ABSTRACT

BHAKTA, RAJ PRAVINBHAI. Direct-write Printed Wearable Textile Electronics. (Under the direction of Dr. Jesse Jur)

Textiles provide a broad range of applications in electronics, particularly as a platform for integrating sensors and displays. A large driver for this momentum is wearable technology for fitness and health applications, as well as home textiles for internet-of-things (IoT) connectivity. Current materials methods, such as the use of conductive yarns, are limited in the ability to manufacture at large scale and breadth of materials function. Printed electronics offers an alternative technology roadmap for textile electronics.

Our direct-write process allows us to print interconnects and other devices onto textiles by manipulating ink rheology for optimal processability and flowability into the textile fiber bulk. It allows for commercially available screen-printable inks to be used with minimal ink waste, minimal post-process clean up, and design flexibility through software driven designs. Ink penetration into the textile can also be controlled using this process by increasing the fluid pressure and tuning the rheology of the ink materials. It has been shown that proper understanding of rheological flow properties of such inks can be used to fabricate stretchable interconnects. This strategy allows for stretchable conductors to be ‘embedded’ into the fiber bulk to match the mechanical properties of the textile substrate enabling direct printing of such conductive inks straight onto the textile without any pre-treatment process. This technology presents a new manufacturing paradigm for printed electronics on textiles. Furthermore, curing strategies that substantially decrease the curing time of the ink were explored ranging from thermal oven to infrared oven. Finally a smart garment that monitor one’s electrocardiogram for mobile health and wellness applications in a passive, accurate, real-time, and low-cost manner...
was fabricated with 5 min production time, the lowest known production time for a smart garment in the current literature and among market products.

In this research work, a novel direct-write printing process was developed to fabricate textile electronics such as an ECG sensing smart garment in 5 min utilizing an automation strategy.
Direct-write Printed Wearable Textile Electronics

by
Raj Pravinbhai Bhakta

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Fiber & Polymer Science

Raleigh, North Carolina 2019

APPROVED BY:

___________________________
Dr. Jesse Jur
Committee Chair

___________________________
Dr. Lokendra Pal

___________________________
Dr. George Hodge

___________________________
Dr. Michael Dickey

___________________________
Dr. Ericka Ford
DEDICATION

To my parents, Pravinbhai and Sharmisthaben Bhakta:

My parents came to one of the greatest countries in the history of human civilization all the way from the entrepreneurial state of Gujarat, India. As the story goes with every emigrant, my father came with only $5 USD in his pocket and a dream to create a better future for his family. After getting married to my mother in 1989, my father dropped out of medical school in India and came to California to start working as a manufacturing manager at a medical device manufacturer called CPI Plastic Molding in Irvine, CA which made heart valves and needle-free devices for applying insulin. At the time, his company was making devices for healthcare companies like Medtronic, Baxter, and Alcon. However, in order to bring my mother to California, he worked an additional job as an office clerk for my uncle’s motel. My mother was finally able to make it California in 1991. My parents had me in 1992 in Riverside, CA and then moved to Houston, TX after a year to start their American dream. They had saved up enough to buy a motel in a rough part of Houston. It wasn’t picturesque as the American dream goes but it was something that they would be able to make into their own. As a family, we struggled financially but one thing my parents had was grit – it’s a common ingredient that leads to overcoming struggles. We couldn’t always afford the best food, the best schooling, or the best neighborhood but that didn’t preclude them from giving to me the best values, the best support, and highest freedom in letting my imagination run free. I owe it to them for letting me choose my own path, having the confidence in me to ‘change the world’, and being there in the ups and downs of this thing we all call Life. I wish onto others that have lived through my situation to have the parents I did. Much love to my parents and this great country.
To my high-school chemistry teacher, Mr. Daniel Montgomery:

From when I was able to remember, I was interested in learning about this thing we call ‘reality’. I was always a curious kid and excited by science. I absorbed books, TV shows, and anything else I could get my hands on that had anything to do with science. Science was my getaway to a ‘virtual reality’ full of atoms, cells, and galaxies that were projections of the ‘reality’ we lived in. When I got to high-school, as every other high-schooler I took Chemistry and AP Chemistry classes. I was an excellent and passionate learner but the reality was I was getting terrible grades in the AP Chemistry class. Mr. Montgomery believed in me but he was realistic – mid-semester he said I wouldn’t be able to pass his AP Chemistry class let alone pass the AP Chemistry exam. This was heart-breaking to hear from one of my mentors but it was much, much needed. I always had a ‘different’ type of learning style – the rote memorization learning style of our modern education which was built for a manufacturing and assembly driven industrialization era just didn’t work for me. I was more of a non-linear thinker that needed my own time to grasp a given body of knowledge from first-principles and connect the disparate nodes to create network connections to the mental models. I took it to prove him wrong and to myself that I would one day become a scientist and inventor, no matter what anyone said, thought, or no matter what life events happened. Immediately I changed my strategy to work from 1 AM – 5 AM in the quietest hours of the night to learn everything from quantum mechanics to equilibrium reactions. It was unorthodox but I taught myself by imagining where I wanted to be in life, regardless of the cards in front of me. I went from below average in the class to a top 4 student ultimately getting a 4 on the AP Chemistry exam and not having to take a Chemistry class again. To this day, if it wasn’t for Mr. Montgomery mentoring me, talking to me everyday after school about the crazy physics of quantum particles or galaxies, and continuously...
giving me the support to be ambitious I wouldn’t have been on the path towards a scientist and inventor. Thanks Mr. Montgomery – I hope you rest in peace in whichever plane of existence you may be in.

To my uncle, Dr. Bipen Bhakta, Emeritus and Charterhouse Professor of Rehabilitation Medicine at University of Leeds, UK:

Growing up, I couldn’t afford all the latest tools for education nor speak to other kids about the crazy visions and ideas I had about the science I was learning. Fortunately, as I was growing up my uncle would bring me books to read and toys that would spark my imagination. When I was 5 years old, he brought me a lego set. I will not forget the impact that had on me till this day. My parents couldn’t always afford to give me the newest toys so I built them from this lego set. I would build houses that I would see on TV. I would build cars I would see on the road. And I would build power ranger and Gundam action figures which were the hottest toys at the time. He would bring to me books of Isaac Newton, Albert Einstein, and other great scientists that have advanced humanity forward. Every time he would come visit, I would save up my crazy questions about how the heart worked, why we were all made up of atoms, and what the future looks like. Some of these questions he had answers for and some he would defer to me to explore. He was a key mentor of mine and was constantly encouraging me to learn as much as I could about anything. As I grew up, I would visit him and my cousins in Leeds, UK and he would visit us regularly. He was a world leader in the field of Rehabilitation Medicine and I am honored to have had a mentor like him. He passed away in December 2014 due to brain cancer. He will be remembered by all as a warm, intelligent, and caring individual that sought to create a better humanity. May you rest in peace in whichever plane of existence you may be in.
BIOGRAPHY

Raj Pravinbhai Bhakta was born in Riverside, California on January 28, 1992 as the only child to Pravinbhai and Sharmisthaben Bhakta. In 1993, his family moved to Houston, TX to start their own version of the American dream. He was always the type of kid that would ask ‘Why?’—never ceasing to wonder at the stars and ponder about life’s existence. As a curious builder, he would make things he couldn’t readily afford like toys and would hack together computer parts to soup up his hold eMachines computer (700 MHz, 256 MB Ram). As a curious thinker, he would dabble in physics and philosophy. In high-school he discovered quantum mechanics and the study of metaphysics, philosophy of science, and philosophy of physics. He wanted to one-day become a scientist, philosopher, and inventor that could set humanity onto a path where the future looks more like Star Trek than Star Wars.

He received enough scholarships to attend The University of Texas-Austin and graduate with a B.S. in Physics, a concentration in Radiation Physics and Nuclear Engineering, and a custom minor in Philosophy of Physics where he completed a thesis studying ‘The Nature of Space in the Quantum Wave Function’ with his advisor Dr. Cory Juhl. Initially he wanted to receive a PhD in Philosophy of Physics & Science to better understand what it means to study Science and to one-day come up with answers to the most pressing questions about the nature of our physical reality. He quickly realized that the most practical route to create positive change for humanity was by studying engineering and inventing real-world solutions to humanity’s most pressing problems like healthcare, natural resource depletion, and access to meaningful work for all. In his junior year he pivoted into studying Nuclear Engineering and studied abroad at TU Delft through a scholarship where he took a class with Dr. Sheldon Landsberger from UT-Austin. He immediately fell in love with Nuclear Engineering as he saw promise to create
security solutions for nuclear non-proliferation and energy security. Thereafter, he began doing research with Dr. Landsberger with a 14 MeV neutron interrogation project for nuclear forensics with a research scientist at Sandia National Labs. This allowed him to apply for and receive a $10,000 research fellowship to work at Y-12 National Security Complex in Oak Ridge, Tennessee where the nation’s uranium material is stored, processed, and safeguarded for national security purposes. His research mentor, Dr. James Bradshaw a fellow Physicist himself encouraged him to keep pursuing inventorship and entrepreneurship as a budding scientist. His experience at Y-12 cemented his decision to apply for graduate school and he eventually came to NC State University for a PhD in Nuclear Engineering. After spending a semester there, he knew this field wouldn’t be the best fit for his strengths and ultimate ambitions. In the summer of 2015, he left to Mumbai, India to make it as a top 10 contestant on the Indian Dance Reality show called ‘Dance India Dance: North America’. As a long-time dancer, he knew he couldn’t say no to this ‘once in a lifetime opportunity’ so he left his research to embark on this dance journey to take time off to think deeply about the next adventure. After coming back to NC State in Fall 2015, he began pitching his inventions for a self-powered wearable radiation sensor to numerous professors from materials science to textiles. He found a young, energetic, and entrepreneurial professor Dr. Jesse Jur in summer 2015. After spending an additional semester taking business classes in Engineering Management and Technology Commercialization (where he was one of the only students to receive the highest grade in the history of the class), he knew entrepreneurship was for him. A week before he was running out of funding, Dr. Jesse Jur called him into his office to offer him a position in his research group. After learning about the world of textiles, he was immediately fascinated about the opportunity to fill a huge gap – he realized that humanity had smartphones, smart TVs, and smart cars but didn’t have smarter clothing or
textiles. He immediately took the position as a funded researcher in the ASSIST wearables research center and sought to create a platform technology that could enable him to create a positive social impact on humanity through smarter clothing and textiles. Along the way, he's been through entrepreneurship classes, start-up accelerators, pitch contests, and in October 2017 started his company Funxion which aims to usher in a world of smarter clothing and textiles. The road to completing his PhD in Fiber & Polymer Science and starting up his company to translate his research from lab-to-marketplace has been exciting, painful at times, and incredibly rewarding. He owes it to all of his mentors, friends, family, and world-class resources at NC State University for giving him the opportunity to truly ‘Think and Do the Extraordinary’. What starts here, changes the world and there’s no other way to do it than by ‘Thinking and Doing’.
ACKNOWLEDGMENTS

Acknowledgements go out first and foremost to Dr. Jesse Jur who took a chance, believed in my crazy ideas, and who gave me the creative freedom to pursue entrepreneurship, ultimately leading to the creation of a new venture called Funxion whose mission is to usher in a world of smarter clothing. I would also like to acknowledge my PhD committee with whom I have shared intellectual discussions and feedback about this research work. I would also like to thank everyone at the ASSIST research center, College of Textiles, and of course my research group. All the research group members I have interacted with and worked with have taught me many things about various fields including fashion, product development, design, electronics, materials science, chemistry, and mechanical engineering among others. The future of education is truly interdisciplinary so I thank NC State University for cultivating a culture of inclusion from all walks of life, a culture where thinking and doing is celebrated, and a culture where pursuing entrepreneurship along one’s path towards inventorship is encouraged and supported.

I would also like to thank the NC State MBA TEC program which gave me the foundation of business fundamentals and taught me how to evaluate new venture opportunities, the NSF I-Corps program which gave Dr. Jesse Jur and I a $50,000 grant to conduct customer discovery on over 100+ stakeholders in the value chain of wearable technology and smart textiles markets, the NC IDEA Labs start-up accelerator which allowed me to learn so much about consumer products and sales/marketing, and finally NSF SBIR Phase I program which has given my company Funxion its startup funds of $225,000 to start our dream towards creating smarter clothing for all. I would also like to acknowledge my Co-Founder/CTO Dr. Hasan Shahariar with whom I started Funxion and have enjoyed dreaming and inventing the craziest of ideas.
# TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................... xi
LIST OF FIGURES ......................................................................................................... xii

## Chapter 1: Motivation of Research

1.1. Market Research done via I-Corps ................................................................. 1
1.2. Customer Discovery done via NSF I-Corps Program ............................. 3
1.3. Alternative Solutions to Functionalizing Textiles ................................. 7
1.4. Techno-economics of Direct-write Printing ........................................... 10
1.5. Fundamental Research and Device Validation Questions .................. 12

## Chapter 2: What is Textile Electronics?

2.1. Why wearable textile electronics? ................................................................. 15
2.2. Functionalization Strategies for Biosensing Textile Electronics: Conductive Fibers/Yarns ............................... 16
2.3. What are biosensing fibers? ........................................................................ 17
2.4. Biocompatibility with the skin .................................................................... 21
2.5. Effect of material and processing on property values of biosensing fibers – An Overview ................................. 23
2.6. Material Properties of optical fibers ......................................................... 25
2.7. Manufacturing effects for optical fibers ................................................. 26
2.8. Integration into wearable textiles ............................................................... 29
2.9. Future trends and outlook of this field ................................................... 30
2.10. Trends in functionalization of polymer fibers ........................................ 31
2.11. Trends in polymer multi-material semiconductor fibers .................. 34
2.12. Wearable Biosensing Fibers ..................................................................... 36
2.13. Functionalization Strategies for Biosensing Textile Electronics: Printed Electronics ................................. 39
2.14. Screen printing and the state-of-the-art: ................................................ 39
2.15. Conductive Ink Printing via Direct-write Printing ............................... 41
2.16. Direct-write Printing and Automation ....................................................... 42
2.17. Principles of Direct-write printing ............................................................. 46
2.18. Ink Rheology for Direct-write Printed Electronics ............................. 47
2.19. Direct-write Printing and Automation ....................................................... 47
2.20. Material-Process-Device Relationships ................................................... 53
2.21. Conclusion ................................................................................................. 54

