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Hybrid Nanomanufacturing Process for High-Rate Polymer Nanofiber Production

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HYBRID NANOMANUFACTURING PROCESS FOR HIGH-RATE POLYMER NANOFIBER PRODUCTION

By
Chad Thomas Peterson

A Thesis

Presented to the Faculty of
The Graduate College at the University of Nebraska
In Partial Fulfillment of Requirements
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Nanotechnology and nanomaterials have the potential to revolutionize existing and create entirely new industries. Unique physical, mechanical, chemical, and biological properties of nanomaterials have been extensively documented in the last two decades. However, most nanomaterials are discontinuous in nature, creating problems with their processing and manipulation into devices and raising health concerns. Continuous nanofibers represent an emerging class of nanomaterials with critical advantages to applications. Continuous nanofibers are readily produced by electrospinning process comprising spinning polymer solutions in high electric fields. Electrospinning is a very economic top-down nanomanufacturing process that has been used to produce ultrafine continuous nanofibers from several hundred polymers, ceramics, carbon, and metals. The process allows integrated electromechanical nanofiber alignment and assembly into macroscopic 2D and 3D nanostructures. One issue with the classical single-jet electrospinning is its low production rate insufficient for most industrial applications.
The objective of this research was to design, develop, study, and optimize a novel hybrid nanomanufacturing process for high-rate production of quality polymer nanofibers. The process combined centrifugal mechanical and electrical forces in an integrated single-step fashion. Initial design, development, and testing of the hybrid process were conducted. Comprehensive systematic parametric studies were performed on two important polymers, i.e. polyethylene oxide and polyacrylonitrile. Optimal parameters were determined for attaining the highest nanofiber production rate while maintaining high quality of the nanofibers. Nanofiber deposition density was studied and methods for obtaining a consistent deposition were determined. Exploratory analysis of several advanced process configurations, including configurations resulting in aligned nanofibers, wound nanofiber yarns, and nanofiber deposits on non-electroded surfaces was performed. The results demonstrated the feasibility of hybrid nanomanufacturing of high quality nanofibers with significant increases in nanofiber production rates, in comparison with the single-jet electrospinning. Integrated high-rate nanomanufacturing of aligned nanofiber sheets, wound yarns, and nanofilamentary deposits on non-electroded surfaces were also successfully demonstrated for the first time. The obtained results can be used to manufacture nanofibers for a broad range of applications spanning structural materials, composites, and energy, environmental, and biomedical applications.
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1 INTRODUCTION

1.1 Nanotechnology and Nanomaterials

1.1.1 Nanotechnology

As defined by the National Nanotechnology Initiative, nanotechnology is defined as the understanding and control of matter at nanoscale dimensions where unique material properties and behavior allow for novel applications [82]. Nanotechnology holds special significance because physical, chemical, and biological properties that are not present in bulk materials can be seen in materials at the nanoscale. Nanotechnology covers nanoscale science, engineering, and technology and involves imaging, measuring, modeling, and manipulating nanomaterials, or matter at the nanometer length scale [82].

Nanotechnology is considered a key to multiple scientific communities in the 21st century, and is one of the fastest growing areas of scientific research due to its impact on numerous scientific disciplines [1, 2]. Patent applications with nanotechnological implications have increased from several hundred per year in the 1990’s to around 10,000 per year by 2008 with the majority of patents filed in the United States, China, Japan, and South Korea [59], and research on the production, characterization, and application of nanomaterials has become increasingly significant in recent years. Nanotechnology is expected to have revolutionary effects
on many industries including aerospace, energy, biotechnology, environmental science, information technology, and medicine.

1.1.2 Nanomaterials

Nanomaterials are defined by the National Nanotechnology Initiative as all nanosized materials, including both engineered and natural materials with dimensions in the nanoscale [82]. In general, the nanoscale is defined to range between 1 and 100 nanometers [2, 3, 82], and nanomaterials are defined to have at least one dimension in the nanoscale.

Nanomaterials can take numerous forms, including nanoparticles, nanofibers, nanotubes, nanoplates, thin films, and nanocrystalline and nanoporous materials [1, 3, 4]. Nanomaterials can be classified based on their geometry in to three categories: zero-dimensional nanomaterials (nanoparticles), one-dimensional nanomaterials (nanofibers, nanotubes), and two-dimensional nanomaterials (nanoplates, thin films) [3, 59]. Nanomaterials are of great significance because they have size-dependent properties and behavior that are unseen in bulk materials. These size-dependent properties include unique magnetic, optical, thermal, and surface properties. Nanomaterials also exhibit massive surface to volume ratios and incredible strength and stiffness. Also, their size allows for nanomaterials to be used in the development of miniaturized devices.
Nanomaterials have great potential for use in numerous applications spanning many areas of science and technology. Nanomaterials are currently used to strengthen composites for lightweight sports equipment, in nanostructured catalysts, in some pharmaceutical products, as surface treatments for various materials, in dental implants, in the filtration of air and water, and in many electronic devices [82]. Nanomaterials also hold a large potential for applications in many areas including high performance structural or functional materials, in biomedical and biological engineering applications, and many other areas [3, 4, 82].

1.1.3 Nanomanufacturing

Nanomanufacturing is the production of materials with nanoscale dimensions. Nanomanufacturing techniques can generally be categorized into two classes, bottom-up and top-down, each with its own advantages and disadvantages.

In bottom-up nanomanufacturing, methods are used to assemble nanomaterials from individual atoms. Bottom-up nanomanufacturing techniques allow for increased control over the material structure. However, these processes produce materials slowly and are expensive and labor intensive. Examples of bottom-up nanomanufacturing techniques include molecular self-assembly and chemical vapor deposition.
Top-down nanomanufacturing techniques, nanoscale materials are derived from bulk materials. In comparison to bottom-up nanomanufacturing techniques, these methods allow for simpler laboratory setups and allow for faster production of materials. Examples of top-down nanomanufacturing methods include nanolithography and comminution.

Most nanomanufacturing techniques are expensive and difficult to control. Also, they generally result in non-uniform, discontinuous materials that exhibit difficult implementation and utilization of properties, generally require expensive post-processing, and pose a significant health risk in comparison to continuous nanomaterials.

1.2 Nanofibers

Nanofibers are of interest to many areas of research, as their unique properties make them appealing for a wide number of applications. Nanofibers exhibit extremely large surface area to volume ratios [6, 7] and have shown significant increases in modulus and strength when their diameters are below 500 nanometers [8].
1.2.1 Methods of Nanofiber Production

Several methods exist for the production of nanofibers [5], including bi-component spinning, melt-blowing, flash spinning, and electrospinning. However, electrospinning is a preferred technique. Electrospinning can be implemented with a generally simple setup. It is an extremely versatile technique as the process works with many materials (even polymer blends, polymers with embedded nanomaterials such as carbon nanotubes [13, 14]). Additionally, electrospinning has a relatively low cost compared to other nanomanufacturing techniques. Finally, the ability of the technique to produce continuous fibers adds to the value of electrospinning [6, 9, 10].

1.2.2 A Brief History of the Electrospinning Process

In order for researchers to develop early forms of the electrospinning method, an understanding of the behavior of fluids when subjected to electrostatic forces is required. Early research by Grey (1731) and Larmour (1898) helped in this understanding [6]. As a result, techniques for the dispersion of fluids using electrostatic forces were invented in 1902 by Cooley [60] and Morton [61]. It was also shown that when these methods were used with a viscous fluid having a non-volatile component capable of hardening, the production of long fibers with small diameters is possible [61].
In the 1930’s, multiple devices for the production of yarns formed from electrospun fibers were patented by Formhals [62]. These devices included needleless setups and are most likely the basis for much of today’s research on needleless electrospinning techniques. Also, several other processes and devices patented by Formhals in the 1930’s can be seen as the basis for much of the current research involving multiple nozzle setups, the production of aligned fibers through electrospinning, and the continuous production of electrospun fiber yarns [63, 64, 65]. Research continued by Taylor in the 1960’s with the characterization of the effects of an electric field on liquid jets [66, 67, 68]. In 1971, Baumgarten developed an apparatus to electrospin acrylic fibers with diameters ranging from 0.05 to 1.1 microns [69]. Mathematical modeling of the electrospinning process was performed by multiple groups in the 1990’s, including the development of a general electrohydrodynamic model of an electrospun jet by Spivak, Dzenis, and Reneker [70]. Further research has continued, with over 200 research groups studying various aspects of the electrospinning process worldwide [11].

1.2.3 An Overview of the Electrospinning Method

An electrospinning setup generally consists of three components: a high-voltage power supply, a nozzle, and a collector. A polymer solution is introduced to the electrospinning system through the nozzle. The nozzle can take various forms, such as a pipette tip or a syringe driven by a micropump. The high-voltage power supply
applies a positive voltage in the kilovolt range to the nozzle. Additionally, the collector, generally a flat plate made of a conductive material, is grounded.

Electrospinning produces fibers by using electrostatic forces to uniaxially stretch a viscoelastic solution [6]. As electric forces overcome the surface tension of the polymer solution, a meniscus is formed, and from it a jet of polymer solution is emitted [11, 12]. Then, through a series of bending instabilities, the jet is elongated, its diameter is reduced, and the solvent evaporates leaving a continuous polymer fiber with a small diameter [11, 12].

Electrospinning is an extremely versatile top-down nanomanufacturing technique. Electrospinning has been used to produce nanofibers from hundreds of natural and synthetic polymers. Carbon fibers have been produced through post-processing of certain polymer fibers [48, 49, 71, 72]. The electrospinning process also functions in the production of ceramic [73, 74, 75] and metal [76, 77, 78] nanofibers. Also, modifications to the electrospinning process have allowed for structural modifications of the electrospun fibers. For example, hollow [79, 80, 81, 89], core-shell [88, 89], and composite nanofibers [83, 84, 85, 93] have been produced by various research groups.
1.2.4 Advantages of Electrospun Nanofibers

The electrospinning process has multiple advantages over other techniques for the formation of nanofibers. First, the electrospinning process is inexpensive in comparison to most bottom-up methods. Also, electrospinning is an extremely versatile process, functioning with hundreds of natural and synthetic polymers [86, 88, 92], including biopolymers [89, 90, 91], as well as ceramics and metals. Finally, the electrospinning process produces continuous nanofibers with generally good uniformity [86].

Continuous nanofibers have multiple benefits as compared to discontinuous nanomaterials. First, they allow for improved ease of handling and do not require the expensive post-processing required by other nanomaterials [59]. They allow for the possibility of electromechanical control and integrated nanomanufacturing of macroscopic nanofilamentary assemblies [82]. Finally, they pose a minimal health risk as seen with the exposure to and handling of other nanomaterials.

1.3 Applications of Continuous Nanofibers

The unique properties of nanofibers make them appealing to many areas of research. Continuous nanofibers are expected to have high axial strength and stiffness [8] as well as incredible flexibility [82]. Also, continuous nanofiber assemblies can exhibit very high porosity and extreme surface area to mass ratios [6, 7, 82].
Many possible applications for nanofibers have been proposed, and experimentation and development has been done for many of these applications. Fields of research for the incorporation of continuous nanofibers include composite reinforcement, protective clothing, catalysis, electronics, energy, filtration, and biomedical applications, as well as numerous other possibilities.

### 1.3.1 Nanofibers as Composite Reinforcement

Nanofibers have been used in laboratory studies as reinforcement in composite materials. The mechanical properties allow for the potential use as composite reinforcement [15, 16, 17, 87]. Nanofibers could even allow for the possibility of transparent composite materials due to their small diameters, which are often times smaller than the wavelengths in the visible light spectrum [15]. Also, instead of functioning as the primary reinforcing material in the composite, the combination of their high strength and stiffness along with their high surface area to volume ratio make nanofibers an ideal material for interlaminar toughening [15, 87]. An example of how nanofibers can be used in composite engineering was presented by Teo and Ramakrishna, who designed a multifunctional, hierarchically organized nanocomposite [94]. Their design consists of five hierarchical levels: a composite nanofiber, a composite coating over the core composite nanofiber, surface modification, the formation of these surface modified, coated nanofibers in to an assembly, and finally incorporation in to a bulk material.
1.3.2 Nanofibers in Biomedical Applications

The use of nanomaterials in biomedical applications has become a highly researched area in recent years. Biomedical applications for electrospun nanofibers include use as wound dressings [15, 16, 19] and utilization in drug delivery [15, 16, 19, 95, 97]. However, one specific area that has gotten much recent attention is the use of electrospun nanofibers as scaffolding for tissue engineering [6, 7, 11, 15, 18, 19, 20, 89, 95, 97, 99]. Randomly-oriented or aligned nanofiber sheets essentially produce a porous scaffold which physically mimics the extracellular structure of tissues [7, 18, 20]. Research has been performed on numerous polymeric systems, including homopolymers, synthetic copolymers, and polymer mixtures in order to assess their use as potential scaffolding for biological tissue engineering [95]. Also, studies with scaffolds consisting of oriented nanofibers have been presented and could be useful as scaffolding for specific systems, such as the coronary artery smooth muscle cells and cardiac myocytes [95]. Research has been conducted for the use of electrospun materials as platforms for bone tissue engineering [98]. Some research groups have studied the effects of using nanofiber meshes electrospun from novel designed polymers. An example of this is presented by Puppi, et al. who showed encouraging results in cell adhesion and viability when using electrospun star branched three-arm poly(ε-caprolactone) fibers as scaffolding [96].
1.3.3 Other Uses for Nanofibers

Nanofibers have shown to be applicable in the field of nanoelectronics. The flexibility of electrospinning to be used with various materials allows for the production of conductive nanofibers that can potentially be used as components in nanoelectronics [6, 16, 21]. Electrospun nanofibers have also shown potential for use in developing ultrasensitive sensors for environmental, food inspection, and medical diagnostics applications. Electrospun nanomaterials show the potential for use in these ultrasensitive sensors for a wide variety of sensing approaches, including acoustic wave, resistive, photoelectric, optical, and amperometric approaches [100].

Nanofibers have also found a home in the energy storage and production industry [12, 22]. For example, metal oxide fibers can be used for improved conductivity in solar cells, and fuel cells with nanofibrous electrodes exhibit increased electrocatalytic activity [22]. Because of the versatility of materials that can be formed in to nanofibers through the electrospinning process, electrospun nanofibers have shown potential for use in many other energy applications. These applications include dye-sensitized solar cells (in both the electrode layer and electrolyte membrane), in batteries (anode, cathode, or electrolytes), in capacitors, in fuel cells (catalytic electrode, membrane, and enzyme immobilization), and in hydrogen storage (high-porosity adsorption layer or electrode) [101].

