Towards a 3D-Printed Hydrogel Prosthetic Hand

Charles Alan Hamilton

Follow this and additional works at: https://ro.uow.edu.au/theses1

Recommended Citation
Towards a 3D-Printed Hydrogel Prosthetic Hand

Charles Alan Hamilton

Supervisor:
Prof. Marc in het Panhuis
Co-supervisors:
Prof. Geoff Spinks & Prof. Gursel Alici

This thesis is presented as part of the requirements for the conferral of the degree:

Master of Philosophy

The University of Wollongong
School of Chemistry

July 2017
Declaration

I, Charles Al-Himla, declare that this thesis is submitted in partial fulfillment of the requirements for the degree of Master of Philosophy from the University of Wollo. This document is submitted for qualitative status of the academic status.
Abstract

Tough and actuating hydrogel materials along with recent advancements in processing techniques, such as 3D-printing, give the field of soft robotics the ability to benefit many different areas. One such area is prosthetics and the creation of a soft prosthetic hand, but very little work exploring the use of hydrogel materials for this specific application has been reported. This thesis works towards the development of a soft 3D-printable prosthetic device made primarily of hydrogel materials in three ways.

Thermally active hydrogel materials, such as poly-(N-isopropylacrylamide) (PNIPAM), have stood out as a promising actuating material in soft robotics applications, but have lacked a practical method of actuation. Electrothermal heating using a soft conductor was proposed as a practical method of raising the temperature of these hydrogels. Different soft conductive materials were tested for their suitability as 3D-printable electrothermal heating elements. Eutectic gallium-indium (eGaIn) alloy was identified as the most promising soft conductor, and a novel extrusion tip was developed to incorporate eGaIn into hydrogel materials via 3D-printing methods. Its suitability as an electrothermal heating element for raising the temperature of hydrogels above the lower critical solution temperature of NIPAM was demonstrated.

3D-Printing large scale (human finger-size) multimaterial actuating hydrogel structures has never been reported. A hydrogel precursor ink formulation was optimized for 3D-printing and encapsulating eGaIn ‘wires.’ Multimaterial hydrogel structures were created and issues in producing these structures, namely NIPAM phase separation when curing with UV light and NIPAM monomer diffusion into the bulk gel, were identified. The impact of these issues was minimized and a finger-like structure that bent approximately 10° at each joint was demonstrated.

An ideal user interface for a prosthetic hand may rely on using peripheral nerve signals for communicating the user’s intention to the hand. A soft 3D-printable low-cost hydrogel-elastomer device is presented and its ability to detect simulated “nerve” signals through capacitive coupling is demonstrated. A correlation between contact area and efficiency of coupling was observed and detection capabilities of > 10% efficiency were reported.

The outcomes of this thesis provide the framework for the next steps in the development of a 3D-printable hydrogel prosthetic hand in terms of creating a practical method for actuating PNIPAM hydrogels, producing a multimaterial finger-like structure with 3D-printing, and demonstrating a concept for peripheral nerve signal sensing with soft 3D-printable materials.
Acknowledgments

To my family, for keeping me grounded and supporting me in every decision I make. To my uncle, Dr. Ralph Rubino, for helping me realize that you should never take life too seriously. To Dr. Anthony DeGennaro, for helping me develop the work ethic I have today. To my grandparents, Dr. George & Marguerite Rubino, you may never see the things I will accomplish but know that I do them with you both in mind.

To my supervisors, Profs Marc in het Panhuis, Geoff Spinks, and Gursel Alici. Thank you for challenging me constantly and giving me so many opportunities during my time here. I thank you for your endless support and encouragement throughout my research endeavours and in my choice to pursue a career in medicine.

To Profs Joost Vlassak, Zhigang Suo, and their student Kevin Tian for letting me work alongside them in the labs at the School of Engineering and Applied Sciences at Harvard University.

Lastly, to the Mallee Bulls, I joined to play rugby, but found a second family and the team was invaluable to me during my time here.

“Why are Things as They are and not Otherwise?”
Johannes Kepler

“The greatest thing you can do in life is add to the knowledge of mankind.”
Edward Bechtel
Publications and Presentations

Publications:


Presentations:

ACES Electromaterials Symposium, Feb 2016, Deakin University, Australia, soft robotics showcase talk and poster presentation.

ACES Full Centre Meeting, Sept 2016, Australian National University, Australia, Soft Robotics Showcase Talk.

Fall 2016 MRS Symposium, Boston, MA, United States. Poster Presentation.


Misc:

Additional publication/presentation information on projects not related to the presented thesis can be found in Appendix 4.

Awarded for a highly commended first year talk (Oct. 2016)

Completed a Certificate in Innovation and Entrepreneurship (Nov. 2016)

Received a Staff Encouragement Award and offered an iAccelerate Scholarship as a result of the 2016 UOW Pitch Competition
Contents

Declaration ii
Abstract iii
Acknowledgements iv
Publications & Presentations v
Table of Contents vi
List of Figures viii
List of Tables x
Abbreviations xi

1 Introduction 1
1.1 The Emergence of Soft Robotics ................................. 1
  1.1.1 Traditional Robotics ........................................ 1
  1.1.2 Biologically Inspired Soft Robots ......................... 2
1.2 The Push for a Better Prosthetic ................................ 4
  1.2.1 The Human Hand and Current Prosthetics ................. 5
  1.2.2 User Control of a Prosthetic Device ..................... 6
1.3 Soft Materials .................................................... 10
  1.3.1 Elastomeric Materials ................................. 11
  1.3.2 Hydrogels ............................................... 12
  1.3.3 Soft Actuators ........................................ 17
  1.3.4 Soft Conductive Materials ............................. 20
1.4 Processing Techniques of Soft Materials ..................... 24
  1.4.1 Cast Moulding ........................................ 24
  1.4.2 3D-Printing ............................................. 24
1.5 Aims .............................................................. 26

2 Identification of a Soft Conductor 28
2.1 Brief Overview ................................................. 28
2.2 Experimental .................................................. 28
  2.2.1 Ionically Conductive Hydrogels ......................... 28
  2.2.2 Electrically Conductive Hydrogels ..................... 30
  2.2.3 Eutectic Gallium-Indium Alloy (eGaIn) ................. 31
2.3 Results & Discussion ........................................... 32
CONTENTS

2.3.1 Ionically Conductive Hydrogels .................................. 32
2.3.2 Electrically Conductive Hydrogels ................................ 33
2.3.3 Eutectic Gallium Indium Alloy .................................. 35
2.4 Conclusion ................................................................. 44

3 3D-Printing Multimaterial Actuating .................................. 46
3.1 Brief Overview ............................................................ 46
3.2 Experimental .............................................................. 46
3.2.1 Precursor Ink Development .......................................... 46
3.2.2 Printing a Multimaterial Actuating Fingerlike Structure .... 48
3.3 Results and Discussion .................................................. 48
3.3.1 Ink Development ........................................................ 48
3.3.2 Printing of an Actuating Finger .................................... 54
3.4 Conclusions ................................................................. 57

4 A Soft Stretchable Sensor for Simulated Peripheral Nerve Signals 58
4.1 Introduction ................................................................. 58
4.2 Experimental .............................................................. 58
4.3 Results & Discussion .................................................... 60
4.3.1 Considerations of Creating the Nerve Sensor ................. 60
4.3.2 Quantifying Signal Detection ...................................... 61
4.4 Conclusion ................................................................. 64

5 Final Conclusions and Future Work .................................. 66
5.1 Future Work: Working with Eutectic Gallium Indium Alloy .... 68
5.2 Future Work: Multimaterial Actuating Hydrogel Structures .... 68
5.2.1 Future Work: Connections to the Device ....................... 69
5.2.2 Future Work: Diffusion of NIPAM ............................... 69
5.3 Future Work: Nerve Signal Sensing .................................. 69

Bibliography ................................................................. 71

A Appendix One .............................................................. 80
A.1 G-Code Example ......................................................... 80

B Appendix Two ............................................................. 87
B.1 Additional Rheological Data ........................................... 87

C Appendix Three .......................................................... 90
C.1 Peripheral ‘Nerve’ Sensing Schematic for Prosthetic Control .... 90

D Appendix Four ............................................................ 92
D.1 3D-Food Printing ......................................................... 92
List of Figures

1.1 The iconic BigDog robot ........................................... 2
1.2 Biomimetic soft robotic octopus tentacle .......................... 3
1.3 Different types of prosthetics for varying purposes .............. 5
1.4 3D-Printed hands for children from e-NABLE .................. 6
1.5 Schematic of electromyographic control of a prosthetic ........ 7
1.6 Anatomy of a nerve and propagation of an action potential .... 9
1.7 A parylene cuff electrode for nerve signal sensing .............. 10
1.8 Examples of soft robotics technologies .......................... 11
1.9 Alginate block copolymers cross-linking with Ca$^{+2}$ ions ...... 13
1.10 Free radical polymerization scheme for acrylamide based polymers 15
1.11 Ionic-covalent entanglement hydrogel .......................... 16
1.12 Mechanics of the Mckibben muscle .............................. 18
1.13 Phase transition of poly(n-isopropylacrylamide) ............... 19
1.14 3D-printed hydrogel elastomer strain sensor device ........... 21
1.15 Free-standing eutectic gallium-indium alloy microstructure ... 23
1.16 Schematic of the steps for 3D-printing .......................... 25
1.17 Extrusion printing of a tough hydrogel .......................... 26

2.1 Custom extrusion printer based on a LinuxCNC machine .......... 30
2.2 Temperature change of an ionically conductive ICE gel with an applied voltage .................................................. 32
2.3 Absorbance of a VGCNF containing alginate solution after varying sonication times ................................................. 34
2.4 Printed tracks of a VGCNF containing hydrogel .................. 34
2.5 Emb3d printing of eGaIn in a tough hydrogel ..................... 35
2.6 A preliminary extrusion tip for printing eGaIn .................... 36
2.7 Solidworks models and SLM printed custom extrusion tips for printing eGaIn .......................................................... 37
2.8 Test tracks of printed eGaIn with varying jog speeds .......... 38
2.9 Close up of the 6-prong custom extrusion tip ..................... 39
2.10 Comparing eGaIn extrusion from the standard and custom 6-prong extrusion tip ................................................... 41
2.11 Printing process of encapsulating eGaIn in tough hydrogel .... 42
2.12 Comparison between expected and actual printing of eGaIn turns .. 43
2.13 Electrothermal heating of hydrogels using eGaIn ................. 44

3.1 Comparison of alginate hydrogels .................................. 49
3.2 Viscosity of alginate hydrogels with varying CaCl$_2$ at a shear rate of 0.1 s$^{-1}$ .......................................................... 50
LIST OF FIGURES

3.3 Viscosity of ICE hydrogels at a shear rate of 0.1 s$^{-1}$ .................................. 51
3.4 Comparing 3D-printed structures of different ICE gels ................................. 52
3.5 CAD model of a fingerlike structure ................................................................. 54
3.6 Phase separation of NIPAM when curing with UV irradiation .................. 55
3.7 Quantifying NIPAM actuation of a fingerlike structure ............................ 56

4.1 Schematic and experimental setup for passing simulated 'nerve' signals to a hydrogel elastomer device via capacitive coupling ........................................ 60
4.2 Measured coupling signal detection efficiency ($\% V_{\text{out}}/V_{\text{in}}$) for a sinusoidal waveform over a range of different frequencies ........................................ 62
4.3 Measured signal detection efficiency for a sinusoidal waveform over a range of amplitudes ................................................................. 64

B.1 Viscosity and shear stress of alginate hydrogels at varying shear rates
   - adding alginate last ........................................................................................................ 87
B.2 Viscosity and shear stress for alginate hydrogels at varying shear rates
   - adding CaCl$_2$ last ........................................................................................................ 88
B.3 Viscosity and shear stress of ICE hydrogels at varying shear rates ........ 89

C.1 Schematic for demonstrating control of a fingerlike structure by detecting simulated 'nerve' signals ................................................................. 90
List of Tables

1.1 Properties of liquidmetal eGaIn ............................................. 22
2.1 Comparing printed eGaIn track width to the prong-to-prong distance
of the 6-prong extrusion tip ....................................................... 39
3.1 Series of alginate hydrogel ink formulations .......................... 47
3.2 Series of alginate/polyacrylamide ICE gel precursor ink formulations 47
3.3 Yield stress values of ICE hydrogels ........................................ 53
4.1 Comparison of measured contact areas to signal detection efficiency 63
B.1 Rheological parameters for a series of alginate hydrogels - adding
alginate last ........................................................................... 88
B.2 Rheological parameters for a series of alginate hydrogels - adding
CaCl$_2$ last ........................................................................... 88
B.3 Rheological parameters for a series of ICE hydrogels ................. 89
Abbreviations

$\alpha$-keto $\alpha$-ketoglutaric acid photoinitiator

$\dot{\gamma}$ Shear rate

$\eta$ Viscosity

$\tau$ Shear stress

$\tau_y$ Yield stress

$K$ Consistency index

$n$ Flow behaviour index

.STL Stereolithography file

3D Three-dimensional

AAm Acrylamide

AC Alternating current

APS Ammonium persulfate

CAD Computer aided design

CAP Compound action potential

CNC Computer numerical control

DC Direct current

DN Double network

eGaIn Eutectic gallium-indium alloy

Emax Emax 904 Gel-SC

FDM Fused deposition modeling

ICE Ionic-covalent entanglement

IR Infrared

LCST Lower Critical Solution Temperature

MBAA N,N'- Methylenebisacrylamide
LIST OF TABLES

NIPAM  N-isopropylacrylamide
pAAm  Poly(acrylamide)
PDMS  poly(dimethylsiloxane)
PNIPAM  poly(N-isopropylacrylamide)
SLM  Selective laser melting
TEMED  N,N,N',N'- tetramethylethylenediamine
UV  Ultraviolet
VGCF  Vapour grown carbon nanofibre
VLM  Visual light microscope
Chapter 1

Introduction

1.1 The Emergence of Soft Robotics

1.1.1 Traditional Robotics

The field of robotics has traditionally dealt with rigid machines that are able to move rapidly and precisely while producing a lot of force to perform complex tasks. Innovations in this field have affected just about every aspect of human life in unimaginable ways. At a very basic level, robots all possess similar architecture consisting of a power source, a sensory mechanism able to detect an external stimulus, a processing unit that deciphers and respond to the stimulus, an actuating mechanism, and an element(s) that can interact with the environment. Oftentimes the robot has the ability to interact with the environment in ways and places that humans cannot. For instance, the Djedi Pyramid Explorer Robot was able to traverse through areas inaccessible to humans in the Great Pyramid of Giza. This resulted in the uncovering of writing that has not been seen by a human for thousands of years [1]. Other subterranean robots are able to enter and map areas that are deemed too dangerous for humans to enter, such as caves, mines, and sewers. These robots are often specially designed for their task and the environment that they will be traversing through [2, 3]. The precision of robotics has also influenced the ways in which human beings approach problems in areas such as healthcare and manufacturing. Doctors train specifically to work with robotic systems that help them perform numerous surgical tasks with increased movement and precision [4]. Although the impact of robotics is tremendous and continues to grow with new developments in energy and autonomy, there are some inherent downsides in traditional robotics technologies such as heaviness and the presence of either a very rigid endo- or exoskeleton [5, 6]. “Bigdog”, shown in Figure 1.1, is one of the most iconic rough-terrain robots that represented a tremendous step forward in the field of robotics, but is 1 meter tall, 1 meter long, and weighs over 100 kilograms [7].
Even with recent advancements in materials and increased technological capabilities, the robots are still very heavy and are rigid enough to seriously injure an individual if it fell on top of someone [3]. These drawbacks become problematic when the robot must interact with soft/fragile objects and puts limitations on their use in certain areas/applications. They also generally require many motors and mechanisms to achieve the desired range of motion. In attempts to combat some of these issues, the field of soft robotics has emerged.

1.1.2 Biologically Inspired Soft Robots

Soft robotics uses soft and deformable materials to create devices or instruments that can perform complex tasks. These types of robotic systems perform much better than traditional robotics when handling fragile objects and excel at interacting with dynamic and unpredictable environments. Much of soft robotics is greatly inspired by nature and the soft bodied organisms around us such as annelids and cephalopods [8].

Annelids, more commonly known as worms, possess a hydrostatic skeleton that is supported by pressurized internal fluid. The movement or elongation of their body used to interact with the environment is based upon muscular contraction that changes the shape of the body/appendage itself [8, 9]. This differs greatly from the rigid joint like structures of the many terrestrial creatures that modern robotics was based on and allows for a wider variety of movement [10]. Worms use layers of circumferential and longitudinal muscles to change the length and diameter of their body to change the internal fluid pressure in certain areas. This occurs in waves and results in the stiffening of tissue and exertion of force onto the environment to move in a peristaltic manner [11]. Although not a hydrostatic structure, the deformable mesh surrounding the ‘Meshworm’ presented by Seck et al (2010) mimics this by allowing power to be transferred between the longitudinal and radial direction, which
causes different modes of biomimetic worm locomotion [12].

Cephalopods, namely octopi, also inspire soft robotics due to the intricate ways they can deform their bodies to fit through small spaces and still produce high forces when interacting with the environment (Figure 1.2(A)). The octopus moves its tentacles in a seemingly infinite number of ways by a complex musculature in longitudinal, transverse, and oblique directions that are each responsible for a different method of motion [13]. The octopus is of special interest to those creating new soft robotics systems because it exists as a muscular hydrostat, like the mammalian tongue, which trades the fluid filled cavity for a dense and complicated architecture of muscle fibers [9]. Muscular hydrostats rely on interaction between different muscle fibers and their inherent incompressibility to achieve movement [14, 15]. Recently, Laschi et al presented a soft robotic tentacle modelled after an octopus tentacle, shown in Figure 1.2(B), that was able to bend in all directions, elongate, and vary its stiffness but comes nowhere near capturing the complexity of the organism itself [16].

Figure 1.2: a) A octopus filmed during the discovery channel’s Atoms of the Deep special reaches its tentacles up into a jar to grab prey b) A soft robotic tentacle that is able to mimic the elongation, shortening, and bending motion of an octopus tentacle. (a) Adapted from [17]. (b) Adapted from [16].

A true biomimetic robot with the full capabilities of the soft organisms seen in nature is still in the distant future, but there have been many notable recent advances that are pushing towards that goal. Shepherd et al presented an entirely soft pneumatically driven locomotive robot that is able to traverse through environments using an inchworm type movement. Its body was made using a modular approach alongside a tethered pneumatic system so that when air was pumped in, certain compartments would expand thus causing motion [18]. Advances in fabrication methods have allowed researchers to move towards a fully ‘Emb3d’ printed untethered system that uses gaseous by-products of chemical reactions contained inside the robot itself to produce movement [19]. It is these types of advances in manufacturing techniques and materials science that allows researchers to combine different types of soft materials in unique geometries to create very exciting soft robotics technologies.
1.2 The Push for a Better Prosthetic

Soft robotics is already responsible for many great advances that are often inspired by soft biological organisms around us [8, 18, 20, 21]. An area that can benefit greatly from the advances in soft robotics is the field of prosthetics. To remain in the scope of the presented work, the prosthetics discussed will be limited to upper arm prostheses. A completely soft and fully functional prosthetic device would be a great asset to many amputees whose numerous day-to-day activities require interaction with delicate objects in dynamic environments.

There will be an estimated 2.2 million amputees residing in the US alone by 2020 with the main causes for amputation being vascular diseases, cancer, trauma, infection, and loss at birth [22]. To overcome this traumatic event, amputees acquire a prosthetic device that is meant to artificially replace the missing appendage and serve as an extension of their body. The user will then rely on this prosthetic on a day-to-day basis to complete normal activities for the rest of their life. Due to the integral role that the prosthetic plays, there is often a very long list of characteristics desired by the end-user. The user generally wants it to be lightweight, fully functional, lifelike, cheap, etc., but to have all of these aspects simultaneously is unachievable with the current technologies. To complicate the issue further, insurance companies oftentimes only provide financial support for a low end device and an individual will have to pay out of pocket if they want something more sophisticated. This forces users to then either pay an exorbitant amount or make a trade-off between functionality and aesthetics, which results in a prosthetic that is deemed inadequate by the user from the start [23]. Resultantly, many users abandon their device for a number of reasons such as lack of functionality, rejection, or embarrassment in social environments [24-26]. The user may even possess multiple devices that they will interchange based upon tasks that they anticipate doing at that given moment. For example, an individual with an upper limb prosthesis may opt to use a prosthetic with a grabber during the day to accomplish basic tasks, but when attending a social function later that evening will switch to a different prosthetic that resembles a hand but serves no functional purpose as shown in Figure 1.3.
CHAPTER 1. INTRODUCTION

![Image](image_url)

**Figure 1.3:** A) An ultra-realistic prosthesis created by Touch Bionics that can feature aesthetic touches such as freckles, hairs, and tattoos but serves no functional purpose. B) A man using the AxonHock made by Ottobockus that provides a simple solution to performing daily tasks but does not resemble a human hand. Images adapted from [27], (A) and [28], (B).

To this day, there is no prosthetic device that comes close to effectively mimicking the functionality of the human body. The field of soft robotics has exciting potential to create a low cost, soft, and functional prosthetic device. The prosthesis would be able to mimic human tissue better than conventional robotics, which would allow for better integration into the human body for sensory feedback and a more sophisticated level of user input.