## Chapter 3: Rheological Studies of Conductive Inks for Direct-write Printing

3.1. Experimental Section ..................................................................................... 59
  3.1.1. Ink Rheology Testing ............................................................................. 59
  3.1.2. Experimental Method for testing ink rheology ........................................ 60
  3.1.3. Ink Rheology Results ............................................................................. 60
  3.1.4. Relaxation Time of Jettable Fluids ....................................................... 62
  3.1.5. Ink-to-Textile Interactions .................................................................... 65
  3.1.6. Experimental Method for contact angle studies .................................... 68
  3.1.7. Contact angle results ............................................................................. 69
  3.1.8. Research Conclusion - Experimental Plan 1: ....................................... 70
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>This table benchmarks each separate process in terms of production time, cost, number of steps, and design process.</td>
<td>5</td>
</tr>
<tr>
<td>Table 2.1</td>
<td>Shows the experimental plan for finding the processability regime for direct-write printing onto textiles.</td>
<td>67</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Shows the experimental plan for demonstrating the ECG Shirt.</td>
<td>91</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1.1  IDTechEx’s Wearable Technology forecast based on their customer discovery and financial projections in 2015 ................................................................. 4

Figure 1.2  Depicts the complex/parallel supply chain for textiles and electronic components from IDTechEx ................................................................................ 5

Figure 1.3  The progression of value chain moving from conductive yarn based technologies to conductive ink based technologies .................................................. 6

Figure 1.4  This is the current manufacturing process for a smart garment utilizing conductive yarn technologies ................................................................. 7

Figure 1.5  This shows the primary customers in the value chain and the major interviews we conducted from our 100+ I-Corps interviews ............................... 9

Figure 1.6  This shows the Experience Curve simulating the unit cost of a smart garment per doubling of production quantity for the current technology (conductive yarns) and our technology ......................................................... 12

Figure 2.1  E-textiles in smart clothing production stage .................................................. 15

Figure 2.2  This shows the sensor setup for a typical smart garment made from silver biosensing fibers ................................................................. 18

Figure 2.3  This figure represents the equivalent circuit elements and causes of impedance for a biopotential signal to reach from the body to the electrode on the left and the associated electrocardiogram spectrum on the right ........ 19

Figure 2.4  This figure shows a typical optical fiber sensing setup in a wearable textile system. The figure on the right shows a typical photoplethysmography spectrum ................................................................. 20

Figure 2.5  Optical penetration depth of light vs wavelength of light in relation to the human skin (upper left), optical penetration depth of light vs wavelength of light in relation to human mucous tissue. Schematic of the physical mechanism of light propagation through the skin and the absorption and scattering events in the tissue (upper right). The absorption coefficients relating to the optical penetration depth into mucous tissue (lower right) ........ 25

Figure 2.6  This figure shows the process of fabricating optical fibers at production scale using the thermal drawing process .................................................. 26

Figure 2.7  This figure shows the reaction time and reaction temperature relationships for the optical fiber polymerization process. The precise control of
temperature is paramount to achieving desired physical properties in optical fibers .................................................................................................................................................. 27

Figure 2.8  This figure shows the dip-coating process used to functionalize polyurethane and cotton polymer fibers with silver nanowires and encapsulate (for protection) with PDMS. An intermediate process of hydrogen plasma treatment is used to remove the PVP dispersing agent from the yarn composite for enhanced conductivity ................................................................................................... 31

Figure 2.9  This figure shows the mechanical strain and stretching cycle data with respect to conductivity. The corresponding SEM images show the morphology of the conductive yarn and delamination and cracking effects after 300% strain and 1000 bending cycles ......................................................................................................................... 32

Figure 2.10  This figure shows the SEM images of the microstructured optical fiber with polymer shell with embedded microelectrodes and a semiconductor core ............................................................................................................................................................................. 34

Figure 2.11  This figure shows the optical fiber device utilizing a polymer shell with internal embedded electrodes and a semiconductor core. This device setup can be used as a photodetector. Future possibilities include such a fiber device being assembled into a fabric system for wearable biosensing for PPG ...................................................................................................................................................................................... 34

Figure 2.12  This shows the future multimaterial and multimodal possibilities of hybrid polymer-metallic-semiconductor optoelectronic fibers. Such fibers can have micro to nano level features and devices embedded and be assembled into fabric structures as shown on the right ...................................................................................................................................................................... 35

Figure 2.13  Shows the conventional table-top screen-printing setup wherein ink is flooded over a patterned screen for printing onto a given substrate. B) Shows a rotary screen setup in which a cylindrical patterned screen system is used to print roll-to-roll onto a substrate at high-throughput ........................................................................ 39

Figure 2.14  A) A schematic of the direct-write process with drop-on-demand mode being used to print on the textile substrate that could be used for designing various types of devices B) meshed-patch antenna device being printed using this direct-write drop-on-demand mode directly on a nonwoven textile. C) The process can also be used as direct-write printing on a film such as thermoplastic polyurethane (TPU) heat-laminted onto a polyester-spandex knitted textile for application in smart garments D) heat laminated interconnects in a meandering pattern and an electrocardiogram shirt as concepts for wearable devices for health monitoring E) The direct-write process enables a vision to achieve automated printing of textile electronics for multi-modal sensing and/or energy harvesting in a garment ......................................................................... 42
Figure 2.15 Shows the throughput of similar direct-write systems used for printed, flexible, and stretchable electronics applications .......................................................... 45

Figure 2.16 A) The continuous filament extrusion mode wherein the functional material such as a shear-thinning conductive ink is extruded. The throughput is limited in this case at high velocities (10 mm/sec +) due to breakage of the filament on rough surfaces such as textiles; B) the drop-on-demand mode which allows an ‘inkjet’ like approach to droplet deposition of conductive inks ................................................................. 46

Figure 2.17 Left: Ag volume fraction in relation to the viscosity, observed to be in accordance to the percolation network theory of particle suspensions for 3D printing. Middle: The apparent viscosity profile of the AgTPU and TPU materials. It can be observed that the TPU material behaves much more like a newtonian fluid where there is no observed change in viscosity during the shear-rate sweep, while the AgTPU material behaves like a non-newtonian power-law fluid. Right: The viscoelastic flow behavior of the Ag ink with thermoplastic polyurethane binder (TPU) and its native fluid material set without any additive particle suspension. The rheological profiles are quite different where the TPU native behaves much like ‘water’ and the AgTPU behaves like a viscoelastic material with a yield stress around 10 Pa.................................................................................. 47

Figure 2.18 The power-law model for shear-thinning viscoelastic systems.......................... 48

Figure 2.19 The various solvent’s effect on penetration depth into the textile’s fibrous structure due to their vapor pressure values. A lower vapor pressure showed a higher penetration depth due to capillary action ......................................................... 49

Figure 2.20 The ECG spectrum by a printed dry electrode .................................................. 51

Figure 2.21 Inkjet-printing reactive silver inks on textiles for textile heater.......................... 51

Figure 3.1 Rheology characterization of conductive ink, where A) & B) shows the viscosity vs. shear rate and the elastic modulus vs. shear stress of the ink diluted with different weight ratios of solvent. C) & D) show the similar data for stretchable conductive ink with PU binder in it ......................................................... 59

Figure 3.2 Shows the on-off DoD actuation period based on the jetting frequency............. 60

Figure 3.3 Shows the relaxation modulus (Pa) decay as a function of time (s). The ideal relaxation time for our fluid ejection system is less than 5 ms ......................... 61

Figure 3.4 Shows the linear relationship of relaxation time (ms) and Viscosity (Pa*s) at 77 ........................................................................................................... 61
Figure 3.5  This figure shows the ink penetration phenomena as a function of the fluid pressure and ink viscosity/dilution.................................................................62

Figure 3.6  D) This shows the ink permeation into the fiber bulk for a Nylon knitted textile and E) & F) the associated electromechanical properties as a function of strain and strain cycles done at 30% strain.................................................63

Figure 3.7  This shows the permeation depth into the textile fiber bulk as a function of the vapor pressure. The ink used in this work is DuPont PE873 Intexar Ag conductive ink. Its solvent system is Glycol Ether which is in the middle of the solvents used in Jin’s study ...........................................................................64

Figure 3.8  The top figure shows the contact angle as a function of time for the various aforementioned ink dilutions. The bottom figure shows the ink’s flow properties into the textile system as a function of viscosity.................................................66

Figure 4.1  This figure shows the TGA (Thermogravimetric Analysis) of the polymer binder or interface material used in the conductive inks which is a thermoplastic polyurethane based material with silica particles as filler for enhanced processability and Glycol Ether as the solvent. This material is DuPont Intexar PE773. The scale is from 20 C to 700 C (with 100 C increments)............................................................................................................70

Figure 4.2  This is the TGA (Thermogravimetric Analysis) data for the Ag Ink. This indicates the optimal curing temperature before thermally induced degradation occurs. This indicates that the optimal curing temperature for such a material is 160 C - 250 C. This material is DuPont Intexar PE873 .............71

Figure 4.3  This study done by Park et al looked at the relationship of sintering time vs sheet resistance of printed lines using their Ag nanoparticle and micro-flake particle based ink. Our conductive material set will undergo a similar experiment but with various temperatures..........................................................72

Figure 4.4  Shows the electrical resistance as a function of time for various curing methods such as thermal oven and infrared based curing. A kapton substrate was used as a control due to its low surface roughness in comparison to the polyester-spandex knit textile. Heat-press post-process was also studied indicating that the combination of infrared curing with subsequent heat-press at the same temperature allows for lower electrical resistance... ........................................................................................................72

Figure 4.5  Shows the curing profiles as a function of curing time for various temperatures for direct-write printed silver ink on polyester-spandex knit .......... 73
Figure 4.6 Shows the optical images of the various curing temperatures and curing times at mechanical strains of 0% and 50% for comparison of ink-to-fiber bundle morphologies ................................................................. 74

Figure 4.7 Shows the SEM cross-sectional view of the ink penetration into the fiber bulk of the knitted textile. The Ag ink penetrates into fiber bundles forming a composite ................................................................. 75

Figure 4.8 Shows the SEM X-S image and zoom-in of the ink-to-fiber bundle composite structure formed. As can be observed, the bundles are coated conformally with the ink with a good coating amongst the fiber bundle. .............. 76

Figure 4.9 Shows the SEM X-S image and zoom-in of the ink-to-fiber bundle composite structure formed. As can be observed, the bundles are not as well coated with ink as the 120 C and 160 C samples ........................................... 76

Figure 4.10 Shows the SEM X-S image and zoom-in of the ink-to-fiber bundle composite structure formed. As can be observed, the bundles are coated with the ink well, however, the individual fibers are more closely packed together indicating localized heating induced fiber agglomeration. This may affect electromechanical behavior ................................................................. 77

Figure 5.1 Process flow chart of the proposed test method ................................................................. 82

Figure 5.2 a) The change in resistance and, b) the composite failure index as a function of strain composite ........................................................................................................ 83

Figure 5.3 Thermal images of interconnects under 0%, 25%, and 175% strain, with brighter spots indicating crack formation ................................................................. 85

Figure 5.4 a) The change in resistance and, b) the composite failure index as a function of strain composite ........................................................................................................ 85

Figure 5.5 Thermal images of interconnects under 0, 150, and 1000 cycles of 20% strain at 20 mm/s, with brighter spots indicating crack formation ........................................... 87
CHAPTER 1

1.0. Motivation of Research:

Smart textiles are a burgeoning class of textiles within the greater market of the textile industry. There has been increased focus on innovating functionality offered by the textiles that are worn on the human body, that are used in industrial settings for use-cases such as filtration, and within mobilized transportation environments such as automotive, air travel, and sub-ground travel. Functionality such as sensing, heating, cooling, self-cleaning, color changing, and the like are increasingly being researched by material scientists and being aimed at commercialization for the benefit of society and the human condition.

As such, there is an inherent need to satisfy the needs of realizing such systems in a low-cost and scalable fashion, two of the most fundamental criteria for mass adoption of textile technologies.

In the coming years, the internet-of-things (IoT) will transform the way commerce and data flows through the world, especially as it relates to the coming upgrade of internet infrastructure known as ‘Web 3.0’. Within the socio-economic fabric of society, IoT will weave living sensor nodes through wearable technologies and make inanimate objects such as clothing, backpacks, and filters active objects that stream data to anyone and anywhere. This will be the next technology wave after the industrial revolution and will be enabled by co-technologies such as artificial intelligence, self-driving vehicles, and smart cities among other technology classes.

Within this context of technology disruption, textiles will also begin to be connected to this living fabric of information flow/commerce and personal data will be utilized for the mass benefit of humanity. For example, what if all humans were wearing a smart garment that was detecting ECG in real-time and onset of disease/sickness was being tracked for free? What if all
humans were wearing this smart garment and were being passively heated/cooled? What if all humans were wearing these smart garments and didn’t have to spend time, money, and valuable natural resources like water washing their clothing? What if all humans were wearing color changing clothing so that they would not have to buy multiple garments? This is the fundamental value proposition smart garments offers to humanity and is at the core of this fundamental research. Thus, the compliance, comfort, user-experience, form factor, and ubiquity of textiles being at the core of the human condition, justifies the pursuit of research that allows for manufacturing and disseminating smart textile electronics to the masses. The amount of data that can be harnessed from textiles is incredible given the proximity and acceptance to the human body. However, in order to realize this technological vision, the manufacturing technologies must allow for smart garments to be produced at similar cost to traditional textiles, a hypothesis that was empirically validated by the qualitative customer discovery done through the National Science Foundation’s I-Corps program for technology commercialization. This is the fundamental purpose of the research described in this doctorate thesis.

