

**INSTITUTO TECNONÓLOGICO Y DE ESTUDIOS
SUPERIORES DE MONTERREY**

Campus Estado de México
School of Engineering and Sciences



**Fabrication of Suspended Nanowires
Through Mechano-Near-Field
Electrospinning of Polymers in Solution
for the Production of Glass-like Carbon**

A thesis presented by:
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*Submitted to the
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in partial fulfillment of the requirements for the degree of
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in
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Estado de México, Atizapan de Zaragoza, December 02, 2020

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Antonio Osamu Katagiri Tanaka

Estado de México, Atizapan de Zaragoza, December 02, 2020

*“Carbon is a simple element but
one branch of chemistry is devoted to its compounds!
... one branch of science is devoted to the many forms of the element as a solid material.
The best of this is that although most carbon materials are grey or black to the naked eye and
the uninitiated. A closer examination reveals the form, beauty and even color of carbon
science.”*

Marsh, Harry
Universitat d'Alacant, Alicante, Spain
scopus.com

Dedication

To my parents, who believed in me no matter the outcome. Mom, dad, this work is possible because of you, for always telling me to believe in my dreams.

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**Fabrication of Suspended Nanowires Through Mechano-Near-Field
Electrospinning of Polymers in Solution for the Production of Glass-like Carbon**

by Antonio Osamu Katagiri Tanaka

Abstract

Carbon nano-wires are versatile materials composed of carbon chains with a wide range of applications due to their high conductivity. Regardless of the high interest in the implementation of carbon nano-wires in several applications and devices, no feasible processes have been developed to fabricate carbon nano-wires with spatial control at a reasonable cost. Carbon nano-wires have been fabricated with the use of a photoresist, but little is known about polymers that can produce more conductive carbon nano-wires after pyrolysis. Various polymer solutions have been tested in near field electrospinning (NFES) and photopolymerization separately, however, few have been tested for nano-wire fabrication purposes through pyrolysis. The intention behind the thesis proposal is to implement rheology analyses of different polymer solutions to determine if they can be easily electrospun at low voltages and then fabricate nano-wires with them. This thesis work arises from the need to test a greater variety of polymers with the goal to design a polymer solution to fabricate carbon nano-wires with better conductivity than the current SU-8 polymeric nano-fibers. The research process will include the design of polymer solutions that can be electrospun, photopolymerized, and then pyrolyzed into conducting carbon nanowires. On the other hand, it is intended to engineer a newly designed polymer solution to achieve mass scale manufacturing of conductive carbon nano-wires in an inexpensive, continuous, simple and reproducible manner as central components for nano-sensors.

keywords: nanotechnology, carbon, nano-wires, Near-Field Electrospinning, NFES

List of Figures

1.1	Fabrication Process of Carbon Nano-wires	2
1.2	Fingerprint of Carbon-based Nano-materials	3
1.3	Carbon sp-hybrid Nano-materials	4
1.4	Ternary Diagram of Carbon Allotropes based on sp Content	4
1.5	Ternary Diagram of Carbon Allotropes based on Porosity and Structural Order	5
1.6	Diameter comparison of various types of fibrous carbon materials	6
1.7	Components of SU-8 2000 Series Resists	9
1.8	Types of Nano-sensors	10
2.1	Electrohydro-dynamic techniques	15
2.2	Typical setup used in pressurized gyration processes	17
2.3	Dispensing nozzle used for solution blow spinning or melt blowing. [104]	18
2.4	Typical mechanical fiber drawing process. First the needle makes contact with the substrate to break the polymer drop. Then the needle leaves the substrate and the collector moves to create and deposit the fiber. Once the fiber is written the needle makes contact with the collector to fix the fiber deposition.	19
2.5	Touch-spinning technique. First rod is attached to a rotating stage and a polymer solution droplet is administrated through a needle. Then the rotating rod ‘touches’ the polymer precursor. Finally, as the rod rotates, the polymer solution is stretched and creates a fiber between the rod and the needle.	19
2.6	Microfluidic device used by Kang et al. [110]	20
2.7	Needle configurations in coaxial electrospinning. (a) the outer needle encasing the inner; (b) the inner needle protruding from the outer; (c) both needles inline with each other;	21
2.8	Typical Melt Electrospinning Setup	22
2.9	NFES setup for controlled fiber deposition on pre-patterned conductive electrodes. [130]	26
2.10	Schematic illustration of the electrohydrodynamic process. [131]	26
2.11	The geometry distribution of linear array multi-nozzle system [133] . .	27

2.12	schematic diagram of leap direct-writing: the ink first accumulates at contact point and then gets stretched by mechanical drawing force. At a critical distance, the ink leaps to the next contact point, and gets stretched again [135]	28
2.13	Near-Field ES Process Parameters	28
2.14	a) Typical Far-field Electrospinning (FFES) Setup. b) Typical Near-field Electrospinning (NFES) Setup.	31
2.15	Different Electrospinning Methods in Terms of Spatial Control, Fiber Throughput and Resolution	33
2.16	WebPlotDigitizer home-screen	34
2.17	Image Analysis Algorithm to Measure Fiber Diameters from SEM images	35
2.18	Validation of the developed image analysis measurement tool	36
2.19	NFES correlation matrix of process parameters and fiber morphology .	37
2.20	Scatter Plot of Polymer Concentrations and Fiber Diameters from Literature Experimental Results	38
2.21	Scatter Plot of Nozzle Inner Diameters and Fiber Diameters from Literature Experimental Results	39
2.22	Scatter Plot of NFES Working Distances and Fiber Diameters from Literature Experimental Results	40
2.23	Scatter Plot of NFES Applied Voltages and Fiber Diameters from Literature Experimental Results	40
2.24	Scatter Plot of Polymer Solution Flow Rates and Fiber Diameters from Literature Experimental Results	41
2.25	Scatter Plot of Collector xy Stage Velocities and Fiber Diameters from Literature Experimental Results	41
2.26	Syntheses and Applications of Nanofibers	43
2.27	Image Analysis Algorithm to Measure Fiber Diameters from SEM images	45
3.1	Studied Polymers by Zhenan Bao et al. [225]	47
3.2	Selection of Polymer-Solvent Systems to Investigate in this Work	48
3.3	Polymer Chain Entanglement in Function of Polymer Concentration .	49
3.4	Effect on Solution Viscosity and Related Electrospinning Capability .	50
3.5	Rheometer - Solvent Trap Setup	54
3.6	Estimation of the Critical Concentration of the PEO in SU-8 solutions .	55
4.1	NFES experimental setup	57
4.2	Diameter of fibres for all the experiments	58
A.1	Viscosity as a function of shear rate for Poly(Ethylene Oxide) (PEO) and SU-8 2002 solutions	64

A.2 Viscosity as a function of shear rate for Polystyrene (PS) and Tetrahydrofuran (THF) solutions	65
A.3 Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB) and 1-Methyl-2-Pyrrolidinone (NMP) solutions	65
A.4 Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB), Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF) solutions	66
A.5 Viscosity as a function of shear rate for Poly(Styrene-co-alpha-Methylstyrene) (PSMS) and N,N-Dimethylformamide (DMF) solutions	66
A.6 Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and Chloroform (CHL) solutions	67
A.7 Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and SU-8 2002 solutions	67
B.1 Viscosity as a function of shear rate for Poly(Ethylene Oxide) (PEO) and SU-8 2002 solutions	68
B.2 Viscosity as a function of shear rate for Polystyrene (PS) and Tetrahydrofuran (THF) solutions	69
B.3 Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB) and 1-Methyl-2-Pyrrolidinone (NMP) solutions	69
B.4 Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB), Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF) solutions	70
B.5 Viscosity as a function of shear rate for Poly(Styrene-co-alpha-Methylstyrene) (PSMS) and N,N-Dimethylformamide (DMF) solutions	70
B.6 Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and Chloroform (CHL) solutions	71
B.7 Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and SU-8 2002 solutions	71
C.1 Morphology and Characterization of Electrospun Fibers at Different Voltages : Poly(Ethylene Oxide) (PEO) and SU-8 2002	72
C.2 Morphology and Characterization of Electrospun Fibers at Different Voltages : Polystyrene (PS) in Tetrahydrofuran (THF)	73
C.3 Morphology and Characterization of Electrospun Fibers at Different Voltages : Poly(Styrene-co-Butadiene) (PSB) in Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF)	74
C.4 Morphology and Characterization of Electrospun Fibers at Different Voltages : Poly(9-Vinylcarbazole) (PVK) in Chloroform (CHL)	75
C.5 Morphology and Characterization of Electrospun Fibers at Different Voltages : Poly(9-Vinylcarbazole) (PVK) and SU-8 2002	76

List of Tables

1.1	Prepared Polymer Solutions in Previous Work	8
1.2	Advantages of Nano-sensors	9
1.3	Classification of Nano-sensors	11
2.1	Approximation process to estimate the critical polymer concentration. Several polymer concentrations are tried and the resulting jets are observed until a continuous stream is achieved.	23
2.2	Near-Field Electrospinning Process Parameters	42
3.1	Poly(Ethylene Oxide) and SU-8 2002 : Control Sample Preparation . .	50
3.2	Polystyrene in Tetrahydrofuran : Sample Preparation	51
3.3	Poly(Styrene-co-Butadiene) in 1-Methyl-2-Pyrrolidinone : Sample Preparation	51
3.4	Poly(Styrene-co-Butadiene) in Tetrahydrofuran and N,N-Dimethylformamide : Sample Preparation	51
3.5	Poly(Styrene-co-alpha-Methylstyrene) in N,N-Dimethylformamide : Sample Preparation	52
3.6	Poly(9-Vinylcarbazole) in Chloroform : Sample Preparation	52
3.7	Poly(9-Vinylcarbazole) and SU-8 2002 : Sample Preparation	52
3.8	Calculated Critical/Spinnable Concentrations for each Polymer-Solvent System	56
D.1	Average Fiber Diameter for All the Experiments	78

Contents

Abstract	vi
List of Figures	x
List of Tables	x
1 Introduction	1
1.1 Carbon Nanowires Research Developments in Terms of Published Papers, Synthesis and Fabrication	2
1.1.1 Carbon and carbon-based nanomaterials	3
1.1.2 Carbon Nano-wires	6
1.2 Problem definition and motivation	9
1.3 Hypothesis	12
1.4 Research Questions	12
1.5 Objectives	13
1.5.1 General objective	13
1.5.2 Specific objectives	13
1.6 Dissertation Outline	13
2 Near-Field Electrospinning as an Affordable Way to Gain Spatial Control	14
2.1 Review of Polymer Solutions for NFES with Spatial Control	14
2.1.1 Stretching forces	15
Electric Field	15
Centrifugal force	16
Blowing forces	18
Mechanical force	18
Microfluidic forces	19
2.1.2 Dispensing nozzle	20
2.1.3 Polymer Reservoir (Polymer Melt & Polymer Solution)	21
2.1.4 Polymer Solution	23
Polymers	23
Solvents	24
2.2 Properties that Improve Accuracy of Nano-Fiber Deposition	25
2.2.1 Nozzle spinneret	29
2.2.2 Applied Voltage	30
2.2.3 Nozzle-to-substrate distance	31

2.2.4	Substrate	32
2.3	Data collection of NFES fiber morphology and process parameters	33
2.3.1	Image Analysis - Data extraction from plots	34
2.3.2	Image Analysis - Data extraction from Scanning Electron Microscopy Images	34
2.4	Discussion & NFES Challenges	36
2.5	Diameter Prediction of Electrospun Fibers	43
3	Selection of Compatible Polymer-Solvent Combinations for Near-Field Electrospinning and Pyrolysis	47
3.1	Selection of Candidate Spunable Polymer Solutions	48
3.2	Rheology of candidate polymer solutions	49
3.2.1	Materials and Sample Preparation	50
3.2.2	Rheological Characterization of polymer Solutions	53
4	Fabrication and Characterization of Polymeric Fibers through Near-Field Electrospinning	57
4.1	Materials and Methods	57
4.2	Results	58
4.3	Conclusions and Future Work	60
A	Flow Curves	64
B	Critical Concentrations	68
C	Optical Microscopy Characterization of Electrospun Fibers	72
D	Average Fiber Diameters, Minimums and Maximums	77
	Bibliography	79
	Curriculum Vitae	107

Chapter 1

Introduction

Carbon nano-materials are subjected to great interest for research purposes due to their various potential applications in diverse areas that take advantage of the nano-scale properties. Carbon nano-materials are suitable for catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing, and cancer detection. Some matchless properties that allow carbon nano-materials to be utilized within multiple functionalities include high porosity, distinguished structures, uniform morphologies, high stability, high magnetic properties, and high conductivity. [1–8]

This document bestows a thesis project to perform research to engineer a polymer solution to achieve mass scale manufacturing of high conductive carbon nano-wires with a reduced diameter in an inexpensive, continuous, simple and reproducible manner. The research intends to involve several manufacturing processes such as near field electrospinning, photo-polymerization, pyrolyzation, and carbonization, as they have shown to be promising methods for the fabrication of carbon nano-materials. [9] See Figure 1.1. A number of processes have been developed for specific purposes of polymeric nano-fibres, some include surface deposition, composites, and chemical adjustments. Polymeric nano-fibers must be also pyrolyzed to generate carbon nano-wires with conductive capabilities [10] for electrochemical sensing and energy storage purposes.

Nanotechnology has led to the study of different polymer patterning techniques to integrate carbon nano-wires structures. One technique is known as far-field electrospinning (FFES), a process in which electrified jets of polymer solution are dispensed to synthesize nano-fibres which are then pyrolyzed at high temperatures. One sub-technique derived from

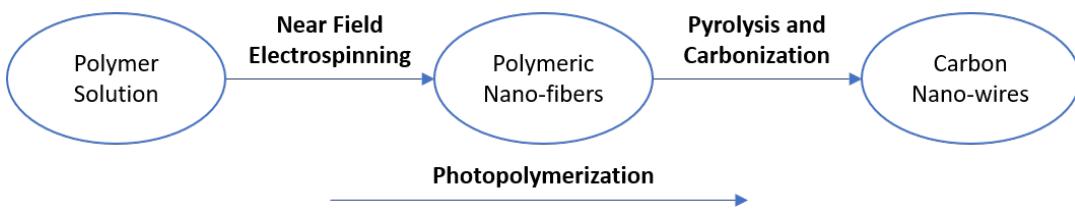


FIGURE 1.1: Fabrication process and characterization techniques of conductive carbon nano-wires to achieve through the dissertation.

electrospinning is near-field electromechanical spinning or NFEMS. Unlike FFES, NFEMS has proved to deliver high control in patterning polymeric nano-fibres. [9]

The proposal is to continue the previous work done in regards to the synthesis of carbon nano-wires. Previous work includes the fabrication of suspended carbon nano-wires by two methods: electro-mechanical spinning and multiple-photon polymerization with a photoresist. [9, 11] This work is intended to focus on electro-mechanical spinning processes only, to bring off polymer solutions that can be electrospun by NFEMS, photo-polymerized and pyrolyzed into conducting carbon nano-wires. The polymer solutions described by Cárdenas and Flores [9, 11] are to be amended to achieve the goal mentioned in the previous statement.

Traditional near-field electrospinning or NFES allows large scale manufacturability combined with spatial control of material deposition. [10] However, the reported efforts required the use of electric fields in excess of 200 kV/m for continuous operation, resulting in limited control for nano-fiber patterning in traditional NFES processes. Madou et al. [10] conclude that the current state-of-the-art synthesis processes for polymer nano-fibers lack to yield precise, inexpensive, fast, and continuous manufacturing properties.

1.1 Carbon Nanowires Research Developments in Terms of Published Papers, Synthesis and Fabrication

Nanotechnology ability to control and piece together materials at the nano-scale has enabled the development of various carbon nano-materials and carbon nano-structures, such as nano-dots, nano-fibres, nano-tubes and nano-wires. [12–15] This chapter bestows on the applications at

the micro-scale and nano-scale levels, as well as the current research of carbon-based nano-materials (CBNs).

1.1.1 Carbon and carbon-based nanomaterials

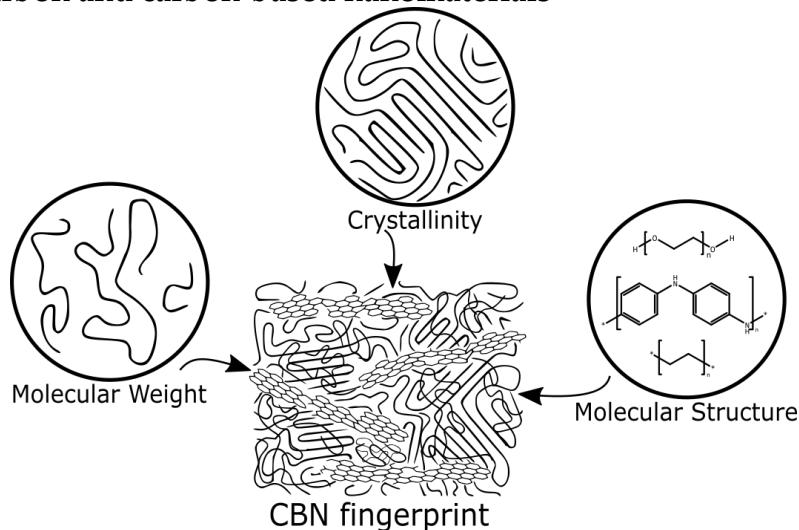


FIGURE 1.2: Molecular to meso-scale structural features of synthetic polymers influence the emergence of specific micro-structural features in polymer-derived carbon materials after pyrolysis.

Carbon is a versatile element capable to form a number of bonds with other elements or with itself. Cabon-based nano-materials (CBNs) exist in diverse forms, depending on the precise values of each degree of freedom that specify the material proclivity at multiple scales. Hybridization, crystallization, percolation, anisotropy, porosity, impurities and imperfections are some of the relevant features that determine the CBN set of properties. The combination of these features at the micro- and meso-scale burst a variety of macro-scale properties that comprise the CBN fingerprint (1.2). The interminable collection of possible CBN fingerprints range from soft, conductive lubricants to very hard, low conductivity solids; and from black colour, bulks to transparent, disordered thin films. [1] Figures 1.3 and 1.4 shows the existence of different types of allotrope as carbon orbitals have the ability to hybridize in sp^1 , sp^2 and sp^3 configurations, assembling different types of allotropes.

In terms of porosity, CBNs exhibit different properties according to the degree of 'open' and 'closed' pores. A 'closed pore' is a void or empty space in solid materials where a discontinuity is present within the array of atoms and molecules. On the other hand, an 'open pore' refers to a void which is connected to the outer surface of the solid, in other words a 'open pore' is a

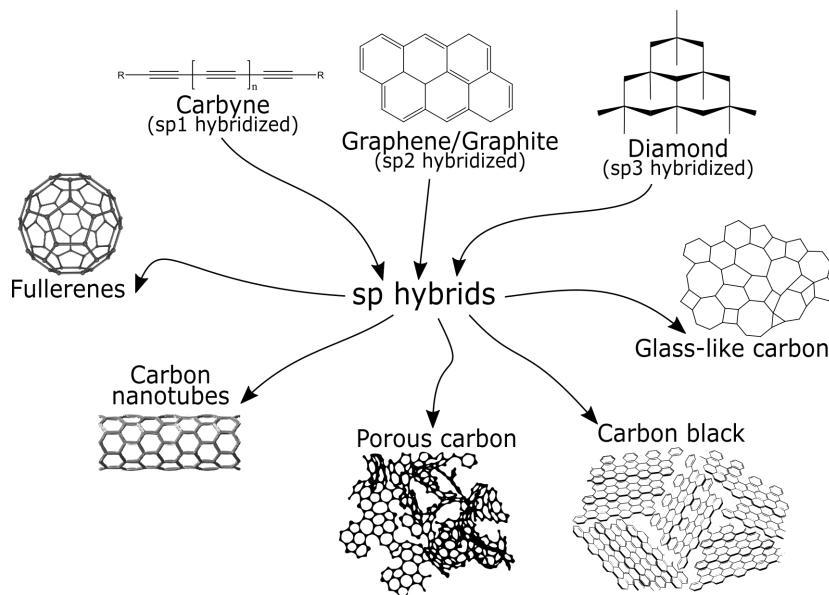


FIGURE 1.3: Three carbon allotropes (diamond, carbyne and graphene) are the building blocks of additional deriving carbon types such as fullerenes, porous carbon and glass-like carbon.

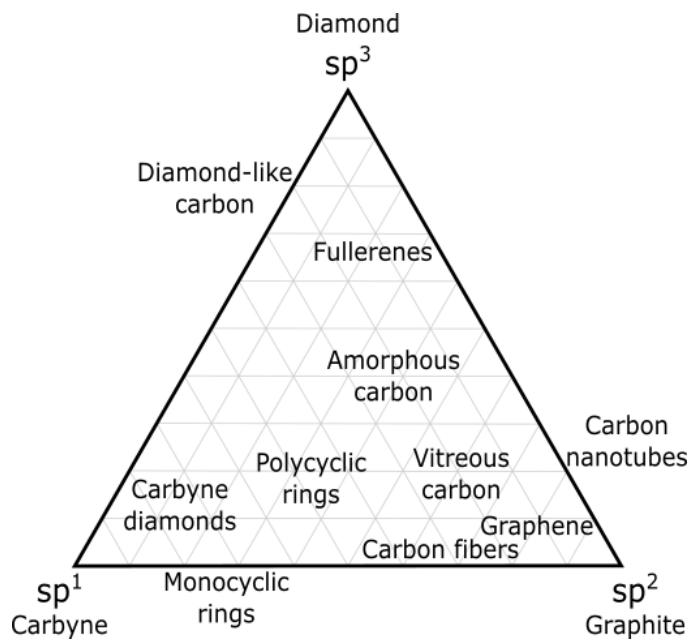


FIGURE 1.4: Ternary phase diagram of amorphous carbon regions based on hybridization degree. Adapted from [16–22].

'closed pore' with an opening to the external surface. [23] Figure 1.5 shows a classification of carbon allotropes according to their porous content.

Thermal conductivity and electrical conductivity decrease with increasing porosity due to the reduced amount of material to conduct electrons and

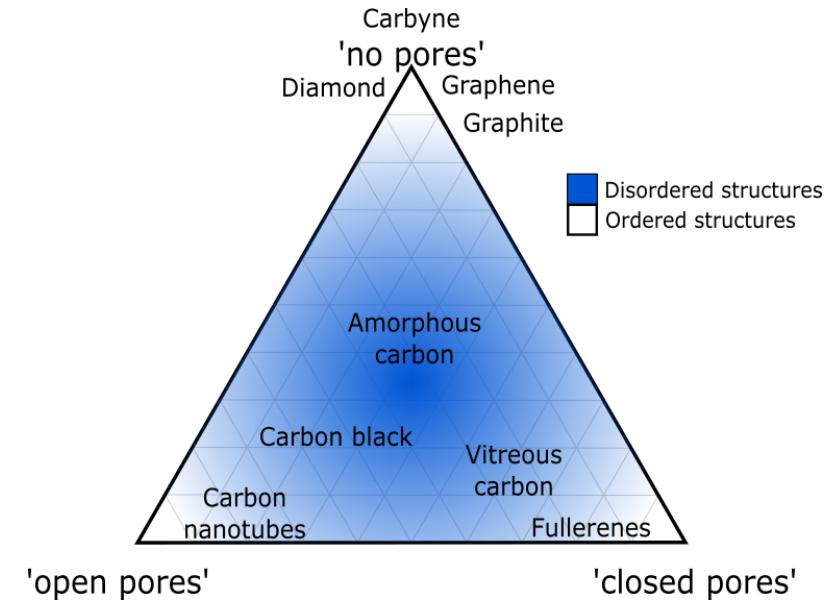


FIGURE 1.5: Ternary phase diagram of amorphous carbon regions based on structure order and porosity. Regions are colored by the degree of crystalline order within the carbon structure. White represents highly ordered structures, whereas white represents disordered structures. [23, 24]

energy. Furthermore, porosity negatively affects the mechanical properties like strength and elastic modulus as it reduces the volume in which stresses are distributed. Moreover, stresses are concentrated at the pores which makes the material prone to mechanical failure. [23, 24]

Due to the versatility and variety of CBNs, CBNs have been fabricated and implemented for various purposes. [2, 4–8]. For instance, field effect transistors (FET) have been studied by Novoselov [25] and Heersche et. al. [16]. Carbon FET devices have reported field-effect mobility one order of magnitude higher than that of silicon FETs. Other literature suggests CBNs to be favorable to detect a variety of gases and bio-molecules. [26, 27] As molecules are absorbed by the CBN, the carrier density and electrical resistivity of the carbon material changes. Moreover, CBNs have showed good performance in applications in energy (prevent wastage of energy), water (purification) and diagnostics (lab-on-chip systems and nano-sensors). [15, 28] As mentioned above, the morphology of CBNs has an impact on the electrochemical and mechanical properties. [23, 24, 29] In this regard, carbon nano-structures, such as nano-wires [30, 31], have been fabricated to achieve improved electrochemical characteristics.

1.1.2 Carbon Nano-wires

As depicted in Figure 1.4, carbon nano-fibers (CNFs) have been classified as linear, sp₂-based structures. [16–22] Nano-fibers own good electrical, optical and mechanical characteristics, however those properties are highly dependent on the morphology of the fibers. [32] The material properties of 1D nano-structures depend on fiber diameter, porosity, crystallization degree and crystallization orientation. Consequently, the fabrication parameters and environment conditions have an impact on the reproducibility of high quality fibers. [32] Carbon nano-fibers (CNFs) have diameters of several micrometers (Figure 1.8) and are different from carbon nano-tubes (CNT). [33–37] Unlike carbon nano-tubes with hollow cores, carbon nano-fibers can be represented as stacked layers along the thread length. [37–39] The stacked geometry of carbon nano-fibers results in unique electrical, chemical and mechanical properties. [40–42] Unlike CNFs, carbon nano-tubes inherent problems such as high cost and low effective surface area, which limit their practical use. [22]

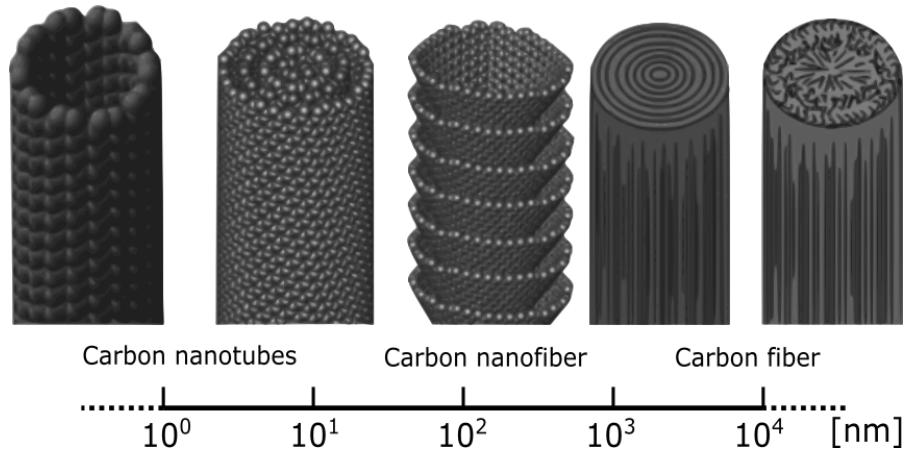


FIGURE 1.6: Various types of fibrous carbon materials bear different characteristics according to their molecular structure. Adapted from [22]

sp₂ carbon nano-wires have been used for the improvement of power density and specific energy in lithium-ion batteries. [43–45] Authors posit that the performance and capacity of Li-ion batteries depend on the CNF structure and texture. Through the right combination of electrospinning and carbonization parameters, electrically conductive, mechanically tough and with thin diameter fibers have been achieved by Yoon et al. [39]. Yoon reported 431 mili-ampere-hour per gram batteries with vitreous carbon nanofibers. Yoon states that the battery capacity highly depends on the

pyrolysis process parameters as the morphology of the fiber develops pores and hence different surface properties. CNFs supercapacitors have been investigated as energy storage devices due to their high power bearability and long lifecycles. [46–49] The studies' authors posit that carbon nano-fibers can be implemented as high-power supercapacitors due to their large surface area and high electrical conductivity.