Nanofibers have shown applications in many other areas as well. These applications continue to span numerous industries and academic disciplines. As some
examples, nanofibers have shown applicability in air and water filtration [6, 11, 15, 19, 22], as biosensors [11, 16, 19], in protective clothing [6, 11, 15], and even in cosmetics [15, 16].

1.4 Methods for High-Rate Electrospinning

Nanofibers have shown great possibilities in a large number of areas. However, the production rate of nanofibers through single-jet electrospinning methods is too slow and the deposition area is too limited for use in industrial applications. The flow rates of bulk material in to the system, generally through a syringe tip, are generally low [23, 29]. In order for nanofibers produced via electrospinning to be a viable option for various industries, methods must be developed to allow for a faster processing of the polymer solution. Several methods have been developed to increase the production rate of nanofibers via electrospinning.

1.4.1 Arrays of Electrospinning Nozzles

One form of electrospinning augmentation is to electrospin using arrays of multiple nozzles. Several designs for multi-nozzle arrays have been developed [24, 25, 26]. However, several drawbacks exist for this method. First, in order to significantly improve nanofiber production, many nozzles must be used, and the size
of the apparatus would be huge, as the improvement of production is linear with the increased number of electrospinning heads [25]. Also, research has shown that the interactions between electrospinning jets complicates the electric field and leads to inconsistent nanofiber deposition [23, 27, 28].

1.4.2 Electrospinning from a Free Fluid Surface

Another category of electrospinning augmentation includes methods in which numerous electrospinning jets are formed from a fluid surface via the application of high voltage. One example of this type of electrospinning is to partially submerge a charged rotating drum or disk in the polymer solution [14, 29, 30, 31, 32, 33]. The electric charge across the surface area of the drum or disk causes many electrospinning jets to form from the thin fluid layer on the surface of the drum or disk. Experimentation has shown up to 125 times increase in nanofiber production from this type of electrospinning [31]. Other methods of forming electrospinning jets from fluid surfaces have also been developed. Some methods utilize the rising of gas bubbles to create cones on the polymer solution surface [34, 35]. A method was developed by Miloh, Spivak, and Yarin for creating multiple jet initiation points on a polymer solution-covered spherical surface [36]. In this method, approximately ten electrospinning jet initiation points are formed when a spherically symmetric electric field is applied to the fluid-covered spherical surface. Lukas, Sarkar, and Pokomy used a surface with specified geometry to induce jet initiation points [37]. By placing
an electric charge on a fluid-covered surface with ridged geometry, numerous jet initiation points are formed. A method developed by Wang, Niu, Lin, and Wang utilizes very high voltages (up to 70 kilovolts) to produce many electrospinning jet initiation points from the surface of a coiled wire [44]. They have shown the ability to create nanofibers at a rate up to 2.75 grams per hour.

However, techniques that electrospin from a free fluid surface also have drawbacks. First, they require a polymer solution bath which can be bulky and requires large amounts of materials. Also, there is little to no control of the rate at which polymer solution delivered to the system. Finally, many of these methods are limited to vertically-upward electrospinning and cannot deposit nanofibers horizontally or downward.

1.4.3 Hybrid Electrospinning Methods

Several research groups have studied the possibility of developing hybrid electrospinning methods to increase the production rate of nanofibers. These methods utilize a secondary force (pressure, air-flow, magnetic, etc.) to aid in the production of nanofibers. However, the nanofibers produced through many of these methods can be highly irregular.

One such method developed by Yarin and Zussman utilizes magnetic forces to induce electrospinning jets [38]. A ferromagnetic layer is placed below a layer of
polymer solution. By subjecting the system to a magnetic field, fluid spikes are formed and function as electrospinning jet initiation points.

Several air-assisted methods also exist. One system developed by Dosunmu, Chase, Kataphinan, and Reneker utilizes air pressure to force polymer solution through many micropores on a tubular surface [39]. As the polymer solution passes through the pores, the electric field produces electrospinning jets from each fluid source. This method has shown approximately 250 times improvement over single-jet electrospinning. Another air-assisted method, called solution blow spinning, was developed by Medeiros, Glenn, Klamczynski, et al. [40]. This method combines electrospinning with aspects of melt blowing by creating a gas flow around the polymer solution nozzle tip. This draws the solution in to a cone and increases the nanofiber production rate.

Another hybrid method utilizes a pulsed laser in conjunction with electrospinning. Sahay, Teo, and Thoroddsen used a pulsed laser focused at the polymer solution droplet to cavitate the fluid, which eases the initiation of the electrospinning jet [57].

Finally, hybrid methods utilizing centrifugal forces have been developed. Weitz, Harnau, Rauchenbach, et al. have shown that nanoscale fibers are created from polymer solution during a standard spin-coating process [41]. This fiber-forming characteristic of fluid shear-off from a rotating disk is the basis for which the hybrid method developed in this thesis is built. Other electro-mechanical systems have also
been developed. Teng, Zeng, and Weng created many electrospinning jets by dropping polymer solution on to the surface of a charged metal roller [42]. Lu, Wang, Liu, et al. utilized a rotating cone to produce many electrospinning jets [43].

1.5 Proposed Hybrid Process and Objectives of Research

A hybrid electrospinning process that utilizes centrifugal forces was proposed by Dr. Yuris Dzenis. The method combines centrifugal forces from a rotating disk with electrostatic forces to produce numerous electrospinning jets. The rotating disk replaces the standard syringe or pipette tip used in traditional electrospinning setups, allowing for an increased feed of polymer solution to the system. From the increased number of electrospinning jets, the combination of mechanical and electrical forces, and the possibility for increased feed of polymer solution to the system, it was expected that the hybrid nanomanufacturing process would result in significant increases to nanofiber production as compared to single-jet electrospinning methods. The goal of the research included in this thesis was to design, build, and study a hybrid nanomanufacturing system for the high-rate deposition of continuous polymer nanofibers, to optimize the system parameters for the electrospinning of polyethylene oxide and polyacrylonitrile nanofibers, to assess and improve the consistency of deposition density, and to assess the potential for the use of the hybrid system with advanced modifications generally utilized with single-jet electrospinning.
Research began by examining the possibility of developing a hybrid nanomanufacturing process in order to augment nanofiber output as compared to single-jet electrospinning. Fluid shear-off from a flat disk rotating at high speeds will be analyzed. A system will then be constructed using components that allow for good control of all system parameters.

The hybrid process will be tested and optimized parametrically using polyethylene oxide in order to obtain the highest nanofiber output but without reducing the quality of the nanofibers. Nanofiber deposition will be compared to single-jet electrospinning by measuring the mass of nanofibers deposited on a specified area over a specified duration of time. Nanofiber quality will be determined qualitatively through the use of scanning electron microscopy.

Once the optimal parameters are determined, the consistency of deposition will be measured. Methods will be used to analyze the prospects for improving deposition consistency, and the system’s overall applicability for continuous production of nanofiber sheets will be assessed.

Next, a study on the deposition of aligned nanofibers will be performed. Single-jet electrospinning samples collected between gapped electrodes will be analyzed by scanning electron microscopy to determine the overall quality of alignment. Then, a similar study will be performed using the hybrid nanomanufacturing process for aligned fiber production.
The hybrid electrospinning process will be examined for its potential use in creating structurally significant nanofibers (polyacrylonitrile). As this polymer may behave differently than polyethylene oxide, the process will again be optimized to yield the best nanofiber production. Again, nanofiber production will be assessed by measuring the mass of the deposited fibers on a specified surface area for a specified duration of time. Fibers will again be analyzed qualitatively through scanning electron microscopy.

Finally, two exploratory studies will be performed using the hybrid electrospinning process. The first study will assess the ability of the process to produce wound nanofiber yarns. The second study will determine the possibility of depositing nanofibers on surfaces with no electrical connections. Both studies will compare single-jet samples with samples obtained using the hybrid nanomanufacturing process.
2 HYBRID NANOMANUFACTURING SYSTEM DESIGN

2.1 Design of Hybrid Nanomanufacturing Process

This fiber-forming fluid shear-off from a flat disk rotating at high speeds is the basis for the design of the hybrid nanomanufacturing process. The rotational motion and centrifugal forces create many fluid exit points from the disk surface, each of which functions at an electrospinning jet initiation point. The numerous jet initiation points are the primary reason for augmented nanofiber formation. Instead of the production of a single nanofiber, as is the case with a standard single-jet electrospinning process, the hybrid technique allows for many electrospinning jets to form as the polymer solution reaches the edge of the disk. This also allows for much higher polymer solution flow rates into the system, and as a result, higher nanofiber production rates.

The hybrid nanomanufacturing system is designed around a desktop precision spin-coating system. The spin-coating system was chosen because it includes a built-in digital control for rotational speed. The spin-coating system requires both a vacuum pump and a compressed nitrogen feed to function. In addition to the spin-coating system, the hybrid electrospinning system requires a micro-pump for polymer solution delivery, a DC power supply to charge the system, a voltage amplifier to achieve the high voltage required for electrospinning, and a collection surface.
The polymer solution is deposited on to the rotating disk of the spin-coating system via the micro-pump. For initial testing, a cylindrical collection surface is placed around the rotating disk. The rotating disk, or head, is charged via the power supply while the collection surface is grounded (Figure 2.1). Special notice is taken to the numerous system parameters available for study. These parameters include the polymer solution feed rate, the head rotational speed, the electrospinning voltage between the head and collector, the polymer solution concentration, and the electrospinning distance. All of these parameters have effect on the quality and consistency of the electrospinning process, the rate of nanofiber deposition, and the quality of the nanofibers produced.
2.2 System Components

The hybrid nanomanufacturing system was designed and built from commercially available components. The desktop spin-coating system selected for use in the hybrid electrospinning system is the P-6708D Desktop Spincoater from Specialty Coating Systems, Inc. (Figure 2.2). A 6-inch diameter circular head was cut from sheet aluminum and was affixed to the rotary shaft of the P-6708D system. The vacuum pump selected to be used by the spin-coating system is Model 0523-v3-g588dx from Gast Manufacturing Inc. The micro-pump used to deliver the polymer
solution to the system is the EW-74900-00 Single Syringe Infusion Pump from Cole-Parmer. The DC power supply selected for the system is the E3611A from Agilent. Finally, the voltage amplifier used to obtain the required high voltage for electrospinning is the UC5-20N HV Power Supply from Gamma High Voltage Research.
2.3 Materials and Methods

2.3.1 Materials

The majority of the design and testing of the hybrid electrospinning system was performed with a solution of poly-ethylene oxide (PEO) in water. PEO was selected because it is water soluble, making it easy to use in the laboratory, and because it is a widely studied polymer important in several areas, including biological sciences. The PEO has an approximate molecular weight of 300,000 and was obtained from Scientific Polymer Products, Inc.
All polymer solutions were prepared using the same method. The proper amount of polymer was precisely weighed for the desired solution concentration using a digital scale (Fisher Scientific A-250). The required amount of solvent was measured using a graduated cylinder. The polymer and solvent are combined in a 100 mL glass jar along with a magnetic stir bar. The polymer and solvent are concurrently stirred and heated on a combination magnetic stirrer and hotplate (Corning PC-620) for 5 to 6 hours or until the polymer is completely dissolved in to the solvent.

2.3.2 Scanning Electron Microscopy

Scanning electron microscopy was used for detailed observation and analysis of nanofibers collected by the hybrid nanomanufacturing process. Both the Hitachi S4700 Field-Emission Scanning Electron Microscope (Figure 2.3) and the FEI Quanta 200 FEG Environmental Scanning Electron Microscope (Figure 2.4) were used for observation and analysis of nanofibers.
Figure 2.3 – Hitachi S4700 Field-Emission Scanning Electron Microscope
Figure 2.4 – FEI Quanta 200 FEG Environmental Scanning Electron Microscope

Low magnifications ranging from 30X to 1000X were used to observe the qualities of the overall collection of nanofibers including the consistency of nanofiber deposition and the presence of bulk fluid in the sample. High magnifications, some over 100,000X, were used to observe the properties of individual nanofibers including nanofiber diameters, the consistency of nanofiber diameters along the fibers, and the structural quality of the nanofibers.

2.3.3 Mass Production Rate Analysis

As the primary objective of the hybrid nanomanufacturing process is to increase the rate at which nanofiber can be produced, extensive analysis of the mass of nanofibers collected per time unit is needed. In order to obtain comparable data, a consistent method was used for all analysis of nanofiber production.

All analysis of nanofiber production was performed by measuring the difference in mass between a collection surface before nanofiber deposition and after nanofiber deposition. Aluminum foil sheet was cut in to one-inch squares. Each aluminum foil square was then weighed using a digital scale (Mettler Toledo AT201). Next, the aluminum foil squares were adhered to the electrospinning collection surface using cellophane tape. Then, nanofibers were deposited on to the collection surface, including the aluminum foil squares, by the hybrid nanomanufacturing process. The duration of deposition was recorded. Next, the foil squares were
carefully removed with special care taken to ensure that adhesive from the cellophane tape does not remain on the foil. The nanofiber-covered aluminum foil squares were then weighed once again. Using the pre- and post-deposition masses of the squares, the mass of the deposited nanofibers was calculated. Then, the mass of the deposited nanofibers, the area of the foil square, and the duration of deposition were used to calculate the nanofiber deposition per unit area over a specific duration of time in units of milligrams per hour per square centimeter.

2.3.4 Characteristics Studied

Throughout the testing and analysis of the hybrid electrospinning system, several characteristics of both the deposition and individual nanofibers were studied. These include the density, area, uniformity, and quality of the deposition and the quality and diameters of the nanofibers produced.

The overall goal of the study was to perform a systematic parametric analysis of the hybrid process, and to determine the optimal parameters for a good quality nanofiber output. A good output is defined as having a high nanofiber deposition rate, well structured, consistent nanofibers, and a high quality deposition with minimal presence of detrimental deposition artifacts, such as bulk fluid and wet fiber deposition.
2.4 Validation of Hybrid Nanomanufacturing Process

Initial testing of the hybrid nanomanufacturing process was performed in order to test its validity. First, the fluid shear from a disk rotating at high speed was observed visually and with a high speed video camera (Redlake MotionXtra HG-100K). From this analysis, the fiber-forming qualities of the process and the manner in which the polymer solution leaves the disk can be determined.  