In order to reliably understand a starting point for this vision, a smart garment that can detect one’s electrocardiogram was chosen to be developed and validated in a low-cost and scalable fashion as part of the National Science Foundation’s ASSIST self-powered wearable technology research center. The reason an electrocardiogram sensing garment is of interest is because within the greater market of digital healthcare, cardiac disease is the number one cause of deaths worldwide.
1.1. Market Research done via I-Corps

The $30 B wearable technology market is growing at a rate of 17% CAGR and encompasses wearable platforms such as wrist-worn devices, hearables, skin patches, and smart clothing (Figure 1). The market has grown substantially as a result of the interest in wrist-worn devices and now hearables. However, as trends in miniaturization of sensor technologies, flexible form factors, accuracy of sensor data, and passive user-experiences become a forefront need for the user, many sensor technologies will migrate to skin patches or smart fabric platforms. For example, skin patches are ideal for acquiring biophysical signals such as electromyogram and electrocardiogram due to their close contact with the skin however cannot be used for long-term monitoring due to their maximum lifetime of 7 days. There are also comfort issues with the skin adhesives which cause skin irritation for many users during sweating. Smart garments on the other hand are much more comfortable and compatible with long-term physiological monitoring however have issues with motion artefacts which affect ultimate signal quality. In addition, manufacturing costs of smart biometric garments are high due to complex embroidery processes or multi-step human-assisted labor based processes.
The market for textile electronics on the other hand is still in its infancy at a market value of only $90 Million. It is fragmented with respect to product consulting companies, product development companies, materials suppliers, and small to large brands. There have been many first movers in the market but they have not grown as initially projected. There are three main problems facing current textile electronics companies:

- the demand from the market has not been there for high priced products ($100+/unit garment devices)
- the manufacturing processes have not been able to scale beyond 1000 units/week
- the supply chain is very complex and fragmented (Figure 2)
These issues have led to a lack of organic growth in the market. However, trends in the market towards solving many of these problems are promising. For example, in 2016 around 70% of stakeholders in the textile electronics value chain primarily utilized conductive yarn based materials and manufacturing processes. However, after 2017 around 70% of the market flipped to the usage of conductive inks and printed electronics manufacturing processes (Figure 3). This abrupt switchover in materials usage and processes towards printed electronics was mainly driven by the ease of manufacturing and the potential to achieve low-cost offered by printed electronics. After interviewing 100 stakeholders in the textile electronic market we realized that printed electronics will be the dominant technology roadmap for achieving low-cost textile electronic devices. However, it’s not good enough because automation processes are still not in place.
Figure 1.3: The progression of value chain moving from conductive yarn based technologies to conductive ink based technologies (Hayward, 2017).

Lastly, numerous government funds have been allocated for investment for smart fabric based technology with the vision being to usher in advanced manufacturing of smart textiles in the USA to create a new industry altogether. AFFOA (funded by Department of Defense) is the largest with $250 M in committed funding with industry matching (CITE). NSF has also made many research investments but on the conductive yarn side (CITE). Both of these mentioned investments have been on conductive fiber and conductive yarn technologies which as shown in
figure 4, the smart textiles supply chain is moving away from. Furthermore, both technologies from a TRL standpoint will take many years to become commercialized. To put it in perspective, the need for the problem of manufacturing must be solved now and thus there is a great imperative to solve this problem to grow a market that stakeholders can then participate in.

1.2. Customer Discovery done via NSF I-Corps Program

The commercial opportunity thus arises to create a manufacturing platform that can allow clothing manufacturers to make smart textile products. The business model is hypothesized to be a razor-razor blade model wherein the machine is sold to companies like MAS Holdings, Flextronics, Jabil (Clothing+), AiQ, Hexoskin, Sensoria, or OMSignal. The most immediate application within smart textiles as discovered during I-Corps is a smart garment with biosensing capabilities for measuring ECG, heart rate, and heart rate variability.

Our customer is the garment manufacturer. In this case, there are around 7 actively participating smart garment companies. All of these companies have the aforementioned problems of production scale and cost. The fundamental problem is that smart garment manufacturers are taking a multi-step, laborious process in manufacturing smart garments as shown in Figure 1.4 below:

![Figure 1.4](image)

**Figure 1.4:** This is the current manufacturing process for a smart garment utilizing conductive yarn technologies.

Our proposed solution seeks to decrease the current time it takes from 174 min (2.9 hours) to 5 min. This would mean a 36x reduction in production time and a 5x reduction in cost
as needed for our customers like MAS Holdings, for example (MAS Holdings). The reason for the large production time is due to laborious stitching, embroidery, and packaging techniques used for textile electronics currently that are borrowed from traditional textile manufacturing and not yet fit for scaling more than 1000 units/week (Figure CO-1). For example, we interviewed two key decision makers within MAS Holdings to dive into this problem from a techno-economic standpoint. Kosala Jayasundra is the Director of Wearable Technologies at MAS Holdings and is the lead product developer for 3 out of the 4 smart garments sold on the market currently from companies like Athos, OMSignal, and Polo Ralph Lauren. He concluded that there needs to be a breakthrough involving automation and materials developments to substantially lower the cost of production for many consumers to enter the smart garment market (Figure 1.4). To further understand the need for automation and materials developments, we talked to Dr. Chandrika Wickramatillake the GM of Automation at MAS Holdings. He is very bullish on the need for automation for garment manufacturing (Figure CO-2). We discussed the vision for our innovation for the textile electronics market, specifically starting with the smart garment market segment. As a potential customer and stakeholder, he understood the value of our innovation for his company’s business model.
Customer Discovery in the Value Chain for Smart Textiles

![Value Chain Diagram]

**Figure 1.5:** This shows the primary customers in the value chain and the major interviews we conducted from our 100+ I-Corps interviews.

In the value chain for textiles and apparel, ultimately it is the brands that drive the market demand. One of these brands is PVH, a $10 B umbrella for brands like Calvin Klein, Tommy Hilfiger, and Michael Kors among others. Their Innovation Next division is a key partner in our ASSIST ERC and has visited our labs as well. We talked to *Chris Kelly and Kashif Noor, Directors of Innovation at PVH* whose interest in the next wave of innovation is in smart garments (Figure CO-2). Ultimately, a brand like PVH would like a turn-key product solution from their manufacturing partner MAS Holdings. For such a brand to come out with an innovative product, a company like ours would have to produce a proof-of-concept while showing the manufacturing efficacy of our solution. They have expressed great interest in our solution given the need for innovation in the garments space and the excitement from their consumer base.

These interviews were key given our mutual partnership with MAS Holdings and PVH through the ASSIST ERC. The value of entering the textile electronics space through a large
smart garment manufacturer like MAS Holdings and a brand like PVH is key to our strategy to test our MVP solution and move forward to other smart garment manufacturers.

1.3. Alternative Solutions to Functionalizing Textiles

Conductive yarns are used to manufacture many textile electronics products and are currently used to knit or weave silver or stainless steel based conductive yarns into smart garments (Dion, 2013). This technology exists currently either in full-garment knitting or in multi-step embroidery based processes. In full-garment knitting, it is projected that an entire seamless smart garment can be knitted in 45 minutes with interconnects and sensors, however this process has not yet been demonstrated or commercialized (Dion, 2013). Furthermore, this process is still not reliable for manufacturing due to the incompatibility of current conductive yarns with such knitting machines (Schwarz, 2016). On the other hand, embroidery of conductive yarns onto a cut-and-sew garment takes around 3 hours and is currently the state of the art process for creating a smart garment at MAS Holdings, the largest smart clothing manufacturer in the world. These methods are currently not feasible to meet market demands in the next 5 years as discussed previously.

Furthermore, challenges of current printed electronics on textile processes such as screen-printing are threefold: lack of complete automation, requires interface films for printing, and design process is not software based. Screen-printing is a versatile process for printing conductive patterns onto films that can then be heat-laminated onto textiles, however, there is still labor required to do so at the right area on the garment, especially as it relates to the placement of sensors.
Table 1.1: This table benchmarks each separate process in terms of production time, cost, number of steps, and design process.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Production Time</th>
<th>Production Cost</th>
<th># of steps</th>
<th>Design process</th>
<th>Materials Breadth</th>
<th>Durability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductive yarns – Full</td>
<td>45 min</td>
<td>$60</td>
<td>1</td>
<td>Software CAD</td>
<td>Multi-material yarns</td>
<td>N/A</td>
</tr>
<tr>
<td>garment knitting</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductive yarns –</td>
<td>180 min</td>
<td>$60</td>
<td>5+</td>
<td>Software CAD</td>
<td>Multi-material yarns</td>
<td>50 washes</td>
</tr>
<tr>
<td>Embroidery</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Screen-printing</td>
<td>30-45 min</td>
<td>$90</td>
<td>5+</td>
<td>Stencil</td>
<td>Multi-material dielectric and</td>
<td>50 washes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>conductive</td>
<td></td>
</tr>
<tr>
<td>Direct-write printed electronics</td>
<td>5 min</td>
<td>$12</td>
<td>6</td>
<td>Software CAD</td>
<td>Multi-material dielectric and</td>
<td>50 washes</td>
</tr>
<tr>
<td>(Our Process)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>conductive</td>
<td></td>
</tr>
</tbody>
</table>

1.4. Techno-economics of Direct-write Printing

To show how our innovation compares techno-economically to the current technologies, we simulated the unit costs as production scale doubles using the ‘Experience Curve’ methodology (Lloyd, 1979). As shown below in Figure TI-2, our projected unit cost will be very competitive with current production methods for producing a smart garment with economies of scale. Thus, this bodes well for our technology to disrupt the market in a fast manner and communicates our value proposition to smart garment manufacturers and brands alike.
Figure 1.6: This shows the Experience Curve simulating the unit cost of a smart garment per doubling of production quantity for the current technology (conductive yarns) and our technology.

1.5 Fundamental Research and Device Validation Questions

The research methodology employed utilized qualitative customer discovery insights from interviewing 100 stakeholders in the textile electronics and wearable technology space to direct fundamental technology development. It was understood that a production time of 5 minutes and production cost of around $12 per smart garment would be sufficient in allowing for increased mass adoption among consumers (allowing a consumer retail cost of ~$70 per smart garment). From a fundamental research standpoint, two key relationships were employed: the physical/chemical properties of materials employed within the Direct-write process (Materials-to-Process properties) and the device validation outcomes (Process-to-Device properties). This
As such, we will study the following research and device validation questions:

- **Research Question 1**: What is the rheological processability regime for direct-write printing onto textiles?
- **Research Question 2**: How does jetting, wetting, and thermal curing process selection influence mechanical durability?
- **Device Demonstration**: ECG Shirt will be direct-write printed in 5 minutes by selecting optimal ink dilution and thermal curing process.
  - Can an ECG shirt be realized?
- **Device Validation Question 1**: Can a direct-write printed ECG shirt be realized in a production time of 5 minutes?
References

1. IDTechEx. Hayward 2017
CHAPTER 2

2.0. What is Textile Electronics?

Within the field of smart textiles, textile electronics encompasses the entire materials value chain from polymers all the way to full garments (Figure 2.1 below). The functionalization strategies for conductive yarn knitting, weaving, or embroidery differ from the post-process printed electronics functionalization strategy. There are benefits to both and there are a plethora of researchers pursuing both strategies as well. The literature review described herein will follow this materials value chain from ‘Atoms-to-Apparel’ to understand the breadth of this field, the state-of-the-art, and the future trends. This will allow a thorough review to build a picture of the landscape for navigating this realm.

![Figure 2.1: E-textiles in smart clothing production stage (edited figure from ref. [1]).](image)

2.1. Why wearable textile electronics?

Healthcare costs have skyrocketed over the years. Wearable biometric technology offers a new avenue in gathering biometric data about the patient’s vital signs. It has been reported that wearable biometric technology can save up to $200 Billion in healthcare costs by preventing diseases and ailments. This vision of preventative medicine is one that is driving advancements in many sectors ranging from high-tech and software to biotech and medicine. Saving on healthcare costs and preventing diseases before they happen with actionable insights gained
through wearable biometric technologies can increase patient outcomes, lead to longer life expectancies, and be a driver for the democratization of healthcare\textsuperscript{4}.

At the moment, around 20\% of the US population owns a wearable device making the market opportunity ripe\textsuperscript{3}. However, wearable technology today is primarily made out of silicone type rubbery materials that are limited to the wrist as a form factor and lack accuracy in biometric data produced. These materials are limited to mostly wrist based form factors, which at times have issues with comfort and long-term wearability\textsuperscript{5}. Fibers on the other hand offer an entirely new range of form factors that can span the entire body. Furthermore, fibers offer a new technology roadmap to achieve low-cost, scalability, and closeness to the body that allows increased accuracy\textsuperscript{2,4}. Fibers also allow for increased wearability and can be incorporated within textile structures for making smart textiles such as smart garments. Fibers with biosensing abilities can be woven or knitted into clothing or textile materials that can be used to collect biometrics such as electrocardiogram (ECG), photoplethysmography (PPG), or electromyogram (EMG)\textsuperscript{4,5}.

2.2. Functionalization Strategies for Biosensing Textile Electronics: Conductive Fibers/Yarns

As healthcare costs increase more than ever, wearable technology has been touted as a promising solution. Wearable biosensing fibers are promising candidates for enabling wearable smart garment textile systems for continuous biometric monitoring. There are two major types of biosensors: conductive yarn based sensors and optical fiber based sensors. The polymeric material selection and processing conditions during fabrication of such biosensing fibers affect the performance of the biosensing capabilities of these fibers. This literature review will cover how tuning the physical property values allows the proper fabrication of biosensing fibers that
can be used in wearable systems for optimal biometric measurements. In this literature review, it was found that functionalization techniques such as electroless plating were widely used with functional polymers as precursors for silver nanoparticles. For optical fibers it was found poly (methyl methacrylate) (PMMA) was a widely used polymer optical fiber used for biosensing. After surveying the literature, the trends indicate that nanomaterials such as silver nanowires will become a more widely adopted area of research as it relates to fabricating conductive yarns and their fabric based sensors for biosensing. As for optical fibers, hybrid polymer-metal-semiconductor based optoelectronic fiber devices will be used for biosensing applications. These two areas of wearable biosensing fibers are prime candidates for solving many of the problems with current wearable technology solutions.