On the other hand, the low reactivity and unique morphology of CNFs make them promising catalyst supports for metal nano-particles. [50–52] It is well known that the morphology and nano-structure of the supporting material are the main factors that prevent agglomerations of nano-particles. [53, 54] Moreover, in bone tissue scaffold applications, collagen is the most popular scaffold. However, collagen scaffolds bring xenogenicity issues which leads to disease transfer or immunogenic reactions, besides its inability to preserve its shape once placed in the body. [55–62] Currently, carbon fibers have been studied for bone tissue scaffold, however early attempts yield too thick fibers for cell cultivation and tissue regeneration. [63, 64] As depicted in previous research of CNFs for different applications, fiber morphology seems to have a significant impact on their performance.

Typically, carbon nano-fibers (CNFs) are synthesized by a combination of a patterning process and a pyrolysis process. CNFs fabricated by electrospinning of polymer solutions with electrostatic forces. Electrospun CNFs have characteristics such as high surface area, thin morphology with nano-scale diameters. The properties of electrospun fibers allow CNFs to be implemented in nano-sensing devices, energy storage applications, and tissue scaffolds. [28, 65–70] Several patterning techniques have been attempted to achieve the desired fiber morphology. In addition to electrospinning, CNFs have been also fabricated by two-photon polymerization (TPP) and photo-lithography techniques. [71] Cardenas et al. implemented TPP and conventional UV lithography to study the fabrication of CNFs within carbon micro-electromechanical systems (C-MEMS). The fabrication of these kind of carbon devices has been previously reported for techniques, such as electrospinning and photoresist patterning by photolithography using SU-8. The typical fabrication process of C-MEMS begins with a spin-coating of a photoresist unto a substrate (typically SU-8), followed by patterning techniques with UV-exposure by photolithography. Followed by the development of the desired features solvent. Finally, the

device is carbonized in a pyrolysis furnace in an inert environment. [72]

Near-field electrospinning can be regarded as complementary technique, by which polymeric nanofibers can be produced, since the structural geometries created photolithography are restricted by the diffraction limit. [72, 73] SU-8 is designed to produce vitreous carbon structure via photolithography, it is not design for electrospinning procedures as it lacks the right viscosity and solution conductivity. Cardenas [9] and Flores [11] have adapted the SU-8 formulation by the addition of tetrabutylammonium tetrafluoroborate (TBF) and poly(ethylene oxide) (PEO). TBF was added to increase the solution conductivity and PEO provides the required viscosity. Both additions are required to yield smooth solution flow during electrospinning.

TABLE 1.1: Prepared Polymer Solutions in Previous Work [9, 11]

Sample	Concentration wt%		
	SU-8	PEO	TBF
1	99.25	0.25	0.50
2	99.00	0.50	0.50
3	98.75	0.75	0.50
4	98.50	1.00	0.50

The thinnest fibers achieved by Cardenas [9] were achieved with sample 1 of Table 1.1, with the following characteristics: a) Fiber yield rate of 81%; b) Fiber diameter before pyrolysis of $4.966\mu m$; c) Fiber diameter after pyrolysis of $204nm$; d) Average fiber length of $60.54.3\mu m$; and e) Fiber electrical resistance from $407K\Omega$ to $1.727M\Omega$. Cardenas results have areas of opportunity regarding the fiber yield rate and the high variability on the fiber electrical resistance. These undesirable characteristics could be a consequence of the addition of PEO to the solution. Figure 1.7 illustrates the ingredients that comprise the SU-8 formulation. SU-8 based vitreous carbon is obtained after a pyrolysis process in which the oxygen already present in the SU-8 formulation allow the formation of close pores during annealing. However, the further addition of oxygen content present in the PEO molecules may be the cause of the low yield rate and high variability in electric resistivity from sample to sample.

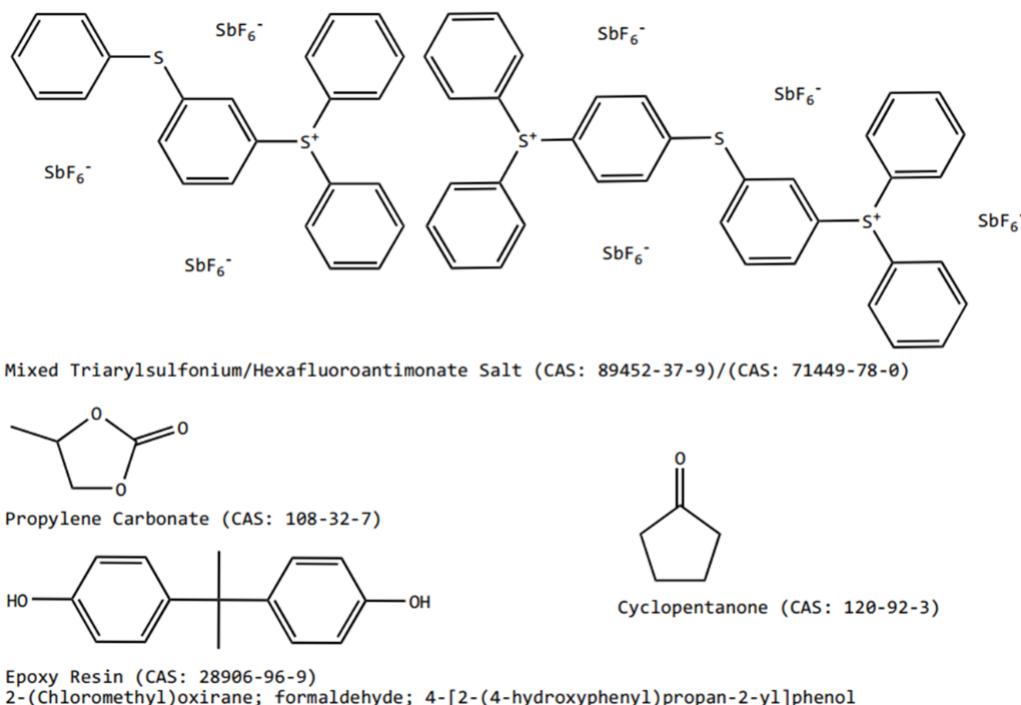


FIGURE 1.7: Components of SU-8 2000 Series Resists. Adapted from [74]

1.2 Problem definition and motivation

The role of carbon nano-fibers in nano-sensor devices play an important role, as portable instruments require light-weight and small-sized components. [28] Table 1.2 lists some advantages of nano-sensors that can be accomplished by the fabrication of CNFs via near-field electrospinning and a thermal treatment in an inert environment.

TABLE 1.2: Advantages of Nano-sensors. Adapted from [28]

Advantage	Description
High sensitivity	More accuracy, single molecule detection
Small size	Light-weight, portability, low-power consumption, small sample size, reduced sample preparation, and ease of use
Low response time	High-frequency, real time analysis
Low cost	Disposable devices

Sensors of small size require less time to output a stable signal as signals require less time to travel shorter lengths, hence signal noise is also reduced. Nano-sized sensors allow data collection and measurements to be performed in real time at faster speeds. [28] The nano-scale also allows sensors

to increase the active surface area, enabling the absorption and detection of analytes in low concentrations. [28] The integration of small-sized sensing devices lean to lower fabrication costs as large-scale production and reproducible fabrication can be achieved when producing nanosensors. [28] Moreover, conventional sensors are bulky and require higher amounts of power to operate. In gas sensing, neither a large sensing surface or a large sample is required to get a readable output signal from the sensor. Power consumption can be saved by reducing the thermal mass of the sensor. [28] Furthermore, if several gases are to be detected, an array of several gas sensors are to be assembled into an array. A multi-gas sensor array can increase the size and cost, whereas an array of gas nano-sensors (each functionalized to detect a specific analyte) can be implemented into a single device. [28] Nano-sensors can be classified by the kind of energy or physical phenomena that is detected, as depicted in Table 1.3 for instance: biological, mechanical, thermal, chemical, and optical sensors. [28, 75]

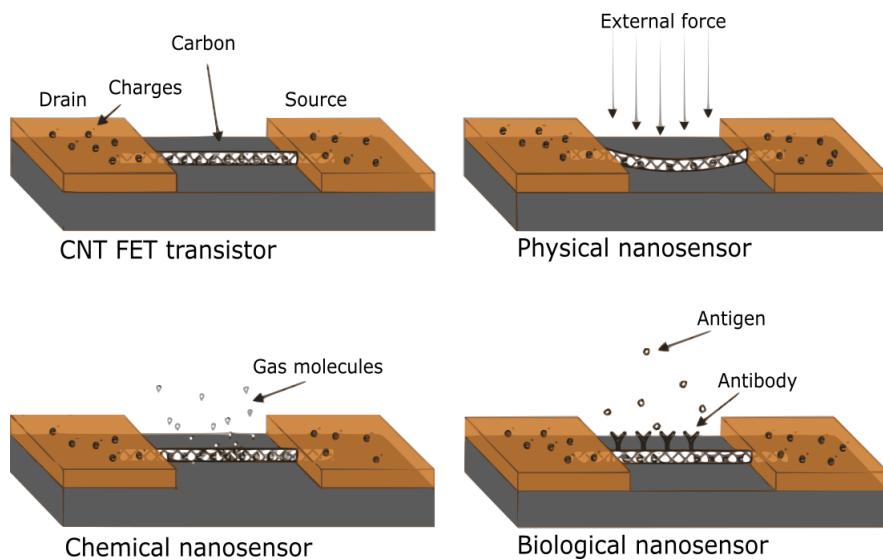


FIGURE 1.8: Diagram examples of carbon-based nano-sensors.
Adapted from [75]

Carbon nanowires have been fabricated with a photoresist by multiple-photon polymerization techniques. However little is known about polymers that can produce conductive carbon nano-wires after pyrolysis, as it is generally believed that most polymers do not form significant amounts of graphitic carbon when carbonized. In the past years, photopolymerization processes have been applied to the fabrication of nano-structures with the use of an epoxy based photoresist. [76] Photopolymerization techniques deliver patterning resolutions with nano-scale tolerances through two-photon

TABLE 1.3: Classification of Nano-sensors. Adapted from [28]

Classification	Phenomena / Energy
Mechanical	Position, acceleration, stress, strain, force, pressure, mass, density, viscosity, moment, torque
Acoustic	Wave amplitude, phase, polarization, velocity
Optical	Absorbance, reflectance, fluorescence, luminescence, refractive index, light scattering
Thermal	Temperature, flux, thermal conductivity, specific heat
Electrical	Charge, current, potential, dielectric constant, conductivity
Magnetic	Magnetic field, flux, permeability
Chemical	Components (identities, concentrations, states)
Biological	Biomass (identities, concentrations, states)

lithography for the production of highly detailed structures [77].

On the other hand, electrospinning has been acknowledged as a process with promising results at nano-structure fabrication [76], yet there is little research regarding the implementation of electrospinning for the fabrication of carbon nano-wires. Electrospinning has the potential to be a more straightforward process for the design and fabrication of nano-structures, as it can achieve mass scale manufacturing in a continuous, simple and reproducible manner. Cardenas [9] showed that electrospinning can be implemented with ease for carbon nano-wire synthesis. Mechano-electrospinning, a new variant of electrospinning shows promising results in the production of ordered carbon nano-wires. As stated in [9], mechano-electrospinning is an early technology invention and brings new challenges, such as the reproducibility of carbon nano-wire production. Furthermore, the study of a new fabrication process to produce carbon nanowires that involves mechano-electrospinning will enable spatial control of the structures' patterning.

Since electrospinning seems to be a better alternative for carbon nano-wire fabrication processes; and for that purpose of its implementation, it is required to develop polymer solutions that can be mechano-electrospun, photopolymerized and pyrolyzed into conducting carbon nano-wires. Carbon nano-materials have been subjected to research due to their various potential applications in diverse areas that take advantage of the nano-scale properties. [8] Carbon nano-materials are suitable for the catalysis,

adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [8] However most applications are not currently feasible due to the lack of a continuous, simple and reproducible fabrication method with inexpensive processes. With the newly designed polymer solution, it would be possible to produce carbon nano-wires in large quantities, and therefore more applications will become feasible. On the other hand, the new technique will overcome some limitations of other methods such as lithography currently has. For instance, patterns created by lithography processes cannot be originated, only replicated, all constituent points of the pattern can only be addressed at the same time, and the process requires the pattern to be encoded into a mask. [78]

1.3 Hypothesis

The rheological properties of polymer solutions along with synthesis parameters (stage velocity, voltage, dispense rate) can be amended through rheological analyses to obtain a low voltage electrospun-able, photopolymerizable and graphitizable fibers for the fabrication conductive of carbon nano-wires with specified dimensions (diameter and length). The rheological properties of polymer solutions along with synthesis parameters are to be amended by replacing the PEO (Poly(ethylene) oxide) component within the existing polymer solutions described in Flores [11] and Cardenas [9] work. PEO is to be replaced as its only purpose is to allow the electrospinning process to take place, but no benefit is obtained from it after pyrolysis.

1.4 Research Questions

- Is there any evidence of conductive carbon nano-wire fabrication though electrospun-able and pyrozable polymer solutions?
- What are the process parameters to consider/control for the fabrication processes of carbon nano-wires?
- What rheological properties are to be controlled/tested to deliver an electrospun-able and pyrozable polymer solution?

- Are there any efforts employed to the design of polymer solutions that can be electrospun, photopolymerized, and pyrolyzed into conducting carbon nanowires?
- What are the optimal fabrication parameters for the synthesis of carbon nano-wires through near-field electromechanical spinning?
- What materials can be used to ease the electrospinning process and favor the carbon nano-wire properties after pyrolysis?

1.5 Objectives

1.5.1 General objective

Study the practice and feasibility of a new fabrication process to achieve mass scale manufacturing of polymeric micro-wires in an inexpensive, continuous, simple and reproducible manner by the integration of near-field electromechanical spinning (NFEMS) and forward-thinking on pyrolysis processes to convert polymeric micro-wires into carbon nano-wires.

1.5.2 Specific objectives

- Design polymer solutions that can be electrospun by NFES, photopolymerized, and then pyrolyzed.
- Through rheological analyses, determine if polymer solutions can be easily employed for conducting carbon nano-wire synthesis.
- Determine and control the polymer solution rheological properties along with the process parameters of carbon nano-wire synthesis.
- Discover a PEO-similar material to allow the electrospinning process as well as input favourable properties to the carbon nano-wire yield.

1.6 Dissertation Outline

Chapter 2

Near-Field Electrospinning as an Affordable Way to Gain Spatial Control

2.1 Review of Polymer Solutions for NFES with Spatial Control

Near-field electrospinning (NFES) is identified to be a technique able to fabricate polymer nano and micro fibers with accurate placement. In the past years (2006-2020), several polymer solutions have been successfully electrospun into fibers through several variants of the conventional NFES process. Each NFES variant intents to tailor the process parameters in order to improve the fibers' properties.

Even though electrospinning is an old invention [79], it is currently a trending topic among researchers [80–82]. One of the reasons electrospinning is to be studied is its potential to fabricate polymer nano fibers from a variety of polymers. The technique allows the production of thin continuous fibers with ease, with micro and sub-micrometer diameters, which is something difficult to achieve by other techniques. Furthermore, the basic setup can be modified with ease to fabricate different fibers with diversified functionalities with different materials. The produced fibers can be aligned or unaligned. Besides, the electrospinning equipment is inexpensive and of small size, compared to the equipment of standard spinning techniques [83]. On the other hand, the understanding of the electrospinning process has improved in the last years.

Current literature dictates the typical spinning setup is comprised by three main components: a polymer reservoir, a fiber collector, and some

way to dispense the fibers onto the collector. The spinning process is an electro-hydrodynamic (EHD) technique that yields continuous polymer fibers. Other EHD techniques are spraying and atomization which produce polymer droplets and polymer particles respectively, see Figure 2.1.

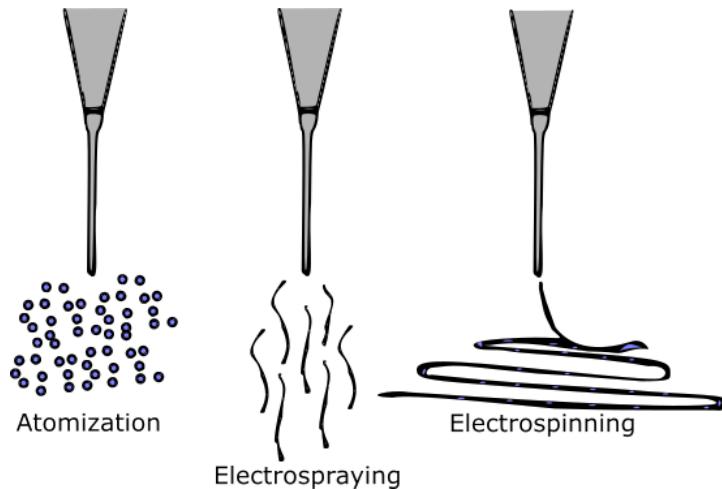


FIGURE 2.1: Electrohydro-dynamic techniques

2.1.1 Stretching forces

Electric Field

Electrospinning (electrostatic fiber spinning) is a fiber fabrication approach that implements an electric field to produce fibers by an electrical potential difference between the syringe needle and the collector. With the influence of high electric fields, the fibers are prone to break into separate layers due to the whipping instabilities as the jet travels to the substrate. The instability can be mitigated by adding additional ring electrodes between the spinneret and the grounded collector. [84]

The typical electrospinning setup applies an electrostatic charge to the polymer fluid at the tip of the needle nozzle, which results in the formation of the Taylor cone [85], from which a single polymer jet is ejected to the grounded collector. From the Taylor cone, the supplied polymer jet (typically a polymer solution) accelerates and reduces in diameter. The fiber finally develops with the complete solvent evaporation. Electrospun fibers are prone to splitting with the increase in acceleration due to high applied voltages, where multiple fibers are yield in a process known as electrospraying [86].

The electrospinning process starts with charging a polymer solution droplet. When a polymer solution is administered with a syringe pump, solution droplets will fall under the influence of gravity. The solution dripping stops when the electric field is strong enough to break the solution's surface tension, causing the droplet to change shape forming a polymer solution jet [87].

Shin et al. [88] reported that the growth of the whipping instability is one important element within the electrospinning technique. As detailed in Shin's work, weak electric fields produce a single uniformly thinning jet, and strong electric fields the jet becomes unstable after traveling a short distance.

High voltage power supply: DC & AC - Direct current (DC) is typically used in electrospinning with the electrons flowing in one direction. Alternate current (AC) implementations are also studied as the AC creates a change in the direction of the current flow. Kessick et al. [89] demonstrated the implementation of AC power supplies in the production of polymer fibers.

The AC electrospinning setup is similar to that for the DC variant. AC electrospinning apparatus do not require a grounded collector as the current alternates. In AC, the produced fibers are prone to carry an electric charge, while those generated shortly after have an opposite charge. The difference in charges lead the fibers to discharge on each other, creating an aerogel plume of fibers [90]. The optimal AC frequency depends on the materials used and is typically within 50Hz and 1kHz [91].

The AC technique has been studied for drug loaded related applications. Balogh et al. [92] compared fibers fabricated by DC and AC spinning techniques. Their work reports that AC and DC electrospinning can produce fibers with all three polymers, where the AC process allowed the implementation of faster flow rates than in the DC setup. The DC electrospinning technique generated fibers with a maximum flow rate of 5 ml/h; on the other hand, the AC setup allowed an increase in flow rate up to 40 ml/h.

Centrifugal force

The spinning processes require the implementation of a force to break the polymer source into a polymer jet. Centrifugal spinning intends to produce

fibers by the use of a rotating polymer source. The centrifugal force generated from typical rotatory speeds above 2000 rpm , results in fiber formation. [93, 94].

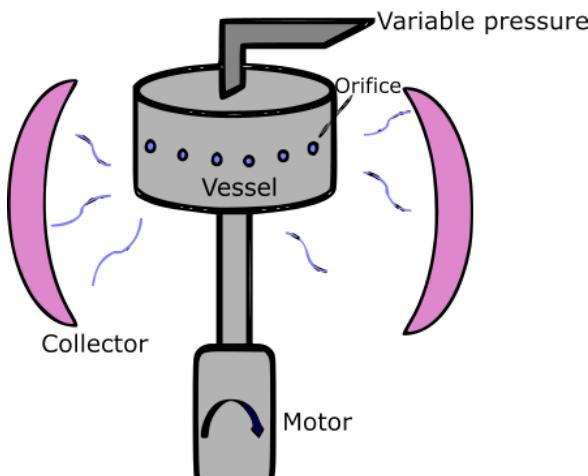


FIGURE 2.2: Typical setup used in pressurized gyration processes

The centrifugal force technique has been applied to polymer solutions and melts. This approach is used in applications where the precise deposition of the fibers is not relevant and production rate is to be maximized [95]. Efforts in centrifugal spinning are focused on drug delivery applications. Zander [96] fabricated polycaprolactone (PCL) fibers using the solution and melt variants of the centrifugal approach. Zander's fibers were produced with rotatory speed between three and 18 thousand revolutions per minute with $10\mu\text{m}$ in diameter.

On the other hand, PCL and PVP fibers were generated by Amalorpava et al. [97]. Amalorpava achieved sub micron/size fiber diameters for drug release purposes and bacteria growth inhibition properties. Literature [98] has shown that centrifugal approach has a simple setup that promises a large scale fabrication of fibers.

In some cases the centrifugal force implementations and pressurized gyration can be combined with an electric field. The implementation of two stretching forces (centrifugal and electrical forces), can help solvent evaporation [99]. Centrifugal electrospinning implements the same setup as the standard centrifugal spinning with the addition of a high voltage power supply between the rotating dispensing nozzle and the collector. The combined method has evidence to yield parallel fibers [100–103] at a higher rate [100, 101] than the standard electrospinning approach.

Blowing forces

Nano fibers can be produced with the implementation of pressurized gas with a polymer solution. The setup used for blow spinning is similar to the one used in coaxial electrospinning, where the polymer precursor is dispensed at a controlled rate. Unlike traditional electrospinning, in the solution blow spinning setup the needle nozzle applies pressurized gas to the polymer solution through an outer spinneret [104], see Figure 2.3.

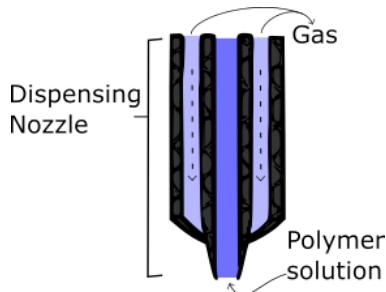


FIGURE 2.3: Dispensing nozzle used for solution blow spinning or melt blowing. [104]

Poly(lactic acid) (PLA) fibers have been produced by solution blow spinning. Oliveira et al. [105] fabricated the fibers from 6wt% PLA solutions with progesterone for live stock reproductive cycle regulation applications. On the other hand, Souza et al. [104] conducted a study to compare the standard electrospinning and the solution blow spinning techniques. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) were fabricated by both methods. The fibers produced by traditional electrospinning had thicker diameters and the size uniformity was higher in the fibers produced by solution blow spinning. The experimental setup requires a coaxial needle nozzle with a pressurized gas flow along with a potential difference between the dispensing needle and the grounded collector.

Mechanical force

Mechanical drawing comprises the simple technique to produce fibers by stretching the polymer solution with a glass pipette. [106] Nevertheless, the drawing technique is not scalable or with practical applications. [107] Touch-spinning methods have been developed to introduce a scalable technique for the production of nano fibers where the fiber is created by stretching the polymer precursor with a moving collector, as depicted in Figure 2.4. Touch-spinning is another mechanical technique that comprises a moving stage with an embedded glass rod (Figure 2.5). Where a polymer

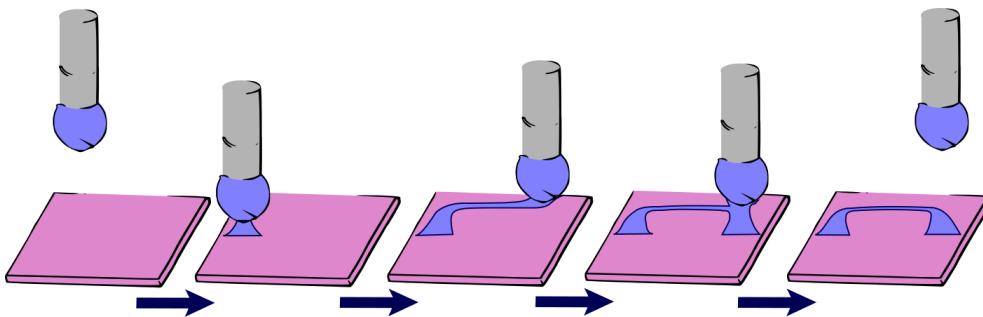


FIGURE 2.4: Typical mechanical fiber drawing process. First the needle makes contact with the substrate to break the polymer drop. Then the needle leaves the substrate and the collector moves to create and deposit the fiber. Once the fiber is written the needle makes contact with the collector to fix the fiber deposition.

solution is supplied from a syringe needle such that the tip of the glass rod makes contact with the polymer solution as it rotates, creating fibers. The rotation stretches the fiber, causing the fiber to increase in length and decrease in diameter. The increase in length causes the fiber surface area to increase and therefore making the polymer solution solvent to volatilize, ending with a dry fiber within the collector.

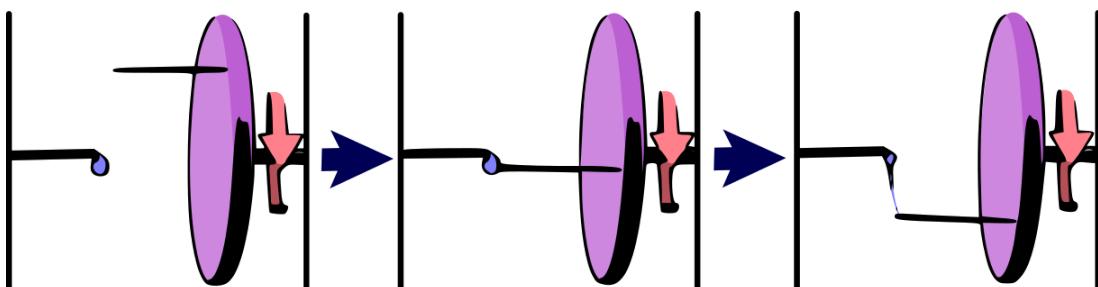


FIGURE 2.5: Touch-spinning technique. First rod is attached to a rotating stage and a polymer solution droplet is administrated through a needle. Then the rotating rod ‘touches’ the polymer precursor. Finally, as the rod rotates, the polymer solution is stretched and creates a fiber between the rod and the needle.

The touch spinning technique implies that the fiber diameter can be controlled by the moving collector’s speed and the polymer solution concentration. The main difference relies on the fact that the touch spinning method implements mechanical control to manipulate and stretch the fibers during the fabrication process, guiding the fiber in the collector enabling better control over fiber alignment. [108]

Microfluidic forces

The microfluidic spinning technique manipulates and controls the polymer solution in networks of micrometer channels. The channel network are

typically embedded in a microfluidic chip, where the solution deposition rate is controlled by active components (pumps and valves) with a computer. Cheng et al. [109] compared and combined the microfluidic spinning and electrospinning techniques. Heterogeneous materials and cell patterning within a single microfiber can be designed by the integration microfluidic channels. Therefore, microfluidic spinning is more suitable for cell encapsulation and tissues generation [109].