1.2.1 The Human Hand and Current Prosthetics

The human hand is an incredibly intricate structure composed of 28 muscles and 27 bones innervated by an even more complex organization of nerves [29]. Finally, all of these are controlled flawlessly by the brain while simultaneously providing sensory feedback. Needless to say, the creation of a perfectly “human” soft robotic hand is a daunting task, but some major efforts have been made to create biomimetic hands and control them with biological signals.

The most basic prosthetic hand was developed hundreds of years ago and closely resembled a hook. It displayed a very limited functionality especially in comparison to the plethora of tasks completed by its biological analogue. Thankfully, recent innovations have provided users with prosthetics that have become increasingly life-like in terms of structure and dexterity. Additionally, computational advances have
allowed researchers to more accurately model the flexure and bending of the finger [36]. As previously discussed, there is always a trade-off between aesthetics, function, and cost but the recent efforts have worked towards decreasing this trade-off tremendously. Most of the more functional robotic hands are multi-digit underactuated systems with numerous motors, linkages, joints, and require a large amount of programming to achieve different gestures [31]. The integration of sensors into the device increases the capabilities of the hand in adapting to a more dynamic environment and decreases the computational power to operate. A more detailed account of the specific advances in prosthetic hands over the past few decades can be found in a review by Saika et al. [39]. It is also worth mentioning the impact that advances in manufacturing techniques have had in the advancement of orthotics, especially for children. Companies such as e-NABLE are using the innovations in 3D-printing to allow individuals to create custom lightweight and cheap prosthetic devices that the users want to wear as shown in Figure 1.4 [33]. However, these prosthetics still lack the optimal functionality desired by the user and succumb to the same downsides as any rigid robotic device when handling soft and fragile objects.

![Figure 1.4: Companies such as e-NABLE work to provide individuals, especially children, with lightweight, appealing, and affordable prosthetic devices that they enjoy wearing. (Image adapted from [33])](image)

### 1.2.2 User Control of a Prosthetic Device

The average user of a prosthetic wants their device to be as lifelike as possible and, most importantly, would like to control it in a similar fashion to how they would control their biological appendage. In order to make this a reality, the prosthetic would need to be controlled with a signal from the user's nerve or muscle, and both of these have been explored as viable options.

#### 1.2.2.1 Muscle Sensing

Myoelectric control of a prosthetic uses muscular contraction on a remaining part of the body to control an external device. At the moment, this is a commercially available, yet expensive, solution that can help an amputee feel as if they have a more lifelike prosthetic device like in the BeBionic hand [34]. In the case of a hand,
sensors in the sleeve of the prosthetic will detect signals from the muscles remaining in the arm. These signals will be processed by the device to signal the movement of certain prescribed prehensile actions such as a handshake or a thumbs-up. Although there is good functionality for a non-invasive process, it provides a much less than ideal solution to the problem as it still does not feel natural to the user [34].

A more sophisticated version of myoelectric control that is generally used in shoulder amputees requires an invasive surgical procedure that attaches severed nerves meant to innervate muscles lower down the limb to a muscle in the shoulder or chest (Figure 1.5). In this manner, the brain of the user sends a signal to move the hand, but this could cause the contraction of the pectoral muscle. A sensor placed on the pectoral muscle then can sense the contraction and signal the prosthetic device to move in a predetermined way [35].

![Figure 1.5: A schematic portraying the process of using reinnervated muscles to control a prosthetic using electromyography in a patient with an upper body amputation. Image adapted from [35]](image)

Current research is looking to improve on the detection of the signals so as to increase the number of distinct motions/gestures available to the user resulting in more lifelike functionality of the device. It is also worthwhile to mention that the more minimally invasive approaches are being further explored for their uses in other areas such as virtual reality. Overall, the technology for controlling a prosthesis in this fashion is relatively advanced but the result is still not ideal. A more sophisticated approach would be to control the prosthetic using detection of the nerve signals themselves.
1.2.2.2 Nerve Signal Sensing

In an ideal neurally interfaced prosthetic device, the signal will go straight from the brain to the prosthetic where it will be processed and movement will be achieved with sensory feedback to the brain. This type of neural interface that directly connects biological nerves to a synthetic structure represents a dream at the forefront of scientific endeavours for the past few decades. Studies have been conducted that look into processing signals from both the central nervous system (CNS), consisting of the brain and spinal cord, as well as the peripheral nervous system (PNS), which consists of the rest of the sensory and motor nerves in the human body. There has been a vast amount of research done in detecting signals in both the CNS and PNS; however, to remain in the scope of the work presented here, only the interface with the PNS will be elaborated on. For interested readers, a comprehensive report on neural interfaces with the CNS can be found in [36]. Before delving into the most recent devices used to sense nerve signals, it is best to briefly understand the anatomy of the nerve and the characteristics of the signal itself.

1.2.2.2.1 Anatomy and Signal of a Peripheral Nerve

The human body interacts with the environment in a few fundamental steps easily described in the situation of a finger touching a very hot object. First, a sensory nerve detects that the body is in contact with the hot object and relays this message to the brain. The brain then processes the received information and sends a signal through to the dendrites of a motor neuron in the PNS. This will signal an action potential to travel down the axon of the neuron and release neurotransmitters from the synaptic cleft into the neuromuscular junction. This will cause the contraction of the muscle that will move the finger away from the hot object. This action potential propagates quickly down the axon of the myelinated neuron in a method known as saltatory conduction shown in Figure 1.6(A). In this method, the signal travels down the axon by the opening of ion channels in between the myelin sheaths which results in a potential difference. This change in potential cascades down the axon as ion gates further down are continually triggered to open. A refractory period ensues in areas to re-establish the standing potential that stops signals from traveling in the reverse direction and helps prepare for the next signal to be sent. In unmyelinated axons, a very similar thing happens but the signal is unable to jump from node to node so the propagation of the signal is much slower.
In actuality, it is not just a single neuron relaying the signal down to the muscle, but an entire group of them organized in a complex biological structure. Neurons are very small cells and exist together in bundles known as fascicles. Numerous fascicles, blood vessels, and surrounding membranes are all bunched together inside an outer membrane known as an epineurium resulting in the final nerve structure shown in 1.6(B). All the individual action potentials of the nerves involved in the process propagate at approximately the same time and the detectable signal that results from this is a conglomeration of all of them known as the compound action potential (CAP). Nerves range in size depending on the type of nerve and organism, but the most common nerve used to test benchtop devices is the sciatic nerve that innervates muscles located in the thigh. Signals from sciatic nerves in different organisms have been easily detected in the past; however, the difficult part of detection is creating something permanent that does not harm the organism [36].

1.2.2.2 Peripheral Nerve Signal Detection

Detecting nerve signals from the PNS is extremely challenging due to many factors including the small amplitude of the signal, the invasiveness in device implementation, and the proximity in which the nerve must be to the electrode. To date, there have been numerous electrodes created with the goal of detecting signals from motor neurons in the peripheral nervous system (PNS). Spiral neural electrodes allow severed nerves to grow into microchannels that also serve as axonal amplifiers, which can be used to effectively detect the signals [39–41]. Alternatively, ribbon or cuff electrodes as shown in Figure 1.7 have been developed, which fit around the nerves and can be used to detect signals from intact nerves [42–44]. However, most
devices to date have many key setbacks. It could be the dependence on expensive metal electrodes, mechanical incompatibility with the biological tissue that they come into contact with, or failure to stretch/bend/flex in ways that the nerve can. We believe that recent advances in soft materials and manufacturing methods such as 3D-printing can be used to create a prosthetic device with a neural interface that could function without the aforementioned problems.

![Diagram of cuff electrode](image)

Figure 1.7: (A) A schematic of a cuff electrode made from parylene structural material and Ti/Au/Pt electrodes with an interlocking mechanism analogous to ratchets on a cable tie. (B) The fabricated cuff electrode (1.7 mm diameter), and its subsequent implementation onto the sciatic nerve of a rat (C). Image adapted from [44].

1.3 Soft Materials

Robotics in the past consisted of machines that were generally organized in segments connected by joints—a “kinematic chain of rigid links.” This allowed for defined axes of movement and the rigid materials used for it not only reflected this, but intrinsically required it [16, 20, 45]. Hard materials excelled at mimicking lever like motions of terrestrial creatures around us, but failed interacting intimately with an environment that they were not specifically programmed for. On the other hand, biological tissue has varied stiffness, innate compliance, large contractile lengths, are highly energy efficient, and can communicate flawlessly with other biological sensors [46].

Researchers use the innate properties of these soft materials in unique combinations and geometrical arrangements to overcome the challenges faced when mimicking bi-
vascular systems and achieving certain applications, for example, biomimetic propulsion in a fish (Figure 1.8(A)) [47]. Organisms learn and adapt to their environment through coupled sensory motor activity; it has been shown that when mapping information, organisms rely heavily on sensory input from the environment to control the flow of information, which dictates the response [48]. The combination of different materials with varying degrees of stiffness and compliance allow the soft robot to use their tissue as a form of sensory input, which makes it so that certain control loops, sensors, or other parts of traditional robotics can be eliminated and make the robot less demanding to control [49]. This creates in a robot with improved sensorimotor networks that in turn result in improved adaptability to a dynamic environment [48]. For instance, the incorporation of soft materials in an underactuating hand with optimised passively compliant joints and adaptive coupling allowed it to grasp various objects that it was not specifically designed to grasp with room for error in positioning (Figure 1.8(B)) [50].

A recurrent theme in using newly developed soft materials is using unique architecture to exploit intrinsic material characteristics. This includes mechanical instabilities, such as buckling, that have been problematic in traditional robotics to the advantage of soft robotics systems. This creates new opportunities in engineering strategies and changes the way in which engineers approach problems [51, 52]. For instance, Yang et al reported a modular approach to a linear pneumatic actuator made entirely of soft materials with actuation based solely on the buckling of the material [46]. To gain a better understanding of how this is possible, a deeper understanding of some of the more commonly used materials in soft robotics applications is required.

1.3.1 Elastomeric Materials

"An elastomer is a polymer stripped of all its molecular complexity," generally with a low modulus, and can undergo large reversible deformations that are ideal for soft robotics applications [53, 54]. Minimizing intermolecular forces is key to achieving large strains in elastomers, therefore it is characteristic of elastomeric materials to limit the amount of polar groups or large side groups that could provide steric hin-
drance when uncoiling. When unstrained, the elastomer network exists essentially as random coils that unravel as it extends until they become linear. Therefore, the strain of an elastomer correlates well to the extent of cross-linking of the polymer and does not necessarily behave according to Hooke’s law where the strain is proportional to stress [55]. Properties of elastomers can be further modified by changing the design of the molecular structures, cross-linkers, or with the addition of filler material. To cross-link an elastomer, the monomer must be in high enough concentration to go above the percolation threshold, but going past this can over cross-link the network and result in a very rigid gel. Synthesis methods and properties vary greatly depending on the polymer, but the most commonly used one in soft robotics is poly(dimethylsiloxane) (PDMS) [53]. PDMS is a polysiloxane elastomer commonly classified under the family of silicone rubbers. PDMS is naturally transparent, hydrophobic, flexible, and works over a broad range of temperatures making it ideal for soft robotics applications [55].

1.3.2 Hydrogels

Another class of materials that is becoming increasingly important in soft robotics are hydrogels. Hydrogels are extremely hydrophilic polymer chains that are cross-linked physically or chemically to form a 3-dimensional network and then swollen in water. These polymers can be synthetically made, but many of them are derived from natural materials [56]. Prior to gelation, various rheological studies are undertaken to understand the flow behaviour of the hydrogels and how these changes as the hydrogel is polymerized [57]. Once cross-linked, they are structurally similar to an elastomeric network in terms of the random coil network cross-linked together, however, the extremely hydrophilic groups allow them retain large amounts of water [53]. Due to their innately low modulus and the ability to retain large amounts of water, they are described as “hydrated and compliant” materials [58]. The water in a hydrogel is stored through hydrogen bonding with polar side chains or filling in the pore spaces in the chemical network [59]. This mixing of water with the hydrogel can be described by thermodynamics when considering the $\Delta G_{\text{mixing}}$ between the polymer and water as well as the $\Delta G_{\text{elastic}}$ of the cross-linked network.

$$\Delta G_{\text{system}} = \Delta G_{\text{mixing}} + \Delta G_{\text{elastic}}$$ (1.1)

Initially, $\Delta G_{\text{mixing}}$ is negative, $\Delta G_{\text{elastic}}$ is positive, and $|\Delta G_{\text{mixing}}| > |\Delta G_{\text{elastic}}|$, therefore the mixing with water is thermodynamically favourable and the hydrogel will swell. Eventually, $\Delta G_{\text{mixing}}$ and $\Delta G_{\text{elastic}}$ will both increase until $|\Delta G_{\text{mixing}}| = |\Delta G_{\text{elastic}}|$ and an equilibrium swollen state is reached [60].

Generally, it is the cross-linking density that governs the tightness of the network, water content when swollen, and mechanical properties of the gel [56]. These mechanical properties are assessed by different techniques such as tensile testing and stress-strain curves, which are used to determine suitable applications [61–63]. Hydrogels are often regarded for their ability to mimic soft tissue and have found many applications in pharmaceuticals, cell culture, drug delivery systems, biomedical implants, wound healing, etc [59, 64–68]. Additionally, many hydrogels possess the ability to respond to outside stimuli that may cause them to either swell or de-swell,
which have been coined ‘smart hydrogels’ [65]. More on ‘smart hydrogels’ will be discussed in subsection 1.3.3.

1.3.2.1 Physical Hydrogels

Physical hydrogels are formed from networks of polymers reversibly crosslinked in a network by forces such as hydrogen bonding, hydrophobic interactions, or electrostatic interactions generally between a cationic backbone and soluble anions [64]. These physical networks tend to be more biologically compatible and have the ability to self-repair, which has resulted in them being more favourable in certain biomedical applications [69, 70]. Many different physical hydrogels exist, but a more in-depth look will only be given to the primary one used in this work, alginate.

Alginate is a well-known anionic water soluble biopolymer that has found applications in many areas such as drug delivery systems, tissue engineering, wound dressings, and more well described in the review by Lee and Mooney [71]. Alginate is found in brown algae and occurs mainly in the form of calcium, magnesium, and sodium salts. It is extracted through treatment with NaOH, precipitated with sodium chloride, and transformed into alginic acid sodium salt after treatment with HCl and a few further purification steps [71]. It exists as two different monomers, (1,4)-β-D-mannuronic acid and (1,4)-α-L-guluronic acid, which are commonly referred to as the M and G monomers, respectively, that can form three different types of block copolymers, as shown in Figure 1.9(A) [72].

![Figure 1.9](image)

**Figure 1.9:** A) The two different monomers of alginate forming the 3 possible block copolymers. B) Tivalent cations cause the formation of an ionically bound network of the G-units of the polysaccharide resulting in the formation of the ‘egg-box’ structure (C). (Image adapted from [72]).

Gelation occurs in the form of ionic cross-linking with divalent cations, most commonly Ca²⁺ (Figure 1.9B). Other multivalent cations such as Al³⁺ and Fe³⁺ have also been shown to cross-link alginate but are used less frequently due to the increased biocompatibility of Ca²⁺ ions [73]. In the case of divalent cations it is the
CHAPTER 1. INTRODUCTION

G-blocks that cross-link and form what is known to be the “egg-box model” Figure 1.9(C) [72]. Many factors influence the viscosity and mechanical characteristics of the alginate gel such as molecular weight distribution, impurities, and the ratio of $G : M$ monomers; therefore it is important that the materials remain consistent batch-to-batch [71, 74, 75]. The rate of cross-linking is also important, as slower cross-linking yields a more uniform network that possesses greater mechanical characteristics [76][75]. An important factor to keep in mind is that cross-linked alginate is known to slowly degrade in conditions where the divalent cross-linkers can be exchanged for monovalent ones, thus dissolving the polymers and dismantling the network [71].

1.3.2.2 Chemical Hydrogels

Chemical hydrogels, more commonly used than their physical counterparts, are polymer networks that are irreversibly crosslinked by covalent bonding [56]. One of the most common chemical hydrogels, and the one primarily used in this work, is the one formed from the synthetic acrylamide (AAm) monomers. Polyacrylamide (pAAm) is a highly stretchable and transparent gel widely regarded for its ability to mimic epidermal tissue [77]. The monomers themselves are considered to be dangerous with cancer-causing and neurotoxic effects so great care should be taken when handling the powder and gel precursor solutions, but the hydrogel is safe when polymerized [78]. The hydrogel network is commonly formed by free-radical polymerization (FRP), where the monomers are linked together with (N, N)-methylenebisacrylamide (MBAA) crosslinker. Most commonly, polymerization occurs through the use of ammonium persulfate (APS) and tetramethylethylenediamine (TEMED) where APS supplies the radicals and TEMED accelerates the formation of them as shown in Figure 1.10. However, by taking advantage of the transparency of the hydrogel, light can be used to polymerize the network with the incorporation of a photo-initiator such as igracure or α-ketoglutaric acid, which are activated by UV irradiation [64, 79].
Acrylamide hydrogels are very versatile materials, but their inherent weakness results in certain drawbacks that have limited its direct use in many soft robotics applications. To combat this issue, there have been many attempts to add in different networks to increase the mechanical characteristics of the resultant gel [58][66].

1.3.2.3 Tough Hydrogels

Hydrogels, although extremely useful, are inherently weak and there has been a large push to create tough hydrogels by methods that incorporate other entities into the structure. The push for tough hydrogels has led to the creation of double
network gels, nanocomposite gels, poly-functional covalent gels, and interpenetrating network gels (IPN) all well described in a review by Naficy et al. [58]. Although many of these exhibit high toughness, they often fail to recover from damage during high strain loading cycles due to breakdown of the polymer network. Therefore, a certain type of IPN gel has drawn much attention in the field of soft robotics known as an ionic-covalent entanglement (ICE) gel.

An ICE gel is an IPN gel that relies on the combination of both physical and chemical cross-links; this creates a very tough gel with the ability to recover from high strain. A very common example of an ICE gel was first reported by Sun et al. (2012) and is comprised of an ionically cross-linked alginate network and a covalently cross-linked pAAm network [80]. As strain is applied to the gel, the crosslinks between the G residues in the alginate chain “unzip” and dissipate energy, which serves to maintain the pAAm network by relieving tension on it as shown in Figure 1.11.

![Figure 1.11: An ionic covalent entanglement gel comprised of polyacrylamide (grey lines), covalently cross-linked by N,N'-methylenebisacrylamide (blue squares), and alginate (green & black lines) ionically cross-linked by divalent cations (red circles). The alginate “unzips” in the pink region to dissipate energy to relieve the stress on the PAAm network as the gel is split. (Image adapted from [81]).](image)

This allows gels to be made with superior fracture toughness and strain recovery with great potential in load-bearing applications that conventional and other tough hydrogels are not suitable for, thus making it an ideal candidate when considering what materials to use in a prosthetic device [61, 63, 89]. Recent research has also been using this concept of an ICE gel alongside stimuli responsive hydrogels resulting
in a tough actuating hydrogel that seems very promising in a variety of applications [62]. More about stimuli responsive hydrogels is discussed in subsection 1.3.3.4.

1.3.3 Soft Actuators

Arguably the most important component of any type of robotic system is the actuator. An actuator is the component of a robotic system that is responsible for generating movement. In standard robotics, this is generally accomplished with different types of steppers, gears, motors, etc. crafted from heavy (generally metal) rigid components. To create an entirely soft robotic system, soft actuators need to be created and implemented into devices. Because many soft robotics systems are based on biologically inspired creatures, soft actuators are often called artificial muscles and have come in many shapes and sizes over the years. Numerous variations of artificial muscles exist so a brief overview of only a few noteworthy or relevant ones is provided.

1.3.3.1 Dielectric Actuators (DEAs)

Electroactive polymers (EAPs) respond to electrical stimulation with a change in shape or size. These polymers are able to produce large actuation strain (over 100%), fast actuation speed, high fracture toughness, and vibration dampening which makes them suitable materials to mimic biological muscle [83]. Dielectric elastomer actuators consist of a dielectric elastomer, such as 3M VHB or PDMS, in between two compliant electrodes. When a voltage is applied to the electrodes, free charges form on the outside of the insulating material causing Maxwell stress. This causes the film to compress and in the process, the electrodes come closer together. This brings opposite charges closer and separates like charges as the area of the film increases to converts electrical energy to mechanical energy resulting in an observable actuation. Current challenges in this technology suffer from finding compliant electrodes able to stay in contact with the entire active region of the elastomer and the extremely large voltages required to drive the actuation [84, 85].

1.3.3.2 Shape Memory Alloys (SMAs)

SMAs are materials that have the ability to return to a set preconfigured shape when heated above a certain transition temperature, which is known as the shape memory effect [86]. They are usually a metallic alloy and the most popular one to date is known as NiTiNOL, a titanium-nickel alloy. The change takes place as the material transitions from one crystalline structure to another based on what is thermodynamically favourable at the current temperature. Martensite is the name of the crystal structure that exists at low stresses and temperatures that can be easily deformed, whereas austenite is the name of the crystal structure when heated. When the deformed martensite is heated above the transition temperature, the material 'remembers' the shape that it was in and reverts to it [87]. A more comprehensive thermodynamical and thermomechanical understanding of this phenomenon can be found in the review by Cianchetti [86]. Over the years, SMAs have found many applications as wires, ribbons, pipes, and springs to operate in small places where a large actuator would be impractical to use. They have been used to model motion in soft biological organisms such as the earthworm, the caterpillar, and muscular
hydrostats [12, 16, 88]. Problematically, SMAs are confined to a very limited number of simple movements and rely on thermal processes to invoke their actuation.

