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Nanomanufacturing and Analysis of Novel Integrated Continuous Nanofibers

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Nanomanufacturing and Analysis of Novel Integrated Continuous Nanofibers

by

John E. Hannappel

A THESIS

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Nanomanufacturing and Analysis of Novel Integrated Continuous Nanofibers

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Complex nanostructured materials have great potential for applications in many areas of nanotechnology. This potential is being unlocked by precise control of their nanoscale architecture and properties. Most current methods of creating these nanostructures are expensive and difficult to control, with the majority of techniques resulting in non-continuous nanostructures and nanoparticles. Electrospinning is an economic nanomanufacturing method resulting in continuous nanofibers. The method consists of spinning fiber-forming liquids in high electric fields. In this work, a modified electrospinning process was analyzed. The process utilized two concentric liquids that resulted in integrated continuous hollow or composite nanofibers. A new adjustable co-axial spinneret nozzle was developed to provide greater control of the nanomanufacturing process. The nozzle was used to manufacture continuous hollow one-dimensional (1D) nanostructures from several materials. The resulting nanostructures were observed and characterized by optical and electron microscopy. Process parameters effecting nanofiber dimensions were identified and their effects were analyzed in extensive systematic parametric studies. The results provide new insight into co-axial electrospinning and can be used for better control of the nanomanufacturing process and nanofibers. Integrated creation of more complex continuous 1D nanostructures that have never been produced before was explored by further process modifications. The challenges of creating such structures where identified for future investigation to succeed.
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Contents

List of Figures .................................................................................................................. vi
List of Tables .................................................................................................................... x
Chapter 1: Introduction ........................................................................................................ 1
  1.1 Nanotechnology ........................................................................................................ 1
  1.3 Nanomaterials ........................................................................................................... 2
    1.3.1 Zero-dimensional Nanomaterials ....................................................................... 2
    1.3.2 Two-dimensional Nanomaterials ....................................................................... 3
    1.3.3 One-dimensional Nanomaterials ....................................................................... 4
    1.3.4 Nanomaterials Applications ............................................................................. 4
  1.2 Nanomanufacturing ..................................................................................................... 5
    1.2.1 Bottom-Up ......................................................................................................... 6
    1.2.2 Top-Down ......................................................................................................... 7
  1.4 Nanomanufacturing Continuous Fibers by Electrospinning ..................................... 8
    1.4.1 Process ............................................................................................................... 8
    1.4.2 History .............................................................................................................. 10
    1.4.3 Setup ................................................................................................................. 11
  1.5 Nanomanufacturing Continuous Co-axial Fibers ..................................................... 13
  1.6 Applications of Continuous Nanofibers ................................................................... 14
    1.5.1 Continuous Co-axial Fiber Applications ......................................................... 15
  1.7 Summary .................................................................................................................... 16
  1.8 Objectives ................................................................................................................ 18
Chapter 2: Nozzle Optimization ......................................................................................... 19
  2.1 Co-axial Electrospinning Problems ........................................................................... 19
  2.2 Design Goals ............................................................................................................ 22
    2.2.1 Adjustability of the Protrusion Distance ......................................................... 22
    2.2.2 Concentricity .................................................................................................... 23
    2.2.3 Durability and Reusability ............................................................................... 23
  2.3 Previous Designs ....................................................................................................... 24
  2.4 High Level Design Options ....................................................................................... 25
    2.2.3 Hierarchy of Flow .............................................................................................. 26
A.3 Observation Methods ........................................................................................................113
  A.3.2 Sample Preparation ....................................................................................................114
A.4 Material Preparation .........................................................................................................118
A.5 Basics Setup ......................................................................................................................119
Appendix B: Effect of Process Variables on Additional Output Parameters ..................121
  B.1 Output Parameters ........................................................................................................121
    B.1.1 Percentage of Fibers Collapsed ..............................................................................123
    B.1.2 Fiber count per area ...............................................................................................123
    B.1.3 Percentage of Visible Fiber Ends ..........................................................................123
    B.1.4 Percentage of Hollow Fiber Ends .........................................................................124
B.2 Results .............................................................................................................................124
    B.2.1 Outer Flow Rate ....................................................................................................125
    B.2.2 Inner Flow Rate ....................................................................................................127
    B.2.3 Voltage ..................................................................................................................129
    B.2.4 Collector Type ........................................................................................................130
    B.2.5 Gap Size ................................................................................................................131
    B.2.6 Spinning Direction .................................................................................................132
    B.2.7 PVP Amount .........................................................................................................133
    B.2.8 Ti (IV) Amount ......................................................................................................134
    B.2.9 Effects of the Meniscus Volume ............................................................................135
Appendix C: SEM images .........................................................................................................138
  C.1 Smallest Outer Diameter Fibers ..................................................................................138
  C.2 Largest Outer Diameter Fibers ....................................................................................139
  C.3 Smallest Wall Thickness ..............................................................................................140
  C.4 Largest Wall Thickness ...............................................................................................141
  C.5 Smallest Relative Wall Thickness ..............................................................................142
  C.6 Largest Relative Wall Thickness ................................................................................143
Appendix D: Co-axial Nozzle Drawing ..................................................................................144
List of Figures

Figure 1: Top-down & Bottom-up approach[40]........................................................................ 6
Figure 2: Electrospinning diagram................................................................................................ 9
Figure 3: Formhals’ Device 1937[71].......................................................................................... 10
Figure 4: Formhals’ Device 1937[71].......................................................................................... 11
Figure 5: Publication search on "electrospinning” from the Web of Science[72]......................... 11
Figure 6: Basic Electrospinning Setup.......................................................................................... 12
Figure 7: Electrospinning Setup Modifications............................................................................ 13
Figure 8: Polymer Electrospun Nanofibers applications[93]....................................................... 15
Figure 9: Published Items of "co-axial electrospinning” search at the web of science[110]........... 16
Figure 10: Co-axial Electrospinning Problems.............................................................................. 21
Figure 11: Protrusion distance Schematic..................................................................................... 22
Figure 12: Co-axial Nozzle Designs............................................................................................. 25
Figure 13: Overview of High Level Design .................................................................................. 26
Figure 14: Hierarchy of Fluid Flow.............................................................................................. 27
Figure 15: Second Fluid Introduction Point .................................................................................. 27
Figure 16: Schematic of the Pre-Existing Design....................................................................... 28
Figure 17: First Co-axial electrospinning Spinneret Nozzle........................................................... 30
Figure 18: Co-axial Nozzle CAD image....................................................................................... 32
Figure 19: Co-axial Nozzle Photo............................................................................................... 32
Figure 20: Co-axial Nozzle Cross-sectional CAD image in extended position........................ 32
Figure 21: Co-axial Nozzle Cross-sectional CAD image in retracted position............................ 32
Figure 22: Sequence of Events .................................................................................................... 35
Figure 23: Screen shoot of video conditional experiment.............................................................. 37
Figure 24: Core position conditional experiment ......................................................................... 38
Figure 25: Core position conditional experiment procedure....................................................... 38
Figure 26: No Drop/Drop Size Triggers....................................................................................... 39
Figure 27: Example of mineral oil being pulled in to the co-axial jet center ................................ 45
Figure 28: Co-axial electrospinning Setup Photo.......................................................................... 47
Figure 29: Example of outer and inner diameter measurements ............................................... 50
Figure 30: Example of outer diameter and wall thickness.......................................................... 50
Figure 31: SEM Images of the Extreme Fiber Dimensions......................................................... 51
Figure 32: Effect of Outer Flow Rate on Outer Diameter w/ 0.75 ml/hr Inner Flow Rate................. 54
Figure 33: Effect of Outer Flow Rate on Outer Diameter w/ 0.75 ml/hr Inner Flow Rate................. 54
Figure 34: Effect of Outer Flow Rate on Inner Diameter w/ 0.55 ml/hr Inner Flow Rate................. 55
Figure 35: Effect of Outer Flow Rate on Inner Diameter w/ 0.75 ml/hr Inner Flow Rate................. 55
Figure 36: Effect of Outer Flow Rate on Wall Thickness w/ 0.55 ml/hr Inner Flow Rate................. 56
Figure 37: Effect of Outer Flow Rate on Outer Diameter w/ 0.75 ml/hr Inner Flow Rate................. 56
Figure 38: Effect of Outer Flow Rate on Relative Wall Thickness w/ 0.55 ml/hr Inner Flow Rate.......................... 57
Figure 39: Effect of Outer Flow Rate on Relative Wall Thickness w/ 0.75 ml/hr Inner Flow Rate.......................... 57
Figure 40: Effect of Outer Flow Rate on Relative Inner Diameter w/ 0.55 ml/hr Inner Flow Rate.......................... 57
Figure 41: Effect of Outer Flow Rate on Relative Inner Diameter w/ 0.75 ml/hr Inner Flow Rate.......................... 57
Figure 42: Effect of Inner Flow Rate on Outer Diameter.......................................................... 58
Figure 43: Effect of Inner Flow Rate on Inner Diameter.......................................................... 59
Figure 44: Effect of Inner Flow Rate on Wall Thickness.......................................................... 60
Figure 45: Effect of Inner Flow Rate on Relative Wall Thickness............................................. 61
Figure 46: Effect of Inner Flow Rate on Relative Inner Diameter............................................. 61
Figure 47: Effect of Voltage on Outer Diameter........................................................................ 63
Figure 48: Effect of Voltage on Inner Diameter........................................................................ 64
Figure 49: Effect of Voltage on Wall Thickness........................................................................ 64
Figure 50: Effect of Voltage on Relative Inner Diameter......................................................... 64
Figure 51: Effect of Voltage on Relative Inner Diameter......................................................... 65
Figure 52: Continuous Collector............................................................................................ 66
Figure 53: Gap Collector.......................................................................................................... 66
Figure 54: Effect of Electric Field Configuration on Outer Diameter........................................... 67
Figure 55: Effect of Electric Field Configuration on Inner Diameter........................................... 67
Figure 56: Effect of Electric Field Configuration on Wall Thickness........................................... 68
Figure 57: Effect of Electric Field Configuration on Relative Wall Thickness.............................. 68
Figure 58: Effect of Gap Size on Outer Diameter....................................................................... 69
Figure 59: Effect of Gap Size on Inner Diameter....................................................................... 69
Figure 60: Effect of Gap Size on Wall Thickness....................................................................... 70
Figure 61: Effect of Gap Size on Relative Wall Thickness......................................................... 70
Figure 62: Effect of Gap Size on Relative Inner Diameter......................................................... 70
Figure 63: Effect of Spinning Direction on Relative Outer Diameter.......................................... 73
Figure 64: Effect of Spinning Direction on Relative Inner Diameter.......................................... 73
Figure 65: Effect of Spinning Direction on Wall Thickness......................................................... 73
Figure 66: Effect of Spinning Direction on Relative Wall Thickness.......................................... 73
Figure 67: Effect of PVP Amount on Outer Diameter............................................................... 75
Figure 68: Effect of PVP Amount on Inner Diameter............................................................... 75
Figure 69: Effect of PVP Amount on Wall Thickness............................................................... 76
Figure 70: Effect of PVP Amount on Relative Inner Diameter.................................................. 76
Figure 71: Effect of PVP Amount on Relative Wall Thickness ............................................. 76
Figure 72: Effect of Ti(IV) Amount on Outer Diameter ................................................... 78
Figure 73: Effect of Ti(IV) Amount on Inner Diameter .................................................. 78
Figure 74: Effect of Ti(IV) Amount on Wall Thickness .................................................. 79
Figure 75: Effect of Ti(IV) Amount on Relative Inner Diameter ................................... 79
Figure 76: Effect of Ti(IV) Amount on Relative Wall Thickness ................................... 79
Figure 77: Tri-liquid Concentric Configuration ............................................................... 83
Figure 78: Island-in-the-sea Configuration .................................................................... 83
Figure 79: Tri-liquid Concentric Problems .................................................................... 85
Figure 80: TLC Nozzle CAD image ............................................................................... 86
Figure 81: TLC Nozzle Photo ......................................................................................... 86
Figure 82: TLC Nozzle Cross-sectional CAD image in extended position .................... 86
Figure 83: TLC Nozzle Cross-sectional CAD image in retracted position ..................... 86
Figure 84: New Tri-Liquid Concentric Nozzle .............................................................. 87
Figure 85: Preliminary Feeder Design .......................................................................... 88
Figure 86: Co-axial Feeder Design ............................................................................... 89
Figure 87: Open “V” Design ......................................................................................... 90
Figure 88: Nested “V” Design ....................................................................................... 90
Figure 89: Island-in-the-Sea Nozzle ............................................................................. 93
Figure 90: Intertwined INS Fibers ................................................................................. 94
Figure 91: Intertwined INS Fibers ................................................................................ 94
Figure 92: Poke Technique .......................................................................................... 111
Figure 93: Fiber transfer method from gap collector ...................................................... 113
Figure 94: Fiber Break Methods Illustration ............................................................... 115
Figure 95: Fiber Transfer Method to SEM .................................................................... 117
Figure 96: Co-axial electrosprinng Setup Photo .......................................................... 119
Figure 97: Extreme Conditions of Additional Output Parameters .............................. 122
Figure 98: Additional Output Parameters Measured .................................................... 124
Figure 99: Effect of Outer Flow Rate on Fiber per Area w/ 0.55 ml/hr Inner Flow Rate ................................................................................................................... 125
Figure 100: Effect of Outer Flow Rate on Fiber per Area w/ 0.75 ml/hr Inner Flow Rate ................................................................................................................... 125
Figure 101: Effect of Outer Flow Rate on Percentage of Fibers Collapsed w/ 0.55 ml/hr Inner Flow Rate ................................................................................................................. 125
Figure 102: Effect of Outer Flow Rate on Percentage of Fibers Collapsed w/ 0.75 ml/hr Inner Flow Rate ................................................................................................................. 125
Figure 103: Effect of Outer Flow Rate on Percentage of Visible Fiber Ends w/ 0.55 ml/hr Inner Flow Rate ................................................................................................................. 126
Figure 104: Effect of Outer Flow Rate on Percentage of Visible Fiber Ends w/ 0.75 ml/hr Inner Flow Rate ................................................................................................................. 126
Figure 105: Effect of Outer Flow Rate on Percentage of Hollow Fiber Ends w/ 0.55 ml/hr Inner Flow Rate ................................................................................................................. 126
Figure 106: Effect of Outer Flow Rate on Percentage of Hollow Fiber Ends w/ 0.75 ml/hr Inner Flow Rate ................................................................................................................. 127
Figure 107: Effect of Inner Flow Rate on Percentage of Fibers Collapsed ................. 127
Figure 108: Effect of Outer Flow Rate on Fiber per Area .............................................. 128
Figure 109: Effect of Inner Flow Rate on Percentage of Visible Fiber Ends ............ 128
Figure 110: Effect of Inner Flow Rate on Percentage of Hollow Fiber Ends .......... 128
Figure 111: Effect of Voltage on Percentage of Fibers Collapsed ..................... 129
Figure 112: Effect of Voltage on Fiber per Area ........................................ 129
Figure 113: Effect of Voltage on Percentage of Visible Fiber Ends ................. 129
Figure 114: Effect of Voltage on Percentage of Hollow Fiber Ends .............. 130
Figure 115: Effect of Collector Type on Percentage of Fibers Collapsed .......... 130
Figure 116: Effect of Collection Type on Fiber per Area .......................... 130
Figure 117: Effect of Collection Type on Percentage of Visible Fiber Ends ...... 130
Figure 118: Effect of Collection Type on Percentage of Hollow Fiber Ends .... 130
Figure 119: Effect of Gap Size on Percentage of Fibers Collapsed ............... 131
Figure 120: Effect of Gap Size on Fiber per Area ...................................... 131
Figure 121: Effect of Gap Size on Percentage of Visible Fiber Ends ............ 131
Figure 122: Effect of Gap Size on Percentage of Hollow Fiber Ends .......... 132
Figure 123: Effect of Spin Direction on Percentage of Fibers Collapsed ........ 132
Figure 124: Effect of Spin Direction on Fiber per Area ............................. 132
Figure 125: Effect of Spin Direction on Percentage of Visible Fiber Ends ...... 132
Figure 126: Effect of Spin Direction on Percentage of Hollow Fiber Ends .... 132
Figure 127: Effect of PVP amount on Fiber per Area ................................ 133
Figure 128: Effect of PVP on Percentage of Visible Fiber Ends .................. 133
Figure 129: Effect of PVP on Percentage of Hollow Fiber Ends .................. 133
Figure 130: Effect of Ti(IV) amount on Fiber per Area .............................. 134
Figure 131: Effect of Ti(IV) on Percentage of Visible Fiber ......................... 134
Figure 132: Effect of Ti(IV) on Percentage of Hollow Fiber Ends ............... 134
Figure 133: Effect of Meniscus Volume on Outer Diameter ....................... 135
Figure 134: Effect of Meniscus Volume on Inner Diameter ....................... 135
Figure 135: Effect of Meniscus Volume on Wall Thickness ....................... 135
Figure 136: Effect of Meniscus Volume on Relative Inner Diameter .......... 136
Figure 137: Effect of Meniscus Volume on Relative Wall Thickness .......... 136
Figure 138: Effect of Total Flow Rate on Meniscus Volume ....................... 136
Figure 139: Effect of Meniscus Volume on Fiber per Area ........................ 137
Figure 140: Effect of Meniscus Volume on Percentage of Visible Fiber ......... 137
Figure 141: Effect of Meniscus Volume on Percentage of Hollow Fiber Ends ... 137
List of Tables