For this initial test, a 12 percent by weight solution of PEO in water is deposited on to the head at a rate of 8.0 milliliters per hour while the head is rotated at a rotational speed of 4000 rotations per minute. The PEO solution passes over the surface of the head in numerous radial lines before leaving the edge of the head. The multiple fluid exit points around the edge of the head (Figure 2.5) each have the potential to be utilized as electrospinning initiation points.
In addition to the visual observation of the polymer solution on the surface of the head after rotation, the process was observed during head rotation by use of a high speed video camera and careful lighting of the head. Screen captures from the recorded video shows the initiation of a fluid jet from the edge of the head (Figure 2.6). This verifies the belief that centrifugal forces from the head rotation can be used to initiate jets of polymer solution for electrospinning.
2.5 Initial Parametric Testing

The first tests to combine the fluid shear from a rotating head with the electrospinning process were performed. A cylindrical collector was placed around the head with spacing of eight inches between the collector surface and the edge of
the head. The polymer solution feed rate was kept low at 3.0 milliliters per hour, the head rotational speed was set between 2000 and 4000 rotations per minute, and the electrospinning voltage was set between 12.5 and 15 kilovolts. SEM imaging of the initial samples collected show that production of high quality nanofibers is possible using the hybrid nanomanufacturing process (Figure 2.7).

![Figure 2.7 – SEM Images from Initial Sample Collected With Hybrid Process](image)

Initial parametric testing of the hybrid nanomanufacturing process was performed in order to obtain a starting point for the extensive parametric testing required to optimize all system parameters. Here, the quality of the nanofiber deposition was the primary focus with special note taken on the density of deposition and the quality of the individual nanofibers.

The polymer solution feed rate was the first parameter studied. Here, the head rotational speed and the electrospinning were held constant at 4000 rotations per minute and 12.5 kilovolts, respectively. The polymer solution feed rate was modified between 20 and 50 milliliters per hour. SEM imaging from samples collected in this study showed that as the fluid deposition rate increased, the rate of fiber production
also increased slightly with minimal effect on the quality of individual fibers (Figure 2.8).

Next, the head rotational speed was tested. Here, the polymer solution feed rate and the electrospinning voltage were held constant at 30 milliliters per hour and 15 kilovolts, respectively. The head rotational speed was modified between 100 and 8000 rotations per minute. This covers the full range allowed by the P-6708D Spincoater system. SEM imaging (Figure 2.9) showed that the deposition is of the best quality at speeds between 1000 and 2000 rotations per minute. Lower speeds result in few fibers and inconsistent diameters of individual fibers. At higher rotational speeds, there is an increased deposition density, but also an increased presence of bulk fluid, an issue that will be addressed later.
Finally, the electrospinning voltage was studied. For this study, the polymer solution feed rate and head rotation was held constant at 30 milliliters per hour and 2000 rotations per minute, respectively. The electrospinning voltage was varied between 5 and 25 kilovolts. SEM imaging showed that as the voltage increased, the individual nanofiber fiber quality and the overall nanofiber deposition density also increased (Figure 2.10). At low voltages, individual nanofibers are poorly formed, exhibiting severe inconsistencies along the length of the fiber. The density of nanofiber deposition is also insufficient. Note that at high voltages, the amount of bulk fluid deposited along with the nanofibers also increased.
From this initial parametric study, a starting point for a comprehensive parametric study was determined (Figure 2.11). Also, throughout the initial study, starting points for polymer solution concentration and electrospinning distance were selected by qualitatively observing the electrospinning. The polymer solution feed rate study showed that high quality nanofibers can be formed even when the polymer solution is introduced to the system at extremely high rates, up to and possibly above 50 milliliters per hour. The head rotational speed study showed that intermediate speeds result in the best quality nanofiber deposition. The electrospinning voltage study showed that high voltages result in good quality fibers and high density depositions. However, the important issue of bulk fluid deposition was also uncovered. The presence of bulk fluid has potential to destroy nanofibers in close proximity and disrupt the continuity of the nanofibers, rendering the collected nanofibers useless.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Solution Feed Rate</td>
<td>40 mL/h</td>
</tr>
<tr>
<td>Head Rotational Speed</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Electrospinning Voltage</td>
<td>25 kV</td>
</tr>
<tr>
<td>Polymer Solution Concentration</td>
<td>10%</td>
</tr>
<tr>
<td>Electrospinning Distance</td>
<td>30 cm</td>
</tr>
</tbody>
</table>

*Figure 2.11 – Initial Parameter Set for Extensive Parametric Study*
2.6 Detrimental Deposition Artifacts

Throughout the initial testing and study of the hybrid manufacturing process, several features present in the depositions were observed. As the hybrid process has an extremely high rate of polymer solution feed in to the system as compared to single-jet electrospinning, excess bulk fluid or wet fibers were sometimes deposited along with nanofibers. The presence of these deposition artifacts occurs when there is a parametric misbalance causing more polymer solution to leave the head than the system can electrospin in to nanofibers. This can occur as an overall characteristic of the electrospinning parameter set. For example, if the fluid feed rate is too high, there is a good chance for bulk fluid or wet fiber deposition. These can also occur sporadically during a “good” electrospinning parameter set when a large amount of polymer solution reaches the edge of the head, causing an excess amount of fluid to leave the head for a short period.

Two deposition artifacts have been observed throughout the study of the hybrid electrospinning system while using PEO solution. Bulk fluid deposition occurs when droplets of polymer solution are expelled from the head along with the electrospinning jets. These droplets are of significant size, often reaching sizes over 0.5 millimeters (Figure 2.12). This bulk fluid splattering could be detrimental to the properties of the nanofibers collected as it leads to areas of the nanofiber sheet that lack the presence of nanofibers. The droplets also break the continuity of the nanofibers.
Wet fiber deposition occurs when the electrospinning parameters cause the nanofibers to be deposited before the solvent can evaporate, resulting in a deposition of large wet fibers (Figure 2.13) that tend to connect at intersection points. The deposition of wet fibers is also harmful to the properties of the fibers as their large size and the joining at fiber intersections would significantly reduce their mechanical properties.
As the presence of detrimental deposition artifacts is unfavorable, care needs to be taken to eliminate or at least significantly reduce their presence in nanofiber depositions. Therefore, during the in-depth parametric study of the hybrid nanomanufacturing process, the presence of these deposition artifacts is noted and used in the determination of the optimal parameters. In addition to carefully noting the presence of these artifacts, a critical modification was made to the layout of the hybrid system to significantly reduce the probability of their occurrence. The initial setup utilized a cylindrical collector surrounding the head. This caused large amounts of bulk fluid deposition as the mechanical forces from the rotating head expelled any excess polymer solution on to the collector. The collector is instead suspended above the head (Figure 2.14). With this layout, the centrifugal forces from the head rotation
are utilized primarily for electrospinning jet initiation rather than for propulsion of the jets.

Figure 2.14 – Collector Surrounding Head and Collector Above Head
3 PARAMETRIC STUDY USING POLYETHYLENE OXIDE

The hybrid nanomanufacturing process features multiple parameters of interest, each of which can be controlled individually. During experimentation, it became apparent that each process parameter has an effect on the characteristics of the nanofibers produced and of the overall deposition. Therefore, extensive parametric testing was performed in order to optimize each parameter for the highest deposition rate and the best quality nanofibers. The parameters analyzed during this study are as follows: polymer solution feed rate, head rotational speed, electrospinning voltage, polymer solution concentration, and the electrospinning distance.

3.1 Nanofiber Production using Single-Jet Electrospinning

In order to assess the enhancement to nanofiber production rate while using the hybrid nanomanufacturing system, productivity data was collected using a traditional single-jet electrospinning setup. Samples were collected in the same manner as with the hybrid setup. Aluminum foil was cut into one-inch squares, the foil was pre-weighed, nanofibers were deposited on the foil for a set amount of time, and the foil squares were weighed once again. The mass of the collected fibers was measured, and using this mass, the area of the foil, and the duration of deposition, the mass production rate was calculated.
The electrospinning parameters for the single-jet samples are as follows:

- PEO solution feed rate = 0.5 milliliters per hour
- Electrospinning voltage = 15.5 kilovolts
- Electrospinning distance = 25 centimeters
- PEO concentration = 10 percent by weight

Nanofiber deposition rates using the single-jet electrospinning setup ranged from 0.037 to 0.186 (mg/h)/cm² and averaged 0.073 (mg/h)/cm² across 30 data points. This information will be used in determining the improvements in nanofiber deposition rate while using the hybrid nanomanufacturing system.

### 3.2 Effects of PEO Solution Feed Rate

The parametric study of the hybrid nanomanufacturing system began by studying the effects of the polymer solution feed rate on nanofiber quality and production rate. During this study, head rotational speed was held constant at 2000 rotations per minute, the electrospinning voltage was held at 25 kilovolts, the electrospinning distance was set to 30 centimeters, and the PEO concentration was 10 percent by weight. Throughout the study the polymer solution feed rate was varied. Data was collected for feed rates of 5, 10, 20, 30, 40, 50, 75, and 100 milliliters per hour. For each data point, the mass of the collected fibers, the area of collection, and
the time of deposition were used to calculate the mass production rate in units of milligrams per hour per square centimeter. For each value of the parameter, 50 samples were collected at points equidistant from the electrospinning head axis.

Data for nanofiber production rates for all PEO solution feed rates studied are shown in Figure 3.1. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.

<table>
<thead>
<tr>
<th>PEO Solution Feed Rate (mL/h)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td>0.80</td>
<td>1.10</td>
<td>0.95</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>1.66</td>
<td>1.90</td>
<td>1.77</td>
</tr>
<tr>
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<td></td>
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</tr>
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<td></td>
<td>4.71</td>
<td>5.39</td>
<td>5.02</td>
</tr>
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<td></td>
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<td>6.70</td>
<td>6.37</td>
</tr>
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<td></td>
<td>6.14</td>
<td>6.79</td>
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</tr>
<tr>
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<td>6.21</td>
<td>6.81</td>
<td>6.51</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>6.25</td>
<td>6.90</td>
<td>6.60</td>
</tr>
</tbody>
</table>

*Figure 3.1 - Nanofiber Production Rates for Various PEO Solution Feed Rates*

This data has also been compiled into a graph. Figure 3.2 plots the nanofiber production rate as a function of PEO solution feed rate.
Based on data in Figures 3.1 and 3.2, it is quite apparent that the rate of nanofiber production reaches a critical value at a feed rate of approximately 40 milliliters per hour. The increase in nanofiber production slows at higher PEO feed rates due to an oversaturation of polymer solution on the head surface. Instead of the polymer solution reaching the edge of the head in a consistent manner allowing it to form in to electrospinning jet initiation points, the excess solution is ejected from the disk in larger droplets. This prevents much of the polymer solution from being electrospun and essentially wastes the material. However, this limit in nanofiber production is most likely related to the size of the head, and scaling up the hybrid nanomanufacturing system would allow for higher polymer solution feed rates to be input to the system.
In addition to nanofiber production rate, the quality of the nanofibers also plays great importance in parameter optimization. The nanofibers were analyzed qualitatively by viewing via SEM microscopy. Attention was directed toward the fiber diameters, the structure of the fibers, and the presence of bulk fluid in the deposition.

SEM images of collected PEO nanofibers are shown in Figures 3.3 and 3.4 for 10 milliliters per hour, Figures 3.5 and 3.6 for 40 milliliters per hour, and Figures 3.7 and 3.8 for 50 milliliters per hour.

Nanofibers collected with a PEO feed rate of 10 milliliters per hour exhibit diameters ranging from 200 nanometers to 1 micron. Note that fiber structures are smooth and that there is no bulk fluid present in the deposition.

Figures 3.3 and 3.4 – SEM Images: PEO Solution Feed Rate of 10 milliliters per hour
Nanofibers collected with a PEO feed rate of 40 milliliters per hour exhibit diameters ranging from 200 nanometers to 1 micron. Again, fibers are well structured and there is also no presence of bulk fluid in the deposition.

Figures 3.5 and 3.6 – SEM Images: PEO Solution Feed Rate of 30 milliliters per hour

Nanofibers collected with a PEO feed rate of 50 milliliters per hour exhibit diameters ranging from 150 nanometers to approximately 1 micron. Note that the fiber structures are irregular and there is a significant presence of bulk fluid in the deposition.

Figures 3.7 and 3.8 – SEM Images: PEO Solution Feed Rate of 50 milliliters per hour
Figure 3.9 shows the range of nanofiber diameters as a function of PEO feed rate. From 10 to 50 milliliters per hour, nanofibers exhibit similar diameters and diameter consistencies. Samples collected at 75 and 100 milliliters per hour showed larger fibers and a wider range of fiber diameters.

A combination of the analysis of deposition rate data and SEM imaging results in the determination of an optimal PEO solution feed rate of 40 milliliters per hour. Feed rates higher than 40 milliliters per hour do not yield better nanofiber production rates. Also, depositions above this level are marred by the presence of bulk fluid and poor fiber structure. A summary of the PEO solution feed rate parametric study is shown in Figure 3.10.
### Figure 3.10 – Summary of PEO Solution Feed Rate Parametric Study

<table>
<thead>
<tr>
<th>PEO Solution Feed Rate (mL/h)</th>
<th>Mass Production Rate ((mg/h)/cm²)</th>
<th>Fiber Diameters (nm)</th>
<th>Bulk Fluid Presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.95</td>
<td>150 - 900</td>
<td>None</td>
</tr>
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<td>None</td>
</tr>
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<td>40</td>
<td>6.37</td>
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<tr>
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<td>6.6</td>
<td>350 - 1500</td>
<td>Significant</td>
</tr>
</tbody>
</table>

#### 3.3 Effects of Head Rotational Speed

The next parameter to be optimized is the rotational speed of the head. For this study, the PEO solution feed rate was held constant at 40 milliliters per hour, the electrospinning voltage was set at 25 kilovolts, the electrospinning distance was set at 30 centimeters, and the PEO solution concentration was 10 percent by weight. The rotational speed of the head was varied throughout the study. Data points were collected for rotational speeds of 100, 500, 1000, 1500, 2000, 2500, 5000 and 8000 rpm. These points span the entire output range of the P6708D desktop spincoater system. For each data point, the mass of the collected fibers, the area of collection, and the time of deposition were used to calculate the mass production rate in units of milligrams per hour per square centimeter. For each value of the parameter, 50 samples were collected at points equidistant from the electrospinning head axis.
Data for nanofiber production rates for various head rotational speeds is presented in Figure 3.11. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.

