Continuous Polymer Nanofibers Using Electrospinning

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Abstract

Electrospinning provides a relatively inexpensive method of creating a variety of nanofibers. An overview of the basic electrospinning process is given. Several experimental setups for building various nanofibers are presented. The electrospinning experimental setup that was developed to produce polymer nanofibers scaffolds is discussed. The parameters influencing the electrospinning process and morphology of the fibers are examined. These parameters include flow rate, concentration, electrode spacing, and voltage potential. The research effort focuses on forming nanofiber scaffolds to be used for tissue engineering.

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Chapter 1

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Chapter 2

Introduction

Engineers have successfully created polymer fibers using mechanical methods for several decades using mechanical processes. Conventional mechanical fiber spinning techniques cannot produce fibers with diameters smaller than about 2μm robustly.[1] Although conventional methods of producing polymer fibers are capable of producing fibers with diameters in the μm range, many applications require nm range. In recent years there has been a push towards nanotechnology in many engineering disciplines. Nanotechnology comprises technological developments on the nanometer scale, usually 0.1 to 100 nm.[2] Fiber creation using polymers has evolved through this growing technology. Recently a process called electrospinning has been developed. This process has produced fibers as small as 5nm in diameter (see fig 2.1) and are appropriately called nanofibers.

2.1 Electrospinning

Electrospinning is a process by which a charged liquid polymer solution is introduced into an electric field. The liquid polymer solution is dispensed via a needle attached to a syringe at a voltage between 10-20kV and is deposited on a conductive material at ground (0V) located between 10-30cm from the needle location. The polymer is ejected from a needle with an inner diameter (ID) between 0.5-1.5mm. The ejected polymer solution forms a continuous nanofiber when the electrical force (due to the high voltage potential of the polymer solution) overcomes the surface tension. At this point the pendant droplet of the polymer solution at the tip of the needle is deformed into

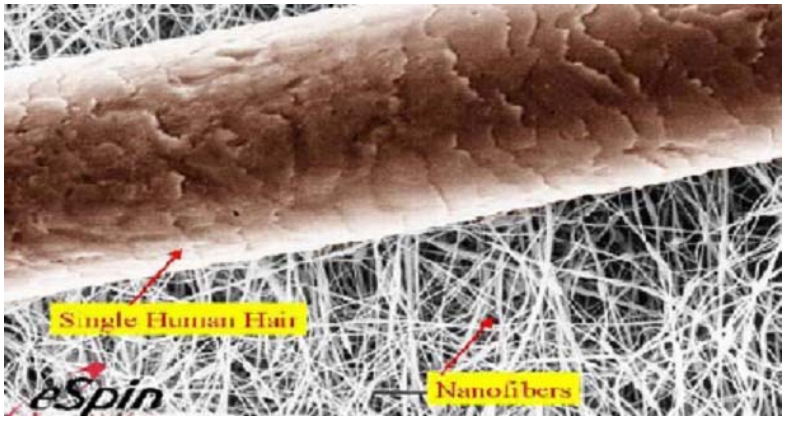


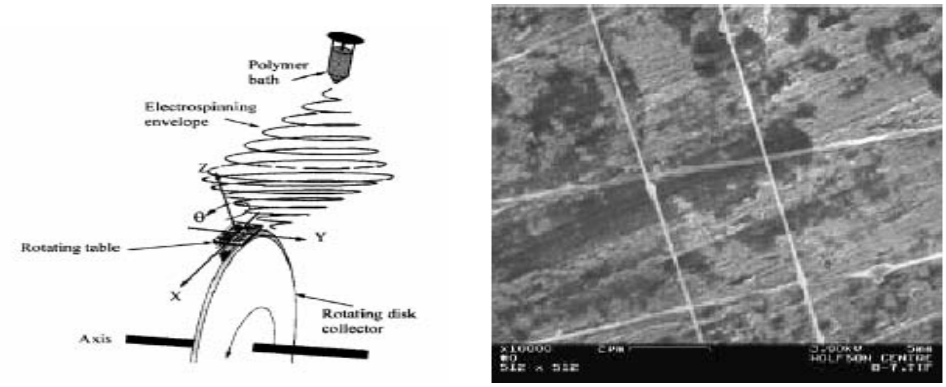
Figure 2.1: Human hair vs. single nanofiber. Image reproduced from [9].