Table 1: Co-axial Feeder Nozzle Flow Rate Test.......................................................... 89
Table 2: Milled Block Tri-liquid Concentric Flow Rate Test........................................ 90
Chapter 1: Introduction

The technology of manufacturing co-axial nanofiber has been improved by the integrated one step process of co-axial electrospinning. Co-axial electrospinning has the ability to produce both hollow and co-axial composite nanofibers with diameters ranging from a few nanometers to microns. A rapidly growing interest in the co-axial electrospinning process is based largely on an extensive of potential applications. In spite of this, systematic studies on the effect of the process variables on the co-axial fibers that are produced do not exist. This chapter presents a brief introduction to nanotechnology and nanomaterials and introduces the electrospinning and co-axial electrospinning process.

1.1 Nanotechnology

As technology advances, scientists and engineers are continuing to discover new methods to solve today’s highly complex problems. One promising area of interest in addressing these problems is nanotechnology.

Nanotechnology covers the study of production, synthesis, manipulation, testing and modeling of nanoscale objects. Nanotechnology provides the ability to create a
nanoscale object with unique properties. The unique properties that the nanoscale objects possess are the driving factor of the interest in this technology.

Nanotechnology can be defined as a use of methods of nanomeasurements and nanomanipulation to create nanoscale objects with unique properties. One specific property advantage of nanomaterials in fibers is the low surface area to volume ratio which results in a stronger fiber.

Being able to manipulate materials at the nanoscale level allows for the miniaturization of material structures and devices. Using nanotechnology will allow for expanded functionality and bring about smaller, cheaper, lighter and faster technology solutions; in turn, reduces the consumption of raw materials and energy. [1] Nanotechnology has yet to be utilized to its full potential of creating such advanced materials and devices.

1.3 Nanomaterials

Nanomaterials are defined as materials with at least one dimension in the nanoscale. There are three main categories that all nanomaterials can be classified into; zero-dimensional, one-dimensional, and two-dimensional. These classifications are based on the geometrical shape of the nanostructure and the number of nanoscale dimensions.

1.3.1 Zero-dimensional Nanomaterials

Zero-dimensional nanomaterials are materials with all three dimensions in the nanoscale. The nanomaterials that fall into this category would include nanoparticles, nanoclusters, and nanodots. These zero-dimensional nanomaterials provide the highest surface area to volume ratio of any nanomaterial.
A zero-dimensional nanostructure can be created by either top-down or bottom-up approaches. Some top-down approaches include milling or attrition, repeated quenching and lithography [2,3]. Some techniques for creating zero-dimensional nanomaterials include homogeneous and heterogeneous nucleation [4], microemulsion [5], aerosol [6], pyrolysis [7], and template-based deposition [8].

The zero-dimensional nanomaterials are commonly embedded into other materials to improve the material properties. However, to fully utilize the nanoparticles’ properties the particles need to be evenly and equally dispersed. Due to the surface chemistry of the nanoparticles agglomeration can make achieving even dispersion of particles challenging.

1.3.2 Two-dimensional Nanomaterials

Two-dimensional (2D) nanomaterials are materials with only one dimension in the nanoscale. Nanofilms are the primary nanostructure that occupies this category, but also include the nanostructure of platelets and graphene.

These nanofilms are nanometers thick coatings which can add desired properties to the material. This surface treatment of bulk materials is a well established process that is widely used in industry. Many of these surface treatments are only nano-size, so these treatments may be considered a two-dimensional nanomaterial. The two most popular deposition methods fall in to either vapor-phase deposition [9] or liquid-based deposition [10].

A two-dimensional nanomaterial that has received many accolades would be graphene. This single sheet of carbon atoms won the 2010 Nobel Prize in physics for the many unique properties with its ultra strength and superior conductivity that it possesses.
1.3.3 One-dimensional Nanomaterials

One-dimensional (1D) nanomaterials are materials with only one dimension in the nanoscale. The nanomaterials that fall into this category would include nanofibers, nanotubes, and nanorods. The additional length of these nanomaterials allows for a larger amount of applications that can be considered over other nanomaterials. There are multiple ways to create a one-dimensional nanostructure. However, there are four major categories that most processes fall into: spontaneous growth [11], template-based synthesis [12], lithography [13], and electrospinning.

The one-dimensional nanomaterials possess many of the same property advantageous as the zero and two-dimensional nanomaterials while providing ultra high axial properties. Similar to zero-dimensional nanomaterials the surface area to volume ratio is maximized for one-dimensional nanomaterials. One of the biggest advantageous for one-dimensional nanomaterials is the high surface area to volume ratio of the nanofiber. This limits the area for defects to occur producing a stronger fiber.

Also the increased strength found in two-dimensional nanomaterials can be produced in a one-dimensional form, simply by rolling a two-dimensional structure into a nanotube. An example of this is the creation of a single walled carbon nanotubes created from graphene sheets[14,15].

1.3.4 Nanomaterials Applications

Due to the unique properties that nanomaterials possess over bulk material, a broad range of potential applications can be achieved. A few applications of interest include electronic application [16], chemical sensors [17], and biological application
[18,19], and energy applications. These topics include only a sampling of some of the exciting research that is taking place in the nano-research community.

Nanomaterials allow standard electronic components, such as the transistor and switch, to be reduced down in size and approached in different ways that could only be accomplished through nanomaterials [20-24]. Biological applications use nanomaterials to help chemotherapy be more effective [25] and provide biological scaffolds [26,27]. By utilizing nanomaterials, nano-mechanical devices can be created to interact and sense many different environmental conditions [19,28,29] and chemicals [30-32]. With the demand to explore alternative sources of energy, the creation of lighter more efficient batteries is one challenge that nanomaterials by developing new, more efficient batteries and electrical storage devices [33,34]. Along with new batteries, new photovoltaic devices that can convert the sun’s energy into electrical energy are being explored using nanomaterials [35-37]. However, to achieve these applications controlled nanomanufacturing methods are needed.

1.2 Nanomanufacturing

There are two general approaches for manufacturing nanomaterials: top-down or bottom-up. These approaches are based on locating where the creation of the material was initiated. The bottom-up approach refers to the build-up of material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by-cluster.[38-40] The top-down approach refers to the reduction in size by removing material to obtain the nanoscale structure.[38-40]
1.2.1 Bottom-Up

The bottom-up approach allows for very precise nanomanufacturing and is the most frequently used nanomanufacturing method. The methods of molecular self-assembly, spontaneous growth, and template-based synthesis are a few of the bottom-up approaches that are available.

Self-assembly is a technique in which specific types of components or constituents spontaneously create an ordered aggregate through their chemical interactions [41]. With the chemical knowledge of certain materials engineers are able to create different combinations of materials accompanied with a functional material allowing the object to act as tiny machines.

Spontaneous growth is a process driven by the reduction of Gibbs free energy or chemical potential due to phase transformation or chemical reaction or the release of stress.[42] These phases include evaporation – condensation [43], vapor (or solution) – liquid – solid (VLS or SLS) growth [44], and stress-induced recrystallization [45].

Template-based synthesis is a very general method that can be used to create different nanomaterials. The basic process of this method requires that a template
material be used as a surface for material to accumulate. When the template is removed, a 1D nanostructure is left behind. There are four main techniques used to perform this process, including electroplating/electrophoretic deposition [46], colloid dispersion [47], melt or solution filling [48], and conversion with chemical reaction.

Currently, this technique is one of the most frequently used techniques in creating hollow nanofiber. Using the template method combined with a nanofiber template, hollow nanofibers can be created. This method requires two separate processes to occur to produce a hollow nanofiber.

The shortcoming to bottom–up manufacturing is the cost required to perform these techniques. These bottom-up processes are very time consuming and energy extensive processes. Also since there is only an incremental growth of the material only discontinuous nanomaterials can be created.

1.2.2 Top-Down

The top-down approach offers many different techniques. Three top-down techniques include comminution, lithography, and electrospinning. The advantage of starting at the “top” level and then removing material to create a nanostructure allows for a bridge between the micro and nano scales, which is one challenge of using nanomaterials in practical applications [49].

Lithography is a technique that nanoimprints nanoscale patterns onto a block of material.[50] Comminution is a process in which solid materials are reduced in size, encompassing crushing, grinding and other techniques.

Electrospinning is also a top-down approach. This process of drawing a polymer jet using an electric field, known as electrospinning, is the only nanomanufacturing
method that allows for the creation of a continuous one-dimensional nanostructure. While all prior nanomanufacturing techniques have length limitations and are discontinuous, this continuous one-dimensional structure creates applications and solves problems that no other nanomanufacturing method can accomplish.

One such problem is the ability to bridge the gap between the material properties of a nanoscale object with the usability of a macro scale object. [51] This problem has been demonstrated by the advanced composites reinforced with high-performance continuous fibers by Dr. Dzenis [52].

1.4 Nanomanufacturing Continuous Fibers by Electrospinning

Due to electrospinning’s unique ability to create a continuous one-dimensional nanostructure, the process of electrospinning will now be reviewed in detail.

1.4.1 Process

The process of electrospinning uses electrical forces to pull and elongate a fiber forming solution into a continuous solid nanofiber. These fibers can be produced with a diameter ranging from less than three nanometers to over one micron.[53] A schematic of this process is demonstrated in Figure 2.

The process of producing an electrospun fiber can be broken down into four stages: 1) jet initiation, 2) steady jet region, 3) instability region and 4) collector. The jet initiation occurs when the electrical force on the meniscus of the polymer solution overcomes the surface tension resulting in the polymer solution being ejected from the meniscus forming a liquid jet. This liquid jet continues in a steady state through the steady jet region. Once the jet has traveled through the steady jet region it enters into the
instability region were the jet begins to bend and randomly whip while the solvent is being evaporated. This jet, turned solid fiber, is than collected.

Figure 2: Electrospinning diagram
Jet initiation occurs when the electrical force on the meniscus of the polymer solution overcomes the surface tension resulting in the polymer solution being ejected from the meniscus forming a liquid jet. The meniscus shape is affected by the fluid’s material properties such as the surface charge and tension of the fluid. The electric field and the surface charges produce both normal and tangential electric stress on the surface of the meniscus \([54-56]\). When the electric field stress can overcome the surface tension of the drop, the jet initiation occurs. This jet initiation occurs at the tip of the conical shape drop, where the highest electrostatic force is located \([57]\). Once the jet is initiated the tangential electrical forces pull the jet towards the grounded collector \([58]\).

The second phase of the process is the steady region. This steady region can be evaluated using electrohydrodynamic principles \([59,60]\). The primary factors in producing a fiber are the molecular structure, surface tension, surface charge, and viscosity. Primarily due to the length of the macromolecular structure of the polymer
solutions used in electrospinning result in a continuous jet of solution that creates a continuous nanofiber. The viscosity of the fluid resists any rapid change in shape [61]. This is one of the major fluid properties in determining the size of the jet that is produced.

The balancing between the surface tension and surface charges determines whether the jet will remain continuous or break into droplets [62,63]. If the surface tension of the fluid is too large the fibers may break into droplets, which transform the process to electrospraying instead of electrospinning [64]. The electrical force on the surface area acts to maximize the surface area, counteracting the surface tension [61].

Once the jet has traveled through the steady jet region it enters into the instability region [55,56,65-67]. The primary source of this instability is due to the bending instability when the jet suddenly bends back and forth and moves irregularly out of the initial flowing direction[68]. This process of multiple bending of the jet produces a whipping effect that is the primary cause of the jet elongation and diameter reduction of the fiber [66].

1.4.2 History

Electrospinning has been around for over a century with the first patent for the creation of fibers by an electric field dating back to 1902 with Williams James Morton’s patent for “Method of Dispensing Fluids”[69]. Then in 1914, John Zeleny published the first article studying the electrified jet [70]. This study was then followed by a series of patents obtained by Anton Formhals from 1934 to 1939.[71,73-76] After Formhals, little interest was shown towards this method until
Electrospinning began with a few sporadic studies by: Baumgarten (1971) [77] and Larrondo (1981) [78-80]. In the early 1990’s the electrospinning process began to create substantial interest due to the research of Reneker[53,54]. Since then, interest in the electrospinning process has grown exponentially [72]. Along with major contributions from Dzenis group at the University of Nebraska on in-depth analysis of the electrospinning process, experimental, theoretically, modeling, and testing[52,81-84].

1.4.3 Setup

One advantage of the electrospinning process is the simplicity of the setup and equipment required to produce a nanofiber. There are only three pieces of equipment that are needed in order to produce an electrospun fiber. The schematic of the basic electrospinning setup can be seen in Figure 6. The first component is a voltage source that provides the needed electric field. The second is the spinning nozzle for holding the polymer solution in the electric field. The spinning nozzle in the basic setup is a capillary tube. This capillary contains the bulk polymer solution and provides the location for the electrical charged meniscus to originate. The final piece is the collector. The collector provides a place for the electrospun fibers to accumulate.
To control the flow rate, a syringe pump can be used. For some polymer solutions with ideal viscosities a capillary nozzle is all that is needed to produce an electrospun fiber. This occurs because the electrical forces provide sufficient force to overcome the capillary forces. However, for fluids with higher and lower viscosities the syringe pump is needed to control the flow rate.

One advantage of the electrospinning process is the simplicity of the setup and procedure in creating the nanofiber. However, the complexity of the process of electrospinning is very complex and must be understood in order to produce a highly controlled nanofiber.

The basic setup for electrospinning can also be easily manipulated and altered. Changing the collector type is a simple way to change the desired orientation of the fiber. The effects of the electric field can be altered by the addition of different electrodes and their position. Configurations to increase the production rates can be achieved by using multiple nozzles or even electrospinning from a pool of polymer solution.

The most substantial change that can be made to the electrospinning process comes in altering the design of the spinneret nozzle. These modifications are used to produce a complex multi-material fiber. From these modifications, the configuration of a
co-axial flow is of most interest due to the co-axial fibers that may be produced. Figure 7 includes many of these alterations.