1.3.3.3 Pressurized Air/Water

Civilizations have been using pneumatic and hydraulic methods of harvesting power for millennia. This has remained a common method of actuation for standard robotics systems. It generally involves the transfer of air or water from one area to another through the movement of a piston or pump. Pushing the air or water into the new area causes a volume change, which results in the movement of a certain part of the machine. It is worth noting that hydraulic systems use an incompressible liquid rather than a gaseous medium and resultantly provide a faster actuation that displays a greater force with less transferred volume. These types of artificial muscles have been the most popular among soft robotics systems, with a very well-known class of pressure driven muscle systems known as McKibben muscles and is shown in Figure 1.12.

![Figure 1.12: The basic structure of a McKibben muscle consisting of a tube and braided mesh with an internal expandable bladder. When the internal bladder is pressurized the muscle contracts longitudinally and causes actuation. Image adapted from [89].](image-url)

First developed in the 1950s, these artificial muscles contain an internal expandable bladder surrounded by a mesh arranged in a double helix. When a liquid or gas is pushed into the internal bladder, it causes a radial expansion and forces the mesh to contract longitudinally [90]. As the artificial muscles contracts, its stiffness also increases much like biological muscle. It was originally used as a lightweight actuator for orthotic systems in wheelchairs or upper limb prostheses and a more in depth analysis of the McKibben muscle as well as the different properties of the mesh/bladder can be found in the review by Bertrand Tendu [91, 92]. Limitations of this system stem from the requirement of a pump with an external bladder to hold the liquid or air when not in the muscle.
1.3.3.4 Hydrogel Artificial Muscles

Certain hydrogels undergo large reversible changes in response to different stimuli such as light, pH, electric and magnetic fields, biological molecules, and temperature. Researchers have been uncovering applications of these gels in numerous fields such as drug delivery, photodegradable materials, biological sensors, gene carriers, aerospace applications, microfluidics, actuators, and more [65–67]. How the material responds to the stimuli depends greatly on the polymer itself but it usually constitutes a change in hydrophilicity, protonation state, polarity, optical chirality, or conformation. A comprehensive review of these gels can be found in [65], but to remain in the scope of the presented work only an overview of poly-N-isopropyl acrylamide (PNIPAM) is given in this chapter.

PNIPAM is the most commonly studied temperature sensitive polymer with a lower critical solution temperature (LCST) of about 31 °C. It consists of N-isopropylacrylamide monomers that polymerize in a very similar fashion to AA monomers through FRP of the vinyl group with MAAA crosslinkers shown in Figure 1.10 [65, 68]. The transparency of the gel allows it to be cured easily with UV light, however, if the radiation causes the gel to heat up, it can undergo a phase separation that turns the transparent gel precursor into a white paste. To the author’s best knowledge, there has been no reported study that offers an in depth analysis of this phenomenon but it is likely related to the LCST of the polymer.

![Diagram of PNIPAM hydrogel behavior](image)

**Figure 1.13:** (A) As NIPAM is heated above its LCST, the chains revert to a hydrophobic state thus breaking the hydrogen bonds with water. (B) A change in chain conformation forces the water out of the hydrogel, which subsequently shrinks in size. [(A) adapted from [69]; (B) adapted from [100]]
The LCST of the polymer is highly tuneable and can be raised or lowered with the inclusion of hydrophilic or hydrophobic moieties, respectively [65]. Below the LCST, the polymer remains in its hydrophilic state and thus stays very swollen, however, when the temperature rises above the LCST, the mixing with water becomes thermodynamically unfavourable [99]. This can be explained further by looking at the free energy of mixing ($\Delta G_{\text{mix}}$) between the polymer chains and H$_2$O:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$  \hspace{1cm} (1.2)

In colder solutions, the amide groups of the NIPAM readily form hydrogen bonds with H$_2$O, however, the nonpolar isopropyl groups contribute large negative effects to the $\Delta H_{\text{mix}}$ and $\Delta S_{\text{mix}}$ [101]. When the temperature rises above the LCST, the $-T\Delta S_{\text{mix}}$ term dominates and the free energy of mixing becomes positive; therefore, the hydrophobic interactions between the polymer chains becomes more thermodynamically favourable than the hydrogen bonding with water. This results in the change of conformation into a more collapsed state; the water is then expelled from the hydrogel as it shrinks in all directions, as shown in Figure 1.13. The fact that this fully reversible phenomenon occurs in a biocompatible material close to body temperature has sparked great interest in its use in biomedical and soft robotics applications. The downside of the material is that since the actuation relies on a change in hydrophobicity of the polymer network to expel water, the speed of actuation is a diffusion limited process. Additionally, practical methods of actuating the NIPAM gels have not been reported yet.

### 1.3.4 Soft Conductive Materials

Another primary component in any robotics system is the connection between the motor and control system that allow for the transmission of signals. In traditional robotics systems, these are simply conductive wires but soft robotics requires that these connections be able to bend, stretch, flex, twist, etc. Therefore, a key component of soft robotics is the inclusion of soft, stretchable, conductive materials. Many different attempts at identifying the proper material have been presented including the use of conductive polymers, nanowires/nanoribbons organized into serpentine shapes, and more [102]. However, to remain in the scope of the work presented here, only a brief overview of conductive hydrogels and liquidmetal gallium-indium alloys will be presented.

### 1.3.4.1 Ionically Conductive Hydrogels

One approach to create a soft stretchable conductor is to take a material that already exhibits the aforementioned mechanical properties and incorporate ions into it so that it also exhibits ionic conductivity. By adding ions into a hydrogel, the ions are able to move throughout the bulk material and carry electrical signals from point A to point B. Although sometimes hydrogels may already contain ions to crosslink certain polymers such as alginate, they are not freely moving and therefore, the hydrogel does not display any notable conductivity. Attempts to increase the ionic conductivity of hydrogels generally involve swelling the hydrogel in a salt solution of high concentration or using a high concentration salt solution to make the gel precursor solution. Once an ionically conductive hydrogel is created, it can be used
for a wide range of soft robotics applications. For example, the Suc Group at Harvard University was able to create an ionic cable that is able to transmit signals of a range of amplitudes and frequencies over large distances (meters) using a hydrogel created with a high concentration of LiCl ions [103]. Other uses of ionically conductive hydrogels presented recently have included pressure and strain sensors [77]. It can be further combined with elastomers in intricate ways to create multifunctional strain gauges that show potential applications in feedback systems of soft robotics devices as shown in Figure 1.14 [104].

![Figure 1.14](image.png)

**Figure 1.14:** A 3D-printed hydrogel elastomer device made from LiCl loaded acrylamide encapsulated in PDMS elastomer (a) that can be placed on the back of the fingers of a glove to be used as a strain sensor (b). The flexion of different finger combinations results in different changes of resistance (c). Image adapted from [104].

An additional advantage of fabricating a soft conductor in this way is that the gel is kept transparent and retains its conductivity over large physical deformations. However, a well-known issue is that the ionic conductivity will always be very low in comparison to electrical conductivity.

1.3.4.2 Electrically Conductive Hydrogels

What would be of benefit to researchers in soft robotics is a soft stretchable conductor that displays similar conductivities to metallic materials such as copper ($5.8 \times 10^7$ S/m). Therefore, there has been a large push to incorporate an electrically conductive network into hydrogel materials using graphene, carbon black, carbon nanotubes, carbon nanofibers, metallic nanoparticles, etc. Accomplishing this requires identifying a solution that will readily form dispersions with the conductive filler material, such as gellan gum [105]. To achieve a conductive network in a hydrogel, the filler material must be included in a large enough quantity that the percolation threshold is met. In relation to the conductive hydrogel, this means
CHAPTER 1. INTRODUCTION

that a large enough amount of conductive filler must be added to form enough interconnecting clusters that will act as a network for the flow of electrons from one side of the hydrogel to another. A more in depth coverage of the statistics and probabilities that govern the concept of percolation theory can be found in [106].

The primary method of dispersing the conductive filler material into hydrogels involves sonication, which uses sound energy to disturb the particles and disperse them throughout the solution. However, much optimization into this is required to find the ideal sonication time; too much of the treatment will damage the polymer chains and conductive network leading to an overall decrease in electrical conductivity and mechanical properties [107, 108]. Overall, this inclusion of conductive filler leads to networks with relatively high conductivities \(7 \pm 2 \text{ mS/cm}\). However, the filler material can complicate certain processing techniques such as extrusion printing because of the clusters of filler material that may block the printing tip [105, 109].

1.3.4.3 Gallium-Indium Alloy

An obvious solution to achieve a soft flexible conductor with metallic conductivity, would be to find a metal that exists as a liquid within the temperature range it will be used. This limits the possibilities to all but a few metals and once those that are not radioactive, explosive, or toxic are no longer considered—there is only one option left. Explored in depth by the Dickey group, gallium and its alloys have been identified recently as very ideal materials for soft robotics. In addition to their inherent metallic conductivity, their low melting points allow them to remain liquid at room temperature where they can stretch and flex [110]. The unique properties of these materials have made them of interest in applications like microfluidics, stretchable electronics, communications, optics, and many more [111–116]. Gallium can be alloyed with a variety of metals, such as indium and tin, but the one used throughout this study is the eutectic combination of 75.5% Ga / 24.5% In (eGaIn). Properties of eGaIn are shown in Table 1.1:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity</td>
<td>(29.4 \times 10^{-6} \Omega \text{ cm} [117])</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>632 dynes/cm (in air) [40]</td>
</tr>
<tr>
<td>Viscosity</td>
<td>(1.99 \times 10^{-3} \text{ Pa s} [117])</td>
</tr>
<tr>
<td>Melting Point</td>
<td>15.7 °C [113]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>40 W/m \cdot K [118]</td>
</tr>
<tr>
<td>Conductivity</td>
<td>(3.4 \times 10^6 \text{ S/cm} [118])</td>
</tr>
</tbody>
</table>

Liquid eGaIn’s most interesting property is that it exhibits a wetting behaviour on certain surfaces and tends to spontaneously form a passivating layer of gallium
oxide a few nanometers thick when exposed to oxygen [112, 117]. In the past, the oxide layer was seen as problematic and made handling the material extremely difficult; however, recent work has seen the oxide layer to be potentially beneficial [119]. It also provides a barrier that stops the metal from making contact with the surrounding environment. The eGaIn is able to flow through its own oxide ‘skin’ as a liquid, inflate/inflate pre-existing oxide skins, and spontaneously repair itself if broken or increase in size to adapt to an increase in liquid metal volume [40]. The ‘skin’ can also be removed/generated using favourable electrochemical conditions to manipulate the interfacial tension and reconfigure the shape of the metal [119]. Arguably, the most important property of the oxide layer in soft robotics applications is that it allows for the formation of stabilizing microstructures as shown in Figure 1.15) [118, 119].

![Image](image-url)

**Figure 1.15**: The oxide skin that spontaneously forms when the eGaIn comes into contact with oxygen allows for the formation of self-containing microstructures. (Image adapted from [120].)

The formation of the oxide layer renders eGaIn compatible with many fabrication techniques such as screen printing, contact printing, co-electrospinning, vacuum filling, pen writing, and extrusion printing. The innate properties of eGaIn combined with these methods of fabrication provide tremendous potential for the use of eGaIn in applications such as microfluidics, reconfigurable devices, electronics, and more well described in the review by Michael Dickey [110]. However, unfavourable interfacial interactions with hydrous materials have restricted eGaIn to be fabricated with primarily silicon based substrates such as glass or PDMS. It has also been shown that an interfacial slip layer forms between the oxide skin of the eGaIn and hydrous surfaces. This can be beneficial for applications in which the metal must flow freely through small tubes and along surfaces, but becomes very problematic when an application requires the eGaIn to stay on a hydrous surface [121]. Overall, eGaIn shows great potential for many soft robotics applications and will play a major role
in the development of numerous stretchable electronics devices.

1.4 Processing Techniques of Soft Materials

Given the large difference in characteristics between materials used in traditional and soft robotics, many different manufacturing techniques are being used. Many of these exploit innate properties of the soft material during the manufacturing process, but the wide variety of properties displayed by the hydrogels makes processing them into complex structures difficult. Tough hydrogels require multiple steps of synthesis, which need to be taken into consideration when determining how to process them. Careful considerations also need to be taken when multiple materials are being used together in the same device. Different materials with varying moduli and hydrophilicities, such as hydrogels and elastomers, may need certain treatments done during the manufacturing process to ensure adhesion and prevent delamination under load cycles [122]. Even devices containing different materials of similar moduli need to be prepared in a certain fashion to ensure that the materials adhere together properly such as tough hydrogels and actuating hydrogels. The details of the processing technique for each device will be material and application specific, but the two most relevant methods of processing materials in the presented work are cast molding and 3D-printing.

1.4.1 Cast Moulding

Cast molding involves pouring the gel precursor into a preformed mold and then applying the material-dependent process to cure the sample. Once cured, it can be removed from the mold in the set structure. However, this method is only viable for materials that possess sufficient mechanical properties to be ejected from the mold without being damaged. Tough hydrogels are robust enough for this to occur and certain variations of these, such as the ICE gel, can be processed with cast molding. However, this is only because the polymerization schemes for the two different networks are different. Both the physical and chemical network can be formed separately and in the presence of one another. In many scenarios of multilayered containing structures, this is not the case and further considerations must be taken. Lastly, cast molding is very restrictive in the type of structures that can be produced, and for many more intricate structures it may not be suitable.

1.4.2 3D-Printing

3D-printing is an additive manufacturing technique that involves the layer by layer deposition of a material to create a 3-dimensional structure [123]. There are many 3D printers on the market; however, the most common ones rely on fused deposition modeling (FDM) to create complex structures. A plastic filament, such as polylactic acid (PLA) or acrylonitrile butadiene styrene (ABS), is stored on a coil and passed through a heating element where it is melted and deposited onto a substrate where it solidifies. The deposition system is generally attached to a movable head where it is given 3 degrees of freedom along a Cartesian coordinate system so that meaningful structures can be created layer by layer as the material is extruded.
The printing process at a very basic level is simple, as shown in Figure 1.16: it begins with the creation of a 3D structure in a modelling program such as SolidWorks. The model is then saved in the form of a .STL file, which stores the triangulized surface geometry of the structure. This .STL file is then placed through a slicing software, such as Slic3r, where the user can input different parameters such as layer height, resolution, nozzle temperature, infill percentage, support material, and more. From this, the sliceer software outputs a Gcode file that instructs the printer of the print conditions, sequential movements, and extrusion parameters to generate the print.

Figure 1.16: A schematic showing the steps generally required in the 3D printing of a user-designed object. Image adapted from [124]

A wide range of materials can be printed and being that most soft robotics technologies exist on laboratory benches, 3D-printing and rapid prototyping has contributed to many recent advancements tremendously. Currently, printers are widely available in many research labs and many of these have been specially customized to print different kinds of materials for assessment of their suitability in a variety of applications.

1.4.2.1 Extrusion Printing

A common additive fabrication technique used for processing viscous materials is known as extrusion printing, shown in Figure 1.17. During this, a material with suitable rheological parameters will be placed into a syringe on a movable printhead with 3 degrees of freedom [69]. The print nozzle will move according to a pre-programmed set of paths, dictated by the Gcode, as the material is pushed out of the syringe, which is often accomplished with a high-resolution piston or pneumatic pressure. The structure will then be built up layer by layer and finalized with post-processing methods specific to the material of the print. The resolution of the printed material depends on a great number of parameters such as the diameter of the extrusion tip, the extrusion speed, the jog speed of the printhead, the z-offset of the nozzle, and the rheological characteristics of the material itself. There are also often environmental controls involved such as a temperature controlled stage or extrusion jacket.
1.4.2.2 Selective Laser Melting (SLM) Systems

Although it is not used to process soft materials, another noteworthy additive fabrication technique that played a large role in the findings presented in this study is known as selective laser melting (SLM). During SLM, a thin layer of metal powder is spread across a print bed and a laser beam is focused in a specific pattern to selectively weld the metal powder together in the desired shape. The build tray is then lowered one layer down, another thin layer of metal powder is spread across the build tray, and the process is repeated until the object has been created. This is done in an inert atmosphere where various metals and alloys can be used, such as titanium, aluminum, copper, nickel, stainless steel, and more [125].

1.5 Aims

The main aim of this study is to further the work towards the creation of a soft 3D-printable prosthetic device primarily made from tough and actuating hydrogel materials. To this aim, the approach taken in this study is to explore the use of electrothermal heating to actuate thermally active hydrogel materials and identify a potential neural interface made from soft 3D-printable materials to be included as a control mechanism. The specific aims are to:

- Identify a soft, stretchable, flexible, printable, and nontoxic conductive material to be used for electrothermal heating of a thermally-responsive tough hydrogel.

- Develop protocols for printing the identified conductive material and incorporate it into a 3D-printed hydrogel structure.

- Observe and quantify the electrothermal heating of the device.
Explore the use of structural and actuating ICE hydrogels to create a multi-material ‘fingerlike structure.’

Demonstrate the presence of capacitive coupling in a 3D-printable hydrogel-elastomer device.

Quantify the capacitive coupling found in the hydrogel-elastomer device from an appropriate simulated “peripheral nerve” signal.
Chapter 2

Identification of a Soft Conductive Material for Electrothermal Heating

2.1 Brief Overview

To electrothermally heat a thermally active 3D-printed hydrogel (PNIPAM), a suitable soft conductive material must be identified and the protocols for extrusion printing this material must be developed. To achieve this, three classes of materials were explored; ionically conductive hydrogels, electrically conductive hydrogels, and eutectic gallium-indium alloy (eGaIn). By introducing ionic species into a hydrogel, a conductive network is created that possesses all the desirable mechanical properties of a hydrogel. Something similar can be done to create an electrically conductive network throughout a hydrogel with the incorporation of conductive filler material, such as vapour grown carbon nanofibers (VGCNFs). An alternate approach would be to identify a metal that would remain liquid in the temperature range that it will be used (approx. 20 - 40 °C), such as eGaIn. Theoretically, a voltage applied to any of the aforementioned conductive materials should yield observable electrothermal heating that may be used to actuate thermally active hydrogel materials. This chapter explores the suitability and challenges of using each of these materials as a heating element in a 3D-printed hydrogel device.

2.2 Experimental

All hydrogel precursors synthesis, printing, post-processing, and experimentation were conducted and at a temperature of 21 °C unless otherwise noted.

2.2.1 Ionically Conductive Hydrogels

Acrylamide (AAm) (Prod #: A8887, Lot #: SLBM1911V), alginic acid (alginate) sodium salt (medium viscosity, Prod #: A2033, Lot #: SLBG9533V, Brookfield Viscosity ≥ 2000 cps 2% in water at 25 °C), calcium chloride dihydrate (CaCl₂ • H₂O) (Prod #: C3306, Lot #: SLBQ3006V), α-ketoglutaric acid photo-initiator (α-keto) (Prod #: 75890, Lot #: BCBL7550V), and N, N’ - methylenebisacrylamide (MBAA) crosslinker (Prod #: 146072, Lot #: MKBS6356V) were purchased from Sigma Aldrich, Australia. Ethylene glycol (ethanediol, Prod #: EA007, Lot...
CHAPTER 2. IDENTIFICATION OF A SOFT CONDUCTOR

# BN284868) was purchased from ChemSupply, Australia. All aforementioned reagents were used as received and all solutions were prepared using Milli-Q water (resistivity 18.2 MΩ cm) unless specified otherwise.

2.2.1.1 ICE Gel Precursor Ink Formulation

The precursor ink formulation was created by adding 39.5 mg MBAA, 35.4 mg α-keto, and 450 mg alginate to a solution consisting of 4.5 mL of 40% (w/v) acrylamide, 5.25 mL H₂O, 1.5 mL .075 M CaCl₂, and 3.75 mL ethylene glycol while stirring with a magnetic stir bar. Alginate was added last with gentle stirring by hand using a spatula in 2 equal parts of 225 mg each.

2.2.1.2 Printing, Post-Processing, and Heating

Prior to printing, the precursor gels were placed under vacuum (RobinAir Vacmaster 2 stage vacuum pump, Model # 15151S2) for 10 minutes. Once removed, the gels were placed into 5 mL syringe barrels and centrifuged for 12 minutes at 4400 rpm with an Eppendorf Centrifuge 5702 to remove air bubbles. All printing was done using a custom-built extrusion printer based on a LinuxCNC-milling machine (Figure 2.1) controlled by LinuxCNC Enhanced Machine Controller Software (2012) and the Gcode to create the device was written by the author in a Gedit text editing software (For more details see Appendix 1). All prints were done using a 23 gauge syringe tip purchased from Nordson EFD. Dimensions of the samples were approximately 33 x 9 x 4 mm³.
Figure 2.1: A LinuxCNC milling machine with 3 degrees of freedom (A) modified into a custom-built 3D-printer with a 3D-printed bracket to hold two Zaber linear actuators (B) and two 5 mL syringe barrels.

After printing, the structure was cured with UV irradiation from a Dymax BlueWave 75 Rev 2.0 UV system with a 19+ W cm⁻² light source. The sample was then immersed in a 0.076 M CaCl₂ solution for 24 hours followed by immersion in Milli-Q H₂O for 24 hours. The gel was then soaked in varying concentrations of CaCl₂ for 24 hours (0.0 M, 0.038 M, 0.076 M, 0.38 M, 0.76 M, 1.5 M). After removing the gel from solution, a potential difference (up to 25 V) was applied to the gel using a DC power source with carbon fibre connections and changes in temperature were recorded using an IR thermometer.