conical shape, typically referred to as Taylor cone. If the voltage surpasses a critical value (depends on the chemical makeup of the polymer solution), the electrostatic force overcomes the surface tension and a fine charged jet is ejected. The formation of the Taylor cone is shown in fig 2.2. After the jet flows away from the droplet in a nearly straight line, it bends into a complex path and other changes in shape occur, during which electrical forces stretch and thin it by very large ratios. After the solvent evaporates solid nanofibers are left.[5]

(a) stage 1 (b) stage 2 (c) stage 3

Figure 2.2: Formation of the Taylor cone. Voltage increases with each stage until equilibrium between surface tension and the electrostatic force is achieved in stage 3. Image reproduced from [4].

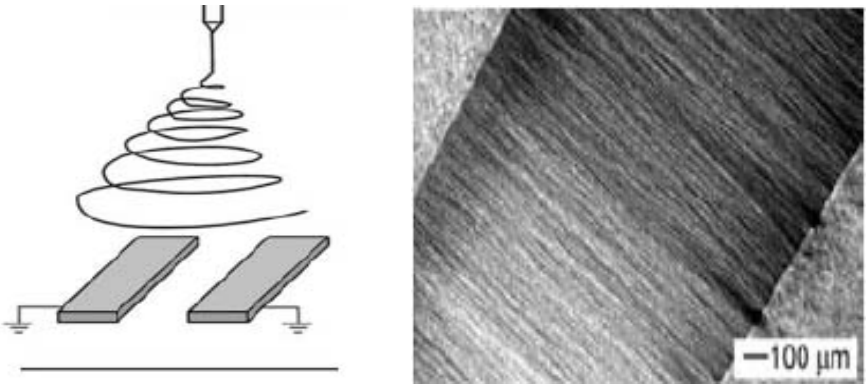
There are several experimental setups that have been developed to produce nanofibers. Each setup attempts to produce scaffolds that are either woven or non-woven. A method to create a woven scaffold is displayed in fig 2.3. This method utilizes a disk that rotates as it collects the continuous nanofiber. The nanofiber is highly attracted to the large electric field created on the sharp end of the disk. Another method to produce aligned fibers is shown in fig 2.4. This method forces the fibers to "straighten" themselves in the region between the two plates. Due to the collection of the fibers within the air gap, the collection of aligned nanofibers is achieved without the possibility of contamination from the ground electrode. This is an ideal collection method for producing scaffolds for tissue engineering.



(a) (b)

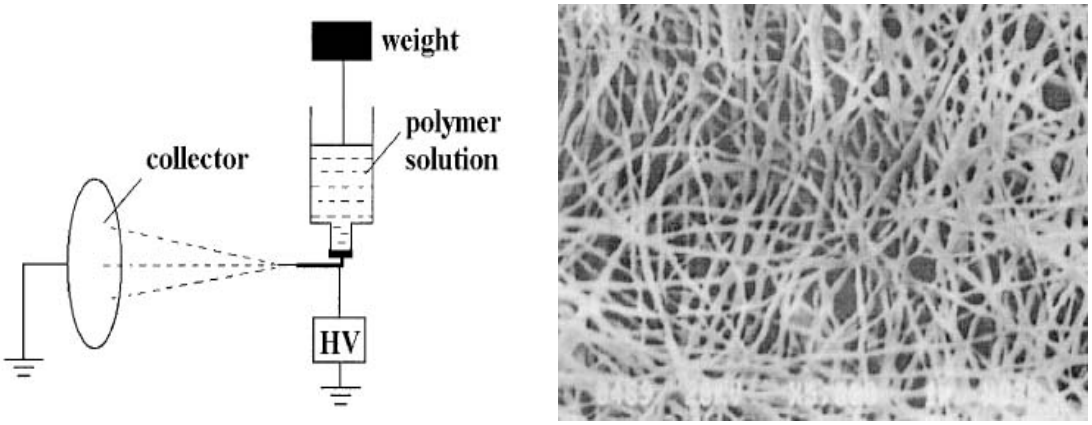
Figure 2.3: An effective method to produce aligned electrospun fibers (a) rotating disk collector (b) resulting woven scaffold. Image reproduced from [5].