On the other hand, Kang et al. [110] managed to fabricate micro fibers by imitating the "silk spinning" process of spiders. Kang's micro fibers properties were modified using a microfluidic system with a programmable flow control (See Figure 2.6). The current microfluidic spinning approach is not scalable to a large fiber production, however it enables the fabrication of high-complex fibers that are not easily achieved by other methods.

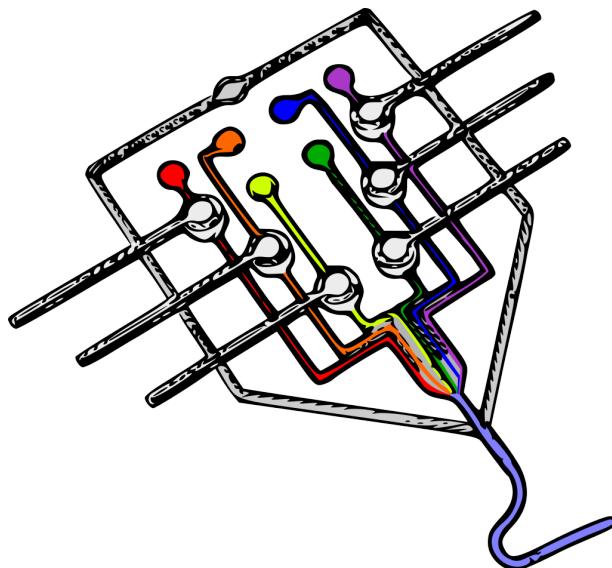


FIGURE 2.6: Microfluidic device used by Kang et al. [110]

Microfluidic techniques offer the possibility to embed several components into a single fiber, where each component can be released at different parts of the fiber.

2.1.2 Dispensing nozzle

Unlike traditional electrospinning, coaxial electrospinning (co-electrospinning) requires de implementation of a dual needle nozzle, where one needle is nested concentrically inside another needle, see Figure 2.7 [111, 112]. The purpose of the co-electrospinning setup is to produce core/shell fibers, unlike mono axial electrospinning that yields

monolithic fibers. Sun et al. [113]. Addressed electrospinning setups, where both the core and shell are comprised by PEO (poly(ethylene oxide)) and for a PEO shell with a poly(dode-cylthiophene) core. Sun et al. state that co-electrospinning has the potential to extend the range of materials that can be used for electrospinning. The shell solution can be modified to make the core solution spinnable. It was also discovered that non-spinnable solutions can be implemented as shell solutions in conjunction with a spinnable core solution. [114]

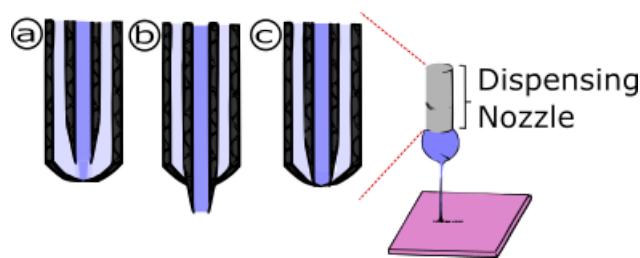


FIGURE 2.7: Needle configurations in coaxial electrospinning. (a) the outer needle encasing the inner; (b) the inner needle protruding from the outer; (c) both needles inline with each other;

Some advantages that co-electrospinning setups can break the polymer drop surface tension, initiating the jet burst from the spinneret nozzle. On the other hand, as the morphology and shape of the fibers depend on the polymer solution properties, the use of a co-axial nozzle allows the amendment of the material properties by producing bubbles, scaffolds and particles. [115, 116]. As in conventional NFES, in co-electrospinning, the needle tip is connected to a high voltage power supply with a grounded collector.

2.1.3 Polymer Reservoir (Polymer Melt & Polymer Solution)

Electrospinning processes can be classified on the polymer reservoir type. As Brown et al. [117] discussed, the polymer melt is equivalent to the polymer solution electrospinning (in place of a polymer solution a melt is used). The use of a polymer melt increases the complexity of the process, because the nozzle syringe and spinneret required to be heated to maintain the polymer in a liquid state. The fibers produced in melt spinning are typically found to have larger diameters than those from the polymer solutions due to the higher viscosity of a polymer melt than its solution. The apparatus used by Brown et al. [117] is depicted in Figure 2.8.

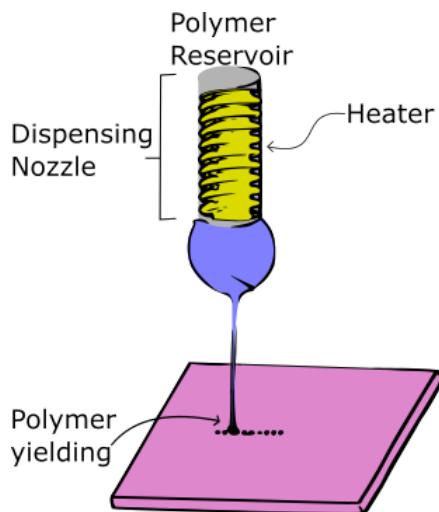


FIGURE 2.8: Typical Melt Electrospinning Setup

Despite the added complexity and thicker diameters, melt electrospinning gets around the need to handle volatile solvents, making the process safer to be performed on larger scales. Furthermore, polymer melt reservoirs get rid of any solvent contamination.

The first report of a melt electrospun drug delivery system came from Nagy et al. [118], who prepared fibers by melt electrospinning of Eudragit EPO with carvedilol. The drug and polymer were melted and mixed to form a homogeneous solid mixture prior to spinning. The melt-spun fibers reached diameters of $5\text{--}30 \mu\text{m}$, compared to $300\text{--}1000 \text{ nm}$ diameters produced from solution-spun fibers [118].

Balogh et al.'s work has been built on to blend plasticizers with the polymer Eudragit EPO and carvedilol active ingredient. [119] The plasticizers Triacetin, Tween 80 and Polyethylene Glycol were investigated in order to reduce the melting point of the polymer-drug mixture. The temperature drop is desirable to minimize the occurring drug degradation.

Lian and Meng [120] performed a comparison of poly(ϵ -caprolactone) (PCL) fibers fabricated by the melt and solution electrospinning techniques. They arrived to the conclusion that melt spinning is preferable when the polymer presents a low solubility. On the other hand the melt fibers were produced in a slower release rate. Gernot et al. [121] demonstrated that submicron-size fibers are possible through melt electrospinning. In their effort, they achieved a precise deposition of PCL fibers with diameters of $817 \pm 165 \text{ nm}$.

In literature, melt electrospinning has less evidence than the solution approach. However, melt electrospinning arises to be as flexible as its solution counterpart in handling multiple polymers, as reported in McCann's work [122]. Currently, the melt electrospinning setup is harder to determine and the lack of research on this technique explains its unexplored potential.

2.1.4 Polymer Solution

In electrospinning, it is typically agreed that the diameter of the fibers increased with higher concentration due to greater viscosity which withstands stretching. In near field electrospinning, similar observations have been reported where concentration increases, fiber diameter increased [123, 124], seeFigure ??.

TABLE 2.1: Approximation process to estimate the critical polymer concentration. Several polymer concentrations are tried and the resulting jets are observed until a continuous stream is achieved.

Observation	Concentration Adjustment
Dripping, no stream	Increase
Splitting small droplets	Increase slightly
Steady stream	No concentration adjustment
Splitting large globs	Decrease slightly
Nozzle clogging	Decrease

Polymers

The polymer selection is in function on the intended application. For example, a fast dissolving hydrophilic polymer such as poly(ethylene oxide) (PEO) is used for fast drug delivery systems. Otherwise, slow dissolving polymers such as poly(ϵ -caprolactone) (PCL) or poly(lactic-co-glycolic acid) (PLGA) are implemented. [125]

The polymer molecular weight along with the polymer concentration and solvent selection have a direct effect on the solution viscosity, conductivity and surface tension, hence the solution behavior in the electrospinning process. The spinnable viscosity range varies with the polymer and solvent.

Solutions with low viscosity are prone to insufficient polymer chain entanglements to produce fibers. [125] On the other hand, if the solution is too viscous, then the surface tension cannot easily be overcome by the electric

field. In both cases, the result can be droplets or particles forming rather than fibers as described in Table 2.1.

Solvents

The solvent used must be capable of dissolving the polymer of interest at an appropriate concentration to form fibers, and must possess a suitable volatility. A low-volatility solvent like water may fail to evaporate completely over the distance between the spinneret and the collector. When the fibers form, they will hence contain residual water owing to this incomplete evaporation. The residue solvent will subsequently evaporate from the fibers upon storage, resulting in ribbon-like (flattened) fibers, wrinkles on the fiber surface or fused fibers. On the other hand, a high-volatility solvent may evaporate very quickly, leading to larger fiber diameters (less time for elongation before solidification) and clogging of the spinneret (due to drying of the liquid at the spinneret before jetting, or drying of the Taylor cone during jetting). Solvents commonly used for electrospinning include ethanol, chloroform, trichloroethane and hexafluoroisopropanol [81, 126, 127].

Mixtures of miscible solvents can be used to ensure that sufficient polymer can be dissolved to give a solution of appropriate viscosity and volatility with suitable dielectric constant range to allow fiber formation. However, care must be taken because using a mixture of solvents with very different volatilities can result in porous fiber structures. As reported by Katsogiannis et al. for organic solvent mixtures with dimethyl sulfoxide (DMSO). [128] DMSO evaporates much more slowly than the organic solvents used, which results in its incorporation into the fibers. The DMSO will eventually evaporate, yielding porous fibers.

It is also important to take into account the surface tension of the solution. Solvents with very high surface tensions (e.g. water) can result in instability arising during the spinning process, and a broad range of fiber diameters in the products. If necessary, a surfactant can be added to reduce the surface tension, but this will be incorporated into the fibers produced.

2.2 Properties that Improve Accuracy of Nano-Fiber Deposition

Near-field electrospinning is considered to be an outstanding technique to fabricate polymer fibers with spatial control and it has suffered several modifications to improve the precision and accuracy of the fiber deposition. This paper intents to collect the NFES variants of electrospun polymer solutions with spatial control in recent research. Table S1 is a collection of the relevant NFES process parameters and achieved fiber morphology.

Some differences have been discovered between LV-NFES and conventional NFES. Low voltage near field electrospinning produces thinner fibers with lower voltages; as shown in Figure ???. Moreover, when implementing a moving stage, the fibers are affected by the mechanical stretching. Bisht et al. and Chang et al. [129, 130] reported that thinner diameters are yield with the increase of the x-y stage velocity, and larger diameters by decreasing the stage velocity.

Bisht and Chang's work [129, 130] reports a controlled technique to fabricate polymeric nano fibers in a continuous manner, using a low voltage setup. Their purpose is to find a workaround to the drawbacks of traditional NFES by using a superelastic polymer precursor, which allow continuous patterning without breaking. In low voltage near-field electrospinning (LV NFES), a visco-elastic polymer is used to allow continuous spinning at about 200V.

Kim et al. [130] experimented with a NFES variation where the fiber deposition is guided by conductive rails, see Figure 2.9. As stated by the authors, the induced electric field is enhanced by the conductive pattern, which allows the fibers to follow the desired deposition path. As the fibers are prone to follow the conductive pattern, additional fibers can be stacked on each other. The stacking process was successfully achieved in high electric field conditions at: 750 μm substrate to collector distance, and a 600 μm needle to rail (offset) distance, see Figure 2.9.

Gupta et al. [131] introduced a new technique to fabricate polymer scaffolds for tissue engineering applications and organ development. As described by Gupta et al. [131], the fiber deposition equipment is comprised by a stainless steel needle with a internal diameter of 750 μm , connected to a high voltage

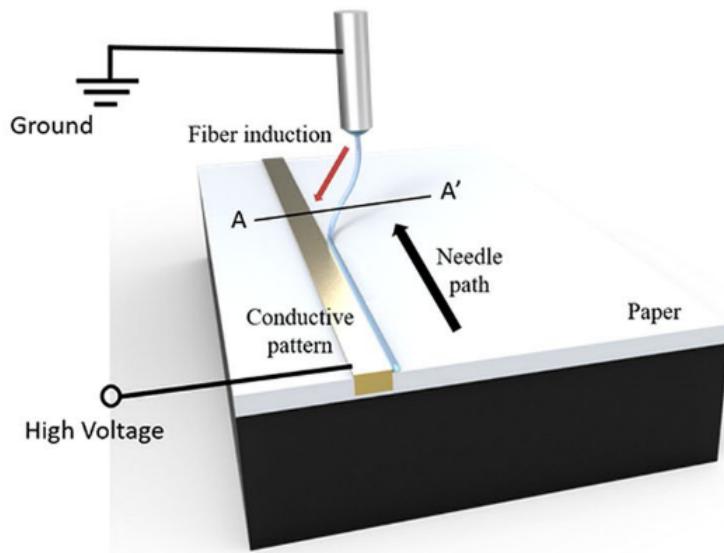


FIGURE 2.9: NFES setup for controlled fiber deposition on pre-patterned conductive electrodes. [130]

power supply of up to 30 kV with a deposition rate of about $\geq 1\mu\text{Lmin}^{-1}$. The setup was embedded to a motorized collector capable of controlled programmable motions, see Figure 2.10. The proposed technique was able to produce fibers of $150\mu\text{m}$ in diameter with pre-designed patterns.

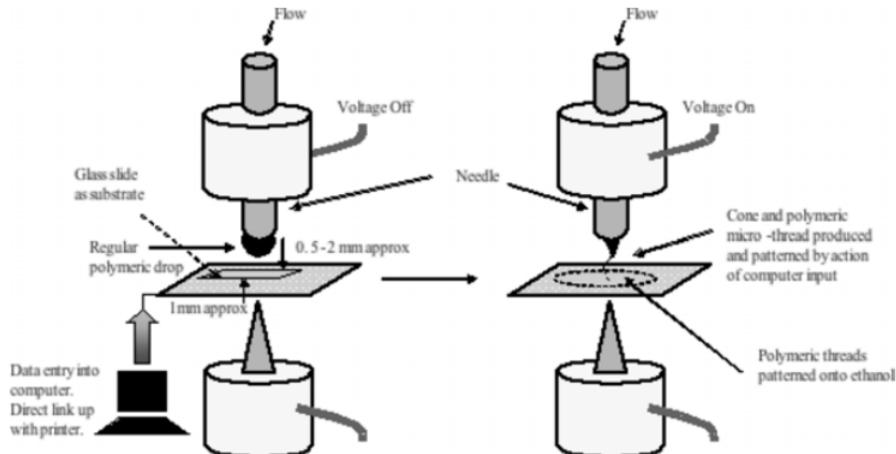


FIGURE 2.10: Schematic illustration of the electrohydrodynamic process. [131]

Wang, et al., Huang, et al., and Chen, et al. [132–134] experimented with several multi-nozzle near-field electrospinning of aligned nano fibers. The multi nozzle NFES apparatus is similar to the one used in conventional NFES with some modifications to the needle nozzle, see Figure 2.11. The authors implemented similar NFES setups where the installed linear array of nozzles is supplied with a constant flow rate of solution.

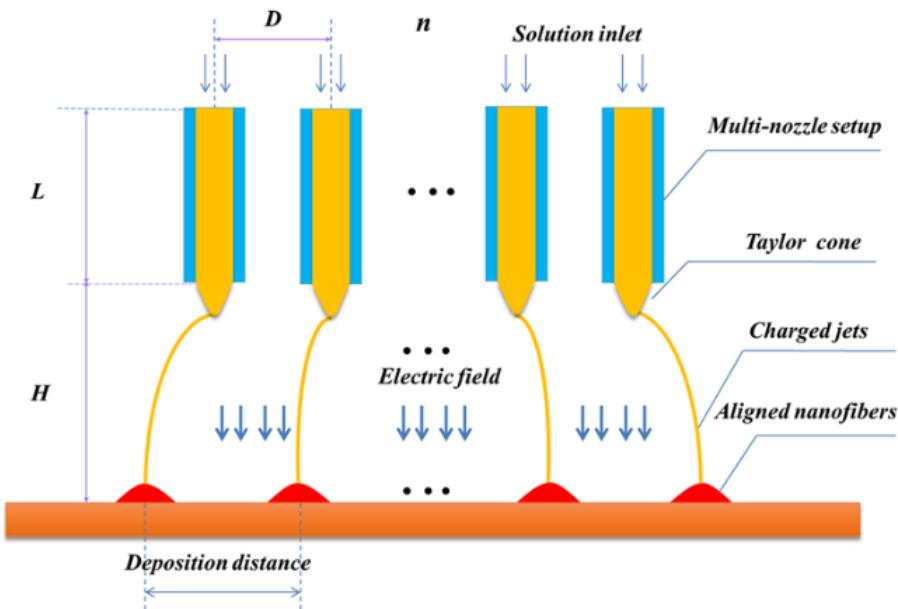


FIGURE 2.11: The geometry distribution of linear array multi-nozzle system [133]

The authors came to the conclusion that the distance between the deposited fibers increase with the increase of the needle-to-collector distance, as the influence of the applied voltage dissipates.

Huang, et al. [135] studied the mechanoelectrospinning (MES) technique for the fabrication of nano fibers. The MES technique tries to improve deposition accuracy by the introduction of a mechanical drawing force. The MES is predominantly controlled by the collector stage velocity, the nozzle-to-collector distance, and the applied voltage. The authors believe that MES can compete as a low-cost, high precision fabrication of electronics and enable the direct writing of structures for nano scale lithography. Figure 2.12 shows the polymer jet behavior when a mechanical force is implemented within the NFES process.

Micro and nano fibers have been written using AC pulse-modulated electrospinning by Bu et al. with polyethylene terephthalate (PET) as substrate [136]. The AC electrical field influences the electrospinning jet. The alternate current tends to decrease the repulsive electrical force allowing a stable straight jet between the dispensing nozzle and the insulating PET substrate. Bu et al. varied the stage velocity; faster stage velocities enable the deposition of straighter fibers [136].

A mechano-electrospinning technique was presented by Nagle et al. [137].

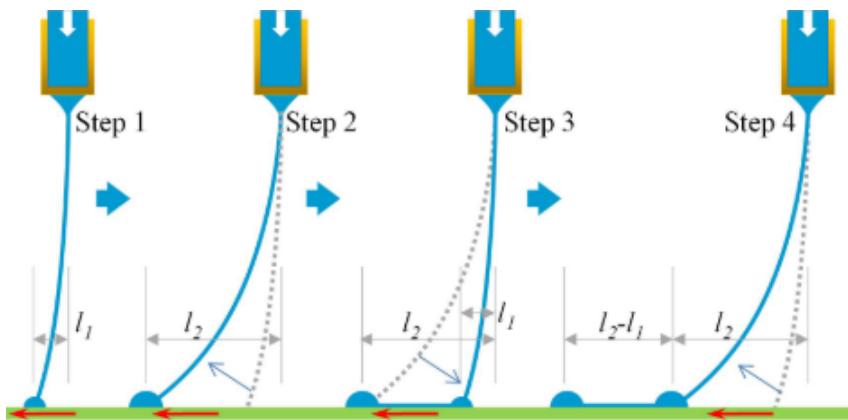


FIGURE 2.12: schematic diagram of leap direct-writing: the ink first accumulates at contact point and then gets stretched by mechanical drawing force. At a critical distance, the ink leaps to the next contact point, and gets stretched again [135]

With the implementation of a mechanical drawing force, a higher resolution nano fibrous pattern can be produced with lower voltages as the Taylor cone becomes more stable. Nagle et al. studied PEO fibers at different nozzle to collector distances. Evidence suggest that better patterning accuracy increases with increasing nozzle to collector distance as the solution is effectively dried [137]. Near field mechano-electrospinning enables the collection of non woven fibers over large areas.

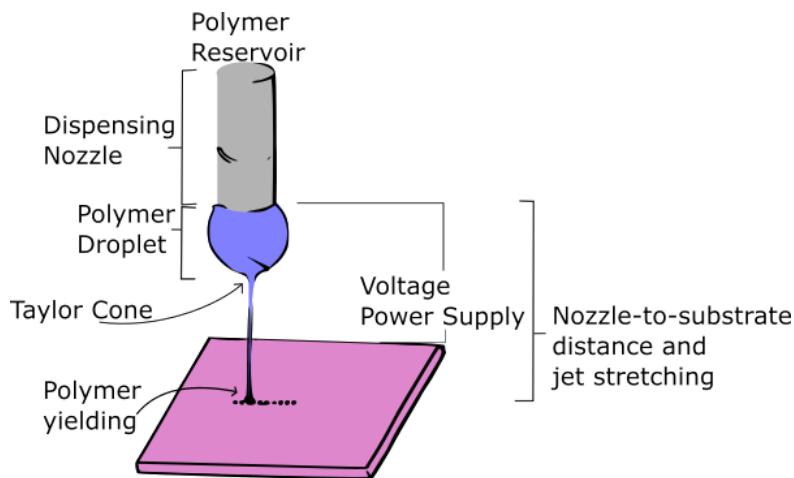


FIGURE 2.13: Near-Field ES Process Parameters

To spin nano fibers at close distances, the initial diameter of the jet is required to be as small as possible since stretching of the thread is limited. Kameoka et al. [138] demonstrated that a small initial spinning radius can be achieved using an atomic force microscope tip with a small polymer solution drop at the tip.

Near-field electrospinning, has exhibited to be capable fabricate nano fibers and nano fiber patterns [139]. Nevertheless, having a small polymer solution drop at the nozzle tip limits the length of the fibers that can be fabricated in a continuous manner. Using a spinneret with a reservoir (e.g. syringe) of solution generally produces fibers with diameter of a few micrometers [131, 140], since it creates a limit to which the nozzle inner diameter can be reduced to allow the solution to flow through. As shown in Figure ??, the implementation of thicker needle nozzles translate into an increase of the resulted fiber diameter

Coppola et al. [141] have showed a NFES variant that allows polymer nano fibers to be deposited directly from a polymer drop, averting the issue of nozzle clogging. The fibers are also prone soaking after deposition thus giving the fibers a semi-circular cross-section as depicted in Xue et al.'s [140] work.

2.2.1 Nozzle spinneret

The thinnest nozzles in literature so far are about 50nm in diameter, by Chang et al. [123] who used a $100\mu\text{m}$ inner diameter needle tip to electrospin poly(ethylene oxide) (PEO). Camillo et al. [142] used a micro-diameter tip Tungsten spinneret in a 26G needle to electrospin co-polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with poly(ethylene oxide) (PEO). The nozzle most commonly comprises a simple narrow-bore, blunt-end metal needle. The diameter of the needle can vary, but most commonly researches work with internal diameters below 1 mm . This translates to needles of gauge 18–22. In general, this simple spinneret design can be used to achieve successful spinning. A blunt-end rather than a tapered-end for the needle exit is important as the size distribution of the products increase with an increase in needle tip angle. However, it should be noted that there will be some interactions between the solvent and polymer molecules in the solution and the metal surface of the spinneret. There will exist some attractive forces between the polar groups in the polymer and the electro-positive metal surface, which can act counter to the drawing force of the electric field and can pull the polymer solution back into the spinneret. It has been found that coating the spinneret exterior in a non-conductive and non-stick polymer such as Teflon or epoxy coating can reduce these interactions. [143, 144] As a result, the electrical energy can be more efficiently used to elongate and narrow the polymer jet, and narrower

fibers can be produced. In addition, strong attractive forces between the polymer jet and the metal spinneret can result in fibers becoming attracted to the needle, leading to lower yields and potentially to blocking of the exit orifice.

2.2.2 Applied Voltage

In recent literature, near field electrospinning has been studied to reduce the fiber diameter and to improve the fiber deposition accuracy. Madou et al. [129] and Chang et al. [123] came to the conclusion higher voltages yield thicker micro-fibers with a loss in jet stability. This relationship between the applied voltage and resulting fiber diameter is influenced by other variables such as nozzle-to-substrate distance and solution deposition rate. For instance, if a high voltage is applied at a low deposition rate then electrospraying is achieved, meaning the formation of several non-continuous fibers. The applied voltage shall be sufficient to break the surface tension and initiate the jet, but low enough to avoid multiple jets at the nozzle tip.

Madou et al. [129] achieved the fabrication of thinner fibers with spatial control by reducing the applied voltage to 200-600 V at a nozzle-to-substrate distance of 0.5-1 mm. The low voltage setting does not create enough charge to break the polymer solution surface tension to initiate the electrospinning process.

Madou et al. [129] and Chang et al. [123] initiated the electrospun fibers by mechanically pull the polymer solution at the nozzle tip using a micro-probe tip. Chang and coworkers reduced the applied voltage from 1.5 kV to 600 V with a nozzle-to-substrate distance of 500 μm to yield a fiber diameter between 3 μm and 50 nm . With an applied voltage of 200 V and a nozzle-to-substrate distance of 1 mm.

In near-field electrospinning, the applied voltage has an impact on the produced fiber morphology. For instance, a voltage higher or lower to the optimum voltage will translate into an increase in fiber diameter. Song et al. [145] demonstrated that a decrease in voltage from 400 to 500 V can reduce the fiber diameter from 160 to about 60 nm with a nozzle-to-substrate distance of 20 μm . A workaround to break the polymer solution surface tension is to initialize the NFES process with a higher voltage and then lower the voltage

once the jet is created. Huang et al. [135] implemented the previous and yield ordered fibers with a distance between adjacent fibers of $50 \mu\text{m}$.

2.2.3 Nozzle-to-substrate distance

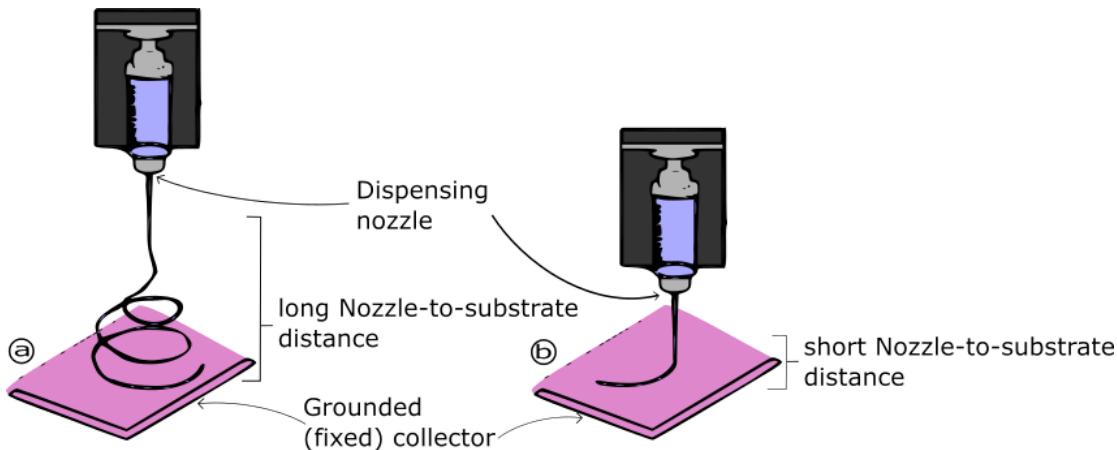


FIGURE 2.14: a) Typical Far-field Electrospinning (FFES) Setup. b) Typical Near-field Electrospinning (NFES) Setup.

Figure 2.14.a, depicts the typical setup for the conventional far-field electrospinning (FFES). As stated in previous sections, the precursor polymer droplet becomes charged with the employment of an electric field between the polymer solution and the collector [146]. When the polymer solution surface tension is overcome by the electric field potential difference a jet is formed, starting the electrospinning process. The electrospinning process can be break down into two steps: i) first the jet travels in a straight line, and ii) the jet begins to curl due to bending and whipping instabilities [89, 147]. The fiber spatial control in far-field electrospinning is limited due to the instabilities, inhibiting the precise deposition of fibers.

