

**INVESTIGATION OF LINEAR
ELECTROSPINNING JETS**

by

Jeffrey A. Knopf

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Honors Bachelor of Chemical Engineering with Distinction.

Spring 2009

Copyright 2009 Jeffrey A. Knopf
All Rights Reserved

**INVESTIGATION OF LINEAR
ELECTROSPINNING JETS**

by

Jeffrey A. Knopf

Approved: _____
Norman Wagner, PhD
Professor in charge of thesis on behalf of the Advisory Committee

Approved: _____
Joseph Deitzel, PhD
Committee member from the Center for Composite Materials

Approved: _____
Norbert Mulders, PhD
Committee member from the Board of Senior Thesis Readers

Approved: _____
Alan Fox, Ph.D.
Director, University Honors Program

ACKNOWLEDGMENTS

I would like to thank my research advisors, Dr. Norman Wagner and Dr. Joe Deitzel, who have provided much needed support and guidance during my project over this past year. I would especially like to thank Joe Deitzel, who initially got me involved in undergrad research and introduced me to the electrospinning process. Without his teaching and support over the past 3 years I would not have been able to accomplish what I have. In addition, I would like to thank Dr. Matt Helgeson for his help throughout the year; without discussions and help from him concerning his recent publication, and also the programs he provided me with and helped me understand, my thesis could not have been completed. I would also like to thank the UD Center for Composite Materials, and everyone who works there. Thanks to the Army Research Laboratory CMR program for the funding that made this research possible.

TABLE OF CONTENTS

LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
ABSTRACT	ix
Chapter	
1 INTRODUCTION	1
1.1 General Electrospinning Background.....	1
1.2 Motivation	5
1.3 PEO-Chloroform: Linear Electrospinning Jet	6
2 MODELING OF THE ELECTROSPINNING PROCESS	10
2.1 Previous Modeling.....	10
2.2 Electrohydrodynamic Modeling	11
2.3 Anticipated Results.....	17
3 EXPERIMENTATION AND MATERIALS	19
3.1 Test Solutions and Experiments	19
3.2 High Speed Imaging	21
3.3 Processing Conditions	24
4 RESULTS AND DISCUSSION.....	26
4.1 Experimental Observations	26
4.2 PEO – Chloroform Radius Profiles	30
4.3 PEO – Chloroform Velocity Profiles.....	35
4.4 Scaling Discussion.....	39
4.5 Future Analysis/Work.....	43
5 CONCLUSION	46
REFERENCES	48

APPENDIX A-ALTERED CONDUCTIVITY	50
APPENDIX B-NOMENCLATURE.....	52

LIST OF TABLES

Table 1—Summary of scaling relationships in different regions of the stable portion of an electrospinning jet.....	14
Table 2--Fitting parameters for various processing conditions	33
Table 3—Experimental data power law fits for equation 6.....	35

LIST OF FIGURES

Figure 1--Typical electrospinning schematic	1
Figure 2--3 Typical electrospinning jet regions.....	2
Figure 3—SEM of electrospun non-woven mat.....	3
Figure 4--Linear jet.....	7
Figure 5--SEM of oriented electrospun fibers	8
Figure 6--Fiber diameter vs. linear drum speed.....	8
Figure 7--Electrospinning jet cylindrical fluid element.....	12
Figure 8--Regions identified in the stable portion of jet.....	13
Figure 9--Plot of Ohnesorge vs. Characteristic stress Ratio.....	16
Figure 10--Structure of poly(ethylene oxide), PEO.....	19
Figure 11--Structure of pyridinium formate	21
Figure 12--Experimental Set-up	22
Figure 13--Representative tracer particle	23
Figure 14--Electrospinning jet splaying	26
Figure 15--Polymer skin formation.	28
Figure 16--Collection target for jet with skin formation.	29
Figure 17--Time evolution of the electrospinning cone	31
Figure 18--Initial jet radius at various processing conditions.....	31
Figure 19--Radius profile of .5 ml/hr, 5.2 kV	32

ABSTRACT

Electrospinning, the process of creating polymeric nanofibers through the use of an electric charge, has attracted significant research recently due to the numerous potential applications of the fibers, such as tissue scaffolds, multi-functional composites, filtration devices, and sensors. One major issue with the process is the lack of a functional model that can link processing parameters to final fiber diameter; most developed models are only functional for a specific polymer-solvent system. A newly simplified electrohydrodynamic model has been developed, and has identified important dimensionless groups and scaling regimes controlling the stable portion of an electrospinning jet. The present work studies a novel polymer solvent system, poly(ethylene oxide) – chloroform, with the aim of further testing the newly simplified model for a completely different system through the use of high speed imaging and velocimetry measurements. The poly(ethylene oxide) – chloroform system is unique because of the fact that a completely linear electrospinning jet without a bending instability can be produced. This allows for the collection of a large volume of highly spatially oriented fibers of uniform diameter, which is not normally possible. Experiments revealed that this linear system followed some of the scaling regimes predicted in the model, and also revealed a significant effect of the evaporation rate on the electrospinning process. With the model partially confirmed for a unique system, more testing should be performed in order to potentially validate the model as viable to link processing parameters and solution properties to final fiber diameter.

Chapter 1

INTRODUCTION

1.1 General Electrospinning Background

Electrospinning is a process by which sub-micron fibers can be produced through spinning under the driving of an electric potential. The process itself has been around for nearly a century with the first patent issued in 1934^[1], but recently it has become more popular and numerous articles are published concerning electrospinning every year. The increased popularity arises from the process' ability to relatively easily, as compared to conventional spinning methods, produce nano-structured materials, specifically non-woven fiber mats. At the most basic level, electrospinning is a relatively simple process: a solution or melt is pumped to a metal syringe where a voltage, normally on the order of 2-20 kV, is applied between the needle and collector causing a jet to emanate from the tip of a needle. The fibers are then drawn onto a grounded collector at a rate determined partly by the applied field.

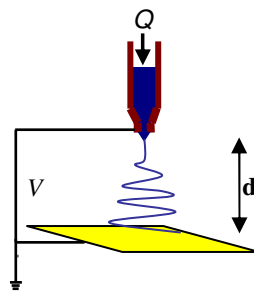


Figure 1--Schematic of a typical electrospinning process. Process parameters include solution flow rate (Q), applied voltage (V), and needle to collector distance (d).

There are three general regions in an electrospinning jet: the Taylor cone, the stable region, and a bending instability. The Taylor cone, first identified and described by Taylor, is a cone like protrusion present in a fluid drop at the tip of the metal syringe.^[2] Compared to the rest of the jet, the Taylor cone occupies a very small region. After the Taylor cone is the stable region of the jet; normally here the jet is linear and emerges from the bottom of the cone. After the Taylor cone is the stable region of the jet; normally here the jet is linear and emerges from the bottom of the cone.

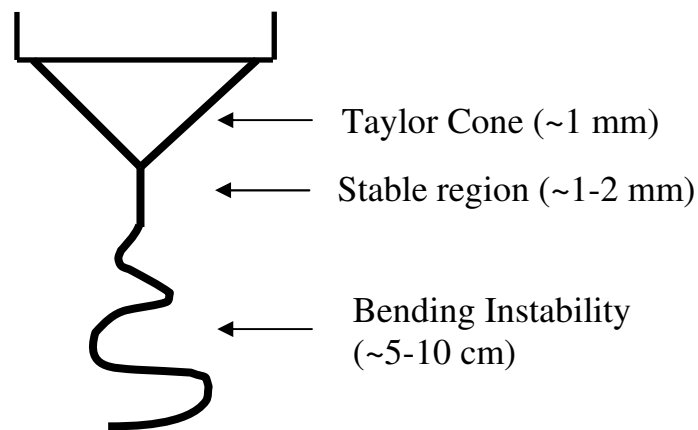


Figure 2--Representation of the three regions in a typical electrospinning jet (Not to scale)

Usually after only a few millimeters at most, a bending instability is observed. The bending instability is a region where the jet bends and whips erratically due to the high electrostatic forces on the surface of the jet. Earlier it was thought that the jet was actually splitting into multiple jets, until high speed imaging was used by Reneker to determine that it was in fact one extremely fast moving jet.^[3] Due to the bending instability, most electrospun material is collected in the form of a random non-woven mat, as shown in figure 3.

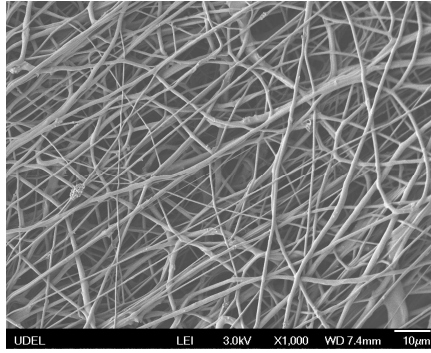


Figure 3—Representative SEM of polyurethane fibers produced through the electrospinning process, x1000.

Electrostatic forces in an electrospinning jet act on the jet surface. In a bending instability, the electrostatic forces have become large enough that they cause the jet to attempt to force it away from itself, thus causing the bending and whipping motion observed. However, electrostatic forces can indeed become large enough to create splitting instabilities, where the jet can split into two or more smaller jets.^[3] If a certain threshold value of the electrostatic forces is reached, the jet splits. This occurs in order to create more surface area; by creating more surface area, the surface charge density is effectively reduced. Electrostatic forces, therefore, play a large role in the mechanics of the bending and splitting instabilities.

Numerous collection methods have been proposed in order to obtain more oriented fibers, including collection between the prongs of a pair of tweezers, using a high speed drum to orient the fibers, or the use of charged rings to create a linear electrospinning jet. A review of some of those methods is presented in [4]. The major problem with most current methods of obtaining oriented fibers is that they either cannot generate large quantities of material or they cannot produce a uniform distribution of fiber diameter.

There are three main forces or properties that govern the electrospinning process: surface tension, electrostatic forces, and viscoelastic forces. It has been understood for a fairly long time that these are the main forces and that the process is essentially a balance of the three; however, the details of exactly how each of these quantities govern the process are an active area of research. The viscoelastic forces are determined by solution properties, such as viscosity. Surface tension depends upon the solvent and solute used in the solution, and the electrostatic forces are determined by the applied voltage and the ability of the solution to carry charge. A more detailed discussion of the forces governing the electrospinning jet will be discussed in Chapter 2.

The electrospinning process is heavily dependent on processing parameters and solution properties.^[5] Major processing parameters include the applied voltage, solution flow rate, and distance of the tip of the syringe to the grounded collector. Important solution properties include viscosity, conductivity, and solvent dielectric, as well as rate of solvent evaporation and solution cooling; however, not much is known about the effect of the two latter properties. Changes to any of these parameters or properties can have a significant effect on the electrospinning process. Property changes can lead to the initiation of an electrospray process where droplets rather than fibers are formed, or an unsteady process where beads can appear in the fibers.