<table>
<thead>
<tr>
<th>Head Rotational Speed (rpm)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td></td>
<td>1.15</td>
<td>1.40</td>
<td>1.27</td>
</tr>
<tr>
<td>500</td>
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<td>1000</td>
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<td>5.00</td>
<td>5.54</td>
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</tr>
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<td>1500</td>
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<td>6.49</td>
<td>6.75</td>
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<td>6.31</td>
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<td>5.71</td>
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</tr>
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</table>

*Figure 3.11 – Nanofiber Production Rate Data for Various Head Rotational Speeds*

Data collected in the parametric study of head rotational speed has been compiled in to a graph (Figure 3.12), representing the nanofiber production rate as a function of the head rotational speed.

The rate of nanofiber deposition increases steadily between 100 and 1500 rotations per minute. Above 1500 rotations per minute, the deposition rate drops off slightly. At higher rotational speeds, excess bulk fluid was observed leaving the electrospinning head without being electrospun, wasting material and accounting for the decrease.
In addition to the analysis of nanofiber production rate, the quality of the fibers needs to be assessed to determine the optimal head rotational speed. Samples were analyzed qualitatively by viewing via SEM microscopy. Attention was directed toward the fiber diameters, the structure of the fibers, and the presence of bulk fluid in the deposition.

SEM images are shown in Figures 3.13 and 3.14 for 1500 rotations per minute, Figures 3.15 and 3.16 for 2000 rotations per minute, and Figures 3.17 and 3.18 for 2500 rotations per minute.
Nanofibers collected with a head rotational speed of 1500 rotations per minute had diameters ranging from 200 to 300 nanometers. Fibers are generally of good quality, have very consistent diameters, and were not deposited with bulk fluid.

*Figures 3.13 and 3.14 – SEM Images: Head Rotational Speed of 1500 Rotations per Minute*

Nanofibers collected with a head rotational speed of 2000 rotations per minute have diameters from 200 to 600 nanometers. Fibers are of good quality, but there are some larger fibers present in the deposition. Also note the presence of some wet fiber deposition.

*Figures 3.15 and 3.16 – SEM Images: Head Rotational Speed of 2000 Rotations per Minute*
Nanofibers collected with a head rotational speed of 2500 rotations per minute exhibited diameters ranging from 200 to 600 nanometers. However, the sample shows some poor fiber structures and a significant amount of bulk fluid deposition.

Figure 3.17 and 3.18 – SEM Images: Head Rotational Speed of 2500 Rotations per Minute

Figure 3.19 shows the range of nanofiber diameters as a function of head rotational speed. Head rotational speeds of 1500 and below exhibit exceptional fiber diameters and diameter ranges. Head rotational speeds of 2000 and above have larger fiber diameters and wider diameter ranges. The larger average fiber diameters and wider diameter distributions can most likely be attributed to the increased centrifugal forces from the increased disk rotational speed forcing excess polymer solution to the edge of the electrospinning head too quickly, resulting in irregular fiber formation.
By combining the nanofiber production rate study and the analysis of SEM images, an optimal head rotational speed of 1500 rotations per minute was chosen. Nanofiber production rates were at a maximum at intermediate head rotational speeds (1500 to 2500 rotations per minute). Lower rotational speeds do not expel the polymer solution from the head quickly enough to take advantage of the high PEO solution feed rate. Head rotational speeds higher than 2500 rotations per minute resulted in large droplets of polymer solution to be thrown from the nozzle without being electrospun into fibers. This accounts for the increasing level of bulk fluid deposition at higher rotational speeds. Also, fiber quality and consistency is best at head rotational speeds less than 2000 rotations per minute. A summary of the head rotational speed parametric study is shown in Figure 3.20.
### 3.4 Effects of Electrospinning Voltage

Next, the electrospinning voltage was optimized for use with the hybrid nanomanufacturing process. For this study, PEO solution feed rate was set to 40 milliliters per hour, head rotational speed was set at 1500 rotations per minute, the electrospinning distance was held constant at 30 centimeters, and the PEO solution concentration was 10 percent by weight. The electric potential between the head and collector was varied. Data was collected for 5, 10, 12.5, 15, 17.5, 20, 25 and 30 kilovolts. For each data point, the mass of the collected fibers, the area of collection, and the time of deposition were used to calculate the mass production rate in units of milligrams per hour per square centimeter. For each value of the parameter, 50 samples were collected at points equidistant from the electrospinning head axis.

<table>
<thead>
<tr>
<th>Head Rotational Speed (rpm)</th>
<th>Mass Production Rate ((mg/h)/cm²)</th>
<th>Fiber Diameters (nm)</th>
<th>Bulk Fluid Presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.27</td>
<td>200 - 350</td>
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<td>Significant</td>
</tr>
<tr>
<td>8000</td>
<td>5.99</td>
<td>300 - 1100</td>
<td>Significant</td>
</tr>
</tbody>
</table>

*Figure 3.20 – Summary of Head Rotational Speed Parametric Study*
Data for nanofiber production rates for the electrospinning voltages studied are shown in Figure 3.21. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.

<table>
<thead>
<tr>
<th>Electrospinning Voltage (kV)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>5</td>
<td>0.09</td>
</tr>
<tr>
<td>10</td>
<td>0.65</td>
</tr>
<tr>
<td>12.5</td>
<td>2.01</td>
</tr>
<tr>
<td>15</td>
<td>4.71</td>
</tr>
<tr>
<td>17.5</td>
<td>5.10</td>
</tr>
<tr>
<td>20</td>
<td>6.21</td>
</tr>
<tr>
<td>25</td>
<td>6.19</td>
</tr>
<tr>
<td>30</td>
<td>6.31</td>
</tr>
</tbody>
</table>

*Figure 3.21 – Nanofiber Production Rates for Various Electrospinning Voltages*

The data collected during the parametric study of electrospinning voltage is shown in Figure 3.22, showing the nanofiber production rate as a function of electrospinning voltage.
The quality of the nanofibers must also be analyzed to determine the optimal electrospinning voltage for the hybrid nanomanufacturing system. Nanofibers were observed by SEM imaging and were analyzed qualitatively. Special attention was given to the nanofiber diameters, the nanofiber structure, and the presence of bulk fluid in the deposition.

SEM images are shown for various electrospinning voltages in Figures 3.23 through 3.28. Figure 3.23 shows fibers collected with an electrospinning voltage of 10 kilovolts. Figures 3.24 and 3.25 show fibers collected with an electrospinning voltage of 15 kilovolts. Figures 3.26 shows fibers collected at 20 kilovolts. Finally, figures 3.27 and 3.28 show fibers collected at 30 kilovolts.
Fibers collected at 10 kilovolts had diameters ranging from 600 nanometers to 2 microns. Very few fibers were produced at this electrospinning voltage, and many of the fibers that were produced were large. Also, note that there was no bulk fluid in the deposition.

![SEM Image - Electrospinning Voltage of 10 Kilovolts](image)

\textbf{Figure 3.23 – SEM Image – Electrospinning Voltage of 10 Kilovolts}

Fibers collected at 15 kilovolts had diameters ranging from 500 nanometers to 1 micron. Fibers are of good quality. Most fibers have diameters near 500 nanometers with only a few larger fibers. Also note that no bulk fluid was deposited with the fibers.
Nanofibers collected at an electrospinning voltage of 20 kilovolts were of the best quality. Fiber diameters ranged between 200 and 300 nanometers. Also, there is no bulk fluid present in the deposition.
Nanofibers collected with an electrospinning voltage of 30 kilvolts were of poor quality. Fiber diameters ranged from 600 nanometers to 1.2 microns. Fiber structure was generally poor, and most of the fibers were deposited wet.

![SEM Images: Electrospinning Voltage of 30 Kilovolts](image)

*Figures 3.27 and 3.28 – SEM Images: Electrospinning Voltage of 30 Kilovolts*

Figure 3.29 shows the range of nanofiber diameters as a function of electrospinning voltage. Low electrospinning voltages (5 and 10 kilovolts) resulted in generally larger fibers and a wide range of fiber diameters. This is most likely because electrospinning at lower voltages can result in inconsistent fiber formation and deposition. Higher voltages yielded decreased fiber diameters and diameter ranges that were narrower, most likely caused by excessive instabilities in the electrospinning jet. The best quality fibers with the smallest and most consistent diameters were produced at an electrospinning voltage of 20 kilovolts.
A combination of the nanofiber deposition rate study and the analysis of fibers through SEM microscopy were used to determine an optimal electrospinning voltage of 20 kilovolts. The nanofiber production was at a maximum at electrospinning voltages of 20 kilovolts and above. Lower electrospinning voltages produced fibers more slowly. Fiber quality was best at intermediate voltages (12.5 to 20 kilovolts). Lower voltages resulted in minimal fiber production, large fiber diameters, and wide diameter ranges. Electrospinning voltages above 20 kilovolts produced fibers at a good rate, but these fibers were generally of poor quality and the depositions contained unacceptable amounts of bulk fluid and wet fiber deposition. A summary of the electrospinning voltage parametric study is shown in Figure 3.30.
### Table 3.30 - Summary of Electrospinning Voltage Parametric Study

<table>
<thead>
<tr>
<th>Electrospinning Voltage (kV)</th>
<th>Mass Production Rate ((mg/h)/cm²)</th>
<th>Fiber Diameters (nm)</th>
<th>Bulk Fluid Presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.3</td>
<td>600 - 1800</td>
<td>None</td>
</tr>
<tr>
<td>10</td>
<td>0.96</td>
<td>600 - 2000</td>
<td>None</td>
</tr>
<tr>
<td>12.5</td>
<td>2.39</td>
<td>500 - 1200</td>
<td>None</td>
</tr>
<tr>
<td>15</td>
<td>4.85</td>
<td>500 - 1000</td>
<td>None</td>
</tr>
<tr>
<td>17.5</td>
<td>5.38</td>
<td>350 - 650</td>
<td>None</td>
</tr>
<tr>
<td>20</td>
<td>6.43</td>
<td>200 - 300</td>
<td>None</td>
</tr>
<tr>
<td>25</td>
<td>6.46</td>
<td>500 - 1000</td>
<td>Yes</td>
</tr>
<tr>
<td>30</td>
<td>6.48</td>
<td>600 - 1200</td>
<td>Yes</td>
</tr>
</tbody>
</table>

**3.5 Effects of Electrospinning Distance**

Next, the distance from the head to the collector, or the electrospinning distance was optimized. For this study, PEO solution feed rate was set at 40 milliliters per hour, head rotational speed was set to 1500 rotations per minute, electrospinning voltage was set to 20 kilovolts, and the PEO solution concentration was set to 10 percent by weight. The electrospinning distance was varied, and data was collected for electrospinning distances of 10, 20, 30, 40, 50, and 60 centimeters. For each data point, the mass of the collected fibers, the area of collection, and the time of deposition were used to calculate the mass production rate in units of milligrams per hour per square centimeter. For each value of the parameter, 50 samples were collected at points equidistant from the electrospinning head axis.
Data for nanofiber production rates for the electrospinning distances studied are shown in Figure 3.31. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.

<table>
<thead>
<tr>
<th>Electrospinning Distance (cm)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>10</td>
<td>6.31</td>
</tr>
<tr>
<td>20</td>
<td>6.40</td>
</tr>
<tr>
<td>30</td>
<td>6.19</td>
</tr>
<tr>
<td>40</td>
<td>3.11</td>
</tr>
<tr>
<td>50</td>
<td>1.00</td>
</tr>
<tr>
<td>60</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Figure 3.31 – Nanofiber Production Rates for Various Electrospinning Distances*

Data from this study is compiled in Figure 3.32. The data is represented as the nanofiber deposition rate as a function of the electrospinning distance.
Next, the quality of the nanofibers produced was examined by SEM microscopy. Attention was directed at the nanofiber diameters, the structure of the fibers, and the presence of bulk fluid in the deposition.

SEM images are shown for various electrospinning distances in Figures 3.33 through 3.38. Figures 3.33 and 3.34 show fibers produced with an electrospinning distance of 10 centimeters. Figures 3.35 and 3.36 show fibers produced at an electrospinning distance of 30 centimeters. Figures 3.37 and 3.38 show fibers produced with an electrospinning distance of 50 centimeters.

Fibers produced with an electrospinning distance of 10 centimeters ranged in diameter from 300 nanometers to 1.8 microns. Fibers are poorly structured with virtually all fibers were deposited wet.
Fibers produced using an electrospinning distance of 30 centimeters yielded the best quality nanofibers. Fiber diameters ranged from 200 to 400 nanometers. The fibers are well structured, and the deposition contains almost no bulk fluid. However, there is a very small amount of wet fiber deposition, but it is not on the level where the overall sample would be affected greatly.
Fibers produced with an electrospinning distance of 50 centimeters had diameters ranging from 200 to 500 nanometers. However, the deposition density is very low. Fibers are well structured and there is no evidence of bulk fluid in the deposition.

Figure 3.39 features nanofiber diameters as a function of electrospinning distance. Electrospinning distances of 20 centimeters and lower result in generally large nanofibers and wide ranges of fiber diameters. This can be attributed to the distance from the electrospinning head to the collector being too short and not allowing the electrospinning jets enough time to elongate and reduce diameter under the bending instabilities. Distances above 20 centimeters result in small diameter fibers and good diameter consistency.

By examining the deposition rate data and the SEM images, an optimal electrospinning distance of 30 centimeters was selected. Electrospinning distances below 30 centimeters result in poor quality fibers due to excessive amounts of bulk fluid in the deposition. Electrospinning distances above 30 centimeters exhibit a
sharp drop in nanofiber production rate. A summary of the electrospinning distance parametric study is shown in Figure 3.40.

![Figure 3.39 - Fiber Diameters as a Function of Electrospinning Distance](image)

<table>
<thead>
<tr>
<th>Electrospinning Distance (cm)</th>
<th>Mass Production Rate ((mg/h)/cm²)</th>
<th>Fiber Diameters (nm)</th>
<th>Bulk Fluid Presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.46</td>
<td>300 - 1800</td>
<td>Significant</td>
</tr>
<tr>
<td>20</td>
<td>6.57</td>
<td>300 - 1000</td>
<td>Significant</td>
</tr>
<tr>
<td>30</td>
<td>6.41</td>
<td>200 - 400</td>
<td>Minimal</td>
</tr>
<tr>
<td>40</td>
<td>3.45</td>
<td>250 - 500</td>
<td>None</td>
</tr>
<tr>
<td>50</td>
<td>1.46</td>
<td>200 - 500</td>
<td>None</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>-------------</td>
<td>-----------</td>
</tr>
</tbody>
</table>

*Figure 3.40 - Summary of Electrospinning Distance Parametric Study*
3.6 Effects of PEO Solution Concentration

The final parameter to be optimized for use with the hybrid nanomanufacturing system is the PEO solution concentration. For this study, PEO solution feed rate was set at 40 milliliters per hour, head rotational speed was set to 1500 rotations per minute, electrospinning voltage was set to 20 kilovolts, and electrospinning distance was set to 30 centimeters. The concentration of the PEO solution was varied. Data was collected for PEO concentrations by weight of 5, 7.5, 10, 12.5, and 15 percent. For each data point, the mass of the collected fibers, the area of collection, and the time of deposition were used to calculate the mass production rate in units of milligrams per hour per square centimeter. For each value of the parameter, 50 samples were collected at points equidistant from the electrospinning head axis.