In the intent to achieve controlled fiber deposition, Sun et al. [139] reported an electrospinning variation known as near-field electrospinning (NFES). Figure 2.14.b, describes the near-field electrospinning setup, where the distance between the dispensing nozzle and the collector is reduced to write fibers while the jet travels in a straight line. Moreover, some mechanical influence is required to deposit fibers precisely. The mechanical force is introduced by moving collector. If the polymer solution jet speed is faster than the speed of the moving collector, the written fiber will curl; on the other hand, if the collector moves faster than the polymer jet, the fiber will gradually diminish [140, 148]. Currently, due to the lack of theoretical models, the near-field electrospinning process parameters (such

as the collector speed) are typically tuned by experience and experimentation only.

The main difference between NFES and FFES is the distance between the needle and the collector which is higher in FFES (about 10 cm) compared to NFES which ranges in the mm scale. The short distance allow the production of well aligned fibers within particular designs. In NFES, the fiber morphology can be altered by the control of the distance between the nozzle and the substrate (collector). With the decrease of the nozzle-to-substrate distance, the electric field strength increases; however it can cause incomplete solvent volatilisation and possible short circuits between the collector and the nozzle tip.

An optimal nozzle-to-substrate distance shall be defined to ensure the fabrication of dry continuous fibers. If the solvent is not well evaporated, the produced fibers are prone to defects; on the other hand if solidification happens too fast, the solids can block the spinneret which can prevent a continuous fiber yield. Furthermore, the polymer jet will discharge itself as soon as possible, therefore long distances can result in low yields.

2.2.4 Substrate

Due to the close distance between the grounded substrate and the charged spinneret in NFES, the set up is prone to electrical shorts. In NFES, when a short circuit takes place, the electrospinning process is interrupted resulting in the fabrication of discontinuous fibers. Two workarounds to avoid electrical shorts is to lower the applied voltage and to use less conductive substrates [149, 150].

Liu et al. [149] discovered that the fiber alignment is improved by using a glass-cooper foil substrate, however the well aligned fibers are spoiled after prolonged depositions due to residual charges. Additionally, the effect of residual charges is amplified with the used collector substrate contains a conductive layer and a non-conductive layer [149].

On the other hand, Choi et al. [150] implemented a hydrophilic substrate to deposit the fibers with plasma treatment to increase the conductivity of selected areas. NFES was carried put with precise deposition as the fibers were placed as per the desired design within the hydrophilic substrate.

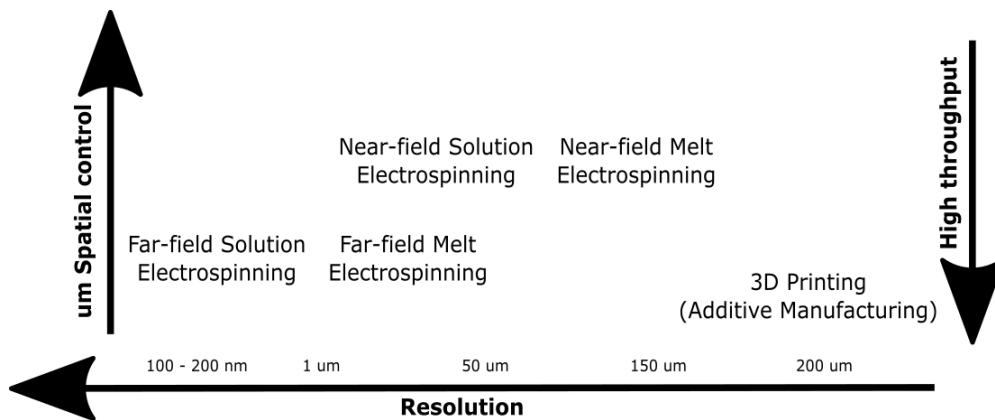


FIGURE 2.15: Different Electrospinning Methods in Terms of Spatial Control, Fiber Throughput and Resolution. Adapted from [151]

As depicted in Figure 2.15, solution electrospinning yields fiber with higher resolution than melt electrospinning techniques, and near-field electrospinning offers greater spacial control on the deposition of fibers than the far-field technique. Moreover, solution electrospinning often involves the use of toxic solvents, whereas melt electrospinning is a solvent free process but with extra complexity as a heater needs to be installed. [151]

2.3 Data collection of NFES fiber morphology and process parameters

Near-field electrospinning process parameters and achieved fiber morphology data was collected into a single database with the purpose to analyze the data and find correlations between the process parameters and the obtained fiber morphology after a NFES process. The analysis comprises from the first reported NFES apparatus built in 2003 by J. Kameoka et al. [152] to recent studies conducted in 2020. [9–11, 152–229] The data collection process was divided in three procedures depending on the format of the available information, as follows:

1. Case 1 : data is collected as is from literature. This procedure was implemented when the data is listed within tables and/or as text format.
2. Case 2 : data is only presented in a figure as plots.
3. Case 3 : data is not available in text format or plots, however Scanning

Electron Microscopy (SEM) images are reported from the obtained fibers.

2.3.1 Image Analysis - Data extraction from plots

Most numerical data of NFES process parameters and fiber diameters is available only in the form of plots. The reported figures provide a visual relationship between the variables of interest, however recovering the numerical values of the data is a tedious process prone to errors. To avoid mistakes and accelerate the collection data from plots, [WebPlotDigitizer](#) was used. WebPlotDigitizer is a HTML5 tool that facilitates accurate data extraction with ease of use. Figure 2.16 is a screenshot of the software in use.

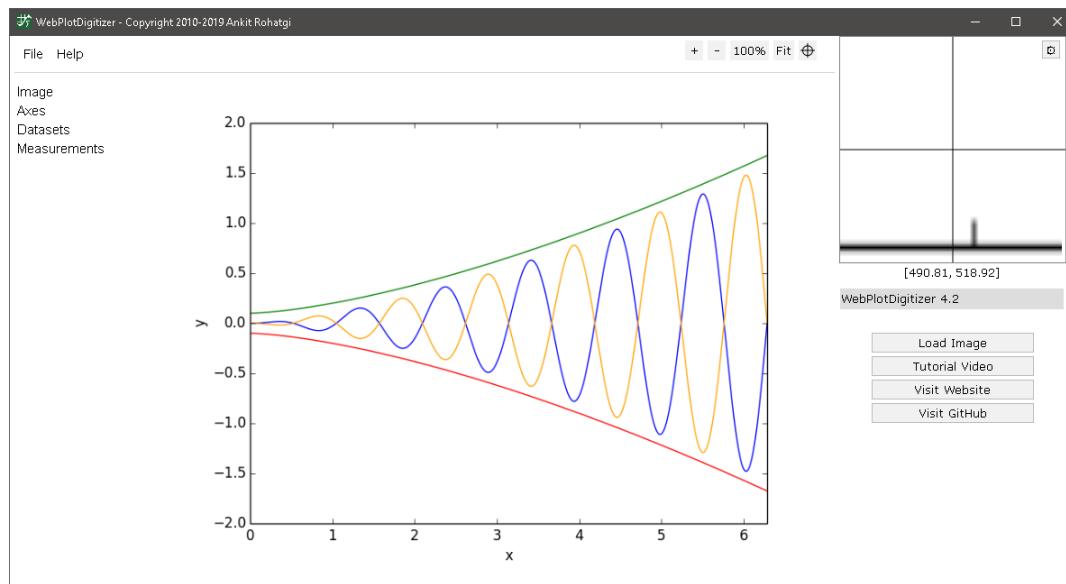


FIGURE 2.16: Open session of WebPlotDigitizer github.com

2.3.2 Image Analysis - Data extraction from Scanning Electron Microscopy Images

Scanning Electron Microscopy Images (SEM) images contain information in a two-dimensional grid that can be extracted using point and line counting techniques, however this can be a laborious process for a large number of images. To decrease the complex and laborious aspect of the counting process, a *Python* script was developed to measure fiber diameters from the available SEM images. As shown in Figure 2.17, the image analysis algorithm follows three main steps: pre-processing, segmentation, object detection, and data processing.

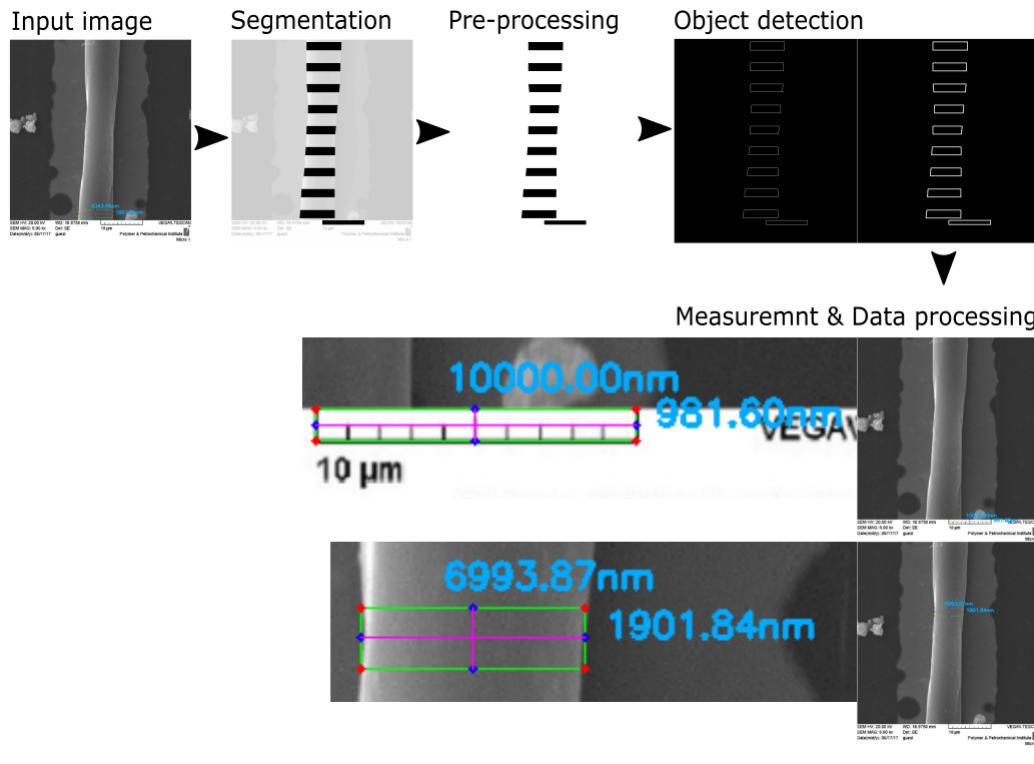


FIGURE 2.17: Image Analysis Algorithm to Measure Fiber Diameters from SEM images. Illustration uses Yousefi et al.'s work as an example. [228]

The adopted image analysis was implemented with the *Python* package *OpenCV*. First a segmentation procedure is executed over an input image to delimit the objects to be measured (fiber sections and scale bar). The segmentation step is the only step needed to be done manually in a image processing software, in this case *Inkscape* was used. Next, the segmented image is passed to the *Pyhton* script, which will convert its input image into a binary image. A binary image is a black and white image (with no gray scale) that ease the detection of the object edges as the color intensity change between the objects and the background is well defined. Once the binary image is computed, the *Canny* edge detection algorithm is executed. Once the edges are well defined, a the image is dilated to make the edges more visible. The final step before measurement, the *OpenCV findContours* function is called to store the objects in memory. The first object to be measured is the scale bar as this is needed as a reference to convert the pixel counts to a metric unit. Finally, the objects are located within the image with four edge points, and the reference object is used to compute the metric length as the ratio of counted pixels between two edge points and the scale bar dimension in meters.

Measurements were validated with Camillo's, Gupta's, Jiang's, Min's, Sun's, Wang's, and Xue's [156, 162, 169, 190, 197, 214, 226] results as those authors reported both, a SEM image and the measured fiber diameter. For instance, Figure 2.18 shows in white the reported diameters by Min and in blue the diameters measured by the *Python script*. The measurement error of the developed script is about 3.2% in average. It is considerable to mention that the reported measurement error is mainly contributed to the fact that most fibers are not of the same diameter along the fiber length. In most cases, measurements at the end of the fibers are thicker than the ones measured in the center.

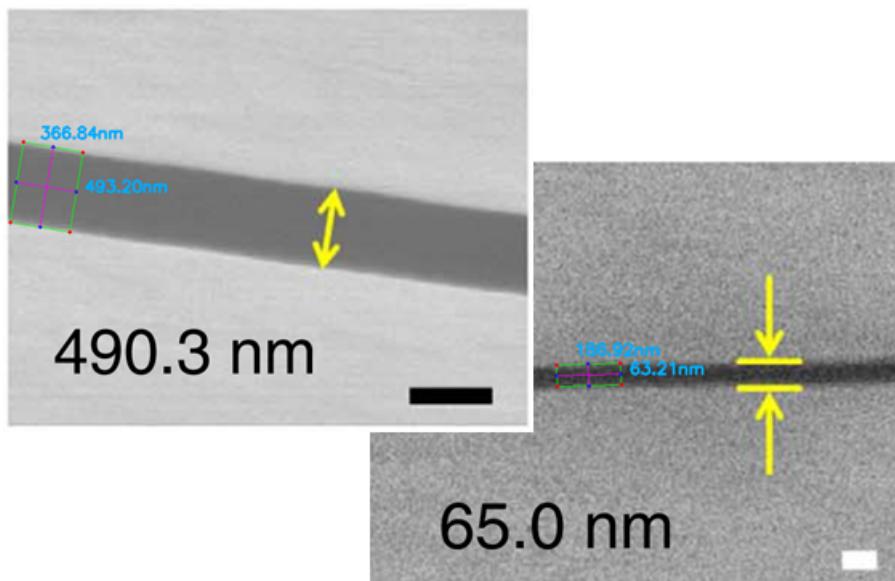


FIGURE 2.18: Validation of the developed image analysis measurement tool. SEM images of Min's work are used as an example. [226]

2.4 Discussion & NFES Challenges

Helix electrodynamic printing (HE-printing) was presented by Duan et al. [230] with the intention of depositing aligned fibers. The authors fabricated a stretchable piezoelectric device using micro and nano fibers to demonstrate the possible applications of HE-printing for electronics manufacturing. Duan et al. concluded that the fiber morphology is mainly driven by: the stage velocity, the applied voltage, and the nozzle-to-collector distance.

Figures 2.20, 2.21, 2.22, 2.23, 2.24 and 2.25 are scatter plots that depict the relationship of various process parameters (polymer concentration $C_{polymer}$,

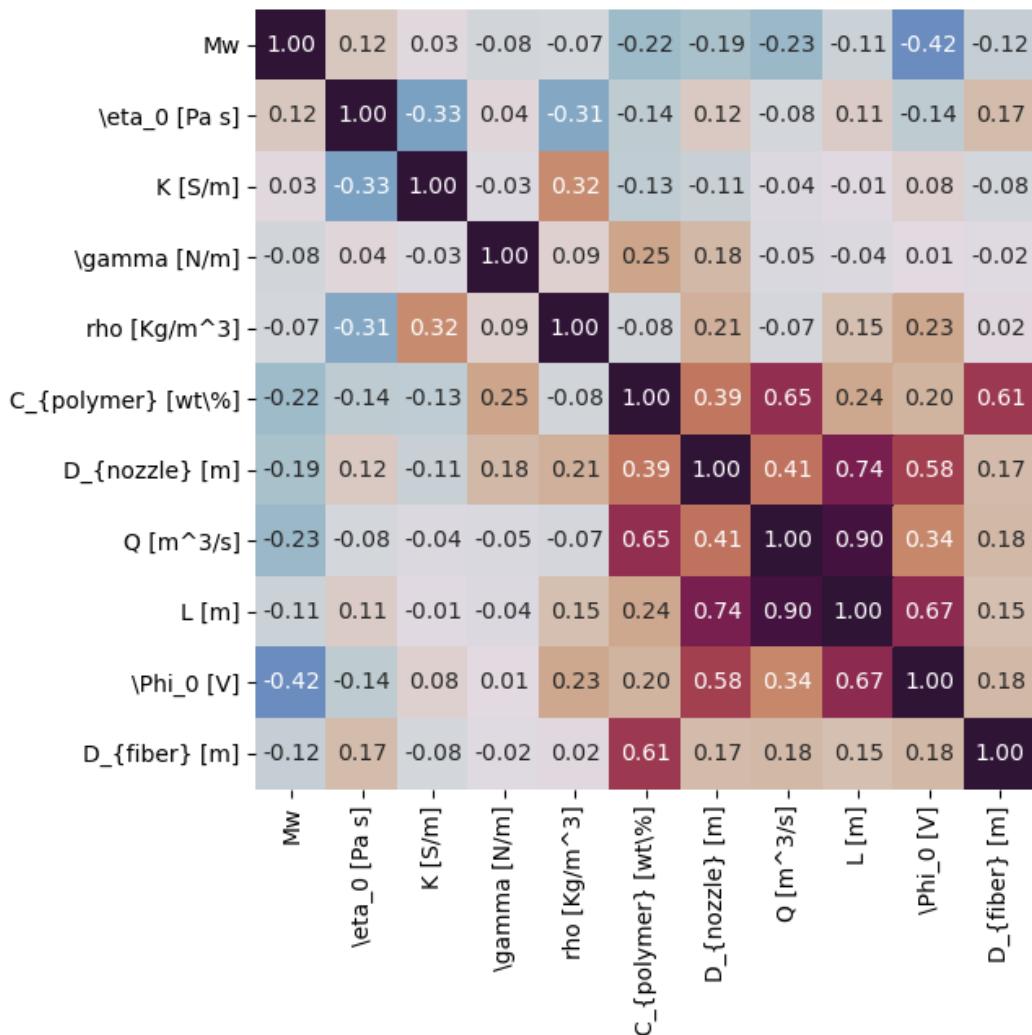


FIGURE 2.19: Correlation matrix comprised by the NFES data from recent literature. [9–11, 152–229] Fiber diameter is highly correlated with polymer solution concentration and slightly correlated with solution flow rate, zero-shear viscosity and nozzle diameter.

nozzle inner diameter D_{nozzle} , NFES working distance L , NFES applied voltage Φ_0 , flow rate Q , and stage velocity v_{stage}) with the final fiber diameter D_{fiber} . In a generalized summary, these figures suggest that thin fibers are produced with the implementation of low polymer concentrations, small nozzle diameters, short working distances, low applied voltages, low flow rates, and high stage xy velocities. Moreover, based on the degree of dispersion of the data points, polymer concentration $C_{polymer}$ is the most reliable process parameter to describe and predict the behavior of the fiber diameter, as most of the data can be grouped in a single cluster. Unlike $C_{polymer}$ in Figure 2.20, various data clusters can be identified within the other scatter plots. For instance, Song's results [223] deviate from the main cluster

in Figures 2.21, 2.22, 2.23, and 2.25, this may be because Song et al. used Au/Pd coated glass capillary nozzles instead of the traditional stainless steel precision tips. However in the $C_{polymer}$ vs. D_{fiber} figure, Song's results fit within the main cluster.

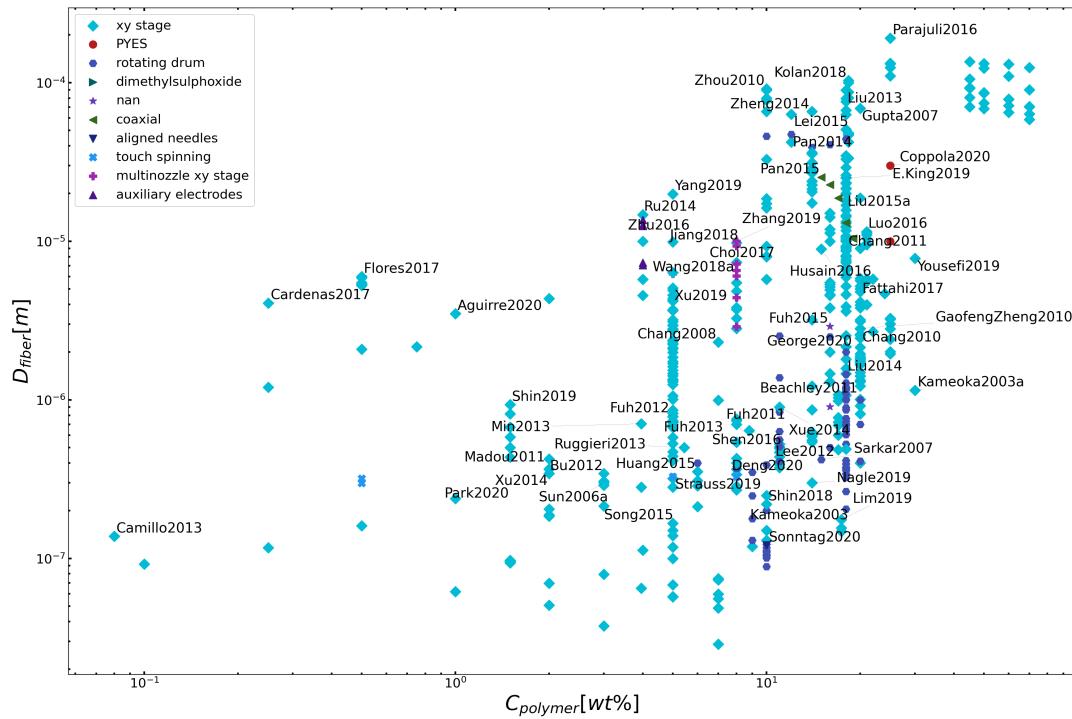


FIGURE 2.20: Scatter Plot of Polymer Concentrations and Fiber Diameters from Literature Experimental Results. [9–11, 152–229]

The trend of Figure 2.21 shows that thicker nozzle diameters yield thicker fibers. However, the final fiber diameter can be reduced without changing the nozzle diameter. For instance Chang et al. [208] achieved the thinnest fibers of about 50nm in diameter even though Chang implemented nozzle needles of similar diameter as Shin, Min and Xu by the implementation different settings on the other process parameters. [155, 164, 226] It is reasonable to notice that Chang's record of achieving the thinnest fiber may be a one time-successful since, neither the yield rate nor the reproducibility of their technique was not reported.

The relationship between the fiber diameter the working distance L and applied voltage Φ_0 can be depicted in Figures 2.22 and 2.23. The near-field electrospinning jet is ejected from the Taylor cone when the applied voltage generates an electric field strong enough to break the solution drop. Changing the applied voltage will amend initial drop and fiber morphology, thereby resulting in a change in the fibers' properties. However, the effect

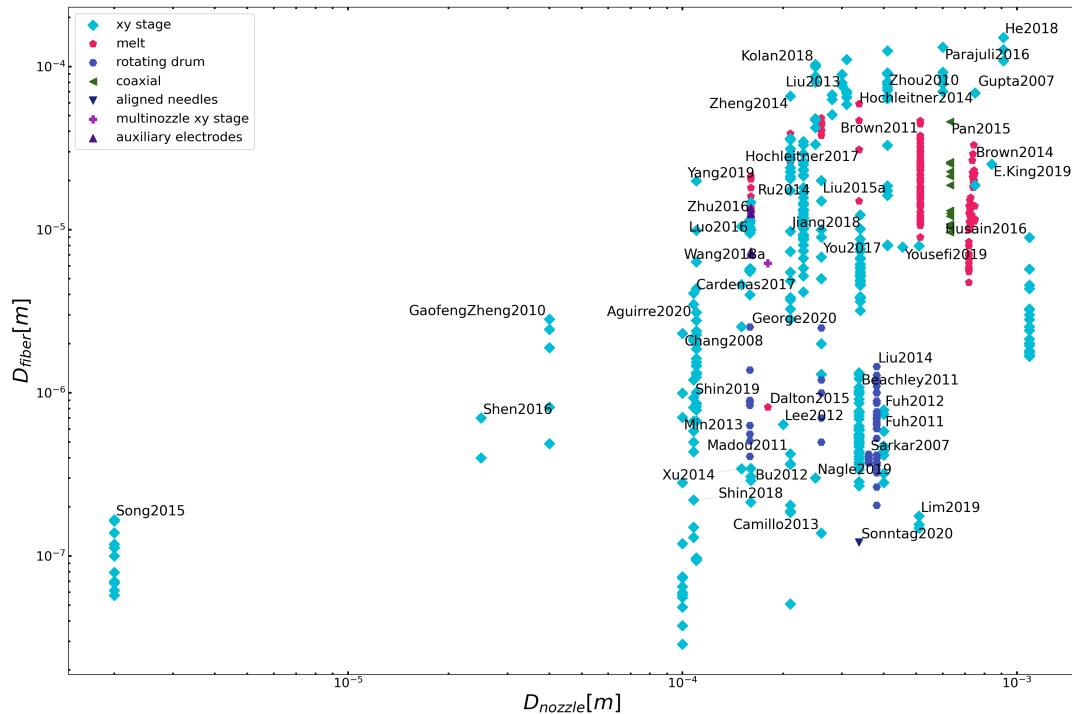


FIGURE 2.21: Scatter Plot of Nozzle Inner Diameters and Fiber Diameters from Literature Experimental Results. [9–11, 152–229]

of the applied voltage on the fiber diameter is not well defined. On one hand, many researchers posit that high applied voltages lead to larger fiber diameters, whereas other researchers have reported reductions in fiber diameter with high applied voltages as the electric field force increases on the charged jet. [231] Furthermore, Reneker and Chun observed that applied voltage does not significantly affect the diameter of electrospun polyethylene oxide (PEO) fibers. [232] Applied voltage has an influence on the fiber diameter, but the degree and direction of influence varies with other process parameters such as polymeric solution concentration and on the working distance [233, 234].

Looking at Figures 2.22 and 2.23, the data points from Husain, Lee and Sonntag [191, 200, 209] experimental results are outside the principal cluster since they implemented working distances around 10^{-1} m, which is considered to be the threshold between NFES and far-field electrospinning (FFES). One can observe that: a) in NFES fiber diameter increase with increasing applied voltage; and b) in FFES fiber diameter decrease with increasing applied voltage. On the other hand, data related to Liu's and Beachey's work [187, 196] do not fit the main trend as they perform the electrospinning process with a rotating drum as the collector, instead of the

typical xy stage.