Methods have also been developed to create non-woven scaffolds. This type of collection involves the same basic setup already described. Non-woven scaffolds are made with randomly oriented nanofibers. This type of collection is typically made using a flat electrode. Using this type of electrode produces a highly uniform electric field. This means that there is no preferred location for the nanofiber to orient itself and is thus random. Two basic methods, a vertical orientation and a horizontal orientation, are presented in figs 2.5 and 2.6 respectively.



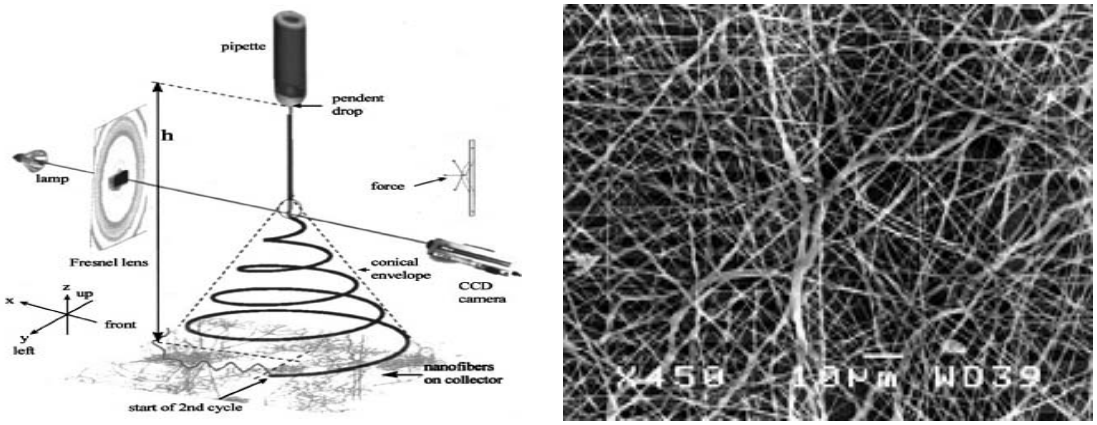
(a) (b)

Figure 2.4: Another effective method to produce aligned electrospun fibers (a) double ground collector (b) resulting aligned fibers. Image reproduced from [10].



(a) (b)

Figure 2.5: Horizontal flat ground collector for random nanofiber collection (a) Horizontal setup with weight as syringe driver and (b) Resulting nanofiber structure. Image reproduced from [3].



(a) (b)

Figure 2.6: Vertical flat ground collector for random nanofiber collection (a) Vertical setup (b) Resulting nanofibers. Image reproduced from [4].

2.2 Nanofiber Use

There are a wide variety of potential uses for nanofibers. According to professor Yarin[4] at the Technion Institute of Technology in Israel:

> Nonwoven systems are of interest for such applications as filter media, fiber-reinforced plastics, solar and light sails and mirrors in space, application of pesticides to plants, biomedical applications (tissue engineering scaffolds, bandages, drug release systems), protective clothing aimed for biological and chemical protection, and fibers loaded with catalysts and chemical indicators.

These are just a few of the numerous ways that nanofibers can be used.

Chapter 3

Experimental

An electrospinning experimental setup was developed at UIC to produce polymer nanofibers. Important aspects such as cost, safety, and flexibility are just a few of the many parameters that affected the design and fabrication of the electrospinning setup. Dielectric and conductive materials were utilized to produce an optimum setup. The former were used to isolate the system from the ground sources and the latter were used for the electrodes and polymer solution.

Polycaprolactone (PCL) was dissolved in acetone with concentrations varying from 6-15 wt% using an ultrasonic bath as a mixing device. This process was carried out at approximately 80^{o}C for 5 h.