2.3. What are biosensing fibers?

Biosensing fibers is a relatively new field within the greater field of sensors. Fiber based sensors are classified in two major categories: conductive fiber based sensors or optical fiber based sensors. Biosensing fibers are imparted with sensing abilities through either conductive coatings or intrinsic optical properties. Body contact sensors made from silver coated yarns are one category of biosensing fibers. Silver coated yarns can be used to sense one’s electrocardiogram, for example, by contacting the skin and directing the heart’s electropotential difference through the percolation network of silver material on the silver coated yarn. This is then sent to an electronic processing unit for analysis and filtering as shown in figure 1 below.
**Figure 2.2:** This shows the sensor setup for a typical smart garment made from silver biosensing fibers\(^2\).

This method of sensing the biopotentials is a popular one with many products out in the market already. On the other hand, optical sensing fibers such as poly(methyl methacrylate) (PMMA) utilize optical properties of fibers by directing light and then detecting backscatter to measure blood flow, and ultimately photoplethysmography\(^6\). Both types of biosensing fibers utilize polymeric properties either through the molecular interaction of the conductive particles with the polymer base or through the intrinsic optical properties of the fibers.

There are advantages and disadvantages to both types of biosensing fibers. For conductive fiber based biopotential sensors, there needs to be adequate skin-to-electrode contact as shown in figure 2 below. With adequate skin-to-electrode contact, there needs to be low impedance for the biopotential signal to have a high signal-to-noise ratio\(^7\). There are issues of motion artifacts for body-contact based sensors which is caused by slippage of the sensor from the body, leading to a loss in signal quality. This can be remedied by increasing the surface area of the fiber based sensor to increase skin contact, by creating three-dimensional conductive structures that can penetrate through skin, or by administering an adhesive polymeric coating\(^7,\(^8\).
These methods all rely on the polymeric surface interactions of the fibers with the top layer of the skin known as the stratum corneum. Most such textile based sensors are fabricated through either chemical functionalization or through printing of conductive inks onto the textile. Readily available inks such as Ag/AgCl inks can provide good skin-electrode impedance that can sufficiently detect biosignals such as electrocardiograms (ECG), electromyograms (EMG), or electroencephalograms (EEG).

![Figure 2.3](image)

**Figure 2.3:** This figure represents the equivalent circuit elements and causes of impedance for a biopotential signal to reach from the body to the electrode on the left and the associated electrocardiogram spectrum on the right.

As for optical biosensing fibers, the sensing mechanism for biometric signal acquisition such as of photoplethysmography (PPG) works through the emission and reflection of photons of the blood flowing beneath the tissue which a characteristic spectrum\(^1,9-13\). For an optical fiber based wearable sensing system, the optical fiber is typically woven into a textile in a detector and emitter setup as shown in figure 3 below\(^9\).
Light penetrates the tissue as shown in figure 4 from the surface of the skin (stratum corneum). Light is either scattered or absorbed in the tissue with blood being the primary absorbing medium within the visible and infrared spectrum of light. Human tissue is known to be anisotropic and not homogenous so light scattering and absorption is variable. As can be observed in the figure 4 (lower left) below, for mucous tissue the absorption coefficient varies with the wavelength with there being peak wavelengths at which the optical penetration depth is highest\textsuperscript{6, 14}. With different tissue types this is even more apparent (figure 4 left). In order to decrease the variation, the distance between the source and detector can be increased so as to allow some of the light to be absorbed into the tissue thereby increasing the signal quality.
**Figure 2.5**: Optical penetration depth of light vs wavelength of light in relation to the human skin (upper left), optical penetration depth of light vs wavelength of light in relation to human mucous tissue. Schematic of the physical mechanism of light propagation through the skin and the absorption and scattering events in the tissue (upper right). The absorption coefficients relating to the optical penetration depth into mucous tissue (lower right).

### 2.4. Biocompatibility with the skin

Biocompatibility is a required property of biosensing fibers. In the case of conductive coating based fibers such as silver coated yarns there is some concern of biocompatibility associated with these yarns. The level of release of the silver particles depends on their size. According to a study done by Kornphimol et al, it was found that there were releases of nano-silver from 0 mg/kg to 322 mg/kg. However, given the anti-bacterial nature of the silver it is known to be safe for skin as long as the particle size is bigger than the pore size of the human skin. Much of the release of metallic particles from coated yarns is due to sweat interactions creating an ionic solution in which the silver particles can exist in aqueous form. Ionic
concentrations of silver can also cause some cytotoxicity issues with skin but passivation coating with a metal such as titanium can decrease the likelihood of these issues\textsuperscript{12}. Long term biocompatibility studies on humans have not yet been done for these sorts of biosensing fibers. A study done by Cheng et al, tested their silver nano-wire based fibers for their biocompatibility\textsuperscript{12}. They implanted one of their fibers underneath the dorsal epidermis in mice for 8 weeks to observe the biocompatibility by measuring inflammation. It was found that there was no observed inflammation underneath the dorsal epidermis area, indicating the biocompatible nature of their silver nano-wire coated fibers\textsuperscript{12}. However, such studies have not been done on humans which have more biological complexity and more stringent guidelines for biocompatibility and cytotoxicity. Possible next steps include conducting biocompatibility studies over long-term monitoring with conductive metallic coated fibers for biosensing and their uptake into the skin and interactions with cells. It is known by some studies that such uptake into the body is minimal at most and is comparable to human uptake of other metals such as magnesium through food and water\textsuperscript{9}.

As for optical biosensing fibers, the biocompatibility is more prevalent due to the polymeric nature of the fiber composition. For example, optical fibers made from PMMA are biocompatible as well as those coated with biocompatible polyelectrolytes such as sodium alginate (SA) and poly (ethylenimine) (PEI)\textsuperscript{9}. Most fiber optic sensors are made from inert polymer materials and thus do not have issues with biocompatibility. In many wearable applications that are close to the skin, optical fiber based biosensors are more fit for biometric measurement\textsuperscript{9}. However, there are issues with signal quality and motion artifacts for optical fiber-based biosensors as will be discussed in later sections.
2.5. Effect of material and processing on property values of biosensing fibers – An Overview

Physical property values of mechanical, electrical, and optical properties can be manipulated by changing the material and processing conditions during fiber fabrication. For example, the mechanical properties of optical fibers extruded from a melt-spinning process depend on the polymer’s viscosity and temperature during the extrusion process. Drawing the fiber with a higher temperature aligns the polymer chains, increasing polymeric crystallinity. This in turn decreases the elongation at break values. However, for biosensing fibers with conductive coatings, the mechanical and electrical properties are largely determined by the coating material and the fiber’s polymer composition. For example, for a cellulose fiber such as cotton it was found that hydrogen bonding was the primary molecular interaction for bonding silver nanoparticles to the cotton fiber. This imparted a conductive coating onto the cotton fibers enhancing the conductivity of the textile. However, the coating solution’s pH greatly affected the agglomeration of the silver nanoparticles on the cotton fibers. Thus, the conductive properties and the biosensing properties can be greatly affected by the processing condition’s pH levels allowing for tunability of the final property values of the fiber. This variability can in turn be used to produce fibers with desired property values.

Fiber and polymer characteristics of biosensing fibers have to be controlled through the material and processing properties to be used in sensing devices. If the fiber and polymer characteristics are not commensurate with the needs for device fabrication then it becomes difficult to make biosensing devices. For example, textile based silver conductive yarn sensors for electrocardiogram measurements have to have good conductivity (low electrical resistance) and must have good contact with the skin to decrease skin impedance and allow the
electropotential biosignals to reach the silver conductive yarn sensors\textsuperscript{5, 16}. The electrical resistance of the yarns is affected primarily by the electrical resistance of the coating material and how well it adheres to the base fiber’s surface. This can be observed in polyethylene terephthalate (PET) based yarns that are coated with silver using electroless plating\textsuperscript{15}. On the other side of biosensing fibers, optical fibers are made through conventional extrusion or melt-spinning processes utilized in the textiles industry\textsuperscript{17}. Fiber and polymer characteristics for optical fiber biosensing devices are dependent more so on optical properties. For example, photonic biosensing fiber devices for photoplethysmography which can be used to infer heart rate, have to have good light transmission through the fiber and low attenuation loss to achieve a high signal-to-noise ratio\textsuperscript{6}. These optical properties can be tuned during the fabrication of the optical biosensing fibers. For example, a bi-component polymer composite is made by using cyclic olefin copolymer (COP) as the core and tetrafluoroethylene (THV) as the sheath\textsuperscript{6}. The optical fiber can be melt-spun to produce low surface roughness for low light attenuation, and good mechanical flexibility for embroidery and wearability. The temperature of the polymer melt, the ratio of the bi-component polymers, and the spinning rate have to be optimized to yield the target fiber characteristics.

2.6. Material Properties of optical fibers

For material properties of optical fibers, the polymer in the optical fiber must have good optical transparency and flexibility for use in wearable systems. Optical transparency is a property of interest when fabricating and formulating optical fibers\textsuperscript{9, 20}. This property is usually determined by molecular structure of the material which in the case of polymer based optical fibers must be amorphous (statistically oriented molecules)\textsuperscript{20}. For polymer based optical fibers the following polymers are used widely in the field: polystyrene, polycarbonate, polyolefin, and
preflourinated polymers\textsuperscript{9}. However, these materials may not always have the optical properties that are desired. As such, dopants must be used to reach the target refractive index during the fiber drawing process\textsuperscript{21}. This alludes to the effect of chemical composition. For optical fibers, the blend of polymers will also have a substantial effect on the optical fiber’s properties in regards to performance. The main performance characteristic that is affected by blending polymers is optical loss\textsuperscript{14}. Optical loss occurs when an optical signal (stream of photons) degrades as it propagates in the optical fiber, resulting in signal loss \textsuperscript{14}. In order to achieve low optical loss, the following material considerations must be taken into account: polymers with no hydrogen groups present, polymers with C-H bonds that have been partially or fully substituted with heavier atoms (deuterium, fluorine, or chlorine), or amplifying the optical signal by increasing photon intensity. Furthermore, material imperfections can also have a great effect. In particular, material imperfections in the polymers processing leading to impurities can lead to a lower glass transition temperature.

\textbf{2.7. Manufacturing effects for optical fibers}

In regards to the production of optical fibers, the process has a substantial impact on the optical properties, many times orders of magnitude impact\textsuperscript{14}. Environmental factors such as humidity and temperature can also affect the properties in sometimes a non-linear manner\textsuperscript{14}. Given this observation, the interdependence and correlation of multiple process parameters can lead to a more durable fiber, especially important for long-term wearability. For example, during the fiber drawing process lowering the temperature can enhance the drawing efficiency. This is because a temperature that is below the optimal drawing temperature decreases the transparency of the fiber. In regards to optical fibers used for wearable textile systems for biosensing, materials such as PMMA, PC, and PS are used even though they are stiff as compared to
conventional textile fibers. However, their material characteristics can be tuned to allow for more flexibility by increasing the viscosity of the polymer blend by increasing the molar mass for instance. For example, PMMA exhibits brittle behavior below a molecular mass of $10^4$ g/mol but is able to be drawn to form a fiber when its molecular mass is above $10^5$ g/mol. Another property that changes with molecular mass is the refractive index$^{21}$.

The simplest manufacturing method for fabricating polymer optical fibers is the extrusion process$^{22}$. This process requires a preform to extrude the fibers as shown in figure 7$^{23}$.

![Figure 2.6](image.png)

**Figure 2.6:** This figure shows the process of fabricating optical fibers at production scale using the thermal drawing process$^{23}$. Such a preform can be either macro, micro, or nanostructured to thermally draw optical fibers at kilometer long production scale. In the case of the widely PMMA optical fiber, a monomer of methyl methacrylate (MMA) is used with Benzoyl peroxide (BPO) as the polymerization initiator, and dodecanethiol (DDM) as chain transfer reagent$^{19}$. MMA has to be polymerized into a pre-polymer form by heating a mixture of MMA-BPO-DDM at 85 Celcius
for 3 hours\textsuperscript{19}. This mixture is then cast in the preform mold to be extruded. This process consists of three major steps: low temperature polymerization, homogenous polymerization and post-polymerization. In this process, the temperature must be precisely controlled for the chemical reactions to take place properly. Property values of the optical fiber will be highly dependent on the processing temperature. Figure 8 shows the relationships of reaction times and reaction temperature during the polymerization process.

![Figure 2.7](image)

**Figure 2.7**: This figure shows the reaction time and reaction temperature relationships for the optical fiber polymerization process. The precise control of temperature is paramount to achieving desired physical properties in optical fibers\textsuperscript{19}.

An issue that must be typically understood during the manufacturing of optical fibers is that of birefringence which is a phenomenon due to the difference in in the indices of refraction for the material as a light wave propagates from the surface of the fiber into and out of the fiber. For many optical fibers, imperfections in the geometry of the fiber or crystallinity due to polymer processing can cause birefringence which when anisotropic can cause differences in optical performance properties. However, birefringence can also be used to control the polarization of light within the fiber and be tuned to control the propagation of light depending on the polymer’s
molecular structure and fiber geometry\textsuperscript{19}. Birefringence can also lead to losses in the light propagation which in turn can lead to signal loss\textsuperscript{24}. Thus, it is important to understand the manufacturing processes and how they can affect the optical properties of polymeric optical fibers.

2.8. Integration into wearable textiles

Considering the textile integration, some polymeric materials are being developed to show considerable strength (similar to conventional yarn) with a high tensile modulus while still being highly flexible. These attributes can be shown in dynamic mechanical analysis (DMA) giving information on the viscous and elastic portion of a material. With this method, it was demonstrated that yarns can have a wide spread of property values. [78b] The polymeric fibers can then be varied and inter-changed to create a property spectrum as similar as possible comparing to yarns. With these, homogeneous textiles with integrated sensors are feasible. In the temperature range which is unproblematic for humans, all common fiber types can be used. While polymers melt or decompose at significantly lower temperatures than other material classes, their usage temperature usually exceeds the application range in which humans exist. The sensors can thus be worn in all climatic situations. Contrary, the resistance to solvents has to be evaluated on a case-to-case basis depending on the exact chemical composition of the fiber.