Normally, there is a processing window for each specific solution where the electrospinning process is viable; however, outside of the window a steady electrospinning jet can be difficult or impossible to achieve. The width of the processing window is dependent on the specific polymer – solvent system being used

and the solution properties of that particular system. Some processing windows, such as those for more ideal solutions, are quite large, while others are fairly narrow. For example, a poly(ethylene oxide) – water system can be electrospun into fibers over a large range of solution viscosities, voltages, and flow rates; however, a system such as nylon 6,6 – formic acid can only form fibers for a limited range of solution viscosities, and the possible flow rates and voltages that can be used are limited. At this time there is no easy way to correctly identify the processing window of a specific system based on processing parameters and solution properties without the use of extensive experimentation.

1.2 Motivation

Recent interest has been generated in the electrospinning process based on the myriad of potential applications for the fibers produced from the process. The ability to consistently produce sub-micron diameter fibers of multiple different polymers, ceramics^[6], and semi-conductors opens the door to applications in multiple different fields. Some of these potential applications include: multi-functional composites, filtration devices^[7], tissue engineered materials^[8], biomaterials^{[9][10]}, and sensors^{[11][12]}, to name a few. For example, previous work at The University of Delaware Center for Composite Materials (UD-CCM) has been aimed at the inclusion of random, non-woven electrospun mats of nylon into transparent composites, as well as the production of biocidal fibers for potential use in biological protection applications.

While small scale laboratory research has spiked in recent years, commercial activity has yet to see the same increase in production. Large scale commercial electrospinning processes currently exist, but most commercial

productions use only one polymer-solvent system and lack the capability to branch out to new systems. These processes have relied on extensive experimentation for a specific system, and cannot or will not expand production to new systems involving new polymers/solvents. This is partly due to the lack of an accurate model that can link processing parameters and solution properties to the final fiber diameter, which could allow processing parameters to be easily identified based on desired fiber properties.

Recently, a simplified electrohydrodynamic model has been generated by Helgeson et al. through analysis of the fairly ideal poly(ethylene oxide) – water system.^[13] The model revealed different flow regions present in the stable portion of the electrospinning jet, and proposed scaling laws for both radius and velocity in each of the identified regions. The proposed model also identified important dimensionless groups that can describe processing parameters and solution properties for the electrospinning process, which may allow for determination of final fiber diameter based on solution properties and processing conditions. The aim of this work is to further test that model through the study of a completely different system, namely that of poly(ethylene oxide) – chloroform.

1.3 PEO-Chloroform: Linear Electrospinning Jet

Most electrospinning jets experience three distinct regions: the Taylor cone, the stable region, and a bending instability. However, previous work performed at UD-CCM has shown that it is possible to produce an entirely linear electrospinning jet through the use of a low dielectric solvent, such as chloroform.

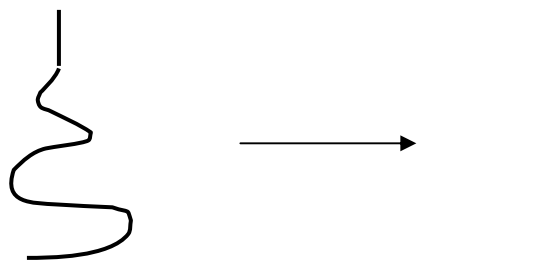


Figure 4--Use of a low dielectric solvent can produce a linear electrospinning jet as opposed to one with a bending instability.

The use of a low dielectric solvent effectively means that the solution has less ability to carry charge. The bending instability arises from the electrostatic forces on the surface of the jet^[3], and a low dielectric solvent effectively reduces these surface electrostatic forces, allowing for a linear jet. Essentially, the electrospinning jet in a low dielectric system is composed only of the Taylor cone and stable region. One method of producing a linear jet that has been previously performed was to force a normal electrospinning jet through charged rings with the same charge bias as the applied voltage, thereby forcing the jet to remain linear.^[14] While a linear jet was produced, this method reduced the amount of collected fiber and is difficult to implement.

The major benefit of a linear electrospinning jet is that it enables collection of highly spatially oriented fibers of uniform fiber diameter in relatively large quantities, as seen in figure 5.

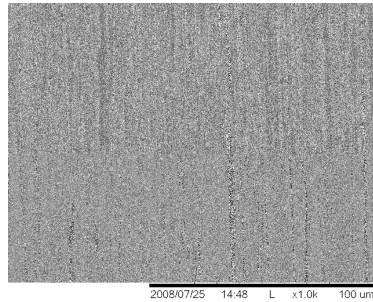


Figure 5--Representative SEM of oriented PEO fibers spun from chloroform, x1000

There have been many previously proposed methods of obtaining linear electrospun fibers^[4]; however, prior to the introduction of a linear jet, the main method of obtaining oriented fibers was the collection of a jet with a bending instability on a rapidly rotating drum. This allowed for collection of highly oriented fibers, but in general there was not a very uniform fiber diameter and there was a large amount of fiber breakage due to the speed of the drum. The rotation speed of the drum has a significant impact on both fiber diameter uniformity and the fiber diameter itself, as shown in figure 6.

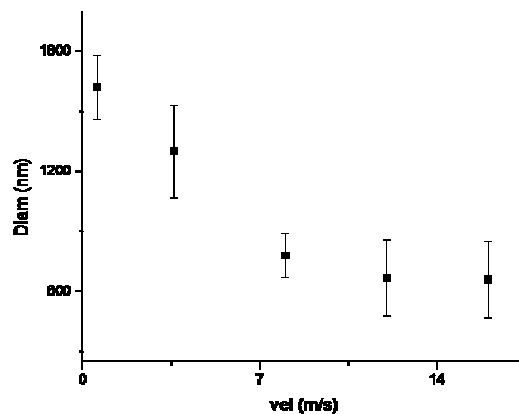


Figure 6--Fiber diameter as a function of face velocity of a rotating drum as the collector. PEO – chloroform was the polymer solvent system under consideration.

Another common method of obtaining oriented fibers has been to collect fibers between the two edges of a tweezer.^[4] The fibers bridge the gap between the two edges, thereby orienting themselves. The major problem with this approach is that a small amount of fibers can be collected. There are two major issues with most methods of oriented fiber collection: lack of collected fiber volume, or lack of uniform fiber diameter. Therefore, use of a low dielectric solvent to produce a linear jet, and thereby oriented fibers, is a possible approach to increase the quantity and quality of oriented nanofibers.

The goal of the current work will be to investigate the flow in the stable region of a linear electrospinning jet. A brief discussion of previous attempts at modeling the electrospinning process as well a more detailed discussion of a recently simplified electrodynamic model will be presented. Experimental methods and materials will describe experiments performed using a high speed camera, and how the images were analyzed. Radius and velocity data will be analyzed in order to determine the recently simplified electrohydrodynamic model's potential compatibility with the linear jet electrospinning system.

Chapter 2

MODELING OF THE ELECTROSPINNING PROCESS

2.1 Previous Modeling

The electrospinning process itself has been around for a fairly long period of time^[1]; however, a model of the process that can successfully link processing parameters and solution properties with final fiber morphology still has not been produced. While several modeling efforts have been undertaken, one major problem with most of the models is that they do not apply to multiple polymer – solvent systems, but only specifically to one experimental system.

Major forces governing the electrospinning process include viscoelastic forces, surface tension, and electrostatic forces. In order to successfully model multiple polymer solvent systems, it is necessary to fundamentally understand the interactions between the different governing forces and the multitude of parameters that are associated with the electrospinning process. Electrostatic forces play a large role in the electrospinning process, hence the name. Several previous research efforts have been aimed at understanding of the bending instability.^{[3][15]} It has been shown that there is a certain charge threshold that must be overcome in order to actually achieve an electrospinning jet rather than a spray; this charge threshold is a function of the solution surface tension and viscosity.^[3] The electrostatic forces on the surface of the jet are also responsible for the bending instability, as the large electrostatic forces on the surface of the jet cause it to repel itself and consequently whip around

uncontrollably.^[3] The viscoelastic forces act somewhat like a counteraction to the electrostatic forces, as they oppose bending of the jet.

Previous models have been developed in a purely theoretical fashion, quantitatively, or a combination of the two. A recent publication by Thompson et al. provides a review of significant previous modeling attempts, as well as a detailed analysis of the effect of processing parameters and solution properties on the electrospinning process through the framework of a model previously developed by Reneker et al.^[16] The model under consideration was presented in [3] & [17]. Out of thirteen parameters in the model, five were identified as having a significant effect on the radius of an electrospinning jet: volumetric charge density, tip to collector distance, initial jet radius, relaxation time, and elongational (extensional) viscosity. However, the author acknowledges that more experiments are necessary to fully validate the model. Thompson's work identified important parameters, but did not bridge the gap from a mathematical model to a functional model that could predict fiber diameter based on processing and solution conditions, a gap that remains to be filled.

2.2 Electrohydrodynamic Modeling

The model under investigation in this work is a recently simplified electrohydrodynamic model of the electrospinning process proposed by Helgeson et al.^[13] The model incorporates forces known to control the electrospinning process, namely viscoelastic and electromechanical forces, along with the surface tension of the solution. This model was devised by simplifying a more complete electrohydrodynamic model ([18][19]), and experimentally verified through high speed imaging of the stable jet region of a PEO – Water system. Using previously

derived dimensionless balance equations on a cylindrical fluid element, figure 7, for the electrospinning process from Feng et al.[19][18], different flow regions were identified in the stable portion of an electrospinning jet in which specific forces were dominant; this allowed the balance equations to be simplified into equations and scaling relationships that could describe the different flow regions of the electrospinning jet.

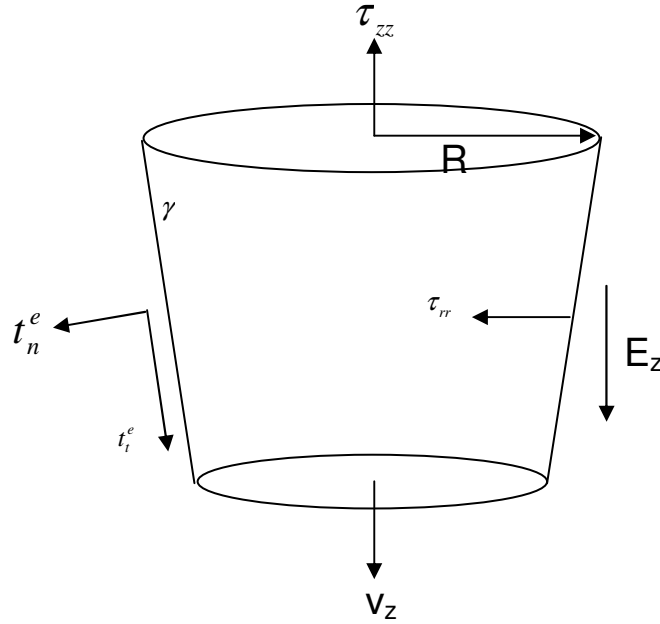


Figure 7--Cylindrical fluid element of an electrospinning jet used in balance equations

A complete discussion of the equations and simplifications used for different regions of the electrospinning jet can be found in [13]. The aim of the modeling was to more fundamentally understand the forces at work in the electrospinning jet and determine when and where the different forces played a large role. This then enables simplifying the model to yield analytical scaling results linking the processing parameters and material properties to the final fiber diameter.