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<tr>
<th>Electric Field Modifications</th>
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<th>Increased Production Rate Modifications</th>
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<tr>
<td>Porous electrospinning device</td>
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<td>Cylindrical collector</td>
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<td>Electrode</td>
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<th>Nozzle Modifications</th>
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<td>Solution B</td>
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<td>Positive high voltage</td>
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Figure 7: Electrospinning Setup Modifications

1.5 Nanomanufacturing Continuous Co-axial Fibers

There are multiple ways of producing a co-axial fiber, some continuous and some discontinuous. Many of the methods of producing co-axial and hollow nanofibers require the use of the bottom-up approaches [85]. Single-wall carbon nanotubes have been produced, although these ultra strong nanotubes are discontinuous due to the bottom-up manufacturing method that is used to create these nanostructures.
In order to create a continuous co-axial composite nanofiber, an electrospun fiber can be electrospun and then coated with a thin film [86]. Similarly, the electrospun fiber can be used as a template and then removed producing a continuous hollow nanofiber [87,88]. These techniques result in a continuous co-axial nanofiber, but require two steps to complete.

A co-axial fiber may also be produced by electrospinning an emulsified polymer solution.[89] Although the fibers are continuous a continuous co-axial fiber is not produced.

Co-axial electrospinning is an electrospinning configuration that can produce a continuous nanofiber from two immiscible fluids using a co-axial spinneret. This process has the capability of producing either a composite co-axial nanofiber, which consists of two materials, or a hollow nanofiber, which consists of having the core material removed. The co-axial electrospinning process is the only nanomanufacturing technique that can produce a continuous nanofiber in an integrated one step process from two immiscible fluids. All other techniques require either a two step process or can only produce a discontinuous one-dimensional nanostructure.

1.6 Applications of Continuous Nanofibers

With the highly controllable electrospinning nanomanufacturing process, multiple applications can be addressed. The advantage over other techniques, besides the continuous nature of the fiber, is the simplicity of the processes. When control can be accomplished, this process can be used in many different applications.

In the area of electronics, the electrospun nanofibers have the ability to produce super capacitors. In addressing different biological and healthcare issues, biosensors,
tissue scaffolds[90,91], medical devices, neural prostheses, drug coated stents[91,92], and artificial heart valves are all possible applications.

As the demand for renewable energy increases, applications such as photovoltaic, fuel cells, battery separators, and hydrogen storage become more desirable. There are many other applications that have been conceived for polymer electrospun fibers that can be seen in Figure 8[93].

![Figure 8: Polymer Electrospun Nanofibers applications][93]

1.5.1 Continuous Co-axial Fiber Applications

With the addition of a second layer to the electrospun fibers a new collection of applications that can be considered. This additional layer is interesting to the biological community for creating functionalized materials [94-97]. The different drug delivery [92,98-100] and scaffold tissue engineering applications [99,101-103] have been improved with the addition of a second fluid. Not only can the single fiber applications be improved with an additional layer of material, but new applications can also be accomplished. One such application is the ability to produce self healing materials [104].
Also, the co-axial electrospun fibers can be used as the next generation of energy storage devices [105,106] and have the ability to create flexible solar cells [107]. Furthermore, the continuous hollow nanofibers have been studied for use as micro fluidic tubes [108,109].

For many of these applications a desired geometry exists that is ideal for the given application. To obtain constant geometry of these co-axial fibers an understanding of the effects of the process variables on the output geometry needs to be established. These effects are the pivotal relationships that can be used to control the geometry of the co-axial nanofibers.

1.7 Summary

Nanotechnology provides the tools to create nanomaterials with unique and advantageous properties. There are three classifications of nanomaterials: zero-dimensional, two-dimensional, and one-dimensional; but only one-dimensional nanomaterial provide the unique advantages of ultra high axial material properties. These nanomaterials are either produced using a top-down or bottom-up approach. From these different nanomanufacturing methods electrospinning is the only one that can produce a continuous nanofiber.

The process of electrospinning uses electrical forces to pull and elongate a fiber forming solution into a continuous solid nanofiber. The basic setup of the
electrospinning setup is simple. However, the understanding of the complex
electrospinning process in order to achieve control of the nanofibers produced is a
common reason for growth in interest for electrospinning, along with the many different
applications that a one-dimensional continuous nanofiber can address.

The flexibility of the electrospinning process allows for the creation of a co-axial
fiber from two immiscible fluids by the process of co-axial electrospinning. The co-axial
electrospinning process is still an emerging nanomanufacturing technique that has been
around for less than a decade. The interest in this process is growing and can be found by
the publication search on “co-axial electrospinning” from the web of science seen in
Figure 9[110].

However, the increased interest has been focused towards the feasibility of
different material combinations[106,111-125] and feasibility of different
applications[89,94-97,99-103,105-109,126-132]. Out of all of the studies that have been
reviewed, there have been no systematic studies on the effects of the process variables on
the fibers produced by co-axial electrospinning. Due to this lack of systematic studies the
coop-axial electrospinning process variables, expected effect has be predicted from the
effects of the single fluid electrospinning process variables effect. The understanding of
these effects is pivotal in controlling the geometry of the co-axial fibers.

This lack of a detailed study about the process of co-axial electrospinning is
noted in a review article were it was stated that “no major review of the co-axial
electrospinning process has appeared to the knowledge of the authors but is needed in
order to develop a fuller understanding of the status of work in this field”[128].
Also missing from the studies on co-axial electrospinning is a nozzle capable of addressing all of the challenges of the co-axial electrospinning process. Bazilevsky, Yarin, and Megaridis addressed the fact that the needed concentricity of the two fluids was difficult to achieve, along with the fact that core entrapment is not automatically guaranteed and that the protrusion of the inner nozzle would help.[89,120,125]

1.8 Objectives

Due to the lack of systematic studies of the co-axial electrospinning process, a comprehensive preliminary parametric study of the co-axial electrospinning process needed to be performed. This parametric study identified the process variables and evaluated the effect of the process variables on the selected output parameters, ensuring that the geometry of the co-axial nanofiber could be more accurately controlled.

In order to complete this parametric study a standardized co-axial electrospinning procedure tailored to address the unique challenges of the co-axial electrospinning process needed to be created. This procedure would set a standardized process that could be repeated for testing the multiple process variables.

Along with a standardized procedure, the creation of a co-axial electrospinneret nozzle was developed. This nozzle was designed to address the specific challenges of core encapsulation and positioning that accompany the co-axial electrospinning process.

With the knowledge that was gained from the parametric studies, some advanced multi-liquid configurations were explored.
Chapter 2: Nozzle Optimization

The co-axial nozzle is a key component in the co-axial electrospinning process. The addition of another material is the key difference from the basic electrospinning process and coaxial electrospinning. Many of the fluid interaction problems in the co-axial electrospinning process originate at the design and capability of the spinneret nozzle.

This chapter will present some of the problems that occur during the co-axial electrospinning process and address how these problems can be solved with an improved co-axial electrospinneret nozzle. Included is the documentation of the evaluation and evolution of the co-axial nozzle which best achieved the design goals.

2.1 Co-axial Electrospinning Problems

The placement of the core fluid in the shell fluid’s meniscus is a critical predictor of whether or not a co-axial fiber will be electrospun. During the formation of the co-axial fiber, the two liquids produce a co-axial flow pattern. In order to produce a co-axial fiber a co-axial or concentric jet needs to be established. Knowing how this concentric jet is created is pivotal in understanding how the co-axial fiber is produced.
To create a concentric jet, the inner fluid must be injected into a laminar flow with a fluid velocity large enough to produce adequate shear force on the surface of the core fluid to result in a concentric flow pattern. Not being considered at this time due to no control of the nozzle design, is the surface forces and interaction/friction between the two fluids, which are large determining factor on the amount of shear forces that will be applied on the core fluid surface.

From this explanation, the desired placement of the core drop should be positioned at the location of largest fluid velocity that can be obtained inside the shell meniscus. Since there is a constant flow rate through the shell meniscus the highest fluid velocity would occur at the smallest cross-sectional area. This is located at the point of the spinning jet.

The spinning jet is located on the surface of the shell meniscus where the largest surface charge is located. In the single fluid electrospinning setup the largest surface charges are located at the tip of the meniscus. It is assumed that, this would be true for the co-axial electrospinning setup as well. To create a co-axial jet the desired location of the core meniscus is at the tip of the meniscus, which is where the largest fluid velocity occurs. This ideal position of the core meniscus can be seen in Figure 10.

If the core fluid is out of position, it will cause the shell polymer solution to electrospin into a single fluid jet without a core. The occurrence of this problem is the result of inaccurate placement of the core drop and indicates design flaws with the nozzle. These two problems can be seen in Figure 10 noted as the short position problem and the non-concentric problem.
In was observed that the jet had the ability to migrate to any point of the meniscus surface, even though the largest surface charge is located on the tip of the shell meniscus. Due to this observed effect, it is critical to minimize the electrospinnable area, where a single fluid jet is electrospun. It was also observed that inaccurate placement of the core resulted in enlargement of the single fluid electrospinnable area. This problem can be seen in Figure 10 as the extended position problem.

The core position is not the only source for increasing the single fluid electrospinnable area. The size of the inner and outer diameter directly affects the
electrospinnable area as well. The single fluid electrospinnable area enlarges as the difference between the inner and outer diameter increases. This problem can be seen in Figure 10 as the diameter problem.

2.2 Design Goals

In the single fluid electrospinning setup, the primary design variable of the nozzle is the diameter of the outlet nozzle. The co-axial spinneret must address both the position of the inner outlet nozzle and the size of the two outlet nozzles. From the co-axial electrospinning problems that have been identified, three design goals were addressing the solution of these problems were established. The three design goals include: the adjustability of the protrusion distance of the inner outlet nozzle, the concentricity of the two outlet nozzles, along with the durability and reusability of the nozzle.

2.2.1 Adjustability of the Protrusion Distance

The protrusion distance is an important dimension as it measures the distance that the inner outlet nozzle protrudes from the outer outlet nozzle. Figure 11 shows a schematic diagram that describes this distance.
The protrusion distance also determines the location of the core fluid within the shell meniscus. The short and extended position problems that are illustrated in Figure 10 can be solved by creating a co-axial nozzle with an adjustable protrusion distance.

### 2.2.2 Concentricity

The ability to maintain concentricity of the two nozzle outlets is pivotal in producing a co-axial fiber. The concentricity of the nozzle is the leading factor in the concentricity problem that was identified in the illustration in Figure 10. It is challenging to maintain the concentricity of outlet nozzles on this scale of nozzle outlets due to the small size of the diameters. These small dimensions leave little acceptable tolerance on the concentricity of the two outlet nozzles.

### 2.2.3 Durability and Reusability

The primary reason for designing this co-axial nozzle is to perform an extensive parameter study on the effects of the process variables on the output parameters. This co-axial electrospinneret must be used for multiple tests in a wide range of parameters and still have the ability to produce a high quality continuous co-axial nanofiber. In order to achieve this goal, the nozzle must be able to successfully electrospin many different chemical combinations and be easy to clean in order to keep all flow paths unobstructed.

To make the device cleanable, the nozzle should be easy to disassemble. Also, any small diameter flow paths should be either large enough for a wire to fit inside to plunge out the excess fluid or short enough so the pressure generated by a syringe is sufficient to remove any excess fluid.
2.3 Previous Designs

To evaluate how others addressed these problems, previous studies were examined. Most articles only provided a high level design and did not include the details of how the nozzle was created. [89,92,94,96,113,115,117,120,125,133-140] Only a few detailed designs with actual photos were found, some of which can be viewed in Figure 12.[121,141-145]

Many of these designs are very similar consequent designs. Wang [141] and Diaz [145] created their nozzles by producing a concentric output by using a standard “T” interconnector for tubing. Song[142] and Sun[121] used the same high level design but created a custom made device to achieve the design. Zhang’s design[143] appears to be created from a plastic dripper with a capillary inserted through the wall and then bent to produce the concentric output. Srivastava’s design[139] was created using etching techniques in order to create multiple concentric outlets. The problem with all of these designs is that they do not have an adjustable protrusion distance function.

Wang’s alternative design [144] created a completely new approach to the co-axial electrospinning technique. In his design, the inner outlet nozzle was inserted into the side of the shell meniscus. However, this design is problematic due to single fluid electrospinnable area expanding as a result of the perpendicular configuration.
2.4 High Level Design Options

To begin the design process of the new and improved co-axial electrospinneret nozzle, all high level design options were identified and evaluated. This evaluation provided the starting point for the detailed lower level designs. The high level designs were identified based upon the hierarchy of flow paths and the fluid introduction point.
2.2.3 Hierarchy of Flow

The hierarchy of flow options consists of two different flow paths. The flow path that is collinear with the outlet nozzle is considered the primary flow while the flow path that must cross into the primary flow path is the secondary flow path. The fluid that is identified as the primary fluid flows into the primary fluid path. The primary inner fluid and the primary outer fluid paths are taken into consideration. These two high level designs can be seen in Figure 14.

The problem with primary inner fluid design was to accomplish the adjustability of the protrusion distance, the adjustment would have to take place after the introduction of the secondary fluid. The primary outer fluid design approach could accomplish the adjustability of the protrusion distance with a sliding mechanism at the point of intersection. Because of this reason the primary inner fluid design was selected.
2.2.4 Second Fluid Introduction Point

The second fluid introduction point is the point at which the secondary fluid is introduced into the primary flow path. This can occur before or after the outlet diameters are reached. These two high level designs can be seen in Figure 15.

Because adjustability is a major design goal, the small size of the inner and outer nozzles prior to the introduction point become more challenging, therefore making a reduction of the diameters prior to the introduction point problematic. To achieve adjustability functionality, a reduction of the diameter after the introduction point is needed to allow for a more reliable and easier to manufacture sliding contact area.

The lengths of the outlet nozzles can also cause problems with holding the two outlet nozzles concentric. The longer the length of the outlet nozzle, the tighter the tolerance of the sliding mechanism at the introduction point needs to be. Though at first it may seem advantageous to reduce the diameter before the introduction point, the manufacturing of such a small sliding mechanism would be a significant challenge and lack in durability. For these reasons, the design option to introduce the secondary fluid prior to the diameter reduction was chosen.
2.5 Design Evolution

Multiple co-axial nozzle prototypes were created and tested. All prototypes were then analyzed and judged using the initial design goals that were previously established. In this section the three main prototypes are evaluated and analyzed, while the evolution of the design is described.

2.5.1 Pre-existing Design

Prior to these studies, a previous co-axial electrospinning test had been performed by a colleague, Chad Peterson. During this study, co-axial electrospinning spinneret was developed. This design was based on similar types of devices often used in co-axial electrospinning research. A schematic of this design, referred to as the pre-existing design can be seen in Figure 16.

In this design, the secondary fluid was introduced after the diameter reduction, while the outer fluid was the primary fluid. The introduction of the secondary fluid resulted in a long length of small diameter tubing being used as the inner outlet nozzle. The long small diameter outlet nozzle was bent and buckled because of the length. The introduction of the secondary flow was performed by using a T-joint. Although this design does obtain a co-axial geometric configuration, a large outer fluid inner diameter of ¼” was used. This large inner diameter is due to the fact that the T-joints are typically manufactured in standard sizes, with the pictured T-joint and tube combination reflecting the smallest size available. For this
design, the input fluids were transported from the syringe pump with a small metal tube with an OD of 2.5 mm and an ID of 0.5 mm. At this size of tubing, the higher viscous fluids had difficulty flowing and were extremely difficult to clean.

The nozzle did not have an adjustable protrusion distance because the inner outlet nozzle was locked into place once the nozzle was assembled. The outlet nozzles were not held concentric due to the length and small diameter of the tube used as an inner outlet nozzle. The force needed to insert the tube through the T-joint to create a liquid tight seal, resulted in the buckling of the inner nozzle outlet. Finally the tubing used to transport the fluid from the syringe pump to the nozzle was not easily cleanable.