However, in regards to integration into textile systems for wearable sensing, polymer materials must show strength and durability to last through textile product processes such as weaving. In particular, high tensile modulus must be exhibited by the optical fiber while remaining flexible. The primary method of testing the mechanical properties and behavior of the optical fibers is through dynamic mechanical testing (DMA). DMA can be used to understand
the viscous and elastic portions of the material and thus relate the polymeric material properties to the mechanical properties. This analysis method can be used to create optical fibers with properties similar to those the textile polymer fibers and yarns that the optical fibers are going to be integrated into. This allows for compatibility during the manufacturing of the optical fiber based wearable textile sensing device as well as for its long-term durability. Ultimately, as more optical fibers related materials research is done that matches mechanical properties of textile fibers with that of the optical fibers, more products in the realm of wearable sensing will gain adoption. Furthermore, from a wearability standpoint, the operating temperature range of humans is far lower than that of the melting points of such optical fibers meaning decomposition or melting during normal wear is not a problem. However, solvent resistance is something that is not uniform across all polymer types so must be understood for the given set of polymers being used for the given use-case.

2.9. Future trends and outlook of this field

The future of wearable biosensing fibers will definitely be two-folded; body-contact sensors and optical fibers field will increasingly be researched further in regards to tuning the physical property values to enhance wearability and durability. As it relates to functionalization of polymer fibers, the research trend has moved towards the utilization of nanomaterials such as silver nanowires which offer higher aspect ratios and durability than nanoparticle based materials. This is primarily due to percolation theory which posits that for nanowire materials the percolation threshold for loaded material with respect to electrical conductivity is lower than for other geometries such as spherical nanoparticles. Such a scientific principle is increasingly being used to guide nanotechnology research as it relates to polymer fiber research from a functionalization and optical fiber extrusion perspective. Thus, the trend for both subsets of
wearable biosensing fibers is to move into utilizing nanomaterials in novel ways to enhance the physical property values of polymer fibers. The following sections will discuss studies that serve as examples of this trend.

2.10. Trends in functionalization of polymer fibers

Functionalization coatings with materials that can withstand washing is of paramount interest in the literature and has not been well studied. As such, many of the current solutions to functionalizing polymer textile fibers are not optimal for long-term durability of wearable devices. Given the review of literature in this field, it can be projected that an approach involving fundamental materials research and processing can solve many of the problems surrounding washability. Materials that have been explored topically but have not been commercialized are nanomaterials. In particular, a study done by Cheng et al, silver nanowires are used as nanomaterial to functionalize cotton and polyurethane yarns. In this study it was found that silver nanowire coated yarns were stretchable with up to 500% strain. This is a very good result that is promising in regards to the durability of such functionalized fibers. Such encapsulation methods utilizing PDMS based polymer materials can be used to prevent nanomaterial loss from the functionalized polymer-metal fiber matrix. This functionalization strategy would allow for a robust conductive yarn that can potentially be resistant to washing while being cost-effective and scalable to manufacture. The unique aspect from the perspective of polymer science is that this functionalization strategy utilizes a treatment with hydrogen plasma to remove polyvinylpyrrolidone (PVP) dispersing agent used to disperse the silver nanowires. Delamination effects of the polymer to the silver nanowire and polyurethane fiber were observed after 1000 cycles of strain at up to 150% strain. Figure 9 shows the images for the mechanical testing data with corresponding SEM images to demonstrate the morphology before and after mechanical
testing. This study is a representation of a trend towards the use of nanomaterials for functionalization of polymer fibers through a low-cost, scalable, and potentially high-throughput process. This process can potentially be less materials intensive compared to electroless plating for functionalizing fibers.

**Figure 2.8:** This figure shows the dip-coating process used to functionalize polyurethane and cotton polymer fibers with silver nanowires and encapsulate (for protection) with PDMS. An intermediate process of hydrogen plasma treatment is used to remove the PVP dispersing agent from the yarn composite for enhanced conductivity.\(^{27}\)
Figure 2.9: This figure shows the mechanical strain and stretching cycle data with respect to conductivity. The corresponding SEM images show the morphology of the conductive yarn and delamination and cracking effects after 300% strain and 1000 bending cycles\textsuperscript{27}.

However, an issue with the functionalization approach is that of sensor accuracy. When such fibers and materials are utilized to knit, weave, or embroider fabric based biosensors, what will the signal accuracy be? It has been demonstrated that silver nanowires can be used for biosensing with respect to electrocardiogram and electromyogram sensing\textsuperscript{23}. However, in this study the silver nanowires were spray coated on the surface of a PDMS film with the conductive element exposed. Biocompatibility is also an issue as it relates to long-term wearability for body-contact sensors. For the study done by Cheug et al, it was found that the silver nanowire coated conductive yarn was biocompatible for 8 weeks when implanted in a mice\textsuperscript{27}. However, studies on human biocompatibility have not yet been completed fully with respect to long-term monitoring as mentioned in a previous section. This where an opportunity lies for further interdisciplinary research bridging the fundamentals of polymer and materials science, device development, and integration into biological environments and form factors.
2.11. Trends in polymer multi-material semiconductor fibers

Future trends in wearable optical biosensing fibers include utilizing conventional extrusion processes for fabricating optical fibers with embedded multimaterial microelectronic devices. This complex but innovative process for optical fibers can be used to detect electromagnetic waves and sound waves as well as emit the same. As it relates to wearable biosensing optical fibers, this approach can lead to polymer optical fibers with embedded micro or nano electronics that can enhance biopotential signals. In addition, it can lead to the manufacturing of multimaterial kilometer scale optical fiber based devices for fabric systems.

In particular, research done by the Fink group at MIT has delved into this new field of multimaterial optical fibers to create scalable hybrid polymer-metallic-semiconductor fibers with robust optoelectronic properties. Such fibers represent a growing class of fiber based devices with tunable photodetection capabilities. These fibers consist of an omnidirectional reflecting polymer shell and a core semiconductor structure with embedded metal electrodes for device interfacing. The omnidirectional reflecting polymer shell can be tuned to let in a specific wavelengths of light and the semiconductor core can be used to measure a photocurrent for a wide variety of applications as shown in figure 11 and figure 12 below. The semiconductor material can be tuned to detect a wide range of wavelengths of light (infrared, ultraviolet, visible) and internally reflect the light in a one dimensional manner through the fiber. In essence, this device can be used for wearable biosensing to capture accurate PPG spectrums.
Figure 2.10: This figure shows the SEM images of the microstructured optical fiber with polymer shell with embedded microelectrodes and a semiconductor core\textsuperscript{23}.

Figure 2.11: This figure shows the optical fiber device utilizing a polymer shell with internal embedded electrodes and a semiconductor core. This device setup can be used as a photodetector. Future possibilities include such a fiber device being assembled into a fabric system for wearable biosensing for PPG\textsuperscript{5,23}. The evolution of these sorts of fibers for wearable biosensing is promising given the complexity of device and fiber architectures that can be created from this novel process to manufacture kilometer scale fibers. Future directions in this field are directed to the realization of various optoelectronic polymeric optical fiber sensing systems embedded in the fiber. This future vision indicates entire optical fiber based devices that can respond to multiple excitation modes and be assembled in fabric based systems as shown in figure 13 below.
Figure 2.12: This shows the future multimaterial and multimodal possibilities of hybrid polymer-metallic-semiconductor optoelectronic fibers. Such fibers can have micro to nano level features and devices embedded and be assembled into fabric structures as shown on the right.

2.12. Wearable Biosensing Fibers

From surveying the literature in the field of wearable biosensing fibers it can be realized that this field is split up into two major biosensing modalities: conductive yarn based sensors and optical fiber based sensors. For conductive yarn based sensors for wearable applications, functionalization methods such as electroless plating of fibers are used to provide conductivity to the fiber. Low electrical resistivity is desired and can be achieved through materials selection and process optimization. The coating method must allow for the conductive material to achieve covalent or ionic bonds to allow for proper adhesion to the surface of the fiber. Once the fiber is coated well with the conductive material it can be used to fabricate electrodes which can contact with the human body for biometric measurement. For optical fiber sensors, the polymer material must be selected with care as well as the corresponding fiber forming process. Thermal drawing is a widely employed technique for extruding fibers with various polymeric features and optoelectronic features that allow for wearable biosensing. The future of wearable biosensing fibers will be projected to grow with more adoption of nanomaterials for functionalization of polymer fibers and micro and nano-structured optical fibers with fiber device modalities. These
fields are developing with exciting innovations and this bodes well for the overarching medical field for wearable biosensing.
References


2.13. Functionalization Strategies for Biosensing Textile Electronics: Printed Electronics

2.14. Screen printing and the state-of-the-art:

Screen-printing is a printing method that has been used for centuries on a range of substrates for applying various fluid materials. It’s one printing technique that is used in the electronics industry for printing circuit boards and for the textile industry in printing onto apparel, for example. Naturally, it is being used for printing functional inks that are used for designs or for imparting conductivity onto textiles such as wovens, nonwovens, and even knits (Khan, S 2015). The throughput for flat-top screen-printing is around 10 mm/sec and for rotary screen-printing is Figure 2.13.

Figure 2.13: A) Shows the conventional table-top screen-printing setup wherein ink is flooded over a patterned screen for printing onto a given substrate. B) Shows a rotary screen setup in which a cylindrical patterned screen system is used to print roll-to-roll onto a substrate at high-throughput (R. R. Søndergaard).

The main parameters for screen-printing are squeegee speed, squeegee pressure, snap off distance, and fluid material viscosity. Most conductive ink based fluid materials that are utilized for screen-printing onto flexible substrates such as textiles exhibit shear-thinning and viscoelastic behavior which is critical for processing and for line resolution (Khan 2015). For most textile substrates micron level line resolution is not a key requirement for textile based electronic systems.
References


2.15. Conductive Ink Printing via Direct-write Printing

Direct-write printing is a promising method for printing continuous roll-to-roll large-area electronics directly onto flexible substrates with a one-step process, ruling out the need for complex and materials-intensive lithographic processes. However, printing conductive circuits on rough textile surfaces is severely limited due to the material’s inherent high surface roughness and porosity and until now no high-throughput strategy has been demonstrated that meets the processing criteria for the electronic textile industry. An on-demand ink dropping system is demonstrated through this work that is a 8x improvement over state of the art conductive printing on textiles. The conductive patterning is able to be tuned according to the dispense velocity and fluid (ink) pressure. The fibrous matrix of the textile substrate helps to absorb the ink solvent and positions each droplet continuously without making any coffee-ring structures and discontinuous lines. This unique feature of textile materials compared to film substrates along with the critical optimization of printing parameters and material characterizations makes it possible to create high-throughput electronic devices on textiles with unique properties.

2.16. Direct-write Printing and Automation

Textile materials are uniquely positioned as substrates for flexible and printed electronic applications due to their absorption and wicking properties, breathability, flexibility, and wearability. Textile-based electronics include sensors, interconnects, heating elements, and antennas that range in application across the automotive, defense, medical, and consumer electronics industries.[1-3] However, technological barriers to any textile electronic device include the need to satisfy high-throughput, low-cost, and high-performance needs of integrating the electronics that are commiserate with the stringent product requirements of the textile. Of particular interest for textile electronics is the ability to leverage the rapidly advancing printed
electronics industry. Due to materials advancements\textsuperscript{[4-6]} in the printed electronics industry, the intersection of printed electronics and textiles is a growing area of research and development within academia and industry. As such, there is a great deal of interest in taking printing techniques from the printed electronics industry and applying them to textile materials which use similar printing techniques such as screen-printing, direct-write, inkjet, and gravure printing\textsuperscript{[7]}. This resonance in printing techniques can allow for high-throughput manufacturing processes to enable low-cost and high-performance textile devices. A barrier to entry of many printing techniques is the issue of scaling production up to industry standards. Thus, this work on direct-write on textiles opens up the possibility for electronic textiles to be realized in a high-throughput manner using software driven designs and one-step material deposition technique without the need for making new screens, rollers, stamps, or masks. The vision for this technology is to automate the fabrication of textile electronics with multi-material deposition based on a software driven design process as shown in figure 1. This process opens up the automated printing of textile electronics such as wearable antennas (Figure 3.2B), interconnects (figure 1D), and multi-modal sensor systems for smart garments (figure 1E) in a single step process.
**Figure 2.14:** A) A schematic of the direct-write process with drop-on-demand mode being used to print on the textile substrate that could be used for designing various types of devices B) meshed-patch antenna device being printed using this direct-write drop-on-demand mode directly on a nonwoven textile. C) The process can also be used as direct-write printing on a film such as thermoplastic polyurethane (TPU) heat-laminted onto a polyester-spandex knitted textile for application in smart garments D) heat laminated interconnects in a meandering pattern and an electrocardiogram shirt as concepts for wearable devices for health monitoring E) The direct-write process enables a vision to achieve automated printing of textile electronics for multi-modal sensing and/or energy harvesting in a garment.

