ABSTRACT

WEI, CHUANG. Investigation of Hierarchical Fabrication Methods for High-Resolution Additive Manufacturing. (Under the direction of Prof. Jingyan Dong).

This study investigates versatile multi-material and multi-scale fabrication approaches for high-resolution additive manufacturing, with a special focus on multi-material and multi-scale 3D scaffolds for tissue engineering and high-resolution conductive traces for low-cost printed flexible electronics.

Firstly, a cost-effective layer-molding method is developed for macroscale 3D tissue engineering applications using photocrosslinkable biopolymers: thermoplastic material is used as supporting mold and functional photocrosslinkable material can be deposited on-demand into the mold in an arbitrary way. The building process is repeated following a layer-by-layer sequence until the desired thickness is reached. The final 3D structure can be obtained by removing the supporting material. In comparison with conventional stereolithography (SLA), the layer-molding method in this study enables highly-viscous functional photocrosslinkable materials to be fabricated into 3D structures and have multi-material integration capability, which are not possible for conventional SLA approach.

Second, Electrohydrodynamic (EHD) hot jet plotting is developed for microscale additive manufacturing. By applying strong spatial electrostatic field, Maxwell stress at the material/air interface results in pointed meniscus (Taylor Cone), from which microscale droplet or fine jet is issued. A 3D microfabrication method is obtained by taking advantage of this microscale material deposition mechanism, coupled with sub-micron position accuracy, augmented by appropriate processing conditions which will suppress inherent EHD instabilities. Moreover, a fully 3D multiscale fabrication method for 3D tissue engineering
scaffold is demonstrated via combination of Solid Freeform Fabrication technology and EHD printing methods.

Third, a long-existing issue for EHD-based printing lies on residual charge on substrate, especially for highly insulated substrate with long characteristic charge decay time. In order to overcome this fundamental challenge, an AC EHD-jet printing method was developed with objective on both charge neutralization and high-resolution. A special AC plus based high voltage is used to drive the material flow. Consequently, a positively-charged droplet and a negatively-charged droplet with equal amount of charge will be ejected from meniscus - overlaying them will eliminated residual charge, making printing continuous features possible. Another advantage for this AC EHD-jet method over EHD printing using constant DC voltage is that printing frequency and printing resolution can be controlled separately.

Lastly, this study investigated the detailed mechanism for EHD-based fabrication. A complete printing process is separated into multiple stages with distinct characteristics, which includes droplet formation, droplet flight, and droplet impact/spreading/solidification. Droplet formation and droplet fight has been successfully addressed in this study. Droplet formation process is modeled by Finite Element Analysis (FEA) with respect to the electrostatic force and surface tension of the resulting pending droplets about to detach from pointed meniscus. The numerical results have reasonable agreement with experimental results obtained from Atomic Force Microscope (AFM), indicating this model can provide guidelines to predict the droplet dimensions at different process conditions. Droplets in-flight velocity and fluidic characteristics (e.g. Reynolds number and Weber number) are modeled
using the results from FEA analysis. Droplet impact/spreading/solidification on non-porous media will be in future study.
Investigation of Hierarchical Fabrication Methods for High-Resolution Additive Manufacturing

by
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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

Industrial Engineering

Raleigh, North Carolina

2014

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DEDICATION

To my parents, Guo Wei and Xiaqin Zhang and my fiancée, Lingjiao Qi.
BIOGRAPHY

Chuang Wei received B.S. degree in Mechanical Engineering from Beijing University of Aeronautics and Astronautics in 2008 before he joined Beijing UPTECH Robotics Co. Ltd group. Then in 2009, he joined Prof. Jingyan Dong’s group in Edward P. Fitts Department of Industrial and Systems Engineering at North Carolina State University. His research focuses on the development of 3D high-resolution printing technologies for tissue engineering applications, low-cost solution-based ultra-resolution digital printing technologies for flexible electronics, and nanomaterial synthesis by Chemical Vapor Deposition.
ACKNOWLEDGMENTS

I’d like to thank my advisor, Prof. Jingyan Dong for providing me such a great opportunity to work on these exciting topics. I also would like to express my gratitude to the rest of my committee, Prof. Richard A. Wysk, Prof. Ola Harrysson and Prof. Xiaoning Jiang for their thoughts and feedback. Finally, I would like to thank to Prof. John H. Kelley for taking the role of Graduate School Representative in my committee.

I express my highest gratitude to my parents and my fiancée, Lingjiao Qi for strong support over my entire graduate study. It has been of great pleasure to work with the most talented and motivated colleagues, Zelin Xu, Jianbing Jiang, Shanshan Yao and Guangming Chen. It is also fun to work with Dr. Li Zhang, Dr. Li Yang, Dr. Martin Samayoa, Guha Manogharan, Yiwei Han, Jia Deng and Xiangcheng Kong. Your presences are of great value for my graduate study.
# TABLE OF CONTENTS

## LIST OF FIGURES

vii

## CHAPTER 1 INTRODUCTION

1

## CHAPTER 2 LITERATURE REVIEW

5

2.1. Traditional Additive Manufacturing Technologies for Tissue Engineering Applications ................................................................. 5
2.2. Advanced Additive Manufacturing Technologies for Hierarchical Fabrication ...... 7
2.3. Advanced Digital Printing Technologies for Flexible Electronics .................. 10
2.4. Development and Modeling of Melt Electrohydrodynamic-Jet Printing of Phase-Change Inks for High-Resolution Additive Manufacturing ................................................. 13

## CHAPTER 3 FLEXIBLE LAYER-MOLDING MULTI-MATERIAL DEPOSITION OF 3D STRUCTURES

16

3.1. Multi-Nozzle-Based Deposition System Description ......................................................... 16
3.2. Deposition of Thermoplastic Polymer ........................................................................ 20
3.3. Layer-Molding Process for Photo-Crosslinkable Material ........................................... 24
3.4. Multi-Material Scaffold Fabrication ............................................................................. 34
3.5. Computational Analysis .............................................................................................. 44
3.6. Conclusion .................................................................................................................. 49

## CHAPTER 4 DIRECT FABRICATION OF HIERARCHICAL THREE-DIMENSIONAL POLYMERIC SCAFFOLDS

50

4.1. Materials and Methods ............................................................................................. 51
4.2. Results and discussion .............................................................................................. 59
4.3. Conclusion .................................................................................................................. 88

## CHAPTER 5 HIGH-RESOLUTION AC-PULSE MODULATED ELECTROHYDRODYNAMIC JET PRINTING ON HIGHLY INSULATING SUBSTRATES

89

5.1 Materials and Methods ............................................................................................. 90
5.2 Results and discussion .............................................................................................. 93
5.3 Conclusions ................................................................................................................ 108
CHAPTER 6 DEVELOPMENT AND MODELING OF MELT ELECTROHYDRODYNAMIC-JET PRINTING OF PHASE-CHANGE INKS FOR HIGH-RESOLUTION ADDITIVE MANUFACTURING

6.1 Materials and EHD Printing system ................................................................. 110
6.2 Melt EHD-Jet Printing of Thermoplastic Phase-Change Material ..................... 112
6.3 Modeling and Analysis of Melt EHD-Jet Printing .......................................... 120

CHAPTER 7 CONCLUSION ..................................................................................... 141

7.1 Summary ........................................................................................................ 141
7.2 Future Work ..................................................................................................... 143

REFERENCES ....................................................................................................... 146
LIST OF FIGURES

Figure 1 (a) Pneumatic syringe for injecting polymer samples. (b) Heated syringe for deposition of thermal plastic wax. (c) Image of the developed deposition system 18
Figure 2 PCL filament width and height as functions of deposition velocity (a) and nozzle-substrate gap (b) 21
Figure 3 (a) Optical image of PCL scaffolds with different shapes and different orientation (b) Optical image of PCL scaffold (c) Top view of PCL under SEM. (d) Tilted view of PCL under SEM 23
Figure 4 Schematic representation of the deposition process for UV-crosslinkable materials. (a) Deposition of thermoplastic wax as an inverted mold. (b) Deposition of photo-crosslinkable poly(propylene fumarate) (PPF) into that layer. (c) UV exposure to cure PPF 25
Figure 5 Width and height of wax filaments (molds for photo-crosslinked PPF) as functions of deposition temperature (a), pressure (b), velocity (c), and nozzle-substrate gap (d) 29
Figure 6 (a) Optical image of PPF scaffold (b) Tilted view of PPF scaffold under SEM (c) Top view of PPF scaffold under SEM 33
Figure 7 (a)-(e) shows the first filling approach, each layer contains two function materials (a) Deposition of wax blends as an inverted mold. (b) Deposition of photo-crosslinkable PCLTA7K and PCLTA10K into that layer then heat-crosslink them (c) Deposition of wax blends in the next layer (d) Repeating these steps results in a 3D structure with structural material (PCLTAs) and sacrificial material (wax blends). (e) Dissolve wax blends in BioAct-VSO yields 3D porous scaffold 37
Figure 8 (a) First filling approach, each layer has two materials, the PCLTA10K filament is opaque while PCLTA7K is transparent (b) Second filling approach, each layer has only one material but adjacent layers have different materials (c) Top view under SEM (d) Side view under SEM 43
Figure 9. Computational domain for steady-state. Include part of the syringe, aluminum foil, nozzle and multi-phase fluid domain in light blue 45
Figure 11 a) Overall PCL distribution. b) PCL distribution around the nozzle 47
Figure 10 (a) Overall PCL velocity distribution (b) PCL velocity distribution around the nozzle 47
Figure 13 (a) Overall pressure distribution. (b) pressure distribution around the nozzle 48
Figure 12 (a) Overall temperature distribution. (b) temperature distribution around the nozzle 48
Figure 14 Schematic of the EHD-jet printing set-up and experimental testbed for EHD-jet printing 52
Figure 15 (a)-(d) show the first type of micro fiber networks, one direction is along the backbone fiber, and the other direction is 90 degree. (f)-(i) show the second type of micro fiber networks, one direction is 45 degree to the backbone fiber and the other is 135 degree. (a, f) Deposition of backbone fiber (b, g) Deposition of micro fiber networks (c, h) Deposition another backbone fiber (d, i) Deposition of another 55
Figure 16  (a) Forces on Taylor cone in EHD processing, (b) Small meniscus without jet or drip at nozzle tip at 600V. (c, d) Stable cone-jet at 900V and 1050V. (d) Unstable multi-jet at high electric field strength. ........................................................................................................ 60
Figure 17 Time sequence of cone-jet formation .............................................................................. 61
Figure 18 The cone-jet shape and jet printed filaments at different voltages. (a1-a3) Results from a nozzle with 152.4 µm orifice. (b1-b3) Results from a nozzle with 51 µm orifice. All scale bars 50 µm. ................................................................................................................................. 63
Figure 19 Filament width at different voltage .................................................................................. 68
Figure 20 The cone-jet shape and the jet printed filaments at different plotting speed. (a1-a3) Results from a nozzle with 152.4 µm orifice. (b1-b3) Results from a nozzle with 51 µm orifice. All scale bars 50 µm. ................................................................................................................................. 70
Figure 21. Filament width at different plotting speed....................................................................... 73
Figure 22 The cone-jet shape and the jet printed filaments at different pressure. (a1-a3) Results from a nozzle with 152.4 µm orifice. (b1-b3) Results from a nozzle with 51 µm orifice. All scale bars 50 µm. ................................................................................................................................. 75
Figure 23. Filament width at different back pressure. ..................................................................... 78
Figure 24. Two dimensional patterns fabricated by electrohydrodynamic jet printing of melted PCL. (a) Spiral-in circle pattern. (b) square shape pattern. (c) a flower pattern...... 80
Figure 25. Three-dimensional scaffold structures fabricated by direct EHD-jet plotting of melted PCL. (a) Overview of the scaffolds. (b) Detailed view of the plotted filaments. (c,d) Tilted views show the layered structure of the 3D scaffold................................................................. 82
Figure 26 (a) 90 degree alignment (b) 45 degree of alignment ......................................................... 84
Figure 27. Schematic of E-jet printing System setup. AC-pulsed voltage is applied between the nozzle and the electrode under the substrate. Droplets are formed under electrostatic stress and printed onto substrate ........................................................................................................ 91
Figure 28. Schematic plot of AC-pulse modulated EHD-jet printing System. Pulse frequency, duration, and peak voltage are input parameters. Intermittent positively and negatively charged droplets neutralize each other and enable reliable printing of continuous features on highly insulating substrates................................................................................................................. 92
Figure 29 Threshold voltages to start EHD printing with respect to the pulse frequency and duty cycle. ......................................................................................... Error! Bookmark not defined.
Figure 30 a) printed droplets at different pulse frequencies. b) Droplet size and printing frequency with respect to command pulse frequency ................................................................. 98
Figure 31 a) printed droplets at different duty cycles. b) Droplet size with respect to duty cycle. ........................................................................................................................................... 100
Figure 32 When duty cycle or duration is too large, satellite droplets can be observed along with the main droplets......................................................................................................................... 101
Figure 33 a) Printed droplets at different voltage. b) Droplet size with respect to the voltage. ........................................................................................................................................... 103
Figure 34 Drop-on-demand printed “ISE” letter demonstrates on-line controllability of the printing process. Letters printed on glass slides with printing speed and droplet dimension controlled by the parameter of the AC-pulse voltage. ......................................................................................... 105
Figure 35 Continuous features printed on highly insulated surface. a) On ABF substrate. b) Closed-up view on ABF substrate. c) Features printed on PET film. d) Features printed on glass slides. ........................................................................................................................... 107

Figure 36 Schematic of the EHD-jet printing set-up and experimental setup for EHD-jet printing ........................................................................................................................................................................... 111

Figure 37 (a) Pulsating (micro-dripping) mode of EHD printing of wax. (b) Footprint of printed droplets from different voltage, from left 560V to right 640V. ................................. 114

Figure 38 Droplets dimension at different process conditions. (a) Morphology and cross-section of a typical droplet (from Tip III printed at 890V). (b) Droplet volume, (c) Footprint diameter, and (d) thickness for droplets printed by three different nozzles at respective working voltage range. Red is Tip I, green is Tip II, and Blue for Tip III. ................................. 116

Figure 39 Drop-on-Demand Wax print ........................................................................................................... 119

Figure 40 a) Schematic configuration for FEA study of the electrostatic force on the droplets. b) Cross section plot of the nozzle, meniscus, and half ejected droplet. c) Electrical filed distribution around the nozzle tip during droplet ejection. ........................................................................................................................... 121

Figure 41 FEA results (dots) and fitted relations from Eq. 1 (line) of electrostatic force at different process conditions for Tip I. (a) Relationship between electrostatic forces and voltages. (b) Relationship between electrostatic forces and droplet diameter. ................................. 125

Figure 42 (a) Intersection points of the line for surface tension force and the curves for electrostatic force give the resulting droplets diameter at different voltage for Tip I. (b) Comparison between droplets dimension from FEA (color lines) and experimentally measured results (data points) for three different nozzles. ................................................. 127

Figure 43 Effective voltage considering the dielectric substrate ......................................................... 129

Figure 44 Experimental results indicate a unified relationship between normalize droplet diameter and electrical bond number when using different nozzles at different printing voltages. ........................................................................................................... 130

Figure 45 a) Schematic configuration for FEA study of electrostatic field strength and charge calculation. b) Electrostatic field distribution along center axis for Tip I at 560V(red), 600V(green) and 640V(blue). c) Charge of a single droplet for three tips at their own working range, Tip I, Tip II, and Tip III are shown in red, green, and blue respectively ..... 132

Figure 46 (a) Typical velocity profile for droplet in-flight for Tip I at 560V, 600V, and 640V (shown in red, green and blue respectively). (b) Impact velocity for three nozzles at different voltage, Tip I, Tip II, and Tip III are shown in red, green, blue respectively. (c) Reynolds Number and (d) Weber Number at impact for three nozzles, Tip I, Tip II and Tip III are shown in red, green, and blue respectively. ......................................................... 136
CHAPTER 1 INTRODUCTION

Additive manufacturing [1-3] and solid freeform fabrication (SFF) [4, 5] have become a fast growing industry that enables rapid prototyping and small volume production of components for automotive, aerospace, medical, and electronic applications. High-resolution additive manufacturing is critical for many emerging applications. Many high precision industrial parts require micron-scale accuracy and high quality surface finish, so as to effectively reduce the time and cost in post-processing.

This study is focused on multi-material and multi-scale high resolution additive manufacturing technologies. One typical application is biomedical application - specifically tissue engineering scaffold. Tissue engineering scaffolds are crucial to support cell functions and provide the evolution of tissues with pre-defined shape and size of the scale ~100 μm. The relatively large structures and pores are important to provide appropriate mechanical integrity, provide cells with sufficient oxygen, nutrient, and growth factors, and remove the waste generated throughout the metabolic process for better cell proliferation and tissue formation. In addition, the micron-scale structures with dimension similar to the size of the cells provides many advanced functions to regulate cell responses to the scaffolds, such as cell alignment and cell contact guidance [6, 7].