2.2.2 Electrically Conductive Hydrogels

VGCMFs (Pyrgraf Products, PR24-IHT, Batch info: PS1345, Bx 8, HT 170), ammonium persulfate (APS) (Prod # A30678) and N.N,N',N' - tetramethylethylenediamine (TEMED) (Prod # T9281, Lot # MKBP4425V) were purchased from Sigma Aldrich. Other materials and procedures required to make any hydrogels in this section were acquired as stated in subsection 2.2.1. All materials were used as purchased without further modification unless otherwise specified. Molds were cut from 6 mm acrylic sheets using a laser cutter (Universal Systems, 10.6 µm CO₂).

2.2.2.1 Gel Precursor Formation

Electrically conductive inks were formed by dispersing 100 mg of VGCMFs into precursor inks described above but with some minor alterations. Instead of adding CaCl₂, an extra 1.5 mL of H₂O was added to keep a consistent final volume and
cross-linking of the alginate would then occur by soaking the gel in a 0.076 M CaCl₂ solution after curing of the acrylamide. Instead of α-keto, 100 mg of APS was dissolved into the solution. To cross-link the acrylamide, 300 μL of TEMED was added to the ink immediately before it required curing in the mould. The sample was soaked in 0.076 M CaCl₂ for approximately 12 hours followed by H₂O for approximately 12 hours. A potential difference of 12 V was then applied to the sample and heating was observed.

2.2.2.2 Optimizing Dispersions

VGCFs were dispersed into the precursor ink using a Branson digital sonifier with a microtapered 1/8th inch horn tip (consonic pty ltd) placed 1 cm from the bottom of the sample vial with a 7 Watt output pulsing on/off every .5 s. To assess the dispersions, a UV-3600 Shimadzu UV-Vis-NIR spectrophotometer (10 mm path length, Spectrosil Quartz) was used to sweep from 600 - 1200 nm. A precursor containing all the same materials aside from the VGCNFs was used as a blank.

2.2.3 Eutectic Gallium-Indium Alloy (eGaIn)

2.2.3.1 eGaIn Formation

Gallium and indium (4N purity) were purchased from Changsha Santech Materials Co., Ltd. and SmaTree Australia, respectively. The eGaIn alloy was made by adding the metals together at a wt. ratio of 75% gallium / 25% indium in an inert atmosphere while stirring with a magnetic stir bar at 65 °C (Stuart heat-stir, Model # CB162). All other materials used were acquired from sources previously stated in subsection 2.2.1 and all gels were prepared as described in subsection 2.2.1.

All extrusion printing of eGaIn and hydrogel materials was done on the custom CNC based extrusion system described in subsection 2.2.1.2. A 23 gauge standard extrusion tip purchased from Nordson EFD was used to print the hydrogels and the custom extrusion tip described in section 2.2.3.2 was used to print eGaIn. Microscope images were taken using a Leica Z16 visual light microscope and profile views were taken using a Dataphysics contact angle system OCE goniometer.

2.2.3.2 Fabrication of a Novel Extrusion Tip

All tip designs were created in SolidWorks 2016 with the luer lock portion of the design adapted from a previous file [126]. The models were printed on a Realizer SLM50 printer with Ti6Al4V titanium alloy powder with particle size ranging from 20-60 μm diameter. The designs were exported from SolidWorks as .STL files and uploaded to the Materialise Magics software where they were “sliced,” and support material was selectively generated. The files were processed by Realizer’s proprietary software and uploaded to the printer where the powder was spread across a titanium build tray and selectively sintered layer by layer to form the 3D structure of the extrusion tip. Following the print, the tips were subject to post-processing steps including reaming of the inner barrel and filing of the luer lock connection.
until it fit flush into the syringe. Finally, the outer portion of the tips were sand-blasted (Burwell Abrasive Blasting Equipment, Model # BHK1, glass beads) until the surface was smooth.

2.2.3.3 Quantifying Electrothermal Heating From eGaIn

Electrothermal heating was accomplished by connecting the eGaIn tracks to a Tektronix PWS4305 programmable DC power supply with an applied voltage of 2, 3, or 4 V using copper wire connections sealed with eMAX UV-curable epoxy. Changes in temperature were measured via thermal imaging by a Micro-Epsilon TIM 160 thermal imager camera with all analysis done in the TIM Connect Software.

2.3 Results & Discussion

2.3.1 Ionically Conductive Hydrogels

Samples soaked in different concentrations of CaCl₂ were subjected to an applied potential difference and the temperature was recorded over time. No heating was observed in any samples until a voltage of 25 V was applied. The samples soaked in 0, 0.038, and 0.076 M CaCl₂ produced no observable heating at any voltage. The temperatures of hydrogels soaked in higher concentrations of CaCl₂ (0.76 M and 1.5 M) were observed to increase over time and this increase is shown in Figure 2.2 for the hydrogel soaked in 0.76 M CaCl₂.

![Graph showing temperature change over time for hydrogel soaked in 0.76 M CaCl₂](image)

**Figure 2.2:** The recorded temperature change of an ICE gel soaked in 0.76 M CaCl₂ solution over time as a potential difference of 25 V is applied to it.

As the potential was applied to the hydrogel, bubbles were observed at the interface between the gel and point of electrical contact, which indicates the splitting of water. Additionally, there was a strong odour of chlorine gas present while the voltage was
applied. Eventually heating of the sample stopped occurring, which is indicative of the power being produced through Joule heating becoming equivalent to the energy being dissipated by the environment. It was also observed that electrical connection was lost for the samples soaked in 0.76 M and 1.5 M CaCl₂ as the point of electrical contact was electrochemically coated. This occurred for the sample soaked in 1.5 M before extended heating could be observed. Theoretically, some of these effects could have been reduced if an AC voltage was applied instead of DC. However, access to an AC power source with a high enough voltage was limited and as these were preliminary experiments it was determined that the DC source was initially suitable.

2.3.2 Electrically Conductive Hydrogels

Initial experiments focused on determining the lowest sonication time that would yield a complete dispersion of conductive VGCNF in the hydrogel precursor solution. It is well known that increased sonication times can lead to damaging the VGCNFs and the dissolved polymers [108, 109]. A hydrogel precursor described above was created with 100 mg of VGCNF added to it and was sonicated for 10 minutes. An aliquot of 50 μL was taken from the vial at time intervals of 0, 30, 60, 120, 240, 360, 480, 600 and 720 seconds. A dilution was made from each aliquot containing 20 μL of sample and 9880 μL H₂O. Each dilution was shaken and used for UV-Vis analysis, which is shown below in Figure 2.3. It is worth noting that the dispersion depends on the input energy and not the sonication time. Therefore, if the required input energy is known then the length of sonication becomes irrelevant as long as the final input energy remains constant. Shorter and more intense sonications may have more detrimental effects on the VGCNF integrity but this was not investigated.

The sonication agitates the VGCNFs and causes them to disperse throughout the gel solution causing an increase in absorbance of the solution. Eventually, the absorbance becomes independent of the input energy indicating that a full dispersion has been reached. As shown in Figure 2.3, the complete dispersion occurs after approximately 1000 Joules. Any input energy beyond this point will potentially damage the VGCNFs and monomers leading to a decrease in conductivity and mechanical properties of the gel. A gel containing 100 mg VGCNF was then produced as previously stated using the optimized sonication energy as per the UV-VIS data and cast into a mold.

A voltage was applied to the sample and heating was observed through the use of an IR thermometer. Being that some heating was observed, attempts to then print “wires” of the material were made. The VGCNF containing precursor ink was added to a 5 mL syringe and printed onto a sample ICE gel prepared as described in section 2.2.1. Note, that this sample was not centrifuged as it was theorized that this would create an inhomogeneous distribution of the nanofibers throughout the syringe. Although the gel was not overly viscous, it was found that the VGCNFs
clogged the needle tip and it printed out in uneven spurts. The printed tracks then spread out onto the gel and the desired lines of fine resolution could not be achieved as shown in Figure 2.4.

![Image](image.png)

**Figure 2.4:** Printed tracks of a VGCNF containing hydrogel on top of a printed ICE gel.

Theoretically, decreasing the amount of VGCNF dispersed into the gel would yield a gel that is less likely to clog the extrusion tip. However, for each new gel made there would have to be further experimentation done to optimize sonication time and with decreasing viscosity it becomes less likely that the gel will be able to hold its printed form. Adding CaCl₂ would help to make the printed structure more stable, but would also further complicate the sonication and print. The VGCNFs also render the conductive gel no longer transparent, so the desired method of polymerization using a photo-initiator and UV irradiation would no longer be feasible. Therefore the only way to cure the gel would have been to touch the tracks with
small amounts of TEMED to initiate the free radical polymerization. The TEMED acts as an accelerator and works very quickly; therefore, there would have been no way to add the TEMED to the syringe and print the lines before the entire syringe polymerized. Due to time constraints and the incompatibility foreseen in the desired manufacturing process, this option was not explored further.

2.3.3 Eutectic Gallium Indium Alloy

Gallium and its alloys show great promise in soft robotics applications. However, the spontaneous formation of the oxide layer and the preference of the metal to flow through the oxide skin like fluid through a tube make the material extremely tricky to work with. In addition to that, the unfavourable interaction with hydrous surfaces added new challenges to its incorporation with hydrogel materials. To use this alloy to electrothermally heat thermally active hydrogel materials, these issues needed to be overcome.

2.3.3.1 Attempting to Print eGaIn

To achieve the maximum amount of heating through the gel, a wire configuration was needed that consisted of the longest amount of the thinnest metal possible. Ideally, this would be printed straight onto the hydrogel substrate, but initial attempts of doing so failed. Whenever the metal was to be printed onto the substrate, it formed a line of beads, shown in Figure 2.6 (A), rather than a continuous ‘wire’ so different approaches were made to combat this issue.

The first attempt was to print with different diameter extrusion nozzles, feed rates, and jog speeds on top of and inside the substrate. The latter is representative of the method of ‘emb3d’ printing proposed by Wehner et al 2016 [19]. However, none of these methods worked out and the result generally ended up as a line of separate liquidmetal beads. It is theorized that one reason the ‘emb3d’ printing did not work was due to lack of oxygen inside the gel and therefore the oxide layer needed to stabilize the wire geometry could not form. It is worth noting that under the proper settings (slow jog speed & fast feed rate) that the metal beads are produced frequently enough to create something resembling a continuous line of metal, as shown in Figure 2.5, but the result is not uniform and may not be electrically connected due to separation by the oxide layer. Being that none of the standard printing methods were successful in producing continuous tracks of eGaIn, a custom extrusion tip was designed to hold print eGaIn.

![Figure 2.5: ‘Emb3d’ printing of eGaIn to form beads in contact with one another inside of a tough hydrogel.](image)
2.3.3.2 Design and Printing with a Novel Extrusion Tip

After handling the eGaIn long enough, it was observed that if the syringe was held at the proper angle, a short but continuous printed line could be achieved. This was understood as the eGaIn having the ability to flow well into its own skin, so it was theorized that if the metal could be extruded laterally onto of the gel it should produce a continuous line. Initially, this was tested by using a 1 mL insulin syringe on a glass slide with the bevel of the syringe pointed in the direction that it was extruding and it was observed that a continuous line could be produced fairly well.

Since handwriting in one direction with the insulin syringe was initially successful, a crude prototype was developed that could print the metal into its skin laterally in all directions. A scalpel was used to carve out notches in a 20 gauge plastic tapered extrusion tip purchased from Nordson EFD as shown in Figure 2.6 (B). The notches on each side allowed for the liquid metal to be extruded in all directions and the initial result was extremely successful as shown in Figure 2.6 (C).

Figure 2.6: (A) A line of eGaIn beads extruded from a standard tip on a glass slide. (B) A 20 gauge tapered extrusion tip with notches cut out by a scalpel allowing for the lateral extrusion of eGaIn into continuous tracks on a glass slide (C).

The method for printing eGaIn using a notched extrusion tip showed great potential, therefore a more sophisticated set of custom extrusion tips were made. There were two main designs; the first had hexagonal lateral openings that would allow the material to flow into its skin and not touch the surface of the gel as shown in Figure 2.7 (A and E). Variations of this tip included increasing the size of the hexagonal openings, which also decreased the total number of circumferential openings available. Openings were hexagonal due to the nature of the 3D-printing process in which they were created. Otherwise unwanted support material would have needed
to be generated in the openings and would not be able to be removed. The second tip had an open top allowing the material to touch the surface of the gel but had prongs on the end to force the material to flow laterally shown in Figure 2.7 (C and D). Variations of this tip included changing the number of surrounding prongs (3, 4, and 6). During post-processing of the extrusion tips, great care had to be taken when sandblasting the tips so as to not break the small pronged features on the top of the tip. In most cases, the extrusion head most likely did not receive enough sandblasting treatment to give it a smooth finish. However, this may have played to the advantage of printing the eGaIn and its potential effects will be discussed later on in this subsection.

![Figure 2.7: The SolidWorks models of the hexagonal (A) and 6-prong (C) extrusion tips and the fabricated 600 μm inner diameter extrusion tips after post-processing (B & D). All scale bars shown are 1 mm in length.](image)

Once the extrusion tips were fabricated, they were each tested to ascertain which tip was the most effective at extruding the liquid metal. Each one was tested by printing eGaIn tracks on a printed ICE gel substrate that was two layers thick (1 mm). It was immediately recognized that the tips with the circumferential hexagonal openings did not print continuous lines and the eGaIn seemed to preferentially flow out of one opening rather than flow between them depending on the direction that the printhead was moving. This observation also served as evidence that there needed to be a certain level of initial contact between the substrate and the liquid metal being extruded from the tip. It was observed that the pronged extrusion tips were much more successful in printing continuous lines, with the most consistent tip being
the 6-pronged one. When printing with the 3-pronged extrusion tip, it was clear that the eGaN preferentially exited out of a certain area and discontinuities were frequent throughout the print. When printing with the 4-pronged tip, discontinuities were less frequent, however, there was still evidence of preferential flow of the eGaN to a certain area. This would result in track widths of different diameters depending on the direction of movement and orientation of the extrusion tip.

Printing with the 6-prong extrusion tip resulted in the most uniform and continuous tracks out of all the custom extrusion tips. Further experimentation was performed to elucidate the factors governing print quality. In most extrusion and FDM 3D-printing methods, the track width is governed by the feed rate of the material and the jog speed of the printhead. Theoretically, this makes perfect sense as extruding more material into the same spot should create a larger amount of material at the area of deposition. However, this is not the case with eGaN due to its tendency to flow through its own oxide skin.

![Figure 2.8: Initial test tracks of printed eGaN at an extension rate of 40 dp/s (2.43 x 10⁻⁴ mL/s) with the jog speed increased incrementally in mm/min from 120 (A), 160 (B), 200 (C), 240 (D), and 280 (F).](image)

If the jog speed is too slow or the feed rate too high, the material will flow through its skin to the beginning of the print and 'balloon' (Figure 2.8A). If the jog speed is too quick or the feed rate too low, then the lines produced will be discontinuous and non-uniform (Figure 2.8E). The extrusion will begin with a thick line, potentially with a starting bead, and the diameter will decrease until the discontinuity ensues. Therefore, the jog speed and extrusion rate must be optimized and the ideal settings were found to be 40 dp/s (2.43 x 10⁻⁴ mL/s) and 310 mm/min with turns taken at 270 mm/min. To determine what governed the track width of the printed lines, a 6-prong extrusion tip was created with the same dimensions except with a different prong-to-prong diameter. It was found that a good correlation existed between the track width and the prong-to-prong distance of the extrusion head as shown in Table 2.1/Figure 2.9. Therefore, smaller track widths could theoretically be achieved if a smaller extrusion tip could be manufactured; however, available equipment is unable to fabricate these features on such a small object at this time. More intricate dimensions of the printed line aside from track width were not specifically measured, but goniometer images of the prints indicate that they were cylindrical. However, rheological properties of the substrate may result into the printed line sinking into
the gel due to the weight of the metal which may affect the geometry of the line. The effects of this on line geometry were not measured as it was deemed unimportant to the presented work but more on this phenomenon can be found in Chapter 3.

Table 2.1: The measured inner ($D_{inner}$)/outer ($D_{outer}$) diameters and prong-to-prong ($D_{P-P}$) distances of two custom extrusion tips and the measured track width ($D_{Tracks}$) from prints with each tip. (All distances are in mm)

<table>
<thead>
<tr>
<th></th>
<th>$D_{P-P}$</th>
<th>$D_{Inner}$</th>
<th>$D_{Outer}$</th>
<th>$D_{Tracks}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tip A</td>
<td>0.97</td>
<td>0.58</td>
<td>1.35</td>
<td>0.93</td>
</tr>
<tr>
<td>Tip B</td>
<td>0.76</td>
<td>0.51</td>
<td>1.24</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Figure 2.9: A close-up of the 6-prong custom extrusion tip under a visual light microscope with the prong-to-prong distance highlighted. Particles of the titanium alloy can be seen extruding from on the sides of the prongs.

The logic behind the development of the tip was to allow the eGaIn to easily flow omnidirectionally into its own ‘skin’ instead of relying on the material to favourably adhere to the hydrogel surface. It is easily understood how the eGaIn is extruded laterally, however, there seem to be some aspects of printing with the custom extrusion tip that are more difficult to understand. One of which is the level of contact required between the substrate and the eGaIn. Although there is an unfavourable surface interaction between the two that allows for the metal to be dragged across the surface, it needs a certain level of contact to actually stick to it. When the nozzle height of the tip is too high, it lacks the contact with the surface and a discontinuous track is formed, however, the tip also cannot be too close to the substrate or it will
force the eGaIn to extrude in an unwanted direction and a discontinuous line will then form. Another way of describing this is that although the tip provides for the omnidirectional lateral extrusion of the metal, continuous printing is also contingent upon the presence of a reservoir of metal in the center of the extrusion tip between and slightly below the prongs.

This theory is heavily supported by the fact that the prong-to-prong distance is closely related to the printed track width. It also brings to light the potential effects that the interfacial interactions between the printed titanium and eGaIn may have on printing. The difference between eGaIn adhesion to the custom tip and the plastic EFD tip is shown in Figure 2.10(A and B). As previously noted, the extrusion tips were subjected to various post-processing techniques including sandblasting, however, the pronged portions of the tip could not be sandblasted without damaging the prongs. By nature of the fabrication method and welding spot size to create the tips, the non-sand blasted portions of the final structure can have particles sticking out of the structure of up to 50 microns in size shown on the prongs in Figure 2.9. Given the large surface area that this creates, it is possible that an increased favourable interaction between the eGaIn and the non-sand blasted portion of the extrusion tip is present. This may allow the extrusion nozzle to act as a transport vessel for the eGaIn that can help ‘drag’ it along (2.10(C and D)). As the eGaIn is dragged across the substrate, more liquid metal is deposited and the oxide layer is constantly being broken and spontaneously repaired so as to increase the length of the ‘wire’ and the stabilizing ‘skin’ surrounding it. Further evidence supporting this is based on the observation that after the print, the extrusion head can be lifted over 1 cm off the substrate and the metal lift off the hydrogel substrate and stretch to stay attached to the extrusion tip without breaking. Lastly, it is worth mentioning that if the diameter of the extrusion nozzle is too large, the eGaIn (once extrusion has started) will continue to flow freely downward due to gravity without the assistance of the Zaber pump.

2.3.3.3 Device Creation

The overall structure was printed in 4 steps and is shown in Figure 2.11. 1) A base layer of the ICE gel was extruded, 2) the eGaIn tracks was extruded on top of the base layer, 3) ICE gel was extruded in the areas surrounding the eGaIn and 4) a top layer of ICE gel would be extruded to encapsulate the device.
Figure 2.10: Goniometer pictures of eGaIn being extruded from a standard 20 gauge extrusion tip (E & D) and the custom 6-pronged extrusion tip (A & C). The metal is extruded as a hanging drop from the tips (A & E) or extruded at a constant rate while moving over the surface of a hydrogel (C & D). Printing of the eGaIn material with the custom titanium tip allows for the liquidmetal to flow laterally into its own skin to produce a continuous “wire” (C) that cannot be achieved with a conventional extrusion tip due to beading (D).
CHAPTER 2. IDENTIFICATION OF A SOFT CONDUCTOR

Figure 2.11: The printing process of the device where the Gcode is interpreted by the LinuxCNC software and the paths that the nozzle will take are produced in three layers (A). The eGaIn wires are printed onto the hydrogel surface after the base layer is produced (B). The top layer of hydrogel is then printed onto the structure to encapsulate the eGaIn (C).

To achieve the maximum electrothermal heating of the bulk gel from eGaIn, the desired printed tracks would need to be as long, thin, and close to one another as possible. However, there were certain issues with the minimum distance that could be achieved between the tracks that were predicated upon the minimum turn radius that could be produced when printing eGaIn. It was observed that if the turn radius was too small, the unfavourable interaction with the hydrogels would allow for the metal to roll over on itself and form something close to a straight line as shown in Figure 2.12. This problem made it impossible to form numerous tracks concentrated in the area meant to be heated.