Conventional printing techniques in the electronics field include: screen-printing, ink-jet printing, transfer printing, gravure printing, and direct-write printing.[8] Each of these printing techniques have specific advantages and disadvantages. Screen-printing is a technique that has been used in the textiles industry for hundreds of years and is well established for printing conductive patterns for circuitry on planar materials.[9, 10] Thus it allows for a low-cost, accurate, and simple process but it is susceptible to substantial ink waste, limited design flexibility, and limited printing area. Furthermore, device-to-device reliability can be limited due to the screen condition over time. Transfer printing is another technique that has been used to print high-resolution conductive patterns, which utilizes a transfer device such as an ink stamp to print conductive patterns onto the substrate. However, prior studies have not demonstrated the scalability of this printing method to meet the high-throughput requirements of the textiles
Direct-write printing is segmented between droplet jetting and continuous filament writing. In droplet jetting (otherwise known as inkjet printing) the ink is deposited in a series of droplets onto the substrate to make a linear structure. With inkjet printing, the advantages lie in printing on flexible substrates with precise control of line-width and film thickness, however with textile substrates inkjet printing has proven to be a difficult process due to the need for multiple layers of ink printing.\textsuperscript{12, 13} Inkjet printing also requires low viscosity inks whose solvents and ink particles are absorbed by the textile substrate’s fiber bulk, often prohibiting conductive percolation in the fibrous structure. In order to use inkjet printing reliably on textile substrates, surface modifications must be made to the textile to reduce the surface roughness and porosity to allow for improved adhesion of the ink particles on the textile surface.\textsuperscript{12, 14}

In continuous filament writing the ink is deposited in a continuous filament structure onto the substrate. This technique allows fabrication with a computer-controlled pressure driven ink-suspension nozzle, permitting control of design and line dimensions on the substrate. This mechanism is very similar to 3D printing. Highly concentrated nanoparticle loaded conductive inks are usually used for direct write printing. In this process the dispenser needle loaded with highly concentrated metallic ink needs to come very close to the substrate in order to make continuous lines of patterns. This direct-write printing method is suitable and widely used for printing high resolution circuits and passive electronics on glass, films, and ceramic materials which have smooth surfaces compared to textiles. However, on textiles it is difficult due to the high surface roughness and because the needle has to be far enough from the textile substrate to avoid friction with the protruding fibers.\textsuperscript{15, 16} Previous work has demonstrated the process of direct-write on textiles, but required up to five print passes to achieve respectable conductivity (0.0667 Ohms/cm) and thickness (110µm).\textsuperscript{17}
This work aims to simplify the direct-write process technique to achieve commensurate line conductivity and thickness in a single printing stage. This study aims to validate the printing process parameters (fluid pressure and dispense velocity) and analyze their relationship to the conductive ink rheology. The direct-write system utilizes a variation of the droplet jetting technique and can potentially meet the high-throughput requirements of the textiles industry with optimum resolution of printed lines. High-throughput printing was achieved by strategically selecting a textile material with specific surface properties that were compatible with commercially available screen-printable conductive inks. Specifically, dispense velocities up to 80 mm/s were examined, whereas, to our best knowledge, previous studies of similar direct-write printing have achieved only up to 10 mm/s.\textsuperscript{[5, 15, 18]} In this work we demonstrate dispense velocities of up to 80 mm/s (more than an 8x increase compared to the previously mentioned work), a one print pass deposition process, and a software driven printing process suitable for rapid prototyping\textsuperscript{[16-19]}.

Figure 2.15: Shows the throughput of similar direct-write systems used for printed, flexible, and stretchable electronics applications.
2.17. Principles of Direct-write printing

Key to the understanding of the direct write process and the available modes of printing is the understanding of the material properties, flow properties, and the process parameters for the extrusion of thixotropic, non-newtonian fluids (such as conductive inks) from a nozzle orifice [20]. Highly concentrated colloidal suspensions of silver micro-flake particle ink shows shear-thinning viscoelastic properties and yield-stress behavior. This thixotropic material flows well under high shear-stress and behaves like a solid below the yield point of the shear-stress. This behavior is best explained by equation 1 and 2 below:

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

$$\tau = \tau_y + K\dot{\gamma}^{n-1} \quad (2)$$

where $\eta$ is the viscosity, $\tau$ is the yield stress, and $\dot{\gamma}$ is the shear-rate. Equation 1 shows that the viscosity is a function of the shear-rate, which decreases with an increase in the shear-rate. Equation 2 shows the stress-strain relationship with a non-zero yield-stress term. This indicates that when the material is at rest, it has an intrinsic yield-stress. As such, given that the conductive ink material is a colloidal suspension of silver micro-flake particles in a polymer binder and solvent, we characterized the material’s ink rheology to understand the viscosity and shear-thinning viscoelastic behavior.

2.18. Ink Rheology for Direct-write Printed Electronics

Printing electronic materials onto polymeric textile systems is a challenge and depending on the given deposition process, the rheology must be tuned. Conceptually, there are material-process property relationships and then material-process-device property relationships. The approach most researchers take is to understand the material and its given process boundaries [2]. In the realm of conductive inks, the ink rheology is an important determinant in how the
given ink can be processed and what the ultimate device characteristics will be. For processes such as direct-write printing or screen-printing, most inks are highly viscous exhibiting shear-thinning and viscoelastic flow behavior [2,10]. This behavior allows the inks to be jetted either in continuous mode or drop-on-demand modes, which has a considerable effect on throughput [10].

![Image of printing processes]

**Figure 2.16:** A) The continuous filament extrusion mode wherein the functional material such as a shear-thinning conductive ink is extruded. The throughput is limited in this case at high velocities (10 mm/sec +) due to breakage of the filament on rough surfaces such as textiles; B) the drop-on-demand mode which allows an ‘inkjet’ like approach to droplet deposition of conductive inks [10].

Most of these aforementioned conductive inks are in colloidal suspensions in which there is a polymer binder, functional particle in the nano or micro regime, and a solvent for dispersion and suspension. The ratios of each of these elements can be tuned according to the target viscosity that is needed. Thus, the inks are designed to be solid-like at low shear rates (1 Hz) and fluid like at higher shear rates (100 Hz), primarily due to the high solid loading fraction. In the case of conductive inks, the conductive particle (Ag, Cu, etc) must be loaded at high weight percentages to attain conductivity [11]. In most cases, silver (Ag) is used due to its high conductivity and low oxidation reactivity relative to that of other metals. It is also versatile for most flexible electronics uses and thus has subsisted as the metal of choice thus far.
Figure 2.17: Left: Ag volume fraction in relation to the viscosity, observed to be in accordance to the percolation network theory of particle suspensions for 3D printing. Middle: The apparent viscosity profile of the AgTPU and TPU materials. It can be observed that the TPU material behaves much more like a newtonian fluid where there is no observed change in viscosity during the shear-rate sweep, while the AgTPU material behaves like a non-newtonian power-law fluid. Right: The viscoelastic flow behavior of the Ag ink with thermoplastic polyurethane binder (TPU) and its native fluid material set without any additive particle suspension. The rheological profiles are quite different where the TPU native behaves much like ‘water’ and the AgTPU behaves like a viscoelastic material with a yield stress around 10 Pa [10],[11],[12].

Many of these ink systems as it relates to shear-thinning behavior can be modeled by the power-law:

\[ \tau = \tau_y + k \gamma^n \]  (2)

The power-law (aka Ostwald de Waale model) can be used to describe highly viscous conductive inks that at a specified range of shear rates (usually 1 Hz to 100 Hz). The power-law is used strictly as a model for describing the flow behavior of some inks and cannot be applied to all ink systems. As such, for inks that are used in the direct-write process, the power-law is adequate in describing the shear-thinning behavior needed at a given shear rate for the fluid to flow and then for it to relax back to its solid-like behavior due to yield stress behavior [10]. This is explicitly shown in Figure 8, where there is an upper newtonian region, a shear-thinning region, and a lower newtonian region [14].
Figure 2.18: The power-law model for shear-thinning viscoelastic systems [14].

As it relates to direct-write printing, the ideal weight percentage of particle loading must be high and the ink viscosity must also be high or else if the weight percentage is too low, the material will spread laterally and if it’s too high it will clog the dispenser needle. This is not true for all substrates and applications, however; especially as it relates to polymeric textile systems which are rough and 3 dimensional in nature. For textile systems, the materials must be highly viscous but can also be tuned to lower viscosities to take advantage of the lateral spreading and allow for the inks to wet through the capillary bundles as shown in Figure 9 above [13]. A lower viscosity of ink or even an ink with a solvent that has a lower vapor pressure can allow for the ink to wet through the textile fibers due to capillary action. The ink penetration phenomena have been shown to allow for ‘embedded electronics’ in fibrous systems, allowing for increased electromechanical performance [13]. This ink-fiber composite structure is uniquely suited for textile electronic devices that have a need for stretchability such as for wearable sensing of biosignals [13]. As shown in Figure 10, the penetration depth can be controlled by altering the choice of solvent vapor pressure and even the weight percentage of the solvent in the ink system.
This can be taken further to hypothesize the effect of conformal coatings onto fibrous structures, much akin to the reactive conductive ink systems described earlier herein.

![Image of solvent effect on penetration depth into textile's fibrous structure]

**Figure 2.19**: The various solvent’s effect on penetration depth into the textile’s fibrous structure due to their vapor pressure values. A lower vapor pressure showed a higher penetration depth due to capillary action [13].

### 2.19. Rheological testing of conductive inks for textile electronic applications

Rheological behavior is usually tested by a Rheometer and consists of a cone and plate setup. The material is typically placed in the center and the cone allowed to spin, shearing the material. The displacement torque (shear stress) is then measured as a function of shear rate to find the yield stress or flow behavior of the material. This is a conventional experiment done for the study of printing conductive inks onto textile systems, especially as they relate to direct-write printing. Apparent viscosity is also similarly measured by the same Rheometer instrument. A popular brand of Rheometers used widely is the Anton-Paar brand.

Connecting the intrinsic rheological flow behavior of a conductive ink to its wetting phenomenon within a textile system is extremely important when processing and enhancing mechanical durability of end device applications [6],[13]. Contact angle is used mostly on planar and smooth surfaces so on textile systems which are inherently rough and have complex surface morphologies it is difficult to properly identify a physical model to predict fluid flow [15]. However, a contact angle analysis can still be done to identify the volumetric flow rate into the fiber system to represent wetting phenomena. In this case, a conventional goniometer setup can be used to visually track the contact angle as a function of time. For inkjet and direct-write
printing methods on textile systems, it is integral to understand the relationship of rheological properties such as yield stress and the change in contact angle with time [15]. For inkjet compatible inks, the viscosity will allow for increased wetting and for direct-write printing with high viscosity inks the wetting will occur as a function of the vapor pressure [15].

2.20. Material-Process-Device Relationships

As discussed in this review of the Rheological behavior of conductive inks for textile electronics, once the material and process relationships are understood a proper device can be fabricated. Some devices of interest are in sensing and heating wherein energy is either transduced or is applied. For example, in biometric sensing applications such as sensing of one’s electrocardiogram (ECG) or electromyogram (EMG), the conductive material can be used as a dry electrode [1]. On the other hand, for applications requiring heating wherein energy is applied as opposed to transduced as in the case of a dry electrode sensing one’s ECG, heating elements can be printed. As shown in Figure 11, a heating element was printed onto textile and various voltage inputs were applied leading to increase in temperature. These fundamental demonstrations show the potential for printing on textiles to be used as a scalable manufacturing method to execute additive manufacturing onto textile systems.

![Figure 2.20: The ECG spectrum by a printed dry electrode.](image-url)
Figure 2.21: Inkjet-printing reactive silver inks on textiles for textile heater [6].

2.21. Conclusion

Printed electronics offers an attractive technology roadmap for achieving low-cost, scalable, customizable, and patternable electronic systems within textile based frameworks. The applications for this core technology platform are far reaching when it comes to the impact on society. In order to understand the fundamental scientific phenomenon governing the processing of inks, the Rheological flow behavior must be understood. Once this component is well understood, a plethora of applications can be harnessed to build devices that solve real-world problems.
References


CHAPTER 3

3.0. Rheological Studies of Conductive Inks for Direct-write Printing

Direct-write printed electronics till now has been used mainly on planar and film substrates. Not much work has been done on direct-write printing on textile systems. Herein we describe work done on textile substrates utilizing the direct-write DoD process for depositing conductive inks. The approach in this research is to utilize a bottom-up understanding to tune the process. The materials-to-process relationships are first studied and then this understanding is used to study the process-to-device relationships.

3.1. Experimental Section

3.1.1. Ink Rheology Testing:

As a first step in achieving a bottom-up understanding of the conductive material set, the flow properties or the rheology is integral to understanding the implications such physical properties have on deposition of such inks within a DoD system such as direct-write.

As seen in table TRD-1, the physical properties of these thixotropic material sets are listed and can be tuned by altering the solvent ratios. A typical rheological setup utilizing a cone and plate setup is used to conduct shear rate (x-axis) vs viscosity (y-axis) and shear stress (x-axis) and elastic moduli. For most conductive inks the rheological properties are a function of the polymer binder, solvent ratio, and the conductive filler loading weight percentage. Many of these conductive inks are shear-thinning and viscoelastic in nature and have a high elastic moduli at low shear rates (~1 Hz). This means these materials are solid like (high elastic moduli) at low shear rates and are viscous at high shear rates (low elastic moduli). In regards to direct-write printing and processing, the dispensing frequency or droplet formation frequency must be sufficiently high for a given shear stress applied to form droplets successively for printing
conductive patterns. For the case of the machine utilized for direct-write DoD printing in this work, a valve frequency of 77 Hz was used for the Nordson C-341 Conformal Coating system.

### 3.1.2 Experimental Method for testing ink rheology:

An Anton-Paar cone and plate rheometer setup was used to measure the viscosity of the DuPont PE873 Intexar Ag conductive ink as shown in Table TRD-1 under a shear rate sweep from 0.1 Hz to 1000 Hz. A cone and plate setup was also used to measure the elastic moduli of the conductive ink under a shear stress sweep from 1 Pa to 1000 Pa. Various ink-to-solvent ratios were studied from the following undiluted to diluted ratios: 1 : 0, 1 : 0.06, and 1 : 0.13, respectively. The same experiment was done for a non-stretchable Creative Materials 124-36 Ag/AgCl ink for comparison.

### 3.1.3 Ink Rheology Results

For the DuPont PE873 Intexar stretchable Ag conductive ink, the rheological flow properties are starkly different from that of a previously studied stretchable Ag/AgCl conductive ink. This stable suspension will maintain the shear thinning properties with an increase in shear rate. The unstable ink will not maintain the consistency of fluid flow as shear rate is increased. As shown below in the preliminary work done, we have already characterized this rheological behavior of conductive inks (colloidal suspension of silver flakes in polymer solution).

Figure FB-1 shows the viscosity and the elastic/storage modulus of two different types of conductive ink with respect to shear rate. It is observed that the ink maintains a consistent shear thinning property and demonstrates a yield stress behavior with the addition of different weight ratios of solvent. This result suggests that within the range of viscosities, the ink will flow easily through the capillary nozzle (shear-thinning behavior) and act like solid as soon as the ink comes
out of the nozzle (yield-stress behavior). This behavior is especially evident when printing onto textile systems and helps to maintain print resolution.