At macroscale, there exists a broad range of traditional scaffold fabrication technologies such as solvent-casting particulate leaching [8], phase-separation [9], gas foaming [10], and solution casting [11]; however, these approaches lack capabilities to engineer the structural features such as porosity and pore size of the resulting scaffolds because are process-
driven rather than design-driven methods. In order to address these basic requirements, Solid Freeform Fabrication (SFF) and Additive Manufacturing (AM) is proposed, which includes 3D printing [12], stereolithography (STL or SLA) [13], selective laser sintering (SLS) [14], and fused deposition modeling (FDM) [15]. The limitation for these approaches lies in the resolution: resolution in SLA and SLS are limited by the laser spot, particle based 3D printing is in particles size, phase-changed 3D printing and FDM are limited in nozzle size. It is quite challenging to fabricate sub-cellular (<10 μm) features, a scale cells are sensitive to. In micron-scale or even below, Electrospinning is a promising process-driven approach only gives feature resolutions; however, the placement accuracy is sacrificed due to whipping instability. Consequently, it is a great challenge to develop a 3D multi-material and multi-scale fabrication method, which does not exist according to our best acknowledgement. Compared to intensive research and development in macroscale additive manufacturing technologies, research advancement on 3D microfabrication methods is slow and limited. Electrohydrodynamic (EHD)-based printing method is a potential 3D microfabrication approach for biomedical applications. For this method, it is advantageous to use phase-change materials which can obtain thick features after quick solidification in microscale. The widely used aqueous or solvent-based inks are inappropriate because only a small fraction of functional materials can be retained after solvent evaporation, leading to very limited feature thickness (~10 nm); phase-changed materials can easily obtain much more thickness (~1 μm).

The objective of this thesis is to develop a versatile multi-material and multi-scale 3D fabrication approach which can significantly enhance tissue engineering scaffold performance;
also shed in-depth insight into this fabrication method from physical mechanism and process optimization.

- At macroscale, a layer-molding fabrication approach was developed for highly viscous photocrosslinkable functional polymers. A thin layer of mold is deposited by using thermoplastic materials, and then multiple functional photocrosslinkable materials can be deposited arbitrarily into the mold; following this sequence in a layer-by-layer fashion till the structure is fully fabricated. Then the mold can be stripped away by appropriate solvent and the final 3D structure is obtained. This approach has significantly advantages over the conventional SLA by not only enabling high-viscous photo-crosslinkable polymers to be used, but also providing multi-material integration capability. In addition, this process is highly cost-effective than SLA due to that functional materials can be deposited locally.

- At microscale, EHD-based printing method is presented with high-resolution and high placement-accuracy in both 2D and 3D. By introduction of strong spatial electrostatic field, Maxwell stress will result in pointed meniscus and minute material will be deposited from the meniscus apex. Also, a multi-scale 3D fabrication method is obtained by combination of using EHD-jet plotting and SFF technology.

- A long-existing critical issue for EHD-based fabrication methods lies in printing continuous feature on highly-insulated substrates, due to long characteristic charge decay time scale. In this study, a new method, AC EHD-jet printing, is developed specifically for this issue. In contrast to widely-used DC-based EHD-jet printing, an alternating short-pulse voltage waveform is adopted to ensure two oppositely charged droplets, with equal amount of charge,
are generated in one period. By overlapping the two successive droplets, the residual charge on substrate will be minimized, making printing continuous features possible on highly insulated substrates. In addition, the printing frequency and printing resolutions controls are separated, compared to EHD printing study using constant voltage signal.

- A EHD-jet model is developed and validated with experimental data to provide insight into the convoluted mechanism as well as to process optimization. The model in this study is divided into multiple stages according to their own physical characteristics: 1) droplet formation around the meniscus apex, 2) droplet flight in space with strong electrostatic field, 3) droplet impact/spreading on non-porous medium, and 4) droplet solidification. Droplet formation process is modeled by Finite Element Analysis (FEA) with respect to the electrostatic force and surface tension of the resulting pending droplets about to detach from pointed meniscus. The numerical results have reasonable agreement with experimental results, which are obtained by using Atomic Force Microscope (AFM), indicating that this model can provide guidelines to predict the droplets dimension at different process conditions. Droplets in-flight velocity and fluidic characteristics (e.g. Reynolds number and Weber number) are modeled using the results from FEA analysis. Droplet impact/spreading/solidification on non-porous media will be in future study.
CHAPTER 2 LITERATURE REVIEW

2.1. Traditional Additive Manufacturing Technologies for Tissue Engineering Applications

Tissue engineering scaffolds are crucial to support cell functions and construct tissues with pre-defined shape and size. In order to provide cells with sufficient oxygen, nutrient, and growth factors, and remove the waste generated throughout the metabolic process for better cell proliferation and tissue formation, a highly connected three-dimensional (3D) structure is required with optimal porosity, pore size, and pore distribution. There are many scaffolding methods such as solvent-casting particulate-leaching, gas foaming, and solution casting [8, 16]. These approaches lack capabilities to engineer the structural features such as porosity and pore size of the resulting scaffolds because they were process-driven rather than methods. In order to address these problems, several solid freeform fabrication (SFF) methods [14, 17-19] have been applied for scaffold fabrication, such as 3D printing, stereolithography (STL or SLA), selective laser sintering (SLS), and fused deposition modeling (FDM).

For powder materials, 3D printing [12, 20-22] and SLS [23, 24] are widely used approaches for creating complex structures. These materials include polymers, ceramics, and composites. The principle of 3D printing is to selectively print liquid binder to a thin layer of powder to form a solid structure. After one layer is selectively solidified, another layer of powder is applied on the top and this process continued until all the layers are finished. SLS follows a similar layer-by-layer fabrication process, in which powder is sintered together by the heat generated from a laser beam. The resolution of fabricated scaffolds from these two
approaches is dependent on the powder size and generally not high. In addition, the requirement of using powder materials limits their applicability to other materials. In order to address the limitation from powder materials, phase-change 3D printing [17] has been developed for scaffold fabrication, in which two types of thermoplastic materials with different melting points (Tm) are involved. One acts as the supporting material, which can be removed later by a specific solvent, and the other acts as the structural material. Over-hang features can be fabricated easily with the help of the supporting structure. The fabricated structure can be used as a mold for indirect fabrication of scaffolds from other materials. The structure resolution of phase-change 3D printing is limited by the thermal interference of two thermoplastic materials [17]. Because two thermoplastics have different Tm, the polymer with a higher Tm can result in local melting when it is printed onto the other polymer with a lower Tm and consequently degrade the fabrication resolution.

FDM and precision extrusion deposition (PED) [15, 19, 25] methods are capable of high-precision fabrication of 3D structures using thermoplastic polymers. In FDM, pre-formed fibers are fed through rollers with a heater, and deposited to a substrate through a nozzle. In PED, a thermoplastic polymer is melted in a syringe and extruded from a nozzle by pressure. The deposited material solidified as the temperature dropped. The materials used in FDM are limited to thermoplastics. Other types of materials such as crosslinkable polymers are difficult to be integrated into this approach because they generally need curing time to solidify and form a structure after dispensing.
Crosslinkable, biodegradable polymers are attractive as scaffold materials because of their good processability [26] in STL. Their properties can be controlled to satisfy specific design requirements such as biodegradability, surface chemistry, and mechanical properties. Commonly used crosslinkable polymers include hydrophobic poly(propylene fumarate) (PPF) [13, 18, 27] and water-soluble poly(ethylene glycol) dimethacrylate (PEGDMA) [28-30]. The principle for STL is to selectively cure a photo-crosslinkable polymer in a layer-by-layer sequence using a UV laser beam. For this approach, the difficulty in scaling down the size of the laser spot results in a resolution limitation. Polymer viscosity is another limitation of this process because a sufficiently low viscosity is required to allow for the movement of the supporting plate in a polymer resin while the ways to reduce the viscosity should not deteriorate the mechanical properties of the fabricated scaffolds [13]. In addition, a large resin volume in the tank introduced cost problems, especially for the materials that can be crosslinked by themselves gradually and the physical properties of the resin can change or even degrade in a normal environment. It is also difficult for STL to integrate two or more different materials in a scaffold because the resin in fabrication needs to be one single-phase mixture of different components.

2.2. Advanced Additive Manufacturing Technologies for Hierarchical Fabrication

Micro-scale periodic three-dimensional (3D) structures have been widely used in many emerging applications, such as tissue engineering scaffolds [31], photonic crystals and meta-materials [32], and sensors and micro-devices [33]. In tissue engineering, scaffolds with highly connected 3D structure are critical to support cell attachment/growth and construct tissues with
pre-defined shape and size. Porous scaffold structures with optimal porosity, pore size, and
pore distribution are required to provide cells with sufficient oxygen and nutrient supply, and
remove the waste generated throughout the metabolic process for better cell proliferation and
tissue formation. While the relatively large structures and pores (generally >100 µm) are
important for providing mechanical support and material transportation, micro-scale structures
with their dimension similar to the size of the cell provides many advanced capabilities to
regulate cell responses to the scaffold, such as cell alignment and cell guidance [6, 7].

Widely used extrusion and ink-jet printing based solid freeform fabrication methods
are limited in their achievable structural resolution that is mainly controlled by the nozzle size.
Fused Deposition Modeling (FDM) [19] and precision extrusion deposition (PED) [25, 34] are
capable of layered fabrication of 3D structures for thermoplastic biodegradable polymers, such
as polycaprolactone (PCL). However, scaling down the nozzle size for better resolution will
make the required extrusion pressure unpractical high for high viscous biopolymers, since the
extrusion pressure scales up much faster when the nozzle diameter is decreased according to
Hagen-Poiseuille equation.

Electrohydrodynamic jet (EHD-jet) printing is a high resolution printing method, in
which the printed materials, ranging from nano particles [35, 36], polymer solution or polymer
melt [37, 38], ceramic solution [39] to composite materials [40], are subjected to high
electrostatic field to form a Taylor-cone structure and a fine jet issued from the cone. The
diameter of the jet is significantly smaller than the nozzle diameter, which can overcome the
limitation of the nozzle size and produce micro and nano-scale feature. Electrohydrodynamic
(EHD) behavior was pioneered by Zeleny back to 1917 [41], and was then investigated both theoretically and experimentally, which provide insightful understanding of the phenomenon along with many important applications.

The parameters for EHD-jet plotting include material properties of the ink (e.g., viscosity, density, conductivity, and permeability) and operational conditions such as applied voltage/electrical field, pressure/flow rate, and substrate to nozzle distance. It is important to point out that widely used electrospray [42-44] and electrospinning [45] utilize the unstable electrohydrodynamic behavior, while EHD-jet plotting needs to avoid unstable behavior to achieve well-controlled placement of the printed structures. EHD-jet printing has been used to fabricate micro/nano scale patterns in the form of droplet in the pulsation mode for the applications of bio-sensing [46, 47], drug encapsulation [48] and AFM cantilever modification [38]. While isolated fine droplets can be flexibly controlled for 2D patterning, it is difficult to be directly used for 3D fabrication. EHD-jet plotting with a stable jet, even though is still predominately used in 2D fabrication, provides good potential for the fabrication of 3D structures by using continuous filaments instead of isolated droplet, if the filament formation and solidification can be well controlled. There are some initial attempts to fabrication 3D polymeric structures using EHD-jet printing [37, 49]. However, due to the difficulty of solvent evaporation, these approaches are still limited in the achievable resolution and controllability.

Working in a stable jet region is critically important for the freeform fabrication of 3D structures using EHD-jet printing. Depending on different process conditions, axis-symmetric instability, in which droplets break-up from the jet, or nonaxis-symmetric instability (i.e.
whipping) will disrupt the stable cone jet[50, 51]. These instabilities are required for electrospray and electrospinning, but devastating for 2D and 3D fabrication requiring precision position control. Process parameters as well as materials used have to be carefully chosen to obtain a stable cone-jet. As pointed [52], very low conductivity liquids such as toluene and hexane may not have any cone-jet mode. There exists a minimum flow rate threshold for cone-jet mode [53], and a maximum flow rate [54] above which whipping instability is developed. For the fabrication of 3D structure, the upper layer filaments need to span over the gap underneath them. Quick solidification of the plotted filaments against sagging down effect is also critical.

2.3. Advanced Digital Printing Technologies for Flexible Electronics

Printable electronics is an emerging industry which aims to fabricate electronics on large area at low cost [55]. Ink-jet printing has been widely used for the deposition of a wide range of low viscosity functional materials over large area with high speed [56]. The ink-jet printers use acoustic or thermal energy to first form monodispersed droplet in the picoliter volume range, of which the radiuses of the droplet are comparable to the nozzle head. Then the droplets obtain initial speed [57] and be deposited over the desired position on substrates by many methods, such as piezoelectric actuation. Many important elements in electronics have been partially or fully fabricated by ink-jet printing, for example, electrical interconnections [58], transistors [59-61] and integrated electronic device, organic photovoltaic solar cells [62] and information display [63].
One specific limitation of the ink-jet printing technique is its limited printing resolution. Generally, the printing resolution in ink-jet printing is mostly determined by the dimension of the printing nozzle, and is typically limited to about 20 μm due to the relatively large droplet volume. Efforts were spent on reducing the nozzle size to obtain smaller droplets. However, the fabrication of the nozzle with micron-scale orifice is challenging and costly [56]. Moreover, reducing the nozzle size for better resolution will required a high actuation effort that is unpractical for many viscous inks, since the printing pressure to form droplets scales up much faster when the nozzle diameter is decreased according to Hagen-Poiseuille equation.

To achieve higher printing resolution, electrohydrodynamic (EHD) jet printing approaches have been developed [64]. In electrohydrodynamic jet printing, the strong electrostatic field imposed between the nozzle tip and the substrate produces surface charge of the ink and form a Taylor-cone structure, and generate picoliter to attoliter droplets [65] when the interfacial electrostatic shear stress at the cone apex exceeds the surface tension. The diameter of the jet/droplet is significantly smaller than the nozzle size, which can overcome the limitation of the nozzle size for better resolution. Many attractive progresses have been reported recently in the application of electrohydrodynamic jet printing, including conductive tracks[66] and transistors [67, 68]. However, compared to the wide applicability of ink-jet printing, there are still some technical difficulties that prevent EHD-jet printing for many applications. In commonly used EHD-jet printing, a high DC-voltage is applied to the nozzle tip to form the Taylor-cone and the droplets. The printing speed and droplets dimension is mostly determined by the fluid properties of the ink, printing head [69], along with the process
conditions, mostly applied voltage and flow rate. Due to the coupled process conditions to the printing process, the droplet size and the printing frequency cannot be controlled independently.

Besides the limited process controllability, a critical disadvantage of electrohydrodynamic jet printing, as pointed out in [64], is the residue charge on the droplet from the EHD printing process. In some conditions [70, 71], the printed charge can be stored on the functional surfaces over days or weeks. The charge on the insulating substrate will change the electrostatic field distribution and the follow-on printing behavior. In DC-based electrohydrodynamic jet printing or pulsed printing using the same polarity of the applied voltage [72-79], the printed droplets on highly insulating substrates retain the same polarity and will reject each other[80, 81]. Certain highly insulating substrates, such as Teflon and PET, have very slow charge decay rates and large time constants of characteristic charge decay. The residue charge makes the control of EHD jet printing very challenging, especially for the printing of high-resolution continuous features. In many electronic applications, such as flexible electronics and electronic packaging, the commonly used substrates, such as Polyethylene terephthalate (PET) and Ajinomoto Fine film (ABF), are highly insulating and can retain charge for a long time. The residue charge issue, if not being well addressed, will impose heavy constraint on the potential applications of the high-resolution EHD jet printing technology.
2.4. Development and Modeling of Melt Electrohydrodynamic-Jet Printing of Phase-Change Inks for High-Resolution Additive Manufacturing

Most of the existing additive processes, including stereolithography, selective laser sintering, electron beam melting, 3D printing, and fused deposition modeling [2, 3], have their best resolution no better than 50µm. The resolution limitations from the existing processes are intrinsic and difficult to be improved. For example, in laser or electron beam based processes, laser spot size, thermal diffusion, and material shrinkage limit the best achievable resolution to be about 100 microns. For deposition or extrusion based approaches (e.g. fused deposition modeling), the resolution is limited by the size of the printing nozzle. Scaling down the nozzle size for better resolution will make the required extrusion pressure impractically high for most liquid phase inks, since extrusion pressure scales up much faster when the nozzle diameter is decreased according to Hagen-Poiseuille equation. New printing technology needs to be developed to meet the increasingly demanding resolution requirements of additive manufacturing.

Electrohydrodynamic (EHD) printing is a high resolution printing method, in which the printing materials are subjected to high electrostatic field to form a Taylor-cone structure, and a fine jet or droplet ejected from the cone. The diameter of the jet/droplet is significantly smaller than the nozzle size, which can overcome the limitation of the nozzle size for better resolution to produce micro and nano-scale features. Depending on different process configurations, there are different EHD printing modes [82], including electrospay [83-85] and electro-spinning [86-94], both of which utilize the unstable electrohydrodynamic
behaviors. In electrospray, axis-symmetric instability breaks up the jet into numerous tiny droplets, while in electrospinning, non-axis-symmetric instability (i.e. whipping) is experienced by the jet to evaporate the solvent to form solid fibers. These instabilities are necessary for electrospray and electrospinning, but devastating for 3D printing of high precision structures. For high precision manufacturing, stable EHD printing modes have to be used, which are EHD direct filament plotting [95, 96] in form of fine filament from the Taylor-Cone, and drop-on-demand pulsated printing [64, 73, 97-99] in form of separate micro droplets.