Data for nanofiber production rates for the various PEO solution concentrations are presented in Figure 3.41. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.
<table>
<thead>
<tr>
<th>PEO Solution Concentration (wt %)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Minimum 3.61</td>
</tr>
<tr>
<td>7.5</td>
<td>Minimum 4.72</td>
</tr>
<tr>
<td>10</td>
<td>Minimum 6.40</td>
</tr>
<tr>
<td>12.5</td>
<td>Minimum 6.34</td>
</tr>
<tr>
<td>15</td>
<td>Minimum 6.36</td>
</tr>
</tbody>
</table>

*Figure 3.41 – Nanofiber Production Rate for Various PEO Solution Concentrations*

The data has also been compiled into a graph in Figure 3.42. The plot shows nanofiber production rate as a function of PEO solution concentration.

*Figure 3.42 – Nanofiber Production Rate as a Function of PEO Solution Concentration*
Nanofiber quality at various PEO solution concentrations was also analyzed. Fibers were examined using SEM microscopy. Figures 3.43 and 3.44 show fibers produced with a PEO solution concentration of 5 percent by weight. Figure 3.45 shows fibers produced with a PEO solution concentration of 10 percent by weight. Figures 3.46 and 3.47 show fibers produced using a PEO solution concentration of 15 percent by weight.

Fibers produced using a PEO solution concentration of 5 percent by weight had diameters ranging from 350 nanometers to 1 micron. Fibers are generally of good quality, but the low magnification image (Figure 3.43) show that a significant amount of bulk fluid is deposited with the fibers.

Figures 3.43 and 3.44 – SEM Images: PEO Solution Concentration of 5 Percent by Weight
Fibers produced using a PEO solution concentration of 10 percent by weight had diameters ranging from 150 to 400 nanometers. Fibers have good consistency of diameters and are well structured. Also, bulk fluid is not present in the deposition.

![Figure 3.45 – SEM Image: PEO Concentration of 10 Percent by Weight](image)

Fibers produced using a PEO concentration of 15 percent by weight ranged in diameter from 700 nanometers to 1.3 microns. Many fibers have good structure, but structural irregularities are visible in some fibers. Also, some fibers were deposited wet.
Figure 3.48 presents fiber diameters as a function of PEO solution concentration. Lower concentrations (5 and 7.5 percent by weight) yield generally small fibers. However, excess solvent resulted in increased deposition of wet fibers and bulk fluid splattering. A 10 percent by weight concentration results in the smallest fiber diameters and the narrowest diameter range. Concentrations above 10 percent by weight result in fibers that are generally large.
Examining the deposition rate data and SEM images, an optimal PEO solution concentration of 10 percent by weight was chosen. Lower concentrations result in decreased nanofiber production rates and an increased presence of bulk fluid in the deposition. Higher concentrations produce large fibers and an increased probability of wet fiber deposition. A summary of the PEO solution concentration parametric study is presented in Figure 3.49.

![Figure 3.58 - Fiber Diameters as a Function of PEO Solution Concentration](image)

<table>
<thead>
<tr>
<th>Concentration (wt %)</th>
<th>Mass Production Rate ((mg/h)/cm²)</th>
<th>Fiber Diameters (nm)</th>
<th>Bulk Fluid Presence</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.84</td>
<td>350 - 1000</td>
<td>Significant</td>
</tr>
<tr>
<td>7.5</td>
<td>4.98</td>
<td>200 - 800</td>
<td>Some</td>
</tr>
<tr>
<td>10</td>
<td>6.51</td>
<td>150 - 400</td>
<td>None</td>
</tr>
<tr>
<td>12.5</td>
<td>6.57</td>
<td>600 - 1000</td>
<td>None</td>
</tr>
<tr>
<td>15</td>
<td>6.48</td>
<td>700 - 1300</td>
<td>None</td>
</tr>
</tbody>
</table>

![Figure 3.49 - Summary of PEO Solution Concentration Parametric Study](image)
3.7 Summary of Hybrid System Design and Parametric Study Using PEO

A systematic parametric study was conducted for the first time using the hybrid process. The extensive study of parameters used in the hybrid nanomanufacturing procedure was a crucial step in developing a reliable method for producing polymer nanofibers with the hybrid process. As a result of this study, parameters of the system were optimized in order to produce the best quality fibers at the highest possible rate. The results of the extensive parametric study are displayed in Figure 2.50.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimized Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO Solution Feed Rate</td>
<td>40 mL/h</td>
</tr>
<tr>
<td>Head Rotational Speed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>Electrospinning Voltage</td>
<td>20 kV</td>
</tr>
<tr>
<td>Electrospinning Distance</td>
<td>30 cm</td>
</tr>
<tr>
<td>PEO Solution Concentration</td>
<td>10 wt %</td>
</tr>
</tbody>
</table>

*Figure 2.50 – Optimized Parameters*

Using the optimized parameters, a final study of nanofiber production was conducted. 50 samples were collected, and using the mass of the deposited fibers, the
duration of deposition, and the area of collection, the optimized mass production rate was calculated.

Samples collected using the optimal hybrid nanomanufacturing parameters yielded production rates ranging from 6.44 to 6.75 (mg/h)/cm². The average mass production rate for these samples was 6.58 (mg/h)/cm². This corresponds to almost a 90 times improvement per unit area as compared to single-jet electrospinning.

Please note that the parameters were optimized for only the setup using a 6-inch diameter head. Higher nanofiber production rates should be possible by scaling up the system. However, this would require additional study of the system parameters. Increasing the size of the head would increase both the surface area and circumference of the head, allowing for even higher polymer solution feed rates. The increased surface area would allow for more polymer solution to be fed to the head, and the increased diameter would allow for a greater number of electrospinning jet initiation points.
4 HYBRID NANOMANUFACTURING FOR CONTINUOUS PRODUCTION OF POLYMER NANOFIBER SHEETS

Polymer nanofiber depositions created using the hybrid nanomanufacturing process were studied. Attention was directed at the consistency of deposition starting at the point collinear with the shaft of the head and extending outward in one direction.

Three studies were conducted to analyze the consistency of nanofiber deposition and the prospects of improving the consistency by various methods. The first study was performed with a stationary collection surface. This study allowed for the collection of data pertaining to how the deposition density changes at various distances from the point collinear to the head axis. The second study consisted of deposition on a collection surface that was moved by hand at specified intervals. This study was conducted in order to verify that the variations in deposition density can be reduced. The third study centered around a simple belt-driven system in which nanofibers were deposited on a looped substrate that traversed at a constant speed, passing over the hybrid nanomanufacturing setup numerous times.
4.1 Study of Deposition Consistency Using the Hybrid Nanomanufacturing Process

In order to study how the deposition density changes with different methods of collection surface manipulation, the variance in deposition density with a stationary substrate must first be examined. The rate at which nanofibers are deposited on the collection surface was examined in the same manner as before. One-inch square pieces of aluminum foil sheet were pre-weighed, affixed to the collection substrate during deposition of nanofibers, removed from the substrate, and weighed again. Using this weight difference, the mass of the deposited nanofibers is determined, and in conjunction with the area of the foil squares and the duration of the deposition, the nanofiber production rate is determined in units of (mg/h)/cm$^2$.

In this study, multiple one-inch square aluminum foil sheets are affixed to the collection substrate with their centers positioned at specified distances from the point collinear with the head axis. Data was collected for 16 distances from the head axis, starting at 0 centimeters and extending outward to 45 centimeters in multiples of 3 (0 cm, 3 cm, 6 cm, 9 cm, ..., 39 cm, 42 cm, 45 cm). Using the data collected, a profile of the deposition rate as a function of the distance from the head axis was created. This deposition rate profile is shown in Figure 4.1.
As seen in Figure 4.1, the deposition rate at the point collinear with the head axis is just below 5.00 (mg/h)/cm². The deposition rate then rises, reaching a maximum at a distance of 21 centimeters from the head axis. Finally, the deposition rate drops steadily as the distance from the head axis is increased. This behavior can be attributed to the hybrid nanomanufacturing system setup and the geometry of the head. The head used with the system was a 6-inch diameter disk (approximately 15 centimeters in diameter). This diameter, along with the centrifugal forces from the head rotation, moves the electrospinning jets and electrospun nanofibers slightly outward, accounting for the lower nanofiber deposition rates close to the head axis. The nanofiber deposition rate reaches a maximum at approximately 13.5 centimeters from the edge of the head. As the distance extends past this point, fewer and fewer
nanofibers reach the substrate, accounting for the steady drop in productivity. A schematic of this proposed deposition of nanofibers is shown in Figure 4.2.

![Schematic of Nanofiber Deposition Using Hybrid Nanomanufacturing Process](image)

Figure 4.2 - Schematic of Nanofiber Deposition Using Hybrid Nanomanufacturing Process

This deposition envelope was verified visually by strategically placing a high-intensity light source behind the hybrid nanomanufacturing setup, and attempts were made to photograph the deposition envelope depicted in Figure 4.2. However, due to the small diameters of the fibers, the rapid changes in their location, and difficulty with proper lighting for photography, this proved to be difficult with the equipment available.
Based on the data collected in this study, it is apparent that there is significant variation in deposition rate dependant on the distance from the head axis. In order for fibers collected using the hybrid nanomanufacturing process to be practical options for use in industrial applications, a consistent deposition density must be achieved.

4.2 Study of Deposition Consistency on a Hand-Moved Substrate

Before constructing a system for a continually moving looped-belt collector, experimentation was performed with a flat collector moved intermittently by hand. This should prove as a sufficient proof-of-concept study to assess how deposition consistency can be improved by moving the collection surface during deposition.

During this study, nanofiber deposition rate data was collected in the same manner as before. The substrate was suspended from a frame that could easily be moved. During each 5 minute deposition, the collection surface was moved a distance of 2 centimeters each 30 seconds. This results in a total traversal of 18 centimeters for each point along the direction of motion. A diagram of the collection substrate is shown in Figure 4.3. Data was collected for 10 points along the direction of motion beginning with the point that starts in line with the head axis and extending outward at intervals of 3 centimeters. The data collected during this study is shown in Figure 4.4.
Figure 4.3 – Schematic of Deposition Substrate

Figure 4.4 – Deposition Rate Profile with a Hand-Moved Substrate
As is shown in Figure 4.4, the deposition rate is fairly consistent up to the point that started the deposition at 18 centimeters from the head axis. Beyond this point, the deposition rate decreases due to the substrate reaching the edge of the nanofiber deposition envelope. A comparison of the data from this experiment with the data collected in the previous study on a stationary substrate is shown in Figure 4.5.

Figure 4.5 – Comparison of a Stationary and Moving Substrate

Figure 4.5 shows that in comparison to deposition on a stationary substrate, the consistency of deposition is much improved. Deposition rates at all points up to and including 18 centimeters from the head axis are within 4 percent of their average. For this same range on with a stationary substrate, only one point was within 5 percent of the average, and there was a maximum deviation of 16.5 percent from the
average. This shows that by moving the collection substrate during the collection of nanofibers, the consistency of deposition rate can be greatly improved.

4.3 Study of Deposition Consistency on an Automated Loop-Belt Collection Substrate

The consistency in deposition rate was improved by intermittently moving the collection substrate by hand. Therefore, an automated system in which the collection surface moves continuously and repeatedly over the electrospinning head should result in greatly improved consistency in deposition rate.

For this study, a small looped-belt collector was constructed. A PVC frame was built, allowing for a 12-inch wide sheet of aluminum to be looped around two axles, one of which is driven by a small DC motor. This motor is controlled by a power supply with variable output voltages, allowing for adjustable belt speeds. A diagram of this system is shown in Figure 4.6.
The goal of this study is to determine how different belt speeds affect the consistency of deposition. For each belt speed, the duration of deposition is held constant at 5 minutes while the number of belt rotations is varied from 1 to 5. This gives belt speeds of 0.2, 0.4, 0.6, 0.8, and 1.0 revolution per minute. For each belt speed, pre-weighed one-inch square pieces of aluminum foil are attached at specific distances along the belt, deposition using the hybrid nanomanufacturing system is performed on the continuously moving substrate, the foil squares are weighed again, and the nanofiber deposition rate is calculated using the study parameters and data. The mass of deposited nanofibers was calculated for starting points that were 0, 9, 18, 27, 36, and 45 centimeters from the head axis in the direction of the belt motion.

Deposition on a substrate with a belt speed of 0.2 revolutions per minute resulted in nanofiber collection with significant variations in deposition rate. Figure
4.7 shows a plot of nanofiber production rate as a function of initial distance from head axis for a belt speed of 0.2 revolutions per minute. The maximum variance in deposition rate for this collection was 43.19 percent.