Desired improvements, were to change the high level design to the desired design of having a inner primary fluid design with an introduction point prior to the diameter reduction of the outlet nozzle as well as adding the adjustable protrusion to the nozzle.

2.5.2 First Improved Design

The first improved design followed the desired high level design that had previously been set forth. The detailed low level design was created by using two syringes placed in a concentric configuration where the smaller syringe would be attached to the plunger of the larger syringe. This design was created using 3 ml syringe and 10 ml syringe and was held together by epoxy. To transport the fluid to the nozzle, plastic tubing that could create a tight fit around the metal tubes was used. On the outer end of the tubing, a disposable syringe needle was epoxied to create a connection point for the syringe in the pump. These tubes were larger than the metal tubing that was previously used to transport the fluid; however the connection of the tubes did not provide a reliable seal. A photo of this design can be seen in Figure 17.
The use of the syringes allowed for a smaller diameter to be used for the inner outlet nozzle, because of the connection point allowed the easy use of a syringe needle to be used as the outlet nozzle. However reducing the outer outlet nozzle was overlooked intentionally because of the focus on achieving an adjustable protrusion length.

This concentric syringe design was able to provide the desired adjustable protrusion distance. This design was effective because of the movable seal that the syringe possessed. The problem with this design was the method that the seal was attached to the inner syringe. The ideal situation of this two syringe setup, is to have the original large syringe seal and plastic mounting frame attached to the tip of the small syringe with the syringe needle protruding out. The actual result was quite different as the most efficient way to create the prototype was to epoxy the seal to the small syringe.

Although this did provide the needed sliding seal, it did not provide the axial alignment needed to maintain the outlet concentricity. This problem of not achieving axial alignment contributed to the failure of the second design goal of maintaining the concentricity of the two outlet nozzles. Having a single seal was the main contributor to the concentricity problem. To provide linear motion to a sliding object, a minimum of three contact points on two different planes are needed to constrain the motion in one
direction. The larger the distance between these two planes of contact, the smaller the axial misalignment that will occur. With the use of only one seal, the two planes of contact are very close to one another which results in the inner syringe not being held concentric with the outer syringe.

The main downfall of this design was the epoxy that was used to assembly the nozzle. The epoxy was good for holding pieces in the proper location, but when solutions with DMF or acetic acid were used the epoxy would become soft and deteriorate. This was an apparent problem because the whole assembly of this design was held together by epoxy. After running a single test, for an extend length of time the nozzle would begin to leak. Because the nozzle could not survive one test, it was deemed unfavorable.

It is reiterated that the quality of this design was dependent on how well the design goals were reached. This design was considered a significant improvement as it solved the primary design goal of providing the adjustable protrusion distance. While the other two design goals were not reached, some detailed low level design modifications would solve these problems.

2.5.3 Advanced Design

This nozzle was created using the same high level design that was used for all of the previous designs. This nozzle was milled from aluminum to remove the need for the epoxy. The nozzle was milled to emulate the same sliding mechanic of the syringe. A CAD image of the design can be seen in Figure 18, Figure 20, and Figure 21, and a photo of the nozzle can be seen in Figure 19. The CAD drawings of the co-axial nozzle can be seen in Appendix C.
For this design, new smaller tubing with smaller diameters were selected. The inner needle was made of an 18 gauge stainless tube. The outer needle was a stainless steel tube with a 0.1875” OD and a 0.09” ID. To provide a sliding motion with less axial misalignment, two contact points were create from Buna-N Dash # 040 O-rings. This sliding seal provided the desired adjustable protrusion distance, while maintaining the outlet nozzle concentricity. For this design Tygon tubes with a 1/16 inch ID where used to transport the fluid from the syringe pump to the nozzle. Tygon was chosen as the material of the tubing because of the chemical resistant properties that Tygon holds. In addition, the clear tubing is a convenient feature in monitoring the flow of the fluid in the tube. On the end of the tubes, male and female luer connectors were attached. This female luer connector allowed the attachment of any syringe. The male connector on the tube was attached to a thread female luer that could be attached and removed with the
threads that were taped into the body of the nozzle. These luers created a mechanical connection point rather than relying on epoxy.

2.6 Conclusions

This final co-axial electrospinneret nozzle addressed and solved all of the design goals that were established. The ability to adjust the protrusion distance was achieved by emulating the sliding motion of a syringe. The ability to maintain concentricity of the two needles was achieved by creating the proper constraint points to reduce the axial misalignment of the sliding motion. Finally, the ability to re-use the nozzle was achieved by creating tight mechanical connections with materials that are chemically resistant as well as being easy to disassemble for cleaning purposes.

The creation of the final nozzle design provides the tools to easily perform a repeatable and reliable test of the co-axial electrospinning process while addressing the unique problems that occur in the co-axial electrospinning process. The ability to be cleaned and quickly prepared for the next test was important in holding the nozzles design constant, while creating minimal change over time between tests.

Unlike all previous nozzle designs, this was the first co-axial electrospinning nozzle that provided an adjustable inner tip distance, while maintaining concentricity. This adjustability provides a flexible nozzle that can be adapted for many different configurations and fluids. This co-electrospinneret nozzle design is the first of its kind that provides adjustability of the protrusion distance and provided the desired features to perform a quality parametric study.
Chapter 3: Co-axial Electrospinning
Experimental Procedure

The co-axial electrospinning process at first glance does not seem that different or more complex than the electrospinning process, but a closer examination of this process reveals that this is not the case. The addition of a second immiscible fluid not only adds more of the same problems from electrospinning but also comes with its own unique set of challenges. The sequence of events that make up the co-axial electrospinning process is one of these unique challenges.

There is a lack of any detailed study on the process of co-axial electrospinning.[128] According to the articles that were analyzed regarding the co-axial electrospinning process the sequence of events that were performed was never addressed. All of the studies regarding co-axial electrospinning describe the process in the same manner as the single fluid electrospinning process, disregarding the sequence of events that occurred to produce the co-axial electrospun fibers. Unlike the single fluid electrospinning process the sequence of events that occur during the co-axial electrospinning process is very important.
In this chapter a detailed analysis of the co-axial electrospinning process was performed and the ideal process for the parametric studies was selected.

3.1 Analysis of Co-axial Electrospinning Procedure

To initiate the co-axial electrospinning processes there are multiple sequences of events that must occur to produce a co-axial jet. Not only will the sequence of these events be addressed but the timing of when each event occurs will also be evaluated.

3.1.1 Sequence of Events

In the co-axial electrospinning process there are four different events that need to occur in order for a co-axial fiber to be produced. The four events include: the starting of the outer fluid flow rate (Outer Flow), the starting of the inner fluid flow rate (Inner Flow), and the starting of the voltage (Voltage), while the collecting of the fibers (Fiber Collection) is the natural end for all of these sequences. The order at which these events occur is considered the sequence of events. There are six unique sequence of events that which can be seen in Figure 22.

![Figure 22: Sequence of Events](image-url)
The reason why these six sequence need to be analyzed is because of the different material properties the inner and outer fluids possess. In the co-axial electrospinning process the two fluids are immiscible and therefore possess very different material properties. This immiscible relationship between the two fluids is one of the driving factors for the importance of the sequence of events.

3.1.2 Timing Sequence

Once all of the sequences of events are established, the point at which the event should occur needs to be decided. The timing of the sequence is what determines when the proceeding event occurs. It was found through the examination of co-axial electrospinning tests that a set amount of time between events could not be held and still produce a co-axial jet.

The major problem of co-axial electrospinning is derived from the position and size of the core drop within the shell meniscus, which was set forth in chapter 2. In order to hold the two menisci position and size constant, it was decided that the timing sequences would depend on the passing of conditional experiments.

3.1.2.1 Video Conditional Experiment

To confirm that the nozzle meniscus was in the proper location the video conditional experiment was performed. The ideal method of confirming the proper core drop position was verified visually with the use of a high speed camera. Figure 23 shows a screen shot of PEO and mineral oil with the core fluid (mineral oil) in the ideal position for producing a co-axial jet, which was previously illustrated in Figure 10.
3.1.2.2 Core Position Conditional Experiment

The core position conditional experiment is the secondary method for confirming the ideal core position. This was performed when the video conditional experiment could not be performed.

This was done by dabbing the tip of the drop with a thin flat metallic plate, i.e. a knife or screw driver. This motion transferred the shell meniscus to the testing surface which could be visually verified to determine whether the core fluid was in the ideal position. If this was the case, then two concentric drops would be seen as demonstrated in Figure 24. If the dabbing of the drop resulted in no concentric drops than two minutes were allowed to expire and then the process was repeated, until the proper core position was established. The process of the dabbing of the drop is illustrated in Figure 25.
Due to the viscosity of the fluids and the narrow flow paths of the inlet tubing from the syringe pump, there was a large response time of the flow rate from the syringe.
pump to the outlet of the nozzle. To overcome this, a no drop/drop size conditional experiment was performed to determine when the flow rate had reached a steady rate. When two identical drop sizes are established, this confirms that the flow rate is constant and triggers the next event.

For the no drop conditional experiment, the desired drop size was no drop present at the outlet of the nozzle, which confirms that the flow rate has completely stopped. A depiction of these two tests can be seen in Figure 26.

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<tr>
<td><strong>Drop Size Conditional Experiment</strong></td>
<td>Clean &amp; Wait</td>
<td>Clean &amp; Wait</td>
<td>Clean &amp; Wait</td>
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</table>

Figure 26: No Drop/Drop Size Triggers

### 3.2 Co-axial Electrospinning Procedures

Now that all the tools and information about the co-electrospinning process has been gathered and examined the actual procedures that were performed can be established.

#### 3.2.1 Pre-spinning Procedure

At the beginning of every experiment the tubing and nozzle needed to be filled with the polymer solution. To expedite this process the continuous pumping function on the syringe pump is used to fill the co-axial nozzle. Once the fluid begins to exit the
nozzle the syringe pump is stopped and the beginning of the co-axial electrospinning procedure will not begin until the no drop conditional experiment passes.

3.2.2 Possible Co-axial Electrospinning Procedure

To further simplify the number of sequences it was determined that the inner and outer flow rates could be assumed as the same event because of the similarity of the events. This assumption reduced the number of possible co-axial electrospinning procedures to three. The three procedures that are used to create the co-axial electrospun fiber are: the Fluid-Voltage-Fluid (FVF) procedure, the Fluid-Fluid-Voltage (FFV) procedure, and the Voltage-Fluid-Fluid (VFF) procedure.

3.2.2.1 Fluid – Fluid – Voltage (FFV) Procedure

In the FFV procedure the ideal core position is established prior to the starting of the voltage. The problem with this procedure is that trying to produce the proper size and position of the core fluid is very challenging, due to the slow response time of the fluid flow. This is a problem because the fluid velocities produced by the electric field assist in maintaining this concentric configuration. For this reason this procedure was not selected to be used for the parametric studies.

3.2.2.2 Voltage – Fluid – Fluid (VFF) Procedure

In the VFF procedure a single fluid electrospinning jet was established prior to the addition of the second fluid. In this procedure the order at which the specific fluid flow is initiated is based on the two fluid properties. In this procedure the fluid, whether that is the inner or outer fluid, which produces the most stable electrospun fiber should be the first fluid flow that is initiated.
The problem with this procedure is that the voltage was turn on prior to the first fluid which can cause problems with the electrospinning of the first fluid. For this reason this procedure was not selected to be used for the parametric studies.

### 3.2.2.3 Fluid – Voltage – Fluid (FVF) Procedure

In the FVF procedure again a single fluid electrospinning jet was established prior to the addition of the second fluid. Again with the order at which the specific fluid flow is initiated is based on the two fluid properties. In this procedure the fluid, whether that is the inner or outer fluid, which produces the most stable electrospun fiber should be the first fluid flow that is initiated. Unlike the VFF procedure the voltage was turned on after the first fluid had been started. With the voltage problem solved this procedure was selected as the procedure to be used in the parametric studies.

### 3.2.3 Collection Procedure

In an attempt to collect only co-axial nanofibers the ideal core position was first verified using either the video conditional experiment or the core position conditional experiment. Once the ideal core position was established the collection of fiber was began. No set collection time was used for the co-axial electrospinning process due to the instability of the co-axial jet that was observed. For this reason once the ideal core position was no longer present the voltage was switched off and the collection of fibers ceased. A detail description of this process can be seen in Appendix A.

### 3.3 Conclusions

In this chapter, the analysis of all the possible procedures that are available were considered and evaluated. This evaluation of all the procedures resulted in concluding that the “Outer Flow – Voltage – Inner Flow” procedure was the best procedure for the
parametric study. Along with this selection the tools for dealing with the specific challenges of co-axial electrospinning process were established.

This procedure that has been selected provides a standard for all co-axial electrospinning tests to follow. This standardized process reduces the variation that may occur when performing multiple tests. For the materials and equipment this procedure creates the greatest opportunity for creating a co-axial fiber in a wide range of different variable parameters.

This procedure is the first of its kind and provides a starting point for which all co-axial electrospinning procedures can be based.
Chapter 4: Parametric Studies of Effect of Process Variables

To access the effect of the many different parameters that contribute to the creation of the hollow continuous nanofiber a standardized process was developed, along with a newly developed co-electrospinneret adjustable nozzle that allows for the nanomanufacturing in many different configurations. With these tools the first systematic preliminary study of the effects of the process variables on the output parameters were analyzed.

Currently the co-axial electrospinning community has focused the bulk of their research on feasibility studies of different material combinations[89,94-97,99-101,103,105,106,106-109,111-114,130,131]. There have also been a couple of studies modeling different unique behavior of the co-axial electrospinning process. One study was created to examine the buckling of co-electrospun fibers due to the evaporation difference of the two fluids[146]. Systematic parametric studies on the effects of the co-axial fibers have not yet been performed before.

Prior to these tests the effect of the process variables were generally accepted to follow the same effects as a single electrospun fiber [128]. This study provides some insight on whether those expectations can be confirmed or denied.
In this chapter the different process variables and output parameters will be described along with methods for collecting the output parameters. The first comprehensive systematic studies of the effects of the process variable and output parameters were analyzed.

4.1 Materials & Methods

Before the results of the effects of the process variables on the output parameters are analyzed, the different process variables and output parameters will be described along with the different methods that were used.

4.1.1 Material Combination Analysis

To focus the study on the parameters of the electrospinning setup one material combination was selected to be thoroughly investigated. From the literature that was found there were multiple combinations that could be used. [134][94,115,147][148][98][125,149][144][113,117][150] The three material combinations that were preliminarily tested were: PEO and Mineral Oil, PVP and PMMA, and PVP-Ti(IV) and Mineral Oil. The creation of these solutions can be seen in Appendix A.

4.1.1.1 PEO and Mineral Oil

The past experience of electrospinning PEO from previous tests provided the understanding of how the material reacts during the spinning process and how the material properties affect the electrospun fiber. Using an aqueous solution, such as PEO, the needed flow pattern of the fluid at the outlet of nozzle could be easily tested.

Some inner flow rate and outer flow rate parametric tests were performed on the PEO and mineral oil. These tests provided the analysis that was used in creating the co-axial electrospinning procedure that was established in the previous chapter.
These tests revealed that the PEO and mineral oil allowed for great visualization of the PEO and mineral meniscus. Figure 27 shows the PEO and mineral oil drop with the mineral oil being pulled into the center of the fiber to create the co-axial electrospun jet.

![Figure 27: Example of mineral oil being pulled in to the co-axial jet center](image)

4.1.1.1 PAN and PMMA

The PAN and PMMA combination were selected to the short list of candidates because of the ability to be carbonized into a hollow carbon nano-fiber. Preliminary testing of the co-axial electrospinning of the two fluids was preformed. During these preliminary test a few complications arose.