A key requirement for direct-write Drop-on-Demand (DOD) systems is the relationship of the actuation frequency on and off time, wherein the on time corresponds to the actual frequency of shear or shear rate imparted on a given fluid material and the off time corresponds to the observed relaxation time (Direct Ink Writing of 3D Functional Materials). In order for the fluid to be extruded or formed into a droplet, the applied shear rate must be sufficiently greater than the relaxation time of the fluid, which in the case of this study will be viscoelastic in nature. The relaxation time of polymer-metal colloidal suspensions like the herein studied conductive ink is a function of the type of polymer and its associated chain length and degree of entanglement. The microstructure of the polymer binder is important but was not the focus of this work given the emphasis on process science. However, the differences in polymer binders is evident in Figure FB-1, especially for non-stretchable and stretchable polymer binders. In particular, the yield stress points (<10 Pa) for the non-stretchable Ag/AgCl ink samples are lower than that of the stretchable Ag Ink indicating that the stretchable ink’s polymer binder has a higher yield point (~10 Pa) due to its ability to stretch.
Figure 3.1: Rheology characterization of conductive ink, where A) & B) shows the viscosity vs. shear rate and the elastic modulus vs. shear stress of the ink diluted with different weight ratios of solvent. C) & D) show the similar data for stretchable conductive ink with PU binder in it.

3.1.4. Relaxation Time of Jettable Fluids

Ink rheology as it relates to the direct-write process is governed by the ink actuation mechanism which forms droplets and the relaxation time of the given material. In conventional DoD jetting mechanisms (shown in Figure 3.2) droplet formation is governed by the shearing time and the relaxation time. If the off time is less than the relaxation time then a droplet cannot be formed (Yang Guo, 2017). If the off time is more than the relaxation time then a droplet can be formed. This phenomena is well studied and is a property of most viscoelastic materials (Yang Guo, 2017).
Figure 3.2: Shows the on-off DoD actuation period based on the jetting frequency.

An experiment was done to validate this phenomena to understand the ideal frequency regime in relation to the relaxation time of the material under various dilutions. This phenomena is critical to understand when ejecting fluids with viscoelastic properties as there are critical regimes of fluid processing which govern process design. In the case of the aforementioned ink dilutions, the relaxation time experiment was done by applying a shear and measuring the decay of the relaxation modulus for each ink dilution. The time at which the relaxation modulus decays to the initial modulus divided by an exponential constant is known as the relaxation time of the material (Yang Guo, 2017). For the fluid ejection system described herein, the on time is 8 ms and the off time is 5 ms. This indicates that the relaxation time for optimal droplet formation must be less than 5 ms. The results for this phenomena are shown for ink-to-solvent dilutions with ratios of 1 : 0, 1 : 0.06, and 1 : 0.13 in Figure 3.3.
Figure 3.3: Shows the relaxation modulus (Pa) decay as a function of time (s). The ideal relaxation time for our fluid ejection system is less than 5 ms.

As shown in Figure 3.3, the ink dilution with the shortest relaxation time is 1 : 0.13, which when plotted as a function of viscosity at the given actuation frequency of 77 Hz, correlates in a linear fashion as shown in Figure 3.3.

Figure 3.4: Shows the linear relationship of relaxation time (ms) and Viscosity (Pa*s) at 77 Hz.

All in all, this indicates that as the viscosity is lowered the relaxation time is also lowered as the polymer binder has less propensity to become entangled due to the increased solvent ratio (Tsuyoshi Yamaguchi, 2014).
3.1.5. Ink-to-Textile Interactions

In order to relate print resolution to the material flow properties studied via rheological experiments, flow phenomena into the textile system must be understood. This is best done in the field of surface science by contact angle or goniometer experiments. Given the non-planarity and 3 dimensionality of textile systems, in-plane and through-plane wetting is normally observed during flow phenomena. This is of particular interest for applications for printing and can be taken advantage of to control ink penetration into the fiber bulk – a phenomena discovered from prior work done on non-woven textile substrates. The ink permeation can be strategically controlled via solvent dilution and applied fluid pressure during direct-write printing to enhance penetration into the fiber bulk for enhanced electromechanical performance as demonstrated by a study done by Jin et al (Hanbit Jin, 2017).

\[\text{Figure 3.5: This figure shows the ink penetration phenomena as a function of the fluid pressure and ink viscosity/dilution.}\]
Figure 3.6: D) This shows the ink permeation into the fiber bulk for a Nylon knitted textile and E) & F) the associated electromechanical properties as a function of strain and strain cycles done at 30% strain.

This phenomena is of particular interest in this study due to the need for enhanced electromechanical performance. As the ink forms a composite with the fiber bundles due to capillary flow, the strain induced is not distributed onto the usual in-plane direction but into the fiber bundles thus as the textile is strained, the ink stretches along with it. This unique structure developed due to controlled ink penetration or permeation is an important hypothesis to validate for knitted textile systems with fiber bundles that allow for capillary flow of inks. Thus in order for sufficient flow to occur, solvent systems with low vapor pressure must be utilized. This is evident in Jin et al’s study as shown here:
Figure 3.7: This shows the permeation depth into the textile fiber bulk as a function of the vapor pressure. The ink used in this work is DuPont PE873 Intexar Ag conductive ink. Its solvent system is Glycol Ether which is in the middle of the solvents used in Jin’s study (Hanbit Jin, 2017).

3.1.6. Experimental Method for contact angle studies

A Reme-Hart goniometer was used to study the change in contact angle over 5 minutes and visual images were analyzed with its associated software. The substrate used was an 88% polyester and 12% spandex knitted textile. The wetting properties of ink-to-solvent ratios were studied from the following undiluted to diluted ratios: 1 : 0, 1 : 0.06, and 1 : 0.13, respectively.

The substrate used herein is a polyester-spandex jersey knit with a thickness of 0.76 mm, and basis weight of 183 g/m². A KES-SE surface properties testing apparatus was used to test the aforementioned substrate properties. This textile substrate is used conventionally for applications in sports & fitness and was thus chosen due to its stretch and compressive properties.
3.1.7. Contact angle results

It is hypothesized that higher viscosity inks will have a higher contact angle and less flow into the textile fiber bulk as compared to lower viscosity inks. In this experiment, the Glycol Ether solvent was used as the diluent which is the same solvent used in the Ag stretchable conductive ink. As shown in Figure 3.8 below, the hypothesis was shown to be correct over a period of 5 minutes or 300 seconds. The greatest change in contact angle occurred for the lowest viscosity which had a 1:0.13 ink-to-solvent ratio. Figure 3.8 also shows the change in contact angle in the first 60 seconds which is a key process parameter that will be observed to keep printing within the 5 minutes target production time for an ECG smart garment. The highest change in contact angle (20%) was observed for the lowest viscosity ink ratio indicating the highest ink penetration and wetting into the fiber bulk. This will be further studied in follow on experiments relating this ink penetration phenomenon with the associated electromechanical properties of direct-write printed textile interconnect devices.
Figure 3.8: The top figure shows the contact angle as a function of time for the various aforementioned ink dilutions. The bottom figure shows the ink’s flow properties into the textile system as a function of viscosity.
3.1.8 Research Conclusion - Experimental Plan 1:

RQ1: What is the rheological processability regime for direct-write printing onto textiles?

Table 2.1: Shows the experimental plan for finding the processability regime for direct-write printing onto textiles.

<table>
<thead>
<tr>
<th>Material Selection</th>
<th>Experimental Apparatus</th>
<th>Rheological Parameters</th>
<th>Experiments</th>
<th>Research Conclusions</th>
</tr>
</thead>
</table>
| • DuPont PEB73 Ag Stretchable Ink | Anton-Paar Rheometer   | • Shear Rate (Frequency Hz)  
• Shear Stress (Pa)  
• Storage/Loss Moduli (Pa) | 1. Shear Rate vs Viscosity 
2. Shear Stress vs Storage/Loss Moduli 
3. Storage/Loss Moduli vs Shear Rate (Frequency) 
4. Fluid Pressures vs Jettability | Flow Properties
✓ Viscosity range with dilution
✓ Yield Stress values
✓ Relaxation time of Ag ink
✓ Jettability |
References


CHAPTER 4

4.0. Curing Strategies for Conductive Inks

Post-processing of conductive inks is a vital process step in converting the ink from a viscoelastic state to that of a cured state in which the conductivity and reliability is enhanced. In most conductive inks, there are metal particles, polymer binder, and solvent suspension system. For these material systems, the solvent must be first evaporated, then the polymer binder cured to allow chains to relax and decrease modulus for stretchability, and the metal particles to increase in their percolation as a result of the polymer binder annealing. There are various curing mechanisms used in the printed electronics space such as convection based thermal oven curing, radiation based infrared curing, and conduction based heat press curing. These processes are also used widely in the textile industry making them amenable in various manufacturing setups.

4.1. Characterization of inks for thermal profile understanding

In order to understand the thermal profiles needed to provide the optimal modulus for textile electronics applications, the time of curing must be minimized and the temperature applied must be below the melting point of the polymer used in the substrate and the ink. These physical properties must be investigated by characterization techniques such as Differential Scanning Calorimetry (DSC) which can give information about the physical properties of a given material such as the heat capacity, crystallization, and degradation and Thermogravimetric Analysis (TGA) which can give information about complete solvent weight evaporation and thermal degradation temperature. These physical properties as a function of the thermal curing profile allows for the optimal tuning of process parameters such as the curing temperature and the time needed to allow for curing to occur.
A TGA experiment was done to characterize the DuPont dielectric ink and conductive ink and their respective thermal profile temperature boundaries as shown in figures SP-1, &2 below. Figures SP-1 & 2 show the thermal degradation of the stretchable dielectric material (DuPont PE773 Intexar), which can be used as encapsulation for textile electronics devices. There are three different slopes of degradation. The first slope can be related to the evaporation of the solvent. The end of the down slope indicates the minimum curing temperature for curing the ink at rate of 10 degree Celsius per minute. Although, the polymer binder degrades at a very high temperature at around 341 degree Celsius for both the conductive and dielectric ink (since both inks have the same polyurethane based binder), the curing temperatures have to be below 140 Celsius so that the polyester based knit textile will not degrade.

**Figure 4.1:** This figure shows the TGA (Thermogravimetric Analysis) of the polymer binder or interface material used in the conductive inks which is a thermoplastic polyurethane based material with silica particles as filler for enhanced processability and Glycol Ether as the solvent. This material is DuPont Intexar PE773. The scale is from 20 C to 700 C (with 100 C increments).
4.2 Comparison of Curing Strategies

The method of curing has a great impact on the end conductivity or electrical resistance of a printed line. There has been much research on how the curing method selection has an impact on the time it takes to have a completely cured sample (Janghoon Park1, 2016).

Figure 4.2: This is the TGA (Thermogravimetric Analysis) data for the Ag Ink. This indicates the optimal curing temperature before thermally induced degradation occurs. This indicates that the optimal curing temperature for such a material is 160°C - 250°C. This material is DuPont Intexar PE873.

4.2 Comparison of Curing Strategies

The method of curing has a great impact on the end conductivity or electrical resistance of a printed line. There has been much research on how the curing method selection has an impact on the time it takes to have a completely cured sample (Janghoon Park1, 2016).

Figure 4.3: This study done by Park et al looked at the relationship of sintering time vs sheet resistance of printed lines using their Ag nanoparticle and micro-flake particle based ink. Our conductive material set will undergo a similar experiment but with various temperatures.
In the previously mentioned study, infrared curing process was used to evaporate solvent and sinter the silver nanoparticles and micro-flake particles into a conductive film with low electrical resistance. In the same respect, this curing strategy can be emulated for other ink systems and substrates. In our case, the substrate is a polyester-spandex knit and the ink system is a polymer-binder, silver micro-flake, and solvent system. An similar experiment to the one Park et al conducted was done to characterize the various curing methods such as thermal oven, infrared, and the influence of post-process heat-pressing for both as shown in Figure 4.

**Figure 4.4:** Shows the electrical resistance as a function of time for various curing methods such as thermal oven and infrared based curing. A kapton substrate was used as a control due to its low surface roughness in comparison to the polyester-spandex knit textile. Heat-press post-process was also studied indicating that the combination of infrared curing with subsequent heat-press at the same temperature allows for lower electrical resistance.

The experiment was conducted by direct-write printing 4 cm lines onto both the substrates at process conditions of 40 mm/s dispense velocity, 57 Psi fluid pressure, and a 3.16
mm dispense height with the ink dilution of 1 : 0.13 as determined through the rheological studies. The results show that infrared curing with subsequent heat-pressing at the same temperature of 160 C allowed similar electrical resistance profiles as a function of curing time to the native Kapton substrate. It can be observed that the shortest curing time with the lowest electrical resistance occurred at 90 seconds. However, in order to understand the effect of various curing temperatures on the electrical resistance as a function of time, three separate curing temperatures must be studied. This was done in a second experiment to understand the curing temperature with the lowest electrical resistance profile as a function of curing time as shown in Figure 4.5.

![Polyester-Spandex Knit - Before/After Heat-Press](image)

**Figure 4.5**: Shows the curing profiles as a function of curing time for various temperatures for direct-write printed silver ink on polyester-spandex knit.

The results show that 140 C had the lowest electrical resistance, 120 C had the highest resistance, and 160 C had the second lowest electrical resistance. It can be observed that the deviation between 120 C and 160 C isn’t as pronounced at lower curing times till around 90
seconds. There is a stark increase in electrical resistance after curing time of 150 seconds indicating there is some degradation occurring in the ink system. This hypothetically could be attributed to micro-crack formation. However, to validate this hypothesis further studies must be done. One method to investigate how these results could influence the ultimate electromechanical durability is via optical microscope. An image matrix of optical images at rest and at a strain of 50% were taken of the cured samples to understand the ink-to-fiber bundle morphologies. This is shown in Figure 4.6 below:

**Figure 4.6:** Shows the optical images of the various curing temperatures and curing times at mechanical strains of 0% and 50% for comparison of ink-to-fiber bundle morphologies.

The ink morphology of the 140 C samples show that the ink forms a composite with the fiber bundles on the top levels of the textile and thus allows more of a ‘film-like’ ink morphology. The images for 160 C show that the ink has penetrated into the fiber bundles forming a conformally coated composite like structure. This behavior is indicative of the high energy deposited over a short amount of time leading to softening of the polymer binder from localized heating of the micron sized silver flake particles due to higher absorption of infrared radiation during the curing process. It can be hypothesized that this feature could increase electromechanical durability.
However, in order to properly hypothesize how ink penetration affects electromechanical durability, one needs to understand the cross-sectional penetration into the fiber bulk of the given textile. Figure 4.7 below shows the SEM (Scanning Electron Microscope) cross-section for direct-write printed samples under various curing temperatures and curing times.