Deposition on a substrate with a belt speed of 0.4 revolutions per minute resulted in nanofiber collection with some improvements in consistency over the deposition rates for a substrate moving at 0.2 revolutions per minute. Figure 4.8 shows a plot of nanofiber production rate as a function of initial distance from head axis for a belt speed of 0.4 revolutions per minute. The maximum variance in deposition rate for this collection was 29.94 percent.
Deposition on a substrate with a belt speed of 0.6 revolutions per minute resulted in nanofiber collection with even more improvements in consistency over the deposition rates for the previous data. Figure 4.9 shows a plot of nanofiber production rate as a function of initial distance from head axis for a belt speed of 0.6 revolutions per minute. The maximum variance in deposition rate for this collection was 10.61 percent.
Deposition on a substrate with a belt speed of 0.8 revolutions per minute resulted in nanofiber collection with nearly uniform deposition in the direction of the belt motion. Figure 4.10 shows a plot of nanofiber production rate as a function of initial distance from head axis for a belt speed of 0.8 revolutions per minute. The maximum variance in deposition rate for this collection was 4.56 percent.
Deposition on a substrate with a belt speed of 1.0 revolution per minute resulted in a uniform nanofiber deposition. Figure 4.11 shows a plot of nanofiber production rate as a function of initial distance from head axis for a belt speed of 1.0 revolution per minute. The maximum variance in deposition rate for this collection was 1.73 percent.
Based on the results of this study, it is apparent that a continuously moving substrate can have great effects on the consistency of nanofiber deposition rate. With a relatively slow belt speed of only 1 revolution per minute, sample with near perfect consistency in fiber deposition rate can be achieved. To better show the results of this study, the previous graphs have been compiled into a single plot in Figure 4.12.
4.4 Summary of Study on the Consistency of Nanofiber Deposition Rates

In order for randomly oriented polymer nanofiber sheets produced using the hybrid nanomanufacturing process to be a practical option for use in various applications, they need to have good consistency in deposition density. Based on the study using a stationary substrate, it is apparent that there are significant variations in the rate of nanofiber deposition at different distances from the head axis. A quick study using a substrate moved intermittently by hand showed that these variations could be reduced. Finally, an automated looped-belt setup showed that nanofiber sheets could be produced with high consistency in the direction of the belt motion.
Based on results of these studies, use of the current configuration of the hybrid nanomanufacturing system could potentially produce nanofiber sheets continuously with consistent deposition density to within 5 percent and a width ranging from 12 to 18 centimeters.
5 COLLECTION OF ALIGNED NANOFIBERS WITH THE HYBRID NANOMANUFACTURING SYSTEM

Aligned nanofibers have several possible applications. For example, they can potentially function as composite reinforcement. Aligned fibers have also shown potential for use in electrical devices [45]. Several methods for the alignment of nanofibers have been researched and developed. Some utilize substrate motion to obtain aligned fibers. Collection on a rotating drum or the edge of a thin disk has shown good aligning properties [6, 8, 15, 16]. Electrospinning of nanofibers doped with magnetic particles has been used to collect aligned fibers between permanent magnets [46]. Perhaps the simplest method for collecting aligned fibers is to deposit nanofibers between spaced electrodes. This method has been used extensively [6, 8, 16, 45] and will be used for fiber alignment in this study.

A study on the potential for the collection of aligned nanofibers using the hybrid nanomanufacturing process was conducted. First, aligned nanofiber samples were collected using a simple single-jet electrospinning technique for comparison. Then, using the same technique with geometrical changes, samples were collected using the hybrid nanomanufacturing system. Samples were viewed by SEM, and fiber angles were measured in order to construct data on the fiber alignment.
5.1 Collection of Aligned Nanofibers with Single-Jet Electrospinning

Several samples were collected using a single-jet electrospinning setup. The samples were viewed by SEM microscopy, and the fiber angles were measured.

5.1.1 Experimental Setup

In order to collect aligned nanofibers, a simple technique was used. Instead of depositing nanofibers on a flat plate collector as is done when a randomly oriented fiber deposition is desired, nanofibers are collected between two parallel grounded electrodes. A diagram of the system setup is shown in Figure 5.1.
5.1.2 Aligned Nanofibers from Single-Jet Electrospinning

Using the experimental setup shown in Figure 5.1, aligned fiber samples were collected. Samples were examined using SEM microscopy, and the fiber alignment was measured. SEM images of some samples are shown in Figures 5.2 – 5.4.
An example of data on fiber alignment for samples collected using single-jet electrospinning is shown in Figure 5.5. This plot shows the measured angle of fibers with the horizontal axis intersecting the vertical axis at the average fiber angle. The fiber angles have been sorted from smallest to largest in order to provide a better representation of the overall quality of fiber alignment.
Alignment data was collected for five samples, and the alignment efficiency based on the percentage of fibers within 5, 10, 20, and 40 degrees of the average fiber alignment has been compiled in Figure 5.6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage of Fibers within:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 degrees</td>
</tr>
<tr>
<td>1</td>
<td>25.0%</td>
</tr>
<tr>
<td>2</td>
<td>13.8%</td>
</tr>
<tr>
<td>3</td>
<td>42.3%</td>
</tr>
<tr>
<td>4</td>
<td>40.0%</td>
</tr>
<tr>
<td>5</td>
<td>44.8%</td>
</tr>
<tr>
<td>Average</td>
<td>33.2%</td>
</tr>
</tbody>
</table>
5.2 Collection of Aligned Nanofibers with Hybrid Electrospinning System

Samples were collected using the hybrid electrospinning setup. The samples were viewed by SEM microscopy, and the fiber angles were measured.

5.2.1 Experimental Setup

A collector setup similar to that used with the single-jet collection of aligned nanofibers was utilized. In order to account for the wider deposition of fibers using the hybrid nanomanufacturing setup, some changes were made. First, the distance between the head and the collector is larger than it was for the single-jet collection. Also, the distance between the parallel grounded electrodes is also larger. A diagram of the system setup is shown in Figure 5.7.
5.2.2 *Aligned Nanofibers from Hybrid Electrospinning Setup*

Using the setup shown in Figure 5.7, aligned fiber samples were collected. Samples were examined using SEM microscopy, and the fiber alignment was measured. SEM images of some samples are shown in Figures 5.8 – 5.11. Two things are immediately obvious when the SEM images from the single-jet and hybrid methods are compared. First, the density of deposition is much greater with the hybrid nanomanufacturing setup. Second, the alignment appears to be better, at least by visual inspection, with single-jet electrospinning. This will be verified by measuring the fiber angles and determining the quality of alignment.
An example of data on fiber alignment for samples collected using single-jet electrospinning is shown in Figure 5.12. This plot shows the measured angle of fibers with the horizontal axis intersecting the vertical axis at the average fiber angle. The fiber angles have been sorted from smallest to largest to give a better representation of the overall quality of the fiber alignment.
Alignment data was collected for five samples, and the alignment efficiency based on the percentage of fibers within 5, 10, 20, and 40 degrees of the average fiber alignment has been compiled in Figure 5.13.

<table>
<thead>
<tr>
<th>Sample</th>
<th>5 degrees</th>
<th>10 degrees</th>
<th>20 degrees</th>
<th>40 degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.5%</td>
<td>30.8%</td>
<td>64.1%</td>
<td>97.4%</td>
</tr>
<tr>
<td>2</td>
<td>21.2%</td>
<td>39.4%</td>
<td>57.6%</td>
<td>84.8%</td>
</tr>
<tr>
<td>3</td>
<td>22.5%</td>
<td>35.0%</td>
<td>55.0%</td>
<td>82.5%</td>
</tr>
<tr>
<td>4</td>
<td>24.1%</td>
<td>41.4%</td>
<td>55.2%</td>
<td>79.3%</td>
</tr>
<tr>
<td>5</td>
<td>31.0%</td>
<td>55.2%</td>
<td>69.0%</td>
<td>96.6%</td>
</tr>
<tr>
<td>Average</td>
<td>23.9%</td>
<td>40.3%</td>
<td>60.2%</td>
<td>88.1%</td>
</tr>
</tbody>
</table>

*Figure 5.13 – Alignment Data: Hybrid Electrospinning*
5.3 **Summary of Fiber Alignment Study**

The possibility of producing aligned nanofibers using the hybrid nanomanufacturing process was demonstrated for the first time, and the alignment quality is similar to that of single-jet electrospinning of aligned nanofibers. The variation in alignment quality between the single-jet and hybrid setups can be seen by comparing Figures 5.6 and 5.13. Fibers collected with the hybrid nanomanufacturing system show a decrease in alignment quality as compared to the fibers collected with the single-jet electrospinning setup. However, many fibers are within 20 degrees of the average fiber direction, and with the massive increase in deposition density, the total number of fibers that are in good alignment is increased significantly. Also, with further study and optimization, the quality of fiber alignment when using the hybrid nanomanufacturing setup could potentially be increased.
6 HYBRID NANOMANUFACTURING OF STRUCTURALLY SIGNIFICANT NANOFIBERS

So far, testing and optimization of the hybrid nanomanufacturing process has been conducted for polyethylene oxide fibers. Next, the same optimization will be performed using polyacrylonitrile in solution with dimethylformamide. Another round of optimization is performed because polyacrylonitrile may behave differently than polyacrylonitrile during electrospinning, and the two polymers will possibly have differing optimal parameters.

Analysis was performed using polyacrylonitrile (PAN) for several reasons. First, PAN produces structurally significant fiber, and is a precursor to carbon nanofibers. PAN fibers also have shown interesting characteristics and are applicable in multiple fields.

6.1 Applications for PAN Nanofibers

Electrospinning of polyacrylonitrile fibers is desired mostly because they are a precursor to carbon fibers [15, 47]. Carbon fibers can be produced by pyrolyzing PAN fibers [48]. PAN-based carbon nanofibers are attractive for multiple reasons including the ability to modify and functionalize their surfaces, their readiness to be blended with other polymers, and the ability to embed them with nanoscale
components [49]. Polyacrylonitrile fibers also have shown applications in supercapacitor electrodes and use during catalysis [47].

6.2 Materials

The parametric analysis and optimization performed was done using polyacrylonitrile (PAN) in solution with dimethylformamide (DMF). PAN from both Sigma-Aldrich and Pfaltz & Bauer, Inc. were used, both of which have an approximate molecular weight of 150,000. DMF was obtained from Sigma-Aldrich.

6.3 Features Observed During Initial Testing of Hybrid Process with PAN

Unlike hybrid nanomanufacturing of PEO nanofibers, bulk fluid deposition is not seen in the production of PAN nanofibers. Instead, two other features were observed.

The first feature is the solidification of the polymer on the head surface. During hybrid nanomanufacturing of PAN nanofibers, some of the polymer congeals on the head surface as shown in Figure 6.1. This solidified polymer clogs the head surface, slowing the flow of PAN solution to the edge of the head. This, in hand,
slows the production of nanofibers. This solidification can most likely be attributed to the high rate at which dimethylformamide evaporates, which is augmented due to the high rate of electrospinning head rotation.

Several methods were tested to reduce the amount of solidification, the most effective being to ensure that the head surface is as smooth as possible. This is done by covering the head surface with a fresh layer of aluminum foil before each deposition. The aluminum foil-covered head after running the system for approximately 5 minutes is shown in Figure 6.2. However, at longer deposition durations, PAN solidification does occur even with the foil covering. The best course of action to prevent this from disrupting nanofiber production is to periodically clean the head.
Figure 6.1 – PAN Solidification on Head Surface

Figure 6.2 – Foil-Covered Head Exhibiting No PAN Solidification
The second feature encountered during the hybrid nanomanufacturing of PAN fibers is fiber bridging between the head and collector. Electrospun fibers remain connected to the center of the head and to the syringe tip used for polymer feed to the system. These fibers extend upward to the collection surface. This congests the area between the head and collector, slowing nanofiber production. This feature is seen with PAN because it produces stronger fibers than PEO, allowing fibers to be connected statically between the head and collector without breaking. This is a factor that will have effects during the parametric study.

6.4 Parametric Study of Nanofiber Quality and Production Using Polyacrylonitrile

As with hybrid nanomanufacturing of polyethylene oxide fibers, the process again features multiple parameters of interest. However, early testing of the hybrid nanomanufacturing system showed that the production using a PAN solution behaves differently than production using a PEO solution. Therefore, another set of parametric studies must be performed in order to optimize electrospinning using the hybrid system with PAN. Again, the parameters analyzed are as follows: polymer solution feed rate, head rotational speed, electrospinning voltage, polymer solution concentration, and the electrospinning distance.
6.4.1 PAN Nanofiber Production using Single-Jet Electrospinning

In order to measure the increases in the nanofiber production rates, data was collected using a traditional single-jet electrospinning setup. The parameters for the single-jet sample collection are as follows:

- PAN solution feed rate = 0.5 milliliters per hour
- Electrospinning voltage = 15.5 kilovolts
- Electrospinning Distance = 25 centimeters
- PAN concentration = 10 percent by weight

Nanofiber deposition rates using the single-jet electrospinning setup ranged from 0.019 to 0.167 (mg/h)/cm². The average deposition rate was 0.068 (mg/h)/cm² across 30 data points.

6.4.2 Effects of PAN Solution Feed Rate

The parametric study of the hybrid nanomanufacturing process with PAN begins by studying the effect of the polymer solution feed rate. During this study, the head rotational speed was set to 1500 rotations per minute, the electrospinning voltage was set at 20 kilovolts, the electrospinning distance was held at 30 centimeters, and the PAN solution concentration was 10 percent by weight. Throughout the study, the PAN solution feed rate was varied. Data was collected for
feed rates of 5, 10, 20, 30, 40, 50, 75, and 100 milliliters per hour. For each data point, the nanofiber production rate was calculated in units of \((\text{mg/h})/\text{cm}^2\).

Data for nanofiber production rates for the PAN solution feed rates studied are shown in Figure 6.3. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.

<table>
<thead>
<tr>
<th>PAN Solution Feed Rate (mL/h)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td>1.69</td>
</tr>
<tr>
<td>20</td>
<td>2.66</td>
</tr>
<tr>
<td>30</td>
<td>3.50</td>
</tr>
<tr>
<td>40</td>
<td>5.00</td>
</tr>
<tr>
<td>50</td>
<td>5.21</td>
</tr>
<tr>
<td>75</td>
<td>5.21</td>
</tr>
<tr>
<td>100</td>
<td>5.15</td>
</tr>
</tbody>
</table>

*Figure 6.3 – Nanofiber Production Rates for Various PAN Solution Feed Rates*
During some of the depositions at 40 milliliters per hour, fiber bridging between the head and collector was observed. For all PAN solution flow rates above 40 milliliters per hour, significant fiber bridging was present in all depositions.

Data collected in the PAN solution feed rate study has been compiled into a graph. Figure 6.4 shows the nanofiber production rate as a function of PAN solution feed rate.

![Graph showing nanofiber production rate vs. PAN solution feed rate](image)

*Figure 6.4 – Nanofiber Production Rate as a function of PAN Solution Feed Rate*

Based on the data presented in the previous plots, an optimal PAN solution feed rate of 40 milliliters per hour was selected. This feed rate provides a nanofiber production rate on par with the maximum value attained. Even though higher feed...
rates do provide increases in productivity, these increases are not significant enough to make them worth the loss of materials due to fiber bridging.

6.4.3 Effects of Head Rotational Speed

The next parameter to be optimized is the head rotational speed. For this study, the PAN solution feed rate is set to 40 milliliters per hour, the electrospinning voltage is set to 20 kilovolts, the electrospinning distance is set to 30 centimeters, and the PAN solution concentration was 10 percent by weight. During this study, the head rotational speed was varied. Data was collected for rotational speeds of 100, 500, 1000, 1500, 2000, 2500, 5000, and 8000 rotations per minute.