Currently, most of the EHD printing applications focus on the fabrication in two dimensions (2D), such as patterns [64, 97], with only some initial investigation towards 3D fabrication [95, 96]. Similar to conventional 3D printing, drop-on-demand EHD printing with thermoplastic phase-change inks in pulsating mode produces a single droplet at a time, which provides promising potential for 3D printing with micro-scale resolution. In contrast to well understood printing principle at conventional-scale, the mechanism of the EHD printing process is still under development from the processing control and plan’s perspective. It is very challenging to predict the droplet dimension from EHD printing at different process conditions. Similar to inkjet printing, there are three stages of EHD printing, which are droplet formation, droplet in-flight, and droplet impact/spreading coupled with either evaporation or solidification [100]. However, experimental investigation of these stages is very difficult due to the micro-scale droplet size and high droplet velocity. On the other hand, computational modeling based approaches for EHD printing provided very promising results from electrospray community
focusing on droplet formation [101-104]. So far, there is still no commercially available numerical solver that can be successfully applied to EHD printing due to its highly sophisticated physics that incorporate coupled electrostatic stress with the fluid dynamics and the singularity events rising from droplet pinch-off. Several groups [101, 103, 104] developed their own complex solver to study many aspects of EHD printing process with intensive computational burden. Some highly simplified models have also been developed to provide an insight from engineering perspective [105, 106].
CHAPTER 3 FLEXIBLE LAYER-MOLDING MULTI-MATERIAL

DEPOSITION OF 3D STRUCTURES

In this chapter, a multi-nozzle versatile deposition approach to flexibly fabricate porous scaffolds using different types of polymeric biomaterials, namely, thermoplastic PCL, photo-crosslinkable PPF and PCLTA is developed. Besides the direct fabrication of thermoplastic PCL scaffolds, I introduce a new approach based on layer molding that enables fabrication of scaffolds with high-resolution features using crosslinkable polymers and multi-material integration. After 3D scaffolds were fabricated using PCL, PPF and PCLTA, their morphologies and microstructures have been characterized using scanning electron microscopy (SEM) and the porosity has been estimated. The compressive mechanical properties of the PCL and PPF scaffolds have also been tested. Furthermore, in order to explore the potential applications as bone tissue engineering scaffolds, mouse pre-osteoblastic MC3T3-E1 cells have been used to evaluate the cytocompatibility of the PCL and PPF scaffolds in terms of cell attachment, proliferation, and ingrowth in the scaffolds. Both the mechanical strength measurement and cell study were conducted by our collaborator. The detail results related will not be discussed in this document, but can be found in [107]. The fabrication method presented in this chapter can be extended to applications that require precise deposition and multiple materials.

3.1. Multi-Nozzle-Based Deposition System Description

In this work, a pneumatically-controlled multi-nozzle deposition system has been investigated. The overall system setup is shown in Figure 1. The high-precision deposition
platform was composed of four sub-systems: 1) a three-axis (XYZ) precision stage, 2) a deposition system which was either pneumatic or based on a syringe pump, 3) a thermal control system, and 4) a surface polishing system (Fig. 1). The XYZ precision stage was located on an optical table to reduce vibrational noise. Three linear stages that were configured in XYZ directions with 100 nm repeatability and accuracy were used to position the deposition nozzles to the programmed locations. The stage provided a displacement range of $100 \times 100 \times 50$ mm. A high resolution camera was used to monitor the deposition process.
Figure 1 (a) Pneumatic syringe for injecting polymer samples. (b) Heated syringe for deposition of thermal plastic wax. (c) Image of the developed deposition system
The material deposition system included two sets of syringes. One syringe was for depositing a crosslinkable polymer; the other syringe was for depositing thermoplastic materials. In the fabrication, deposition nozzles with an orifice size of 250 μm were used with 3 mL syringes for polymer deposition. A pneumatic pressure or pressure from the motor-driven syringe pump was applied to the syringe to extrude a liquid-state polymer out from the nozzle and deposit it on the substrate. The pneumatic system can provide a maximum pressure of 80 psi (corresponding maximum material deposition rate 0.6 mL/min) while the syringe pump can provide a linear pressuring force of 100 N.

After adding heating tape and a thermal control system, the deposition system was capable of processing thermoplastic materials, e.g. PCL, paraffin wax and wax/polyethylene blend in this study. The heating tape was wrapped around the syringe to melt the thermoplastic polymer loaded inside the syringe. A thermocouple was mounted close to the nozzle to provide temperature feedback to a thermal controller. A proportional–integral–derivative (PID) controller in the temperature control system regulated the power of heating tape to achieve the appropriate temperature. The thermal control system has a resolution of ~0.5 °C with a maximum reachable temperature of 250 °C. PCL and paraffin wax were melted by the thermal control system and extruded onto the substrate under the applied pressure.

When needed, an air-powered grinder with a maximum speed of 70,000 rpm was used to flatten the top surface of each deposited layer. The purpose of the optional surface grinding step was to control the height of each layer and to prepare a flat surface of the sample so that the feature of the future layers can be deposited.
3.2. Deposition of Thermoplastic Polymer

PCL used in this study was semi-crystalline and its thermal properties were determined using DSC. Its Tm was 55.4 °C and heat of fusion was 67.2 J/g, corresponding to a crystallinity of 49.8%. It has to be processed at a temperature higher than its Tm. The zero-shear viscosities of the PCL sample were 550, 328, 218, 159, and 115 Pa.s at different temperatures of 60, 80, 100, 120, and 140 °C, respectively.

PCL scaffolds were fabricated using the pressure. The deposition characteristics for PCL scaffolds were investigated first for finding feasible process parameters. PCL filaments were deposited on the substrate using different process parameters and the resulting filaments width and height were measured and analyzed. The process parameters included the deposition velocity, nozzle-substrate gap, deposition flow rate, and temperature of the material. We found that the deposition characteristics were very sensitive to the deposition velocity, nozzle-substrate gap, and nozzle size. In this work, we fixed nozzle diameter as 250 μm, heating temperature as 75 °C, and pressure as 60 psi to simplify the process characterization. Figure 2 shows the results of the PCL filament deposition tests using our deposition system. Both the filament width and height decreased as the deposition velocity increased. As the gap between the nozzle and the substrate increased, the filament height also increased but the width decreased because the flow rate was constant.
Figure 2 PCL filament width and height as functions of (a) deposition velocity and (b) nozzle-substrate gap. Each condition was repeated 5 times.
Porous 3D PCL scaffolds, in Figure 3 with fully interconnected inner structures, uniform pore size were fabricated using the temperature-controlled syringe. The designed scaffold model was converted into the tool path using its geometrical parameters of each layer. The overall scaffold dimension in Figure 6(b)-(d) is 13mm x 13mm, the distance between the centerlines of two filaments is 700μm, the height of each layer is 250 μm, and pore size is 250 microns. The filaments of PCL were deposited with a layered pattern of 90° orientation to the previous layer to create the porous structure. Because PCL was highly viscous and can quickly solidify after being extruded, no supportive material was required. The pore size of the filament dimensions was measured from the SEM images. The porosity of the PCL scaffolds was calculated according to the measured dimensions by a simple gravimetrical method. The PCL scaffolds had a pore size of 243 ± 4 μm and a porosity of 39.2 ± 2.4%, satisfied the minimum requirement for pore size, which was ~100 μm to allow for cell proliferation, migration, and ingrowth into the scaffolds.
Figure 3 (a) Optical image of PCL scaffolds with different shapes and different orientation (b) Optical image of PCL scaffold (c) Top view of PCL under SEM. (d) Tilted view of PCL under SEM
3.3. Layer-Molding Process for Photo-Crosslinkable Material

PPF is amorphous polyester with a relatively high viscosity at room temperature. Mixing with a low molecular weight solvent, DEF, was effective to reduce its viscosity and DEF can also participate in photo-crosslinking of PPF as a crosslinker. The zero-shear viscosities of PPF/DEF mixture with a weight ratio of 85:15 at different temperatures of 25, 37, 60, 80, and 100 °C were determined on a rheometer to be 57.4, 14.7, 3.2, 1.2, and 0.82 Pa.s, respectively. Differential Scanning Calorimetric (DSC) measurements were performed on a Perkin Elmer Diamond differential scanning calorimeter in a nitrogen atmosphere. The same thermal history was applied to all the samples by first heating up to 100 °C and cooling to –80 °C at 5 °C/min. Then a subsequent heating run was performed from –80 to 100 °C at 10 °C/min.

The overall dimension of the PPF scaffold design is about 13mm x 13mm, with distance between two filaments of 400 μm, 200 μm pore size and height of each layer of 250 μm. The pore shape of both PCL and PPF scaffolds is defined by the geometrical shape of the PCL and PPF filaments. The fabrication of cured PPF scaffolds was very different from that for PCL scaffolds because PPF/DEF resin remained as liquid after deposition and UV crosslinking cannot be fulfilled instantly. A supportive structure and a local mold were required to retain its designed structure. The procedure of the layer-by-layer fabrication process for PPF was divided into four major steps, as shown schematically in Fig. 4. The four major steps were elaborated as follows.
Figure 4 Schematic representation of the deposition process for UV-crosslinkable materials. (a) Deposition of wax as an inverted mold. (b) Deposition of photo-crosslinkable poly(propylene fumarate) (PPF) into that layer. (c) UV exposure to cure PPF (d) Polish the surface and control layer thickness (e) Repeat the process from (a) to (d). (f) Remove wax
Step 1: Supportive molding material (paraffin wax) was deposited to make a mold pattern for each layer. This inverted pattern was used as a single layer mold to define the structure of the biomaterial, which was PPF in this study. The thermoplastic wax also provided structural support when the upper layers were deposited. The deposition following the programmed tool path created a layer of wax mold structure on the substrate. The resolution of deposited wax filaments was largely dependent on the nozzle size and the process parameters. Process control over this step to obtain precise features of each wax layer was critical for the final scaffold structures because they were shaped by the inverted wax mold structure. The critical process parameters included temperature, pressure, deposition velocity, and the gap between the nozzle and the substrate. After process parameters were identified, the porosity of the scaffold can be easily adjusted by changing the dimension of the wax mold structure.

Step 2: PPF/DEF resin was deposited into the space of the wax mold using a pneumatic syringe. The liquid state PPF/DEF resin was contained in the wax mold structure. UV light was used to cure PPF/DEF before further processing steps. The sample is placed 10 cm away from an UV light and exposed with an intensity of 10 W/cm2 for about 20 seconds. After curing, the surface of the top layer sometimes was rough because it was difficult to fill the space with extra amount of material. Surface tension of the liquid state PPF/DEF resin and material shrinkage during solidification also contribute to the rough surface.
Step 3: The top surface was ground with an air-powered grinder to control the height of each deposited layer and flatten the surface for the next deposition step. Then, an additional layer was deposited by repeating Steps 1 to 3.

Step 4: After all the designed features and structures were deposited, the resulting scaffold that included structural and sacrificial materials was cut to sharp and soaked in a BioAct-VSO solvent for 12 h. After all the wax was dissolved, the scaffold was dried by air at ambient temperature. Prior to characterizations, cured PPF scaffolds were immersed in a mixture of acetone and alcohol for two days and then completely dried to remove the sol fraction.

For fabrication of crosslinked PPF scaffolds, a pneumatic syringe was used to deposit PPF/DEF resin and the heated pneumatic syringe was used to deposit wax. In this approach, the feature of the final scaffold structure was solely defined by the deposited wax filaments that acted as the inverted sacrificial structures. For the deposition process of paraffin wax, the dimension of the deposited filaments depended predominantly on the nozzle size. However, when a specific nozzle size was chosen, the structural characteristics such as filament width and height were mainly defined by four process parameters: heating temperature, deposition pressure, deposition velocity, and the gap between the nozzle tip and the substrate. In this study, we characterized the effects of these process parameters on the deposited filament width and height. Thus a set of suitable parameters can be chosen to regulate the deposition behavior and deposited features. The deposition characteristics for the paraffin wax were investigated using
single-line deposition on the substrate. The resulting filaments width and height were measured and analyzed, as shown in Fig.5.

The experimental results demonstrated that the wax deposition was very sensitive to the temperature of the heated syringe. When the temperature was below 57.7 °C, it was unable to extrude wax from the syringe. As the heating temperature increased, the viscosity of wax decreased and consequently the flow rate increased and more wax can be extruded from the nozzle under the same pressure. The width of the deposited filament increased, as shown in Fig.8a. The height of the filaments decreased slightly as the result of the reflow of the melted wax on the substrate. When the temperature was too high (> 60 °C), the deposition became uncontrollable and the melted wax was jetted out with a small pressure.

Pneumatic pressure was also important in the deposition process. As the pressure increased, the flow rate increased. A larger volume of wax was dispensed and deposited. As shown in Fig. 5b, the filament width increased from 130 to ~300 µm when the pressure increased from 20 to 60 psi. The relationship between the filament height and the applied pressure was not as sensitive as the relationship between the width and the pressure. In fact, as the pressure increased, the filament width decreased only slightly. This effect was different from the expectation that a larger flow rate resulted in larger filament width and height. This trend can be explained by the reflow effect of the melted wax. When a hot thermoplastic material is extruded from the syringe, it needs time to cool down and solidify. The material reflowing before its solidification counteracts the effect of a larger flow rate.
Figure 5 Width and height of wax filaments (molds for photo-crosslinked PPF) as functions of deposition temperature (a), pressure (b), velocity (c), and nozzle-substrate gap (d). Each condition was repeated 5 times.
Figure a: Graph showing the change in dimension (μm) with temperature (°C). The graph indicates an increase in both width and height with temperature, with error bars indicating variability.

Figure b: Graph showing the change in dimension (μm) with pressure (Psi). The graph shows a clear increase in both width and height with increasing pressure, with error bars indicating variability.
The deposition was also affected by the deposition velocity, as shown in Fig 5c. As the deposition velocity increased, the filament width also increased slightly. This phenomenon might be due to the uneven temperature distribution inside the nozzle and syringe. The material close to nozzle had a lower temperature while the material inside the syringe had a higher temperature. Because the filament deposition was a continuous process, the material flow during deposition was driven by both the pressure and the pulling force from the deposited filaments. When the deposition velocity was increased, the filament that was already attached to the substrate can draw more melted wax from the nozzle with the help of the air pressure. A larger material flow resulted in a larger filament width. The filament height did not change significantly with respect to the velocity because of the material reflowing.

The last important process parameter we identified was the gap between the nozzle and the substrate. This parameter significantly impacted the height of the deposited filaments. Because of the larger space from the increased nozzle-substrate gap, the filament dimension increased as well. As shown in Fig. 5d, when the gap increased, the height of the deposited filaments increased significantly from 100 to 200 µm in an approximately linear manner. The gap roughly determined the height of the deposition. Along with the change in the height, the filament width also increased from 165 to 235 µm.
Figure 6 (a) Optical image of PPF scaffold (b) Tilted view of PPF scaffold under SEM (c) Top view of PPF scaffold under SEM
As demonstrated in the optical and SEM images in Fig. 6, porous 3D lattice-structure crosslinked PPF with fully interconnected inner architectures were fabricated using the layer-molding technique. The gaps, filaments, and internal pore connectivity were observed in the SEM images of the micro-structures of crosslinked PPF scaffolds. Figure 6 clearly demonstrated the layered pattern and the fully interconnected pores of the fabricated scaffold micro-architecture. The uniformity of the pores and the filaments indicated the applicability of using the developed deposition process to fabricate scaffolds at the micron scale using PPF.

The pore size of the filament dimensions was measured from the SEM images. The porosity of PPF scaffolds was calculated according to the measured dimensions by a simple gravimetrical method. PPF scaffolds had a pore size of 210 ± 18 µm and a porosity of 61.6 ± 1.6%, which satisfied the minimum requirement for pore size, which was ~100 µm to allow for cell proliferation, migration, and ingrowth into the scaffolds.

3.4. Multi-Material Scaffold Fabrication

The two functional materials used in this study, PCLTA with molecule weight of 7,000 and 10,000, both of which are photo-crosslinkable biodegradable material and are solid at room temperature so that they cannot be processed by stereolithography. The fabrication of crosslinked PCLTA scaffolds without mold is very difficult because they can only be crosslinked by UV light in liquid state, which needs heating and will not maintain geometry as designed. As a result, wax blends serves as supporting material so that PCLTA can maintain geometry even under high temperatures.
The ideal wax blends need to have reasonable viscosity in favor of deposition, high melting temperature so that it maintains its geometry during heating-crosslinking procedure as well as easy to dissolve into solvent. In this study, the proportion of wax to modifier was around 1:1 fully satisfied requirement mentioned above. The only downside is that heating is needed while dissolving the mold, rather than in room temperature, which would potentially be a problem for integrating low melting temperature biodegradable thermoplastic polymer into structure.