One problem that occurred was the solidification of the solution on the edge of the nozzle outlet which was a major hindrance on the co-axial electrospinning process. Also both materials were visually similar, so verifying if the core fluid was in the optimal position could not clearly be identified. The last big problem was the process of removing the core. To remove the core the PAN needed to be carbonized to degrade the core PMMA, this resulted in a hollow carbon fiber. This carbonization process is an energy extensive and time consuming process. Quick removal of the core was necessary so that multiple tests could be done.
4.1.1.3 PVP-Ti (IV) and Mineral Oil

The PVP-Ti(IV) and mineral oil combination was considered because of the prior studies of this material combination and the applications available for the Ti(IV). The PVP-Ti(IV) was a precursor to ceramic fibers. One specific application of the ceramic fiber that could be produced was the uses of these hollow fibers as a sensor material.[151]

Preliminary tests of the PVP-Ti(IV) were done to study the effect of the inner flow rate on the co-axial fiber. These tests resulted in the creation of some co-axial hollow fibers which could be measured and recorded. During these tests the ability to create co-axial fibers could be reached, and accomplished repeatedly.

One problem that occurred was the solidification of the fluid due to the reaction between the moisture in the air and the Ti(IV). This caused delays and difficulties, however a co-axial nanofiber was still obtainable.

The main reason for the selection of this material combination was because of the positive results of being able to quickly obtain a co-axial nanofiber during the preliminary test. Also the property of PVP-Ti(IV) being a precursor to a ceramic fiber was also advantageous due to the applications that are available for such a fiber. From these choices the PVP-Ti(IV) and mineral oil combination was selected.

4.2 Basics Setup

For all the experiments performed for producing the co-axial continuous nanofibers the basic electrospinning setup co-axial electrospinning was held constant excluding the process variables that will be identified. Similarly to the single fluid electrospinning setup a voltage source, co-axial nozzle, collector and two independent
syringe pumps were used. The full setup can be seen in Figure 28. The details about the equipment used in this setup can be found in Appendix A.

![Figure 28: Co-axial electrospinning Setup Photo](image)

**4.3 Process Variables**

The process variables examined were the adjustable input variables of the co-axial electrospinning setup. In determining the effect of these process variables on the output parameters, each test series that was performed only contained one controlled variable while all others were held constant.

In the co-axial electrospinning process there are multiple variables that can be adjusted that effect the production of the fibers. Here is a list of the process variables that were tested:

- Inner flow rate
- Voltage
- Collection plate type
- PVP amount
- Outer flow rate
- Spinning direction
- Gap size
- Ti(IV) amount
The effect of the process variables on the output was determined by performing a test and collecting a sample for which all the process variables were held constant. Then the process variable of interest was adjusted while all other variables were held constant for the next test. This continued to produce a test series on the process variable of interest. In addition to controlled dependence any possible other correlations were studied. These results are presented in Appendix B.

4.4 Scanning Electron Microscope (SEM) Methods

Once a test for a given set of parameters was collected, they were placed in an octane bath for 8 hours to remove the mineral oil core. The fibers were then transferred to the SEM stage; during this transfer the fibers were broke to expose the cross-section of the fibers. Further details about this procedure can be seen Appendix A.

The sample was viewed using the SEM. The SEM stage was placed in the Quanta 200 FEG Environmental Scanning Electron Microscope and examined. To increase the ability to obtain a cross-sectional view of the fiber breaks the stages was rotated 45° from horizontal.

The method of observation for all samples was held constant. The stage was viewed at a zoomed out state to capture an overall view of the quality of the fibers that were produced for a given set of output parameters. When a co-axial fiber was spotted, a zoomed-in photo was captured. This was repeated until 20 co-axial cross-sections were captured for one sample of a given set of output parameters. Once these images were collected they were analyzed.
4.5 Output Parameters

There are many factors that contribute to the end product of the co-axial electrospun hollow nano-fiber. The parametric tests were performed by varying one of the process variables while holding all other parameters constant. The output parameters were than measured and analyzed. In this section the output parameters will be identified and defined.

In addition to the output parameters that will be reviewed in this chapter there were additional qualitative output parameters that were collected. Information regarding these output parameters can be found in Appendix B.

4.5.1 Fiber Dimensions

To achieve the performance of the desired applications from co-axial fibers the geometry of the co-axial fiber is an important output parameter. Understanding the effect of the process variables on the output parameters is pivotal in controlling the geometry of the co-axial fibers.

The fiber dimensions output parameters include all the measure dimensions of the fiber. The dimensions of the fiber that were recorded were the outer diameter (OD), the inner diameter (ID) and/or the wall thickness (t).

Once the twenty co-axial images had been collected from a sample, as previously described, the images were loaded in to JMicroVision. Using JMicroVision the measurement tool was used to determine and record the pixel length of the desire dimension. The scale for each image was also measured and recorded so the conversion factor could be calculated.
The primary procedure in determining the dimensions of the co-axial fiber was to measure the outer diameter and inner diameter and calculate the wall thickness from the two values. These measurements were collected at the point of the break across the cross-section of the fiber. The dimensions of the fiber varied along the fiber length. An example of how the fiber diameter was measured can be seen in Figure 29.

Figure 29: Example of outer and inner diameter measurements

During the collection of the twenty co-axial images there were challenges. On occasion the SEM image was obstructed from viewing the entire inner contour. When this occurred, the wall thickness was measured instead of the inner diameter, and the inner diameter was calculated. This was considered the secondary procedure. An example of this obstruction can be seen in Figure 30.

Figure 30: Example of outer diameter and wall thickness
Throughout these tests a large range of sizes were observed. The extremes of these hollow fibers can be seen in Figure 31, and larger images can be seen in Appendix C.

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Figure 31: SEM Images of the Extreme Fiber Dimensions
4.5.2 Fiber Ratios

In addition to the diameters and wall thickness, two ratios were determined and analyzed. These ratios determine the relative wall thickness and relative inner diameter to the outer radius and outer diameter. This is important due to the unique information and relationship that can be observed from these two ratios.

The relative wall thickness is the ratio of wall thickness to outer radius. The relative inner diameter is the ratio of the inner diameter to outer diameter. These two ratios are very similar and in fact possess a mathematical relationship between the two ratios of: $\frac{t}{r_{out}} = 1 - \frac{ID}{OD}$

4.6 Parametric Process Analysis

Now that all the process variables and output parameters have been identified, the effect of the process variables on the output parameters can be analyzed. The process variables that were used in the testing these parameters and the results will be examined in this section.

4.6.1 Effects of Flow Rate

There were two different flow rates that were tested in this parametric study, the inner and outer flow rate. The inner flow rate is the flow rate of the core material of the fiber. The outer flow rate is the flow rate of the shell material of the fiber. These flow rates were controlled by two independently operated syringe pumps.

4.6.1.1 Effects of Outer Flow Rate

To test the effect of the outer flow rate on the co-axial fibers the continuous collector at a distance of 25 cm away from the nozzle tip was used in the upward
spinning direction. The voltage was held constant at 15.8 kV and the inner flow rate was held constant at 0.75 ml/hr. The outer flow rate range for this test series was from 0.4 to 1.9 ml/hr with test being performed at every 0.1 ml/hr increment.

Another test series was performed under a similar setup. In this test series all thing were the same except the inner flow rate was held constant at 0.55 ml/hr during this test series. The outer flow rate range for this test series was from 0.4 to 1.8 ml/hr with test being performed at every 0.05 ml/hr increment. As described before, twenty images from each test were collected and analyzed. From these images the effect of the dimensional output parameters could be evaluated.

The effect of the outer flow rate on the outer diameter can be seen in Figure 32 & Figure 33. For the test series with the constant inner flow rate of 0.55 ml/hr it was observed that the average outer diameter decreased when the outer flow rate increased for flow rates lower than 1 ml/hr, while the outer diameter did not change for flow rates larger than and equal to 1 ml/hr. The test series with the inner flow rate constant at 0.75 ml/hr was observed that the average outer diameter decreased when the outer flow rate increased. Another interesting trend that can be seen from the test series with an inner flow rate of 0.55 ml/hr was that the variation of the outer diameters was smaller when the outer flow rate was higher than 1 ml/hr than the variation of the outer diameter for outer flow rates lower than 1 ml/hr.
The effect of the outer flow rate on the inner diameter can be seen in Figure 34 & Figure 35. From these results it was observed that for the test series with the inner flow rate constant at 0.55 ml/hr the inner diameter decreased when the outer flow rate increased for flow rates lower than 1 ml/hr, while no change of outer diameter was observed, within the experimental error for flow rates larger than 1 ml/hr. The outer flow rate test series with the inner flow rate constant of 0.75 ml/hr was observed that the average outer diameter decreased when the outer flow rate increased.
The effects of the outer flow rate on the wall thickness can be seen in Figure 36 & Figure 37. From these results it was observed that for both test series with the inner flow rate constant at 0.55 and 0.75 ml/hr the average inner diameter decreased when the outer flow rate increased.

Another interesting trend that can be seen from the test series with an inner flow rate of 0.55 ml/hr was that the standard deviations of the inner diameters were smaller when the outer flow rate was higher than 1.2 ml/hr than the standard deviation of the inner diameter for outer flow rates lower than 1.3 ml/hr.

Figure 34: Effect of Outer Flow Rate on Inner Diameter w/ 0.55 ml/hr Inner Flow Rate

Figure 35: Effect of Outer Flow Rate on Inner Diameter w/ 0.75 ml/hr Inner Flow Rate
To further understand the effects of the outer flow rate on the fiber dimensions the relative wall thickness and relative inner diameter can be seen in Figure 38 & Figure 41. From these results it was observed that the average relative wall thickness slightly increased as the outer flow rate increased. While the relative inner diameter decreased as the flow rate increased.
Figure 38: Effect of Outer Flow Rate on Relative Wall Thickness w/ 0.55 ml/hr Inner Flow Rate

Figure 39: Effect of Outer Flow Rate on Relative Wall Thickness w/ 0.75 ml/hr Inner Flow Rate

Figure 40: Effect of Outer Flow Rate on Relative Inner Diameter w/ 0.55 ml/hr Inner Flow Rate
The overall conclusions about the effect of the outer flow rate on the co-axial fibers were from the two unexpected observations that were made. It was observed that both the average outer and inner diameter decreased when the outer flow rate increased for the test series with a constant inner flow rate of 0.75 ml/hr. The expected relationship was that the outer diameter would increase as the flow rate increases. This however was not the observed effect.

The smallest individual wall thickness and relative wall thickness was observed during the outer flow rate test at 1.3 ml/hr. This fiber had an outer diameter of 815 nm, inner diameter of 789 nm, wall thickness of 13 nm, and a relative wall thickness of 0.03 nm/nm.

4.6.1.2 Inner Flow Rate

To test the effect of the inner flow rate on the co-axial fibers a continuous collector at a distance of 25 cm away from the nozzle tip was used in the upward spinning direction. The voltage was held constant at 15.8 kV and the outer flow rate was
held constant at 1.75 ml/hr. Then the inner flow rate range for this test series was from 0.55 to 1.00 ml/hr with tests being performed at every 0.05 ml/hr increments.

The data from these tests were then graphed with the standard deviations of these measurements being displayed as the error bars in the graph. The effect of the inner flow rate on the outer diameter can be seen in Figure 42. From these results it was observed that the average outer diameter increased when the inner flow rate increased for flow rates less than 0.8 ml/hr, while the effect of the inner flow rate on the outer diameter was inconclusive for flow rates in the range of 0.8 to 0.9 ml/hr.

The effect of the inner flow rate on the inner diameter can be seen in Figure 43. From these results it was observed that the average inner diameter increased when the inner flow rate increased. From Figure 44 no change of the average wall thickness was seen, and even more so when the test at an inner flow rate of 0.75 is eliminated due to the large variation. The smallest wall thickness average from all the process variables was observed at 0.8 ml/hr with an average wall thickness less than 100 nm.

Figure 42: Effect of Inner Flow Rate on Outer Diameter
To further understand the effects of the inner flow rate on the fiber dimensions the relative wall thickness and relative inner diameter can be seen in Figure 46 & Figure 45.

From these results it was observed that the average relative wall thickness decreased slightly almost linearly as the inner flow rate increased. It was also seen that the average relative inner diameter increased almost linearly when the inner flow rate increased.
The overall conclusions about the effect of the inner flow rate on the co-axial fibers were from the strongest relationship that was observed this far in the parametric study. It was observed that the average outer diameter increased when the inner flow rate increased for flow rates less than 0.8 ml/hr. Also both ratios were almost linearly affected by the increase in the inner flow rate.

The smallest wall thickness average from all the process variables was observed at 0.8 ml/hr with an average wall thickness less than 100 nm. This is a significant
achievement as other areas of research only consider nanomaterials to objects with dimensions less than 100 nm.

4.6.2 Electrospinning Configuration Variables

There are different ways that the co-axial electrospinning equipment can be setup. In this section the effect of electrospinning configuration variables on the output parameters will be evaluated. These electrospinning configuration variables include the voltage, the collector type, and spinning direction.

4.6.2.1 Voltage

The voltage induced in the co-axial electrospinning process plays a very important role. The voltage is the driving force that produces the fiber. The electrical force is what causes the fluid to flow into the jet. It is expected that as the voltage is increased a stronger electric field will be created resulting in a smaller fiber.

To test the effect of the voltage on the co-axial fibers a continuous collector plate at a distance of 25 cm away from the nozzle tip was used in the upward spinning direction. The inner flow rate was held constant at 0.55 ml/hr and the outer flow rate was held constant at 0.9 ml/hr. These flow rates were chosen from the observations that were made in the previous experiments. The test began by taking the first sample at every different voltage tested. The voltage range for this test series was from 13 to 19 kV with tests being performed at every 1 kV increment.

The data from these tests were then graphed and the standard deviations of these measurements are displayed as the error bars in the graph. The effect of the voltage on the dimensions of the fiber can be seen in Figure 47 thru Figure 51. It was observed that the average outer and inner diameters were inconclusively effected by the inner flow rate,
due to the complicated nonlinear pattern, best characterized with a fourth order polynomial approximation. This odd behavior could be caused by the high variation of the nature of the electrospinning process. To overcome this issue a large sample size being collected from multiple samples from one test should be preformed.

In addition the smallest inner and outer diameter averages from all of the process variables was reached at the 15 kV tests with an outer diameter average of approximately 600 nm and an inner diameter average of approximately 300 nm.

It was observed that the average wall thickness decreased when the voltage increased for voltages larger than 13 kV. The 13 kV data point was excluded because of the large standard deviation of the sample. It was seen that relative wall thickness decreased when the voltage increased. While it was also observed that the relative inner diameter increased when the voltage increased. It should also be noted that the same nonlinear effect observed in the inner and outer diameter relationships could also weakly be seen in both of the ratios.

Figure 47: Effect of Voltage on Outer Diameter
Figure 48: Effect of Voltage on Inner Diameter

Figure 49: Effect of Voltage on Wall Thickness

Figure 50: Effect of Voltage on Relative Inner Diameter
The overall conclusions about the effect of the voltage on the output parameters were the unusual shape of the inner and outer diameters. It was observed that the voltage followed a fourth order polynomial curve in relationship with the outer and inner diameters. In addition the smallest inner and outer diameter averages from all of the process variables was reached at the 15 kV tests with an outer diameter average of approximately 600 nm and an inner diameter average of approximately 300 nm.

From these test and previous ones it appears that the voltage adjustment is a parameter that should be adjusted during the co-axial electrospinning process. The voltage should be adjusted to finely control the flow rate of the fluid exiting the meniscus. This flow rate is influenced by the electric field and the meniscus size can be controlled by the voltage. It should be adjustable so that a constant meniscus size can be controlled. The desired exit flow rate of fluid from the meniscus (controlled by the voltage) should be equal to the input flow rate of the meniscus (controlled by the syringe pump). Match these two flow rates provide better control on the core position problem.