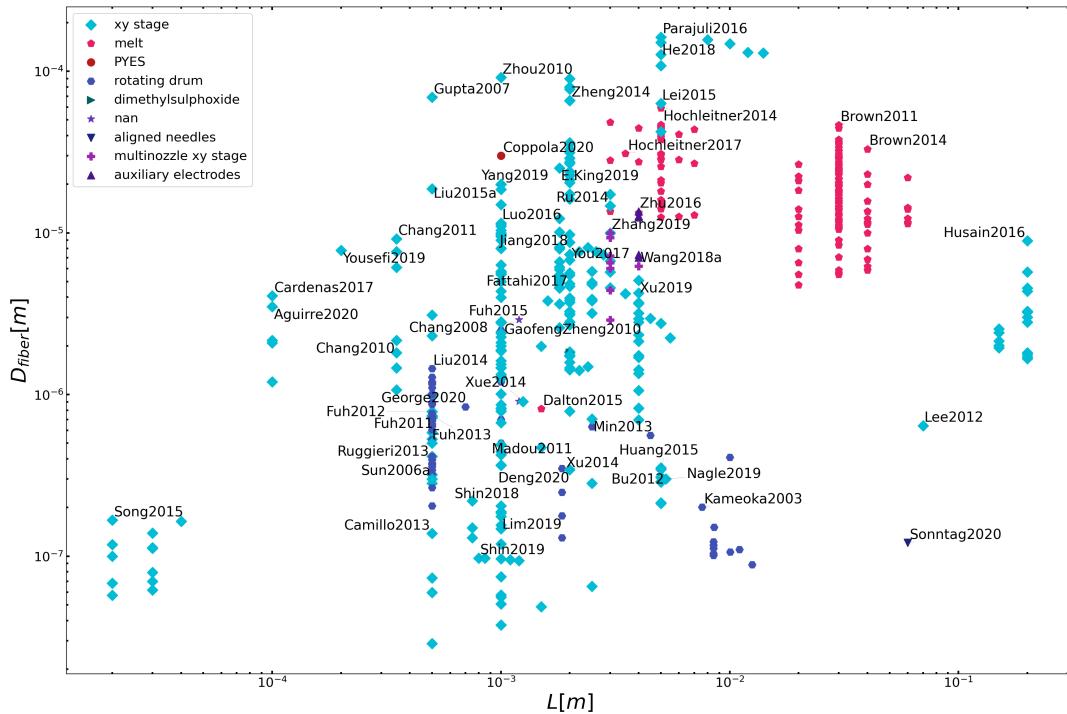


FIGURE 2.22: Scatter Plot of NFES Working Distances and Fiber Diameters from Literature Experimental Results. [9–11, 152–229]

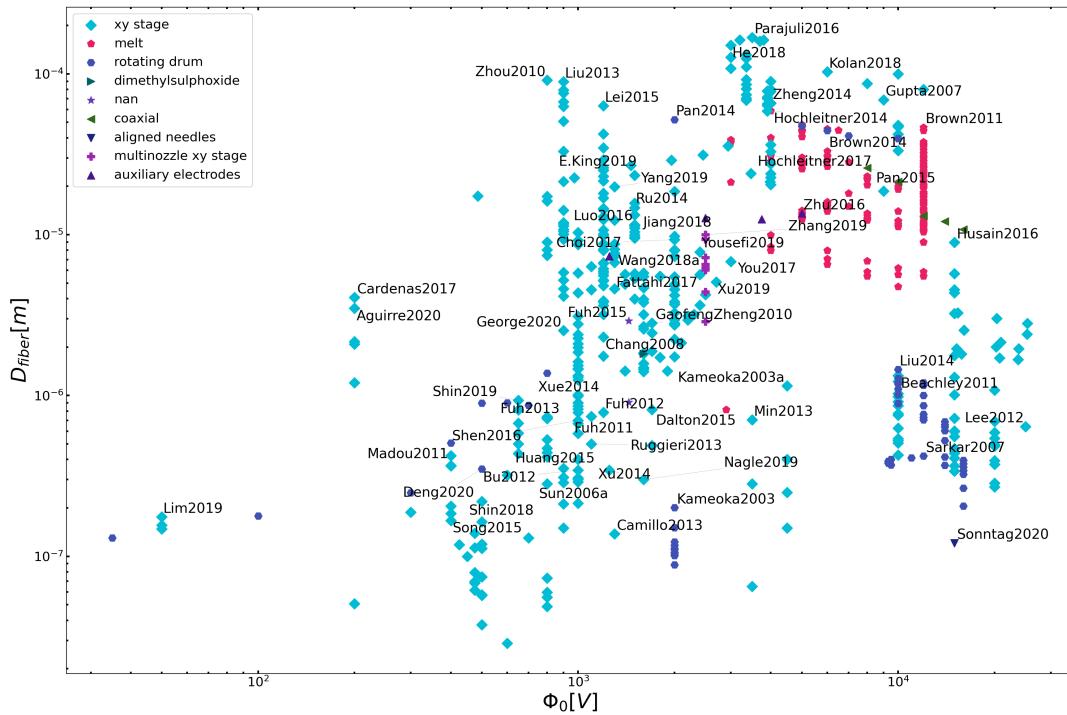


FIGURE 2.23: Scatter Plot of NFES Applied Voltages and Fiber Diameters from Literature Experimental Results. [9–11, 152–229]

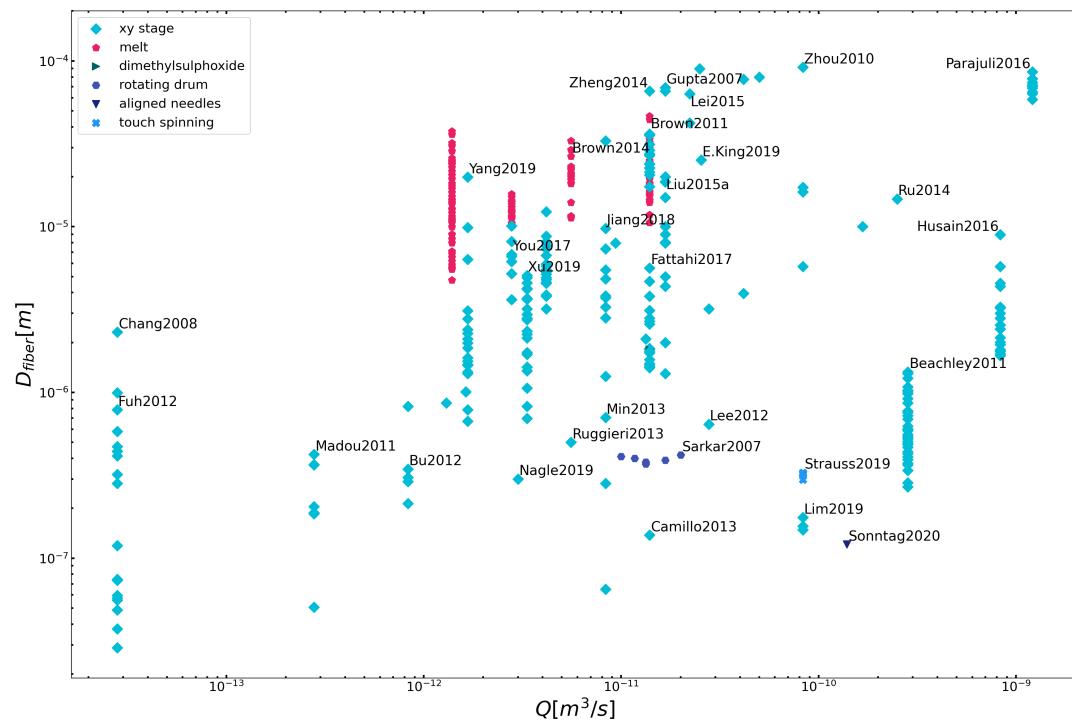


FIGURE 2.24: Scatter Plot of Polymer Solution Flow Rates and Fiber Diameters from Literature Experimental Results. [9–11, 152–229]

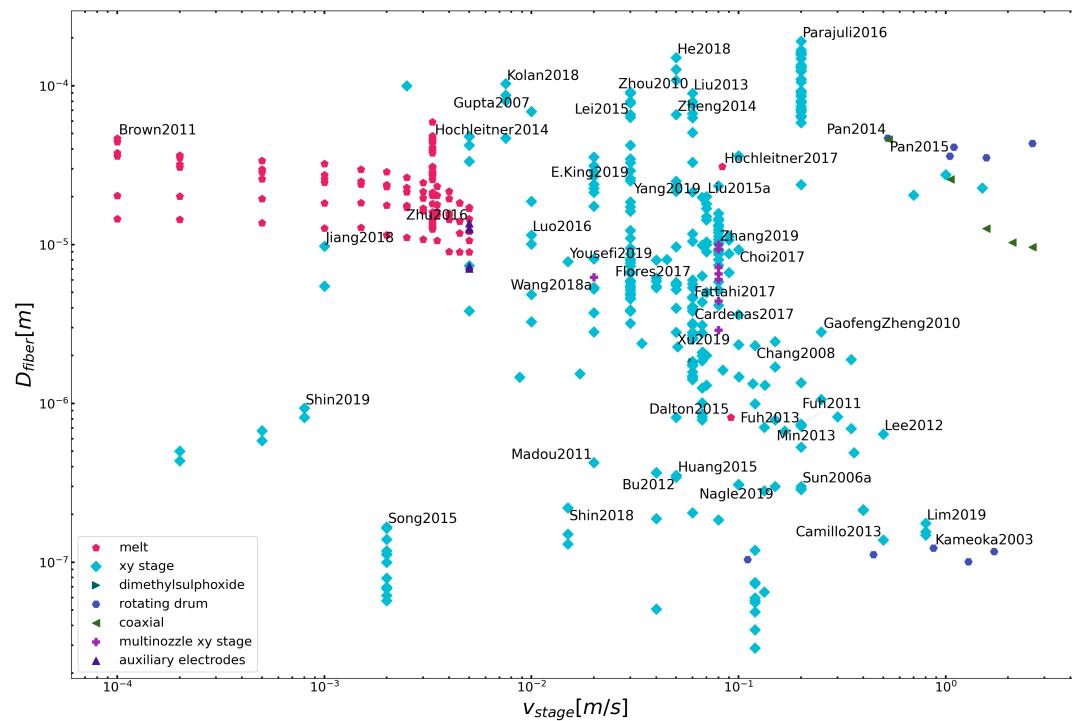


FIGURE 2.25: Scatter Plot of Collector xy Stage Velocities and Fiber Diameters from Literature Experimental Results. [9–11, 152–229]

The effect of parameters such as ink concentration, working distance, applied voltage, and stage speed on the diameter of the printed nano-fibers was investigated, a summary is presented in Table 2.2.

TABLE 2.2: Summary of the main parameters that drive the electrospinning process, ordered by: polymer solution parameters, process parameters, and ambient parameters. Adapted from [235, 236]

NFES Process Parameters	Effect
Solution Parameters:	
Concentration	Concentration shall be high enough to produce uniform nano-fibers, but low enough to give the correct viscosity
Molecular weight	High molecular weight polymers yield smoother fibers
Viscosity	Zero-shear viscosity shall be optimal to generate a constant jet from the needle
Conductivity	Solution shall be conductive enough for the electric field to have influence on the jet
Process Parameters:	
Applied voltage	Higher voltages eject more material from the nozzle
Flow rate	Slow flow rates yield thinner fibers, but it shall be fast enough to prevent clogging and keep the Tailor cone in a constant size and shape
Working distance	Long distances result in thinner fibers, however the spatial control is harmed
Ambient Parameters:	
Humidity	Increasing humidity produces thicker diameters
Temperature	Increasing temperature yields thinner fibers, however high temperatures make the nozzle prone to clog as the solvent evaporates at a faster rate

Near-field electrospinning (NFES) is known as a versatile nano-fabrication technique, suitable for several applications such as tissue engineering, chemical sensing, filtration, energy storage, besides others (see Figure 2.26). Fast developments in electrospinning has been observed in recent years. However, this process is limited by the electric field wiping instability effects during polymer deposition. This leads to a major challenge: how to surpass this limitation of planar two-dimensional prints. The current trend in this area lies on the research of new materials, techniques to increase precision patterning in NFES systems.

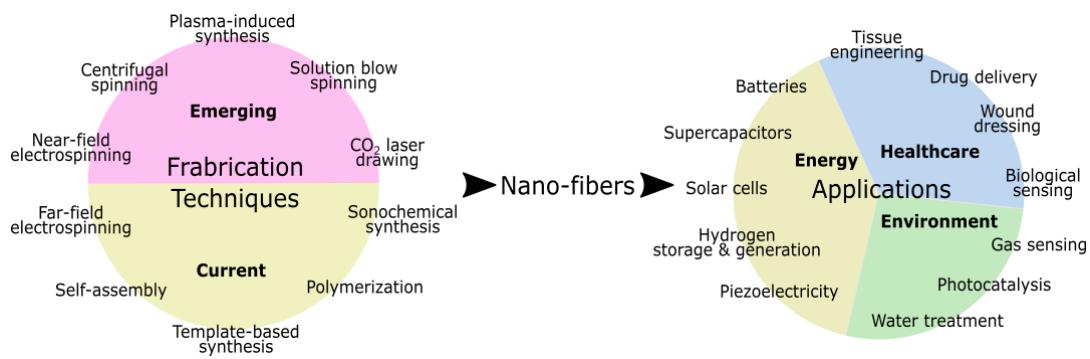


FIGURE 2.26: Syntheses and Applications of Nanofibers. Adapted from [237]

2.5 Diameter Prediction of Electrospun Fibers

Electrospinning is a simple process to fabricate fibers of different morphology. However, the final morphology of a fiber depends on various solution, process, and ambient parameters (Table 2.2) with interaction with rheology and fluid dynamics. Given the connection of various parameters, it is not trivial to derive a mathematical model to describe the complete electrospinning process. Current attempts involve limited models that can only describe the steady jet region for specific polymer solutions. [66, 238, 239] From literature [196, 240–242] and as described in Figure 2.19, zero-shear viscosity, flow rate and applied voltage are the main drivers that determine the final fiber morphology and dimensions. Other parameters such as solution surface tension, conductivity and working distance have less impact on the electrospun fibers. [65] As shown in Figures 2.24 and 2.20, literature states that flow rate Q and solution concentration $C_{polymer}$ are directly proportional to the fiber diameter D_{fiber} . [243–245]

As mentioned in the previous section, the correlation between the final fiber diameter D_{fiber} and the applied voltage Φ_0 is not well defined. Most authors posit that the fiber diameter decreases with increasing voltage. [231, 246–253] Nevertheless, other publications state the inverse correlation. [254, 255] This discrepancy between the final fiber diameter D_{fiber} and the applied voltage Φ_0 may be attributed to the fact that Φ_0 is also related to the electric field Φ_0/L , which in turn is related to the working distance L . As the electric field Φ_0/L increases, the electric field forces loose influence under the polymer jet as the increased force results into faster evaporation of the solvent promoting faster solidification. On the other hand, polymer concentration $C_{polymer}$, and conductivity K also have an effect on the electric field. [248, 256]

On the other hand, Zhang et al., Kim et al., and Mitappatham et al. studied the relationship between the solution surface tension γ and its conductivity K . [231, 257, 258] Kim's and Mitappatham's work report a increase in fiber diameter with increasing conductivity in the polymer solution, while Zhang's reports the inverse relationship. The existing interdependence between the process and solution parameters adds complexity and ambiguity to the effect of each parameter. The fiber morphology not only depends on the process parameters, but also on the type of electrospinning process and on polymer-solvent system. [259]

Helgeson and Wagner [260] have presented an adimensional analysis to predict the fiber diameter with conservation equations of momentum, mass, electric charge and four dimensionless numbers: Peclet number $Pe = \frac{2\bar{\varepsilon}v_0}{KR_0}$, Reynold number $Re = \frac{\rho v_0 R_0}{\eta_0}$, Weber number $We = \frac{\rho v_0^2 R_0}{\gamma}$, and the dimensionless electric field strength $\Psi = \frac{\bar{\varepsilon}E_0^2}{\rho v_0^2}$. Where $\bar{\varepsilon}$ is the dielectric permitivity of the atmosphere, K the solution conductivity, ρ the density, η_0 the zero-shear viscosity, γ the surface tension, E_0 the applied electric field, R_0 the initial jet radius, and v_0 the initial jet velocity. Since R_0 and v_0 can neither be controlled nor measured, Helgeson arrived to a correlation between the electrostatic and viscous forces Π_1 describing the stress directing the polymer jet elongation from the source to the collector plate. [260]

$$\Pi_1 = RePe\Psi = \frac{2\bar{\varepsilon}^2\Phi_0^2}{K\eta_0 L^2} \quad (2.1)$$

Ohnesorge number, resulting from the manipulation of the Reynolds number Re and the Weber number We , is used to explain the behavior of the polymeric solution jet under small disturbances, due the voltage presence, leads to the capillary rupture of the fluid jet. [260]

$$Oh = \frac{Re^2}{We} = \frac{\eta_0}{\sqrt{\rho\gamma R_{jet}}} \quad (2.2)$$

Where $R_{jet} = R_f \sqrt{\frac{1}{w_s}}$ is the wet radius of the jet solution, which is calculated

from the radius of the dry fiber R_f and the mass fraction of the polymer in solution w_s . [260]

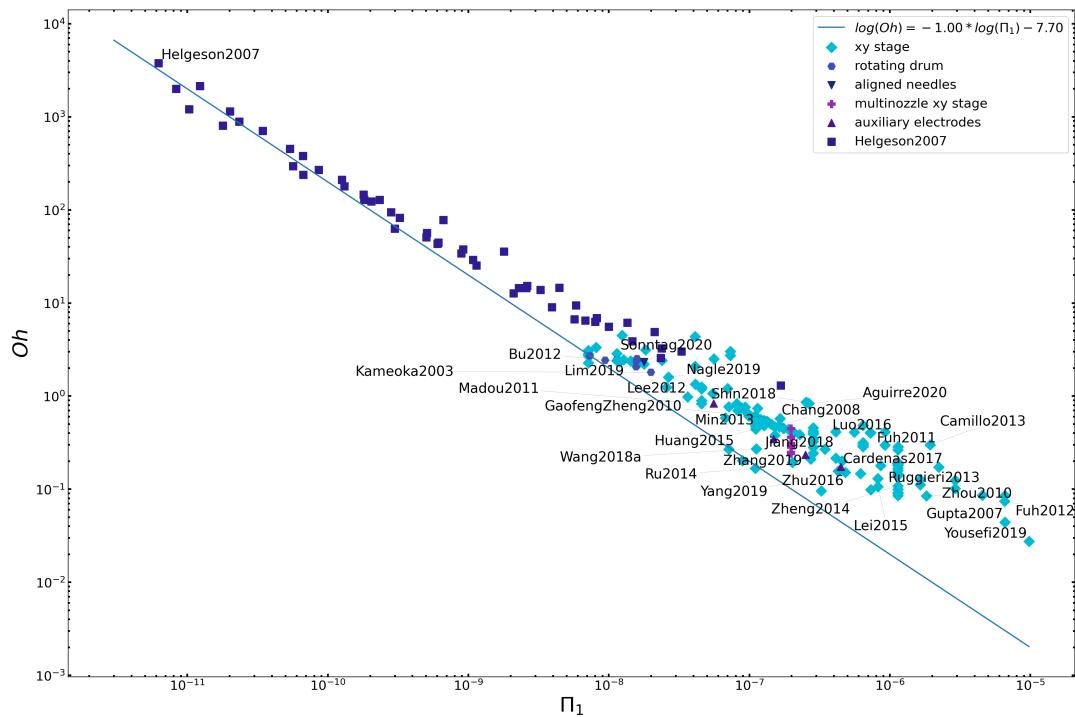


FIGURE 2.27: Image Analysis Algorithm to Measure Fiber Diameters from SEM images. Illustration uses Yousefi et al.'s work as an example. [9–11, 152–229, 260]

Figure 2.27 plots the Π_1 and Oh values reported by [260] along with new data points from the previous data collection of NFES fiber diameters and process parameters. It is possible to observe the predominance of the viscous and the electrostatic forces within the solution by the magnitude Π_1 (Equation 2.1), on the other hand Oh (Equation 2.2) reflects the capacity of the viscous forces over the polymeric jet, which allows stability in the electrospinning process. The data points gathered by Helgeson et al. are from far-field electrospinning studies, whereas the new data points belong to near-field electrospinning studies.

The collected data suggest that both types of electrospinning behave in a similar manner, where the FFES data fits better a linear behavior of slope -1 . As the working distance closes in NFES, the data points fit a shallower slope with higher Π_1 values and lower Oh values. This suggests that in NFES less viscous solutions have been used, since in long working distances a higher viscosity is needed to keep the integrity of the fiber in the whole traveling distance until it reaches the collector. For high Oh values and elevated

viscosity, the entanglement of the polymeric chains is higher, resulting in the formation of individual fibers; also, the jet is prone to faster solidification, due to an early evaporation of solvent, due to the resistance to the change of momentum, caused by the high viscosity in the polymeric solution, hence the need of higher voltages in FFES. Helgeson et al. suggest that with the following relationship in Equation 2.3 can be used to predict the fiber diameter, as in the trend in Figure 2.27 Oh has an inverse linear relationship with Π_1 . [260]

$$\Pi_1 Oh = \frac{2\bar{\varepsilon}^2 \Phi_0^2}{KL^2 \sqrt{\rho \gamma R_{jet}}} = 2.5 \pm 0.2 \times 10^{-8} \quad (2.3)$$

The absence of the solution zero-shear viscosity in Equation 2.3 suggests that η_0 by its own is insufficient to predict the fiber diameter. The solution conductivity, process parameters and surface tension are the main drivers to describe the diameter of electrospun fibers. [260]

Chapter 3

Selection of Compatible Polymer-Solvent Combinations for Near-Field Electrospinning and Pyrolysis

Zhenan Bao et al. [225] investigated the effect of the polymer chemical structure (the effect of benzene rings) on the morphology, dimensions, composition, graphitization degree, crystallinity, and electrical conductivity of graphene nano-ribbons derived from four different types of electrospun polymers. The authors studied four polymers polystyrene (PS), poly(vinyl alcohol) (PVA), polyvinylphenol (PVP), and a phenolic resin known as Novolac. See Figure 3.1. The authors created electrospun polymer fibers out of the four selected polymers. PVP, Novolac and PVA have hydroxyl groups that can be functionalized with metal cations, while PS does not have such binding capability. On the other hand, PVP and Novolac have one benzene ring in each repeating unit, whereas PVA is mainly made out of sp³ carbon.

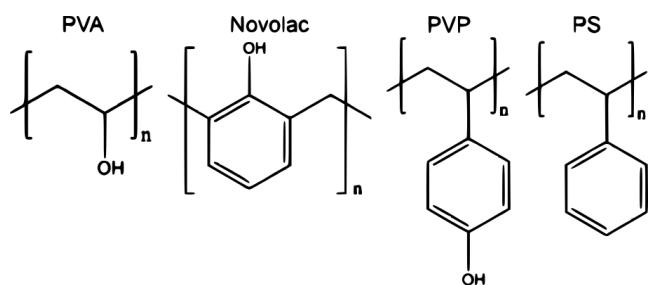


FIGURE 3.1: Studied Polymers by Zhenan Bao et al. [225]

Zhenan Bao et al. [225] found that higher sp² carbon content (or more benzene rings) in the polymer chemical structure translates into higher graphitization degree and higher electrical conductivity in the final carbon structures. This finding can be used as a guide when choosing polymer

precursors for the fabrication of carbon structures. Furthermore, the authors posit that polymers with functional groups are required for the creation of smooth and continuous fibers through electrospinning. [225]

3.1 Selection of Candidate Spunable Polymer Solutions

Given the conclusions from Zhenan Bao et al. [225] along with the extensive literature review and data analysis of Chapter 2, the following polymer solutions were selected to be studied in this work. Polymer selection was based on their high carbon content and presence of benzene rings. The purpose of the polymer selection is to focus the efforts to maximize the likelihood of polymers to yield carbon structures with high electrical conductivity and high graphitization degree; as testing every possible polymer-solvent system is not a practical way to carry on this research. Figure 3.2 lists the polymers that are going to be investigated. The selected polymers have been electrospun via far-field electrospinning for the fabrication of fibrous mats [226, 228, 261], but no records of being spunable by NFES.

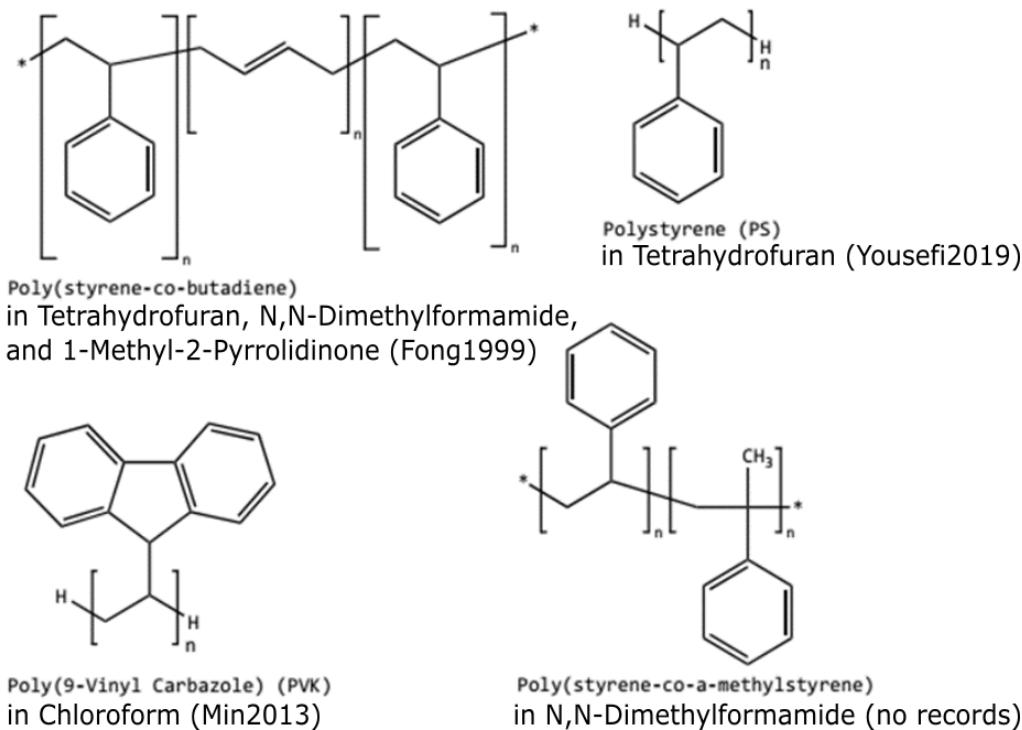


FIGURE 3.2: Selection of Polymer-Solvent Systems to Investigate in this Work. [226, 228, 261]

3.2 Rheology of candidate polymer solutions

As stated in previous sections, near-field electrospinning requires the control of several parameters to obtain fibers with the desired properties. One of the main parameters are related to the polymer precursor such as molecular weight and its concentration in solution. The evaluation of polymer chain entanglements is an effective way to address the spunability of a polymer-solvent system. [262] Polymer concentration and molecular weight are the main factors in determining the entanglement degree between polymer chains.

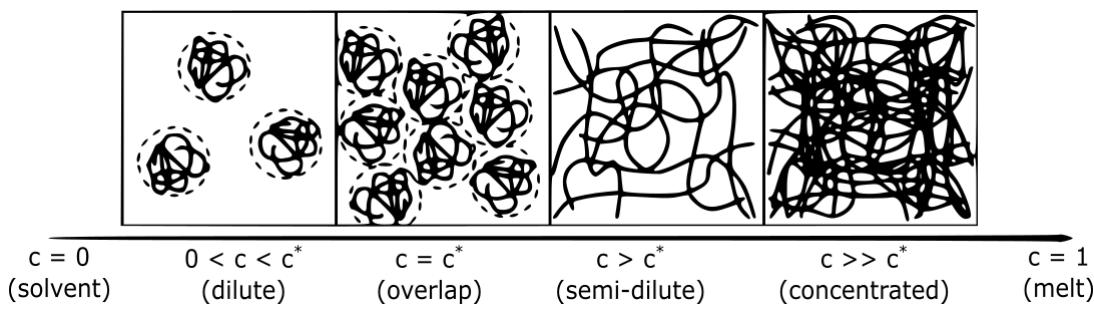


FIGURE 3.3: Effect of the polymer concentration on the structure of polymer chains in solution. Adapted from [263]

Solutions at low concentrations do not allow polymer chains to entangle leading the viscoelasticity of the solution dependent only on individual polymer chains. As the polymer concentration increases, the chains overlap and become entangled. The concentration at which the entanglement initially takes place is the critical concentration c^* . Concentrations above the critical concentration c^* generate a fast increase in chain entanglement (Figure 3.3). This rapid change in chain entanglement is translated into a fast increase in the viscoelasticity of the solution. Figure 3.4 illustrates the relationship between polymer concentration and viscoelasticity. [245, 263]

Electrospinning of smooth, continuous fibers require a polymer concentration higher than the critical concentration. As shown in Figure 3.4, the critical concentration can be estimated from the change in slope. [212, 245, 263] Therefore, in order to find the critical/spinnable concentrations of the candidate polymer-solvent solutions (poly(styrene-co-butadiene) in tetrahydrofuran, poly(9-vinyl carbazole) in chloroform, polystyrene in tetrahydrofuran, and poly(styrene-co-a-methylstyrene) - See Figure 3.2), it is necessary to build the appropriate viscosity vs. concentration plots as described in the following sections.