Four different regions were identified, the Taylor cone and three distinct sub-regions within the previously described stable region of an electrospinning jet: jet initiation, jet stretching, and jet thinning regions. For the purposes of the Helgeson model the Taylor cone, region i, was not analyzed. The jet initiation region (ii) is the portion of the jet where the radius of the jet shrinks drastically and there is a correspondingly large increase in the extensional viscosity of the jet due to strain hardening. Figure 8 shows the increase in extensional viscosity associated with the decrease in jet diameter.

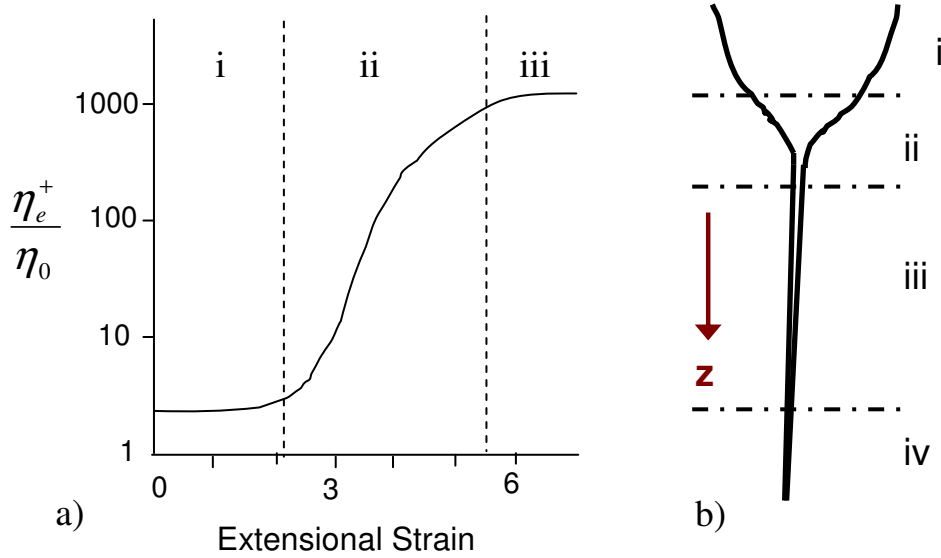


Figure 8--Different regions identified in the stable portion of an electrospinning jet, the z direction points along the jet axis. (a) – representative plot of typical extensional viscosity/zero-shear viscosity vs. extensional strain in the z direction; (b) Typical electrospinning jet for PEO-water

The jet stretching portion, region iii, is where the extensional viscosity in the jet reaches a pseudo steady-state, shown as the plateau at the right of figure 8a. The model theoretically predicted and it was experimentally verified that in this region of the electrospinning jet the radius would scale with $z^{-1/2}$, and that the velocity would scale with z^1 . The fourth identified region in the jet is the jet thinning portion, region iv. In this region electromechanical forces and jet inertia dominate, minimizing the effect of the extensional viscosity. In this region it was theorized and experimentally verified that the radius would scale with $z^{-1/4}$ and velocity with $z^{1/2}$. Experimental verification of the proposed theoretical scaling was performed using velocimetry data acquired through high speed imaging and particle tracking, as well as jet radius measurements. Table 1 presents a summary of the scaling results obtained by Helgeson et al.

Table 1—Summary of scaling relationships in different regions of the stable portion of an electrospinning jet. Scaling values are for axial position, z , down the jet.

<i>Region</i>	<i>Dominant Forces/Phenomena</i>	<i>Radius</i>	<i>Velocity</i>
ii	Electromechanical stress, strain hardening	-	-
iii	Pseudo steady extensional viscosity	-1/2	1
iv	Jet Inertia, tangential electromechanical stress	-1/4	1/2

It was verified that the assumptions made in the analysis, namely plug flow in the jet and no solvent evaporation, were correct through comparison of calculated velocities to experimentally observed velocities for the PEO-water system. Experimental velocities were shown to follow a calculated velocity from the following relationship:

$$v = \frac{Q}{\pi \cdot (R(z))^2} \quad (1)$$

Experimental velocities followed the calculated velocities and observed the predicted theoretical scaling regimes.

Through simplification of the dimensionless balance equations that had previously been derived, two important dimensionless groups were identified that could potentially characterize the electrospinning process: the Ohnesorge number, and the characteristic stress ratio. The Ohnesorge number, equation 2, includes the solution properties of zero-shear viscosity, surface tension, and solution density. It also contains the final fiber diameter. The Ohnesorge number is a ratio of the viscous to surface forces: as viscosity increases the Ohnesorge # will also increase.

$$Oh_f = \frac{\eta_0}{(\rho R_f)^{1/2}} \quad (2)$$

Use of the Ohnesorge # allows for the incorporation of the final fiber diameter into a model that links processing parameters and solution properties. The characteristic stress ratio, equation (3), was determined through simplification of the previously developed balance equations. The characteristic stress ratio incorporates important processing variables as well as other terms that can describe the stable portion of the electrospinning jet such as jet radius at initiation and the pseudo steady extensional viscosity.

$$\Pi_\infty = \frac{(\epsilon - \bar{\epsilon})E_0^2 R_0^3}{\eta_{e,\infty}^+ Q} \quad (3)$$

Included processing variables are: solution flow rate, electric field strength, and the difference in dielectric constant between solution and surrounding medium, usually air. The characteristic stress ratio is important because it contains the extensional viscosity and a measure of the initial jet radius, which were both identified by Thompson et al. as important in controlling the radius of an electrospinning jet.

It was experimentally verified for the PEO – Water system that the Ohnesorge number and the characteristic stress ratio were related through a power law correlation. Figure 9 shows data from previously reported literature and work performed by Helgeson, all fit to a plot of Ohnesorge vs. characteristic stress.^[13]

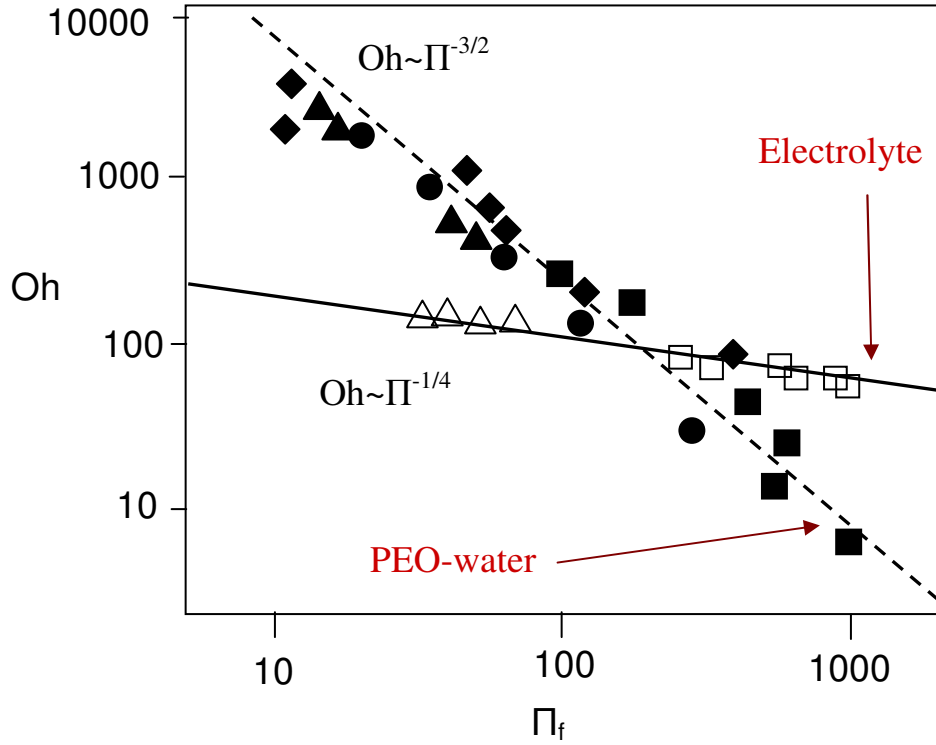


Figure 9--Plot of Ohnesorge vs. Characteristic stress Ratio. Filled shapes represent PEO-water, while empty have NaCl added. Originally compiled by Helgeson et al. [13] (□,■ [20]; ▲,△ [13]; ♦ [21]; • [22])

For the PEO – Water system, a fairly good correlation of $Oh \sim \Pi^{-3/2}$ was observed for several different data sets. Another interesting observation presented in Figure 9 is that through the addition of an electrolyte to a PEO – Water system, the relationship

between the Ohnesorge number and characteristic stress was observed to have a lower slope, $-1/4$.

The relationship presented by Helgeson et al., namely the relationship between the Ohnesorge # and the Characteristic stress ratio, could potentially be a means to successfully link electrospinning processing parameters and solution properties to the final fiber diameter.

2.3 Anticipated Results

Experimentation performed in this work examined a linear jet at various processing conditions, as well as several solutions of the same weight percent polymer but of differing conductivities. It is expected that for all solutions, the radius and velocity profiles should scale similarly to the PEO – Water system examined by Helgeson et al. Specifically, in the jet stretching region, region iii, the radius should scale with $z^{-1/2}$, and the velocity should scale with z^1 . In the jet thinning region, region iv, the radius should scale with $z^{-1/4}$ and the velocity with $z^{1/2}$. These scaling laws were determined theoretically, and thus it is hoped that they will be valid when describing a completely different electrospinning system than was previously examined, namely the linear PEO-chloroform system under consideration. It is unclear a priori what effect the bending instability may or may not have on the scaling laws.

It is also expected that the PEO – Chloroform system examined in this work will follow a correlation between the Ohnesorge number and the characteristic stress ratio identified by Helgeson et al. While it is expected that the system will follow some type of correlation between these two dimensionless groups, the particular scaling it will follow is unclear. Previous experimentation demonstrated

that variation of solution conductivity changed power law scaling between the two, so it is expected that the PEO – chloroform system will follow a different power law scaling value. Chloroform has a much lower conductivity than water, as well as a much lower dielectric constant, so it is anticipated that the power law should be larger than the $-3/2$ observed in the PEO – water system.

Chapter 3

EXPERIMENTATION AND MATERIALS

3.1 Test Solutions and Experiments

Experimental work performed in this study consisted of imaging the initial region of an electrospinning jet with a high speed camera. The polymer solutions examined in this study consisted of Poly(ethylene oxide) and chloroform.