Paraffin wax obtained from McMaster and modifier, C17 from Westlake Chemical Corporation, which is used to highly increase the viscosity wax blends at elevate temperature, reduce surface tension and improve final surface quality. The wax blends are so stable that it does not have any interaction with photo-crosslinkable materials used in this case during the whole fabrication process and it can be removed by solvent later on. Consequently, this wax blends can serve as a good candidate for sacrificial supporting material. The melting point of paraffin wax is about 130° to 132° F. The Paraffin wax beads are FDA compliant. They're furnished in a 1-lb. package that contains approximately 17,000 beads. The modifier C17 which is a branched low density polyethylene with a relatively high melt point and viscosity compared has a soften point temperature 133 °C. The solvent to dissolve paraffin wax was a cleaner solution BIOACT VSO (Petroferm Inc.).

The porous 3D PCLTAs scaffold with fully interconnected channels were fabricated following a layer-by-layer sequence which involves depositing wax mold, filling the mold with un-crosslinked PCLTAs, following by heating-crosslinking PCLTAs. There are two different
ways of filling, either two PCLTAs in one single layer, or one PCLTA in a layer but another
PCLTA in adjacent layer.

The procedure of the layer-by-layer fabrication process for PPF was divided into four
major steps, as shown schematically in Fig. 7. The four major steps were elaborated as follows.

Step 1: Supportive molding material (wax blends) was deposited to make a mold
pattern for each layer. This inverted pattern was used as a single layer mold to define the
structure of the biomaterial, which was PCLTAs in this study. The thermoplastic wax blends
also provided structural support when the upper layers were deposited. The deposition
following the programmed tool path created a layer of wax mold structure on the substrate.
The resolution of deposited wax filaments was largely dependent on the nozzle size and the
process parameters such as the pressure, federate, temperature and gap between the nozzle and
substrate. Process control over this step to obtain precise features of each wax layer was critical
for the final scaffold structures because the final structure was shaped by the inverted wax
mold structure. After process parameters were identified, the porosity of the scaffold can be
easily adjusted by changing the dimension of the wax mold structure.
Figure 7 (a)-(e) shows the first filling approach, each layer contains two function materials (a) Deposition of wax blends as an inverted mold. (b) Deposition of photo-crosslinkable PCLTA7K and PCLTA10K into that layer then heat-crosslink them (c) Deposition of wax blends in the next layer (d) Repeating these steps results in a 3D structure with structural material (PCLTAs) and sacrificial material (wax blends). (e) Dissolve wax blends in BioAct-VSO yields 3D porous scaffold (f)-(j) shows the second filling approach, each layer contains only one function material but adjacent layers have different material. (f) Deposition of wax blends as an inverted mold. (g) Deposition of photo-crosslinkable PCLTA10K into that layer then heat-crosslink it (h) Deposition of photo-crosslinkable PCLTA7K into the next layer then heat-crosslink it (i) Repeating these steps results in a 3D structure with structural material (PCLTAs) and sacrificial material (wax blends). (j) Dissolve wax blends in BioAct-VSO yields 3D porous scaffold.
Step 2: PCLTAs resin were melted and deposited into the space of the wax mold using pneumatic syringes. The liquid state PCLTAs went solidification and was contained in the wax mold structure. Heat the structure again until the resin within change to liquid state then UV light was used to cure PCLTAs before further processing steps. Due to regular wax mold and good surface finish, such flat surface was obtained that no further machining is needed.

Step 3: Repeat above step 1 to 2 until the scaffold reaches to designed height.

Step 4: After all the designed features and structures were deposited, the resulting scaffold that included structural and sacrificial materials was soaked in a BioAct-VSO solvent for more than 96 h above 70°C. After all the wax was dissolved, the scaffold was dried by air at ambient temperature.

PCLAs possessed more reactive acrylate segments on the chain ends with a theoretical number of 2 or 3. Therefore, PCLAs were expected to crosslink more efficiently to form networks with better-defined crosslinking density and distance between two neighboring crosslinks. As the molecular weight of PCL precursor increased within the range studied here, the crystallinity and melting point of both PCLA and PCLA network formed increased significantly. Thus a wide range of material properties can be achieved using this series of PCLAs.

For fabrication of crosslinked PCLTAs scaffolds, two pneumatic syringes with heating element are used to deposit them and another pneumatic syringe with heating control is used for wax blends as mold. The feature of final scaffold structures was primarily determined by the wax blends filament. When a certain filament width and height is decided, it turned out to
be there is a good solution and needs no tuning at all. All the variables related to filament are: gap between nozzle tip and substrate, velocity, temperature, and pressure, providing nozzle size and materials are chosen already. If height is fixed such as in our case 250 μm height a layer is designed, then the gap is fixed to be 250 μm. The faster the velocity the shorter the time to finish a sample, however if it’s faster than the camera can respond or operator can intervene, it may crash the nozzle which is dangerous. As a result, choose the deposition velocity to 1mm/s. The lower the temperature, the lower the internal stress which would peel off the structure from the substrate; however, the filament needs to melt the layers underneath to get good bonding. So the reasonable deposition temperature was chosen to be around 190F. As for the pressure, it was also fixed because the deposition velocity and the gap were predefined, which means flow rate was fixed. Hence, there was one good solution and there were no variables for process if nozzle size and materials were predefined. In our case, the gap was 250 μm, velocity was around 1mm/s, temperature was about 190 F and pressure was around 20 psi.

As demonstrated in the optical and SEM images in Fig. 8, porous 3D lattice-structured scaffolds of crosslinked PCLTAs with fully interconnected inner architectures were fabricated. PCLTA10K filament was opaque while PCLTA7K was quite transparent. The whole scaffolds were slightly red. The gaps, filaments, and internal pore connectivity were demonstrated in the SEM images of the micro-structures of the fabricated PCLTAs scaffolds. Figure 8c,d clearly demonstrated the layered pattern and the fully interconnected pores of the fabricated scaffold macro-architecture. The uniformity of the pores and the filaments fully demonstrated the
feasibility of using the developed deposition process to fabricate scaffolds at the micron scale using two different polymers into a single scaffold. The pore size of the filament dimensions was measured from the SEM images. The scaffolds had a pore size of 250± 50 µm and uniform pore distribution. Clearly the pore size is larger than the minimum requirement (~100 µm) to allow for cell proliferation, migration, and ingrowth into the scaffolds.
Figure 8 (a) First filling approach, each layer has two materials, the PCLTA10K filament is opaque while PCLTA7K is transparent (b) Second filling approach, each layer has only one material but adjacent layers have different materials (c) Top view under SEM (d) Side view under SEM
3.5. Computational Analysis

In order to systematically analysis the deposition process, we set up a multi-phase conjugate heat transfer problem. The major objective of this analysis is to identify the heat transfer, the flowrate, and pressure drop. It is quite challenging to take every physical effect into account in the model because several reasons list below:

1. Multi-phase fluid is introduced with large density ratio and huge viscosity ratio, which makes this problem very computational intensive.
2. The polymer flow around the nozzle tip can be stretched or compressed by the filament on the substrate, which increase the difficulty to describe the force interaction.

In order to understand the basic process, we make several simplifications so that we can still understand the process without too much detail modeling and exhausted computation.

1. The interaction between the polymer melt and the substrate will be ignored. So that axisymmetric quasi-3d model can be setup, highly increases the computational efficiency
2. The polymer phase change will be ignored. And the polymer will be regarded as pure liquid. Below 60 C, the viscosity will be treated as constant, 550 Pa*s and above 140 C degree, the temperature will also be treated as constant 115Pa*s
3. The geometry is measure by a caliper and then precisely modeled in Solidworks. Then the geometry is simplified in order to take advantage of the structured grid.
4. Both the polymer melt and the air will be treated as incompressible flow. The specific heat and heat conductivity for both air and PCL will be considered as constant.
Based on the simplification, we investigated the steady-state solution of a large domain, which includes part of the syringe, heating tape, aluminum foil and the whole nozzle (in Figure 9). The boundary condition for this study is straightforward: The melted PCL flows into the syringe at 170 F degree under pressure of 60 psi and the environment is 72 F degree with 1 bar pressure. The interface between the polymer melt and the air is in Fig 10. It shows that PCL will swell outside the nozzle due to stress relaxation; the velocity profile at the same attitude will become the same, which is confirmed in Fig 10. The pressure distribution is in Fig 12. It clearly shows that almost all the pressure drop happens inside the nozzle. The temperature distribution is in Figure 13. It clearly shows that the temperature distribution in the whole
syringe assembly is quite uniform. And the green zone indicates that the PCL starts to solidify (132.8F).

The result from CFD model has less flow rate than in reality. The error here comes from several factors. The first factor is that the cross section of the PCL filament is treated as rectangle, which obviously overestimates the flowrate. The second important reason is that when feedrate exceed the jet speed, the filament already on the substrate will stretch the jet, result in more flowrate. Moreover, there can be that PCL has maintained in elevated
Figure 10 (a) Overall PCL velocity distribution (b) PCL velocity distribution around the nozzle

Figure 10 a) Overall PCL distribution. b) PCL distribution around the nozzle
Figure 11 (a) Overall temperature distribution. (b) temperature distribution around the nozzle

Figure 13 (a) Overall pressure distribution. (b) pressure distribution around the nozzle
temperature for long time so that degradation happens, reducing the viscosity. The specific heat is treated as constant and enthalpy of fusion is ignored. The simplification of these two parameters will underestimate the polymer melt temperature, which effectively increases the computational viscosity and lowers the material flowrate.

3.6. Conclusion

In this chapter, a layer-molding, multi-material integration versatile deposition system based on multiple nozzles fabrication processes have been developed to flexibly construct porous tissue engineering scaffolds for different types of polymeric biomaterials, i.e. thermoplastic materials and crosslinkable materials. Traditionally precision deposition systems are used for the manufacturing of thermoplastic materials or materials in curing agents, and crosslinkable materials are fabricated using stereolithography. The layer molding process developed in this study enabled rapid and accurate fabrication of precise 3D microstructures using different polymer types. Compared with stereolithography that generally works with a single resin since the resin needed to be stored and photo-cured in a processing tank, the deposition-on-demand and curing approach in this study leads to multiple materials integration and reduced the material consumption. Because the structural material is selectively deposited to a wax mold, we can easily and flexibly use different materials at different layers and even at different locations in one layer. Heterogeneous scaffolds composed of multiple materials with different physicochemical characteristics can be also fabricated using this method in order to achieve novel properties and functionalities for diverse tissue engineering applications.
CHAPTER 4 DIRECT FABRICATION OF HIERARCHICAL THREE-DIMENSIONAL POLYMERIC SCAFFOLDS

This chapter presents direct three-dimensional (3D) fabrication of polymer scaffolds with sub-10 µm structures using electrohydrodynamic jet (EHD-jet) plotting of melted thermoplastic polymers. Traditional extrusion-based fabrication approaches of 3D periodic porous structures are very limited in their resolution, due to the excessive pressure requirement for extruding high-viscous thermoplastic polymers. Electrohydrodynamic jet (EHD-jet) printing has become a high-resolution alternative to other forms of nozzle deposition-based fabrication approaches by generating micro-scale liquid droplets or a fine jet through the application of a large electrical voltage between the nozzle and the substrate. In this study, we successfully apply electrohydrodynamic jet (EHD-jet) plotting technology with melted biodegradable polymer (polycaprolactone, or PCL) for the fabrication of 2D patterns and 3D periodic porous scaffold structures in potential tissue engineering applications. Process conditions (e.g. electrical voltage, pressure, plotting speed) have been thoroughly investigated to achieve reliable jet printing of fine filaments. We have demonstrated for the first time that the EHD-jet plotting process is capable of the fabrication of 3D periodic structures with sub-5µm resolution, which has great potential in advanced biomedical applications, such as cell alignment and guidance. Also we present a hybrid scaffold fabrication platform by taking advantage of pneumatic control and EHD printing technology that both macro feature and micro feature can be well controlled.
4.1. Materials and Methods

4.1.1. Materials

Polycaprolactone (PCL) pellets were purchased from Sigma-Aldrich (Milwaukee, WI) with average Mn of 45000 g/mol and melting point from 56-64 °C. As a biocompatible and biodegradable polymer that has been approved by the Food and Drug Association (FDA), polycaprolactone has been widely used for the fabrication of tissue engineering scaffolds. The thermal as well as rheological properties has been extensively covered in[8] , which make PCL a great candidate to be used in the fabrication of micro-scale structures by EHD-jet plotting in its melting phase. The temperature gradient can quickly solidify the jetted PCL to form well controlled fine 3D structures with sub-5um resolution.

4.1.2. System Setup

The EHD-jet plotting platform was composed of four sub-systems: a three-axis (XYZ) precision stage, a pneumatic dispensing system with precision pressure regulator, a thermal control system, and a high voltage supply (Figure 14). The XYZ precision stage was located on an optical table to reduce vibrational noise. Three linear stages that were configured in XYZ directions with 100 nm repeatability and accuracy were used to position the plotting nozzles to the programmed locations. The stage provided a displacement range of 100 × 100 × 50 mm. A high resolution camera with a maximum resolution of 0.5μm was used to monitor the deposition process.
Figure 12 Schematic of the EHD-jet printing set-up and experimental testbed for EHD-jet printing
A pneumatic syringe was used to provide the pressure of the EHD-jet plotting process and keep the required flow rate. Two deposition nozzles (one stainless steel nozzle with ID of 152.4 µm and OD of 304.8 µm, one conical shape nozzle with ID of 51 µm and OD of 152µm) were used with 3 mL syringes for EHD-jet printing. The pneumatic system with a precision regulator can provide a maximum pressure of 10 psi with 0.05 psi resolution. After adding a heating tape and a thermal control system, the e-jet printing system was capable of processing thermoplastic materials (e.g. PCL) in this study. The heating tape was wrapped around the syringe to melt the thermoplastic polymer loaded inside the syringe. A thermocouple was mounted close to the nozzle to provide temperature feedback to a thermal controller. A proportional–integral–derivative (PID) controller regulated the power of heating tape to achieve the desired temperature. The thermal control system has a resolution of 0.5 °C with a maximum reachable temperature of 250 °C. PCL were melted and printed onto the substrate under the applied electrical voltage between the nozzle and the grounded plate. The electrical potential between the nozzle and the substrate is controlled by a high voltage source meter (Keithley 2410) which can provide voltage up to 1100 volts. The substrate (1 mm thick glass slide) rests on an aluminum coated silicon wafer that provides an electrically grounded support. The substrate and the underneath ground electrode was displaced by the XY-stage.

4.1.3. EHD-jet plotting process

In this study, short nozzle-substrate distance (170 µm) was chosen to utilize the stable jet region and avoid potential whipping instability. The effects of other process parameters (applied voltage, pressure, printing speed) on the EHD-jet plotting process was investigated to
obtain the most appropriate set of process conditions for 2D patterning and 3D structure fabrication. Two types of printing nozzles (with orifice sizes of 152.4 μm and 51μm) were used to evaluate the effect of nozzle size to the plotting results.

4.1.4. Two-dimensional Patterning and 3D freeform fabrication using EHD-jet plotting

After a stable jet is obtained, two-dimensional PCL patterns were directly plotted on the substrate like using a fountain pen. Complex 2D patterns such as spiral-in circle and square, and a freeform flower pattern, were printed to demonstrate the capability of the EHD-jet plotting. Porous 3D PCL scaffolds with fully interconnected inner structures were fabricated using EHD-jet plotting. The PCL pellets were melted at 80 °C and then e-jet plotted. The overall scaffold dimension is 2.5 x 2.5 mm, the distance between the centerlines of two filaments is 30 μm. The filaments of PCL were deposited with a layered pattern of 90° orientation to the previous layer to create the porous structure with 8-layers. Because PCL was highly viscous and can quickly solidify after being extruded, no supportive material was required. The G-code program is used to generate the tool path of the printing system for both 2D and 3D pattern in this study. In case of complex pattern, computer-aided design (CAD) software package can be used to generate the G-code for a specific structure design then feed into the motion controller to provide the motion of the printing system.
Figure 13 (a)-(d) show the first type of micro fiber networks, one direction is along the backbone fiber, and the other direction is 90 degree. (f)-(i) show the second type of micro fiber networks, one direction is 45 degree to the backbone fiber and the other is 135 degree. (a, f) Deposition of backbone fiber (b, g) Deposition of micro fiber networks (c, h) Deposition another backbone fiber (d, i) Deposition of another micro-layer
4.1.5. Hierarchical Scaffold Fabrication

The fabrication process of PCL hierarchical structures follows a layer-by-layer fashion as in Figure 15. Step 1: a thick layer of fiber with centerline space 500um is dispensed by using pneumatic dispensing unit. The dispensing follows the programmed tool path. The detailed parameters include: the pressure 60 psi to 70 psi, feedrate 1.0 mm/s, and the nozzle-to-substrate distance is kept at 250 um. Step 2: several micro-fiber layers are dispensed by EHD dispensing unit in either of the following way: 1) 1 layer along the thick fiber layer with 40um spacing and another layer orthogonal to the thick layer, the centerline difference is 75um. 2) 1 layer 45 degree to the thick fiber, the other layer 135 degree to the thick layer with 85um spacing. Either of the approaches mentioned above deposit a well-connected micro fiber net over the backbone, and the backbone serves as the supporting materials for the micro-fiber. The pressure is chosen to be 16 psi, the feed rate is 3.0-5.0 mm/s, and the standoff height is 250um, voltage for each layer is from 1600 to V 2000V. Step 3: change the orientation and repeat Step 1 and Step 2 until the desired thickness is reached.