**Figure 4.7:** Shows the SEM cross-sectional view of the ink penetration into the fiber bulk of the knitted textile. The Ag ink penetrates into fiber bundles forming a composite.

It can be observed that the ink penetrates into the fiber bundles well for temperatures of 120 C and 160 C but not so much for 140 C. This may be due to inconsistencies in the ink formulation or in the fabrication process. The yellow lines indicated the level of ink penetration into the fiber bulk. It can be observed that the ink penetration is qualitatively similar, indicating that the ink’s wetting phenomena isn’t influenced by curing effects as much as it is in the initial time period after printing where most of the wetting into the fiber bulk occurs as validated by contact angle experiments discussed previously.

As shown in the following figures, the ink penetration into the fiber bundles can indicate electromechanically behavior of the printed samples. In Figure 4.8, the samples are cured at 120
C, the lowest temperature but the conformality of the ink-to-fiber bundles was higher than that of the samples with higher temperatures. The relationship of this ink-to-fiber phenomena will be analyzed with electromechanical experiments.

**Figure 4.8:** Shows the SEM X-S image and zoom-in of the ink-to-fiber bundle composite structure formed for 120 C cured samples. As can be observed, the bundles are coated conformally with the ink with a good coating amongst the fiber bundle.

**Figure 4.9:** Shows the SEM X-S image and zoom-in of the ink-to-fiber bundle composite structure formed. As can be observed, the bundles are not as well coated with ink as the 120 C and 160 C samples.
**Figure 5.0:** Shows the SEM X-S image and zoom-in of the ink-to-fiber bundle composite structure formed. As can be observed, the bundles are coated with the ink well, however, the individual fibers are more closely packed together indicating localized heating induced fiber agglomeration. This may affect electromechanical behavior.
References


CHAPTER 5

5.0. In-situ Testing of Direct-write Printed Devices: In-situ test method for identifying cracks in conductive printed materials used in textile electronics

5.1. Introduction:

Reliability of printed devices within the field of textile electronics is a significant roadblock to their widespread market adoption. This problem is further exacerbated by the lack of test methods for evaluating the failure modes of printed devices such as interconnects under mechanical strain. A simple but effective thermo-electro-mechanical method for identifying cracks within printed conductive pathways (interconnects) on textiles is described in this study. This method utilizes resistive joule heating to isolate conductive areas where cracks can form in-situ. It requires only a DC power source, thermal imaging device, tensile testing setup, and printed conductive samples. It has been shown that along a printed interconnect, cracks can form along print directions that endure high localized strain such as at curved junctions or at connection points for many sinusoidal based interconnect geometries. Compared to post visual inspection utilizing optical microscopy, SEM microscopy, or atomic force microscopy which can be time-consuming and expensive, our method is simple and cost-effective as a first pass for identifying device failure modes. In this study we will outline this new test method and results for interconnects printed directly onto a knit textile substrate.

Printed, Flexible, and Stretchable Electronics (PFS) have become attractive paradigms for obtaining electronics with form factors, geometries, and functionalities that hitherto have not been explored. In context of grand challenges such as passive health monitoring of human physiology, implantable interfaces for connecting the human to the internet-of-things, and distributed sensing of infrastructure on the internet-of-things these electronic structures have the
potential to become a part of the growing need for utilizing data to better understand and predict physical phenomena. However, most devices in this field have poor electromechanical durability or may have lab-scale durability in isolated conditions but may not necessarily exhibit similar durability when say put onto the human body. In order to scale PFS electronics, electromechanical durability must be understood deeply and in particular the failure modes of a given device. There are many _a posteriori_ methods of understanding the failure of a PFS conductive device but there aren’t many in-situ methods that are time efficient, cost-effective, and at the same time in-situ [1-2]. There has been some work on detecting failure modes such as conductive film cracking in-situ via methods such as Confocal Laser Microscope Spectroscopy or Scanning Kelvin Probe Microscopy, however, when such PFS electronic structures are fabricated on textile structures such as knits, there is an added layer of complexity [1-4]. Textile structures are three-dimensional by nature and thus have unique requirements for device fabrication such as for interconnects [4]. Furthermore, their electromechanical properties differ due to their unique structures and material constituents. For example, when conductive inks are printed onto a knit structure, the fiber bundles serve as channels for the ink to wet into (at a given viscosity) and after curing form ink-to-fiber composite structures. This has been shown to enhance electromechanical durability by a study done by Jin, et al [3]. However, identifying the crack propagation, location, and intensity of the cracks requires a simple, cost-effective, and in-situ method of characterization. Herein we propose a thermal imaging based method for characterizing the crack propagation based on interconnect design, location of cracking, and the intensity of the cracking. This is employed as a result of joule heating phenomena which occurs in a conductive device at resistive areas and increases in intensity or temperature as cracks propagate.
5.2. Experimental Methods

5.2.1. Sample Preparation

Fabrication of interconnects was performed via direct jet printing on an Asymtek Conformal Coating Machine. Dupont PE874 stretchable silver ink, which consists of microsize silver flakes suspended in a thermoplastic urethane binder solvent, was printed onto an 88% polyester 12% spandex knit fabric. The knit fabric was laser cut to shape and placed into the direct jet printer with the knit structure aligned with the edges of the printer platform and in the direction in which the interconnect was to be printed. The silver ink was diluted with glycol ether in a 1:0.13 ratio to be direct jet printed. The pressure valve for ink flow was set to the maximum allowable pressure, and a program was made in the direct jet printer for the interconnect to be printed. Once the sample was printed, it rested at room temperature for 1 minute, then cured in an infrared heater for varying time and temperature. Once cured, the sample was heat pressed for 30 seconds at the same temperature it was cured. For any electromechanical testing, a coating of silver epoxy was added to each end of the interconnect to allow for a stable connection between the interconnect and the test leads.

5.2.2. Sample Preparation

Characterization of the interconnects was performed using an Instron tensile tester, National Instruments USB-6001 Data Acquisition (DAQ) voltage divider circuit, and FLIR thermal imaging camera. The interconnect was connected to each end of the tensile tester, with leads connected from the ends of the interconnect to the voltage divider. The tensile tester underwent two functions: strain and cyclical strain. Under strain, the interconnect was stretched 0.5 mm/sec until the resistance peaked. Under cyclical strain, the interconnect was stretched 20 mm/sec up to 20% strain for 1000 cycles. For each test, the normalized resistance and
temperature data was recorded by the voltage divider and the thermal imaging camera, respectively.

Both before and after strain and cyclical strain, the interconnects were observed under an optical microscope and scanning electron microscope to identify areas in which cracks occur, and the severity in which cracks occur.

Figure 5.1: Process flow chart of the proposed test method.

5.3.0. Results and discussion:

Figure 5.2: a) The change in resistance and, b) the composite failure index as a function of strain.

In the context of a wearable device, the method developed herein was used to understand two key requirements for device function: device strain to failure and device lifetime under strain.
cycling at a certain frequency. These two requirements are critical in understanding when the device will fail at a given input voltage. In this method, an input voltage of 5 V was kept constant to simulate a wearable device and a strain frequency of 0.5 mm/sec (at gauge length of 100 mm) was simulated.

As can be observed in Figure 2a, the electrical resistance begins to increase exponentially around 20%. This can be observed from the thermal images in Figure 3 as well. Most notably, the onset of crack formation begins to occur around 25% strain. This crack formation behavior can also be measured as a function of joule heating temperature and the total area of the cracks. This phenomena indicates the severity of the cracks formed. This is expressed as a Composite Failure Index (CFI) in the formula below:

\[
CFI = AT
\]

*where A is the total area of cracks and T is the highest temperature observed in the crack area*

This CFI measure will guide the understanding of device function in real-time and allow for real-time detection of cracks and locations of highest likelihood of device failure. The printed interconnects exhibited the highest crack formation around the curved sinusoidal pattern in the course direction of the textile. This is expected as the localized strain is high around this curved region, causing more cracks to form than in the wale direction of the textile. There are three key regions of interest in the CFI measure in relation to the strain imposed on the printed interconnect device. The first region is the onset of the crack formation up till the peak of CFI. This region is represented as the dramatic increase in crack formation and joule heating temperature at the crack regions. This indicates the minimum strain after which cracks begin to form and the localized areas which have the highest propensity to failing. The second region is
the peak of the CFI, which indicates that the device is at an inflection point, beyond which it will begin on a trajectory towards complete failure. The third region is the decay towards complete failure which can be observed as the decrease in joule heating temperature. It must be noted that the joule heating phenomena is a function of the input voltage so beyond a certain resistance value electron flow will be impeded so greatly that there will be no current and thus no joule heating. If the input voltage is increased more cracks can indeed be imaged but in the context of this study our device was constrained in a setup akin to that of an operational device under in-situ mechanical deformation.

Figure 5.3: Thermal images of interconnects under 0%, 25%, and 175% strain, with brighter spots indicating crack formation.
Figure 5.4: a) The electrical resistance and b) composite failure index as a function of cyclical strain.

In this method, an input voltage of 5 V was kept constant to simulate a wearable device and a strain rate of 20 mm/sec (at gauge length of 100 mm) under 20% strain was simulated. A total of 1000 cycles were performed for each sample, and the resulting electrical resistance and composite failure index was measured.

From the Electrical Resistance vs Cyclical Strain plot, the resistance fluctuates as the device is strained, with the resistance increasing exponentially over time. Cracks begin to form and propagate from the first cycle, but the device only appears to begin failing after 200 seconds, as the resistance begins to deviate substantially from the initial resistance. By around 150 cycles, the thermal images indicate significant crack formation. This is supported by the Composite Failure Index vs Cyclic Strain graph, in which the CFI begins to decrease or decay at 10 minutes, indicating that the joule heating phenomena also begins to decrease. This is a result of the increase in electrical resistance and crack formation as shown in Figure 4. The result of this decay indicates that the device fails to perform at the input voltage of 5 V after this number of strain cycles. This can be seen in the Electrical Resistance vs Cyclical Strain plot, as the resistance no longer remains close to the initial resistance after this point. Additionally, the
thermal images begin to show a decrease in temperature around the crack areas, further indicating the decrease in joule heating due to a lack of conductivity.

This method can be used to understand both where the interconnect is failing due to crack formation, and the device operating lifetime as a function of the frequency of mechanical deformation. This combination allows for a robust method to determine the lifespan of a device due to these two mechanical stimuli.

**Figure 5.5**: Thermal images of interconnects under 0, 150, and 1000 cycles of 20% strain at 20 mm/s, with brighter spots indicating crack formation.

5.4.0. **Conclusion:**

PFS devices are of great interest for technology platforms like wearables for health monitoring. However, a bottleneck to scalability and adoption is the electromechanical durability of such devices. In this study, an in-situ test method for identifying crack location, formation, and the onset of device failure utilizing a Composite Failure Index was developed. This new test
method is a reliable, real-time, and cost-effective way of identifying device failure causes without employing expensive and complex characterization techniques after the device fails. The impact of this method will help iterate on PFS devices faster and allow for simulation of device operation.
References


6.0. Device Demonstration of Direct-write Printed ECG Shirt

To demonstrate that a smart garment can be direct-write printed in 5 minutes, the ideal process parameters optimized for reduced production time and maximum durability must be done. This device demonstration will be done to validate if an ECG smart garment can be fabricated using this process.

The following process parameter selection flow was used to demonstrate a proof-of-concept ECG Shirt:

**Figure 6.1:** Shows the process flow for selecting the optimal parameters to fabricate the ECG smart garment.
Research Conclusion – Device Demonstration:

Table 3.1: Shows the experimental plan for demonstrating the ECG Shirt.

<table>
<thead>
<tr>
<th>Material Selection</th>
<th>Experimental Apparatus</th>
<th>Experimental Parameters</th>
<th>Experiments</th>
<th>Research Conclusions</th>
</tr>
</thead>
</table>
| • DuPont P873 Ag Stretchable Ink  
  • GDW Glycol Ether Solvent  
  • TPU film  
  • Polyester-Spandex (88%/12%) Jersey Knit | • Direct-write Printer (Nordson C-341)  
  • Infrared Oven  
  • Heat Press | • ECG (mV)  
  • Signal-to-Noise ratio  
  • Fluid pressure, Dispense Velocity  
  • Ink Viscosity | 1. Physical Testing Demonstration  
  2. Walking | Wearable Demonstration  
  ✓ Direct-write printing can be used to automate ECG Shirt  
  ✓ Direct-write printed ECG Shirt can detect a working ECG signal |

The following direct-write printing process parameters were used to fabricate the ECG smart garment:

<p>| |</p>
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispense Velocity = 40 mm/sec</td>
</tr>
<tr>
<td>Fluid Pressure = 57 Psi</td>
</tr>
</tbody>
</table>
| IR Curing Temperature and Time = 120 C for 90 sec  
  Post-process Heat-Press = 120 C for 30 sec |

In order to fabricate the garment, a fabric swatch was cut according to predetermined dimensions and design. This swatch was aligned on the printing stage in accordance to the print program file. The machine parameters were set, the conductive ink was printed on the fabric swatch directly with no pre-treatment process, and subsequently cured in an IR oven set at the curing temperature and time. Each interconnect and electrode took around 1 min for a total printing time of around 3 min. After printing, the fabric swatch was cured in an IR oven at 120 C for 90 sec and heat-pressed for 30 sec to allow for the ink to penetrate into the fiber bundles.
Once the fabric swatch was cured, it was assembled into a full-garment. The garment was then worn to acquire ECG signals while standing to show the demonstration of a fully direct-write printed smart garment.

Figure 6.6 shows the ECG spectrum while standing:

![ECG Spectrum](image)

**Figure 6.1:** Shows the ECG spectrum taken while standing.

### 6.1 Conclusion

The goal of this PhD research was to ultimately create a novel process, interconnect devices that are durable, and utilize this process to fabricate a ECG smart garment to demonstrate the manufacturability of a smart garment. This was achieved but further work must be done to demonstrate better signal quality, washability, and wearability. Furthermore, this process can be optimized even further to reduce the fabrication time and increase the durability of the garment.