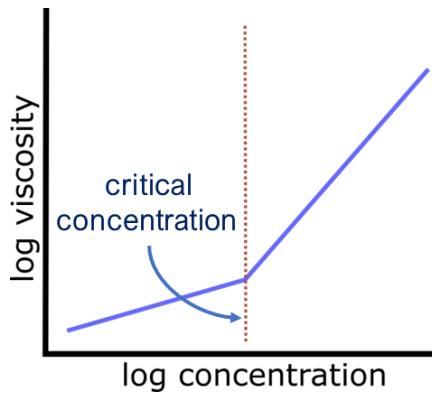


FIGURE 3.4: Effect on solution viscosity, polymer concentration and spinnability. Adapted from [212, 245, 263]

3.2.1 Materials and Sample Preparation

Seven polymer-solvent combinations are to be tested. The Poly(Ethylene Oxide) and SU-8 2002 combination is what has been used in past work [9, 11], and will be used as the control sample set. The selected polymer-solvent combinations are to investigate the ability of oxygenless polymers to be electrospun and then carbonized into vitreous carbon. Tables D.1, 3.3, 3.4, 3.5, 3.2, 3.6, and 3.7 list the prepared polymer systems. Tetrabutylammonium tetrafluoroborate (TBF) was added to all solutions to increase the conductivity of the solution. SU-8 contains 71% of cyclopentanone (CPO), which acts as the solvent (Figure 1.7) [74].

TABLE 3.1: Poly(Ethylene Oxide) and SU-8 2002 : Sample Preparation

Sample	Weight Percent <i>wt%</i>		
	SU-8	PEO	TBF
1	99.50	0.00	0.50
2	99.25	0.25	0.50
3	99.00	0.50	0.50
4	98.75	0.75	0.50
5	98.50	1.00	0.50
density [g/ml]		1.123	

TABLE 3.2: Polystyrene in Tetrahydrofuran : Sample Preparation

Sample	Weight Percent wt%		
	THF	PS	TBF
6	99.25	0.25	0.50
7	94.50	5.00	0.50
8	89.50	10.00	0.50
9	84.50	15.00	0.50
10	79.50	20.00	0.50
11	69.50	30.00	0.50
12	64.50	35.00	0.50
13	59.50	40.00	0.50
density [g/ml]	0.888		

TABLE 3.3: Poly(Styrene-co-Butadiene) in 1-Methyl-2-Pyrrolidinone : Sample Preparation

Sample	Weight Percent wt%		
	NMP	PSB	TBF
14	98.50	1.00	0.50
15	95.50	4.00	0.50
16	91.50	8.00	0.50
17	87.50	12.00	0.50
density [g/ml]	1.027		

TABLE 3.4: Poly(Styrene-co-Butadiene) in Tetrahydrofuran and N,N-Dimethylformamide : Sample Preparation

Sample	Weight Percent wt%			
	THF	DMF	PSB	TBF
18	70.875	23.625	5.00	0.50
19	69.000	23.000	7.50	0.50
20	67.125	22.375	10.00	0.50
21	65.250	21.750	12.50	0.50
22	63.375	21.125	15.00	0.50
23	59.625	19.875	20.00	0.50
24	55.875	18.625	25.00	0.50
density [g/ml]	0.888	0.950		

TABLE 3.5: Poly(Styrene-co-alpha-Methylstyrene) in
N,N-Dimethylformamide : Sample Preparation

Sample	Weight Percent wt%		
	DMF	PSMS	TBF
25	99.00	0.50	0.50
26	94.50	5.00	0.50
27	89.50	10.00	0.50
28	84.50	15.00	0.50
density [g/ml]		0.950	

TABLE 3.6: Poly(9-Vinylcarbazole) in Chloroform : Sample Preparation

Sample	Weight Percent wt%		
	CHL	PVK	TBF
29	99.50	0.00	0.50
30	99.49	0.01	0.50
31	84.50	15.00	0.50
32	79.50	20.00	0.50
33	69.50	30.00	0.50
density [g/ml]		1.492	

TABLE 3.7: Poly(9-Vinylcarbazole) and SU-8 2002 : Sample Preparation

Sample	Weight Percent wt%		
	SU-8	PVK	TBF
34	99.50	0.00	0.50
35	99.495	0.005	0.50
36	98.75	0.75	0.50
37	94.50	5.00	0.50
38	79.50	20.00	0.50
density [g/ml]		1.123	

SU-8 2002 was obtained from MicroChem (Newton, MA, USA), while Tetrabutylammonium Tetrafluoroborate (TBF) of 99% purity were, Poly(Ethylene Oxide) (PEO), Polystyrene (PS), Poly(Styrene-co-Butadiene) (PSB), Poly(Styrene-co-alpha-Methylstyrene) (PSMS), Poly(9-Vinylcarbazole) (PVK), Tetrahydrofuran (THF), 1-Methyl-2-Pyrrolidinone (NMP), N,N-Dimethylformamide (DMF), and Chloroform (CHL) were obtained from Sigma-Aldrich (Saint Louis, MI, USA). PEO has a viscosity-average molecular weight M_v of 4,000,000, with less than 1000 ppm of Butylated Hydroxytoluene (BHT) as an inhibitor. PS has an average molecular weight M_w of 192,000. PSB has a melt index of 6g/10min(200°C/5kg), where the butadiene comprises 4 wt% PSMS has a melt viscosity of 10Pa · s at 161°C. PVK has an average molecular weight M_w of 1,100,000 in powder form. THF is anhydrous and contained no inhibitor with 99.9% purity. NMP is anhydrous with 99.5% purity. DMF is anhydrous with 99.8% purity. CHL has 99.5% purity, a melting point of -63°C, boiling point of 60.5°C, and a density of 1.492g/ml at 25°C. CHL contains between 100 to 200 ppm amylenes as stabilizer. SU-8 is a high contrast, epoxy-based negative photoresist. All of the reactants were used as received.

Samples of 3 milliters were prepared with the adequate amounts of polymer, salt and solvent. Solutions were stirred at 160rpm for 2hours at 60°C. Samples with higher polymer concentrations often required more stirring time to eliminate all polymer aggregates. All solutions were left undisturbed for 3hours in 4 ml vials to eliminate bubbles from the solution.

3.2.2 Rheological Characterization of polymer Solutions

All of the rheological tests were performed in a rotational rheometer (Discovery Hybrid Rheometer DHR, TA Instruments) equipped with a cone-and-plate (CP) geometry (diameter of 60mm, angle of 0.9969°, and truncation of 23μm) in a steel Peltier plate (Figure 3.5a). The experiments were conducted at 20°C and 3hours after polymer solution preparation. Flow curve (FC) tests were conducted to obtain viscosity curves in function of the shear rate. Analysis were performed at shear rate range from 10⁻³ 1/s to 10⁴ 1/s. A solvent trap cover (Figure 3.5f) and solvent trap geometry (Figure 3.5a) were used to create a thermally stable vapor barrier, virtually eliminating any solvent loss during the rheological experiments and improving temperature uniformity. Distilled water was used to create a seal between the CP geometry and the solvent trap cover (Figure 3.5e).

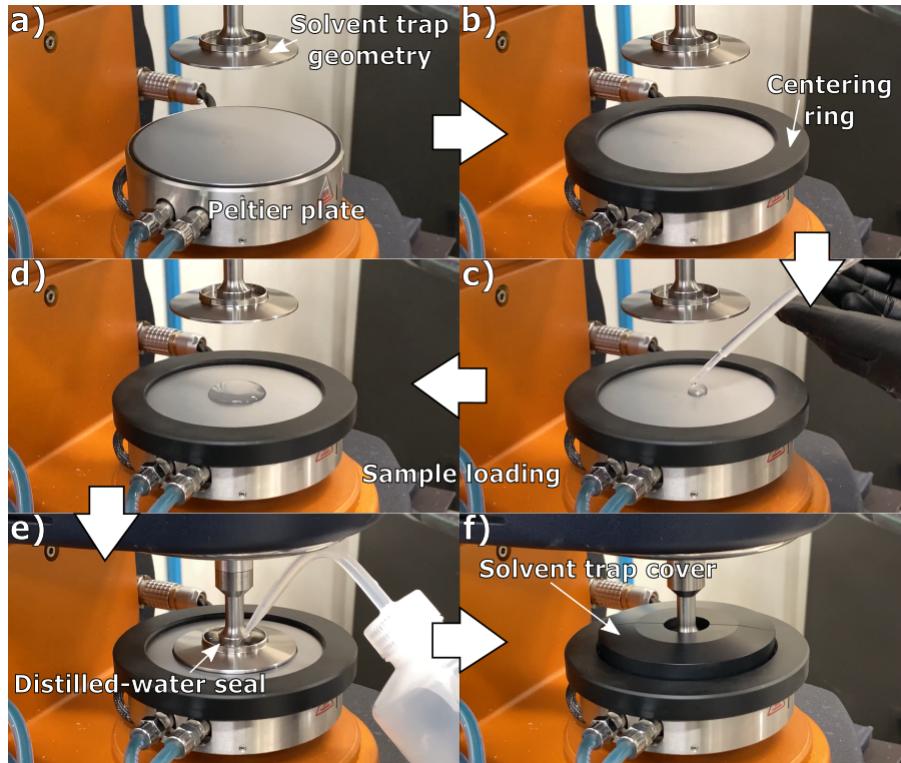


FIGURE 3.5: Rheometer - Solvent Trap Setup

Flow curves determine the flow behaviour of a sample by measuring the viscosity as a function of shear rate. For shear rates under $10^{-2.25}$ 1/s the rheometer was unable to take viscosity measurements, on the other hand for shear rates over $10^{-3.5}$ 1/s the measurements are discarded. At high shear rates, several factors such as inertial effects, and viscous heating can alter the rheometric measurements [264, 265]. As the shear rate increases, the centrifugal stresses become large enough to overcome the surface tension stresses that keep the sample within the gap between the geometry and the plate. High centrifugal stresses result in the sample being thrown out of the measuring area; a phenomenon known as 'radial migration effect' [266]. Once the 'radial migration effect' partially ejects the sample, the viscosity measurements are lower than expected due to a drop in torque. [267]

As depicted in the rheological results in Figures A.1, A.2, A.3, A.4, A.5, A.6 and A.7, the constant-viscosity (Newtonian-like) behavior before the shear thinning onset was captured. In all samples, a noticeable shear-thinning behavior is observed with an increase in viscosity with concentration increments. The shear-thinning behavior can be interpreted as the alignment of polymer chains to the flow in the direction of the applied shear stress.

[268] The Carreau-Yasuda model (Equation 3.1) [264] was fitted to the cone-and-plate measurements to compute the zero-shear viscosity of each sample.

$$\eta = \frac{\eta_0 - \eta_\infty}{[1 + (\kappa\dot{\gamma})^a]^{\frac{(1-n)}{a}}} + \eta_\infty \quad (3.1)$$

Where: η is the viscosity, $\dot{\gamma}$ the shear rate, η_∞ the infinite shear rate viscosity, η_0 the zero shear rate viscosity, κ is the time constant, n the Power Law index, a the width of the transition region between the zero shear viscosity and the Power Law region. The model was fitted to the rheological data to estimate η_0 . Then, η_0 values are used to create diagrams that describe the effect of polymer concentration on the solution viscosity, as described in Figure 3.4. The critical concentrations are calculated from the change in slope in the zero-shear viscosity to concentration relationship as depicted in Figure 3.6 for the PEO in SU-8 solutions. Appendix B contains the diagrams of the other polymer-solvent systems.

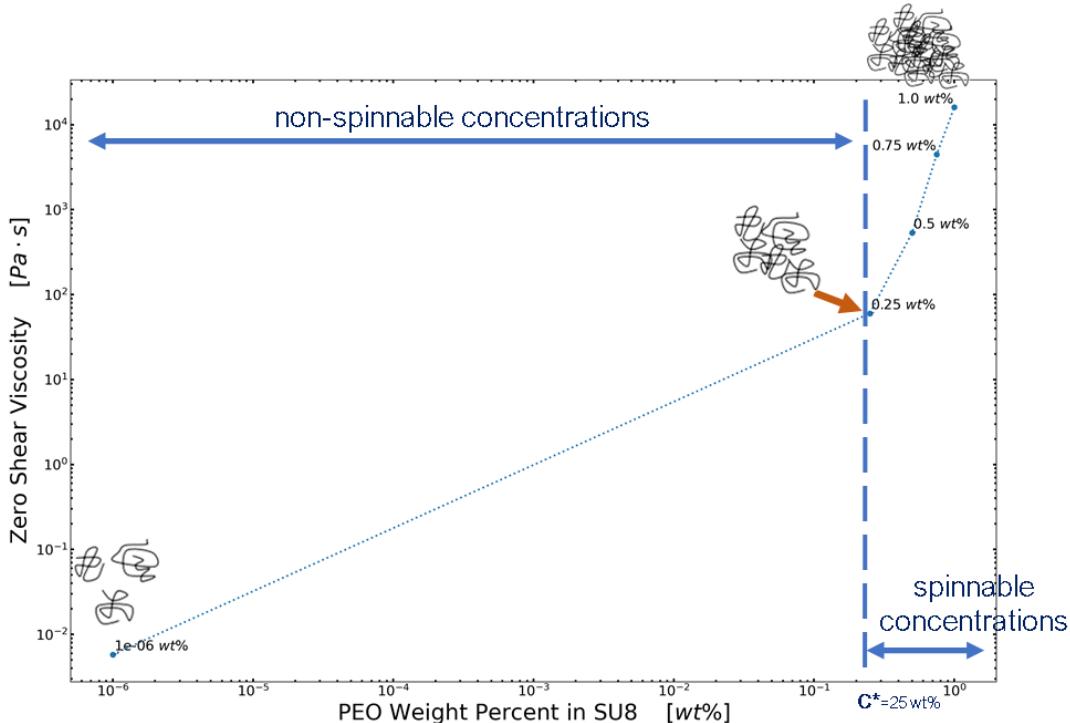


FIGURE 3.6: The change in slope is given at 25 wt% PEO, which suggests that at 25 wt% the polymer chains are entangled.

Table 3.8 summarizes the calculated critical concentrations for each system.

TABLE 3.8: Calculated Critical/Spinnable Concentrations for each Polymer-Solvent System

Polymer	Molecular Weight [g · mol]	Solvent	c^* [wt%]	η_0 [Pa · s]
PEO	4,000,000	CPO (SU-8)	0.25	60.022
PS	192,000	THF	20.00	0.166
PSB	490,000 [269]	NMP	8.00	0.028
PSB	490,000 [269]	THF and DMF	15.00	0.092
PSMS	2,658,076 [270]	DMF	5.00	0.282
PVK	1,100,000	CHL	15.00	41.861
PVK	1,100,000	CPO (SU-8)	0.75	49.657

In general, the critical concentration c^* has proportional relationship with the polymer molecular weight, as a polymer's molecular weight greatly influences the solution viscosity. First, the structure of the polymer chain has an effect on its solubility as the intermolecular interactions between long molecules are stronger and the solvent molecules take longer to diffuse within the polymer aggregates. [65, 268] Second, the viscosity of a polymer solution will be smaller when a polymer of low molecular weight is dissolved than a solution of the same polymer but of a higher molecular weight. [65] The molecular weight of the polymer describes the length of the polymer chain, which has an effect on the viscosity of the solution. Since the polymer length defines the amount of entanglement of the polymer chains in the solvent, a lower molecular weight shall be compensated by higher concentrations to reach the desired viscosity.

Chapter 4

Fabrication and Characterization of Polymeric Fibers through Near-Field Electrospinning

4.1 Materials and Methods

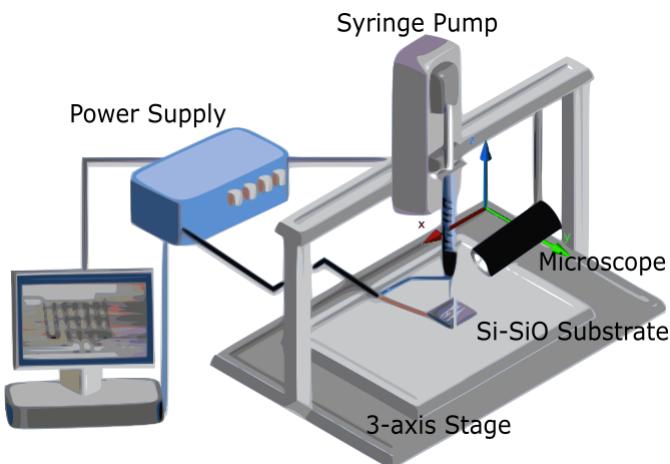


FIGURE 4.1: NFES experimental setup. Adapted from [268]

The near-field apparatus (Figure 4.1) is comprised by a high voltage supply (HVS448 3000 V, LabSmith, Livermore, CA, USA), a three-axis stage, syringe pump (Pump 11 Elite, Harvard Apparatus, Cambridge, MA, USA). Samples were prepared as per the rheology measurements in Chapter 3. Experiments were conducted with 1 milliliter slip-tip insulin syringes with 21 gauge precision tips (Nordson Engineered Fluid Dispensing, Westlake, OH, USA). The power supply and 3-axis stage are controlled through a desktop computer, while the syringe pump is controlled manually. Fiber depositions were placed on a Si – SiO₂ wafer. The voltage between the nozzle tip and the collector was varied between 200[V] and 600[V] in increments of 100[V],

keeping a constant current of $10\mu A$. For applied voltages under $400[V]$, the electric field was not strong enough to overcome the surface tension of the polymer solution and initiate the jet. To enable the fiber deposition at low voltages, the polymer jet was manually initiated by breaking the surface tension with a sharp glass tip. The working distance L and stage velocity was set at a constant values for all the experiments at $0.5mm$ and $10mm/s$ respectively. The syringe pump was set at a steady flow rate of $0.04\mu L/min$.

The calculated critical concentrations in Chapter 3 (Table 3.8) are used for the fabrication of polymeric fibers. One set of experiments was conducted for each polymer-solvent system to study the effect of applied voltage on fiber diameter. The morphology of the fibers were characterized with an optical microscope (Correct, Seiya Optical, Dallas, TX, USA). Each sample was measured at $30+$ points within the microscope field of view (Appendix C).

4.2 Results

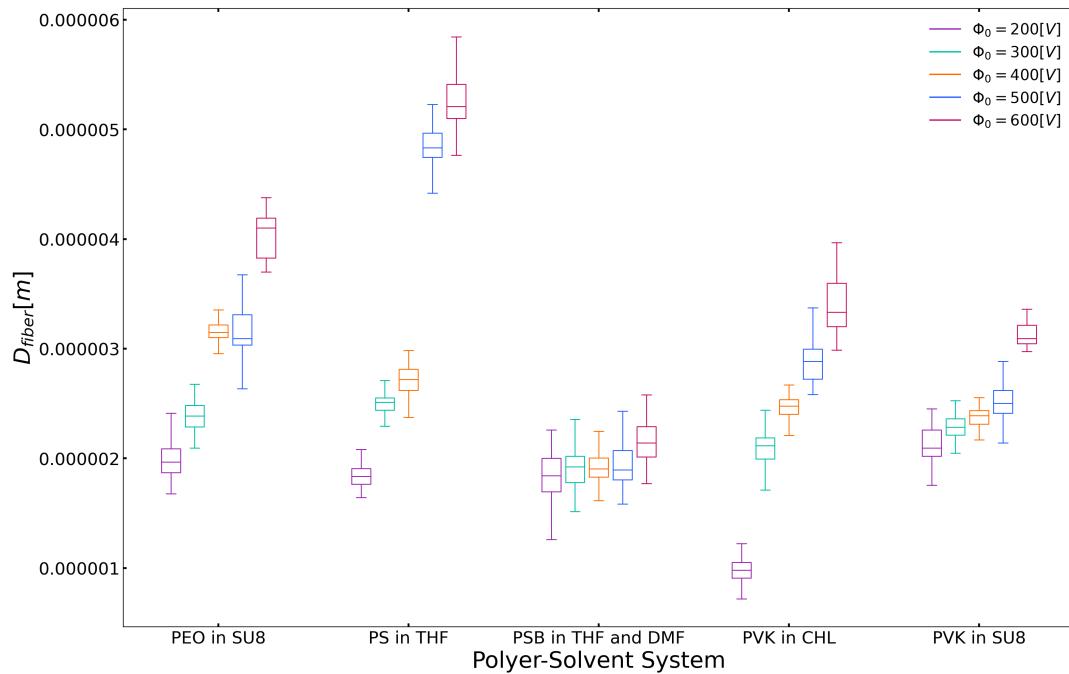


FIGURE 4.2: Diameter of fibres for all the experiments with varying applied voltage Φ_0 . Appendix D

Figure 4.2 shows a dependence of fiber diameter as a function of the applied voltage and confirms what was already noticed in the correlation matrix in Chapter 2, as lower voltages yield fibers with thinner diameters. This

results verify the electro-spinnability of oxygen-less polymers by NFES into fibers of $1\mu\text{m}$ to $5\mu\text{m}$ in diameter. PS presented complications during the NFES process as fibers of this polymer do not adhere onto the substrate making them prone to fracture or substrate abandonment, specially when printing fibers of thin diameters. To ease this complication the working distance L can be reduced to let the fibers dry on the surface and prevent complete solidification while traveling the distance L . The increase in applied voltage can also help with this problem as more material is pulled out of the dispensing needle, however this two fixes will translate into thicker fibers.

The PVK and CHL system was the one that behaved with more similarity as the control sample of SU-8 and PEO. Uniform, 700nm diameter fibers were achieved with PVK and CHL at the lowest voltage setting (200V). Given the similarities with the control sample, PVK was chosen to replace the PEO to increase the spinnability of SU8. Therefore, the PVK in SU-8 system was tested in the same conditions as the previous experiments. Both polymers (PEO and PVK) in SU-8 yield parallel results in fiber morphology and in electrospinning preformanc. However, at high voltages, the PVK solution produced thinner fibers than those produced by the PEO solution. Moreover, as PVK does not contain any additional oxygen content in its structure, adding PVK can be a better alternative to electrospun SU-8 based fibers intended for carbonization as thinner fibers will have better opportunities to survive the pyrolysis process without breaking.

On the other hand, the polymer-solvent systems comprised by Poly(Styrene-co-Butadiene) (PSB) in 1-Methyl-2-Pyrrolidinone (NMP) and Poly(Styrene-co-alpha-Methylstyrene) (PSMS) in N,N-Dimethylformamide (DMF) were unable to yield fibers. In the case of the PSB/NMP solutions, a hard shell was formed around the polymer drop at the tip of the nozzle preventing the jet to initiate, which causes clogging. Seems that rapid volatilization of NMP is not the case as PSB was successfully electrospun with higher volatile solvents (THF and DMF). Notice that vapor pressure of NMP is around 39Pa at 25°C , THF and DMF have vapor pressures of about 19.3kPa at 20°C and 0.49kPa at 25°C respectively. [271] On the other hand, PSMS in DMF was not able to produce fibers as the jet was not initiated. After noticing that the calculated critical concentration c^* is not spinnable the solutions of 10 and 15 wt% were also tested in the NFES apparatus with no success. The cause of the non-spinnable nature of PSMS can be laid on the

fact that PSMS pellets were brittle and capable of making fine PSMS dust with ease, unlike PS and PSB pellets which have an elastic behavior.

4.3 Conclusions and Future Work

A series of experiments were carried out in order to find a correlation between the rheological properties of different polymer solutions in near-field electro-mechanical spinning for carbon structures. Flow curve measurement tests were carried out in an oscillatory rheometer to estimate the critical concentrations of various polymer-solvent systems at which they are spinnable by NFES. Since the formulation is 0.25 *wt%* PEO in SU-8 2002 has been studied in the past and is known to yield good polymer solutions but fails at the pyrolysis, this work intends to find spinnable and pyrolyzable systems as well as a method to discover new spinnable polymer solutions.

From the flow curve measurements, the zero-shear viscosity was estimated using the Carreau-Yassuda model. For all solutions, a shear thinning behavior was noticed. It was found that the viscosity-concentration plot is a good method to find the critical concentration at which the solution is able to produce fibers through NFES. However the method failed at calculating the spinnable concentration of PSMS. A significant takeaway is that a polymer does not have elastic properties in the pellet form, it will probably not work as a NFES polymer precursor.

Fibers were fabricated at different applied voltages for each set of solutions in order to verify that in NFES fiber diameter increases with increasing applied voltage, whereas the inverse relationship is true for FFES. Other parameters such as working distance, stage velocity, nozzle diameter, flow rate were kept constant for all experiments; however, for low applied voltages the jet shall be initiated by manually breaking the polymer drop. The thickest average fiber diameter was achieved with the PS in THF system ($\Phi_0 = 600V$, $D_{fiber} = 5.304\mu m$) and the thinnest was $0.976\mu m$ using the PVK in CHL system and an applied voltage of 200V. It was proved that attainable rheological information can be used to modify the NFES process parameters to yield the desired fiber morphology.

Moreover a data analysis was done on the NFES publications of the last 13 years to identify relationships between fiber diameter and the process parameters. For instance, it was confirmed that thin fibers are achieved with

los polymer concentrations, small nozzle diameters, low applied voltage, slow flow rates and high stage velocities. Also, using the collected data and the input of Helgeson's work [260], an dimensionless analysis was done to predict fiber diameters with easy to get parameters. Apart from the work done, this dissertation opens pending research to enable NFES for the fabrication of carbon structures. The following lists future work that could be done as a continuation of this thesis.

- Helgeson's model [260] was thought to work with far-field electrospinning, hence the deviation of the NFES data from the model trend. For an accurate NFES fiber diameter prediction, the mechanical stresses introduced by the moving stage shall be considered in the model (Equation 2.3).
- This work verifies the electro-spinnability of four new formulations, however fibers were not carbonized into carbon structures. Further work shall study the pyrolysis process of the proposed fibers to get carbon structures with good electrical conductivity. A photo-polymerization process could be introduced before pyrolyzation to increase the order of the molecules and achieve carbon with higher conductivity.
- Near-field electrospinning solutions require specific viscosities to initialte a polymer jet. The viscosity-concentration plot is a helpful tool to estimate the critical spinnable concentration of a polymer-solvent system. However there is room for improvement as this method only considers reological data. Other methods could be adopted to better tune other process parameters such as stage velocity, and applied voltage.

Acronyms and Abbreviations

CEM	Campus Estado de México
CNWs	Carbon Nano-wires
DC	Direct Current
EMS	Electromechanical Spinning
FFES	Far Field de Electrospinning
ITESM	Instituto Tecnonólogico y de Estudios Superiores de Monterrey
MA	Massachusetts
MEMS	Microelectromechanical Systems
MNT	Maestría en Nanotecnología (<i>Master of Science in Nanotechnology</i>)
MTY	Monterrey or Campus Monterrey
NFEMS	Near-Field Electromechanical Spinning
NFES	Near Field de Electrospinning
USA	United States of America
UV	Ultraviolet

Variables and Symbols

Symbol	Name	Unit
M_w	Molecular Weight	g/mole
η_0	Zero-shear Viscosity	Pa · s
K	Electrical Conductivity	S/m
γ	Surface Tension	N/m
$\dot{\gamma}$	Shear Rate	1/s
ρ	Density	Kg/m ³
$C_{polymer}$	Polymer concentration	wt%
D_{nozzle}	Nozzle Inner Diameter	m
Q	Flow Rate	m ³ /s
L	NFES Working Distance	m
Φ_0	NFES Applied Voltage	V
v_{stage}	Collector/Stage velocity	m/s
D_{fiber}	Fiber Diameter	m
$FiberGap$	Distance between fibers	m
R_{jet}	NFES Jet Radius	m
Oh	Ohnesorge number	NA.
Pe	Peclet number	NA.
Re	Reynolds number	NA.
We	Weber number	NA.
Ψ	Dimensionless Field Strength	NA.