4.1.6. SEM and microscope morphology characterization

The shape of the cone-jet of the EHD-jet printing was observed by the high resolution video camera. The morphology of EHD-jet plotted PCL patterns and 3D scaffolds were characterized using SEM (S-3500, Hitachi Instruments Inc., Tokyo, Japan). The scaffolds were sputter-coated with gold, and viewed at 10 kV accelerating voltage. The filament size and spacing were measured and calculated from SEM images using the image analysis software.
4.2. Results and discussion

4.2.1. Stable Cone-jet Formation of melted polycaprolactone (PCL)

In EHD printing, the applied electric field, and the resulting electric stress (Figure 16a) deforms the meniscus at the nozzle end into the Taylor cone, and eventually produce drops or a jet from the cone shape. Generally, as the applied electric field strength increases, different electrohydrodynamic printing modes can be observed, transitioning from pulsating mode to stable jet, unstable multiple jets. For the melted polycaprolactone at 80°C, when the nozzle to substrate gap was kept at 170 µm, as we increased the voltage from 500 volts, a meniscus and Taylor cone was gradually forming at the tip of the nozzle (Figure 16b). However at a voltage lower than 800 volts, there is no observed drip and jet generated from the cone. When the voltage was increased to about 825 volts, a stable jet began to be ejected from the cone. The stable jet remained well, but both the radius and elongation of the electrified cone became smaller (Figure 16d), as voltage increased. When the applied voltage was increased to about 1100 volts unstable multi-jets appears, as shown in Figure 16e. In our experimental condition, we did not observe any pulsating printing mode (single drop printed onto the substrate), partially due to the high viscosity of the melted polycaprolactone. It is difficult for melted PCL to obtain enough electric stress to overcome the surface tension at the meniscus to form a fine drop.
Figure 14  (a) Forces on Taylor cone in EHD processing, (b) Small meniscus without jet or drip at nozzle tip at 600V. (c, d) Stable cone-jet at 900V and 1050V. (e) Unstable multi-jet at high electric field strength.
Figure 15 Time sequence of cone-jet Formation.
Due to the high viscosity of the melted PCL, the stable cone-jet formation requires relatively long transient time (about 25 seconds) to reach equilibrium, which indicates any serious disruption of cone-jet structure may end up with defects in the fabricated structures. Figure 17 shows a typical cone-jet formation sequence after which the stable cone-jet mode is remained and precise patterning and plotting can be performed continuously.

4.2.2. Characterization of EHD-jet plotting process

Obtaining stable electrohydrodynamic cone-jet mode requires the proper selection of the process parameters that include electrical voltage, pressure and plotting speed. These process conditions need to be thoroughly investigated to achieve reliable jet printing and filament formation. In this study, the nozzle-substrate gap was fixed at 170 µm to achieve large enough electric strength to form the stable cone-jet. At this small standoff height, the jet is kept at the stable and straight region, and the effect of whipping instability is minimized. Small standoff height also enables the process to response promptly to the abrupt path change when fabricating complex features with sharp turns and small corners. In contrast, if a large nozzle-substrate gap is used, the long unsettled partially-solidified filament between the nozzle and the substrate increases the difficulty in plotting patterns with large curvature. To observe the effect of different process conditions on the cone-jet shape and the plotted filaments, one process parameter (from electrical voltage, pressure and plotting speed) was changed at a time while keeping others constant.
Figure 16 The cone-jet shape and jet printed filaments at different voltages. (a1-a3) Results from a nozzle with 152.4 µm orifice. (b1-b3) Results from a nozzle with 51 µm orifice. All scale bars 50 µm.
(a1) 825V

(a2) 900V

(a3) 975V
(b1) 850V

(b2) 925V

(b3) 1025V
4.2.2.1. The effect of voltage on EHD-jet plotting process

The applied voltage played the most important role in the EHD-jet printing process. As shown in Figure 18, as the voltage increased, we can observe the formation of the meniscus at the nozzle tip below the critical voltage, a stable cone-jet within a proper range of the applied voltage, and then unstable multi-jets with too high voltage. Unstable jet is not practically useful for precision fabrication. In the section, we tried to investigate the effect of the applied voltage at the stable-jet region on the printing process and the fabricated filaments. Filaments were plotted onto the substrate with a spacing of 40µm. As the effect of the voltage was investigated, a pressure of 4.0 psi and a plotting speed of 1.6 mm/s is chosen for the nozzle with 152.4 µm orifice, a pressure of 1.8 psi and a plotting speed of 1 mm/s is chosen for the nozzle with 51 µm orifice.

The voltages between 700 V to 1050 V with a step of 25 V were applied to the nozzle, and the resulting cone-jet shape was observed from the high-resolution camera along the plotting direction and from the side. Clearly there exists a lower bound threshold voltage (between 800V and 825V for this configuration) to continuously jet melted polymer, under which the stable cone-jet structure cannot maintain. At a relative low voltage (825V for the 152.4 µm nozzle and 850 for the 51 µm nozzle), a skewed cone-jet was observed (Figure 18), in which the jet was inclined to the substrate along the plotting direction. As voltage increased, the skew cone-jet mode was switched to straight cone-jet with minimal feature variation at around 900V and 925V respectively for two nozzles. After the voltage was further increased, although a straight and stable cone-jet was observed from the camera, the plotted filaments
became winding and lose controllability for precision fabrication. Moreover, the amplitude of winding increased with the increase of the voltage. This behavior can be explained by the specific material property of PCL and the jetting speed. In electrohydrodynamic printing, the jetting speed increases with a larger voltage and the resulting larger electric field strength. At the low voltage, the jetting speed was lower than the plotting speed of the stage, the high viscous force of the melted PCL deformed the cone-jet. As a result, the skewed cone-jet was observed. When the jetting speed matched the plotting speed, a straight cone-jet was obtained. When the voltage was too high, the jetting speed exceeds the plotting speed. The high viscosity of the plotted and semi-solidified PCL filaments makes it difficult to reflow on the substrate. Thus the winding filaments were obtained to absorb the over-plotted length due to speed mismatch.

The plotted filaments at different voltages were observed in a SEM, and their dimension was measured, as shown in Figure 19. The average strand width of about 22 µm and 13 µm were obtained respectively for two nozzles. Statistically it does not show any significant difference at different voltage. For the large nozzle, when the applied voltage is very low (825V) and closed to the threshold voltage, a large variation in filaments dimension was observed. However, the filaments plotted by other skewed cone-jets modes at 850V and 875V have almost the same variation in their dimension when compare to the filaments plotted by the straight cone-jet from 900V to 950V, which indicates that the skewed cone-jet can also be possibly used for precision fabrication to enlarge the operation range.
Figure 17 Filament width at different voltage. Each condition was repeated 5 times.
4.2.2.2. The effect of plotting speed

As observed from previous section, the potential mismatch between the jetting speed and the plotting speed will affect the cone-jet shape and the plotted filaments on the substrate. In this section, we directly investigated the effect of the plotting speed on the printing process and fabricated filaments, while keep the jetting speed constant by using the fixed voltage and pressure. A pressure of 4.0 psi and a voltage of 900V were chosen for the nozzle with 152.4 µm orifice, and a pressure of 1.8 psi and a voltage of 925V were chosen for the nozzle with 51 µm orifice.

When plotting at a small plotting speed for both nozzles, winding filaments were observed (Figure 20). As the plotting speed increased, the filaments become straight gradually. After the plotting speed was further increased, the skewed cone-jet appeared with straight filaments left on the substrate. This specific behavior indicated the importance of matching the plotting speed with the jetting speed. When the plotting speed is lower than the jetting speed, the over-plotted filaments were buckled on the substrate, since these high-viscous PCL filaments are hard to be compressed and reflow on the substrate. A vibrating cone-jet, similar to whipping instability, was observed due to the viscous dragging force from the winding settlement of PCL filament. The jet vibration gradually disappeared with the increased plotting speed, and the stable cone-jet and straight filaments were obtained, which confirm that the jet vibration at low plotting speed are not whipping instability, but from the interaction between the cone-jet and the printed winding filaments.
Figure 18 The cone-jet shape and the jet printed filaments at different plotting speed. (a1-a3) Results from a nozzle with 152.4 µm orifice. (b1-b3) Results from a nozzle with 51 µm orifice. All scale bars 50 µm.
(a1) 1mm/s

(a2) 1.6 mm/s

(a3) 2.4mm/s
(b1) 0.6 mm/s

(b2) 1 mm/s

(b3) 2 mm/s
If the plotting speed is too high, the viscous dragging force from the printed features deformed the cone-jet to the skewed cone-jet. For the straight filaments fabricated by the stable cone-jet and slightly skewed cone-jet, the plotting speed significantly changed the plotted filament width. For 152.4 µm nozzle, the line width decreased from about 25 µm to 17 µm, as plotting speed increased from 1.2 mm/s to 2.4 mm/s. For 51 µm nozzle, the line width decreased from about 13 µm to 7 µm, as plotting speed increased from 0.8 mm/s to 2 mm/s (Figure 19). The results indicate that the PCL jet or semi-solidified filament can be stretched
with reduced filament diameter. The plotting speed can be used a method to adjust of the
dimension of the fabricated features.

4.2.2.3. The effect of pressure

It is well known that the pressure or the flow rate can affect cone-jet shape and jet
stability. The required pressure range for maintaining stable-jet plotting is determined by the
nozzle size and other process conditions. The pressure from 3.6 psi to 5.6 psi was applied to
the large nozzle with the applied voltage of 900V and a plotting speed of 1.6 mm/s. For the
small nozzle, the pressure from 1.2 psi to 3 psi was applied with a voltage of 925V and a
plotting speed of 1 mm/s. In electrohydrodynamic printing, generally larger flow rate will make
the jet less stable and produce whipping instability. However, for EHD-jet printing of melted
PCL, we observed vibrating jet and winding filament at the low pressure (Figure 21). As
pressure increased, the stable jet and the skewed cone-jet appeared gradually, and straight
filaments were achieved. This phenomenon is again the result of the high viscosity of the
melted PCL jet and interaction between the cone-jet and the printed filaments on the substrate.
With a small flow rate at low pressure, a thin jet was obtained. The electric stress provided
large acceleration and high speed of the ejected jetting. This jetting speed was larger than the
plotting speed, thus winding filaments and vibrating jet were observed. As pressure increased,
large flow rate produced a thick jet. With similar electric stress (from the same voltage), less
acceleration was applied to the jet, resulting smaller jetting speed. Thus the jetting speed
gradually matched the plotting speed, and then was lower than the plotting speed. As a result,
straight filaments and skewed jet were observed.
Figure 20 The cone-jet shape and the jet printed filaments at different pressure. (a1-a3) Results from a nozzle with 152.4 µm orifice. (b1-b3) Results from a nozzle with 51 µm orifice. All scale bars 50 µm.
(a1) 3.6 psi

(a2) 4.2 psi

(a3) 5.6 psi
(b1) 1.2 psi

(b2) 1.8 psi

(b3) 2.7 psi
This explanation was further supported by the increased filament width (indicating larger flow rate) along with the increase of the pressure, as shown in Figure 23.

4.2.2.4. The scaling effect of the nozzle size

The size of the nozzle orifice greatly impacts the dimension of the EHD-jet printed structures. The previous research mentioned a general scaling relationship between the nozzle size and the jet diameter that the jet diameter is proportional to the square root of the nozzle size [36]. It is difficult to directly apply this scaling law to the melted EHD-jet printing, since the previous models were built on pure liquid phase ink. For the EHD-jet printing of melted PCL, the temperature-induced viscosity change and even phase change in the jet can make the
theoretical modeling very complex and different. But we did observed the better resolution by using a 51 µm nozzle compared with using a 152.4 µm nozzle. The filament dimension was roughly reduced by a factor of 2.

4.2.3. Fabrication of 2D patterns and 3D structures

One of the most critical steps in EHD plotting is to match the plotting speed with the jetting speed; the latter is affected by the applied voltage and the pressure. Small plotting speed can result in winding filaments and jet instability, while too large plotting speed can result in the severely skewed jet and large lag in plotting, which will degrade the controllability and precision of plotting. In our plotting practice, the straight cone-jet or the slightly skewed jet were used for the fabrication to avoid the winding of the filaments.

High resolution precisely controlled fabrication of 2D patterns and 3D structures were achieved using the EHD-jet plotting of melted polycaprolactone. Using the small nozzle with 51 µm inner diameter, various complex two-dimensional patterns were printed onto a glass substrate. Figure 24 shows a spiral-in round-shape pattern, a spiral-in square-shape pattern, and one freeform flower pattern plotted by polycaprolactone filaments. The smallest line width was less than 5 µm, which are at least one to two orders of magnitude smaller than direct melt extrusion based fabrication approaches. Because a small nozzle-substrate gap was chosen at 170 µm, there is less lagged jet/filament in-between the nozzle and the substrate. As a result, the EHD-jet plotting process can respond well to sharp geometric change. Patterns with a turning radius as small as 10 µm can be achieved reliably.
Figure 22. Two dimensional patterns fabricated by electrohydrodynamic jet printing of melted PCL. (a) Spiral-in circle pattern. (b) squarel shape pattern. (c) a flower pattern.
Three-dimensional woodpile scaffold structures were fabricated using EHD-jet plotting of melted PCL. The overall scaffold dimension is 2.5 x 2.5 mm, the distance between the centerlines of two filaments is 30 µm. The filaments of PCL were deposited with a layered pattern of 90° orientation to the previous layer to create the periodic porous structure. During the fabrication, we kept the standoff height of 170 µm while slightly adjusting the applied voltage to count for the change of electrostatic field strength due to the plotted layers on the substrate. In the plotting of 3D structures, selection of plotting speed is even more important, as the plotted filaments were plotted across a large gap without any support. To prevent the sagging effect, the plotting speed needs to be high enough so that the viscous force from the jet and filament can produce a self-supported structure. Figure 25 demonstrates a porous 3D lattice-structured scaffold of PCL with fully interconnected inner architectures that were fabricated using the direct electrohydrodynamic hot jet plotting approach. Figure 25b-d clearly demonstrated the layered pattern and the fully interconnected pores of the fabricated scaffold micro-architecture. The uniformity of the pores and the filaments indicated the applicability of using the developed electrohydrodynamic hot jet plotting process to fabricate structures at the micro-scale. The diameter of the filament is about 5 µm.
It is very difficult, if not at all impossible, to achieve such resolution with traditional fabrication approaches, such as fused-deposition modeling (FDM), in which the deposited filament diameter is largely determined by the nozzle diameter. Scaling down the nozzle size for better resolution with traditional fabrication approaches will make the deposition pressure impractical high for high viscous biopolymers.

Figure 23. Three-dimensional scaffold structures fabricated by direct EHD-jet plotting of melted PCL. (a) Overview of the scaffolds. (b) Detailed view of the plotted filaments. (c,d) Tilted views show the layered structure of the 3D scaffold.
4.2.4. Fabrication of 3D hierarchical structures

In this study, we have fabricated two groups of scaffolds having the same macrostructure but microstructure with different orientation in Figure 26. The macro pore size and porosity is exactly the same, 250 µm and 50% respectively. The micro fiber network has no significantly difference in terms of fiber size, which is about 10 µm in diameter. SEM images of the fabricated scaffolds confirmed the both macro structure and micro structure is well under control.

For the pneumatic dispensing unit, the only concern is the thick fiber has tendency to wrap towards the center and peel off from the substrate once the thermal stress induced overcomes the adhesion force between the structure and the substrate. As a result, the temperature should be minimized to reduce the thermal stress but the bottom line would be the rheology is favorable for dispensing. As a result, the 180F degree is a reasonable good choice. For the micro fiber, it is overwhelmingly complicated since so many process variables, such as temperature, voltage, standoff height, pressure, feedrate are highly coupled. However, there are some simplified relationships that would help to determine the optimized conditions.

It is best to decide the processing temperature first, since that material property can be largely fixed. Here in this study temperature is to be 180F degree based on the two types of stress during dispensing, one comes from jet surface charging and the other one originated from cooling and solidification, which plays counterbalancing roles. The electrical surface tension will be immediately released at the interface between the jet and the substrate.
Figure 24 (a) 90 degree alignment (b) 45 degree of alignment
Compared to electrostatic tension, the thermal induced stress plays a long-term role and a devastating role that ultimately leads to fiber breakup and results in “broken” network. The reason could be that thermal induced stress increases faster than the mechanical strength increased. And this conclusion exactly explained that why severely sagging micro fiber gets straight immediately and then breakup slowly. The solutions include lower down temperature in the first place and increasing the cooling rate so that fiber mechanical strength could drastically increase in a short time. As long as fiber mechanical strength increases faster than the thermal induced stress releases, the micro fiber would remain intact.