![Figure 51: Effect of Voltage on Relative Inner Diameter](image-url)
4.6.2.2 Electric Field Configuration

The modification of the electric field due to different collector geometries was evaluated in these tests. The basic continuous collector setup is a grounded flat plate. The flat plate creates an axisymmetric electric field that allows the fibers to accumulate randomly and create a nonwoven random orientated fiber mate. If more control of the direction of the fibers is desire a non-axisymmetric electric field can be created by using a split-electrode or gap collector. This non-axisymmetric electric field produces fibers that are orientated perpendicular to the parallel gap.

For the continuous collector a flat plate of aluminum wrapped in aluminum foil was used as the grounded collector. This continuous collector can be seen in Figure 52. To achieve the split-electrode collector two small plates of aluminum where attached to two bridge pieces using bolts. This created a narrow parallel gap for the fibers to accumulate. To allow for an adjustable gap size one of the aluminum plates had multiple holes insert at equally space distances apart. This allowed the gap size to be adjusted when deemed necessary. This gap collector can be seen in Figure 53.

![Figure 52: Continuous Collector](image1)

![Figure 53: Gap Collector](image2)
To test the effect of the collector type on the co-axial fibers a collector plate at a distance of 25 cm away from the nozzle tip was used in the upward spinning direction. The inner flow rate was set at 0.55 ml/hr and the outer flow rate was set at 1.0 ml/hr with a voltage of 17 kV. These parameters were chosen because of the observations that were made in the previous experiments. Four samples were taken while using the continuous plate collector and four samples were taken while using the gap collector with a gap size of 5.5 cm.

The data from these tests were then graphed and the standard deviations of these measurements are displayed as the error bars in the graph. The effect of the collection type on the dimensions of the fiber can be seen in Figure 54 thru Figure 57.
Overall the effect of the collector type on the output parameters was consistent for all fiber dimensions. It was observed that the average inner diameter, outer diameter and wall thickness were larger for the gap collector. Also, it was seen that the average relative wall thickness did not change. Also the standard deviation of the inner diameter, outer diameter and wall thickness were smaller for the continuous collector.

4.6.2.3 Gap Size

To analyze the effect of the gap size on the co-axial fibers a gap collector at a distance of 25 cm away from the nozzle outlet was used in the upward spinning direction. The inner flow rate was set at 0.55 ml/hr and the outer flow rate was set at 1.0 ml/hr with a voltage of 16 kV. These parameters were chosen because of the observations that were made in the previous experiments. One test consisted of the collection of two samples for every gap size. The initial plate distance was 5 cm. Then the plate distance was decreased by increments of 1 cm until the final distance of 1 cm was reached.
The data from these tests were then graphed and the standard deviations of these measurements are displayed as the error bars in the graph. The effect of the gap size on the dimensions of the fiber can be seen in Figure 58 thru Figure 62. From these results it was seen that the average outer diameter, inner diameter and wall thickness increased as the gap size increase. While the relative wall thickness and relative inner diameters were seen to be insensitive to the increase of the gap size. The highest wall thickness average of all process variables was observed at a 5 cm gap size, with an average wall thickness of 600 nm.
Figure 60: Effect of Gap Size on Wall Thickness

Figure 61: Effect of Gap Size on Relative Wall Thickness

Figure 62: Effect of Gap Size on Relative Inner Diameter
Overall it was observed that the average outer diameter increased as the gap size increased. Also the highest wall thickness average of all process variables was observed at a 5 cm gap size, with an average wall thickness of 600 nm.

The smallest individual inner diameter was observed during the gap size test at 1 cm. This fiber had an outer diameter of 517 nm, inner diameter of 93 nm, wall thickness of 212 nm, and a relative wall thickness of 0.82 nm/nm. The smallest individual relative inner diameter was also observed during the gap size test at 1 cm. This fiber had an outer diameter of 912 nm, inner diameter of 116 nm, wall thickness of 398 nm, and a relative wall thickness of 0.87 nm/nm.

4.6.2.4 Spinning Direction

The spinning direction is another electrospinning modification that can be change in the setup. The spinning direction is the direction that the electrospinning takes place. The down spinning direction occurs when the flow of the liquid/jet is down. The spinning direction can be performed at any angle off of the horizontal plane.

The biggest variable that the spinning direction changes, is the effect of the gravity. It is known that the gravitation force is not a significant effect on the single fluid electrospinning process. However, in the co-axial electrospinning the density difference of the two materials can either produce an advantage or a disadvantage depending of the densities of the two fluids and the spinning direction.

For the co-axial electrospinning setup the two choices that were tested was up and down spinning directions. To determine if the spinning direction has any effect on the
output process parameters some tests were performed to determine if any relationships could be observed.

To test the effect of the spinning direction on the co-axial fibers a gap collector with a 1 cm gap, at a distance of 25 cm away from the nozzle outlet. The inner flow rate was set at 0.55 ml/hr and the outer flow rate was set at 1.0 ml/hr with a voltage of 16 kV. These parameters were chosen because of the observations that were made in the previous experiments. Three samples were taken during the spinning up test and three samples were taken during the spinning down test. The best sample that was collected was used and twenty images were collected for the respective test. The best sample was chosen visually from the SEM overall images that were taken.

The data from these tests were then graphed and the standard deviations of these measurements are displayed as the error bars in the graph. The effect of the spinning direction on the output parameter of the fiber can be seen in Figure 63 thru Figure 66. From these results it was seen that the average outer diameter, inner diameter, wall thickness and relative wall thickness was larger for the spinning down direction. However it was also observed that the variation of the outer diameter and inner diameter decreased for the up spinning direction. The relative wall thickness was observed to be insensitive to the spinning direction.
In conclusion the most unusual effect that was observed was the difference in the two spinning directions as the gravitational forces are insufficient compared to the electrical forces. However it was observed that the standard deviation of the outer diameter and inner diameter decreased for the up spinning direction and the fiber dimensions decreased for the up spinning direction.
The smallest individual outer diameter was observed during the down test. This fiber had an outer diameter of 221 nm, inner diameter of 124 nm, wall thickness of 48 nm, and a relative wall thickness of 0.44 nm/nm.

4.6.3 Material

The amount of the materials in the fluid solution has a large effect on the output parameters. The conductivity, viscosity, and surface interactions of the material are all very important aspects in the co-axial electrospinning process. In this section the amount of that impact within a single solution is investigated. In the entire previous test performed the material composition was held constant at the following values: PVP: 0.3 g, EtoH: 5 ml, Ti(IV): 3 g, Acetic Acid: 2 ml

4.6.3.1 PVP Amount

It is known that as the PVP amount is lowered, a smaller diameter of nano-fibers can be obtained, due to the lower viscosity of the PVP solution. To test the effect of the PVP amount on the co-axial fibers a gap collector with a 1 cm gap, at a distance of 25 cm away from the nozzle outlet, was used. The inner flow rate was set at 0.55 ml/hr and the outer flow rate was set at 1.0 ml/hr with a voltage of 16 kV. These parameters were chosen because of the observations that were made in the previous experiments. The three PVP amounts that were tested were 0.1, 0.3, and 0.5 g. From each test two samples were collected. From these two samples, twenty total images were examined. The rest of the material amounts were held constant at: EtoH: 5 ml, Ti(IV): 3 g, Acetic Acid: 2 ml.

The data from these tests were then graphed and the standard deviations of these measurements are displayed as the error bars in the graph. The effect of the PVP amount on the output parameters of the fiber can be seen in Figure 67 thru Figure 71. It was
observed that the outer diameter and inner diameter remain constant for 0.1 and 0.3 g of PVP and then rose for 0.5 g of PVP. These outer and inner diameter averages at 0.5 g were the largest outer and inner diameter averages observed from all of the process variable tests.

It was observed that the wall thickness increased slightly as the PVP amount increased. It was also seen that the average of the relative inner diameter increased for each step increase of PVP. Similarly it was observed that the average of the relative wall thickness decreased for each step increase of PVP.

![Figure 67: Effect of PVP Amount on Outer Diameter](image1)

![Figure 68: Effect of PVP Amount on Inner Diameter](image2)
Figure 69: Effect of PVP Amount on Wall Thickness

Figure 70: Effect of PVP Amount on Relative Inner Diameter

Figure 71: Effect of PVP Amount on Relative Wall Thickness
4.6.3.2 Ti (IV) Amount

From the previous experience it was seen that the reaction with the moisture in the air with the Ti(IV) is a major challenge to overcome during the co-axial electrospinning process. It was the hope that as the Ti(IV) amount was lowered the amount of solidification at the nozzle outlet would reduce, resulting in a better co-axial nanofiber.

To test the effect of the Ti(IV) amount on the output parameters a gap collector with a 1 cm gap, at a distance of 25 cm away from the nozzle outlet, was used. The inner flow rate was set at 0.55 ml/hr and the outer flow rate was set at 1.0 ml/hr with a voltage of 16 kV. For these test, the parameters were chosen because of the observations that were made in the previous experiments. The test began by taking two samples for every Ti(IV) amount tested. The three Ti(IV) amounts that were tested were 2, 3, and 4 g. Two samples were taken for each set of parameters and twenty total images were gathered from the two samples. The rest of the material amounts were held constant at: PVP: 0.3 g, EtoH: 5 ml, Acetic Acid: 2ml.

The data from these tests were then graphed and the standard deviations of these measurements were displayed as the error bars in the graph. The effect of the Ti(IV) amount on the output parameters of the fiber can be seen in Figure 72 thru Figure 76.

From these results it was seen that the average outer diameter and inner diameter increased as the Ti(IV) amount increased. Along with this, it was also observed that the variation of the outer diameter and inner diameter also increased as the Ti(IV) amount increased.

The average wall thickness was observed to be unchanged by the Ti(IV) amount. It was also seen that the average of the relative inner diameter increased for each step
increase of Ti(IV). Similarly it was observed that the average of the relative wall thickness decreased for each step increase of Ti(IV).

Figure 72: Effect of Ti(IV) Amount on Outer Diameter

Figure 73: Effect of Ti(IV) Amount on Inner Diameter
Figure 74: Effect of Ti(IV) Amount on Wall Thickness

Figure 75: Effect of Ti(IV) Amount on Relative Inner Diameter

Figure 76: Effect of Ti(IV) Amount on Relative Wall Thickness
In conclusion the most interesting relationship regards the standard deviations of the outer and inner diameter. It was observed that the standard deviation of the outer diameter and inner diameter also decreased as the Ti(IV) amount decreased.

4.7 Conclusions

From all of these tests the most interesting observations that were made are as follows:

- It was observed that both the average outer and inner diameter decreased when the outer flow rate increased. The expected relationship was that at least the outer diameter increases as the flow rate increases. This however was not the observed effect.

- It was observed that the average outer diameter increased when the inner flow rate increased for flow rates less than 0.8 ml/hr.

- The smallest individual wall thickness and relative wall thickness was observed during the outer flow rate test at 1.3 ml/hr. This fiber had an outer diameter of 815 nm, inner diameter of 789 nm, wall thickness of 13 nm, and a relative wall thickness of 0.03 nm/nm.

- The smallest wall thickness average from all the process variables was observed at the inner flow rate of 0.8 ml/hr with an average wall thickness less than 100 nm.

- From these test it appears that the voltage adjustment is a parameter that should be adjusted during the co-axial electrospinning process to adjust the flow rate of the jet.
• The smallest inner and outer diameter averages from all of the process variables was reached at 15 kV with an outer diameter average of approximately 600 nm and an inner diameter average of approximately 300 nm.

• It was observed that the average inner diameter, outer diameter and wall thickness was larger for the gap collector.

• It was observed that the average outer diameter almost linearly increases as the gap size increases.

• The smallest individual inner diameter was observed during the gap size test at 1 cm. This fiber had an outer diameter of 517 nm, inner diameter of 93 nm, wall thickness of 212 nm, and a relative wall thickness of 0.82 nm/nm.

• The smallest individual relative inner diameter was also observed during the gap size test at 1 cm. This fiber had an outer diameter of 912 nm, inner diameter of 116 nm, wall thickness of 398 nm, and a relative wall thickness of 0.87 nm/nm.

• It was observed that the standard deviation of the outer diameter and inner diameter decreased for the up spinning direction and the fiber dimensions decreased for the up spinning direction.

• The smallest individual outer diameter was observed during the down test. This fiber had an outer diameter of 221 nm, inner diameter of 124 nm, wall thickness of 48 nm, and a relative wall thickness of 0.44 nm/nm.

• It was observed that the standard deviation of the outer diameter and inner diameter also decreased as the Ti(IV) amount decreased.

The two most interesting results were the unexpected observation between the inner diameter and the outer flow rate. It is commonly expected that as the outer flow
rate increases the dimensions of the fiber should also increase. This was not what was observed.

From the experience of collecting the fibers it was concluded the parameters do affect the ease of the co-axial electrospinning process. Many of the samples that were collected at the beginning of these tests required an extensive amount of time to collect and find the hollow fibers. At the end of these tests that process was much easier and quicker. It could be the fact that the operator gained experience which allowed for smoother operation of the test, but it is believed that the parameters used were a bigger factor than the operator.
Chapter 5: Preliminary Investigation of Advanced Multi-liquid Process Configurations

From the knowledge that was obtained from the previous chapters a better understanding of how two fluids interact and are affected by different process parameters was established. The natural next step of this process is to explore other advanced multi-liquid process configurations.

There were two novel multi-material fiber configurations that were of interest. This included the tri-liquid concentric (TLC) configuration and the island-in-the-sea configuration. Illustration of these two configurations can be seen in Figure 77 & Figure 78.
5.1 Tri-liquid Concentric Fiber Configuration

The idea of creating a tri-liquid concentric fiber is a new idea that has only been accomplished once to this date[132]. Creating a nozzle that will provide the opportunity to create such a fiber was the ultimate goal. Exploration and analysis of the challenges associated with achieving such conditions were performed in this section.

5.1.1 Tri-liquid Concentric Nozzle Problems

The experience of the co-axial electrospinning process provided the tools to identify the problems that would occur for the tri-liquid concentric nozzle. All of the same problems that occurred during the co-axial electrospinning process are present and in fact multiplied during the tri-liquid concentric electrospinning process. The many different challenges that may occur during this process can be seen in Figure 79.

Similar to the co-axial nozzle, the position of the core material is critical in producing a tri-liquid concentric fiber. For the tri-liquid concentric nozzle the importance of the position of the middle shell is just as critical. Also the addition of the outer shell causes a larger size of the overall meniscus, which resulted in a larger single fluid electrospinnable area.

An additional problem that was observed from the testing of these nozzles was the added importance of the concentricity of the nozzle due to the immiscibility of the three fluids. All the fluids that were tested were immiscible in pairs but not as a group. This meant that the core would be immiscible with the middle shell but miscible with the outer. While, the middle shell fluid was immiscible with both the core and outer shell fluids. For this reason the concentricity of the nozzles was pivotal in maintaining the immiscible buffer of the middle shell fluid between the core and outer shell.
5.1.2 Design Goals

From these tri-liquid concentric nozzle problems the design goals that are required in producing a tri-liquid concentric fiber were identified. The two main design goals were to reduce the outlet diameters and maintain concentricity of all three outlet nozzles.

5.1.3 First Tri-liquid Concentric Nozzle Design

The first attempt to produce a tri-liquid concentric electrospun fiber was performed by a redesign of the co-axial nozzle. This redesigned nozzle was simply the co-axial nozzle with the addition of a third nozzle. A CAD image of the design can be seen in Figure 80, Figure 82, & Figure 83, also a photo of the nozzle can be seen in Figure 81.
At this point in the testing the primary goal was to try to create a tri-liquid concentric electrospun fiber. The materials that were used in this setup were PEO-Mineral Oil-PEO in a spinning down configuration with a continuous collector 25 cm away from the tip of the nozzle. All other parameters were adjusted on the fly to obtain optimal spinning conditions. The large outlet diameter was the key factor in the failure of this design.