Poly(ethylene oxide), or PEO, is a polymer with a repeat unit consisting of C_2H_4O ; its structure is shown below.

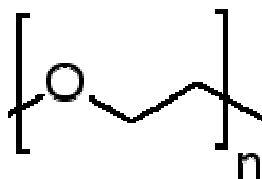


Figure 10--Structure of poly(ethylene oxide), PEO. (www.sigmaaldrich.com)

PEO is an ideal polymer for use in the electrospinning process. In most cases there is a large window of processing parameters, and fibers can easily be generated for a wide range of solutions. Chloroform is an organic solvent with the formula $CHCl_3$.

Chloroform is a low boiling, low dielectric, toxic solvent. The potential harmful effects of the solvent were mitigated through the use of very small amounts during the electrospinning process, as well as conducting the actual experiments in a well ventilated enclosure to avoid inhalation of the chloroform vapors.

Solutions created for experimentation were mixed based on mass.

Chloroform has a density of 1.492 g/ml, and approximately 100 ml of each wt% stock solution was created. The required mass of polymer, in grams, for a specific weight percent solution was determined through the following equation, shown with 2 wt% as an example:

$$.02 = \frac{x}{x + 149.2} \quad (4)$$

For this work, stock solutions of 1, 2, 3, 4, and 5 weight percent solutions were created. It was later determined that the 3, 4, and 5 weight percent solutions were not viable for the electrospinning process, as they were too viscous. Stock solutions were created by mass using 400,000 MW PEO (Scientific Polymer Products) and 99.8% HPLC chloroform (CHROMASOLV, Sigma-Aldrich). The required mass of chloroform, namely 149.2 g, was massed and added to the required amount of PEO powder. A stir bar was then inserted and the solution was allowed to stir overnight.

In order to create viable solutions for high speed imaging and particle tracking, tracer particles needed to be added to the solutions. Originally, it was thought that polyurethane tracers from previous work would be used^[13]; however, it was found that the polyurethane did not completely disperse in the chloroform, and thus large chunks were formed which disrupted the electrospinning process. Therefore, silica particles were chosen as trackers since it was thought that they would more completely disperse in the PEO/Chloroform solution. Hollow silica particles with a nominal diameter of 8-12 um were added to 20 ml of each stock polymer solution at a concentration of 500 ppm by mass. The silica particles functioned well as trackers as they were easily dispersed and could be discerned easily in the high speed images. In order to ensure complete dispersion of the particles, solutions containing

the silica particles were placed on a roll mixer and allowed to mix for several days before experimentation.

In order to create PEO-chloroform solutions with altered conductivities pyridinium formate (Py.FA), an organic salt, was used.

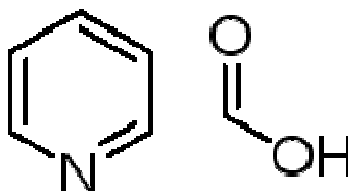


Figure 11--Pyridine shown at left, formic acid on right. When mixed, the proton from formic acid protonates the nitrogen on pyridine, forming pyridinium formate. (www.sigmaaldrich.com)

This organic salt was created by mixing pyridine and formic acid in a 1:1 molar ratio. Desired amounts of Py.FA were then added by mass to sample solutions of 2 wt% PEO/chloroform so that each solution would have a different conductivity. Four altered conductivity solutions were created, all in 2 wt% PEO: 2, 3.75, 5.5, and 8 wt% Py.FA.

3.2 High Speed Imaging

In order to perform the desired analysis of the radius and velocity profiles in an electrospinning jet, high speed imaging capabilities were required. The jet itself cannot be easily seen using normal photography techniques, and the velocity of the fluid inside the electrospinning jet is fast enough that conventional photography could not successfully obtain images of the tracer particles: they simply move too fast. The images were obtained using a RedLake MotionXtra HG-100 high speed camera and

MotionCentral Image analysis software. Particle tracking was performed using ImageXpress MotionPlus software.

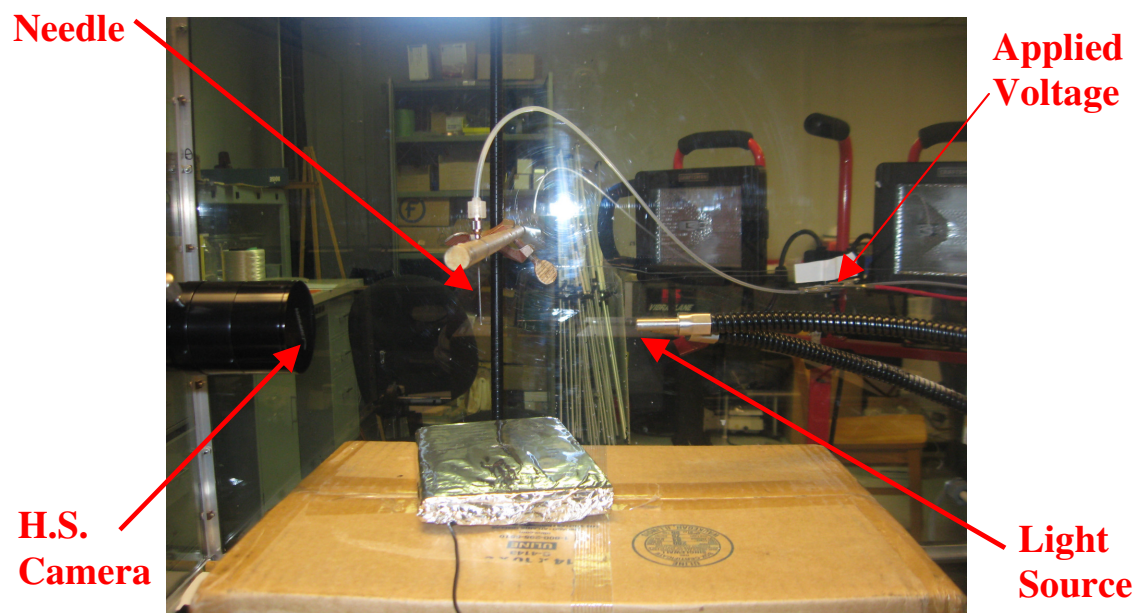


Figure 12--Experimental Set-up

In order to obtain usable images, the electrospinning jet required a significant amount of backlighting. This was obtained through the use of a halogen light source (Fiber Lite MH-100) that was shone through the jet directly into the iris of the camera.

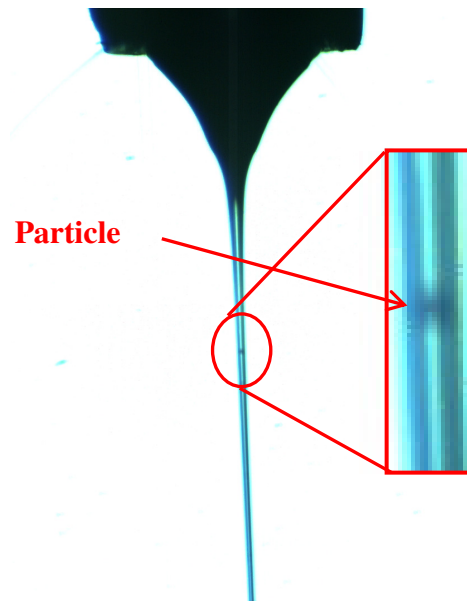


Figure 13--Representation of a tracer particle seen in the electrospinning jet

Tracking of the particles over time allowed for velocity vs. position in the jet to be determined. The ImageXpress MotionPlus software allowed for the generation of velocimetry data by tracking the particles in successive frames. The tracker reticule had to be placed manually over the particle in each successive frame in order to obtain a velocity profile. In order to visualize the particles a high degree of backlighting was required in order to make the tracer particles in the jet visible.

The settings of the high speed camera affected the quality, clarity, and usefulness of the obtained images. Two of the main variables controlling the high speed camera were the frame rate and the exposure time, or shutter speed. The frame rate determines how many frames are captured by the camera per unit time, and the exposure time controls the amount of light that reaches the lens during imaging. Since the particles are fast-moving, the highest frame rate available was chosen, 2000 fps. The frame rate had a smaller impact on the quality of the obtained images and didn't

significantly affect the ability to actually see the particles. The exposure time, however, significantly affected the quality and usefulness of the images. Too high an exposure time and ‘motion blur’ appeared; once the particles reached the lower region of the jet they became blurry and difficult to track. Too low an exposure time and there was not enough lighting present, so the particles could not be seen in the jet. Therefore, in an attempt to strike a balance between these two problems, an exposure time of 250 μ s was chosen.

3.3 Processing Conditions

The electrospinning process in general is extremely sensitive to process variables such as flow rate, applied voltage, and tip to ground distance. Even for the same polymer solution, the application of different processing conditions can make it impossible to produce consistent fibers. For the purposes of this study, most of the process variables remained in the same general range. For all experiments, the needle tip to grounded surface distance was 8 cm. The collection target was a piece of aluminum foil approximately 15 x 10 cm directly underneath the needle. Experiments were conducted at room temperature, approximately 25 °C. Humidity during experimentation ranged from essentially zero to almost 45%; however, humidity seemed to have little effect on the system since similar results with respect to solvent evaporation were obtained over the entire humidity range. Applied voltages normally ranged from about 4 kV to 7.5 kV. In all experiments, the voltage was applied to the polymer solution far away from the needle where the jet erupted in order to minimize any possible electrical disturbances that could have been caused by the voltage clip. Flow rates of the polymer solution ranged from .5 ml/hr to 1 ml/hr, although most experiments took place around .5 ml/hr. Solution flow rate was controlled using a

syringe pump (Harvard Apparatus PHD 2000), and the voltage was applied using a power supply from Gamma High Voltage Research.

Chapter 4

RESULTS AND DISCUSSION

4.1 Experimental Observations

Experiments were performed in order to verify a theoretically predicted and experimentally verified model of the electrospinning process. Experimental goals included studying the affect of varying viscosity by testing 1, 3, and 5 wt% PEO – chloroform solutions, and also studying the effect of the bending instability on the stable jet region through the addition of organic salts to a single weight percent solution. It was hypothesized that the PEO – chloroform system would correlate well with the model, namely that predicted radius and velocity scaling factors would be observed, and that a characteristic stress ratio describing the stable region of the jet would correlate with the Ohnesorge number.

Initially experiments were performed as intended on 1, 3, 5 wt%; however, it immediately became apparent that the viscosity of the 3 and 5 wt% solutions was too high to achieve successful electrospinning, and odd results were obtained, as shown in figure 14.