Then the voltage and the standoff height could be determined. For a fixed standoff height, there is a threshold on voltage, above which the cone-jet formation can be maintained. However, as shown before if the voltage continue to increase, the jet gradually becomes straight and then start to vibrating, possibly due to the mismatch between jet speed and feedrate. At low voltage, the jet speed is low then the feedrate, so the jet is skewed. Then as voltage increases, the jet speed increases and jet becomes straight. If voltage further increase, the jet speed will be larger than feedrate, the semi-solidified fiber is hard to reflow on the substrate and starts to vibrate. So the requirement for voltage is that under a certain standoff height, the cone-jet will always remain on thick fiber and on free space and will not vibrating. The standoff height could possibly related to fiber breaks up since the observation from the camera indicate that low standoff height has higher fiber breakup probability; on the other hand, the higher standoff height may results in faster jet speed as well as thinner fiber, which also has a tendency to breakup. The former breakup could be explained that micro fiber
breakup starts with necking, a small fragile portion gets thinner and charge will highly accumulate on this region. If the standoff height is small there would be large electrostatic attraction force that pulls the fiber up to the nozzle, which is exactly the case we observed in camera. The latter breakup could be explained that the thinner fiber has less cross-section area so that the time from necking to breaking is short, and slowly mechanical strength increase could not keep pace with this breaking process. As a result, the standoff height in this study is chosen to be 250um under any circumstance. Voltage is chosen according to the height of the overall structure.

Also the feedrate needs to be optimized. There are three lower bounds on the feedrate, corresponding to no jet vibration, free standing, and micro fiber orientation respectively. The first constraint is that, as indicated, the jet tends to vibrate when the feedrate is low because more semi-solidified material is hard to reflow on the substrate. The second constraint is that the micro fiber needs to span over more than 250um space. If the speed is slow, the jet could quickly touch the layers underneath and bond with them, comprising the free standing structure as designed.

The last constraint comes when a certain angle across the two thick fibers is required, since the underneath thick fiber is acting as electrodes and will accelerate the jet around the vicinity. The jet velocity in the free space is much lower than the vicinity around the thick fibers, which is the reason why the angle on large fibers is steeper while the angle over space is smaller. There is also an upper bound for feedrate, since the large the feedrate will result in thin fiber, which tends to breakup. As a result, the feedrate is optimized in this way: 1) if the
micro fiber is along the thick fiber, the feed rate is 4-5 mm/s 2) if the micro fiber is 90 degree across the thick fiber, the velocity is 2-3 mm/s 3) if the micro fiber is 45 degree from the thick fiber, the velocity is 3 mm/s. In this way, the fiber is still thin with strong mechanical strength and the orientation could be under good control.

Pressure is also an important factor that it could not only decide the fiber morphology but also the resistance to breakup. As pressure increases, the vibrating jet becomes straight first and then skewed. This could be explained that jet at low flowrate associated with low pressure could be accelerated more so that jet speed becomes higher than feedrate. Consequently, the extra semi-solidified PCL will be difficult to reflow on the substrate. Moreover, it is observed in the experiment that pressure also determine that whether the micro fiber will remain intact or breakup. This could also be explained in terms of necking process. If the fiber becomes thicker, the cross-section area increases, the more time needs to breakup which gives rise to more mechanical strength increase, which prevents the breakup issue. However, for the benefits of tissue engineering, it is desirable to have thinner fiber, which is another constraint. As in this study, the pressure is chosen to be 18 psi to balance these two contrary requirements.

It is complicated to balance these highly coupled processing parameters. A detailed EHD dispensing model is highly desired and we are currently investigated it. However, by taking advantage of the relationship and constraint as mentioned above, it is not that challenging to obtain good quality micro fiber networks. The parameters for each single layer are different because the backbone fiber is essentially changing the collector geometry and perturb the electrostatic field and distribution. However, based on the parameters relation
mentioned above, it is not too difficult to find reasonable operational conditions. Once these parameters are well-adjusted, the process is robust enough to obtain well-connected micro fiber network with good quality.

4.3. Conclusion

In this study, we applied electrohydrodynamic hot jet plotting technology with melted biodegradable polymer (polycaprolactone, or PCL) for the fabrication of 2D freeform patterns and 3D periodic porous scaffold structures for potential tissue engineering applications. Stable cone-jet formation, cone-jet shape and plotted filaments at different process conditions (e.g. electrical voltage, pressure, plotting speed) have been thoroughly investigated to achieve reliable jet printing. The most important step in selecting the proper set of process parameters is to match the plotting speed and jetting speed that are controlled by the applied electrical voltage and pressure. We have demonstrated for the first time that 3D periodic structures with the layered pattern and the fully interconnected pores can be fabricated by electrohydrodynamic hot jet plotting process with sub-5µm resolution using high viscous biodegradable polymers. The achieved filament diameter is one to two orders of magnitude smaller than traditional melt extrusion based fabrication approaches. The EHD-jet plotted micro-scale structures have great potential in advanced biomedical applications, such as cell alignment and guidance of cell growth. Also we present a hybrid scaffold fabrication platform by taking advantage of pneumatic control and EHD printing technology that both macro feature and micro feature can be well controlled.
CHAPTER 5 HIGH-RESOLUTION AC-PULSE MODULATED ELECTROHYDRODYNAMIC JET PRINTING ON HIGHLY INSULATING SUBSTRATES

This study presents a new high-resolution AC-pulse modulated electrohydrodynamic (EHD) jet printing technology on highly insulating substrates for drop-on-demand fabrication of electrical features and interconnects using the silver nanoparticle. In traditional EHD jet printing, the remained charge of the printed droplets changes the electrostatic field distribution and interrupts the follow-on printing behavior, especially for highly insulating substrates which have a slow charge decay rates. The residue charge makes the control of EHD jet printing very challenging for high-resolution continuous features. In this paper, by using the modulated AC-pulsed voltage, the EHD jet printing process switches the charge polarity of the consequent droplets to neutralize the charge on the substrate. The effect of the residue charge is minimized, which enables high resolution printing of continuous patterns. Moreover, by modulating the pulse frequency, voltage, and duration, the EHD jet printing behavior can be controlled with respect to printing speed/frequency and droplet size. Printing frequency is directly controlled by the pulse frequency, and the droplet dimension is controlled by the voltage and the duration of the pulse. We demonstrated that AC-pulse modulated EHD jet printing can overcome the long-predicated charge accumulation problem on highly insulating substrates, and potentially be applied to many flexible electronics applications.
5.1 Materials and Methods

5.1.1 Materials

The silver NP ink used in this study is DGP 40LT-15C (Advanced Nano Products, Co., Ltd, South Korea) with 30-35% solid content stabilized by proprietary stabilizer. The viscosity is in the range of 10-17 cP and surface tension between 35~38 dyn/cm. Three types of substrates used in this study are microscopic glass slides (75mm x 25 mm x 1mm), and two highly insulating substrates, 1mm-thick insulating Ajinomoto Fine film (ABF) coated on glass slides and 1mm-thick Polyethylene terephthalate (PET) film, which are widely used for high density circuits, electronic packaging, and flexible electronics applications.

5.1.2 System Setup for AC-pulse modulated electrohydrodynamic (EHD) jet printing

The AC-pulse modulated EHD-jet printing system is composed of three sub-systems, as shown in Figure 27: a precision three-axis motorized stage, a pneumatic dispensing system with precision pressure regulator, and a high voltage supply. The XYZ motion stage is placed on a vibration-isolation table to reduce vibration noise. Three linear stages are configured in XYZ directions with 100 nm repeatability and are used to move the printing nozzles to the programmed locations. The stage provided a displacement range of 100 × 100 × 50 mm in XUZ directions. A video camera was used to monitor the printing process.

A pneumatic syringe was used to provide the pressure of the electrohydrodynamic jet printing process and keep the required flow rate. The pneumatic system with a precision regulator can provide a maximum pressure of 5 psi with 0.05 psi resolution. The nozzle tip is obtained by pulling a borosilicate capillary and dicing the tip to expose open end under
microscope. The glass capillary is then glued to gauge 25 stainless steel nozzles (inner diameter of 250µm and outer diameter of 500 µm), which is served as the nozzle electrode. The substrate electrode is obtained by coating 50nm-thick aluminum on a heavily doped silicon wafer by thermal evaporation. Different substrates are directly placed on top of the substrate electrode. The substrate and the underneath electrode is displaced on demand by the XY-stage. A function waveform generator (Agilent 33220A) is used to generate the modulated AC-pulse voltage command signal with desired voltage, frequency and duration, which is then amplified by a high voltage amplifier (Trek 610A) for EHD-jet printing. The AC-pulse voltage waveform signal is shown in Figure 28.
In this paper, to improve the controllability of the EHD-jet printing process and reduce the issue of residue charge accumulation, a modulated AC-pulse voltage signal is used for EHD-jet printing. The typical waveform of the command voltage is given in Figure 2. In this AC-pulse modulated EHD-jet printing process, three process parameters are used to control the printing process, which are pulse frequency, pulse voltage amplitude, and pulse duration.

The AC pulse frequency is used to control the printing frequency. When the voltage and the pulse duration are properly selected, each positive or negative pulse will produce a droplet. The resulting printing frequency is expected to double the frequency of the command pulse signal. The voltage amplitude needs to be selected with enough electrical field to form the

\[ T_d = \frac{1}{f} \]

\[ +V \quad -V \]

Figure 26. Schematic plot of AC-pulse modulated EHD-jet printing System. Pulse frequency, duration, and peak voltage are input parameters. Intermittent positively and negatively charged droplets neutralize each other and enable reliable printing of continuous features on highly insulating substrates.
meniscus and provide large enough electrical stress to eject the droplets. The duration of the voltage pulse controls the size of the droplets. With larger pulse duration time, more surface charge is accumulated, which results in larger droplet volume. Due to the intermittent positive and negative pulses, the charge from the consequent droplets neutralizes each other, which effectively minimize the effect of residue charge to the printing process. As the result, continuous features can be reliable printed onto highly insulating substrates. Compared with widely used DC voltage based EHD-jet printing, in which the voltage is the only parameter to control the process with respect to printing frequency and droplet size, the AC-pulse modulated printing offers the capability for charge neutralization, and reliable and independent control over the printing frequency and droplet size.

5.1.4 Pattern fabrication and characterization

The process characterization was performed on glass slides. After the process conditions are properly identified, continuous electrical interconnects are directly printed onto the glass substrates, as well as two highly insulating substrates, Polyethylene terephthalate (PET) and Ajinomoto Fine film (ABF), which are difficult to be printed on using EHD-jet printing with a constant voltage as well as DC pulsed printing. The shape and dimension of the printed droplets and patterns was observed directly by the high resolution microscope.

5.2 Results and discussion

5.2.1 Onset Conditions for Droplet Formation

In AC-pulse modulated EHD-jet printing, the electric stress resulting from the applied voltage deforms the meniscus at the nozzle tip into the Taylor cone, and eventually produce
droplets from the cone shape. Identifying the required voltage to initiate the EHD-jet printing process with respect to the frequency and duty cycle of the pulsed signal is a critical step for process development.

In EHD-jet printing, both the electrostatic stress applied on the meniscus and the duration time when the electrical stress is applied play the important role on the droplet generation. As a result, the voltage (defining the electrostatic stress), and the pulse duty cycle along with the frequency (together defining the voltage duration time) are critical parameters and coupled together to determine the start of the printing process. We experimentally characterized the threshold voltage amplitude needed for EHD-jet printing with respect to the pulse frequency and duty cycle in Figure 29.

![Onset Voltage Diagram](image)

Figure 29 Threshold voltages to start EHD printing with respect to the pulse frequency and duty cycle.
It can be clearly found that for each fixed duty cycle, using a larger pulse frequency will result in increased threshold voltage to start printing. At a very low pulse frequency, the EHD-printing is very close to the condition where a constant DC voltage is used. For all the duty cycles used (6% to 10%), the threshold voltage to start the printing process is around 300V. As the signal frequency gradually increases, the threshold voltage increases as well. At each specific signal frequency, the signal with smaller duty cycle required larger threshold voltage for EHD-jet printing. The reason for this behavior is due to the different duration time for each signal. For high frequency voltage pulse or pulse with small duty cycle, with less time for charge accumulation at the tip of the nozzle, a larger voltage and the resulting electrostatic stress is needed to produce the meniscus and the droplets.

As the relatively low frequency range, we observed the slow increase rate of the threshold voltage with respect to the pulse signal frequency. However when the pulse frequency is increased to above 1000 Hz, a sharp increase in the threshold voltage is observed. Although the physics behind it can be very complicated, this phenomenon can be explained by the time for charge migration and meniscus formation. The charge or mobile ions will need some time to migrate from the inner volume of the ink to the surface of the liquid at the nozzle tip to overcome the surface tension and form the meniscus. When the frequency is higher enough, the duration of the voltage become close to the time constant of charge migration, and then a very large voltage is needed to provide enough electrical stress to form the meniscus and produce the droplets. This time constant of charge migration and meniscus formation generally determines the printing frequency. In electrohydrodynamic jet printing with a
constant high voltage [64] or high baseline voltage with modulated voltage pulse voltage [73], the Taylor-cone is maintained and printing speed of tens of kHz is obtained. In this AC-pulse modulated EHD-jet printing, there is no DC voltage to keep deforming the ink and to maintain the Taylor cone, which results in a relatively smaller range of printing frequency. However, considering the small duty cycle used in this study, the printing behavior and speed are still comparable to previously reported results[73]. Moreover, by using AC pulses in EHD-jet printing, the charge carried by the consequent droplets is capable to be neutralized, which is extremely important for the printing of continuous features on highly insulating substrates.

5.2.2 Characterization of AC-pulse modulated EHD-jet printing process

Obtaining stable electrohydrodynamic jet printing requires the proper selection of the process parameters that include pulse frequency, pulse voltage, and duty cycle. The effect of these process parameters to the printing process needs to be thoroughly investigated to achieve reliable EHD-jet printing. In this study, the nozzle-substrate gap was fixed at 100 µm. To observe the effect of different process conditions on the printing process, one process parameter (from pulse frequency, pulse voltage, and duty cycle) was changed at a time while keeping others constant.

5.2.2.1 Pulse Frequency

To figure out the relationship between command pulse frequency and printing frequency, a pulse voltage and the duty cycle are fixed at 370 Volts and 6%. When the speed of stage is known, by measuring the spacing of the printed droplets, the printing frequency can be measured. We observed that the printing frequency is precisely controlled by the pulse
frequency with the factor of two. As shown in Figure 30, the printing frequency is two times of the pulse frequency, and the two frequencies follow a linear relationship. This relationship indicates that both positive pulse and negative pulse are engaged in droplet formation. The charge carried by two consequent droplets is of opposite polarity, and can be neutralized in the substrate for continuous feature fabrication. Compared to other EHD printing approaches using single polarity voltage, the approach using AC-pulse is robust for material deposition, because no net charge is printed onto the substrate surface regardless of their capability to dissipate the charge quickly or not. Generally for substrate materials of glass, silicon, or SiO2 thin films, charge can escape in short amount of time and will not affect the EHD-jet printing process. However, for highly insulating substrates, including ABF, PED, Teflon, and PDMS, which are widely used for flexible electronics and electronic sealing and packaging, charge can stay on the surface for a long time (from a few minutes to a few weeks). The residue charge will reject incoming charged droplet, rendering the high resolution deposition of electronic interconnection very difficult.
Figure 27 a) printed droplets at different pulse frequencies. b) Droplet size and printing frequency with respect to command pulse frequency. Each condition was repeated 5 times.
As the increase of the printing frequency, a reduced droplet dimension was observed, from about 30 um at 25 Hz to below 10 um at 350 Hz. Since the same duty cycle is chosen, larger pulse frequency indicates smaller duration time for each voltage pulse. Thus even though the same voltage amplitude is used, the produced droplets became smaller due to less time for charge collection at the nozzle tip.

For the given voltage amplitude and duration, there is no noticeable printing results for pulse frequency above 400 Hz. At this frequency, the duration time becomes too short to gather enough charge. At the given voltage, the generated electrical stress is not large enough to overcome the surface tension to produce droplets. However, by using a larger voltage or choosing a larger duty cycle, a higher printing speed can still be achieved.

5.2.2.2 Pulse Duty Cycle

To evaluate the effect of duty cycle or duration time on the EHD-jet printing, especially on the control of the size of the droplets, a set of printing tests were performed with the pulse frequency and voltage fixed at 200Hz and 370 volts. When the duty cycle is too small, there is no noticeable droplet printing, due to insufficient charge accumulation and electrical stress to produce the droplets. As duty cycle increases, the size of the printed droplets also gets increased, as shown in Figure 31. The size of the droplets and the duty cycle follows a roughly linear relationship in the range of the duty cycles used in the experiments.
Figure 28 a) printed droplets at different duty cycles. b) Droplet size with respect to duty cycle. Each condition was repeated 5 times.
When the duty cycle or duration is too large, satellite droplets is observed around the main droplets, which indicates unstable electrohydrodynamic printing modes. Figure 32 shows examples of such observation. This behavior can be explained by the large voltage used in AC-pulse based EHD-jet printing. When the pulsed voltage is used for EHD-jet printing, the voltage used is generally larger than the constant DC voltage required for EHD printing, especially at relatively higher frequencies. When the duration of the voltage pulse is very long, it becomes similar to EHD-jet printing with a constant voltage. However, since a larger voltage is used, unstable EHD-jet printing will be possibly observed.