5.1.4 Second Tri-liquid Concentric Nozzle Design

In order to solve the problem found in the previous design the primary goal for this design was to reduce the outlet diameters. Two needles at the gauges of 23 and 18 were found to fit concentrically with each other. These combined with a pipette nozzle was used to create the second tri-liquid concentric nozzle design. This nozzle can be seen in Figure 84.
The improvement to this design was the reduced size of the outlet nozzles. However, the downfall of this design was the epoxy. Since the needles and syringes were held together by epoxy, the precision of the placement of the outlet nozzles could not maintain a concentric configuration. Therefore the two miscible fluids of the core and outer shell frequently combined.

Because of the many difficulties of tri-liquid concentric nozzle design it was decided that a completely different approaches needed be considered to eliminate some of these problems.

5.1.5 Two-dimensional Feeder Designs

Since there had been numerous complications and an entirely new approach was taken. Currently it was thought that in order to produce a tri-layered concentric flow pattern the nozzle must be arranged in the same pattern. However it was found that the two dimensional flow paths of micro fluidic devices possessed the capability of producing a three dimensional co-axial flow pattern. This two-dimensional feeder design idea was inspired by the practice of creating micro emulsion drops from a micro fluidics device.[152-154]
The two-dimensional feeders were milled from the PMMA block had a cross-section area of 0.065 inches wide and a depth of 0.047 inches. The fluid channels were created by using a mill with a 1/16 inches bit. The 2-axis stage allowed for semi-precise control of the fluid channels pattern. It was classified as semi-precise control due to the large tolerance of about ±0.005 inches that could be felt in the handles.

In the test the fluids used were water, mineral oil, and isopropyl alcohol. These combinations were select due to the densities of the three fluids. With the density and immiscibility of these fluids, naturally three layers would be produced. All three fluids remain immiscible as long as the mineral oil can keep the alcohol and water separated.

5.1.5.1 Preliminary Feeder Designs

The biggest problem with creating the two-dimensional feeder design was the lack of knowledge of how to create such a device. As well as, acquiring the required flow rates needed to produce a three dimensional concentric flow path from a two-dimensional flow path. In these preliminary designs the method of creating the two dimensional feeders were explored, along with the examination of the fluid flow in the two dimensional feeders. Some design iterations that were explored can be seen in Figure 85.

![Figure 85: Preliminary Feeder Design](image-url)
5.1.5.2 Co-axial Feeder Design

The first usable design that was created can be seen in Figure 86. This design was used to test both the flow characteristic of creating a co-axial flow pattern and its ability to be used as to create a co-axial electrospun fiber. In this design the outlet point was chamfered to create a tip at which the fluids could be electrospun from.

From this design the desired flow rates of the fluids that are required to obtain a co-axial flow pattern were established. The flow of the fluid at the point of fluid intersection was monitored with the use of a high speed camera.

The test was performed by increasing the outer flow rate until a concentric flow pattern could be seen. Then the inner flow rate was reduced until the concentric pattern disappeared. Once this limit was established the inner flow rate was set and increased above this limit until the concentric pattern returned. Then the outer flow rate was lowered until the concentric flow pattern was eliminated to find its limit. From these tests, the lowest possible flow rates needed were established and can be seen in Table 1.

<table>
<thead>
<tr>
<th>Outer</th>
<th>Flow rate</th>
<th>Inner</th>
<th>Flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>3.5 ml/hr</td>
<td>Mineral Oil</td>
<td>0.3 ml/hr</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>20 ml/hr</td>
<td>Alcohol</td>
<td>10 ml/hr</td>
</tr>
</tbody>
</table>

Table 1: Co-axial Feeder Nozzle Flow Rate Test

Once it was confirmed that the concentric laminar flow pattern could be created the ability to co-electrospin the fibers were tested. These tests resulted in positive results with both material combinations being able to be electrospun in the up direction. The
proper positioning of the core fluid was confirmed visually and with the core position conditional experiment. No SEM images of the fibers were taken to verify the co-axial structure.

5.1.5.3 Preliminary Tri-liquid Feeder Design

Once there were signs that the feeder design had the ability to create a co-axial flow pattern that could be electrospun the additional third fluid was added to the design. There were two flow paths that were explored when dealing with three different fluids. There was the open V design that can be seen in Figure 87 and the nested V design that can be seen in Figure 88. From testing these two designs the nested V design provided the better results in creating the concentric flow pattern.

![Figure 87: Open “V” Design](image)

![Figure 88: Nested “V” Design](image)

Using the nested V design the flow limits were calculated in the same fashion as the two fluid combinations were tested. From these test the limits can be seen in Table 2.

<table>
<thead>
<tr>
<th>Outer Fluid</th>
<th>Flow rate</th>
<th>Middle Fluid</th>
<th>Flow rate</th>
<th>Inner Fluid</th>
<th>Flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>25 ml/hr</td>
<td>Mineral Oil</td>
<td>20 ml/hr</td>
<td>Alcohol</td>
<td>10 ml/hr</td>
</tr>
</tbody>
</table>

Table 2: Milled Block Tri-liquid Concentric Flow Rate Test

Since the tri-liquid concentric flow pattern was able to be obtained using these flow rates the desire to modify the sixth design to include a point tip was the next step.
Due to problematic feeder assembly the attempts to this tip resulted in the epoxied Plexiglas cover being detached.

From the flow rate test it was determined that oil within PEO needed flow rates of: PEO: 3.5 ml/hr; oil: 0.3 ml/hr. For the combination of alcohol in oil the needed flow rates were: Oil: 20 ml/hr; Alcohol: 10ml/hr. For the tri-liquid concentric combination the flow rates were: PEO: 25 ml/hr; Oil: 20 ml/hr; Alcohol: 10m/hr. From these flow rates and the dimensions of the channels the fluid velocity at a given points in the feeder was calculated. The average velocity of the oil and alcohol mix at their exit was found to be 7.052 mm/s while the velocity of all three fluids at the tip exit was 14.10 mm/s. These speeds are the theoretic velocities at which the fluids need to travel in order to create a concentric flow with the given feeder design. It should be noted that the rough edges of the fluid channels walls and glue flash could be the cause of some turbulent flow, which may have raised the required flow rates.

After testing the electrospinning capabilities of co-axial feeder design it was found that a flow rate of PEO: 0.4 ml/hr (x2) and Oil: 0.15 ml/hr were needed to produce the ideal core position during the co-axial electrospinning process. The desired cross section of the fluid channels were calculated from the desired fluid velocities needed, and the given output flow rates that were needed to be electrospun. To create a junction with the flow rate of the mineral oil at 0.15ml/hr with the desired fluid velocity, the cross sectional area would have to be 1.65 mm x 1.1938 mm. Dimensions at this level are beyond the precision of the current manufacturing methods that were being used, but could be achieved in future designs.
5.1.6 Future design options

The future design for the feeders should come from established techniques of creating these designs. One option that was explored was the use of the micro fluidic products that inspired this design. The use of micro fluidics to produce emulsion drops and double emulsion drop is currently an option that is available in micro fluidic chip designs. It is also believed that if the solutions are set with the correct flow rate that a concentric flow pattern can be produced. It is believed that these micro fluidic chips could be altered to create a desired feeder design.

5.2 Island-in-the-Sea Fibers

Due to the similarities of the co-axial configuration to the island-in-the-sea configuration the electrospinning of this unique configuration was explored. Specifically the island-in-the-sea configuration was investigated due to its potential of creating continuous nanobundles of nanofibers. The novel idea of creating continuous nanobundles of nanofibers through the island-in-the-sea electrospinning process has never been accomplished to this date.

The creation of an island-in-the-sea (INS) electrospinning nozzle was designed and tested. The basic setup was the same as the co-axial electrospinning setup. The only difference is that a different spinneret nozzle was includes that has multiple inner nozzles instead of one. Figure 78 illustrates this configuration.

5.2.1 Nozzle Design

For these test the combination of a PMMA as the shell solution with PAN as the core solution was selected. This combination was selected because of the practical applications of creating a nano-yarn of the carbonized fibers. The degradation
temperature of the PMMA during the stabilization of the PAN resulted in the disappearance of the PMMA and revealing of the PAN fibers.

For these preliminary tests a nozzle was created. The nozzle can be viewed in Figure 89. This nozzle was created out of three 22 gauge needles and epoxied to three bent 18 gauge needles for a proper attachment point that these large needles provided with their luer connections. These needles were placed inside the plunger of a 30 ml syringe, and the syringe was altered to allow access to the needles inlets and outlets. This nozzle was used for all test performed in these preliminary studies.

From these test some fibers were able to be produced, carbonized, and collected. The following SEM images show the fibers that were produced. The desired structure of the process is to create a nanofiber that is intertwined with one another. Some images that illustrate the intertwined fibers can be seen in Figure 90 and Figure 91. It is assumed that these intertwined fibers were created due to the island-in-the-sea method. However more investigation on these fibers needs to be performed before any conclusions can be made due to the frequent entanglement of fibers that occur during the electrospinning process.
5.3 Conclusions

The problems of the tri-liquid concentric design were identified and evaluated. It was observed that these problems were much more challenging to overcome than the problems of the co-axial design. To overcome these challenges a smaller nozzle with highly precise positioning is needed.

For these reasons a new approach was investigated. This two dimensional feeder design was capable of obtaining the ideal core position during the electrospinning of two fluids. It was found that to apply this design to the tri-liquid concentric configurations
that smaller scale flow paths beyond the capability of current manufacturing technique are needed. It was concluded that there is a strong possibility that the PMMA and PAN fluids can be utilized to create an island-in-the-sea fiber.
Chapter 6: Overall Conclusions

Co-axial electrospinning has the ability to produce both hollow and co-axial composite nanofibers with diameters in the range from a few nanometers to microns. Rapidly growing interest in the co-axial electrospinning process is based largely on a large number of potential applications. In spite of the rapidly growing interest there have been no systematic studies on the effect of the process variables on the co-axial fibers that are produced. This thesis focused on process variables of the co-axial electrospinning process and its effects on the output parameters.

An improved co-axial electrospinneret nozzle was designed, built, and tested. The nozzle provided an adjustable protrusion distance and concentricity, and could be easily cleaned/reused.

A tailored procedure was identified for co-axial electrospinning process. The procedure and the improved nozzle were applied to and proven effective on a wide range of material combinations.

Both of these two tools were then used and a comprehensive systematic parametric study of the co-axial electrospinning process was conducted for the first time.
The study quantified the effects of liquid flow rates, electrospinning configuration parameters, and liquid composition parameters on hollow nanofiber diameters and wall thickness. Several unexpected qualitative variations were observed and described for the first time.

Several advanced multi-liquid process configurations were explored. Preliminary designs of advanced nozzles were performed and tested.

The results provide new quantitative insight into co-axial electrospinning process and can be used for better process control and for controllable production of hollow and composite nanofibers for a variety of nanotechnology applications.

6.1 Recommendation for Future Studies

To draw stronger conclusions on the effect of the process variables and output parameters larger sample sizes need to be analyzed. Instead of having all measurements come from one sample for a given set of process parameters, the fibers measured could be extracted from multiple samples.

Stronger conclusions could also be seen if the variability of the sample would be reduced. Co-axial electrospinning process is a very complex process with more variables effecting output parameters than were tested in this study. However with the knowledge gained from these tests it is believed that the variability of the samples could be reduced by obtaining a more stable meniscus with a stable core fluid position.

In order to hold the meniscus in a co-axial electrospinning configuration the co-electrospinneret nozzle must be able to quick adjust and hold this configuration. One way to achieve this is by altering the co-axial electrospinning processes, specifically by adding the adjustment of the voltage to regulate the size of the meniscus.
The meniscus size can be simplified as a tank problem, may be considered the meniscus size as the volume of the tank with an inlet rate (syringe pump) and outlet rate (electrospinning jet). By adjusting the voltage, the outlet rate can be more quickly adjusted. To maintain a constant co-axial jet the meniscus size needs to be held constant. To obtain these conditions it is believed that for a given combination of fluids with two constant flow rates, there exist a voltage range that will produce a stable co-axial electrospinning jet.

Also some incremental improvements to the nozzle could be done. This would be achieved by reducing the length of the output nozzles. This reduction of length would improve to concentricity of the needles. The long length was initial thought to be needed to achieve a laminar flow in the needles. It was realized later that a much shorter length would still be able to produce a laminar flow. With the shorter length of the output nozzles the diameters of both outlets should be possible. By shrinking the overall outlet the single fluid electrospinnable area would be reduced.

With these improvements and a more extensive study, stronger effects of the process variables on the output parameters could be observed.

In addition to these recommendations a new possible approach to the co-axial electrospinning was discovered. The use of a two-dimensional co-axial feeder was seen to produce a stable meniscus with the proper core placement. It is recommended that further investigation of the feasibility of this design on the creation of co-axial fibers be pursued.
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Appendix A: Methods

A.1 Poking Technique

A.2 Collection Methods A sequence of photos displaying this technique can be seen in Figure 92.

**Poking Technique**

Figure 92: Poke Technique
A.2 Collection Methods

As described earlier there are two types of collectors that were used the continuous collector or the gap collector. To collect the fibers samples only when the core meniscus is in the ideal position during the collection time a quick a repeatable method for collecting fibers was created. When using the continuous collector an aluminum plate was used as the collector. To provide a repeatable collecting surface for the sample, one side of the plate was covered in aluminum foil. To collect the fibers the collection plate was flipped over to allow the fibers to accumulate on the foil surface.

When using the gap collector a similar approach was taken. In this setup both a cover plate and the gap collector were used. These two plates were stacked on top of each other at the beginning of the procedure so the cover plate would stop the collection of fiber on the gap collector. To collect the fibers the cover plate was removed allowing the fibers to accumulate on the gap collector.

Once the fibers were collected across the parallel gap they were transferred on to foil. This was done to add support for the fibers. This was performed by taking a narrow strip of foil that was slightly narrower than the gap and pulling the foil through the gap. While doing this the foil could be moved up and down while being pulled through the fibers to distribute the fibers across the foil more evenly or more densely. A sequence of photos describing this process can be seen in
For the case when the material combination included a mineral oil core an additional step to remove the mineral oil was preformed. To remove the mineral oil core the samples were soaked in octane for 8 hours. The samples where then removed, dried out, and ready to be examined.

A.3 Observation Methods

Once the fibers were collected on foil the fibers need to be examined. This is a challenge due to the nanoscale of the object. To observe these co-axial nanofibers and determine different dimensions of these fibers the traditional light microscope cannot be used, because the dimensions are smaller than the wavelength of light. To view such small objects an electron microscope is needed.

One problem is that the hollow co-axial fiber has core that surrounded by material. This is a problem for the SEM since it only creates a topographical image of the surface. The solution this problem is that the fibers need to be broke so a cross-
sectional view of the fibers can be seen using the SEM. The alternative solution would be to use the TEM.

Given these two choices, the option of using the SEM and breaking the fibers to view the cross-sectional was chosen. It was chosen for the following reasons:

- The cost to operate the SEM was much lower for our lab. Combine that with multiple samples that needed to be examined the cost savings added up.
- The change over time for one sample for the TEM took thirty minute, while the SEM change over time for five samples took around two minutes. So in regards to sample change over the SEM saves time and money.
- The area of fibers that can be examined with the SEM (628 mm$^2$) is much larger than the TEM’s (14.6 mm$^2$).
- The TEM’s sample has to be collected directing during the co-axial electrospinning process and may not be transferred onto a TEM stage from a different collector. Combine this with the small stage area and the short collection time of some tests would result in a low number of fibers collected on a stage. In contrast using the SEM collection method, which will be reviewed in the following subsection, allows for a much broader area of the collector surface to be examined on a single SEM stage.