Data for nanofiber production rates for the head rotational speeds studied are shown in Figure 6.5. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.
<table>
<thead>
<tr>
<th>Head Rotational Speed (rpm)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>100</td>
<td>1.62</td>
</tr>
<tr>
<td>500</td>
<td>3.57</td>
</tr>
<tr>
<td>1000</td>
<td>4.72</td>
</tr>
<tr>
<td>1500</td>
<td>5.21</td>
</tr>
<tr>
<td>2000</td>
<td>4.22</td>
</tr>
<tr>
<td>2500</td>
<td>5.06</td>
</tr>
<tr>
<td>5000</td>
<td>4.20</td>
</tr>
<tr>
<td>8000</td>
<td>2.81</td>
</tr>
</tbody>
</table>

*Figure 6.5 – Nanofiber Production Rates for Various Head Rotational Speeds*

At a head rotational speed of 2500 rotations per minute, fiber bridging from head to collector was observed in some depositions. Fiber bridging was significant for all fiber depositions with head rotational speeds greater than 2500 rotations per minute.

The data from this study is shown as a graph in Figure 6.6. This graph shows the nanofiber production rate as a function of head rotational speed.
Using the data collected in this study, an optimal head rotational speed of 2000 rotations per minute was selected. This rotational speed was chosen because it provided the highest nanofiber production rate, and depositions using this rotational speed did not exhibit fiber bridging between the head and collector.

6.4.4 Effects of Electrospinning Voltage

Next, the electrospinning voltage will be optimized for the hybrid nanomanufacturing of PAN fibers. In this study, the PAN solution feed rate was set to 40 milliliters per hour, the head rotational speed was set to 2000 rotations per minute, the electrospinning distance was set to 30 centimeters, and the PAN solution concentration was 10 percent by weight. Throughout the study, electrospinning
voltage was varied. Data was collected for electrospinning voltages of 5, 10, 12.5, 15, 17.5, 20, 25, and 30 kilovolts.

Data for nanofiber production rates for the electrospinning voltages studied are shown in Figure 6.7. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.

At an electrospinning voltage of 5 kilovolts, no nanofibers were produced. This voltage is too low to initiate electrospinning jets from the PAN solution. Fiber bridging was not an issue for depositions using electrospinning voltages of 25 kilovolts or lower. Fiber bridging from head to collector was prevalent in depositions using 30 kilovolts electrospinning voltage.

The data from this study is plotted in Figure 6.8. This graph plots the nanofiber production rate against the electrospinning voltage.

<table>
<thead>
<tr>
<th>Electrospinning Voltage (kV)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>5</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>3.91</td>
</tr>
<tr>
<td>12.5</td>
<td>4.26</td>
</tr>
<tr>
<td>15</td>
<td>4.46</td>
</tr>
<tr>
<td>17.5</td>
<td>4.74</td>
</tr>
<tr>
<td>20</td>
<td>5.02</td>
</tr>
<tr>
<td>25</td>
<td>5.28</td>
</tr>
<tr>
<td>30</td>
<td>4.63</td>
</tr>
</tbody>
</table>

*Figure 6.7 – Nanofiber Deposition Rates for Various Electrospinning Voltages*
Using the data obtained during this study, an optimal electrospinning voltage of 25 kilovolts was selected. This value was chosen because at this voltage, nanofiber production was maximized. At higher voltages, nanofiber production dropped due to the influence of fiber bridging.

**6.4.5 Effects of Electrospinning Distance**

Next, the distance between the head and collector was studied. For this study, the PAN solution feed rate was set at 40 milliliters per hour, the head rotational speed was set at 2000 rotations per minute, the electrospinning voltage was set at 25 kilovolts, and the PAN solution concentration was 10 percent by weight. During this
study, the distance from head to collector was varied. Data was collected for
distances of 10, 20, 30, 40, 50, and 60 centimeters.

Data for nanofiber production rates for the electrospinning distances studied
are shown in Figure 6.9. Data is presented for the minimum, maximum, and average
nanofiber production rates obtained during the study.

For electrospinning distances of 10 and 20 centimeters, fiber bridging was a
significant factor in all depositions. At 30 centimeters, fiber bridging was only
observed in some depositions. Above 30 centimeters there was no observation of
fibers bridging from head to collector during deposition.

<table>
<thead>
<tr>
<th>Electrospinning Distance (cm)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>10</td>
<td>3.35</td>
</tr>
<tr>
<td>20</td>
<td>4.50</td>
</tr>
<tr>
<td>30</td>
<td>5.15</td>
</tr>
<tr>
<td>40</td>
<td>4.20</td>
</tr>
<tr>
<td>50</td>
<td>5.00</td>
</tr>
<tr>
<td>60</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Figure 6.9 - Nanofiber Production Rates for Various Electrospinning Distances
The data collected in the study is plotted in Figure 6.10. The graph shows the nanofiber production rate as a function of electrospinning distance.

![Graph](image)

*Figure 6.10 – Nanofiber Production Rate as a Function of Electrospinning Distance*

Using the data obtained in this study, an optimal electrospinning distance of 40 centimeters was selected. Smaller distances are plagued with the issue of fiber bridging that slows the production of nanofibers. Distances greater than 40 centimeters reach the limit of the electrospinning process and the production rates drop off.

### 6.4.6 Effects of PAN Solution Concentration

Finally, the last parameter to be optimized is the PAN solution concentration. For this study, the PAN solution feed is set at 40 milliliters per hour, the head
rotational speed is set at 2000 rotations per minute, the electrospinning voltage is set at 25 kilovolts, and the electrospinning distance is set at 40 centimeters. Throughout this optimization, the PAN solution concentration is varied. Data was collected for PAN solutions of 5, 7.5, 10, 12.5, and 15 percent by weight.

Data for nanofiber production rates for the various PAN solution concentrations studied are shown in Figure 6.11. Data is presented for the minimum, maximum, and average nanofiber production rates obtained during the study.

<table>
<thead>
<tr>
<th>PAN Solution Concentration (wt %)</th>
<th>Nanofiber Production Rate (mg/h)/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>5</td>
<td>2.51</td>
</tr>
<tr>
<td>7.5</td>
<td>3.70</td>
</tr>
<tr>
<td>10</td>
<td>5.54</td>
</tr>
<tr>
<td>12.5</td>
<td>5.00</td>
</tr>
<tr>
<td>15</td>
<td>3.39</td>
</tr>
</tbody>
</table>

*Figure 6.11 – Nanofiber Production Rates for Various PAN Solution Concentrations*
Depositions using 12.5 percent by weight concentration of PAN exhibited significant polymer solidification on the head surface, and there was a considerable presence of fiber bridging between the head and the collector. Depositions using 15 percent by weight concentration of PAN were the only depositions in the entire parametric study that exhibited bulk fluid. Large droplets of PAN solution left the head surface frequently, accounting for the significant decrease in productivity. Fiber bridging and polymer solidification on the head surface were also factors.

The data from the concentration parametric study is plotted in Figure 6.12. The graph shows the nanofiber production rate as a function of PAN solution concentration.

![Figure 6.12 – Nanofiber Production Rate as a Function of PAN Solution Concentration](image-url)
Based on the data from this study, a 10 percent by weight PAN solution is the obvious choice for the optimal concentration. Depositions using this concentration yielded the best nanofiber production, and there was not a significant presence of fiber bridging from the head to the collector.

### 6.5 Summary of Parametric Study for the Hybrid Production of PAN Nanofibers

The hybrid nanomanufacturing process has proven a successful option for the production of PAN nanofibers. Extensive analysis of the hybrid system parameters during the production of PAN nanofibers has been performed. As a result of this study, all parameters were optimized to produce nanofibers at the highest possible rate. The results of the parametric study are outlined in Figure 6.13.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimized Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO Solution Feed Rate</td>
<td>40 mL/h</td>
</tr>
<tr>
<td>Head Rotational Speed</td>
<td>2000 rpm</td>
</tr>
<tr>
<td>Electrospinning Voltage</td>
<td>25 kV</td>
</tr>
<tr>
<td>Electrospinning Distance</td>
<td>40 cm</td>
</tr>
<tr>
<td>PEO Solution Concentration</td>
<td>10 wt %</td>
</tr>
</tbody>
</table>

*Figure 6.13– Optimized Parameters*
Using the parameters optimized to provide the greatest nanofiber production rate, a study of the PAN nanofiber quality was performed. Multiple samples were collected using the optimized parameters, and the nanofibers were observed using SEM imaging. SEM images of the PAN fibers collected are shown in Figures 6.14 – 6.19.

Figures 6.14 and 6.15 – SEM Image: Lower Deposition Density Section from Edge of Sample
Note that for all samples, fiber quality is excellent. The fibers have smooth edges and are generally free from irregularities. Also, the nanofiber diameters are extremely consistent, falling in the range from 200 to 500 nanometers.

For this study, the highest average nanofiber production rate obtained was 5.86 (mg/h)/cm². This value corresponds to an approximate 85 times increase in production per unit area as compared to single-jet electrospinning.
As was with the parametric study using PEO solution, the system was optimized using a 6-inch diameter head. Therefore, higher production rates should be possible by scaling up the system. A larger head would allow for a higher polymer solution feed to the system, and the increased head diameter would allow for a greater number of electrospinning jet initiation points.
In addition to the parametric optimization with two important polymers, the study on deposition consistency and its improvement, and the assessment of the prospects of fiber alignment, two exploratory studies were performed using the hybrid nanomanufacturing process. The first study focuses on the ability to produce nanofiber yarns using the hybrid nanomanufacturing process. The second is a proof-of-concept experiment for the deposition of nanofibers on a substrate free from electrical connection.

7.1 Hybrid Manufacturing of Nanofiber Yarns

In this study, an existing configuration was used to collect nanofiber yarns using single-jet electrospinning. The configuration was then tested with the hybrid nanomanufacturing process to produce yarns. The system was then modified geometrically to improve the quality of the yarns and was again tested using the hybrid nanomanufacturing process. Yarns were examined by SEM microscopy, and a qualitative comparison between the different yarn production methods was formed.
Several methods exist for the production of nanofiber yarns [6, 50 – 56]. Fibers can be deposited between parallel rings and then post-wound into yarns [6]. Randomly-oriented nanofibers can be deposited on to the surface of water and then slowly taken up via a roller to produce fiber bundles [6, 51]. A rod can be used to slowly pull fiber bundles from an electrospinning field [52]. A grounded needle placed near a rotating drum can induce electrospun fibers to form bundles that are taken up by the drum [53]. Deposition on the circumference of a ring induces fiber alignment and can produce short yarns [54]. Finally, methods have been developed that collect aligned fibers between spaced collectors and twist them into yarns simultaneously by rotating one of the collectors [55, 56]. This is the method that will be tested in the following experiment as it has a fairly simple setup for creating nanofiber yarns.

7.1.1 Experimental Setup

For the single-jet electrospinning collection of nanofiber yarns, an electro-mechanical system is used to simultaneously collect aligned nanofibers and twist them into yarns. This collector is has the same configuration as a standard single-jet electrospinning setup. However, the collector is replaced by two electrodes spaced at a specified distance. The electrospun nanofibers are collected and aligned between these electrodes. One electrode is stationary while the other is rotated via a small DC
motor. This twists the aligned fibers into a bundle of nanofibers, a nanofiber yarn. A schematic of the yarn collector for single-jet electrospinning is shown in Figure 7.1.

![Figure 7.1 - Schematic of a Single-Jet Electrospinning Nanofiber Yarn Collector](image)

The same setup was used for collection of nanofiber yarns using the hybrid nanomanufacturing process. However, after initial testing it became apparent that some geometrical changes needed to be made. The electrode disk was increased in size, the electrode spacing was increased, and the distance between the head and electrodes was also increased. A diagram of the setup for collection of nanofiber yarns using the hybrid electrospinning process is shown in Figure 7.2.
7.1.2 Single-Jet Electrospinning of Nanofiber Yarns

Using the setup in Figure 7.1, nanofiber yarns were collected. The parameters for the yarn collection are shown in Figure 7.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO Solution Feed Rate</td>
<td>0.5 mL/h</td>
</tr>
<tr>
<td>Electrospinning Voltage</td>
<td>15 kV</td>
</tr>
<tr>
<td>PEO Solution Concentration</td>
<td>10 wt %</td>
</tr>
<tr>
<td>Distance from Head to Collectors</td>
<td>25 cm</td>
</tr>
<tr>
<td>Distance Between Collectors</td>
<td>18 cm</td>
</tr>
<tr>
<td>Diameter of Rotating Collector</td>
<td>8 cm</td>
</tr>
<tr>
<td>Duration of Deposition</td>
<td>15 min</td>
</tr>
</tbody>
</table>

Figure 7.3 – Parameters for Yarn Collection Using Single-Syringe Electrospinning
SEM images of a yarn collected using single-jet electrospinning are shown in Figures 7.4 – 7.6. Nanofibers are generally of good quality, having smooth edges, small diameters, and good consistency of diameters. Individual fiber diameters range from 200 to 400 nanometers. The diameter of the entire yarn is approximately 90 microns. With an ideal hexagonal packing of fibers, this would allow for more than 80,000 nanofibers per yarn. However, it is apparent that the packing density is far from optimal, so an approximation of 20,000 to 40,000 nanofibers per yarn would be better.

Figure 7.4 – SEM Image: Yarn Collected Using Single-Jet Electrospinning
7.1.3 Hybrid Nanomanufacturing of Nanofiber Yarns

Using the setup in Figure 7.2, nanofiber yarns were collected. For the initial test, the geometric setup of the collector was kept the same as it was during the single-jet electrospinning collection of nanofiber yarns. The parameters for the yarn collection are shown in Figure 7.7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO Solution Feed Rate</td>
<td>40 mL/h</td>
</tr>
<tr>
<td>Head Rotational Speed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>Electrospinning Voltage</td>
<td>20 kV</td>
</tr>
<tr>
<td>PEO Solution Concentration</td>
<td>10 wt %</td>
</tr>
<tr>
<td>Distance from Head to Collectors</td>
<td>25 cm</td>
</tr>
<tr>
<td>Distance Between Collectors</td>
<td>18 cm</td>
</tr>
<tr>
<td>Diameter of Rotating Collector</td>
<td>8 cm</td>
</tr>
<tr>
<td>Duration of Deposition</td>
<td>5 min</td>
</tr>
</tbody>
</table>

Figure 7.7 – Parameters for Yarn Collection Using Hybrid Nanomanufacturing
SEM images are shown in Figures 7.8 and 7.9 for yarn collected using the hybrid nanomanufacturing process. Again, nanofibers are generally of good quality, having smooth edges, small diameters, and good consistency of diameters. Individual fiber diameters range from 200 to 300 nanometers. The diameter of the entire yarn is approximately 85 microns. With an ideal hexagonal packing of fibers, this would allow for more than 100,000 nanofibers per yarn. However, the packing density is again far from optimal, so an approximation of 25,000 to 50,000 nanofibers per yarn would be better.