Engineers have had success producing nanofibers using various polymers. Proper selection of the polymer is an important detail that must be considered and is determined by the specific application the fibers are being created. PCL is a biodegradable polymer that is useful in tissue engineering. Although the degradation rate is slow for PCL, the rate can be increased by increasing the surface area of the nanofibers.[3] The surface area to volume ratio increases as fiber diameter decreases.[11]

3.1 Apparatus

The main focus of the research is to produce nanofibers for tissue engineering, specifically cartilage tissue engineering. There are three layers of cartilage tissue. The top layer is highly ordered in a horizontal fashion, the middle layer is randomly oriented, and the bottom layer is highly ordered in a vertical

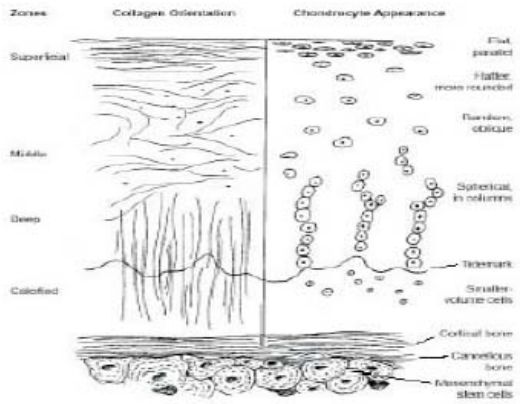
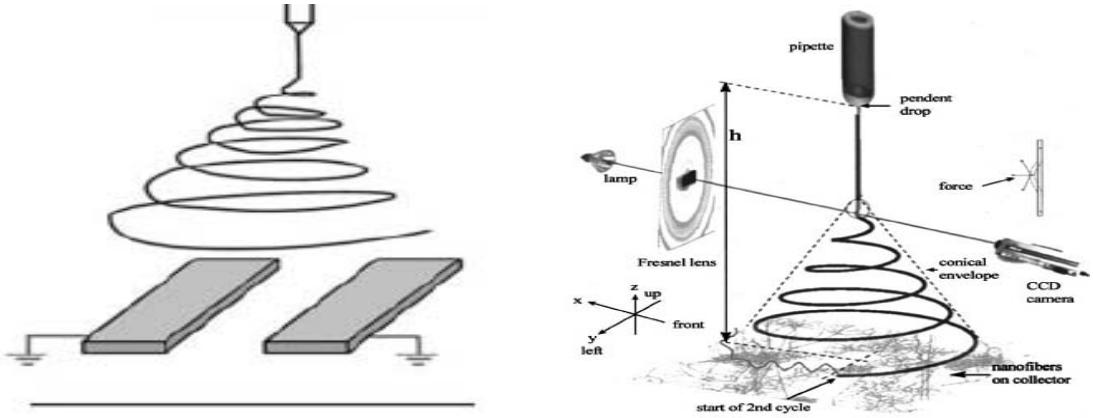


Figure 3.1: A schematic of three distinct zones of natural articular cartilage is shown. Collagen fibrils and chondrocyte organization in each zone are depicted to point out the relevant but distinguishable features in each zone. The bone boundary is portrayed as the calcified layer at the bottom. Image reproduced from [12].

fashion (see fig. 3.1). Due to the fact that there are both random and ordered layers in the cartilage tissue, it is necessary to produce both ordered and random scaffolds. The two basic setups that were used for the electrospinning experiments performed are shown in fig 3.2.

In order to produce electrospun fibers, an experimental setup was developed. The designed experimental setup is shown in fig 3.3. Figs 3.4, 3.5, and 3.6 show the electrospinning setup in more detail. This setup has been modified through the progression of the experiments to eliminate problems that occurred during the initial experiments. The electrospinning process takes place in a large Plexiglas box that has very limited exposure to elements exterior to the box. This box helps control the environment in which the electrospinning is taking place namely the unpredictable air currents in an uncontrolled environment that can dramatically alter nanofiber production. The inside of the box also contained an acetone bath that was used to saturate the electrospinning environment with acetone (the solvent used in all experiments.) This bath was used to help reduce the evaporation rate of the acetone in the PCL-acetone solution that was ejected from the needle during the experiments.