The printed heating element of eGaIn was limited to tracks with a turn radius of 2.3 mm. Overall, great care needs to be taken when printing, as even with the increased turning radius the extrusion head ‘pulls’ on the metal track and it rolls into the turn. Therefore, even if rolling is not observed there is still a force being exerted that causes a slight deviation and can cause an increased chance of track discontinuity. Any printed turn will have this slight deviation and therefore the code for the printed gel surrounding the eGaIn needs to be adjusted to compensate for this. After these considerations are taken into account, the printing of the device is relatively straightforward. It was then fully cured with UV irradiation, and swollen in 0.076 M CaCl₂ for 24 hours followed by H₂O for 24 hours with final swollen dimensions of approximately 72 x 24 x 4 mm³.

2.3.3.3.1 Connections to eGaIn

The largest unsolved issue in the device is the creation of a connection between the eGaIn in the hydrogel and the power supply. This relies on creating an interface between a hard (wire) and soft (gel) material with strong adhesive properties, which is a very well-known and difficult challenge in soft robotics. For the work presented in this section, the wires were placed into the gel prior to curing and swelling the
sample. Once the sample was cured, the device was very delicately picked up and UV curable Emax elastomer was put around the wires and used to seal them onto the gel. The device expanded as the hydrogel was swollen in CaCl\textsubscript{2} and H\textsubscript{2}O. As the hydrogel expanded, so did the holes that were created when the wires were inserted into the gel. Problematically, the diameter of the wire itself was unable to expand to match the increase in diameter from the holes. This creates a geometrical mismatch between the two and produced a prevalent failure point in making the samples. Initially, this did not seem problematic, however, the channels that hold the eGaIn inside the device also increased in diameter. Given that it is a closed system and the volume of eGaIn stays constant during the swelling process, a small vacuum is created inside the eGaIn channels. If the vacuum is broken (most likely at the wire-gel interface), the metal will come together due to its high surface tension and a discontinuity will be formed in the track. If this happens, the only way to repair the sample is to pull out the wires, remove all the metal inside of the hydrogel, inject new metal into the tracks, and reinsert/reattach the wires. Alternatively, the wires can be inserted after the device is cured/swollen but that still runs a very high probability risk of disrupting the vacuum and forming a discontinuity. Many different attempts have been made to provide a proper seal between the wires and the hydrogel including different types of glues and gels, but none have been successful so far. Ideas to improve this connection are proposed in Chapter 5, but have not been tested. Although the connection is a daunting task, efforts were made to be very gentle with the samples as to not disrupt the connection. In the event that the seal was broken, it was repaired as stated above.

2.3.3.3.2 Electrothermal Heating

To investigate the use of eGaIn for electrothermal heating, two samples were made as per the method described above and potentials of 2, 3, and 4 V were applied for
15 minutes for three separate cycles. The change in temperature was recorded with an IR camera and is shown in Figure 2.13. Between cycles, the samples were left to rehydrate in H2O for 30 minutes and were found to have lost an average of 4% weight assumed to be water content during the 15 minutes.

![Image of hydrogel device with temperature graphs](image)

**Figure 2.13:** The 3D-printed hydrogel device with eGaIn wires immediately after printing. After the insertion of connecting wires and post-processing previously described, a potential difference of 2, 3 and 4 V were applied and the temperature change was recorded over time (b). Three separate heating cycles were conducted at each applied voltage. Average temperature of the selected region (box) was recorded with an IR camera and is shown at 0 (c), and 900 seconds after a voltage of 4 V was applied (d).

It was observed that the temperature of the bulk gel rose above the LCST of NIPAM when a potential of 4 V was applied. The asymptotes in the temperature curve can be explained as the equilibrium state at which the power produced through electrothermal heating is equivalent to the energy being dissipated to the environment. The highest applied voltage was 4 V corresponding to an average current of 4.6 Amps due to a current limit on the power supply of 5 Amps. Theoretically, the hydrogel could heat up quicker and to a higher temperature if a higher voltage was applied, but there was no equipment readily available to test this.

### 2.4 Conclusion

Previously published studies have addressed the wide uses for ionically conductive hydrogels and it is presented here that they can be used to temporarily raise the temperature of a printed hydrogel structure. However, there were many unfavourable issues with the process such as electrolysis of water, production of chlorine gas, loss of connection, and a relatively low final temperature when heated. Overall, ionically conductive hydrogels did not seem suitable for applications of electrothermal
heating of gels above the transition temperature of NIPAM hydrogels. The afore-
mentioned issues can be succinctly expressed in the fact that large voltages and salt
concentrations are needed to heat the gel up and the voltage required to achieve
the electrolysis of water is extremely low (∼ 1.2 V). Therefore, other materials were
explored for electrothermal heating purposes.

The incorporation of VGCNFs into hydrogel materials did create a soft conductor
produced heat when a voltage was applied across it, however, it was not chosen to
serve as an electrothermal heating element for this study. Conductive hydrogels show
great potential in future applications, but making it compatible with 3D-printing
is extremely difficult. First and foremost, there would have been a lot of further
optimization to develop a final precursor ink. It would have required a fine balance
between finding the lowest amount of VGCNFs to not clog the extrusion tip but still
remain above the percolation threshold to establish a conductive network. Further
considerations would have been needed to ensure that the minimum sonication time
was being used as to not damage the VGCNFs or the polymer. Even if all this was
achieved, the final result would still be a material that cannot be polymerized by UV
light. In the end, it was determined that time would be better spent exploring other
more promising areas in search of a soft stretchable conductor for electrothermal
heating.

eGaIn was identified as a suitable stretchable, flexible, soft conductive material and
a method for its incorporation into hydrogel materials was successfully developed
and understood. eGaIn itself is a very tricky material that does not follow the
standard rules that govern extrusion printing of standard viscous materials. The
6-prong extrusion tip allows for the omnidirectional lateral flow of material into
its own oxide skin to form continuous lines and overcome the unfavourable surface
interaction between the eGaIn and hydrous substrate. The overall theory of how
it works is easily understood, however, some of the more intricate reasons for its
success can only be supported by observation and have not been quantified. This
has been the most promising soft conductor found for the proposed application and
eGaIn was chosen as the material of choice for future experiments. However, further
work is still required to develop a robust connection between the liquid metal and
external power supply.
Chapter 3

3D-Printing Multimaterial Actuating Hydrogel Structures

3.1 Brief Overview

A critical aspect of the proposed hydrogel finger will be the arrangement of structural and actuating hydrogel materials in the appropriate geometrical structure to produce the largest actuation. Up to this point, the structural hydrogel used for printing was modelled off ink formulations previously reported in recent work at the University of Wollongong by Shannon Bakarich [62, 63]. However, the inks presented in Chapter 2 contained a lower (0.076 M) [CaCl$_2$] than reported in the publications (0.1 M). When [CaCl$_2$] was raised to match the previous ink formulations, it was observed that the gel could no longer support the eGaIn tracks. Investigating this problem uncovered an issue with past gelation methods for the alginate that could have ramifications in terms of resultant mechanical properties, but should not affect the thermal properties of the gel. This chapter will focus on revisiting the structural ICE gel precursor ink formulation to be used and optimizing it for incorporation with eGaIn. Lastly, the chapter documents the performance of the fabricated fingerlike multimaterial 3D-printed actuating hydrogel structure.

3.2 Experimental

3.2.1 Precursor Ink Development

Oxygen is known to inhibit the curing process of acrylamide-based hydrogels because it readily reacts with the radicals formed during the process and inhibits the polymerization reaction. Oxygen inhibition is prevented by placing the hydrogel samples under vacuum for 10 minutes prior to loading them into the syringe barrels and curing in a N$_2$ filled environment.

3.2.1.1 Refining Gel Formation Process

All materials were purchased from the same companies and were prepared as described in section 2.2 unless otherwise stated. Two series of alginate hydrogels (A and B) were made with the same materials (Table 3.1), but added together in a different order.
Table 3.1: Series of alginate hydrogel formulations while varying the [CaCl₂] and keeping the amount of alginate constant (450 mg).

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂O</th>
<th>0.1 M CaCl₂</th>
<th>Final [CaCl₂] (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>1</td>
<td>6.67</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>2</td>
<td>13.3</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>3</td>
<td>20.0</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>4</td>
<td>26.7</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>5</td>
<td>33.3</td>
</tr>
</tbody>
</table>

In series A, the H₂O and 0.1 M CaCl₂ solutions were mixed together into a sample vial and the alginate was added last in 2 equal parts by stirring with a spatula until fully dissolved. In series B, the alginate was dissolved into the H₂O in 2 equal parts first, followed by the addition of CaC₂ in 1 mL aliquots with gentle stirring by hand with a spatula for approximately 30 seconds in between each aliquot.

3.2.1.2 Reformulating ICE Gel Precursor

All materials were purchased from the same companies and prepared as described in section 2.2 unless otherwise stated. A series of ICE gel precursor inks were created in a sample vial containing 4.5 mL 40% (w/v) Aam solution, 38.7 mg MBAA, 36.9 mg α-keto, 450 mg alginate with varying amounts of 0.1 M CaCl₂ and H₂O according to Table 3.2 by stirring with a magnetic stir bar until the solution became viscous enough that the stir bar had no effect. At this point, the solution was gently stirred by hand with a spatula until fully dissolved. The CaCl₂ was added in 0.250 mL aliquots with gentle stirring by hand with a spatula for approximately 30 seconds in between each aliquot.

Table 3.2: A series of alginate/polyacrylamide ICE gel precursor inks made by varying the amount of CaCl₂ used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂O</th>
<th>0.1 M CaCl₂</th>
<th>Final [CaCl₂] (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>8.75</td>
<td>0.25</td>
<td>1.90</td>
</tr>
<tr>
<td>3</td>
<td>8.50</td>
<td>0.50</td>
<td>3.70</td>
</tr>
<tr>
<td>4</td>
<td>8.25</td>
<td>0.75</td>
<td>5.60</td>
</tr>
<tr>
<td>5</td>
<td>8.00</td>
<td>1.00</td>
<td>7.40</td>
</tr>
<tr>
<td>6</td>
<td>7.50</td>
<td>1.50</td>
<td>11.0</td>
</tr>
</tbody>
</table>
3.2.1.3 Rheological characterization & 3D-Printing

Rheological analysis was carried out using an Anton-Paar Physica MCR 301 Digital Rheometer with a cone and plate measuring system (40.072 mm diameter, 0.992° angle, 97 μm truncation) at 21 °C. The shear rate was ramped from 0.1 to 100 s⁻¹ with 20 seconds per measuring point after preshearing at 0.1 s⁻¹ for 2 minutes. The viscosity and shear stress of the samples were then plotted separately against the shear rate.

3D-Printing was done on the same LinuxCNC based printer described in subsection 2.2.1.2. Once the print was complete a drop of eGaIn was placed into the structure by hand and left for 10 minutes to determine if the liquid metal sank into the hydrogel.

3.2.2 Printing a Multimaterial Actuating Fingerlike Structure

All materials were purchased from the same companies and prepared as described in section 2.2 unless otherwise stated. All inks were prepared at 21 °C. The ICE gel precursor inks were created by mixing together 9 mL 40% (w/v) Aam solution, 77.4 mg MBAA, 73.8 mg α-ketoglutaric acid, 900 mg alginate, 17.5 mL H₂O, and 0.5 mL of 0.1 M CaCl₂ in a sample vial with a magnetic stir bar. The CaCl₂ was added in 250 μL aliquots with gentle stirring with a spatula for approximately 30 seconds in between each aliquot. The actuating hydrogel precursor ink was created by mixing together 2.25 g NIPAM, 15 mg MBAA, 90 mg α-ketoglutaric acid, 450 mg alginate, 14.7 mL H₂O, and 330 μL of 0.1M CaCl₂ stirred together in a sample vial with a magnetic stir bar. The CaCl₂ was added last in 2 equal parts with gentle stirring with a spatula for approximately 30 seconds in between each part. If any solution became too viscous that the stir bar had no effect, the solution was stirred by hand using a spatula until completely dissolved. All printing and post-processing was done as previously described in subsection 2.2.1.2 except the samples were cured in a portable refrigeration unit (Powertech 12VDC Portable Cooler & Warmer, JayCar Electronics) filled with N₂ and set to a temperature of 10 °C. The chamber was pre-purged with N₂ for approximately 15 minutes before the sample was placed inside.

3.3 Results and Discussion

3.3.1 Ink Development

3.3.1.1 Refining Gel Formulation

It is well known that alginate cross-links ionically with divalent cations and therefore, the addition of more calcium ions to the precursor solution should cause an increase in crosslinking and viscosity of the gel [71]. When adjusting from the low [CaCl₂] to the one reported in [63], it was observed that the tracks of eGaIn printed on top of the gel were not supported and the liquid metal sank into the gel. The reason for this behaviour was unclear and the following tests were done to further investigate.
Series A (alginate added last) was made and it was observed that with increasing [CaCl$_2$], the appearance of the gel changed and small almost granular particulates were observed, as shown in Figure 3.1 (A and C). The material in the sample vial would readily flow like a liquid at high [CaCl$_2$]. After a period of a few hours it was observed that there was some sort of phase separation occurring in the material in the sample vial, indicating that the gel was not homogeneous.

**Figure 3.1:** Alginate hydrogels of the same formulation but with either alginate (A and C) or CaCl$_2$ (B and D) added last.

After observation using a microscope, it seemed as if the gel being formed showed characteristics of a microgel and not a uniformly crosslinked hydrogel. The inhomogeneous microgel structure could have formed if the alginate was cross-linked immediately upon addition to the solution in discrete ‘packets’ and would explain the granular nature of the resultant gel. As the [CaCl$_2$] increased in the alginate solution, the size of the granules decreased and the gel became cloudier. This evidence supports the above hypothesis as it could be theorized that increasing [CaCl$_2$] could lead to alginate crosslinking in a more localized environment and result in the smaller microgel granules. Overall, it seemed that the alginate microgel formation was a result of the crosslinking process happening too quickly (almost instantaneously) so that highly crosslinked granules formed before the alginate could be uniformly dispersed throughout the solution. A method to control the crosslinking speed would be to add the CaCl$_2$ to an alginate containing solution; therefore, series B was made and is shown in Figure 3.1 (B and D).
The differences between series A and B were observed immediately upon creating the two gels side-by-side. When the CaCl₂ is added last in small increments the gel that forms appears clear and much more homogeneous as shown in Figure 3.1(B). To quantitatively assess what was happening, viscosity measurements of both series A and B were taken and results are shown in Figure 3.2. Additional rheological measurements including full flow curves, consistency indices (K), flow behaviour indices (n), shear stress (τ) curves, and the yield stress (τ₀) values can be found in Appendix 2. Viscosity measurements for the sample containing 5 mL of 0.1 M CaCl₂ where CaCl₂ was added last are not reported as it was impossible to get the gel evenly spread along the plate of the rheometer due to its very high viscosity. Overall, this material had a tendency to non-uniformly crumble and squeeze out of the measurement area.

![Graph](image)

**Figure 3.2:** The measured viscosity of alginate gels with varying [CaCl₂] at a shear rate of 0.1 s⁻¹. The two types of hydrogels either had alginate added last (blue diamonds) or CaCl₂ added last (red squares).

Viscosity measurements reaffirm the observation that for samples in which alginate was added last, the viscosity decreases with increasing [CaCl₂]. Whereas for samples with CaCl₂ added last, the viscosity of the sample continues to increase with [CaCl₂] until the issues with measurement became structural. From this point onwards, it was noted that the order in which alginate and Ca²⁺ is added dictates whether formation of a homogeneous hydrogel or a microgel will occur. The rheological data suggests microgel formation may only occur for [CaCl₂] above a certain threshold and, below this level, the gel structure may be similar regardless of the method of forming the gel. However, further experimentation into the microstructures will be required to prove this hypothesis. It would also follow that the same behaviour would occur for divalent cross-linkers other than Ca²⁺. However, the concentration
threshold at which microgel structures form would depend greatly on a number of factors including the ratio of the \( G/M \) blocks in the alginate and the affinity between the alginate and the chosen cation.

3.3.1.2 Reformulating ICE Gel Precursor

For a material to be compatible with extrusion printing, it needs to possess adequate rheological properties to allow it to be smoothly extruded through the syringe and still hold its 3D structure once printed. In this specific case, an additional requirement was imposed on the material in which it must be stiff enough to support an overprinted track of eGelu. Finding a balance between these properties was achieved by adjusting the amount of alginate gelation induced in the precursor ink. Therefore, a series of ICE gel precursor inks with varying CaCl\(_2\) amounts were made using the method where CaCl\(_2\) was added last. Figure 3.3 shows the viscosity (at 0.1 s\(^{-1}\)) as a function of CaCl\(_2\) concentration. Rheological measurements are not reported for the samples containing 11.1 mM CaCl\(_2\) as too much gelation had occurred to obtain accurate measurements.

![Figure 3.3: The measured viscosity at a shear rate of 0.1 s\(^{-1}\) for ICE gels with different amounts of [CaCl\(_2\)].](image)

The viscosity of the gel increases with increasing \([\text{CaCl}_2]\) as is expected and the values are larger than those in 3.2, which is most likely due to the other substances in the precursor ink. A 3D object was then printed with each hydrogel ink to assess what produced the best structure. As a general trend, as the \([\text{CaCl}_2]\) increased, the uniformity of printed lines and quality of the overall structure decreased. All samples were able to hold the structural integrity of the print, but the printed lines became much more globular with an occasional stop-start pattern in the gel as shown in Figure 3.4 (A & B). These defects were the result of too much gelation and the tip
getting partially clogged on occasion. Eventually the pressure built up and caused more gel to spurt out than desired. Given that the gel precursor ink is transparent, the smoothness of the print could be assessed by the ability to read a given line of text on a piece of paper through the hydrogel as shown in Figure 3.4 (C & D).

![Figure 3.4: 3D-Printed alginate/polyacrylamide hydrogels containing final CaCl₂ concentrations of 0 (A & C) and 7.4 mM (B & D). Samples were placed over text to observe the transparency of the printed structure (C & D).](image)

On the samples with lower [CaCl₂], the ink is extruded smoothly and light is able to pass through the sample very well as shown in Figure 3.4 (C). However, as the concentration increased and the printed lines got more globular, the structure as a whole became less smooth and the light passed through the hydrogel in a distorted fashion causing the text to appear irregular as shown in Figure 3.4 (D).

On a side note, it is worth briefly mentioning that the original gel precursor ink proposed by Bakarich et al. [63] used ethylene glycol as a rheological modifier to prevent evaporation and was not used in the ink formulations presented above. All prints were done in a humidity controlled laboratory environment and there were never any detrimental effects of evaporation observed in the absence of ethylene glycol. In an effort to keep the system as simple as possible, ethylene glycol was replaced with H₂O in the ink formulation. Compared to the previous literature, it does not seem as if the presence of ethylene glycol had significant effects on the rheological parameters. Furthermore, it is unknown if it had any significant effects on the mechanical properties of the printed structure as this was not tested.

Given the high density of eGaIn (6.25 g/mL), the liquidmetal tracks can sink through to the base of the device due to gravitational effects, i.e., the gel network is not strong or stiff enough to support the weight of eGaIn. If this were to occur, the eGaIn would no longer be encapsulated in the hydrogel and freely flow out of the channels as soon as the printed structure is removed from the glass substrate. Therefore, an additional requirement of the ink is that the printed structure must be able to support the eGaIn wire. Mathematically, this can be represented by comparing the
pressure exerted by the normal force of the eGaN tracks to the yield stress of the ICE gels under the assumption that the yield stress, determined from shear rheology, can be used as an approximation of the compressive yield stress. The pressure can be expressed as:

\[ P = \frac{F}{A} \]  

(3.1)

where \( P \) is the pressure (Pa), \( F \) is the normal force (N) exerted by the eGaN, and \( A \) is the contact area (m²). The yield stress can be approximated from the low shear rate region (<1 s⁻¹) of the rheological data using a Bingham Model [57]:

\[ \tau = \tau_y + \eta \dot{\gamma}^n \]  

(3.2)

where \( \tau \) is the shear stress (Pa), \( \tau_y \) is the yield stress (Pa), \( K \) is the consistency index (Pa sⁿ), \( \dot{\gamma} \) is the shear rate (s⁻²), and \( n \) is the flow index. The yield stresses of the different ICE gel precursors can be found in Table 3.3 and a more comprehensive array of full flow curves, shear stress curves, and rheological parameters can be found in Appendix 2.

**Table 3.3:** The measured yield stress of the ICE gel precursors as approximated by a Bingham Model:

<table>
<thead>
<tr>
<th>[CaCl₂] (mM)</th>
<th>0</th>
<th>1.85</th>
<th>3.70</th>
<th>5.56</th>
<th>7.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau_y ) (Pa)</td>
<td>83 ± 2</td>
<td>199 ± 1</td>
<td>218 ± 2</td>
<td>257 ± 4</td>
<td>281 ± 4</td>
</tr>
</tbody>
</table>

Consider a conservative estimation of an eGaN track weight with a track width of 0.9 mm and height of 1.5 mm. By using the density of eGaN and Eq. 3.1, a pressure value of 91.8 Pa can be calculated, which serves as an approximate lower threshold for the compressive yield stress of an appropriate ICE gel precursor for supporting the eGaN tracks. This would predict that the sample with no CaCl₂ would not be able to support the eGaN, but the ones with higher CaCl₂ should. To test this, a small drop of liquid metal was placed on top of the gel and observations were made as to whether or not it sank into the gel after 10 minutes had elapsed. It was observed in all samples, except for the one lacking CaCl₂, that the eGaN was supported and would be suitable to hold liquid metal wires. The ideal precursor ink would be the one containing just enough CaCl₂ to support the eGaN wires, but not enough to adversely impact the print quality. Therefore, the hydrogel precursor containing 1.85 mM CaCl₂ was selected as a suitable ICE gel precursor ink for the creation of the hydrogel finger.
3.3.2 Printing of an Actuating Finger

The chosen ICE hydrogel precursor ink is very compatible with extrusion printing, making the printing process extremely simple. The goal was to print a structure similar to the one shown in Figure 3.5. The structural material, shown in blue, would be made of the alginate/pAAm hydrogel. Two 'joints' placed along the finger, shown in gray, would contain the actuating FNIPAM hydrogel. Therefore, when the printed FNIPAM undergoes a phase transition and shrinks, the fingerlike structure should bend at the 'joints.' The ICE gel structure was printed first at an extrusion rate of 40 dp/s (2.16 x 10^{-4} mL/s) with a jog speed of 400 mm/min. Following the print of the ICE gel, the syringe barrel was swapped out and the NIPAM ink was printed into the 'joints' of the finger. Although the printing process is relatively straightforward, the post-processing required can complicate the process.