Note that the consistency of fiber pitch is less than with single-jet electrospun yarns, and the yarn is more akin to a bundle of randomly oriented fibers. This is believed to be because of the geometry of the collector. With the collector electrodes fairly close to each other, the large output of fibers was able to deposit without significant alignment.
Since the first trial for the collection of nanofiber yarns using the hybrid nanomanufacturing process yielded good quality fibers but a poor overall yarn structure, a second test was performed. This time, the size of the collector disk, the spacing between electrodes, and the distance from the head to the collector were all increased. Parameters for yarns collected with this setup are outlined in Figure 7.10.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO Solution Feed Rate</td>
<td>40 mL/h</td>
</tr>
<tr>
<td>Head Rotational Speed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>Electrospinning Voltage</td>
<td>20 kV</td>
</tr>
<tr>
<td>PEO Solution Concentration</td>
<td>10 wt %</td>
</tr>
<tr>
<td>Distance from Head to Collectors</td>
<td>30 cm</td>
</tr>
<tr>
<td>Distance Between Collectors</td>
<td>30 cm</td>
</tr>
<tr>
<td>Diameter of Rotating Collector</td>
<td>13 cm</td>
</tr>
<tr>
<td>Duration of Deposition</td>
<td>5 min</td>
</tr>
</tbody>
</table>

*Figure 7.10 - Parameters for Yarn Collection Using Hybrid Nanomanufacturing with Adjusted Geometry*
SEM images are shown in Figures 7.11 and 7.12 for a yarn collected with hybrid nanomanufacturing and adjusted geometry. Again, most nanofibers are of good quality. Fiber diameters range from 200 to 300 nanometers, and the diameter of the entire yarn is approximately 60 microns. Note the significant improvement in the consistency of fiber pitch (Figure 7.12). The increased geometrical parameters allowed for better initial fiber alignment as they were deposited between the electrodes. Based on the dimensions of the nanofibers and the yarn, an ideal hexagonal packing of fibers would yield more than 50,000 fibers per yarn. However, the packing density is far from ideal, so an estimated 10,000 to 25,000 fibers per yarn would be better.

*Figures 7.11 and 7.12 – SEM Images: Yarn Collected Using Hybrid Nanomanufacturing with Adjusted Geometry*
7.1.4 Conclusions of Yarn Collection Experimentation

The hybrid nanomanufacturing process has been tested for its ability to produce nanofiber yarns, and wound nanofiber yarns were produced using the hybrid nanomanufacturing process for the first time. Note that yarns using with the hybrid process were produced approximately 3 times faster than yarns using the single-jet electrospinning setup, and that the yarns had similar dimensions. This high-rate production of yarns is promising, as the hybrid electrospinning process for the collection of nanofiber yarns could potentially be modified into a continuous system where electrospun nanofibers are collected, twisted into yarns, and spooled for later use in the textile or other industries.

7.2 Nanofiber Deposition on Non-Electroded Surfaces

The majority of electrospinning research has been performed on conductive substrates with some form of electrical connection. However, there may be applications where nanofiber deposition is wanted, but the conditions do not suit this type of setup. For example, deposition on electrically sensitive substrates or non-conductive substrates would require some form of system modification to allow for the direct deposition of nanofibers by electrospinning.
One possible method for depositing nanofibers on non-electroded surfaces is to electrospin the fibers through an electrically grounded ring placed close to the collection substrate. This is a proof-of-concept experiment, showing the possibility of depositing nanofibers on both conductive and non-conductive substrates that do not have electrical connections.

7.2.1 Experimental Setup

In order to electrospin nanofibers on to a surface that does not have electrical connections, an electrically grounded ring was placed close to the collection surface. This ring directs the electrospinning toward the substrate. This configuration was tested for both conductive (aluminum foil) and non-conductive (paper) substrates. Also, for both categories of substrates, testing was done with both a single-jet electrospinning setup and the hybrid nanomanufacturing process. Diagrams of these setups are shown in Figures 7.13 and 7.14 for the single-jet and hybrid configurations, respectively.
Figure 7.13 – Deposition on a Non-Electrified Substrate Using Single-Jet Electrospinning

Figure 7.14 – Deposition on a Non-Electrified Substrate Using Hybrid Nanomanufacturing
7.2.2 Experimentation for the Deposition of Nanofibers on Non-Electrified Substrates

The parameters for this study were determined through trial-and-error experimentation. Several parameter sets were experimented with until parameters that gave good deposition on the substrate were found. The parameters used in this study are outlined in Figure 7.15. For all depositions, a 10 percent by weight solution of PEO was used. For the hybrid nanomanufacturing collections, head rotational speed was 1500 rotations per minute.

<table>
<thead>
<tr>
<th>Electrospinning Technique</th>
<th>Substrate Type</th>
<th>PEO Solution Feed Rate</th>
<th>Electrospinning Voltage</th>
<th>Distance from Head to Ring</th>
<th>Distance From Ring to Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-Jet</td>
<td>Conductive</td>
<td>0.5 mL/h</td>
<td>15 kV</td>
<td>10 cm</td>
<td>5 cm</td>
</tr>
<tr>
<td></td>
<td>Non-Conductive</td>
<td>0.5 mL/h</td>
<td>25 kV</td>
<td>15 cm</td>
<td>2 cm</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Conductive</td>
<td>30 mL/h</td>
<td>20 kV</td>
<td>30 cm</td>
<td>5 cm</td>
</tr>
<tr>
<td></td>
<td>Non-Conductive</td>
<td>30 mL/h</td>
<td>25 kV</td>
<td>40 cm</td>
<td>2 cm</td>
</tr>
</tbody>
</table>

*Figure 7.15 - Parameters for Nanofiber Deposition on Non-Electrified Surfaces*

Samples collected using single-jet electrospinning and a conductive substrate resulted in nanofibers ranging in diameter from 150 nanometers to 1 micron. SEM images of collected fibers are shown in Figures 7.16 and 7.17.
Samples collected using single-jet electrospinning and a non-conductive substrate resulted in nanofibers ranging in diameter from 200 nanometers to 1 micron. The deposition density is significantly lower than the deposition using a conductive substrate. SEM images of collected fibers are shown in Figures 7.18 and 7.19.
Samples collected using hybrid nanomanufacturing method and a conductive substrate resulted in nanofibers ranging in diameter from 150 to 800 nanometers. The deposition density is significantly higher than the depositions using single-jet electrospinning. SEM images of collected fibers are shown in Figures 7.20 and 7.21.

Samples collected using hybrid nanomanufacturing method and a non-conductive substrate resulted in nanofibers ranging in diameter from 100 nanometers to 2 microns. The deposition density and fiber quality is lower than with the deposition on a conductive substrate. SEM images of collected fibers are shown in Figures 7.22 and 7.23.
7.2.3 Conclusions: Study of Nanofiber Deposition on Non-Electroded Substrates

The proof-of-concept experiment on the deposition of nanofibers on a non-electroded substrate was a success. It was proven that by placing a grounded ring close to a non-electroded surface, the electrospinning of PEO fibers can be initiated and directed toward the substrate. The best deposition and fiber quality was obtained using the hybrid nanomanufacturing process. Further experimentation and development could lead to the development of a so-called “electrospinning gun” that would allow nanofibers to be deposited on any surface.
8 CONCLUSIONS

One of the major roadblocks in the implementation of continuous polymer nanofibers in to industrial applications is the relatively slow rate at which they are produced using the single-jet electrospinning. The method works well for producing laboratory samples, but the method falls short for any application that requires larger amounts of nanofibers.

In order to achieve high-rate continuous nanofiber production, an increase in the base material is required. In the case of electrospinning, this base material is the polymer solution. Various techniques are available to boost the amount of polymer solution fed to the system. However, in the interest of simplicity and size, a straightforward hybrid nanomanufacturing method was selected.

The combination of the fiber-forming fluid shear-off from a rotating disk with the fundamentals of electrospinning has allowed for a method to produce continuous polymer nanofibers at a high rate. The surface area of the rotating disk serves as the polymer solution delivery system for the electrospinning system, and the size of this head allows for large amounts of polymer solution to be fed to the system. The polymer solution shears to the edge of the head and exits at many points. Each of these points serves as an initiation point for an electrospinning jet.
The hybrid nanomanufacturing system was first tested and optimized using a solution of polyethylene oxide in water. This optimization covered all major parameters of the system. Samples were collected and analyzed both for nanofiber production rate and nanofiber quality. Using the data obtained, optimal values were determined for the polymer solution feed rate, the head rotational speed, the electrospinning voltage, the electrospinning distance, and the polymer concentration. As a result of the study, the average nanofiber production rate using optimized parameters was 6.58 (mg/h)/cm$^2$. This corresponds to an approximate 90 times improvement per unit area as compared to single-jet electrospinning, which produced nanofibers at 0.072 (mg/h)/cm$^2$. Keep in mind that this result was obtained using a six-inch diameter head, and larger heads would allow for even higher polymer solution flow in to the system, and as a result, even greater increases in nanofiber production.

Once the hybrid nanomanufacturing process was optimized for the production of polyethylene oxide fibers, the consistency of deposition was measured. By studying depositions on a stationary substrate, it was determined that nanofiber deposition density varies as a function of the distance from the head axis. Studies with an intermittently moved substrate resulted in depositions that were fairly consistent at distances up to 18 centimeters from the head axis in the direction of motion. Finally, a study on an automated looped belt collector showed that a consistent deposition in the direction of motion could easily be obtained by passing
the deposition surface over the hybrid nanomanufacturing system multiple times. Using this setup, nanofiber mats of consistent density could potentially be produced continuously with a width ranging from 12 to 18 centimeters.

The hybrid nanomanufacturing process was tested for its ability to produce aligned nanofibers, and the collection of aligned nanofibers was demonstrated with the hybrid process for the first time. Samples were collected between gapped electrodes using both single-syringe electrospinning and the hybrid nanomanufacturing process. The samples were analyzed by scanning electron microscopy, the fiber angles were measured, and a comparison between the single-jet and hybrid system was made. Samples collected with the hybrid nanomanufacturing process showed alignment quality comparable to that of single-jet electrospinning of aligned fibers. Also, further study and optimization could result in samples with excellent alignment properties.

The production of polyacrylonitrile fibers was tested and optimized with the hybrid nanomanufacturing system. As polyacrylonitrile solution behaves differently than polyethylene oxide solution during electrospinning, a full parametric study was conducted, and optimized parameters were determined for use with this polymer. As a result of the study, the average nanofiber production rate using optimized parameters was 5.86 (mg/h)/cm$^2$. This corresponds to an approximate 85 times improvement per unit area as compared to single-jet electrospinning, which produced nanofibers at 0.068 (mg/h)/cm$^2$. Again, keep in mind that this result was obtained...
using a six-inch diameter head, and larger heads would allow for even higher polymer solution flow into the system, and as a result, even greater increases in nanofiber production.

Finally, two exploratory studies were carried out. The first study analyzed the hybrid nanomanufacturing process’s applicability to the production of wound nanofiber yarns. The study showed that yarns with fairly good qualities could be produced using the same technique for collection and winding as single-jet electrospinning. The second study functioned as a proof-of-concept experiment for the deposition of nanofibers on surfaces with no electrical connections. The study showed that deposition on both conductive and non-conductive substrates was possible, and that the hybrid method may function better for this application than single-jet electrospinning.

The results of this research have shown that a simple hybrid nanomanufacturing process can be used to produce nanofibers at high rates in comparison to single-jet electrospinning. The hybrid process has also shown to function for the collection of continuous nanofibers in various configurations usually obtained through single-jet electrospinning, including randomly-oriented sheets with good deposition consistency, aligned samples, and nanofiber yarns.
With further development of the hybrid nanomanufacturing process, the implementation of continuous polymer nanofibers in many applications spanning multiple industries could quickly become a possible.
BIBLIOGRAPHY


[16] Li, D., Xia, Y., "Electrospinning of Nanofibers: Reinventing the Wheel?", Advanced Materials, 16(4), (2004), 1151-1170


[25] Tomaszewski, W., Szadkowski, M., "Investigation of Electrospinning with the Use of a Multi-Jet Electrospinning Head", Fibres & Textiles in Eastern Europe, 13, 4(52), (2005), 22-26

[26] Zhou, F.L., Gong, R.H., Porat, I., "Polymeric Nanofibers Via Flat Spinneret Electrospinning", Polymer Engineering and Science, 49(12), (2009), 2475-2481


[34] Liu, Y., He, J.H., "Bubble Electrospinning for Mass Production of Nanofibers", Journal of Nonlinear Sciences and Numerical Simulation, 8(3), (2007), 293-396


[38] Yarin, A.L., Zussman, E., "Upward Needleless Electrospinning of Multiple Nanofibers", Polymer, 45, (2004), 2977-2980


[51] Smit, E., Buttner, U., Sanderson, R., "Continuous Yarns from Electrospun Fibers", Polymer, 46, (2005), 2419-2423


[73] Li, D., McCann, J.T., Xia, Y., "Electrospinning: A Simple and Versatile Technique for Producing Ceramic Nanofibers and Nanotubes", Journal of the American Ceramic Society, 89(6), (2006), 1861-1869


[75] Ramaseshan, R., Sundarrajan, S., Jose, R., Ramakrishna, S., "Nanostructured Ceramics by Electrospinning", Journal of Applied Physics, 102, (2007), 111101


Electrical Conductivity Thermal Hysteresis of Silver Nanofibers Produced by the Electrospinning Technique", Langmuir, 24, (2008), 11982-11987


[80] Li, D., McCann, J.T., Xia, Y., "Use of Electrospinning to Directly Fabricate Hollow Nanofibers with Functionalized Inner and Outer Surfaces", Small, 1(1), (2005), 83-86


[94] Teo, W.E., Ramakrishna, S., "Electrospun Nanofibers as a Platform for Multifunctional, Hierarchically Organized Nanocomposite", Composites Science and Technology, 69, (2009), 1804-1817