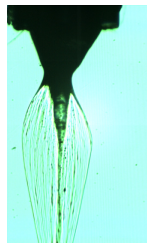


Figure 14--High speed image of 5 wt% PEO – chloroform system, .2 ml/hr, 17.5 kV displaying an odd 'splayed jet' phenomenon

It seemed that the jet splayed outwards immediately following the cone region, only to return back to a more normal cylindrical jet shortly after the stable region. This splaying was experimentally verified by using the high speed camera to view further down the jet and watch the splaying decrease until there was none apparent. It is unclear what caused this phenomenon, and it has not been previously observed. The appearance of this unnatural jet at higher viscosities led to the decision to only experiment with a previously prepared 2 wt% PEO – chloroform system. The 2 wt% was viscous enough to electrospin, but not so viscous as to cause a splaying of the jet.

One major experimental observation was the realization that solvent evaporation played a large role in the electrospinning process for the PEO – chloroform system, and potentially plays a role in many other systems. Solvent evaporation meant that it was difficult to obtain a pseudo steady state jet for an extended period of time. When a jet was initiated, it looked like a normal electrospinning jet; however, over time a polymer ‘skin’ began to form as the cone grew bigger and bigger. The cone would therefore effectively be covered by what seemed to be dried polymer, and the solution flowed through the interior of the cone through to the jet initiation point. After a certain amount of time, usually on the order of a few minutes, the skin would completely cover the tip of the needle, stopping the jet.

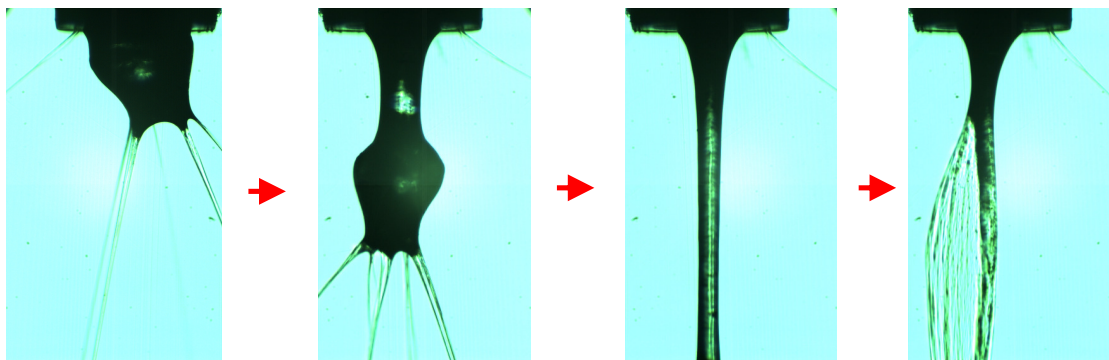


Figure 15--Extreme case of formation of polymer skin and subsequent removal of said skin. Jet is from a 5 wt% PEO – chloroform system.

Eventually, this dried jet would then be forcibly removed from the tip of the needle due to the continued flow of solution through the syringe. After the dried cone fell off, a new jet would emerge. Figure 15 shows the extreme case of this phenomenon for a 5 wt% PEO solution; as the viscosity increased, drying of the cone became more prominent and problematic.

The drying of the cone and subsequent release of the dried up cone occurred regularly for the higher wt% polymer solutions due to the high viscosity. Therefore, the collection target was peppered with what looked like bumps covered with fibers. This morphology of the fiber mat, shown in figure 16, shows that in cases where collection mats may be speckled with bumps all over them the jet may be drying up and causing large clumps of dried polymer to hit the collection mat. This may indicate that the system under consideration was undergoing a significant effect from solvent evaporation, and/or that the viscosity of the chosen solution was too high.

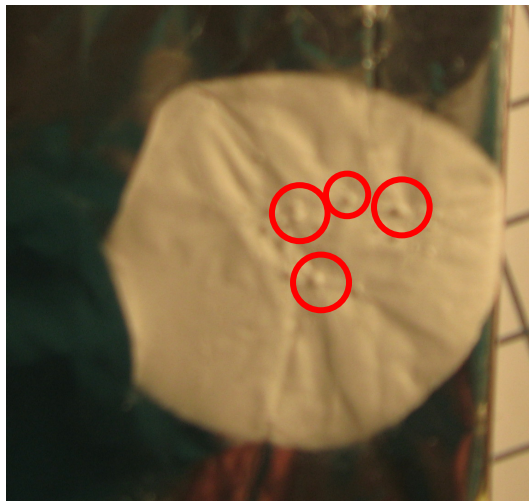


Figure 16--Collection target for a 5 wt% PEO-chloroform system. Circles show locations of raised areas on the collection target.

At lower viscosities, such as the 2 wt% PEO solution, skin formation was still present but it occurred over a longer time scale. The formation of this polymer skin indicates that solvent evaporation likely plays a large role in the electrospinning process. Previous analysis of PEO – water did not take into account solvent evaporation, but chloroform has a much higher vapor pressure and therefore evaporated more readily. While it was not possible to achieve a steady state jet for this system, the formation of a polymer skin and the growth of the cone were fairly predictable and reproducible over time for a given set of processing conditions.

In addition to the inability to study the 3 and 5 wt% solutions, it was also difficult to analyze the images obtained for the 2 wt% solutions with altered conductivity through the addition of organic salt; this was mostly due to the fact that the salt caused the jet to be less stable and move in and out of the plane of focus of the high speed camera. This movement between focal planes made particle tracking and radius determination difficult. Some preliminary observations and results for altered

conductivities are presented in Appendix A. In light of these difficulties, the main analysis performed was on 2 wt% PEO at different processing conditions and different stages of jet evolution due to cone growth and skin formation.

4.2 PEO – Chloroform Radius Profiles

The Helgeson et al. model proposed that the radius scaled with different powers of z , axial position down the jet, depending on the electrospinning jet's flow regime. It was proposed that radius scaled with $z^{-1/2}$ in the jet stretching region, and $z^{-1/4}$ in the jet thinning region. In order to experimentally verify these scaling laws for the PEO – chloroform system, it was necessary to determine the radius profile as a function of z distance from the tip of the needle. This was performed using a method previously described by Helgeson et al. using Matlab as the computing package^[13]

High speed images were output as .tif files. The radius was calculated by converting the image to a binary file where the jet appeared white and the environment appeared black. The number of black pixels per row was then counted and subtracted from the total number of pixels in a row leaving the number pixels in the jet, which represented the jet radius. Radius data was calculated over 40 images to yield statistical significance. In order to determine the radius in millimeters rather than pixels it was necessary to calibrate the image. This was done by scaling the measured number of pixels by the known diameter of the needle; this value was found to be 427 pixels/mm.

2 wt% PEO – chloroform was analyzed at various processing conditions where voltage and flow rate were varied, as well as at different stages of cone evolution due to skin formation. The polymer skin formation made it impossible to

achieve a traditional pseudo steady jet; that is, a jet that is consistent for approximately 15 to 20 minutes.

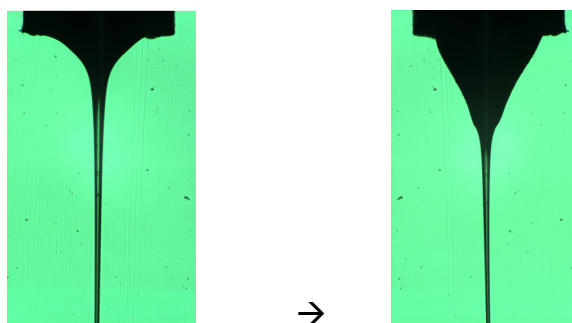


Figure 17--Time evolution of the electrospinning cone. The second image was taken approximately 2 minutes after the first.

In most cases, images were obtained immediately upon jet initiation, and then approximately 2 minutes later. Representative images of the jet upon initiation and two minutes after initiation are shown in figure 17. It was seen in all cases that increasing the voltage caused the radius to decrease more quickly, which has been previously observed.^[5]

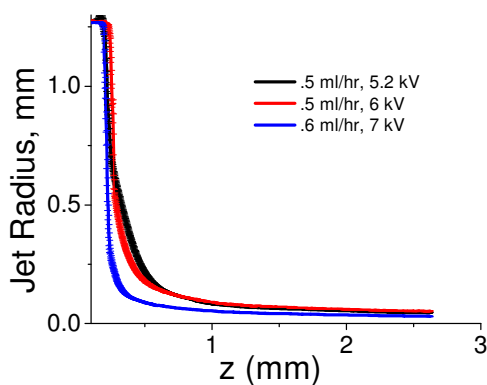


Figure 18--Initial jet radius at various processing conditions. Increasing the voltage reduces the jet radius

All of the radius profiles follow the same general trend, as they only shifted slightly horizontally or vertically due to variation of processing conditions. While all of the initial radius profiles followed the same trend for the entirety of the electrospinning jet, the radius profile of jets 2 minutes after initiation showed significant deviation from the initial jet profile. As can be seen in figure 19, the radius profile of the cone changed significantly 2 minutes after initiation of the jet. However, upon analysis of the radius profile, it was discovered that for the same processing conditions, the radius after the jet initiation region is nearly identical for both the initial jet and the jet after 2 minutes, shown in figure 19 after a z distance of approximately 1.2 mm.

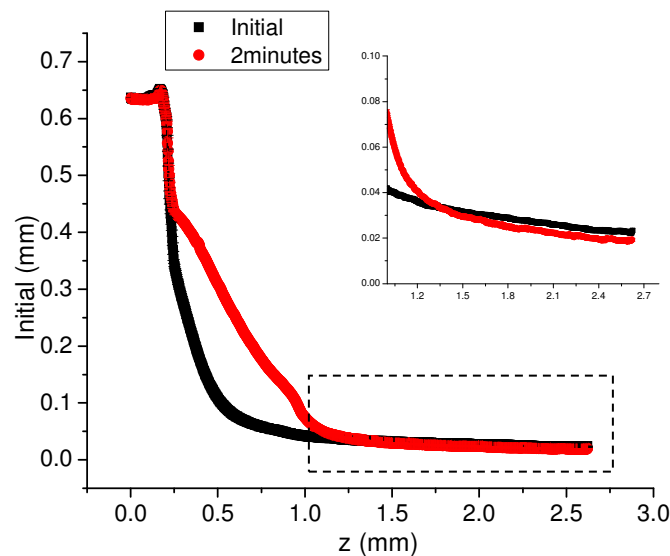


Figure 19--Radius profile of .5 ml/hr, 5.2 kV system at jet initiation and 2 minutes after initiation. Inset is a close up of the boxed area.

Therefore, while the formation of a polymer skin had a significant impact on the growth of the cone region of the electrospinning jet, it seems that the polymer skin and cone growth may not have had a large affect on the radius further down the jet.

In order to verify the scaling laws observed by Helgeson et al., it was necessary to fit the obtained radius profiles to the equation previously proposed, namely:

$$R(z) = Az^{-n} + Bz^{-1/2} + Cz^{-1/4} \quad (5)$$

In order to fit the radius profiles, data was input into Microsoft Excel software. Fitting was begun at the inflection point in the radius profile. In order to obtain values of n, A, B, and C, the sum of least squares error of the difference between the calculated and experimental radius points was minimized using the Excel solver function. Table 2 presents the results of fitting for several different processing conditions.