![Image](image1.png)

**Figure 3.5:** An example model created in solidworks for a hydrogel 'finger' to be 3D-printed cut of structural alginate/pAAm hydrogel (blue) and actuating alginate/FNIPAM hydrogel (gray).

A large issue when fabricating the multi-material fingerlike structure comes from the intrinsic property of the NIPAM precursor ink to phase separate and form a white paste rather than a uniformly cross-linked hydrogel during the curing process as shown in Figure 3.6. This occurs when the temperature of the NIPAM gets too high before being fully cured and produces a phase separated structure that does not actuate. Given that the chosen curing method involved UV irradiation, which raises the temperature of the hydrogel, this phase separation occurred readily. It was observed that phase separation would repeatedly occur in the printed sample when cured at room temperature (21 °C) with an intensity of approximately 5 mW/cm². Alternatively, the gel can be cured in a temperature controlled environment. This would negate the temperature rise in the gel from the UV irradiation given a low enough surrounding temperature. Initial attempts at this involved printing the multi-material structure as previously described and curing it in a portable DC powered cooler system kept at 10 °C. It was observed that doing this alone was not adequate enough to prevent the phase separation. The approach was modified and it was found that the printed samples must be placed in the freezer (-18 °C) for 6 minutes prior to curing in the portable cooler. The sample could then be fully cured after exposure to 5 mW/cm² UV irradiation for 17 minutes.
Figure 3.6: Alginate/NIPAM ICE hydrogel was extruded into the joints of an alginate/pAAm ICE hydrogel that was fully cured beforehand. The temperature increase of the NIPAM during the curing process caused a phase separation resulting in a white paste that did not adhere to the alginate/pAAm gel.

The logical next step in the creation of the hydrogel finger is to determine the geometrical organization of actuating and structural material to achieve the largest actuation. Actuation of PNIPAM hydrogels can easily be induced upon immersion into a water bath above 30 °C. Each sample was placed in a 65 °C water bath to observe actuation of the hydrogel, indicated by a color change from clear to white. However, it was observed that none of the printed hydrogels showed any color change/actuation when immersed in the water bath for 10 minutes. This provided evidence towards the fact that the concentration of the PNIPAM chains was too low in the joints to cause any favorable reconfiguration of the polymer chains to occur when heated. It was theorized that during the time between when the sample was in the freezer and being fully cured, the NIPAM monomers were dispersing into the rest of the bulk gel away from the hinge. In order to minimize the diffusion of the NIPAM monomers into the bulk gel, the NIPAM precursor ink was kept in contact with the other gel for the least amount of time possible prior to being fully cured.

The most successful approach to minimizing the contact time was by reducing the 6 minute pre-cooling time in the freezer. This was achieved by printing the structural ICE gel and then placing the printed structure and the syringe containing NIPAM in the freezer prior to printing the NIPAM in the joints. The structure was cured in the portable cooling system immediately after the NIPAM was printed, but still showed evidence of phase separation. This indicated that the complete printed structure still needed to be left in the freezer prior to curing. Overall, pre-cooling the printed structural gel and NIPAM syringe reduced the amount of time the complete printed structure needed to be placed in the freezer by 3 minutes and thus reduced the amount of time the NIPAM precursor was in contact with the bulk gel. This resulted in a printed fingerlike structure with PNIPAM actuation that caused the tip of the finger to move by approximately 5 mm as shown in Figure 3.7 (A & B).
For reference, PNIPAM is located on the right hand side of the finger-like structure shown in Figure 3.7. It should be noted that the 'finger' appears more bent in 22 °C water (Figure 3.7 (A)) than in 65 °C water (Figure 3.7 (B)). This indicates that the swelling ratio of PNIPAM gel is larger than that of the structural gel when fully swollen in 22 °C water. When subsequently heated to 65 °C, the PNIPAM swelling decreases and produces a smaller bending angle in the finger.

**Figure 3.7:** A finger-like structure (emphasized with a black line), composed of structural and actuating hydrogel material is immersed in water at 22 °C (A) and 65 °C (B) with a protractor for reference. A top view (C) of the finger-like structure indicates where actuating material was printed (between the solid black lines) and where it showed actuation (between dashed lines), indicated by a color change to white. An example of how the angles were measured to quantify actuation is shown in (A).

It was anticipated that the entire section of printed PNIPAM would actuate. However, as shown in Figure 3.7 (C), less than half of the printed PNIPAM (between the solid black lines) underwent the phase transition and is indicated by the white coloured gel between the hashed lines. The bending of each joint was analyzed by measuring the angle change in ImageJ as shown in an example in Figure 3.7 (A). The angles of the 'joints,' \( \phi_1 \) and \( \phi_2 \), changed by 11 ± 2.7 and 9 ± 2.4 degrees respectively. It was observed that one PNIPAM 'joint' (farthest from the hand, \( \phi_1 \)) may actuate more so than the other, but this could not be considered significant without further experimentation. A factor that may play a role in this would be the order in which the joints were printed. This would give the PNIPAM monomers in one of the joints slightly more time to diffuse into the surrounding structural gel and the lower NIPAM concentration would result in a smaller actuation. It could also be possible that by nature of the second 'joint' having less gel to move at the end of the finger than the more central 'joint,' less force is required to provide larger movement on that area.
3.4 Conclusions

It was observed that the order of adding CaCl₂ and alginate plays a fundamental role in the gelation process when creating alginate hydrogels. Adding alginate last to a solution with high enough [CaCl₂] results in something resembling a microgel, whereas adding it first results in a uniformly crosslinked hydrogel. Alginate has been extensively studied and it has been widely reported in the past that many different factors affect its gelation [71]. Overall, anything that is able to slow the gelation process will form a more uniform gel with superior mechanical properties. Therefore, adding CaCl₂ at the end in small increments should produce the most uniformly crosslinked gel, which was supported with rheological measurements.

It was apparent that for the ICE precursor ink to be suitable for extrusion printing, it would need to contain a certain level of alginate gelation to support the eGaIn wires and hold its 3D structure. Overall, rheological analysis followed by observing if the printed structure could support eGaIn tracks helped to determine the final hydrogel precursor ink formulation for encapsulating eGaIn wires in a 3D-printed structure. Only a very small [CaCl₂] (1.85 mM) is required to give enough gelation to result in a suitable ink for extrusion printing and this amount can easily be varied depending on the purpose. For instance, less CaCl₂ could have been used if the hydrogel did not need to support the liquid metal.

Many factors that play into the fabrication of multimaterial hydrogel structures containing NIPAM. It was found that precautions need to be taken when curing to avoid the phase separation of the actuating gel. One method that proved effective was to pre-cool the structure in the freezer (-18 °C) and cure it in a temperature controlled environment (10 °C). Another factor that needs to be taken into account is the diffusion of the NIPAM monomers into the bulk gel prior to curing. Even with the optimum conditions in the current experimental setup, an estimate of less than 50% of the printed NIPAM gel was observed to undergo the conformational change and actuate the fingerlike structure. The observed finger angle actuation of 10° demonstrated the feasibility of 3D-printing a hydrogel actuating finger. Further improvements in the processing methods would produce larger bending displacement.
Chapter 4

A Soft Stretchable Sensor for Simulated Peripheral Nerve Signals

4.1 Introduction

One of the key aspects of a prosthetic limb is the interface it will have with the body to transmit and receive information. Peripheral nerves are composed of an extremely complex organizational hierarchy of neurons surrounded by different membranes and structures that provide blood flow and nutrients. Replicating such a complex structure is extremely difficult, and mimicking the compound action potential (CAP) that is propagated down the nerve adds to the challenge. This chapter focused on determining if simulated ‘nerve’ signals could be detected in a proposed capacitive coupling system. The ‘nerve’ signals were replicated by passing a signal from a waveform generator through a line of LiCl loaded pAAm hydrogel. The fully soft, stretchable, and transparent device was made from poly(dimethylsiloxane) (PDMS) and LiCl loaded pAAm hydrogel and was used to detect the simulated ‘nerve’ signals through capacitive coupling.

4.2 Experimental

PDMS and curing accelerator (Shin-Etsu Silicones) were combined in a 10:1 ratio and mixed for 2 min in a planetary centrifugal mixer (Thinky, ThinkyMixer ARE-300) at 2000 rpm. The PDMS precursor was extruded by hand onto a pre-cut 5 mm acrylic sheet using a 5 mL syringe and cured for approximately 12 hours in an oven at 65 °C. The PDMS was then treated with O₂ plasma (SPI Supplies, Plasma Prep II) at an O₂ pressure of 982 mTorr, vacuum pressure of 275 mTorr, and radio frequency power of 80 W for 60 s. After treatment, the PDMS was submerged in a sealed container filled with DI H₂O (resistivity = 18.2 MΩ cm) for storage.

The hydrogel precursor to be extruded onto the PDMS surface was created as per previously reported methods (Tian et al 2017) [104]. Prior to extrusion, the PDMS was removed from the H₂O and blown dry with N₂ gas. The hydrogel precursor was deposited onto the PDMS via a hand-held printing method. After printing, it was exposed to UV light (8 W 365 nm, UVP, UVLS-28 EL, effective dose of 6 mW cm⁻²) until fully cured in a N₂ filled humidity controlled environment (43%) made
by blowing N₂ gas through a saturated solution of potassium carbonate. Once cured, the sample was covered in another layer of PDMS by hand-held printing and cured by baking for approximately 12 hours in an oven at 65 °C. The sample was removed from the oven and left to soak in DI water for at least 12 hours (until testing).

To simulate peripheral nerve detection, a sample ‘nerve’ made of the same conductive hydrogel described above was deposited onto the device using hand-held printing. The sample was suspended vertically with an insulated gripper and wires were connected from a function generator (Keysight Technologies, Model 33500B) to the ‘nerve’ that passed a sinusoidal signal with varying peak-to-peak amplitude (0.1 – 1 V) and frequency (1 kHz – 10 MHz). Wires were connected from an oscilloscope (Keysight Technologies, Model DSO1004A) and were pierced through the PDMS by hand to be in contact with the hydrogel encapsulated in the PDMS. All leads to ground were grounded together and a schematic of the final experimental setup is shown in Figure 4.1. A total of 3 samples were made and the signal output from each of the printed hydrogel sensors were recorded from the oscilloscope relative to the input signal. The recorded signal was analyzed in relation to the contact area between the ‘nerve’ and the PDMS above the electrode, which was measured in ImageJ.
Figure 4.1: (A) Schematic of passing simulated nerve signals through a model 'nerve' made of conductive LiCl loaded pAAm hydrogel (orange) through PDMS (blue) to a soft electrode made from the same LiCl loaded pAAm hydrogel (green) via capacitive coupling. $S_1$ and $S_2$ indicate the output from each electrode pad to be displayed on an oscilloscope. (B) The vertically suspended hydrogel-elastomer device (indicated by white box and arrow) for sensing simulated nerve signals in the current experimental setup. (C) where a signal is passed from a waveform generator (1) through the device (2) to an oscilloscope (3).

4.3 Results & Discussion

4.3.1 Considerations of Creating the Nerve Sensor

A function generator passing a sinusoidal signal through a line of conductive hydrogel (approx. 1 mm track width) was used to simulate a nerve signal after the following considerations were made. This is the same conductive hydrogel used by Tian et al. 2017 and the geometry of the extruded lines was similar to what was previously reported [104]. Sensory nerve signals propagate down the axon at speeds of up to 120 m/s, but peripheral nerve signals travel at much slower speeds of about 50 - 60 m/s [127, 128]. In a cuff electrode implanted inside an animal on a peripheral nerve, the two electrodes are spaced at an approximate distance of 2 mm apart [43]. A conservative estimate could be made to consider a CAP passing down the axon
of a nerve at 95 m/s. This signal would reach the second electrode approximately 0.2 ms after the first. Therefore, for the proposed system to be able to distinguish a peripheral nerve signal, it would need to resolve signals of at least 50 kHz. The only other consideration that would need to be made is determining if the device can detect signals of a comparable amplitude to the CAP of a peripheral nerve, so attempts to find the smallest possible detectable amplitude were made.

The proposed device uses capacitive coupling to detect a signal in a non-contact method through a dielectric material (PDMS). In this specific case, the ‘nerve’ passes a signal down through it, which is in contact with the PDMS. The signal passes through the PDMS and is transmitted through the conductive hydrogel wires to the oscilloscope. The fabrication of the device was relatively straightforward; it should be noted that the materials were extruded by a hand-held printing approach, but all materials have been shown to be compatible with 3D-printing methods [104]. The PDMS was deposited and thermally cured in a straightforward manner, but required surface modification with O₂ plasma prior to printing the hydrogel onto the surface. The treatment increased the adhesion between the hydrogel precursor and the PDMS. The plasma treatment of the PDMS causes the formation of hydroxyl groups on the surface allowing for the hydrogel to adhere via hydrogen bonding. The plasma treatment is only temporary when exposed to atmosphere, so the PDMS was stored in H₂O to preserve the orientation of the hydroxyl groups to the external surface until immediately before the extrusion of the ‘nerve.’ Once the hydrogel was printed and cured, a final layer of PDMS was extruded, by hand, on top and cured to encapsulate the gel. Being that the PDMS is thermally cured, the hydrogel dries out in the curing oven and must be rehydrated. During this step it is critical to ensure that the PDMS layer on top of the hydrogel is uniform, otherwise when the hydrogel begins to swell it may burst out of the system via a weak point in the PDMS. During the experiment, the device was suspended vertically with an insulating gripper to reduce external noise and ensure that the signal would pass through the device and not to any other potentially grounded surface.

4.3.2 Quantifying Signal Detection

A range of frequencies and amplitudes of a sinusoidal waveform were generated and passed through the device. The initial noise of the system was measured on the oscilloscope to be around 12 mV_{pp}, where V_{pp} is the peak-to-peak voltage. Initially, 1 V_{pp} was passed through the hydrogel ‘nerve’ at a range of frequencies to determine the highest possible frequency that could be resolved and to determine the effects of frequency on signal detection. The coupling was reported as the signal detection efficiency, (\% \text{V}_{out}/\text{V}_{in}), where \text{V}_{in} is the peak-to-peak input voltage and \text{V}_{out} is the peak-to-peak output voltage. This process was repeated with the signal passing in the opposite direction of the conductive gel to determine if there was any difference in the magnitude of coupling between the two electrodes. The findings for one of the samples is shown in Figure 4.2. The coupling is reported for each electrode pad (S₁ and S₂) relative to the initial input voltage as measured from the function generator when the signal was not passed through the device. The default setup has the input source closest to S₁ and then closest to S₂ when ‘flipped.’ For all samples,
the coupling is significantly stronger at the electrode closest to the signal input.

![Graph](image)

**Figure 4.2:** The measured coupling signal detection efficiency for a sinusoidal waveform over a range of different frequencies. Each electrode pad is denoted $S_1$ (red) or $S_2$ (blue) with either the input signal closest to $S_1$ (squares) or closest to $S_2$ (triangles).

Detection efficiency slowly increased with frequency from 1 kHz to 10 kHz and remains at a maximum of about 10-12% signal detection until 1 MHz. At frequencies past this, the efficiency of the detection dropped off until it was indiscernible from the noise at around 10 MHz. To compare the coupling at each of the two electrodes, the side from which the signal source was coming from was swapped. Theoretically, each electrode should give roughly the same signal detection efficiency when the input source is closest to it. However, when the input was changed, it was observed that different electrodes of certain samples showed better coupling than others given approximately the same distance to the input voltage. One factor that could have played a role in this was variations in the thickness of PDMS between electrodes; the signal strength could decrease if it travels a larger distance through the dielectric. However, measurements of PDMS thickness between the conductive hydrogel electrode and the ‘nerve’ showed no significant difference between them. There may also be some capacitive effects at the electrode interface that could play a role, but this was not measured. A more conclusive explanation of this phenomenon could be provided by relating the detection efficiency to the contact surface area between the PDMS and ‘nerve’ model. The contact area of each electrode was estimated using ImageJ and the results comparing the contact area to the coupling efficiency for a single frequency (50 kHz) are shown in Table 4.1.
Table 4.1: A comparison of the measured contact areas of the conductive hydro-gel ‘nerve’ on the electrode pad to the signal detection efficiency when the power source is closest to S1 (Default) or S2 (Flipped). S1 and S2 refer to the output from each electrode as shown in Figure 4.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact Area mm²</th>
<th>Default % V_{out}/V_{in}</th>
<th>Flipped % V_{out}/V_{in}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>7.8 ± 0.3</td>
<td>9.7 ± 0.1</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>S2</td>
<td>9.2 ± 0.1</td>
<td>4.0 ± 0.2</td>
<td>12.6 ± 0.1</td>
</tr>
<tr>
<td>Sample 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>6.8 ± 0.2</td>
<td>9.8 ± 0.1</td>
<td>4.3 ± 0.2</td>
</tr>
<tr>
<td>S2</td>
<td>4.5 ± 0.2</td>
<td>3.5 ± 0.1</td>
<td>8.1 ± 0.1</td>
</tr>
</tbody>
</table>

It was observed that the electrodes with a larger contact area (Sample 1, S2 and Sample 2, S1) provided better coupling of the signal. For example, in Sample 1, S2 had a larger contact area. When the source was closest to S1, the detection efficiency was 9.7 %, but when the input source was closest to S2, the detection efficiency rose to 12.6 %. These findings agree with the initial expectation that a larger contact area should yield a greater signal detection efficiency. These results proved that the proposed device is able to resolve signals over a large range of frequencies with a conservatively reported value of 10 % efficiency, and that this detection efficiency shows a correlation to the contact surface area between the device and the signal source. It is anticipated that the signal detection efficiency may in fact be greater than the reported values as the V_{in} was measured from the signal source and not on the conductive gel above the electrode pad. The signal amplitude at the point of contact should be lower than that at the waveform generator because the whole line of conductive hydrogel should theoretically act as a voltage divider. Therefore, using the amplitude at the point of contact should lower the input signal magnitude, increase the detection efficiency, and give a more accurate representation of what the device is capable of. This also explains why the coupling values of the further electrodes are significantly smaller than those recorded at the closer electrode.

After establishing the range of frequencies that a signal could be detected over, attempts to determine the lower boundary of detectable amplitudes were made. Sinusoidal waves of 50 kHz with amplitudes ranging from V_{pp} = 100 mV to 1 V were passed through the device and the detected signals were recorded on an oscilloscope (Figure 4.3). A frequency of 50 kHz was chosen based on the speed at which action potentials travel in peripheral nerves as discussed in subsection 4.3.1.
Figure 4.3: The measured signal detection efficiency (\% V_{out}/V_{in}) for a sinusoidal waveform over a range of amplitudes. Each electrode pad is denoted S₁ (red) or S₂ (blue) with the input signal closest to S₁ (squares) or closest to S₂ (triangles).

As the amplitude of the input signal decreased, the efficiency of the coupling remained constant until much lower amplitudes (100 - 300 mV) where it increased slightly. As the signal approached a V_{pp} of around 100 mV, the waveform could still be visualized on the oscilloscope, but the noise was a large enough factor that the results were considered less reliable as indicated by the error bars (measurement standard deviation) in Figure 4.3. Overall, the device detected signals over a range of amplitudes and it is now the experimental setup that must be refined in order to determine the lower boundary for signal detection.

4.4 Conclusion

A hydrogel-elastomer sensor made from 3D-printable materials is proposed and its ability to detect simulated nerve signals through capacitive coupling is explored. The sensor is able to detect signals with a conservative estimate of 10 \% detection efficiency over a large range of frequencies (10 - 500 kHz). Frequencies beyond this range can be detected, but at a lesser efficiency with relatively no signal being detected at 10 MHz. Additionally, it was observed that the efficiency of signal detection shows a correlation to the contact area between the signal source and the electrode. The sensor is able to detect signals of amplitudes input V_{pp} = .1 V to 1 V, but the lower detection threshold could not be determined with the current experimental setup.