Figure 29 When duty cycle or duration is too large, satellite droplets can be observed along with the main droplets.
5.2.2.3 Pulse Voltage

To study the effect of amplitude of the voltage pulse on the EHD-jet printing and the size of the droplets, we performed the printing with different voltage while choosing the pulse frequency and the duty cycle fixed at 200 Hz and 6%. Figure 33 shows the experimental results on printed droplets at different voltage. From the experimental results, it can be clearly observed that larger droplets are produced with larger pulse voltage in general. The effect of the voltage is similar to the printing results based on DC pulsed voltage [72], but is opposite to the results from electrohydrodynamic jet printing with constant voltage [108]. In EHD printing with constant DC voltage, a larger voltage generally results in a higher printing frequency, but smaller droplet size. Although the theoretical explanation about the effect of pulse voltage on droplet generation is still not thoroughly studied in detail, the disparity of the voltage effect between the pulsed voltage and constant DC voltage may come from the different droplet generation mechanism. When EHD-jet printing with the constant DC voltage signal, the droplet formation mechanism is based on tip-streaming [101, 109], in which the droplet is generated in unstable region further away from supercritical region of Taylor-Cone [110]. The droplet generation mechanism in AC-pulse based EHD-jet printing is even more complicated as in [111]. Moreover, in pulse-based printing, the retreat of the meniscus when the voltage pulse is removed may produces the droplets, which is similar to the droplet pinch-off in ink-jet printing. Thus larger voltage indicates larger meniscus, and then larger droplets. Further experimental and computational studies will be performed in future to explore and explain this phenomenon.
Figure 30 a) Printed droplets at different voltage. b) Droplet size with respect to the voltage. Each condition was repeated 5 times.
5.2.3 Drop-on-Demand Printing results

In order to demonstrate the capability and versatility of the process control in AC-pulse modulated EHD-jet printing, we drop-on-demand printed “ISE” letters in the form of separate droplets on glass slides, as shown in Figure 34. The nozzle used here has roughly 10 μm outer diameter. The frequency of the AC-pulsed voltage for printing letter “I” and “E” is two times of the frequency for letter “S”, which is directly reflected by the different droplet spacing between these three letters. For letter “I”, a smaller duty cycle of 8% is used, and 10% duty cycle is used for letter “S”, which can be observed by the difference in the droplet size in these two letters. In the last letter “E”, two duty cycles are used and changed during the printing process. The instant change of the droplet dimension is shown in Figure 33. The results demonstrate good and independent controllability of the printing speed and droplet size by using AC-pulse modulated EHD-jet printing.
Figure 31 Drop-on-demand printed “ISE” letter demonstrates on-line controllability of the printing process. Letters printed on glass slides with printing speed and droplet dimension controlled by the parameter of the AC-pulse voltage.
Traditionally EHD-jet printing using constant or pulsed DC voltage is very difficult to print continuous features on highly insulating substrate, due to the residue charge carried by the printed droplets which remain on the substrate for a long period. For highly insulating substrates, Polyethylene terephthalate (PET) and Ajinomoto Fine film (ABF), we cannot figure out a stable and reliable printing condition when using constant or pulsed DC voltage in EHD-jet printing with our system configuration. The EHD-jet printing using constant or pulsed DC voltage is uncontrollable which keeps switching between either no printing or printing droplet with huge volume. Previous studies[81] also mentioned some other challenges for printing onto highly insulating substrates, such as droplet repulsion, which make the fabrication of continuous features extremely difficult, if not impossible.

Using the AC-pulse modulated EHD-jet printing, we successfully printed continuous features with high resolution on ABF and PET substrates, which both are highly insulating substrates with long characteristic time constant for charge decay, as shown in Figure 35. The contact pad and interconnect are printed by AC-pulse modulated EHD-jet printing. Clearly the contact pad and interconnect line are continuous. The smallest feature dimension (line width) in these patterns is about 3 μm. These simple continuous features indicate that carried charge in droplets is neutralized on these substrates with large characteristic charge decay rate by using AC-pulse modulated EHD-jet printing technology; otherwise residue charge accumulation and repulsion between droplets with the same polarity will make the continuous printing almost impossible.
Figure 32 Continuous features printed on highly insulated surface. a) On ABF substrate. b) closed-up view on ABF substrate. c) Features printed on PET film. d) Features printed on glass slides.
5.3 Conclusions

In this chapter, we introduced a new AC-pulse modulated high-resolution electrohydrodynamic (EHD) jet printing technology and systematically investigated the effect of critical process parameters on the printing behavior. By modulating the pulse frequency, pulse voltage amplitude, and pulse duration, the EHD jet printing behavior can be controlled with respect to the printing speed and droplet size. Printing speed can be controlled by the pulse frequency, and the droplet dimension is controlled by the voltage or the duration of the pulse. Moreover, the AC-pulse modulated EHD jet printing process alternate the charge polarity of the consequent droplets by using the AC-pulse voltage to neutralize the charge on the printed droplets. The effect of the residue charge is minimized, which enables high resolution printing of continuous patterns on electronic insulating substrates. We demonstrated that AC-pulse modulated EHD jet printing can overcome the residue charge problem on highly insulating substrates, and be applied to many flexible electronics and high density packaging applications.
CHAPTER 6 DEVELOPMENT AND MODELING OF MELT ELECTROHYDRODYNAMIC-JET PRINTING OF PHASE-CHANGE INKS FOR HIGH-RESOLUTION ADDITIVE MANUFACTURING

This chapter presents the development and modeling a high-resolution electrohydrodynamic-jet (EHD-jet) printing process using phase-change ink (i.e. wax), which is capable of producing sub-10 micron footprint (sub-10fL in volume) for super-resolution additive manufacturing. Traditional 3D printing approaches are very limited in their resolution, mostly due to the excessive pressure requirement for extruding high-viscous inks. EHD-jet printing is a high-resolution alternative to other forms of nozzle-based printing fabrication approaches by generating micro-scale liquid droplets through the application of an electrical voltage between the printing nozzle and the substrate. In this study, we successfully apply EHD-jet printing with phase-change ink (wax), which is widely used modeling and supporting material for additive manufacturing, to achieve micron-scale droplets. The resolution for single droplet on substrate is as small as 6 microns with the thickness in the range of 1-2 microns, which provides great potential in both high-resolution 3D printing and 2D drop-on-demand micro-fabrication. The droplet formation and droplet dimension of the EHD printing is modeled by Finite Element Analysis (FEA) with respect to the electrostatic force and surface tension of the resulting pending droplets attached to the Tailor cone. The volume and dimension of the droplets printed at different process conditions are measured experimentally to validate model. Furthermore, after introducing a new electrical bond number for our configuration, a dimensionless scaling law is identified to describe the relationship between
dimensionless normalized droplet diameter and electrical bond number, which provides a guideline to predict the droplets dimension at different process conditions. Finally, the droplets in-flight velocity and fluidic characteristics (e.g. Reynolds number and Weber number) are modeled using the results from FEA analysis.

6.1 Materials and EHD Printing system

6.1.1 Materials

The paraffin wax used in this study has a melting temperature of ~55°C. The substrate is microscope glass slides obtained from Fisher Scientific with the relative permittivity ~7.78 measured by Stanford Research System LCR Meter SR715. The glass slides were thoroughly cleaned in ultrasonic bath in water, acetone, and IPA in sequence, then fully dried on hotplate before cooling down to room temperature.

6.1.2 EHD Printing System Setup

The printing system (Figure 36) is composed of three sub-systems: a precision three-axis linear-translational motorized stage, a pneumatic dispensing system with precision pressure regulator and closed-loop temperature control, and a high voltage supply. The motion stage is installed on an optical table to reduce vibrational noise. Three linear stages are configured in XYZ directions with 100 nm repeatability and are used to move the printing head to the programmed locations. The stage provided a displacement range of 100 × 100 × 50 mm. A pneumatic syringe was used but pressure was not applied in this study. EHD-jet printing is self-sustained and highly repeatable without pressure.
Figure 33 Schematic of the EHD-jet printing set-up and experimental setup for EHD-jet printing
The temperature of the syringe was set to 110 °C during printing to melt wax and reduce its viscosity and surface tension. The nozzle tip is obtained by pulling a borosilicate capillary and dicing it to expose open end under microscope. Nozzles with three different sizes (38.2μm, 61.4μm, and 71.7μm, as Tip I, Tip II, and Tip III respectively) are used for this study and their dimensions are examined by SEM. The grounded electrode is obtained by coating 50nm-thick aluminum on a heavily doped silicon wafer by thermal evaporation. The substrate (glass slide) was placed on the grounded electrode. The substrate and the underneath electrode is displaced on demand by the XY-stage. A function generator (Agilent 33220A) is used to generate the voltage command, which is then amplified by a high voltage amplifier (Trek 610A) to be used for EHD-jet printing.

6.1.3 Pattern Characterization

The micro droplets are printed and solidified on the glass slide by the EHD printing process. The droplets on the substrate is inspected under optical microscope, and then scanned by an Atomic Force Microscopy (AFM) to measure footprint morphology with respect to their dimensions and thickness on the substrate. The volume of the droplets can be calculated as well, which is used to verify the FEA model for predicting the droplet diameter at different process conditions. The printed features are also imaged by using Scanning Electron Microscope (SEM).

6.2 Melt EHD-Jet Printing of Thermoplastic Phase-Change Material

In electrohydrodynamic (EHD) jet printing, a high voltage is applied to the nozzle tip, which causes mobile ions in the printed material (melted wax in this study) to gather near the
surface at the tip of the nozzle. The Columbic force causes the meniscus at the nozzle end to deform into a conical shape (i.e., Taylor cone). With sufficiently large electric field, the surface charge repulsion from the electrostatic stress at the cone apex exceeds the surface tension of the meniscus, and a droplet or a jet of fluid is printed from the Taylor cone onto the grounded substrate. The fluid properties of the printed material, along with the process conditions, mostly the applied voltage and flow rate determines the plotting results.

Generally, as the applied voltage or electric field strength increases, different electrohydrodynamic modes can be observed, transitioning from pulsating mode to stable jet, unstable multiple jets. EHD-jet printing in the pulsating mode provides drop-on-demand printing capabilities that have great potential in high resolution micro-scale 3D printing and additive manufacturing when working with wax-based support material and build materials. In the micro-dripping mode, the fine droplet is ejected and can be deposited on demand to form 3D structures layer-by-layer.

In our experiments, three nozzle tips were used for EHD-jet printing with the outer diameter of 38.2μm, 61.4μm, and 71.7μm respectively. In our study, we found that the nozzle outer diameter is more relevant to the printed droplets, compared with the size of the nozzle orifice. The reason comes from the wetting of the printing material at the tip of the nozzle. The size of the Tailor-Cone is mostly determined by the nozzle diameter instead of the nozzle orifice size, due to the wetting at the tip. To simplify the modeling process in the next section, no pressure was applied to the syringe. The fluid system work at the equilibrium state, in which there is no ink flow when the printing voltage is not applied.
For melted wax in EHD printing, when the nozzle to substrate gap was kept at 100 µm (For Tip I) and 150 µm (For Tip II and Tip III), as we gradually increased the voltage, a meniscus and Taylor cone was gradually forming at the tip of the nozzle (Figure 36(a)). When the applied voltage is large enough (around 550V to 800V for different tips), micro droplets were ejected from the Taylor cone and printed onto the substrate. When the voltage is further increased, droplet fission happens. Unlike high viscosity melted polycaprolactone (PCL), we didn’t observe the stable jet printing for wax since the viscosity of wax is several order of magnitude lower than PCL.

Figure 36b) shows the footprint of the droplets on glass slides using different printing voltage from 560V to 640V. 560V is the threshold voltage to initiate ejection, and the 640V is the upper limit above which droplet fission happens. For the results, clearly increasing the voltage and the induced electrical field strength will reduce the droplet dimension (better
resolution) and increase the ejection frequency of the droplets, which can be easily explained by the mechanism of EHD printing. A higher voltage or electrical field strength will increase surface charge density at the Taylor cone. As a result, droplets with smaller volume can obtain large enough electrostatic force to overcome surface tension to be ejected from the cone tip. The high electrical field also increases the migration speed of the accumulation of surface charge, thus the frequency of the droplet formation and ejection is increased too.

To characterize and model the relationship between process conditions (voltage and nozzle size) and the droplet dimension, the printed droplets from different conditions were imaged and scanned by an Atomic Force Microscope (AFM) to measure the specific dimensions (footprint diameter and height) and volume after solidification. Due to the phase-change feature of the wax used for printing, the dimension and volume of the printing droplets can be directly measured after printing, which provide valuable quantitative information for process modeling. From results in Figure 37, small nozzle requires less voltage for EHD printing and produces droplets with smaller volume, which come from the larger electrical field concentration at the sharp tip of the smaller nozzle.
Figure 35 Droplets dimension at different process conditions. (a) Morphology and cross-section of a typical droplet (from Tip III printed at 890V). (b) Droplet volume, (c) Footprint diameter, and (d) thickness for droplets printed by three different nozzles at respective working voltage range. Red is Tip I, green is Tip II, and Blue for Tip III. Each condition was repeated 5 times.
Figure 38(d) shows the thickness of the printed droplets for three different nozzles at respective working voltage range. Apparently the thickness obtained from single droplet is above 1µm, significantly thicker than any aqueous/solvent-based ink, which holds great potential in 3D printing. The reason of such thickness is straightforward that aqueous/solvent-based inks are majorly composed of fugitive solvent, which will evaporate after printing. Phase-change ink, such as wax, will quick solidify without scarifying its volume. Thus a good thickness can be achieved even after droplets with high flying speed impacting and spreading on the substrate.

Similar to conventional phase-change based 3D printing, using EHD-jet printing, when the substrate speed is chosen properly that matches the droplet size and printing frequency, a continuous line can be printed without sacrificing the line resolution (width), as shown in Figure 39. In the SEM picture of Figure 39, a “NCSU” letters were printed by EHD-jet printing using melted wax. The speed for printing “NC” is about two times faster than “SU”. Clearly continuous line features and separated droplets can be identified easily from the SEM. The
smallest feature dimension in Figure 39 is about 3 µm, about 1 to 2 orders of magnitude smaller than conventional 3D printed features using phase-change printing, which indicate great resolution potential of EHD-jet printing process in additive manufacturing.

6.3 Modeling and Analysis of Melt EHD-Jet Printing

6.3.1 FEA modeling of the droplet formation EHD-Jet Printing

Modeling the EHD-jet printing is critically important from the perspective of process control. It is important to predict the droplet dimension at different system configuration and process conditions for planning the printing sequences. It is extremely difficult to obtain the analytical solution to describe the EHD behaviors due to highly complex and coupled physics of the EHD printing process. In this work, instead of studying the complex coupled electrical and fluidic behavior together, we modeled two important forces (electrostatic force, and surface tension force) in EHD printing separately by Finite Element Analysis (FEA).

The scheme of FEA is shown in Figure 40(a). We assume a hemispherical meniscus forming at the end of the nozzle tip, and the diameter of the hemispherical meniscus is same to the diameter of the nozzle tip. The EHD printing process depends on two competing forces, the electrostatic Coulombic force and surface tension force. When the electrostatic Coulombic force exceeds the surface tension force, a droplet is ejected from the meniscus.
Figure 37 a) Schematic configuration for FEA study of the electrostatic force on the droplets. 
b) Cross section plot of the nozzle, meniscus, and half ejected droplet. c) Electrical filed 
distribution around the nozzle tip during droplet ejection.
a) Surface Tension

Counter Electrode

Print Head

~100-150 μm

~600 to 800V

Substrate

Electrostatic Force
In FEA analysis, we study a state that pending semi-hemisphere droplet is about to detach from the meniscus apex. In this state, the droplet with the fixed diameter has the largest surface tension force, and will be ejected from the meniscus if the electrostatic force acting on the droplet surface is larger than the surface tension force.