Appendix A

Flow Curves

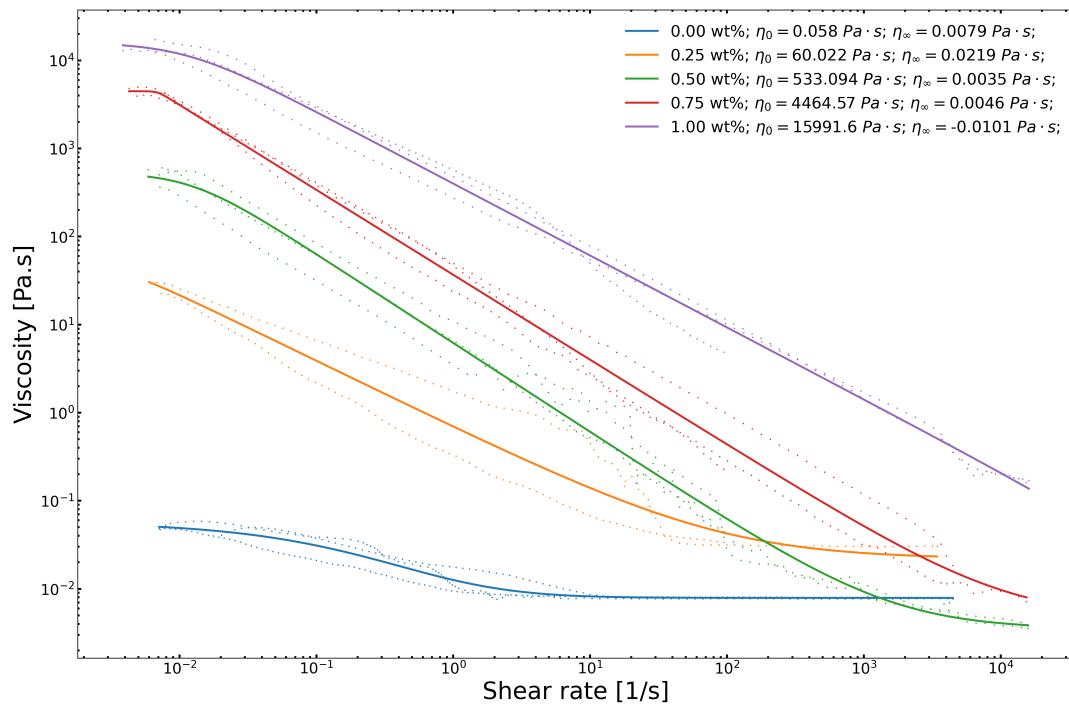


FIGURE A.1: Viscosity as a function of shear rate for Poly(Ethylene Oxide) (PEO) and SU-8 2002 solutions

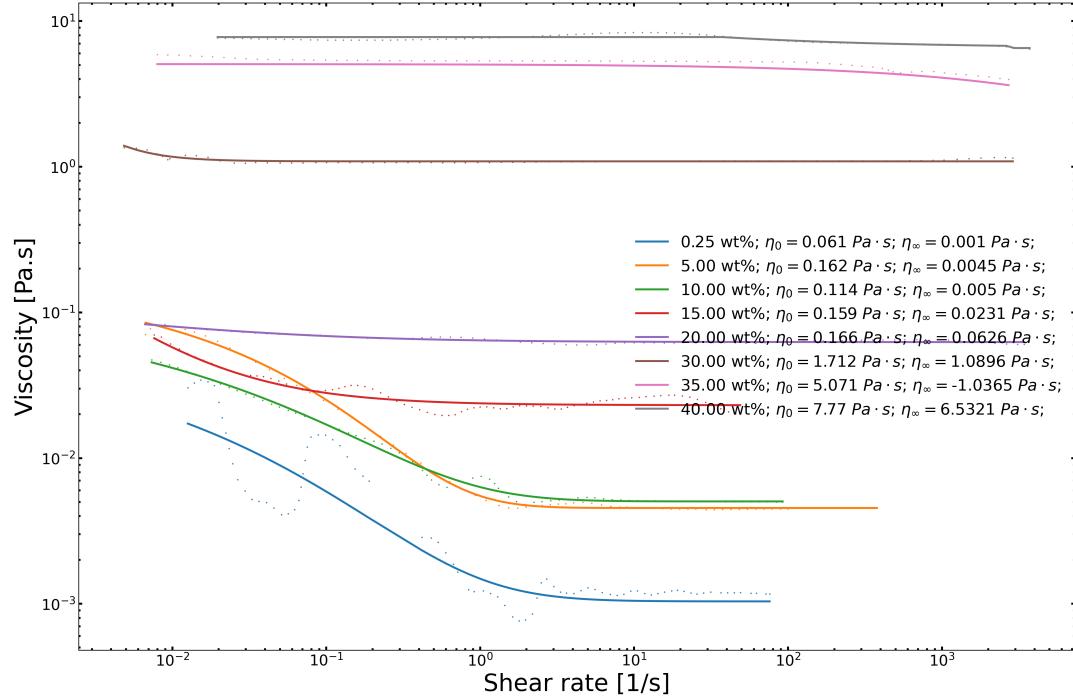


FIGURE A.2: Viscosity as a function of shear rate for Polystyrene (PS) and Tetrahydrofuran (THF) solutions

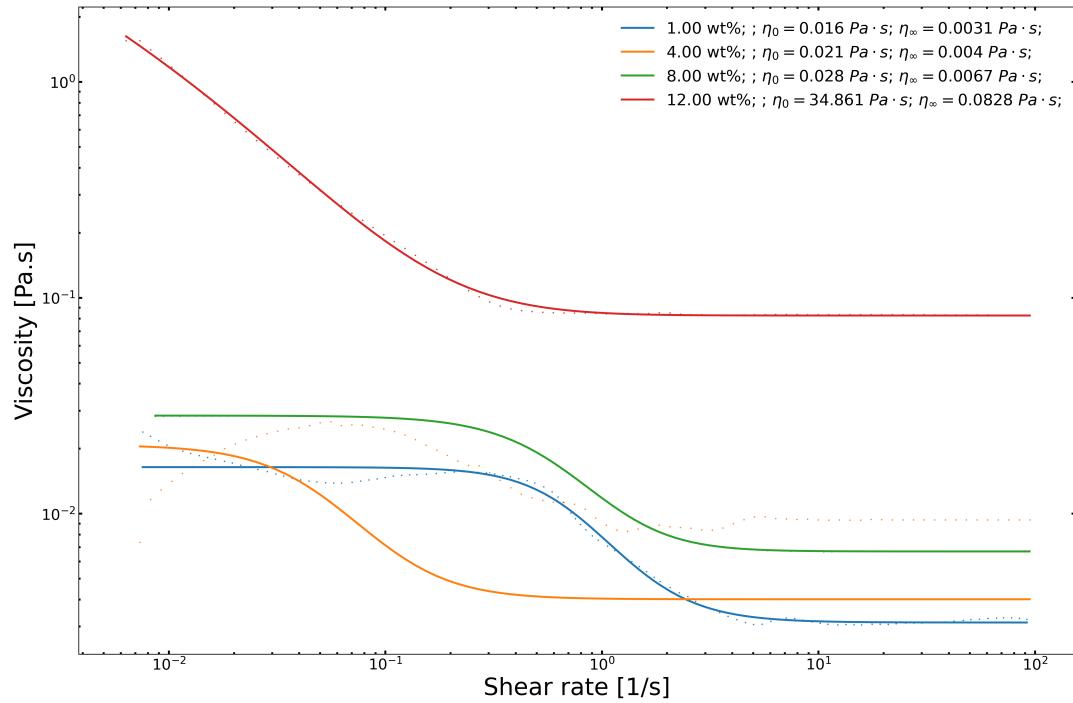


FIGURE A.3: Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB) and 1-Methyl-2-Pyrrolidinone (NMP)

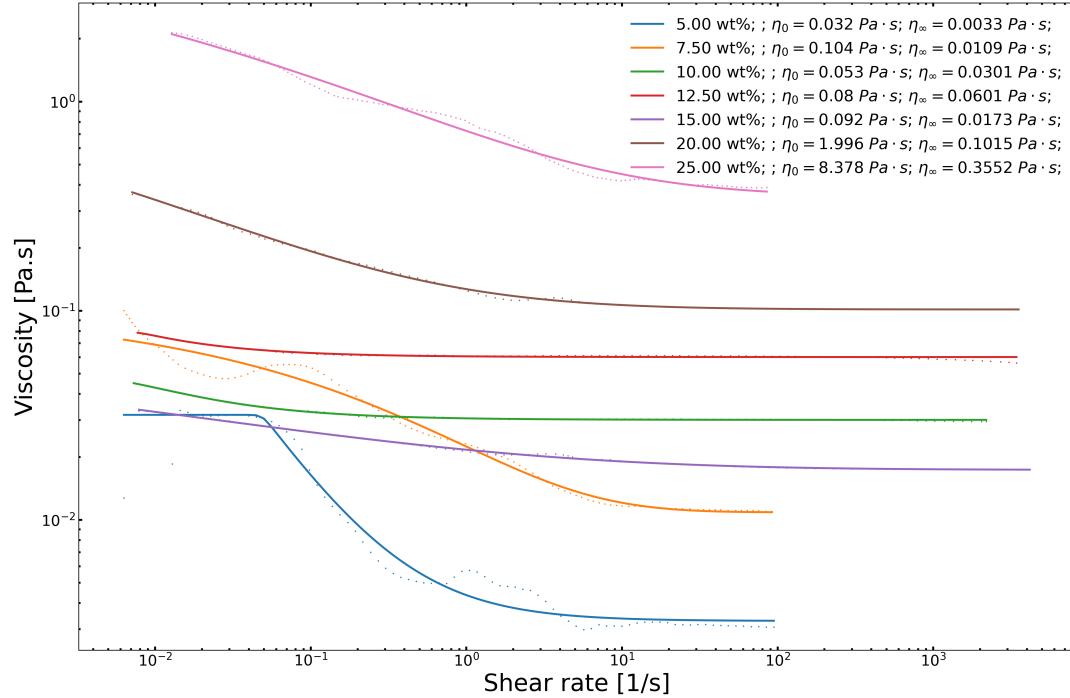


FIGURE A.4: Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB), Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF) solutions

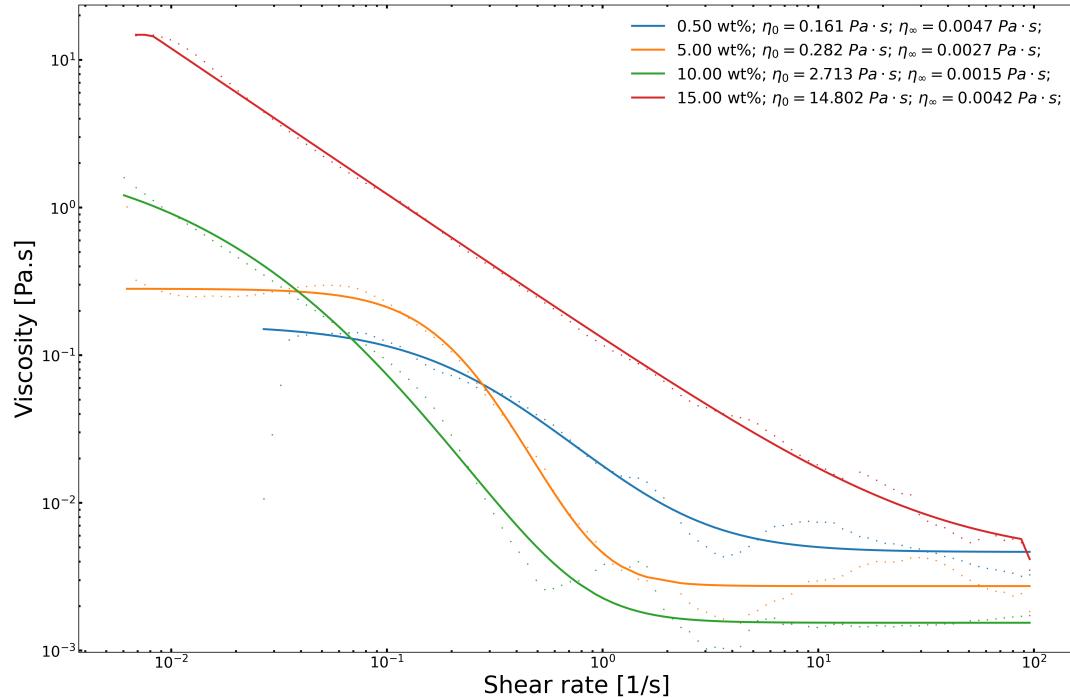


FIGURE A.5: Viscosity as a function of shear rate for Poly(Styrene-co-alpha-Methylstyrene) (PSMS) and N,N-Dimethylformamide (DMF) solutions

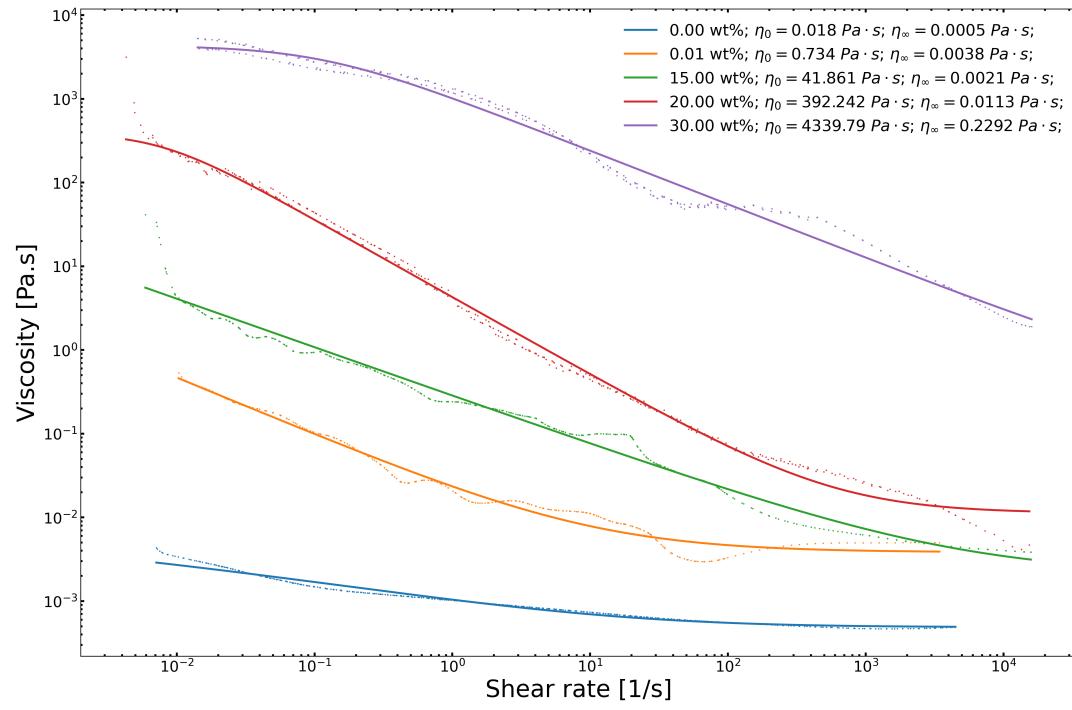


FIGURE A.6: Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and Chloroform (CHL) solutions

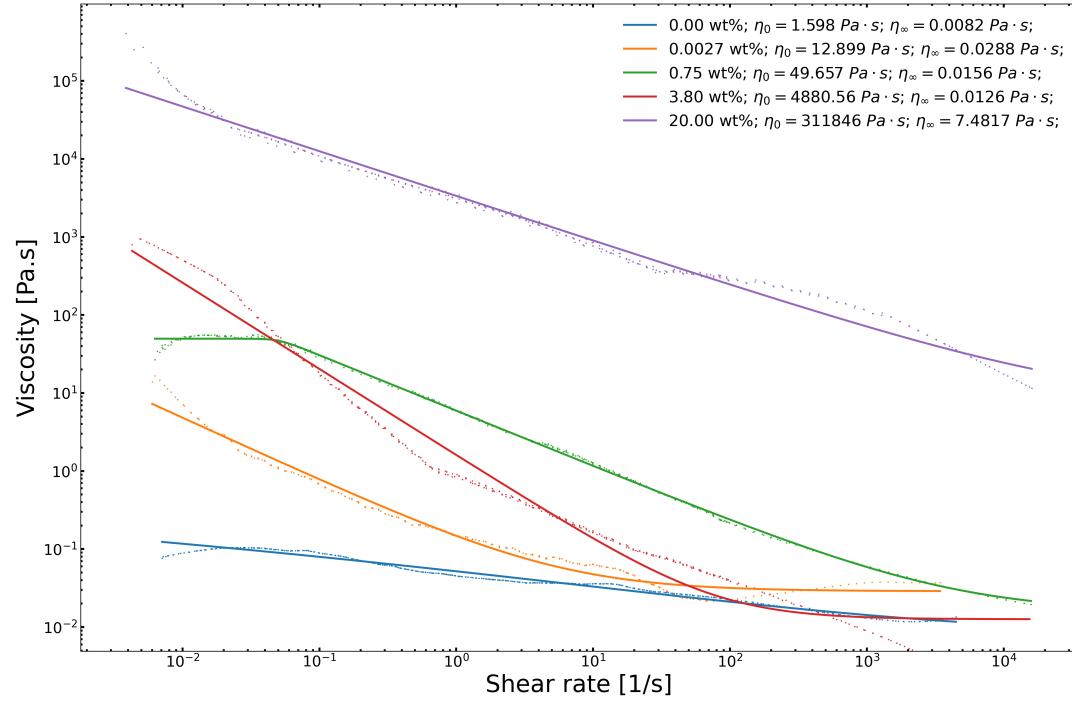


FIGURE A.7: Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and SU-8 2002 solutions

Appendix B

Critical Concentrations

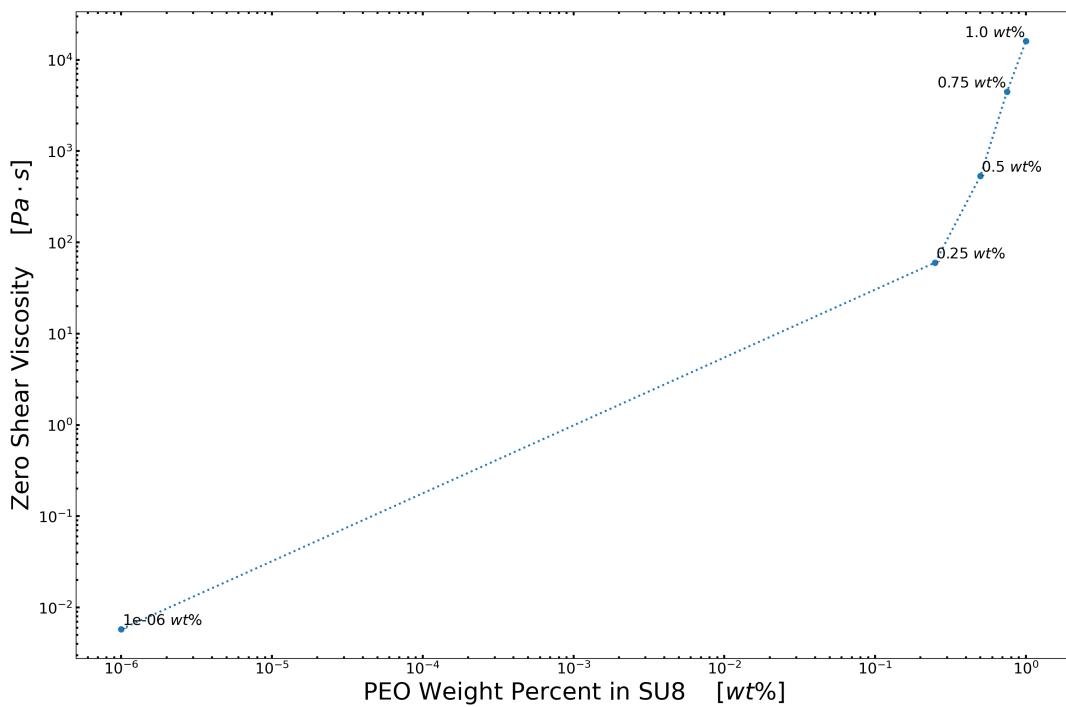


FIGURE B.1: Viscosity as a function of shear rate for Poly(Ethylene Oxide) (PEO) and SU-8 2002 solutions

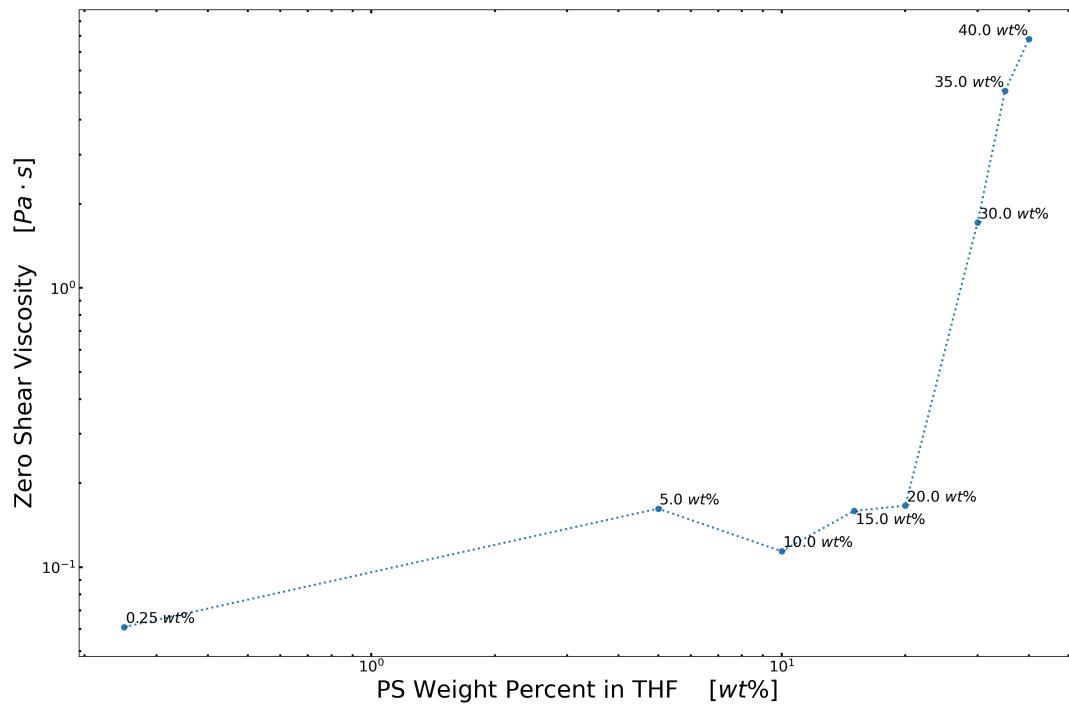


FIGURE B.2: Viscosity as a function of shear rate for Polystyrene (PS) and Tetrahydrofuran (THF) solutions

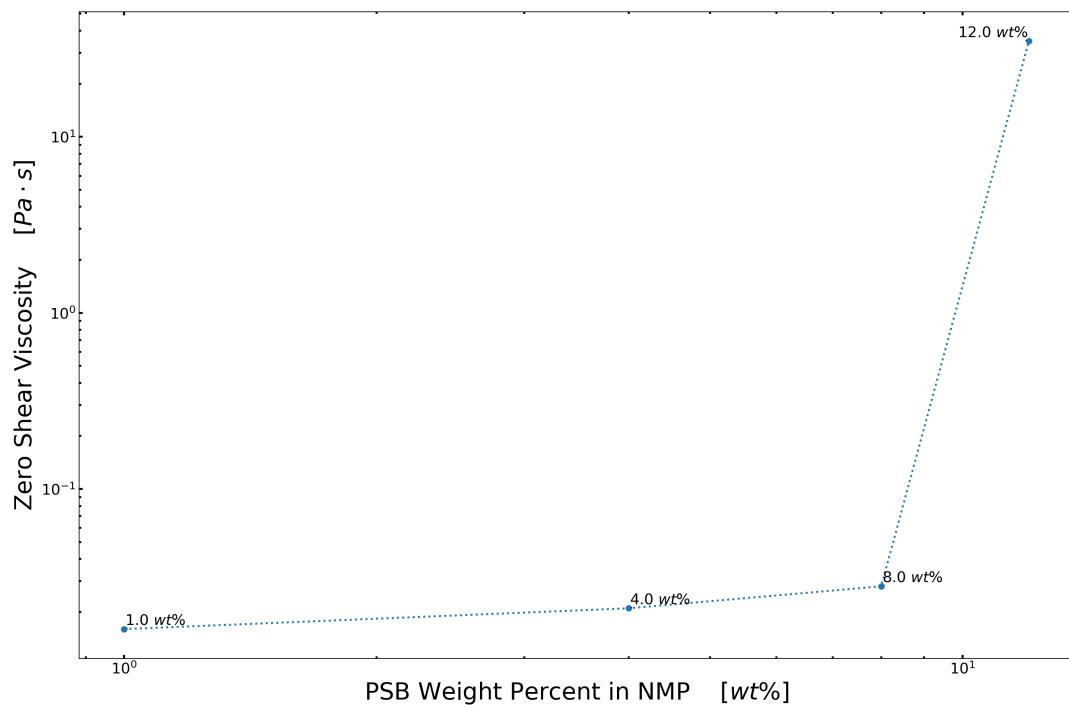


FIGURE B.3: Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB) and 1-Methyl-2-Pyrrolidinone (NMP)

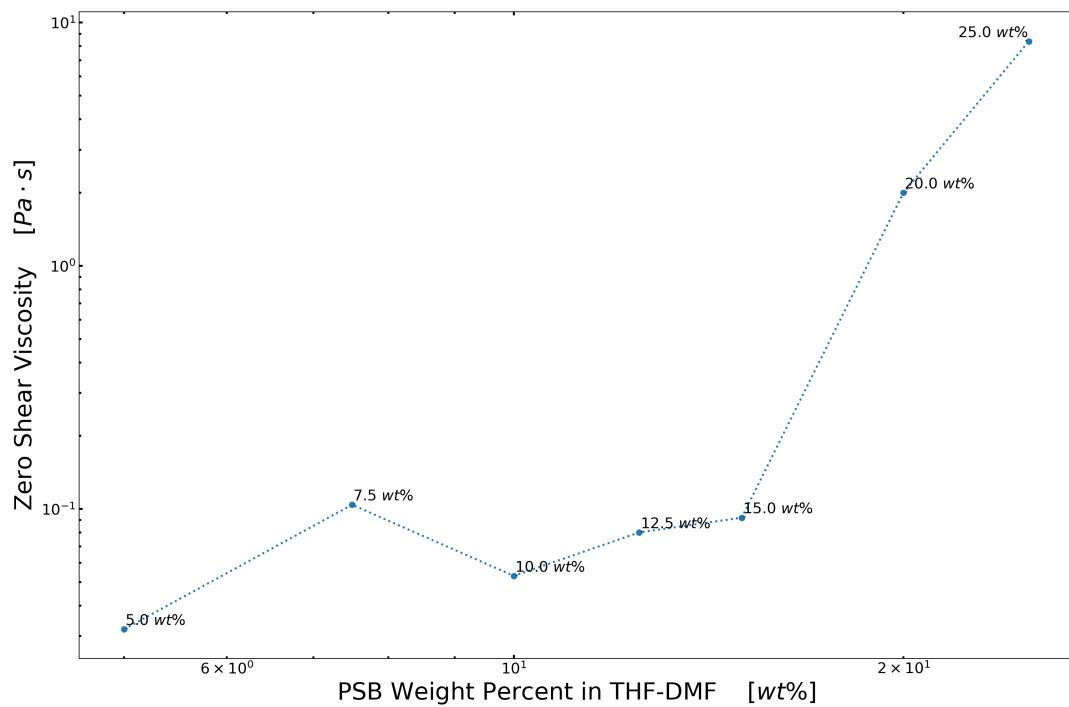


FIGURE B.4: Viscosity as a function of shear rate for Poly(Styrene-co-Butadiene) (PSB), Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF) solutions