Table 2--Fitting parameters for various processing conditions

	<i>.5 ml/hr, 5.2 kV</i>		<i>.5 ml/hr, 6 kV</i>		<i>.6 ml/hr, 7 kV</i>	
	Initial	2 min.	Initial	2 min.	Initial	2 min.
A	0.006	0.041	0.004	0.008	0.0004	0.005
B	0.037	0.031	0.041	0.027	0.027	0.006
C	0	0	0	0	0	0.012
n	3.3	6.2	3.0	5.7	3.9	3.4

Nearly all of the fits showed a minimal dependence on $z^{-1/4}$, indicating that the jet thinning region likely was not present in the PEO-chloroform system. Further evidence of this assertion based on velocity data is presented in the following section.

Once a fit was obtained for a given radius profile and the coefficients were determined, it was then necessary to appropriately identify where each scaling region of the jet should be located. The procedure to determine the location of jet regions was the same as used previously by Helgeson et al. In order to determine where the jet stretching region began (region iii, $z^{-1/2}$), the ‘A’ term in the radius fit equation was set at zero, and region iii was defined to begin when that subsequent fit described the actual experimental radius to within 1% accuracy.

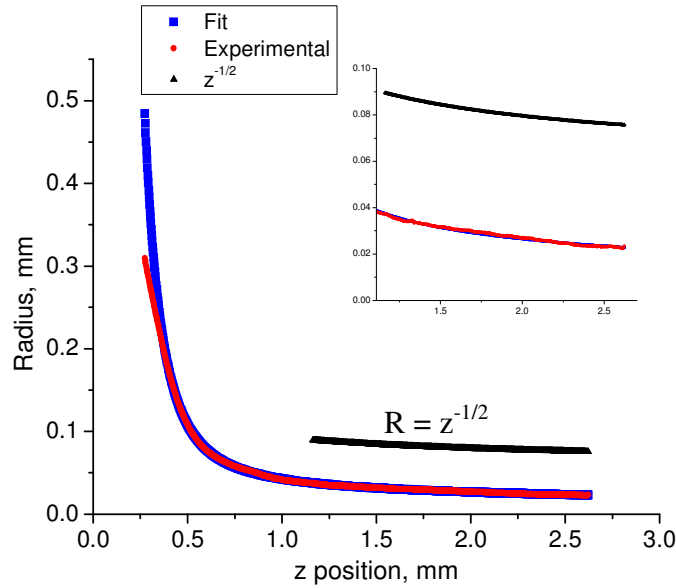


Figure 20--0.5 ml/hr, 5.2 kV Experimental fit using equation 5; black raised line is a plot of $z^{-1/2}$ for region iii for comparison

Visual inspection and comparison would seem to indicate that the radius profile in region iii follows $z^{-1/2}$ fairly well, as shown in figure 20. The small dependence on the $z^{-1/4}$ term and the linear nature of the experimental velocity profiles indicated that there

was no jet thinning region present in experiment. Therefore, once the beginning of region iii was identified, the rest of the jet was taken to belong to that region. Table 3 presents fitting data for the experimentally obtained radius profile identified as region iii fit to the following equation:

$$R(z) = U * z^m \quad (6)$$

Table 3—Experimental data power law fits for equation 6

	<i>.5 ml/hr, 5.2 kV</i>		<i>.5 ml/hr, 6 kV</i>		<i>.6 ml/hr, 7 kV</i>	
	Initial	2 min.	Initial	2 min.	Initial	2 min.
m	-0.61	-0.81	-0.56	-0.60	-0.57	-0.44
U	0.04	0.04	0.04	0.03	0.03	0.02
R²	1.00	0.99	1.00	0.99	0.99	0.98

The power law exponents for the experimental data ranged from -.44 to -.81, with the expected exponent being -.5. Most experimentally obtained exponents were within 20% of the expected value, with the only outlier being the .5 ml/hr, 5.2 kV case. In most cases, there was a low dependence on the $z^{-1/4}$ scaling term in equation 4. The experimental power law fits of region iii also showed little dependence on the $z^{-1/4}$ term; these two observations lead to the assertion that there is no jet thinning region present in the linear jet of PEO-chloroform.

4.3 PEO – Chloroform Velocity Profiles

The velocity of the electrospinning jet was analyzed for the 2 wt% PEO – chloroform system for several sets of processing conditions and at different time evolutions of the electrospinning cone. This was achieved using particle tracking

software to analyze the motion of the particles in the jet itself, which were assumed to represent the velocity of the surrounding fluid. Difficulties arose in tracking due to poor lighting conditions and jet movement issues, with the jet moving in and out of the plane of focus; however, these problems were minimal for the cases without the addition of an organic salt. In any case, due to technical limitations, usually only a few particles were available for tracking for each set of processing conditions; however, the points seem to be fairly precise based on cases when multiple particles were available.

Changes in processing conditions have previously been shown to alter the velocity of the electrospinning jet.^[5] In this analysis, the velocity was examined for a 2 wt% PEO – chloroform solution at .5 ml/hr 5.2 kV, .5 ml/hr 6 kV, and .6 ml/hr 7 kV; all of these conditions were analyzed at jet initiation and 2 minutes after the initiation.

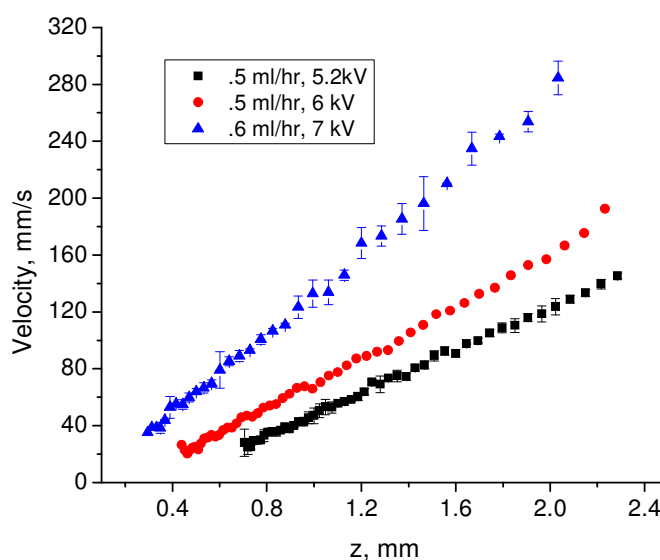


Figure 21--Velocity profile of initial jet formation for various processing conditions.

All of the velocity profiles behave linearly; as can be seen in figure 21, increasing the voltage and/or flow rate resulted in an increase in fluid velocity. Increase of only the voltage seemed to simply shift the curve upwards with little change in slope, while increase of flow rate in addition to voltage changed caused a larger change in slope as well as an increase in the magnitude of the observed velocity. The velocity for the same jets 2 minutes after the initiation is shown in figure 22. Again, all of the velocity profiles behave in a linear fashion.

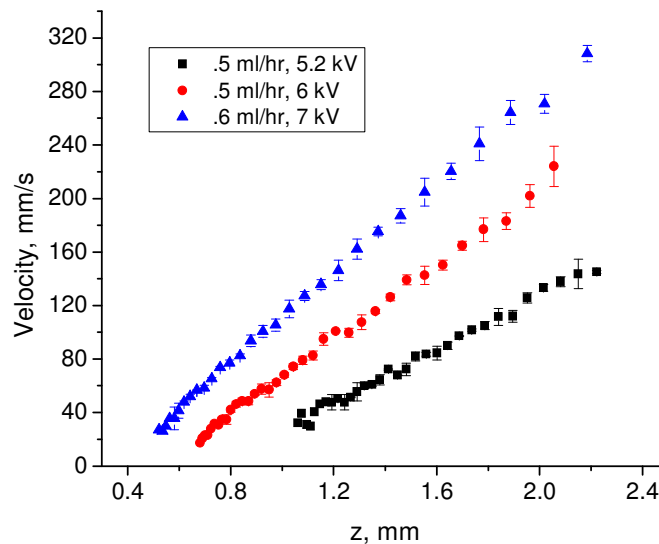


Figure 22--Velocity profile of jets 2 minutes after initiation for various processing conditions.

Velocity measurements were fairly consistent over the time scale of image capture; however, there was a significant change in velocity from the initial images taken at jet initiation to the second set of images taken two minutes after initiation, as shown in figure 23.

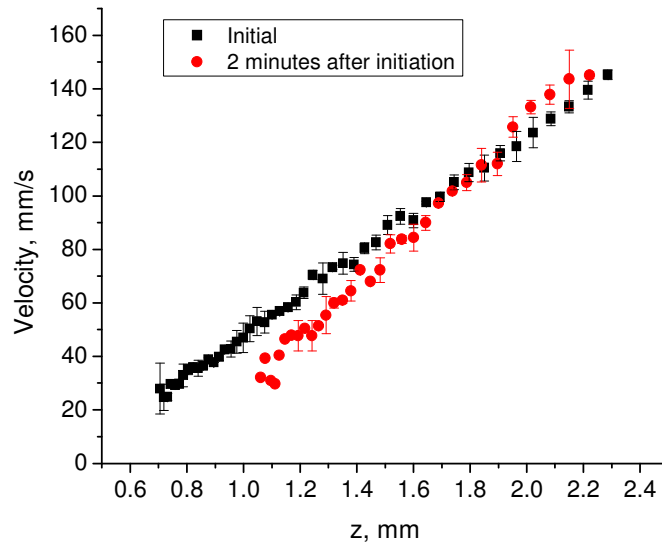


Figure 23--Velocity of .5 ml/hr, 5.2 kV system at jet initiation and 2 minutes after initiation

As can be seen in figure 23, the slope of the velocity curve tended to increase with increasing time as the cone region grew. Also, the difference between slopes at initiation and 2 minutes after initiation tended to increase with increasing voltage. This change in velocity profiles again shows that the growth of the cone due to the polymer skin formation has a significant effect on this electrospinning process. The growth of the cone adds a time dependent component to the electrospinning jet, making it impossible to achieve a pseudo-steady state for this system.

4.4 Scaling Discussion

Previously obtained results for the PEO-water system confirmed that the velocity scaled initially with z in the jet stretching region, followed by the jet thinning region where velocity scaled with $z^{1/2}$. This was an idealized system and had a bending instability present. While the PEO-water system had both scaling regions present, the PEO-chloroform system currently under investigation showed only a velocity dependence that was linear and scaled only with z . This can be seen in all of the figures containing experimental velocity plots: all of the experimental velocities follow a linear trend. This fact, along with the radius dependence on $z^{-1/2}$, seem to indicate that the linear electrospinning jet does not contain region iv, the jet thinning region.