From the configuration in Figure 41, with FEA analysis, we can calculate the electrostatic force acted on the half ejected droplet surface at different conditions, such as voltage, droplet diameter, and the nozzle/meniscus diameter, as shown in Figure 40(a-c). The electrostatic force $F_e$, can be expressed as a function of voltage $V$, droplet diameter $D_d$, and the nozzle/meniscus diameter $D_N$, as

$$F_e = c \cdot V^{k1} \cdot D_d^{k2} \cdot D_N^{k3} \quad (1)$$

By changing one parameter at a time and fixing the other parameters, the FEA result that shows the relationship between the electrostatic force and the process parameters can be obtained. From the FEA results, the exponents in Equation 1 and coefficient $c$ can be identified for a specific tip. For example, for Tip I, the $F_{e, \text{tip I}} = 3.94E^{-6} \cdot V^{2.0002} \cdot D_d^{1.74} \cdot D_N^{-1.08}$. For Tip II and III, power $k1$, $k2$, and $k3$ are very close to the value for Tip I, but the coefficient $c$ is different due to the different configurations for using different nozzle tip diameter. The FEA results of the electrostatic force can be well described by Equation 1 with less than 1% difference, as demonstrated in Figure 40(d), which compared the force given by FEA results and Equation 1 for the droplets in-flight diameter obtained experimentally. The droplets in-flight diameter is derived from the measured volume of the wax droplets on the substrate by assuming perfect spherical droplet when leaving the meniscus.
Figure 38 FEA results (dots) and fitted relations from Eq. 1 (line) of electrostatic force at different process conditions for Tip I. (a) Relationship between electrostatic forces and voltages. (b) Relationship between electrostatic forces and droplet diameter. (c) Relationship between electrostatic force and Tip diameter. d) Relationship between electrostatic force to experimental conditions.
In the EHD printing scenario, the droplet with a certain diameter will be ejected from the meniscus when the electrostatic force becomes stronger than surface tension force, $F_s$, which is

$$F_s = \sigma \pi D_d$$  \hspace{1cm} (2)

The resulting droplets diameter can be derived by equation 3,

$$F_e = c V^{k_1} D_d^{k_2} N^{k_3} = F_s = \sigma \pi D_d$$, and $D_d = \left(\frac{c V^{k_1} D_N^{k_3}}{\pi \sigma}\right)^{\frac{1}{1-k_2}}$  \hspace{1cm} (3)

Where $\sigma$ is surface tension coefficient of the melted wax in mN/m, $V$ is applied voltage. The solution for the resulting droplets diameter can be solved graphically as in Figure 42. When the line of the surface tension force intersects with the curve of the electrostatic force for a certain nozzle tip with applied voltages, the electrical static force is large enough to overcome the surface tension to produce a droplet with certain diameter. Using this method, for each voltage applied and for each nozzle configuration, we can estimate the corresponding droplet diameter by EHD printing at a specific process conditions.
Figure 39 (a) Intersection points of the line for surface tension force and the curves for electrostatic force give the resulting droplets diameter at different voltage for Tip I. (b) Comparison between droplets dimension from FEA (color lines) and experimentally measured results (data points) for three different nozzles.
Due to the phase-change ink (wax) used in EHD printing, we are capable to measure the volume of printed wax droplets on the substrate. Thus we can directly compare and validate the effectiveness of the FEA based modeling approach with respect to the produced droplet dimension. The results for FEA method and experimental results are plot directly in Figure 42(b). The FEA method is in good agreement with the measured droplet dimensions. The small difference between FEA results and the experimental results may come from factors that include the measurement error of the nozzle diameter, the difference in the surface tension for different tips due to the temperature variation.

6.3.2 Dimensionless analysis of droplet scaling in EHD-Jet Printing

FEA results provide reasonable prediction for the dimension of the ejected droplets for each nozzle configuration. We also performed dimensionless analysis to incorporate the results from three independent experiments from three nozzles into a single framework. In EHD printing, electric bond number provide great insight into the voltage effect (electrostatic force) and surface tension effect of the EHD behavior, which characterizes the importance of the liquid deformation due to the electric field. The electric bond number is defined as

$$N_e = \frac{\varepsilon V^2}{2D\sigma}$$ (4)

Where $\varepsilon$ is the electric permittivity of the liquid, and $V$ is the applied voltage, $D$ is the characteristic length scale and is selected to be the nozzle diameter $D_N$, $\sigma$ is the surface tension. Electric bond number indicates the ratio of electrostatic pressure and surface pressure.
Normally the voltage in the electric bond number is defined the voltage or electrical field between the nozzle and the substrate. If the droplets are directly printed onto the ground electrode, we can use the applied voltage to define the electric bond number. For our configuration (Figure 43), we put a glass substrate on the ground electrode to collect the printed droplets. There are two dielectric layers between the nozzle and the ground electrode, the air and the substrate glass. In contrast to printing directly on ground electrode, the introduction of the extra thick dielectric glass layer will significantly change the electrostatic field. Thus the voltage across the nozzle and the substrate is different from the command voltage applied. The effective voltage drop between the nozzle and the surface of the glass substrate can be easily derived as $V_g = \frac{V}{1 + \frac{d_2}{\varepsilon_2 d_1}}$, where $d_1$ is the nozzle to substrate gap, $d_2$ is the thickness of the glass substrate, $\varepsilon_2$ is the relative permittivity of the glass. Using $V_g$ in Eq. 4, the electric bond number for our configuration can be defined.
We can also express the diameter of the droplets using a dimensionless normalized diameter $d = D_d/D_N$, which is the droplets diameter normalized by the nozzle diameter. This normalized droplet diameter indicates the ratio between the droplet diameter and the nozzle dimension, and incorporate the effect of the nozzle size on printed droplets. When the experimental results of printed droplet diameter at different voltage using different nozzles are plotted with the dimensionless electric bond number and normalized droplet diameter, it can be found in Figure 44 that the results from three different nozzle tips can be described in a unified relationship of $d \sim N_e^{-1.1}$. This meaning of this unified scaling relationship is quite straight forward. The normalized droplet diameter has a slight inverse power relationship with the electric bond number. With a large electric bond number indicating that electrostatic pressure is stronger than surface pressure, relatively smaller droplets can be ejected from the meniscus. The unified relationship using dimensionless parameters make process control much
easier. The printed droplet dimension can be estimated and extrapolated even different nozzles, printing voltages, and nozzle to substrate gap are used.

Compare to other scaling law proposed in EHD printing community [32-33], our results are different mostly due to the difference in printing modes that come from specific ink properties in these studies. In [32-33], the EHD printing was operate at the cone-jet mode for liquid phase inks, in which he jet diameter was measured to study their scaling law with respect to process parameters. Our work uses phase change melted wax as the printing material and the volume of the micro droplets are measured to study its relationship with process parameters.

6.3.3 Modeling of the droplet-in-flight velocity in Melt EHD-Jet Printing

Droplet in-flight velocity of EHD-jet printing is critical to address droplet impact/spreading on substrate. The critical variable to be solved is the impact velocity of the droplet. In this study, an analytical model is developed to achieve the impact velocity of the droplets using the results from FEA analysis. The scheme plot of the droplet in-flight modeling is shown in Figure 45(a). The in-flight droplet experiences two forces, electrostatic force that accelerates the droplet towards substrate, and viscous dragging force from air that slow down the droplet movement. The electrostatic force can be expressed as $F_{es} = Eq$; and the drag force is $F_d = \frac{1}{2} \rho v^2 A C_d$, where $\rho$ is air density, $C_d$ is drag coefficient, and $v$, $A$ are droplet velocity and droplet cross-section area. The electrostatic field strength along the axial direction of the nozzle can be obtained from FEA analysis.
Figure 42  a) Schematic configuration for FEA study of electrostatic field strength and charge calculation. b) Electrostatic field distribution along center axis for Tip I at 560V(red), 600V(green) and 640V(blue). c) Charge of a single droplet for three tips at their own working range, Tip I, Tip II, and Tip III are shown in red, green, and blue respectively.
An example of electrostatic field strength along the center axis is shown in Figure 45(b). Obviously the electrostatic field strength rely on the voltage difference between the nozzle and the substrate. The electrostatic field strength is largest around the nozzle tip and gradually decreases when the droplet moves to the substrate. The charge of the droplet is obtained from the charge accumulating on the pending hemisphere droplet, and is uniformly distributed on the droplets surface. Figure 45(c) provides the charge of each droplet at different process conditions for three nozzles. Clearly the charge each droplet carried decreases along with the reduction of the droplet dimension and surface area.

Given the charge and mass of a given droplet and the electrostatic field strength along axial direction, the droplet in-flight velocity can be calculated numerically using both the electrostatic force and drag force as two inputs which provide the net force to accelerate a droplet. After integrating the acceleration operation along z-axis, the velocity of the droplets can be derived as the function of time and travel distance. Figure 46(a) provides representative velocity profiles for Tip I at three different voltages, which clearly shows that the impact velocity is in the range of ~10 m/s and printing or in-flight time is within a few μs. This fast in-flight speed is part of the reason that direct measurement/observation of droplet formation and is very difficult. After leaving the meniscus, the droplet initially has a larger acceleration due to the strong electrostatic field around the nozzle tip and small dragging force due to slow speed. The droplet acceleration is decreasing as it flies toward the substrate due to reducing electrostatic field strength and increasing dragging as velocity increases.
Figure 43 (a) Typical velocity profile for droplet in-flight for Tip I at 560V, 600V, and 640V (shown in red, green and blue respectively). (b) Impact velocity for three nozzles at different voltage, Tip I, Tip II, and Tip III are shown in red, green, blue respectively. (c) Reynolds Number and (d) Weber Number at impact for three nozzles, Tip I, Tip II and Tip III are shown in red, green, and blue respectively.
Figure 46(b) shows final impact velocity of the droplet at different printing conditions. Increasing the printing voltage will increase the impact velocity. Figure 46(c) shows the Reynolds number for different printing conditions. Droplets from large tips have large Reynolds number since larger droplet dimension will be obtained. For each nozzle used in this work, roughly similar Reynolds number is obtained, indicating the droplet moment does not change much for each tip since larger voltage produces smaller droplets but with higher impact velocity. The Weber number shown in Figure 46(d) demonstrates a sharp increase as the voltage increases for each nozzle, since the velocity significantly increased along with the increase of printing voltage, which offset the droplet shrinkage. When comparing the results in Figure 46(c-d) with inkjet wax printing, the Reynolds number is in a similar range, which means the viscous effects tend to be smaller than inertial effects during impact. The Weber number in EHD printing is almost an order of magnitude larger than inkjet printing, which is the reason the droplet thickness (or aspect ratio) is not as high as that obtained from inkjet printing. The achieved Reynolds number and Weber number will enable our future study of droplet settlement on the substrate surface for 3D printing applications.

6.4 Conclusions

In this work, we study and model the melt EHD printing process using a phase-change material (i.e. wax) for micro-scale additive manufacturing, which is capable to produce sub-10 micron droplets for 3D printing. We successfully obtain high resolution EHD jet printing with melted wax, which is a widely used material for additive manufacturing, to achieve
micron-scale droplets. The resolution for single droplet on substrate is as high as 6 microns and the thickness is in the range of 1-2 microns, which provides great potential in both high-resolution 3D printing and 2D digital micro-fabrication. We modeled the droplet formation of the EHD printing by Finite Element Analysis (FEA) with respect to the electrostatic force and surface tension of the ejecting droplets from the Tailor cone. To validate the FEA model of droplet generation, the volume and dimension of the droplets printed with different process conditions are measured experimentally by atomic force microscope. The simplified force-balance based FEA model is capable to predict the diameter of the ejected droplets with good accuracy. Moreover, after introducing a new electrical Bond number, a dimensionless scaling relationship is identified between dimensionless droplet diameter and electrical bond number, which provides a guideline to predict the droplets dimension at different process conditions. Finally, the droplets in-flight velocity and fluidic characteristics (e.g. Reynolds number and Weber number) are modeled using the results from FEA analysis.
CHAPTER 7 CONCLUSION

7.1 Summary

In this study, a versatile multi-material and multi-scale method is developed for high-resolution additive manufacturing with a special focus on multi-material and multi-scale 3D scaffolds for tissue engineering and high-resolution conductive traces for low-cost printed flexible electronics.

Firstly, a layer-molding method is developed for macroscale 3D tissue engineering applications using photocrosslinkable biopolymers: thermoplastic material is used as supporting mold and functional photocrosslinkable material can be deposited on-demand into the mold in an arbitrary way. The building process is repeated following a layer-by-layer sequence until the desired thickness is reached. The final 3D structure can be obtained by removing the supporting material. In comparison with conventional stereolithography (SLA), the layer-molding method in this study enables highly-viscous functional photocrosslinkable materials to be fabricated into 3D structures and have multi-material integration capability, which are not possible for conventional SLA approach. In addition, this method is highly cost-effective and cross-contaminant free because no materials yet will be used, which is of critical importance for expensive biomaterials.

Second, in microscale, EHD hot jet plotting method is developed by using strong electrostatic field-Maxwell stress at the material/air interface results in pointed meniscus (Taylor Cone), from which minute droplet or fine jet is issued. High-resolution features can be obtained by choosing appropriate processing conditions to avoid instability. It has been
demonstrated for the first time in this study that 5μm resolution 2D pattern and 3D structures can be fabricated by using this method. Also multiscale fabrication method is developed by combining FDM method and EHD hot plotting method.

Third, the long-existing challenge for EHD-jet printing continuous features on insulating substrate has been resolved by using AC voltage pulse waveform. Consequently, a positively-charged droplet and a negatively-charged droplet with equal amount of charge will be ejected from meniscus - overlaying them will eliminated residual charge on the substrate that printing continuous feature becomes possible. This method is also high-resolution as DC EHD-jet printing since the basic mechanism is the same if the residual charge issue is successfully addressed - 2μm continuously conductive trace can be fabricated on highly insulated substrate surfaces. Moreover, the printing resolution and printing frequency controls are separated compared to constant DC EHD printing methods.

Lastly, this study investigated the detailed mechanism for EHD-based fabrication. A complete printing process is divided into multiple stages with distinct characteristics, including droplet formation, droplet flight, and droplet impact/spreading/solidification. Droplet formation and droplet flight has been successfully addressed in this study. Droplet formation process is modeled by Finite Element Analysis (FEA) with respect to the electrostatic force and surface tension of the resulting pending droplets about to detach from pointed meniscus. The reasonable agreement between the numerical results and experimental data indicates that this model can provide guidelines to predict the droplets dimension at different process conditions. Droplets in-flight velocity and fluidic characteristics (e.g. Reynolds number and
Weber number) are modeled using the results from FEA analysis. Droplet impact/spreading/solidification on non-porous media will be in future study.

7.2 Future Work

It has been demonstrated in this study the EHD-based printing methods is essentially a high-resolution fabrication approach in both 2D and 3D. And the future development can be categorized into three different ways: to improve resolution down to sub-μm or even to nm, to increase printing throughput, and to further understand the process with detailed process models.

So far in this study, the resolution in both 2D and 3D for EHD printing is sub-5μm which is almost one to two order of magnitude improvement over traditional digital printing method, inkjet printing (~1pL droplet and ~20 μm footprint). For 2D applications, even though the resolution is still not as high as cleanroom-based lithography (~ 0.5 μm) for microfabrication, it is very promising to reach down to this scale by downscale the characteristic length scale. In addition, the EHD-based printing technologies are digital methods which offer great flexibility in mask making-the pattern can be easily adjusted or even changed on-the-fly. Compared to conventional lithography-based microfabrication method, no pre-made mask is required which means much shorter turnaround time. In addition, the functional materials can be deposit drop by drop at exactly the location where they are needed so that material usage can be maximized. The combination of mask making and direct material deposition will make the EHD printing powerful, versatile, and highly cost effective in microfabrication compared to cleanroom-based lithography, and it can play an important role
in micro-fluidic device and MEMS-based device fabrication, such as innovated sensors and actuators. For 3D applications, the interaction between the incoming material and the deposited material needs to be considered because the deposited material is essentially acting as electrode. And the effect is depending on printed structures which is undesired. Printing head design is necessary to obtain robust fabrication performance not depending on printed structures.

The throughput is another important future direction due to the efficiency requirement for any fabrication methods. This requirement can be met by increasing the frequency response for single nozzle and multi-nozzle array approaches. For single nozzle approach, the printing frequency will increase due to the fact that capillary time scale and viscous time scale will be significantly reduced when characteristic length is downscaled; from material perspective, increasing the ink conductivity will also help due to the fact electric relaxation time scale will be reduced when conductivity is increased. As a result, it will be synergetic efforts from both process development as well as material development. The muti-nozzle array approaches heavily deployed in inkjet printing also can be applied to EHD-based printing. However, the electrostatic interference is inherent and universal which means the cross-talk between nozzles may be problematic for printing performance. Excellent engineering practice is required to shield undesired electrostatic field.

It is fundamentally important to understand EHD printing process in the context of multiple stages, which are droplet formation, droplet flight, droplet impact/spreading, and droplet solidification. It is obvious that these multiple stages have their own characteristic.
This study used simplified model to address the droplet formation process, based on which the droplet flight stage is analyzed. It will be extremely important to use advanced model to better estimate the droplet formation process, which can provide droplet size information, charge, and time-scale for inks with different electric and rheological properties. Also the importance of droplet formation lies in the fact that all the other stages require precise information from it. Also droplet impact/spreading and droplet solidification process is important to describe the final foot print morphology. Having a comprehensive modeling approach can significantly predict the performance as well as process trouble-shooting.
REFERENCES


   communications, 2013. 4.
   p. 388-395.
64. Sekitani, T., et al., *Organic transistors manufactured using inkjet technology with 
   subfemtoliter accuracy*. Proceedings of the National Academy of Sciences of the 
   communications, 2013. 4: p. 1773.
66. Stachewicz, U., et al., *Relaxation times in single event electrospraying controlled by 