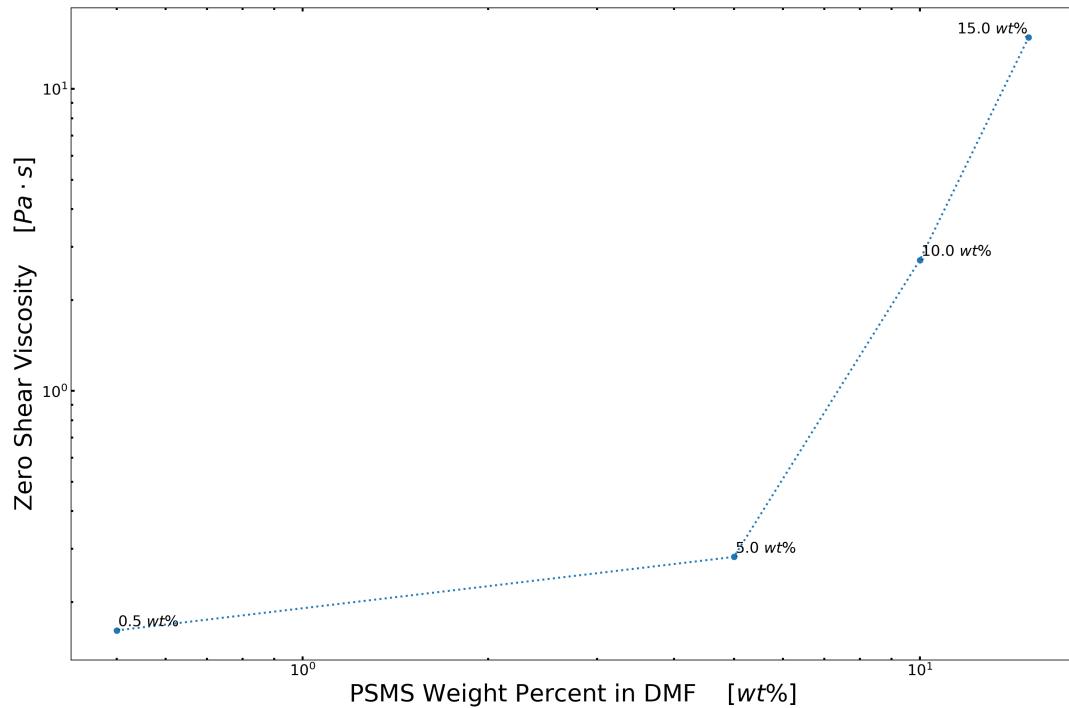


FIGURE B.5: Viscosity as a function of shear rate for Poly(Styrene-co-alpha-Methylstyrene) (PSMS) and N,N-Dimethylformamide (DMF) solutions

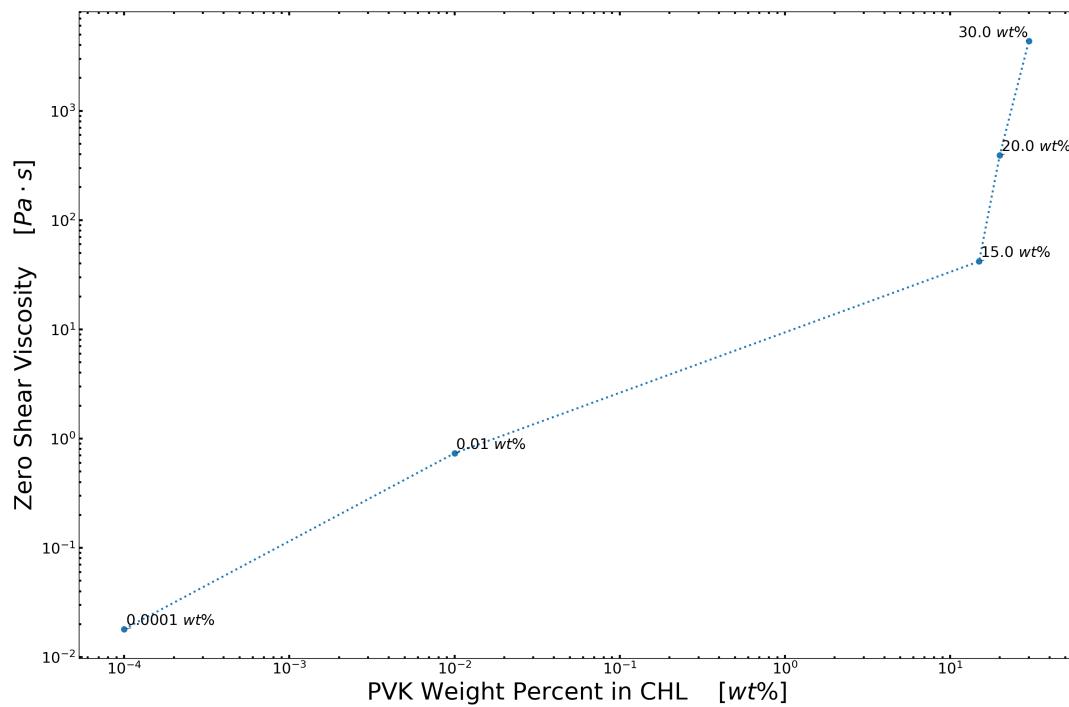


FIGURE B.6: Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and Chloroform (CHL) solutions

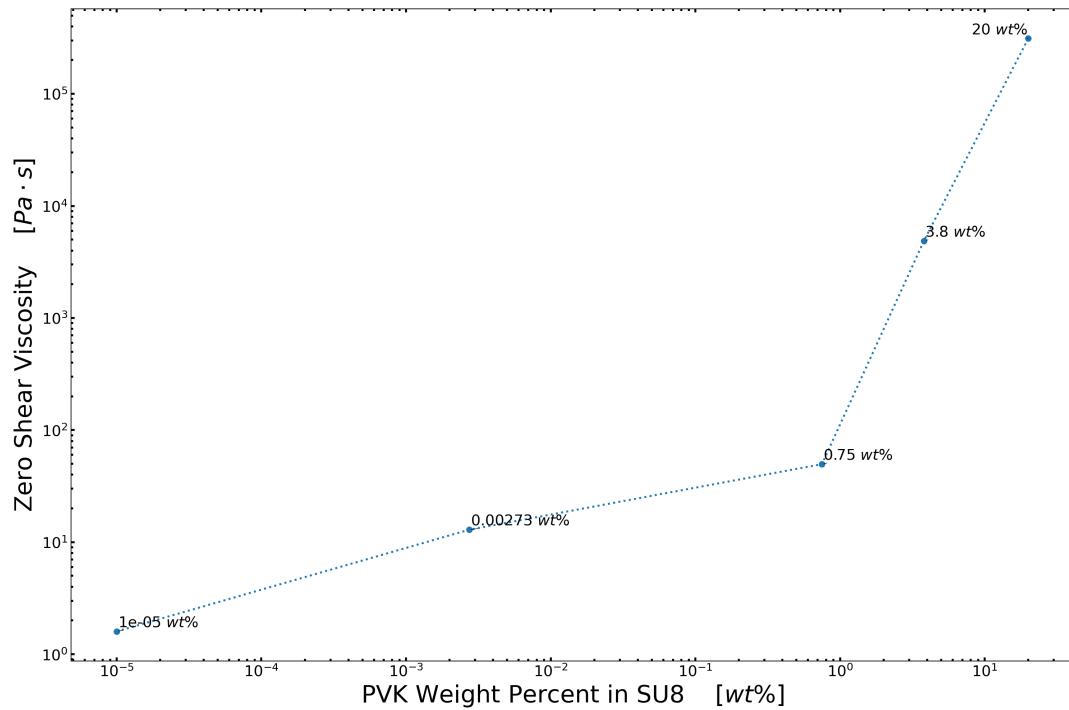


FIGURE B.7: Viscosity as a function of shear rate for Poly(9-Vinylcarbazole) (PVK) and SU-8 2002 solutions

Appendix C

Optical Microscopy Characterization of Electrospun Fibers

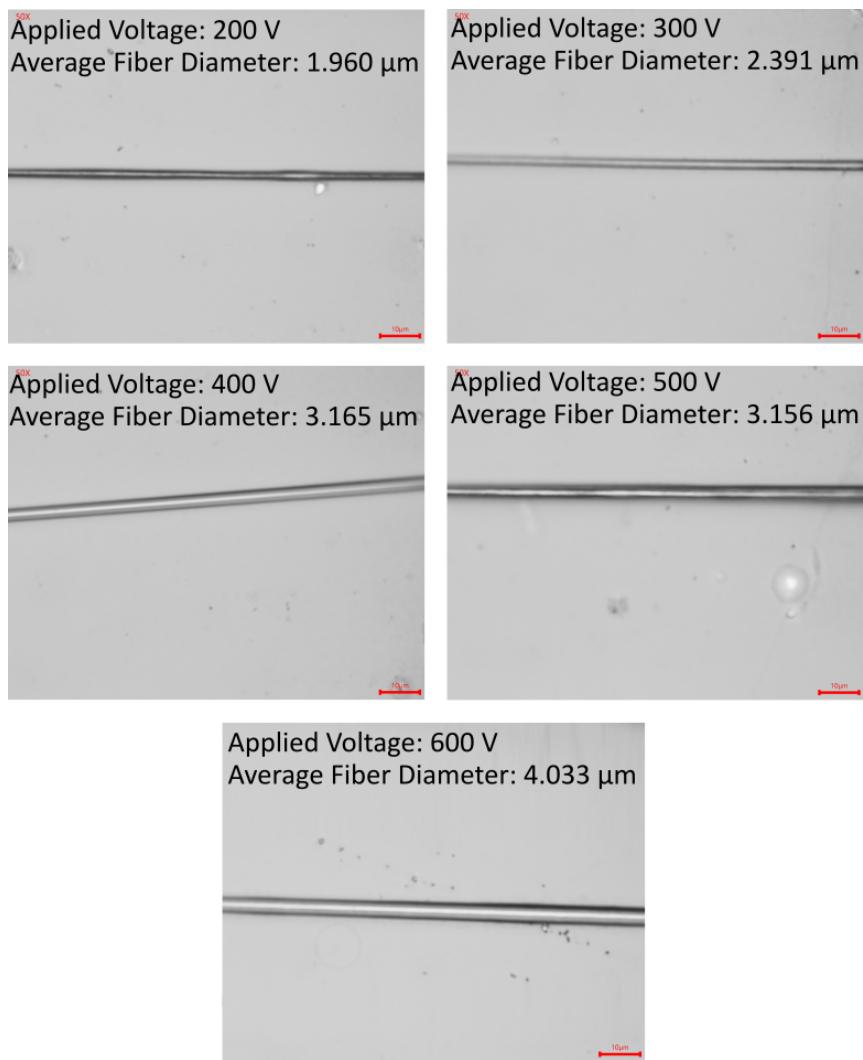


FIGURE C.1: Morphology and Characterization of Electrospun Fibers at Different Voltages : Poly(Ethylene Oxide) (PEO) and SU-8 2002

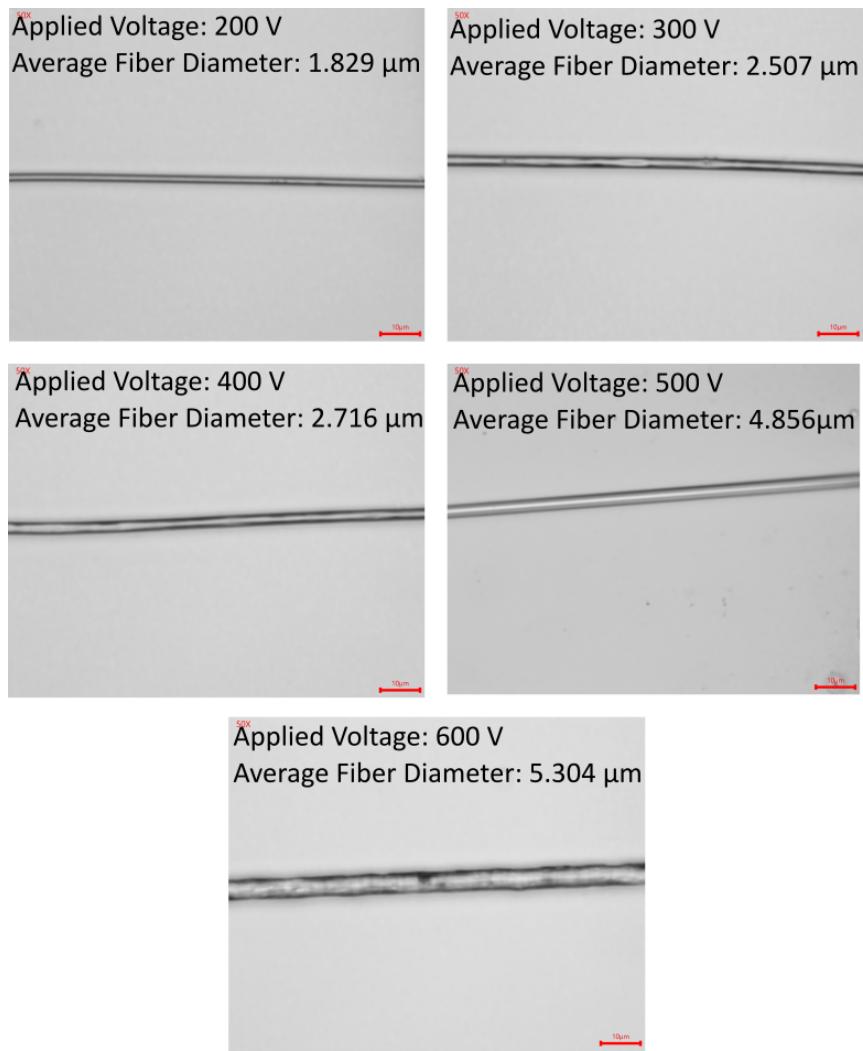


FIGURE C.2: Morphology and Characterization of Electrospun Fibers
at Different Voltages : Polystyrene (PS) in Tetrahydrofuran (THF)

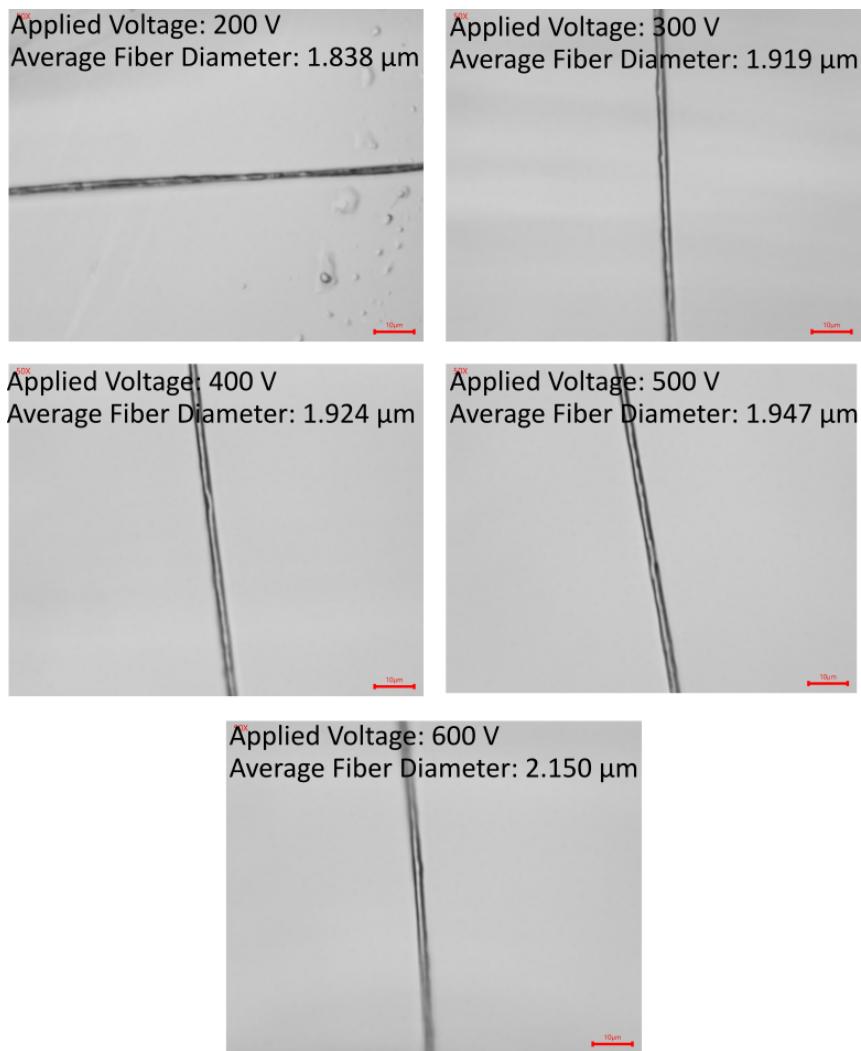


FIGURE C.3: Morphology and Characterization of Electrospun Fibers at Different Voltages : Poly(Styrene-co-Butadiene) (PSB) in Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF)

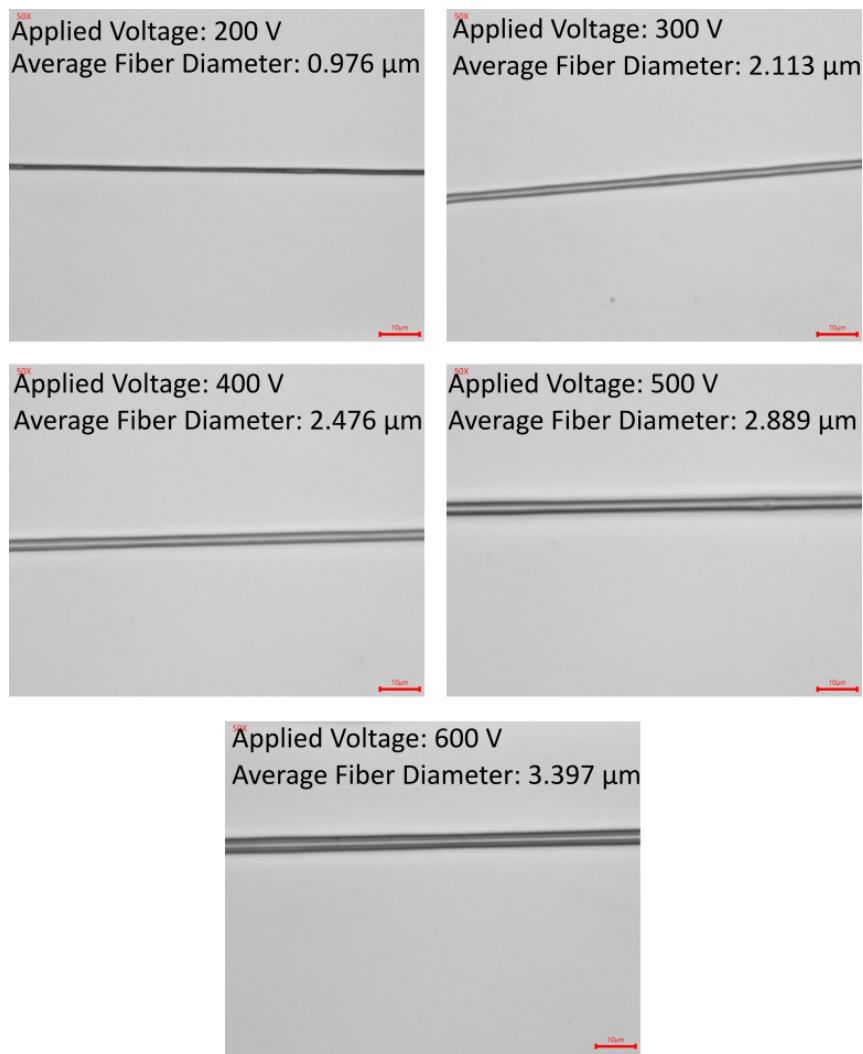


FIGURE C.4: Morphology and Characterization of Electrospun Fibers at Different Voltages : Poly(9-Vinylcarbazole) (PVK) in Chloroform (CHL)

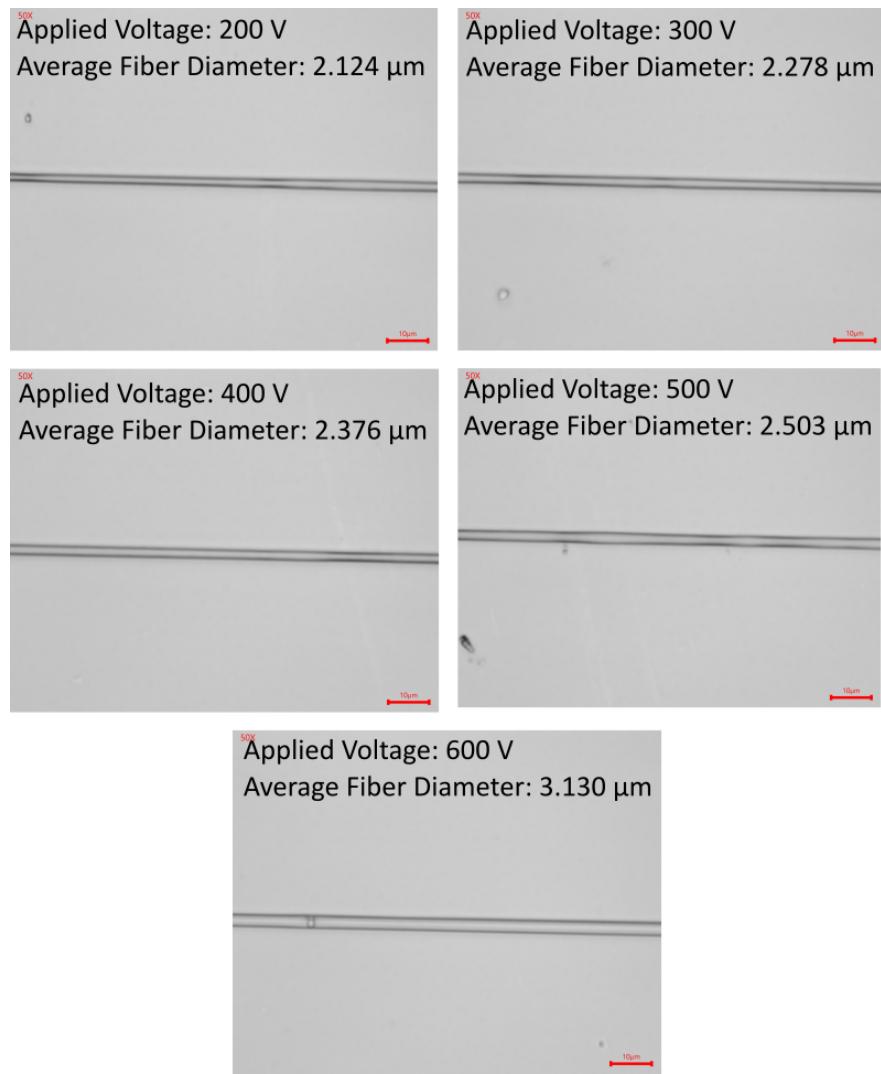


FIGURE C.5: Morphology and Characterization of Electrospun Fibers
at Different Voltages : Poly(9-Vinylcarbazole) (PVK) and SU-8 2002

Appendix D

Average Fiber Diameters, Minimums and Maximums

TABLE D.1: Average Fiber Diameter for All the Experiments

Sample	$C_{polymer}[wt\%]$	$\Phi_0[V]$	average	minimum	maximum
PEO in SU8	0.25	200	1.96 ± 0.185	1.48	2.41
		300	2.39 ± 0.156	2.09	2.67
		400	3.16 ± 0.129	2.81	3.41
		500	3.15 ± 0.247	2.63	3.86
		600	4.03 ± 0.201	3.69	4.37
PS in THF	20.00	200	1.82 ± 0.101	1.64	2.08
		300	2.50 ± 0.105	2.29	2.73
		400	2.71 ± 0.140	2.37	2.98
		500	4.85 ± 0.172	4.41	5.22
		600	5.30 ± 0.388	4.76	6.57
PSB in THF and DMF	15.00	200	1.83 ± 0.251	1.25	2.25
		300	1.91 ± 0.221	1.51	2.54
		400	1.92 ± 0.138	1.61	2.27
		500	1.94 ± 0.201	1.58	2.53
		600	2.15 ± 0.208	1.77	2.76
PVK in CHL	15.00	200	0.97 ± 0.106	0.71	1.26
		300	2.11 ± 0.179	1.71	2.54
		400	2.47 ± 0.134	2.16	2.86
		500	2.88 ± 0.199	2.58	3.37
		600	3.39 ± 0.236	2.98	3.96
PVK in SU8	0.75	200	2.12 ± 0.169	1.75	2.45
		300	2.27 ± 0.117	2.04	2.52
		400	2.37 ± 0.117	2.12	2.65
		500	2.50 ± 0.169	2.06	2.88
		600	3.13 ± 0.109	2.97	3.35

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EDUCATION

TECNOLÓGICO DE MONTERREY

MSc IN NANOTECHNOLOGY

Jan 2019 - Dec 2020 | Estado de México, MX

TECNOLÓGICO DE MONTERREY

BS IN DIGITAL SYSTEMS AND ROBOTICS

Aug 2012 - May 2016 | Querétaro, MX
Cum. GPA: 3.6 / 4.0

LINKS

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COURSEWORK

GRADUATE

Thermodynamics of Materials

Nano-structured Materials

Plastics and Composites Engineering

Rheology & Electrospinning

UNDERGRADUATE

Sensors

Control Engineering

Digital Systems

Computer Architecture

Embedded Systems

Web Application Design

Microcontrollers

Electric Circuits

SKILLS

PROGRAMMING

Over 5000 lines:

Python • Javascript • \LaTeX

Over 2000 lines:

C • C++ • ADA • Verilog • VHDL

Over 1000 lines:

Java • CSS • PHP • Assembly

Familiar:

Android • MySQL

EXPERIENCE

GE AVIATION | EMBEDDED SOFTWARE ENG.

Jun 2018 - Dec 2019 | Querétaro, MX

- At General Electric's Business & General Aviation Power Software team, I develop and test critical software for Aviation Power products. I have high responsibility in the development and in the documentation of the features and interactions with other systems.

GE AVIATION | SW EDISON ENGINEERING DEVELOPMENT PROGRAM

June 2016 – May 2018 | Querétaro, MX

- EEDP is an intensive program for people who have a passion for technology, a drive for technical excellence, and share in GE's core values. It is designed to accelerate participants' professional development through intense technical training.

GE POWER | SOFTWARE EID INTERN

May 2015 – May 2016 | Querétaro, MX

- Support and improve engineering projects and activities.
- Worked on the analysis and optimization of +20 wind turbines for every GE wind farm worldwide.

RESEARCH

MACROPHOTOSCIENCE RESEACH GROUP | MSc STUDENT

Jan 2019 – Dec 2020 | Nuevo León, MX

Worked with Phd. Alan Aguirre and Phd. Dora Medina to determine the electro-spunability of various polymer solutions for the fabrication of carbon nano-wires.

AWARDS

May 2018 top 4% Software EEDP graduate at GE Aviation

Aug 2015 1st/1000 GE 9th Lean Challenge

Nov 2014 1st/50 GEIQ's Robotics Project

PUBLICATIONS

- [1] Saeed Beigi-boroujeni, Osamu Katagiri-tanaka, Braulio Cardenas-benitez, O Sergio, and Alan Aguirre-soto. Pyrolytic Carbon from Novolac Epoxy Resin Compressed before Photocrosslinking and Pyrolysis. *Materials Today: Proceedings*, 2020.