Overall, this paves the way for peripheral nerve signal sensing with a soft, stretchable, transparent device that is low cost and 3D-printable. Although the simulated nerve signals detected were not action potentials, the frequencies resolved by the
device indicate that it should theoretically be able to detect compound action potentials from the peripheral nervous system. Suggested improvements will be covered in the future work section of Chapter 5.
Chapter 5

Final Conclusions and Future Work

Traditional robotics has generally revolved around the use of heavy rigid systems that are problematic in applications requiring interaction with delicate objects. Soft robotics has emerged alongside newly developed soft materials and processing methods, such as 3D-printing, which can help to overcome these problems and have an impact in areas that traditional robotics is not suited for. One area that could greatly benefit from advances in soft robotics is in prosthetic devices, such as in the creation of a soft prosthetic hand. Key components of a soft prosthetic hand include the actuating materials (such as thermally active hydrogels), the multimaterial structure of the hand, and the interface used in communication with the hand.

This thesis aims to further the work towards the development of components for a soft prosthetic hand primarily made from hydrogel materials. Overall, it presents a practical method of actuation for thermally active hydrogels, refinement of a structural hydrogel precursor ink, printing of a multimaterial hydrogel structure, and a proposed interface for detecting peripheral nerve signals.

Chapter 2 of this thesis addressed Specific Aims 1, 2, and 3, i.e., focusing on the need for a more practical method of actuation for thermally active hydrogel materials. To achieve this, three types of different soft conductive materials were explored and their compatibility as a 3D-printable electrothermal heating element was assessed. Material 1: I onically conductive hydrogels were created by soaking gels in CaCl₂ solutions. It was determined that applying a voltage of 25 V was observed to temporarily raise the temperature of the printed hydrogel structure to approximately 29.5 °C. However, unfavorable electrochemical processes occurred that split water, evaporated chlorine gas, and caused a loss of connection between the gel and the power source. Additionally, printing ‘wires’ of the ionically conductive hydrogel was not feasible as the ions would diffuse throughout the rest of the bulk gel.

Material 2: Electrically conductive hydrogels were created by dispersing vapour grown carbon nanofibers (VGCNFs) in the hydrogel precursor, but remained incompatible with 3D-printing techniques. In particular, it was observed that the VGCNFs clogged the extrusion tip and ‘wires’ of the desired resolution could not be fabricated. Finding the correct balance between an ink containing enough VGCNFs to extrude properly, remain above the percolation threshold to exhibit a conductive network, and possess the correct rheological properties to remain in a stabilized ‘wire’ structure was deemed too time consuming and remained out of the scope of this thesis.
Additionally, even if this balance could be achieved, the addition of VGCNFs rendered the ink no longer transparent, and therefore, no longer compatible with the desired polymerization technique involving UV irradiation.

Material 3: Eutectic gallium-indium alloy (eGaIn) possesses all the desired properties of a soft conductive material and its suitability as an electrothermal heating element was explored. Its incorporation into hydrogel materials using 3D-printing was not previously established; therefore, custom extrusion tips were developed as a part of this project to allow for the printing of eGaIn onto hydrogels. A 6-prong extrusion tip with features allowing for omnidirectional extrusion was the most successful in printing eGaIn and factors responsible for this success were analyzed. The custom extrusion tip allowed printed eGaIn wires to be encapsulated in a hydrogel device and an applied voltage caused the eGaIn to heat the bulk gel up above the LCST of NIPAM. This proved the suitability of eGaIn as an electrothermal heating element for actuating NIPAM hydrogels.

Chapter 3 addressed Specific Aim 4, i.e., the incorporation of eGaIn in alginate/pAAm gels and beginning the development process of finger-sized multimaterial actuating structures. It was observed that past ink formulations created a microgel-like substance at higher CaCl₂ concentration and the process of creating the hydrogel ink precursor was altered. This was supported by rheological data demonstrating that the order of adding CaCl₂ and alginate dictates the internal structure of the gel, and that incremental addition of CaCl₂ to an alginate solution creates a more uniformly cross-linked hydrogel. The [CaCl₂] in the ink precursor was then adjusted to create an ink that produced the most uniform 3D-printed structure while still supporting printed eGaIn wires. This ink was printed alongside NIPAM hydrogels in an attempt to produce an actuating finger-like structure. It was reported that the structure must be pre-cooled prior to curing with UV irradiation to avoid phase separation of the NIPAM. However, printing a multimaterial structure with the current setup yielded structures where only a small portion (<50%) of the printed NIPAM volume underwent the phase transition. It is believed that this is primarily due to the migration of the NIPAM monomers into the bulk gel. Overall, each joint in the finger actuated by rotating at the hinge joints by approximately 10 degrees. Given the previously reported correlation between NIPAM concentration and actuation [62], controlling the monomer diffusion will be critical to comparing the expected and observed actuation of multimaterial structures. No further progress was able to be made into reducing the amount of NIPAM diffusion and, as far as the author is aware, there is no current literature on 3D-printing actuating multimaterial hydrogel structures of this scale. Overall, the findings presented in Chapter 3 provide a solid basis for the future development of actuating multimaterial hydrogel structures, and sheds light on areas that will need improvement as progress towards the final soft prosthetic device continues.

Chapter 4 addressed Specific Aim 5 and 6, i.e., exploring the development of a new soft device that could be used in the future to create a new cuff electrode for detecting peripheral nerve signals. The printable hydrogel-elastomer device presented in this thesis introduces a non-contact method of detecting peripheral nerve signals through capacitive coupling. It was observed that this device was able to detect sinusoidal waveforms over a range of frequencies (1 kHz - 1 MHz). The detection efficiency, %
$V_{out}/V_{in}$ was over 10% in some cases and was correlated to the contact area between the ‘nerve’ and the PDMS above the electrode pad. Additionally, intrinsic properties of these materials such as flexibility, stretchability, and transparency offer different areas of interest to explore and may provide greater mechanical compatibility with biological tissue. Conceptually proving this functionality with a simulated peripheral ‘nerve’ signal provides the first step towards creating a soft, 3D-printable, electrode device that can be used as an interface in the soft prosthetic hand.

The work presented in this thesis helps pave the way towards the creation of a soft prosthetic hand by providing the groundwork in some critical areas to the project. The final device will be the product of numerous researchers over the course of many years of work and the author is proud to be a part of it. However, applications of the findings presented in this thesis are not restricted solely to the prosthetic hand. Overall, the work in this thesis has not only helped further the creation of a soft prosthetic device, but it has helped improve aspects of the soft robotics field as a whole. The rest of this chapter details suggestions by the author that will either improve upon the work presented here, provide direction towards the next step, or provide a basis for other interesting research projects that are worthwhile to pursue.

### 5.1 Future Work: Working with Eutectic Gallium Indium Alloy

The combination of eGaIn properties, namely the high surface tension, spontaneous formation of an oxide layer, and the ‘slip layer’ make it extremely difficult to process and incorporate into hydrogel devices through 3D-printing [121]. The spontaneously forming oxide layer that helps to stabilize microstructures is arguably the most defining characteristic of eGaIn, but also the least well understood in some cases. For instance, when in contact with hydrous materials, the layer that spontaneously forms is not gallium oxide and published work supports the formation of a gallium hydroxide layer [121]. Whether this hydroxide layer is passivating or not (and at what thickness the formation stops) is up for debate and no long term study was done throughout the course of the presented work to determine this. To date (and to the best of the author’s knowledge), there are no published reports indicating that it is not passivating, however, it has been suggested that unpublished results hint it may not be [129]. In regards to the prosthetic hand project, determining if the gallium hydroxide layer is passivating or not will be critical to its potential inclusion in future work as the continued production of gallium oxide will continue to change the electrical properties of the wires greatly. Therefore, research into the formation of the hydroxide layer should be a top priority.

### 5.2 Future Work: Multimaterial Actuating Hydrogel Structures

Large 3D-printed multimaterial actuating hydrogel devices have not been reported in the past and there is no set protocol for their creation. Adding in active materials that respond to stimuli, such as NIPAM, further complicates things. Moving
forward, there are a few areas that will require a certain level of attention, namely improving the electrical connections and developing processing methods to localize specific materials. This aspect was hampered in the present study by the unwanted diffusion of monomers throughout the bulk gel.

5.2.1 Future Work: Connections to the Device

Conductive materials inside of any hydrogel device require robust connections to the outside world. In the presented work, the connections to the eGaIn were the most fragile aspect and caused many issues when not handled delicately. A potential solution to this problem would be a bioinspired approach based on the adhesion of bivalve molluscs, specifically the mussel. Mussels are able to adhere to a wide variety of surfaces using a proteinaceous glue containing numerous L-3,4-dihydroxyphenylalanine (dopa) amino acids that are structurally similar to poly(dopamine) [130]. Consequently, poly(dopamine) has been widely investigated for many purposes including a strong adhesion between different materials in aqueous and non-aqueous environments [131]. Therefore, poly(dopamine) may help provide a robust connection between hydrogels and electrical connections to the outside world.

5.2.2 Future Work: Diffusion of NIPAM

Any diffusion of NIPAM monomer in the printed structure will cause the observed actuation to deviate from the expected actuation based on the established correlation between actuation and NIPAM concentration [62]. This makes it extremely difficult to predict the actuation in terms of modelling fingerlike movement in the structure. It also poses problems in terms of reproducibility unless the timing of producing the structure is exact and the experimental setup is further refined as follows.

The two major factors inhibiting the 3D-printing of multi-material actuating hydrogel structures detailed in this thesis are (i) the phase separation upon curing the sample and (ii) the diffusion of the NIPAM monomers into the bulk gel. The most successful attempt at inhibiting these came from reducing the contact time between actuating and non-actuating hydrogels by pre-cooling the gels. Therefore, an obvious solution is to incorporate a temperature controlled jacket/stage to the printer. A more creative solution would follow the trend in many notable soft robotics findings of exploiting a potentially unwanted phenomenon (or mechanical instability) in an advantageous way. The diffusion coupled withinks high in NIPAM concentration can be printed strategically to create a concentration gradient of NIPAM throughout the gel. These gradients could produce structures with actuation and stiffness gradients to result in unique modes of movement. However, this will result in nonlinear systems; therefore, finding accurate ways to model the expected actuation will be crucial.

5.3 Future Work: Nerve Signal Sensing

The initial capacitive coupling results were extremely promising and there is great potential in this area for soft, transparent, non-contact sensing applications. The next step in the project would involve a number of alterations to the device and
the experimental setup as well as provide a more systematic measuring of the effect of contact area on coupling efficiency. The same type of device should be 3D-printed on a smaller scale (similar to previously reported cuff electrodes [44]) and different dielectric materials, such as 3M VHB tape, should be used in place of PDMS to ascertain what properties of the dielectric yield the greatest coupling. The experimental setup could be altered by using a signal generator that is able to produce smaller signals, and ideally the simulated signal could be modified to better represent a nerve signal. Additionally, a higher resolution oscilloscope should be used so that the amplitudes of smaller signals can be accurately detected. If the results of the experiments continue to be successful, the end goal would be to try and detect signals from the sciatic nerve of an animal.
Bibliography


[37] Web Page. URL: http://w3.shorecrest.org/“Lisa%5C_Peck/anatomy%5C_phys/ch7%5C_nervous/images/07.20%5C_NerveStruct%5C_1.jpg.


[40] J. J. FitzGerald et al. “Microchannels as Axonal Amplifiers”. In: *IEEE T e c tic s o Biomedic l E gi ee i g 55.3* (2008), pp. 1136–1146. DOI: 10.1109/tbme.2007.909533.


[75] Hyun-Joon Kong, Kuen Yong Lee, and David J. mooney, “Decoupling the dependence of the rheological/mechanical properties of hydrogels from solids concentration”. In: *Pol me* 43.6293-6246 (2002).


BIBLIOGRAPHY


[100] Sina Naficy et al. “4D Printing of Reversible Shape Morphing Hydrogel Structures”. In: M c o m o l e r i t i s d E g i ee i q (2016). DOI: 10.1002/mame.201600212.


[103] Can Hui Yang et al. “Ionic Cable”. In: Ext e m e M e c h a n i cs Lette s 3 (2015), p. 7. DOI: 10.1016/j.eml.2015.03.001.


BIBLIOGRAPHY


[126] C stom Lc Lock Desig . STL File.


Appendix A

Appendix One

A.1 G-Code Example

The Gcode used to print all of the structures from the custom built LinuxCNC printer was written by the author. Below is Gcode of the separate structures presented here compiled together into one program. Most general changes are extremely user-friendly and depending on the input variables required by the comments in the beginning of the program, it can produce small or large versions of a rectangular prism, encapsulated eGaIn structure, or a multimaterial hydrogel finger (all of varying heights). The multimaterial hydrogel finger has input options to either include eGaIn or not. Each of these structures can have any certain aspects of the structure omitted. Further modifications of box width/length are slightly more complex but everything is customizable. Overall, this code provides a solid foundation for any individual looking to continue the work presented in this thesis.

For reference, a few quick facts concerning the syntax/code will be provided:
1) Variables are declared using the '#*' and a number. ie #101 = 5 will create the variable '#101' and give it the value 5.
2) All commands were done in a relative coordinate system
3) The code could be 'blackboxed' but the author felt that it would make others less likely to alter it.

A full guide to the syntax as well as a guide to downloading the EMC2 software and acquiring the user manual/more information can be found online at: http://linuxcnc.org/docs/2.4/html/common/_Getting/EMC.html
G21 G53 G01 X0.000000 Y0.000000 Z0.000000 F300.000000
(These variables initiate the program with an arbitrary jog speed and tell it to start at 'home')
G4 P3 (pause to ensure Full extrusion)
G91 (Set relative positioning)

(User Input Time)
(Suggested Jog Speeds are 40 mm/min for gel and 45 mm/min FOR eGaln)
(What do You want to print? encapsulated eGaln or a 'Finger')
******************************************************************************
(IF You want encapsulated eGaln, enter 1 below)
#651 = 0 (--- right there)
(Now let's be more speclFic:)
O931 IF [#651 EQ 1]
#163 = 0 (1 for large 70 X 24, 0 for small 70 X ~15)
#156 = 0 (How many layers BELOW eGaln do you want?)
#534 = 0 (1 to include metal)
#159 = 0 (How many layers coinciding with egain do you want? Ignore if you said no metal)
#158 = 0 (How many layers ABOVE eGaln do you want? Ignore if you said no metal)
O931 ENDIF
******************************************************************************
(if You want a 'Finger,' enter 1 below)
#650 = 0 (--- right there)
(Now let's be more specific:)
O930 IF [#650 EQ 1]
#163 = 0 (1 for large 70 X 24, 0 for small 70 X ____)
#156 = 0 (How many layers BELOW eGaln do you want?)
#534 = 0 (1 to include metal)
#159 = 0 (How many layers coinciding with egain do you want? Ignore if you said no metal)
#732 = 0 (1 if you are printing ICE Finger portion)
#275 = 0 (1 if you are printing NIPAM 'joints')
O930 ENDIF
******************************************************************************
*****DO NOT TOUCH THE REST OF THE CODE UNLESS YOU KNOW WHAT YOU'RE DOING*****
*****I mean it*****
*****DON'T DO IT*****

#101 = .75 (Step Size/Track Width)

(Conditional Base Layer Variables)
O924 IF [#163 EQ 1] (Large)
#202 = 23.95 (length of vert steps)
#151 = 16 (number of horizontal steps bottom to top)
O924 ELSE (**small***, need to change some vars)
#202 = [#101 * 20] (length of vert steps)
#800 = [#101*2] (CHANNEL WIDTH, TRY TO KEEP MULTIPLE OF STEPSIZE)
#151 = 10 (number of horizontal steps bottom to top)
O924 ENDIF

(Unconditional Base Layer Variables)
#115 = 1.5 (priming length 1)
#102 = 70.5 (length of horiz steps)
#153 = 47 (number of vertical steps...left to right)
#111 = 400 (Feedrate)
#110 = 385 (next to eGeln feedrate)
#201 = .75 (width of vert steps)
#199 = .5 (Z displacement of different layers)
#157 = 0 (DONT CHANGE)
#150 = 0 (don't change)
#152 = 0 (don't change)

(ICE NIPAM Variables)
#339 = 4 (layer counter)
#333 = #801 (y travel Distance)
#101 = 0.75 (gel track spacing)
#334 = .5 (Layer height)
#335 = 4 (how many layers do you want)
#303 = 0 (i1 counter)
#304 = 26 (i1 Top Var)
#305 = 0 (i2 counter)
#306 = 9 (i2 Top Var)
#307 = 0 (i3 counter)
#308 = 9 (i3 Top Var)
#210 = [0.75*3] (N dynamic distance)
#211 = 3 (N spacing change)
#111 = 400 (Feedrate)

#344 = [#210 + .75 + [#304 + #306 + #308]*.75*2] (Return to origin var)

(Metal Variables)
O562 IF [#772 EQ 1]
O562 ENDIF

(Variable Declaration)

*******************************************************************************
(Base Layer Code)

(This Prints the Base Layer)
O195 WHILE [#156 GT #157]

O191 WHILE [#150 LT #151] (horizontal layer)

G01 X#102 F#111
G01 Y#101 F#111
G01 X[-#102] F#111
G01 Y#101 F#111
#150 = [#150 + 1]
O191 ENDWHILE

G01 X[#102] F[#111]
G01 Z[#199] (go up to next layer)

O192 WHILE [#152 LT #153] (vertical layer)
G01 Y[-#202] F[#111]
G01 X[#201] F[#111]
G01 Y[#202] F[#111]
G01 X[#201] F[#111]

#152 = [#152 + 1]
O192 ENDWHILE
#150 = 0 (Resets H & V counters)
#152 = 0 (Prepare for next layer)
G01 Y[-#202] F[#111]

#156 = [#156 - 1]
O195 ENDWHILE

G01 Z[#199] (GOES UP TO EGAIN LAYER)

(*******************************************************)
(Gel Surrounding eGaIn)
O535 IF [#534 EQ 1]
O535 ENDIF

(*******************************************************)
(eGaIn Code)
O535 IF [#534 EQ 1]
O535 ENDIF

(*******************************************************)
(Gel on Top of eGaIn)
O535 IF [#534 EQ 1]
O535 ENDIF

(*******************************************************)
(ICE Finger CODE)
O900 IF [#732 EQ 1]

O169 WHILE [#335 GT 0]
#970 = 3

O180 WHILE [#970 GT 0] (Cycle through 3 areas)
O181 IF [#970 EQ 3] (First area)
O160 WHILE [#303 LT #304]
G01 Y#333 F#111
G01 X#101
G01 Y=#333
G01 X#101

#303 = [#303 + 1]
O160 ENDWHILE
O181 ENDIF

O182 IF [#970 EQ 2] (Second area)
O161 WHILE [#305 LT #306]
  G01 Y#333 F#111
  G01 X#101
  G01 Y=#333
  G01 X#101

#305 = [#305 + 1]
O161 ENDWHILE
O182 ENDIF

O183 IF [#970 EQ 1] (Third area)
O162 WHILE [#307 LT #308]
  G01 Y#333 F#111
  G01 X#101
  G01 Y=#333
  G01 X#101

#307 = [#307 + 1]
O162 ENDWHILE
O183 ENDIF
(Skip over gap with NIPAM)
G01 X[-.75] Y-2
G01 X[#210]
G01 Y2

#970 = [#970 - 1]
O180 ENDWHILE
(Finish layer)
G01 Z#334
(Return to start)
G01 Y-2
G01 X[-#344]
G01 Y2
(Update Counters to Account for new NIPAM Spacing)
#303 = 0 (Reset count for different areas)
#305 = 0
#307 = 0
#304 = [#304 - 1] (Less tracks for different areas)
#306 = [#306 - 2]
#308 = [#308 - 1]
#210 = [#210 + #211] (NIPAM Gap Spacing)
#335 = [#335 • 1]
O169 ENDWHILE

(Return to area to change tool)
G01 Y#333
G01 X[26*2*.75]
G01 Z[1-#334*4]
O900 ENDF

G01 Z10

*****************************************************************************

(NIPAM Joint)
O901 IF [#275 EQ 1]

#509 = 2 (Number of NIPAM Areas)

O906 WHILE [#509 GT 0]
(Set or Reset Counters)
#500 = 4 (Layer Counter)
#501 = 1 (Track Counter)
#505 = 1 (Invisible Counter)
#502 = 3 (Return Counter)
O902 WHILE [#500 GT 0]

O903 WHILE [#501 GT 0]
O905 IF [#501 NEQ 1]
G01 Y-#333 F#111
G01 X#101
G01 Y#333
G01 X#101
O905 ELSE
G01 Y-#333 F#111
G01 X#101
G01 Y#333
G01 Z#334 (Go up to next layer)
O905 ENDF

#501 = [#501 - 1]
O903 ENDFWHILE

G01 X[-#101*#502] (Return to Start, cycles 3, 7, 11)

(Reset Counters & Increment)
#505 = [#505 + 2]
#502 = [#502 + 4]
#501 = [#505] (1, 3, 5, 7)
#500 = [#500 - 1]
O902 ENDFWHILE
(Need code to get me to next NIPAM Area, then copy & Paste the Above)

G01 Y2
G01 X[(4.5 + 4.5)]
G01 Z[-#334*#339]
G01 Y-2

#509 = [#509 - 1]
O906 ENDWHILE

O901 ENDIF

(******************************************************************Finished*************************************************************************)
N1001 M2 (end code)
Appendix B

Appendix Two

B.1 Additional Rheological Data

Below is supplementary rheological data of refining the ICE hydrogel precursor solutions. All experiments occurred as described in subsection 3.2.1 and all graphing/analysis was done using OriginPro. The viscosity (η) and the shear stress (τ) were plotted separately against shear rate (γ). The consistency (K) and flow index (n) were determined by modeling the measured viscosity values to that of a Power Law Fluid [57]:

\[ η = K \dot{γ}^{n-1} \]  

(B.1)

The yield stress (τ_y) was determined by modeling the shear stress at low shear rates (<1 s^{-1}) to a Bingham Model [57]:

\[ τ = τ_y + η \dot{γ}^n \]  

(B.2)

Figure B.1: Viscosity and shear stress plotted against the shear rate for alginate hydrogels with varying amounts of CaCl₂ where alginate was added last.
**Table B.1:** Rheological Parameters for a series of alginate hydrogels with varying [CaCl₂] where alginate was added last.