There are several potential reasons for the linear jet's lack of a jet thinning region: increased solvent evaporation rate and formation of polymer skin due to chloroform's high vapor pressure, lack of the bending instability, or accumulation of charge density at the initiation of the electrospinning jet. High speed images measured approximately 2.5-3 mm down the jet, but visual verification ensured that there was no bending instability present. In order to determine the effect of the solvent evaporation on the velocity curves, experimental velocities were plotted against a calculated velocity. The calculated velocity was found from equation 1, and is based on the assumption that the jet velocity was plug flow with no solvent evaporation, similar to the analysis used by Helgeson et al.^[13] In all cases for the PEO – chloroform system, for both the initial jets and the jets analyzed after 2 minutes, experimental velocities were higher than the calculated velocities that assumed no solvent evaporation, indicating the solvent evaporation could play a significant role in the PEO-chloroform

system. Figure 24 shows the both the experimental and calculated velocities for the initial jet at .5 ml/hr, 5.2 kV

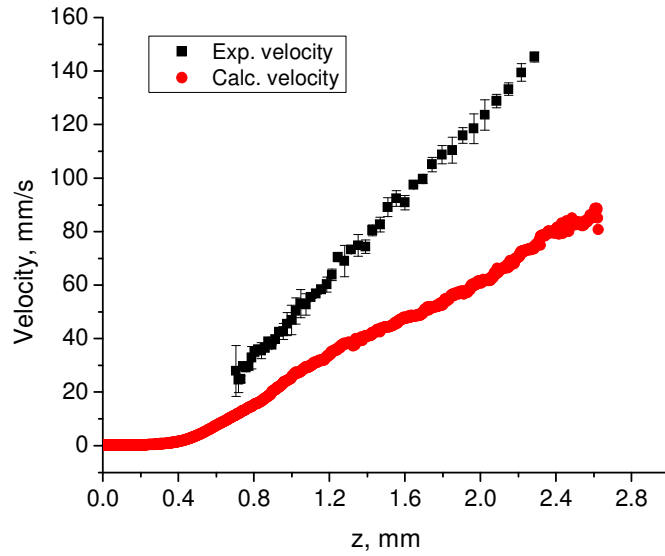


Figure 24--Initial experimental and calculated velocity for .5 ml/hr, 5.2 kV system

While both profiles appear linear, the experimental velocity has a larger slope as well as larger magnitudes at the same z position. The initial jet for these processing conditions has a larger slope than the calculated velocity over the entire range studied; however, experimental and calculated velocities for the jet 2 minutes after initiation for the same processing conditions seems to have a region from $z \sim 1$ -1.5 mm where the slope appears to be equal, as presented in figure 25.

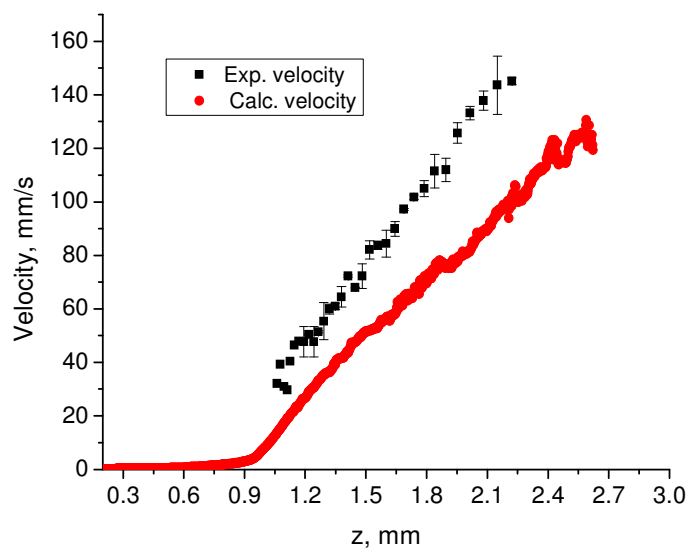


Figure 25--2 minute experimental and calculated velocity for .5 ml/hr, 5.2 kV system

In addition, the difference between the experimental and calculated slopes is less in the jet 2 minutes after initiation than the difference observed for the jet immediately after initiation. It is possible that the growth of the cone with time and the subsequent formation of the polymer skin on the cone partially negated the effects of solvent evaporation in the cone region, thereby yielding similar slopes for experimental and calculated velocities. This point is illustrated more clearly in figure 26, which presents data for the .6 ml/hr, 7 kV system two minutes after jet initiation.

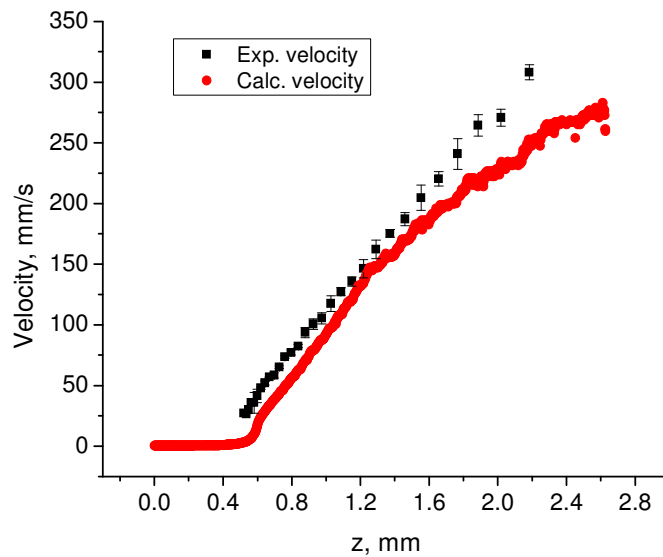


Figure 26--2 minute experimental and calculated velocity for .6 ml/hr, 7 kV 2 system

The calculated velocity assuming no solvent evaporation has a linear initial region and seems to also have a region that scales with $z^{1/2}$. The experimentally obtained velocity has essentially an identical slope and similar magnitude to the linear region of the calculated velocity, and only deviates further down the jet where the experimental velocity continues in a linear regime. Based on uncertainty in the radius measurements used to calculate a velocity, the experimental and calculated velocities are still statistically different. The data shows that the formation of the polymer skin on the cone region may provide an effective barrier to solvent evaporation, making an assumption of no mass transfer more reasonable. It also could show the time dependency of the formation of a pseudo steady jet. However, all of the experimentally obtained velocity data shows that solvent evaporation may play a large role in the electrospinning process. In addition, results of both velocimetry

measurements and radius profiles suggest that the linear jet does not experience a jet thinning region.

While solvent evaporation may play a role, the effect of charge build up may also be important. At jet initiation, evaporation of the solvent could have potentially caused a temporary increase in the viscosity of the solution. Therefore, a higher charge density may have been required to initiate the jet. This higher charge density could potentially account for the increased viscosity, and the fact that over time the experimental and calculated velocities seemed to approach each other. With time, the excess charge density in the jet could have been reduced. Even as the experimental and calculated velocities began to approach each other, they still seemed different at the furthest z position measured in the jet. Given more time, it is possible that both profiles could meet; however, more experimentation must be performed in order to analyze that possibility.

4.5 Future Analysis/Work

Due to time constraints and problems experienced with the electrospinning process for PEO-chloroform, it was not possible to obtain enough experimental results and data to conduct the analysis of the Ohnesorge vs. characteristic stress ratio. If zero shear viscosity measurements were made in addition to surface tension and final fiber diameter estimations, it would be possible to estimate whether or not the PEO-chloroform system could be correlated through the use of those two dimensionless groups. Also, in order to further confirm the assertions that the linear system only experienced radius scaling of $z^{-1/2}$ and velocity of z^1 , more measurements need to be taken. The reproducibility of both the radius and velocity experimental data seemed to be good, but only a small number of trials were able to be analyzed. In order to

achieve a higher degree of statistical significance, more sets of images will need to be analyzed at processing conditions already studied and additional processing conditions.

Also, further work should be performed in order to further elucidate the effect of solvent evaporation on the linear system. It may be possible that solvent evaporation plays a large role in keeping the jet linear, rather than the previous assertion that a low dielectric constant was the only requirement for a linear jet. Further experiments should be performed using a higher boiling low dielectric solvent than chloroform so that the effect of solvent evaporation could effectively be eliminated, as seemed to be the case for PEO-water. In this way, further study of linear jets could be performed, and scaling could be studied in the jet for yet another system. It would also allow for a determination of the effect of solvent evaporation on scaling and linear jet formation. In addition to experimentation with a higher boiling low dielectric solvent, more experiments should be performed exploring the effect of the bending instability on the electrospinning jet and the different scaling regions. It may be that use of a higher boiling low dielectric solvent will allow for a more stable jet, which could lead to easier measurement conditions for the altered conductivity solutions.

While more experimentation should be performed to continue to test the recently proposed electrospinning model, testing of applications should also be performed. Linear nanofibers have the potential to be used in numerous potential applications; one application of specific interest is the differentiation of neural stem cells along oriented nanofibers.^{[10][23]} However, one major problem with that research is the lack of a high quantity of uniform, spatially oriented nanofibers. Use of a low

dielectric solvent along with a biodegradable polymer might provide the capability to produce large quantities of oriented nanofibers. One specific system that should be investigated is the poly(ϵ -caprolactone)-chloroform system, as poly(ϵ -caprolactone) has already been shown to increase differentiation and is readily dissolvable in chloroform. Eventually it may be possible to create some type of biodegradable composite for spinal therapies using this technique.

Chapter 5

CONCLUSION

High speed imaging experiments were performed on a linear electrospinning jet system, poly(ethylene oxide)-chloroform, in order to further test a recently proposed electrohydrodynamic model of the electrospinning process. The model simplified existing balance equations based on important forces in different regions of the stable portion of an electrospinning jet. The previous model identified four regions in the stable portion of the jet, and radius and velocity scaling parameters for two of the regions (iii & iv) were identified. High speed images were obtained of a 2 wt% PEO-chloroform system at several processing parameters in order to determine the scaling in the stable portion of the jet. It was determined that the linear jet only had three distinct regions in stable portion of the electrospinning jet; specifically, there was no jet thinning region (region iv). After the jet initiation region, the radius was found to only scale with $z^{-1/2}$, while the velocity scaled linearly with z . Experimentation with PEO-chloroform identified that solvent evaporation plays a large role in the electrospinning process. A polymer skin was seen to develop as the electrospinning cone grew with time. Solvent evaporation was confirmed to have a significant effect on the system through comparison of calculated velocities based on a no evaporation assumption to experimentally obtained jet velocities. Agreement was found with the recently proposed Helgeson et al. model, with the exception that the linear electrospinning system currently under consideration did not undergo one of the expected regions. This indicates that, with more study, the model might have the

potential to serve as a link between solution properties & processing parameters and the final fiber diameter. Future work should include study of a larger number of trials to increase the statistical significance of the obtained data, as well as measurement of several solution properties in order to determine the potential correlation between the Ohnesorge # and characteristic stress ratio. Also, experiments should be performed with a high boiling low dielectric solvent to further investigate the effect of solvent evaporation on the electrospinning process. The creation of nanofibers, in particular oriented nanofibers, presents the opportunity to create new materials for a multitude of high tech applications; therefore, the model under consideration should continue to be tested and confirmed in order to provide a potential link between final fiber diameter and processing conditions. With a functional model, the electrospinning process can potentially be brought to a commercial scale and have a positive impact in multiple industries.