A.3.2 Sample Preparation

In order to view the cross-section of the fiber in the SEM, the fibers need to be broken. To do this a small study was performed to determine the best way of breaking and mounting the fibers on the SEM stage. In this study multiple fibers breaks and mounting approaches where performed.
To reduce the toughness and increase the breakability, the fibers were placed in liquid nitrogen. For most of these methods the fiber sample that was deposited on the foil was submerged in liquid nitrogen. While submerged the sample were cut apart in various ways. There were three ways used to break the fibers: ripped, stabbed, and cut. An illustration to assist in distinguishing these techniques from one another can be seen in Figure 94.

<table>
<thead>
<tr>
<th>Stab</th>
<th>Cut</th>
<th>Rip</th>
</tr>
</thead>
</table>

Figure 94: Fiber Break Methods Illustration

The stabbing method occurred by submerging the sample in the nitrogen and then stabbing the foil sample with a knife. The cutting method occurred by submerging the sample in the nitrogen and then by holding the foil against the wall of the container. Then a dragging motion of the knife across the fibers was performed to cut the fibers. The last method was to submerge the foil sample and then grip two places of the sample and pull them apart until a rip in the material formed.

Once the fibers were broken the next step was to transfer the fibers on to the SEM stage. To do this, two different methods were explored. The first was to take the pieces of foil with the fiber break and directly adhere the foil onto the stage. The second was to peel the fibers from the foil onto the stage. The fibers were attached to the stage in this process in various ways. One was to cover the entire surface of the stage with double sided adhesive tape. The other ways was to attach the double sided adhesive tape
on the edge of the stage in various configurations. SEM images of all these samples were taken and then reviewed.

From performing the test it was concluded that stabbing the foil in nitrogen and then peeling the fibers from the foil and placing them on a surface of double sided adhesive on the SEM stage was the best method. The main problem to this method was the difficulty of peeling the fibers from the foil and placing them onto the stage. In order to peel the fibers from the foil a thick layer of fibers is needed. To accumulate a thick layer of fibers a longer collection time is required. Unfortunately in these tests, the collection time for the co-electrospun fibers at times maybe very short, not allowing for a thick layer.

To try to solve the peeling problem a new transfer method was tested. This method took the SEM stage with the adhesive and pressed the stage against the foil. When the stage was pulled away from the foil the fibers would be transferred on to the SEM stage. After examining these images a surprise result was found. During the transfer of the fibers on the stage, other fiber breaks outside of the nitrogen break zone were discovered. These discoveries lead to the method that was used in the experimental procedure.

This new method of adhesive fiber transfer occurred without the nitrogen cutting. The nitrogen was removed because multiple breaks, equally distributed across the stage, could be seen just from the adhesive transfer, rather than only local breaks that the cut created. Also this method was not limited by the number of fibers. If the fiber density of the sample was low on the foil it could be increased on the stage by performing multiple
transfers on the same stage. With more fibers the probability of finding a co-axial fiber increases.

Figure 95: Fiber Transfer Method to SEM
A.4 Material Preparation

From the literature review multiple materials combinations have been produced. For these experiments three different material combinations were selected based on past experience with these materials, application possibilities, and ease of use. The main three combinations that were tested and evaluated were PVP-Ti(IV)/Oil, PEO/Oil, and PAN/PMMA.

To create the PEO solution Poly(ethylene oxide with 900,000 molecular weight from Scientific Polymers Products was dissolved in distilled water and mixed for 4 hours to insure proper dispersion of the material. For different tests different amounts of PEO were combined with the water.

For most of the experiments heavy liquid paraffin oil or mineral oil as it is known, was used as the oil. However to increase the interfacial forces between the outer solution and the mineral oil a surfactant Triton-X100 was added when noted. An amount of surfactant was added to create a 4% amount of surfactant in the mineral oil and then the solution was heated and stirred for 8 hours to insure complete disbursement of the surfactant in the mineral oil.

To create the PAN solution Polyacrylonitrile from Sigma-Aldrich was dissolved in Dimethylformamide from Sigma-Aldrich. It was then stirred for 8 hours to allow the PAN to be completely dissolved in the DMF.

To create the PMMA solution acetone was combined with DMF and also mixed in with Poly(Methylmethacrylate) with a 120000 molecular weight from Sigma-Aldrich. The solution was then stirred for 8 hours to ensure proper dispersion.
To create the PVP-Ti(IV) solution two steps were taken. First titanium(IV) isopropoxide was mixed with acetic acid and stirred and heated for 20 minutes. At the same time polyvinylpyrrolidone was dissolve in ethanol and stirred for 20 minutes. Then these two solutions were combined, heated and stirred for 20 minutes.

**A.5 Basics Setup**

For the setup seen in Figure 96 an observational element was added to allow for a closer examination of the co-axial electrospinning process. This observational element was a MotionXtrs HG-100k high speed camera with a 7000 Navitar TV Zoom lens accompanied with a back light. The voltage source that was used was an Agilent DC Power supply. The syringe pump that was used was a Cole-Parmer syringe pump with a 3ml B&D disposable syringe. The collector plate in this setup is the continuous collector. The nozzle that was used was co-axial nozzle design specifically for these parametric tests.

The syringe was attached to 1/16 inch ID Tygon tubing used to transport the fluid to the spinneret nozzle. The tubing length was held to 11 and 14 inches. The tubing from the syringe pump to the spinneret nozzle plays an important role in controlling the fluid flow rate. To reduce the amount of fluid needed for spinning, the smallest diameter that
still could be clean by wire was selected to conserve material. The downside of having
the small diameter tubing is that it causes a greater response time for the flow rate,
esspecially with the higher viscous fluids. That is the reason why the tubing was held
under 14 inches length, because it was the minimum working length that the current setup
allowed.

The co-axial nozzle is not only used as a fluid outlet, but also used as the positive
electrode. The nozzle was connected by alligator clips and wires to the voltage source to
produce the positive electrode. While the collector was also connected with alligator
clips and wire and connected to the negative charge outlet of the voltage source.
Appendix B: Effect of Process Variables on Additional Output Parameters

There was an additional set of output parameters that were also evaluated. However, because of

B.1 Output Parameters

These output parameters are all observations made from the overall images taken from the SEM. These parameters describe the result and the overall quality of the sample that was collected. The samples that were collected varied greatly in the overall fibers produced to the amount of hollow fibers produced. Some SEM photos of the extreme qualitative parameters can be seen in Figure 97.
Smallest Fibers per Area

Largest Fibers per Area

Smallest Percentage of Visible Ends

Largest Percentage of Visible Ends

Smallest Percentage of Hollow Fibers from the Visible Ends

Figure 97: Extreme Conditions of Additional Output Parameters
B.1.1 Percentage of Fibers Collapsed

It was noticed during the SEM observations that some of the fibers with small relative wall thickness had collapsed. So to find any correlations between the collapsed fibers and the process variables, the percentage of collapsed fibers for a given sample set was recorded. To be classified as a collapsed fiber, the fiber needed to be visually identified as flat. The best way to verify this was to examine the end. If the fiber was collapsed it would resemble a dog bone shape.

This variable was collected from the individual fiber images. After the fiber dimensions had been collected it was than noted whether the fiber was collapsed or not. From this the percentage of collapsed fibers could be determine for each sample set.

B.1.2 Fiber count per area

The fiber count per area output parameter is the number of visible fibers in the overall image. The fiber count was conducted by drawing lines over all the visible fibers tracing the fibers path. Once all of the fibers had been traced the number of lines drawn would be counted. This count included all types of fiber segments. So if one continuous fiber was broke into three pieces than the fiber count would be three. This number was then recorded along with the pixel to length conversion factor. Knowing the overall pixel size of the image the total area could be calculated. With this information the amount of fibers per area could be determined. An example of the collection of this data can be seen in Figure 98.

B.1.3 Percentage of Visible Fiber Ends

To determine the co-axial fiber amount of a sample two counts needed to be collected: the amount of fiber ends that could be seen in the overall image and the amount
of those fiber ends that were hollow. In the zoomed out image not all of the fiber ends are visually distinguishable. If the fiber end could be clearly distinguished as solid or hollow it would be counted as a fiber end. If the fiber end could not be clearly distinguished as solid or hollow it would not be counted. To count all the fiber ends when a fiber end was identified a square was placed near the fiber end. Once all the ends were identified they were counted and recorded. An example of the collection of this data can be seen in Figure 98.

![Image of fiber ends with marked squares and circles]

Figure 98: Additional Output Parameters Measured

**B.1.4 Percentage of Hollow Fiber Ends**

Once all of the visible fibers ends had been identified the number of these ends that were hollow fibers ends were recorded. This was done by placing a circle next to every fiber end that could be distinguished as hollow. Once all hollow fibers were found the number was recorded and the percentage of hollow fibers out of the visible fiber ends was calculated. An example of the collection of this data can be seen in Figure 98.

**B.2 Results**

The effects of the process variables on these additional output parameters were presented.
B.2.1 Outer Flow Rate

Figure 99: Effect of Outer Flow Rate on Fiber per Area w/ 0.55 ml/hr Inner Flow Rate

Figure 100: Effect of Outer Flow Rate on Fiber per Area w/ 0.75 ml/hr Inner Flow Rate

Figure 101: Effect of Outer Flow Rate on Percentage of Fibers Collapsed w/ 0.55 ml/hr Inner Flow Rate
Figure 102: Effect of Outer Flow Rate on Percentage of Fibers Collapsed w/ 0.75 ml/hr Inner Flow Rate

Figure 103: Effect of Outer Flow Rate on Percentage of Visible Fiber Ends w/ 0.55 ml/hr Inner Flow Rate

Figure 104: Effect of Outer Flow Rate on Percentage of Visible Fiber Ends w/ 0.75 ml/hr Inner Flow Rate
### B.2.2 Inner Flow Rate

**Figure 105**: Effect of Outer Flow Rate on Percentage of Hollow Fiber Ends with 0.55 ml/hr Inner Flow Rate

**Figure 106**: Effect of Outer Flow Rate on Percentage of Hollow Fiber Ends with 0.75 ml/hr Inner Flow Rate

**Figure 107**: Effect of Inner Flow Rate on Percentage of Fibers Collapsed
Figure 108: Effect of Outer Flow Rate on Fiber per Area

Figure 109: Effect of Inner Flow Rate on Percentage of Visible Fiber Ends

Figure 110: Effect of Inner Flow Rate on Percentage of Hollow Fiber Ends
B.2.3 Voltage

Figure 111: Effect of Voltage on Percentage of Fibers Collapsed

Figure 112: Effect of Voltage on Fiber per Area

Figure 113: Effect of Voltage on Percentage of Visible Fiber Ends
B.2.4 Collector Type

Figure 114: Effect of Voltage on Percentage of Hollow Fiber Ends

Figure 115: Effect of Collector Type on Percentage of Fibers Collapsed

Figure 116: Effect of Collection Type on Fiber per Area

Figure 117: Effect of Collection Type on Percentage of Visible Fiber Ends

Figure 118: Effect of Collection Type on Percentage of Hollow Fiber Ends
B.2.5 Gap Size

Figure 119: Effect of Gap Size on Percentage of Fibers Collapsed

Figure 120: Effect of Gap Size on Fiber per Area

Figure 121: Effect of Gap Size on Percentage of Visible Fiber Ends
B.2.6 Spinning Direction

Figure 122: Effect of Gap Size on Percentage of Hollow Fiber Ends

Figure 123: Effect of Spin Direction on Percentage of Fibers Collapsed

Figure 124: Effect of Spin Direction on Fiber per Area

Figure 125: Effect of Spin Direction on Percentage of Visible Fiber Ends

Figure 126: Effect of Spin Direction on Percentage of Hollow Fiber Ends
B.2.7 PVP Amount

Figure 127: Effect of PVP amount on Fiber per Area

Figure 128: Effect of PVP on Percentage of Visible Fiber Ends

Figure 129: Effect of PVP on Percentage of Hollow Fiber Ends
B.2.8 Ti (IV) Amount

Figure 130: Effect of Ti(IV) amount on Fiber per Area

Figure 131: Effect of Ti(IV) on Percentage of Visible Fiber

Figure 132: Effect of Ti(IV) on Percentage of Hollow Fiber Ends
B.2.9 Effects of the Meniscus Volume

Figure 133: Effect of Meniscus Volume on Outer Diameter

Figure 134: Effect of Meniscus Volume on Inner Diameter

Figure 135: Effect of Meniscus Volume on Wall Thickness
Figure 136: Effect of Meniscus Volume on Relative Inner Diameter

Figure 137: Effect of Meniscus Volume on Relative Wall Thickness

Figure 138: Effect of Total Flow Rate on Meniscus Volume
Figure 139: Effect of Meniscus Volume on Fiber per Area

Figure 140: Effect of Meniscus Volume on Percentage of Visible Fiber

Figure 141: Effect of Meniscus Volume on Percentage of Hollow Fiber Ends
Appendix C: SEM images

This Appendix displays the extreme dimensions of the fibers that were collected.

C.1 Smallest Outer Diameter Fibers

(smallest outer diameter taken from Down test)
C.2 Largest Outer Diameter Fibers
C.3 Smallest Wall Thickness

(smallest wall thickness taken from outer flow rate test at 1.3 ml/hr)
C.4 Largest Wall Thickness
C.5 Smallest Relative Wall Thickness

(smallest relative wall thickness taken from outer flow rate test at 1.3 ml/hr)
C.6 Largest Relative Wall Thickness

(Largest relative wall thickness taken from gap size test at 1 cm)
Appendix D: Co-axial Nozzle Drawing
Subassembly 1

S1 | 1
NT1 | 1

Press Fit

DIMENSIONS ARE IN INCHES
TOLERANCES:
FRACTIONAL ±
ANGULAR: 3/16 BEND ±
TWO PLACE DECIMAL ±
THREE PLACE DECIMAL ±

MATERIAL

QA

COMMENTS

NAME

DATE

DRAWN

3/10/09

CHECKED

END APPR.

MAN APPR.

NOTES

DO NOT SCALE DRAWING

SCHEDULE 1

A

WSM2

REV.

1/2 SCALE
0.001
SHEET 2 OF 3
Subassembly 2

<table>
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<th>Quantity</th>
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<tr>
<td>NT2</td>
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Mat'l
Aluminum Alloy 6061
1" OD, .75" ID
McMaster #89965K313

Shell 2

UNLESS OTHERWISE SPECIFIED:
DIMENSIONS ARE IN INCHES
tolerances
FRACTIONAL ± 1/64
ANCHOR 15-05
TWO PLACE DECIMAL ± 0.001
THREE PLACE DECIMAL ± 0.0001

INTERPRET GEOMETRIC TOLERANCES FOR:
MATERIAL:
Aluminum Alloy 6061

NEXT ISSUED USED ON
FINISH
APPLICATION DO NOT SCALE DRAWING

SIZE: A
Dwg. No.: S2
Rev.: 1
Scale: 2:1
Weight:
Sheet 1 of 1
Mat'l
Aluminum Alloy 2024 Tube
3/4" OD, .510" ID
McMaster #1968T333

Shell 1

SIZE: A
DWG. NO: S1
REV: 1

SCALE: 2:1
WEIGHT:
SHEET 1 OF 1
Mat'l: Stainless Steel 304 Tube
18 GA, .05" OD, .033" ID
McMaster #8988K417

Grind End

0.052

0.033

3.138

0.250

0.0000 - 0.0003

Needle Tip 1

<table>
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<tbody>
<tr>
<td>A</td>
<td>NT1</td>
<td>1</td>
</tr>
</tbody>
</table>

Scale: 1:1
Weight:
Sheet 1 of 1
Grind End if Tube OD is out of tolerance

Material: Stainless Steel 304

Stainless Steel 304 Tube
3/16" OD, .09" ID
McMaster #89895K219