<table>
<thead>
<tr>
<th>Final [CaCl₂] (mM)</th>
<th>K (Pa sⁿ)</th>
<th>n</th>
<th>τ₀ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>12 ± 1</td>
<td>0.77 ± 0.02</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>6.67</td>
<td>122 ± 1</td>
<td>0.34 ± 0.01</td>
<td>114 ± 2</td>
</tr>
<tr>
<td>13.30</td>
<td>195 ± 8</td>
<td>0.29 ± 0.01</td>
<td>164 ± 3</td>
</tr>
<tr>
<td>9.00</td>
<td>139 ± 1</td>
<td>0.35 ± 0.02</td>
<td>191 ± 3</td>
</tr>
<tr>
<td>26.7</td>
<td>75 ± 1</td>
<td>0.38 ± 0.01</td>
<td>71 ± 2</td>
</tr>
<tr>
<td>33.3</td>
<td>72 ± 1</td>
<td>0.28 ± 0.01</td>
<td>65 ± 1</td>
</tr>
</tbody>
</table>

**Figure B.2:** Viscosity and shear stress plotted against the shear rate for alginate hydrogels with varying amounts of CaCl₂ where CaCl₂ was added last.

**Table B.2:** Rheological Parameters for a series of alginate hydrogels with varying [CaCl₂] where CaCl₂ was added last.

<table>
<thead>
<tr>
<th>Final [CaCl₂] (mM)</th>
<th>K (Pa sⁿ)</th>
<th>n</th>
<th>τ₀ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>19 ± 1</td>
<td>0.77 ± 0.02</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>6.67</td>
<td>110 ± 2</td>
<td>0.33 ± 0.01</td>
<td>110 ± 2</td>
</tr>
<tr>
<td>13.3</td>
<td>140 ± 1</td>
<td>0.23 ± 0.01</td>
<td>141 ± 1</td>
</tr>
<tr>
<td>26.0</td>
<td>144 ± 10</td>
<td>0.10 ± 0.02</td>
<td>151 ± 2</td>
</tr>
<tr>
<td>26.7</td>
<td>146 ± 3</td>
<td>0.22 ± 0.01</td>
<td>144 ± 2</td>
</tr>
</tbody>
</table>
Figure B.3: Viscosity and shear stress plotted against the shear rate for alginate/poly(acrylamide) hydrogels with varying $[\text{CaCl}_2]$. 

Table B.3: Rheological Parameters for a series of alginate/poly(acrylamide) hydrogel precursor inks with varying amounts of CaCl$_2$. 

<table>
<thead>
<tr>
<th>Final $[\text{CaCl}_2]$ (mM)</th>
<th>$K$ (Pa s$^n$)</th>
<th>$n$</th>
<th>$\tau_v$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>$86 \pm 2$</td>
<td>$0.39 \pm 0.01$</td>
<td>$88 \pm 9$</td>
</tr>
<tr>
<td>1.85</td>
<td>$190 \pm 3$</td>
<td>$0.25 \pm 0.01$</td>
<td>$190 \pm 1$</td>
</tr>
<tr>
<td>3.70</td>
<td>$202 \pm 8$</td>
<td>$0.20 \pm 0.02$</td>
<td>$218 \pm 2$</td>
</tr>
<tr>
<td>5.56</td>
<td>$240 \pm 9$</td>
<td>$0.21 \pm 0.02$</td>
<td>$257 \pm 4$</td>
</tr>
<tr>
<td>7.41</td>
<td>$267 \pm 11$</td>
<td>$0.20 \pm 0.02$</td>
<td>$281 \pm 4$</td>
</tr>
</tbody>
</table>
Appendix C

Appendix Three

C.1 Peripheral ‘Nerve’ Sensing Schematic for Prosthetic Control

No matter what stage the capacitive coupling sensor is in, it can be incorporated into a simple demonstration for the eventual prosthetic finger/hand fairly easily through the schematic shown in Figure C.1 or a variation of it.

![Schematic Diagram]

Figure C.1: A schematic where an Arduino allows the signal (a) to be sent from a waveform generator to the ‘nerve’ (orange wire) through a latch relay (b) to be detected by the capacitive coupling device (c). The output signal of the device triggers another latch relay (d) to put a voltage across the eGIn in the ‘finger’ (e) and produce heating. The Arduino is then able to reset the system by flipping off the latch relays.

The schematic is relatively straightforward and can be extensively modified depending how far along the project is or what is required of it at the time. These modifications could include replacing the Arduino/first latch relay with a feedback
mechanism to start/stop heating of the finger, a sophisticated method of differentiating ‘nerve’ signals from others to flip on the second latch relay, signal amplification of the output signal from the capacitive coupling device, or modifying the ‘nerve’ signal source.
Appendix D

Appendix Four

D.1 3D-Food Printing

A big responsibility of scientists is to communicate what they are doing to the general community in an engaging, accurate, and digestible manner. A side project that has helped me do this and has played a large role in these two years has been the work with 3-D printing Vegemite and Marmite. Through this, we have engaged in outreach activities at different schools, put on demonstrations at AIIM, participated in the 2015 UOW Big Ideas Festival, and helped create the ‘Electronics for Breakfast’ youtube video with almost 4,000 views.

On a more academic note, I have given a talk at the 3D Foodprinting Conference at Monash University in May 2017:

![3D Foodprinting Conference](image)

and published a first author paper in Elsevier Journal of Food Engineering:

3D printing Vegemite and Marmite: Redefining “breadboards”

Charles Alan Hamilton\textsuperscript{a,b}, Gursel Alici\textsuperscript{a,c}, Marc in het Panhuis\textsuperscript{a,b,*}

\textsuperscript{a} Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, AllM Facility, University of Wollongong, Wollongong, NSW 2522, Australia
\textsuperscript{b} Soft Materials Group, School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia
\textsuperscript{c} School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

**Abstract**

The ability to use Food Layered Manufacturing (FLM) to fabricate attractive food presentations and incorporate additives that can alter texture, nutrition, color, and flavor have made it widely investigated for combating various issues in the food industry. For a food item to be FLM compatible, it must possess suitable rheological properties to allow for its extrusion and to keep its 3D printed structure. Here, we present a rheological analysis of two commercially available breakfast spreads, Vegemite and Marmite, and show their compatibility with FLM in producing 3D structures onto bread substrates. Furthermore, we demonstrated that these materials can be used to fabricate attractive food designs that can be used for educational activities. The inherent conductivity of the breakfast spreads was used to print edible circuits onto a “breadboard.”

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

There is a constant need for innovative methods of food processing to address various problems in caring for those with specialized dietary needs. Physiological changes that occur with aging such as dysphagia, decreased sensory perception, and changing nutritional needs require the elderly to have specialized diets (Goldman et al., 2014). Consequently, many elderly patients in hospitals and long-term care facilities suffer from underdiagnosed malnutrition, which causes comorbidities in the patients (Wells and Dumbrell, 2006). Other groups, such as children, have specialized dietary requirements and studies have been conducted to determine methods to ensure children eat balanced meals. An effective method to meet their nutritional needs has been arranging food into attractive presentations and it has been reported that children prefer to eat a wider variety of food if it is plated in a fun and appealing way (Zampollo et al., 2012). There is also a call for new food manufacturing techniques to satisfy the food-based desires of astronauts who have their gustation altered due to the environment in the line of duty. The mental health and morale of astronauts is critical for successful completion of their long-term missions and it is reported that they crave good food more than other comforts (Terfansky and Thangavelu, 2013). Recently, 3D printing has been explored as an innovative food-manufacturing technique that has the ability to meet these special dietary requirements.

3D printing is an additive manufacturing technique that involves the layer-by-layer deposition of materials to form a 3D structure that may not have been achievable with conventional manufacturing techniques. Coined “Food Layered Manufacturing” (FLM), 3D printing showed its first application in the food industry with the development and use of the extrusion-based Fab@home system (Wegrzyn et al., 2012; Malone and Lipson, 2007; Periard et al., 2007; Lipton et al., 2015). Most extrusion-based systems consist of a syringe containing a viscous material that is hooked up to a nozzle that is able to move with 3 degrees of freedom. The material is then pushed out of the syringe by either pneumatic pressure or a piston to deposit material layer-by-layer until a 3D shape is formed (Wegrzyn et al., 2012; Godoi et al., 2016).

FLM has been used to print edible materials into complex shapes and gives the user the ability to modify properties like texture, colour, flavour, and nutrition. It has also been used to fabricate conductive devices using edible materials that may eventually play a role in future novel drug delivery systems and GI monitoring...
devices (Keller et al., 2015). A wide range of materials have been printed, including cake frosting, processed cheese, meat purees, chocolate, dough, and more (Periard et al., 2007; Lipton et al., 2010, 2015; Godoi et al., 2016; Sun et al., 2015a; Sun et al., 2015b). FLM allows these materials to be fabricated into attractive food presentations that can incorporate multiple materials and additives to enhance nutrient value catered to individual needs. Depending on the food that is created, it can either be cooked by various post-processing methods and still retain its structure or remain soft to meet texture requirements of an individual unable to consume hard food (Lipton et al., 2010; Goulbourne et al., 2014). All of this provides a tremendous platform of opportunity for schools, parents, food service managers, child care centres, old age homes, and food manufacturers to incorporate this technology into their production lines to combat malnutrition and address specific dietary needs of different demographics (Zampollo et al., 2012; Sun et al., 2015a, 2015b). In order for a food material to be compatible with FLM, it must possess suitable rheological characteristics to allow for its extrusion. In the future, an in depth understanding of the rheological properties of food materials for their use in FLM will be critical, especially when considering the rheological effects of certain additives (Fischer and Windhab, 2011).

In this study, we present a rheological analysis of commercially available Australian breakfast spreads, Vegemite and Marmite, and demonstrate their compatibility with FLM through the creation of attractive food designs printed onto edible (bread) substrates. Furthermore, we show how the rheological properties of these spreads can be modified and how the resolution and integrity of the printed structures are affected. Lastly, we use the inherent electrical conductivity of the breakfast spreads to fabricate edible circuitry through the creation of a “breadboard.” This example of conductive food patterning is used to demonstrate the potential of FLM and commercially available food products in edible electronics and as a learning tool for students during outreach activities.

2. Materials and methods

Vegemite and Marmite, produced by Mendelez International and Sanitarium Health and Sanitarium Health and Food Company, respectively, were purchased from Woolworths Supermarkets (Wollongong, Australia) and used without any further modification. The edible white bread substrate, also purchased from Woolworths, was modified before use by slight downward pressure by hand (using a rectangular acrylic plate) to create a flatter substrate. Following this, the bread was inserted in a typical household toaster (HomeMaker T358 Bread Toaster) until golden brown. The bread was left to equilibrate to room temperature (21 °C) prior to any printing.

2.1. Rheological characterization

Rheological characterization of Vegemite and Marmite were conducted on an Anton-Paar Physica MCR 301 Digital Rheometer with a conical plate measuring system (49.972 mm diameter, 0.992° angle, 97 μm truncation) and a heat-controlled sample stage (Julabo Compact Recirculating Cooler AWC 100). Temperature sweeps of Vegemite and Marmite were done at a constant shear rate of 100 s⁻¹ while decreasing the temperature from 40 °C to 4 °C at a rate of 2 °C/min.

Viscosity profiles of Vegemite and Marmite were obtained at temperatures of 4, 10, 20, and 37 °C by ramping the shear rate (γ) from 0.1 to 500 s⁻¹. The apparent viscosity was measured and plotted as a function of the shear rate. The resultant curve was modeled to a power law (Eq. (1)), and used to calculate the consistency (K) and power law index (n) of the materials at different temperatures:

\[ \eta = K\gamma^n . \]  

(1)

The shear stress (σ) was plotted as a function of the shear rate and a Bingham model was used to determine the yield stress (σγ) as follows:

\[ \sigma = \sigma_y + \eta \gamma. \]  

(2)

2.2. 3D printed structures

3D printed structures of Vegemite and Marmite were fabricated onto edible (bread) substrates using a commercially available BioBot 1 extrusion printer purchased from BioBots and controlled with the Repetier Host software. A pyramid structure (base of 3 cm × 3 cm) was modeled in SolidWorks 2016 and exported as an STL file that was subsequently sliced with Slic3r, converted to Gcode, and loaded into Repetier Host. The pyramid was printed with Vegemite and Marmite onto toasted bread at temperatures of 25 and 45 °C, respectively.

2.3. Direct writing of attractive food presentations

Attractive food presentations of Vegemite and Marmite were printed onto edible bread substrates at 25 °C using the BioBot printer. Images of a smiley face, a fish, and a stick figure were created using Solidworks and uploaded to the printer as described above.

2.4. Edible circuits

The edible circuits were printed onto the bread substrates using a custom made 3D printer based on a CNC milling machine and controlled by LinuxCNC software. Sets of Gcode were written in a Linux Gedit program and Vegemite or Marmite was extruded out of a 5mL syringe by a T-N08A25Zaber linear actuator. After printing, red, yellow, and green LEDs purchased from Jaycar Electronics (Wollongong, Australia) were added. The “breadboard” was connected to a power supply set to 12 V to represent the lights at a traffic stop.

3. Results & discussion

3.1. Rheology

Rheological studies were used to look into suitable viscosities for the 3D printing of Vegemite and Marmite into shapes that can retain their structure post-printing. The temperature profiles of Vegemite and Marmite, (Fig. 1), show the expected behavior of decreasing viscosity (η at constant shear rate) with increasing temperature. It was observed that the behavior can be modeled to a power law (data not shown).

To understand the flow behavior of Vegemite and Marmite, viscosity profiles (shown in Fig. 2) were measured at varying temperatures and fit to a power law shown in Eq. (1), where η is the viscosity, γ is the shear rate, K is defined as the flow consistency index, and n as the flow behavior exponent. The flow behavior exponent and consistency behavior index are especially important in determining if a material is compatible with FLM and determining the desired extrusion rates. The flow consistency indices of Vegemite and Marmite represent the viscosity of the material at a shear rate of 1 s⁻¹ and decrease with rising temperature as would be expected (see Table 1). Flow behavior exponents less than 1 indicate that both Vegemite and Marmite are shear-thinning materials. For Marmite, this value decreases with...
decreasing temperature, indicating an increase in shear-thinning behavior and a further deviation from Newtonian fluid behavior. When plotting the shear stress versus the shear rate (see Fig. 2), the material exhibited pseudoplastic behavior and a Bingham model (Eq. (2)) was used to determine the yield point, \( \sigma_y \), of the materials at varying temperatures (see Table 1).

An observed yield point can be explained by the presence of particulates throughout the material that form a stabilizing network. Once the applied pressure is large enough to break this network, the yield point has been overcome and the material will begin to flow like a liquid (think the amount of “squeezing” necessary before toothpaste begins to flow out of a tube). The existence of a yield point and the minimum pressure needed to overcome it is a very important parameter that must be tuned for each material in FLM, especially when using pneumatically driven printing systems.

Our results indicate that, in general, Vegemite has lower yield points than Marmite (Table 1). In other words, less pressure is required to start the extrusion process of Vegemite compared to Marmite. As expected, the yield point decreases significantly with increasing temperature and appears to follow exponential behavior.

3.2. Dependence of print quality on viscosity

Understanding how rheological properties of food materials will influence resultant printed 3D structures will be critical as FLM...
continues to find additional applications. Here, we demonstrate the use of commercially available Vegemite and Marmite in the fabrication of 3D structures and attractive food presentations. We also show how the integrity of the printed structure depends on the rheological properties of the materials.

### 3.2.1. 3D printed structures

To demonstrate the use of Vegemite and Marmite with FLM techniques, a pyramid was printed at temperatures of 25 and 45 °C (see Fig. 3). The substrate used was toasted bread to replicate the usual circumstances under which the breakfast spreads are usually consumed. All print conditions were kept constant aside from the pneumatic pressure used to extrude the materials. At 25 °C, 25 psi (172 kPa) of pressure was used to extrude both materials but needed to be decreased to 15 psi (103 kPa) to print the structures at 45 °C. When attempting to use 25 psi (172 kPa) to print the structures at 45 °C, the flow rate was too large and the printed structure resembled a puddle of material. When attempting to print the structure at a higher temperature of 65 °C, the material was extruded too quickly even with very low pressures (<5 psi or 34 kPa) being used to extrude the material. It was observed that Vegemite and Marmite retained the integrity of the printed structures at 25 °C much better than at 45 °C. This demonstrates that the breakfast spreads possess rheological characteristics that are compatible with FLM techniques. In other words, it is possible to 3D print self-supporting structures in Vegemite and Marmite (at temperatures below 45 °C).

### 3.2.2. Attractive food presentations

An attractive food presentation is beneficial in a wide range of applications, and could soon become an easily accessible commodity in modern households with advances in FLM. We show that commercially available Vegemite and Marmite can be used to create fun designs suitable for celebratory events such as birthday parties. Similar to the 3D structures presented above, the designs were printed onto toasted and buttered bread to simulate conditions under which the FLM product would be consumed. Vegemite and Marmite were both found to possess suitable rheological characteristics to print the attractive designs (Fig. 4).

### Table 1

The rheological parameters (including standard deviations) of Vegemite and Marmite at various temperatures where \(\sigma_y\) represents the yield stress, \(K\) represents the flow consistency index, and \(n\) represents the flow behaviour index.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Vegemite</th>
<th>Marmite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\sigma_y) (Pa)</td>
<td>(K) (Pa s(^n))</td>
</tr>
<tr>
<td>37</td>
<td>419 ± 2</td>
<td>333 ± 27</td>
</tr>
<tr>
<td>20</td>
<td>687 ± 2</td>
<td>590 ± 35</td>
</tr>
<tr>
<td>10</td>
<td>987 ± 6</td>
<td>697 ± 69</td>
</tr>
<tr>
<td>4</td>
<td>1168 ± 5</td>
<td>905 ± 49</td>
</tr>
</tbody>
</table>

![Fig. 3. Photographs of Vegemite and Marmite printed into pyramid shapes on toasted bread. (A) Vegemite printed at 25 °C, (B) Vegemite printed at 45 °C, (C) Marmite printed at 25 °C, and (D) Marmite printed at 45 °C. All scale bars shown are 1 cm in length.](image-url)
3.3. Edible electronics — redefining breadboards

We have routinely used printed 3D structures on bread in our educational activities. For example, during a visit to a daycare center, attractive food presentations were used to teach children about 3D printing technologies (see Fig. 5). It was observed that the fabrication of food into designs is favored greatly by the younger children, and serves as a great method for encouraging them to consume healthy food and get engaged in educational activities.

We observed that Vegemite and Marmite are able to conduct DC electricity due to the presence of salt ions. Vegemite and Marmite were found to exhibit conductivity values of $20 \pm 3$ S/cm and $13 \pm 1$ S/cm, respectively (data not shown). We demonstrated that Vegemite and Marmite can be used to make circuits resulting in the fabrication of a literal “breadboard.”

The potential to use commercially available food products to create electronic circuits has enabled us to create fun educational outreach activities. For example, here we present a Vegemite circuit consisting of a red, yellow, and green LED to simulate a traffic light (Fig. 6). Similar results could be obtained using Marmite (data not shown). After the experiment, the non-edible metal circuit components (LEDs & wires to power supply) were removed and the edible components of the “breadboard” (Vegemite/Marmite & toasted bread) were consumed either by the authors or by children during educational activities. Videos of our functioning circuits can be found in the supplementary information and online (youtube.com).

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.jfoodeng.2017.01.008.
4. Conclusion

In this paper, we have shown that the compatibility of commercially available food products, Vegemite and Marmite, with FLM techniques can be used to produce 3D structures, such as attractive food designs and edible circuitry onto bread substrates. We demonstrated the importance of characterising the rheological behaviour of the food products in retaining the structural integrity of the printed materials (e.g. pyramids on bread). The electrical conductivity of Vegemite and Marmite was used to print edible circuits on “breadboards.” It was shown that printed FLM designs are suitable in outreach activities to teach young learners about electronic circuits and 3D printing.

Our work contributes to the development of food processing techniques that have the potential to be used in a wide range of applications such as space missions, aged-care facilities, and hospitals. FLM has a lot to offer for these applications due to the potential to modify flavour, nutrition, and texture through the incorporation of combinations of food additives. In addition, FLM can be used to fabricate food into attractive designs suitable for special occasions such as children birthday parties.

Acknowledgements

This work was supported by funding from the University of Wollongong (UOW) and the Australian Research Council (ARC) Centre of Excellence for Electromaterials Science (CE140100012). We thank Chris Richards and Dr. Steve Beitme from the Materials Node of the Australian National Fabrication Facility (ANFF) at UOW for the use of the BioBot printer. Reece Gately and Alex Keller are thanked for assistance with electronic characterisation.

References

https://www.youtube.com/watch?v=TPCDsg6bhjE.

Fig. 6. Photographs of a 3D printed Vegemite electronic circuit extruded onto edible (bread) substrate, simulating the (A) red, (B) yellow, and (C) green lights of a traffic light. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)