REFERENCES

- [1] A. Formhals, "Process and Apparatus for preparing Artificial Threads," U.S. Patent 1,975,504.
- [2] G. Taylor, "Electrically Driven Jets," *Proceedings of the Royal Society of London Series A-Mathematical*. Vol. 313, 1969, pp. 453-&.
- [3] D. Reneker, A. Yarin, H. Fong, and S. Koombhongse, "Bending instability of electrically charged liquid jets of polymer solutions in electrospinning," *Journal of Applied Physics*. Vol. 87, May. 2000, pp. 4531-4547.
- [4] S. Tan, X. Huang, and B. Wu, "Some fascinating phenomena in electrospinning processes and applications of electrospun nanofibers," *Polymer International*. Vol. 56, 2007, pp. 1330-1339.
- [5] J.M. Deitzel, J. Kleinmeyer, D. Harris, and N.C. Beck Tan, "The effect of processing variables on the morphology of electrospun nanofibers and textiles," *Polymer*. Vol. 42, Jan. 2001, pp. 261-272.
- [6] P. Panda, "Ceramic nanofibers by electrospinning technique - A review," *Transactions of the Indian Ceramic Society*. Vol. 66, Jun. 2008, pp. 65-76.
- [7] B. Veleirinho and F. Lopes-da-Silva, "Application of electrospun poly(ethylene terephthalate) nanofiber mat to apple juice clarification," *Process Biochemistry*. Vol. 44, Mar. 2009, pp. 353-356.
- [8] T.J. Sill and H.A. von Recum, "Electrospinning: Applications in drug delivery and tissue engineering," *Biomaterials*. Vol. 29, 2008, pp. 1989-2006.
- [9] H. Tong and M. Wang, "Electrospinning of Aligned Biodegradable Polymer Fibers and Composite Fibers for Tissue Engineering Applications," *Journal of Nanoscience and Nanotechnology*. Vol. 7, 2007, pp. 3834-3840.
- [10] S. Chew, R. Mi, A. Hoke, and K. Leong, "The effect of the alignment of electrospun fibrous scaffolds on Schwann cell maturation," *Biomaterials*. Vol. 29, Feb. 2008, pp. 653-661.
- [11] R.F. Kessick and J. Fenn, "Microscale Electrospinning of Polymer Nanowires for Sensing Applications," 2005.
- [12] B. Ding, M. Wang, J. Yu, and G. Sun, "Gas Sensors Based on Electrospun Nanofibers," *Sensors*. Vol. 9, Mar. 2009, pp. 1609-1624.
- [13] M.E. Helgeson, K.N. Grammatikos, J.M. Deitzel, and N.J. Wagner, "Theory and kinematic measurements of the mechanics of stable electrospun polymer jets," *Polymer*. Vol. 49, Jun. 2008, pp. 2924-2936.

- [14] J.M. Deitzel, J.D. Kleinmeyer, J.K. Hirvonen, and N.C. Beck Tan, "Controlled deposition of electrospun poly(ethylene oxide) fibers," *Polymer*. Vol. 42, Sep. 2001, pp. 8163-8170.
- [15] M. Hohman, M. Shin, G. Rutledge, and M. Brenner, "Electrospinning and electrically forced jets. I. Stability theory," *Physics of Fluids*. Vol. 13, Aug. 2001, pp. 2201-2220.
- [16] C. Thompson, G. Chase, A. Yarin, and D. Reneker, "Effects of parameters on nanofiber diameter determined from electrospinning model," *Polymer*. Vol. 48, Nov. 2007, pp. 6913-6922.
- [17] A. Yarin, S. Koombhongse, and D. Reneker, "Taylor cone and jetting from liquid droplets in electrospinning of nanofibers," *Journal of Applied Physics*. Vol. 90, Nov. 2001, pp. 4836-4846.
- [18] J. Feng, "The stretching of an electrified non-Newtonian jet: A model for electrospinning," *Physics of Fluids*. Vol. 14, Nov. 2002, pp. 3912-3926.
- [19] J. Feng, "Stretching of a straight electrically charged viscoelastic jet," *Journal of Non-Newtonian Fluid Mechanics*. Vol. 116, Dec. 2003, pp. 55-70.
- [20] H. Fong, I. Chun, and D. Reneker, "Beaded nanofibers formed during electrospinning," *Polymer*. Vol. 40, Jul. 1999, pp. 4585-4592.
- [21] J. Deitzel, C. Krauthauser, D. Harris, C. Pergantis, and J. Kleinmeyer, "Key parameters influencing the onset and maintenance of the electrospinning jet," *Polymeric Nanofibers*. Vol. 918, 2006, pp. 56-73.
- [22] V. Daga, M. Helgeson, and N. Wagner, "Electrospinning of neat and laponite-filled aqueous poly(ethylene oxide) solutions," *Journal of Polymer Science Part B-Polymer Physics*. Vol. 44, Jun. 2006, pp. 1608-1617.
- [23] S. Chew, R. Mi, A. Hoke, and K. Leong, "Aligned protein-polymer composite fibers enhance nerve regeneration: A potential tissue-engineering platform," *Advanced Functional Materials*. Vol. 17, May. 2007, pp. 1288-1296.

APPENDIX A

ALTERED CONDUCTIVITY

Difficulties arose with particle tracking for the altered conductivity series because of jet movement in and out of the high speed camera's plane of focus. While hard to track the particles in the best lighting and non-movement conditions, this movement in focal planes made it nearly impossible. However, two particles were able to be tracked for a small region after the cone during the initiation of a bending/whipping instability.

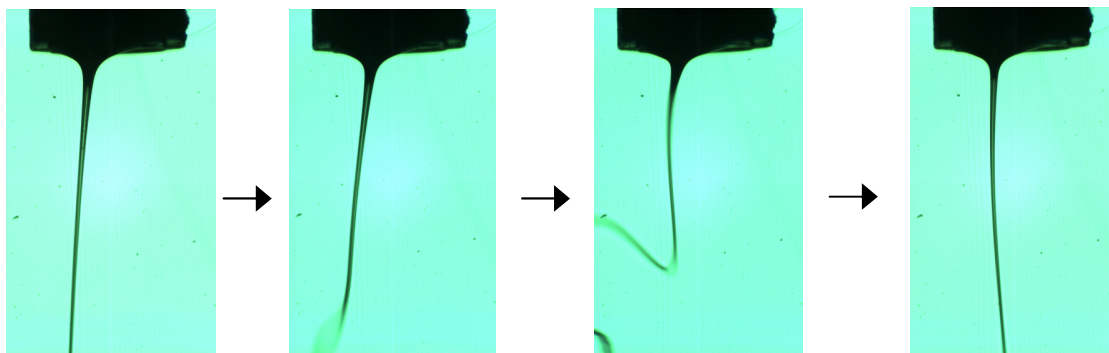


Figure A1—Initiation of a whipping in the electrospinning jet, 8 wt% Py.FA in 2 wt% PEO-chloroform

The velocity tracking showed the particle accelerating in accordance with previously obtained data, but then as the whipping instability materialized the particle began to slow down, potentially indicating that the bending instability is necessary to have a jet

thinning region where the radius scales with $z^{-1/4}$ and the velocity scales with $z^{1/2}$; however, more experimentation will be needed to prove this observation.

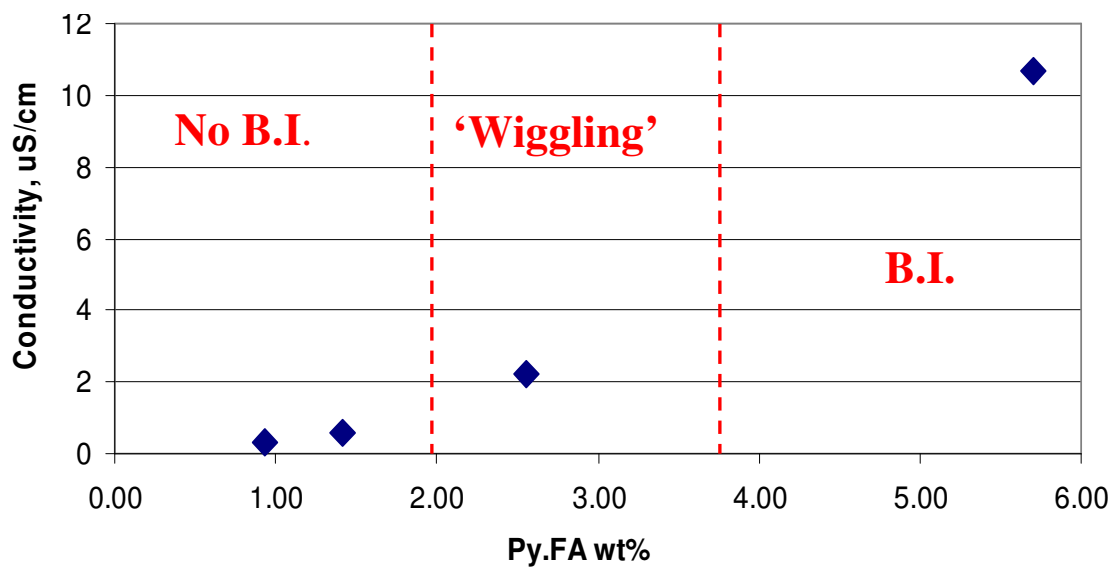


Figure A2—Conductivity of 2 wt% PEO-Chloroform solutions with various added amounts of Py.FA organic salt.

Addition of the organic salt pyridinium formate allowed for the linear jet to be transformed from completely linear to a jet with a bending instability, as shown in figure A2.

APPENDIX B

NOMENCLATURE

Oh_f = Ohnesorge number

Π = Characteristic stress ratio

ρ = Solution density

γ = Solution surface tension

R_f = Final fiber diameter

ε = Solution dielectric constant

ε_0 = Surrounding medium dielectric constant

η_0 = Zero-shear solution viscosity

$\eta_{e,\infty}^+$ = Pseudo-steady extensional viscosity

E_0 = Electrical potential between needle tip and collection plate

Q = Solution volumetric flow rate

z = Axial position down the length of electrospinning jet

R = Radius of the electrospinning jet

v = Linear velocity of the electrospinning jet

d = Needle tip to collection plate distance

V = Applied voltage

t_n^e = Surface normal electrostatic traction

t_t^e = Surface tangential electrostatic traction

τ_{zz} = Normal stress in the axial direction

τ_{rr} = Normal stress in the radial direction