A computer-controlled device controls the electrode separation distance. The computer software allows the user to use a PC to control the location



(a) (b)

Figure 3.2: Experimental setup used to create nanofiber scaffolds (a) Setup used to collect ordered fibers (b) Setup used to collect random fibers. Image reproduced from [10] and [4] respectively.

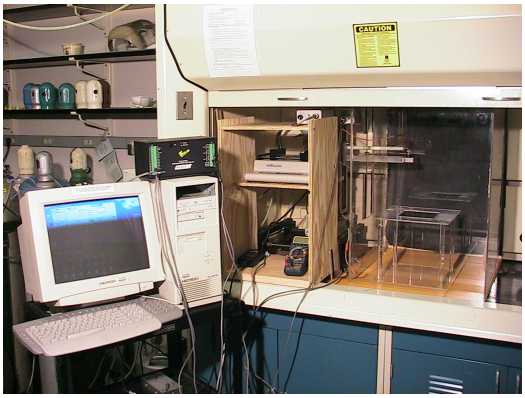


Figure 3.3: Experimental setup developed at UIC for electrospinning.

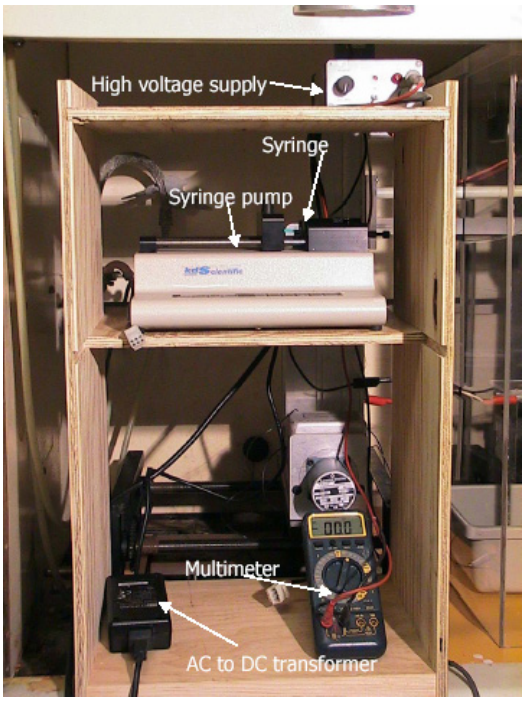


Figure 3.4: Detailed view of electrospinning setup.

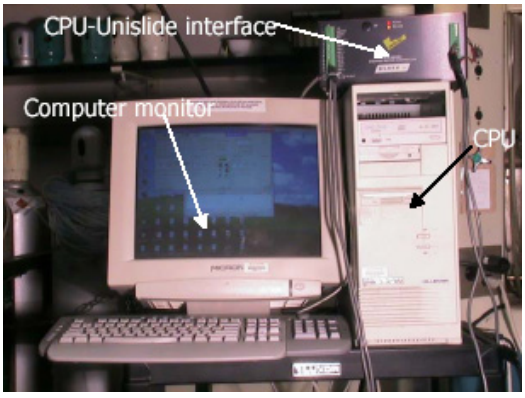


Figure 3.5: Detailed view of electrospinning setup.

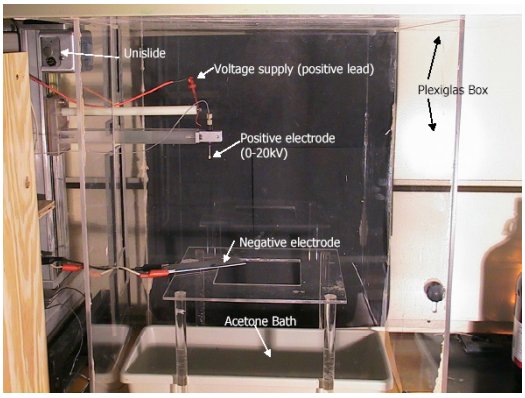


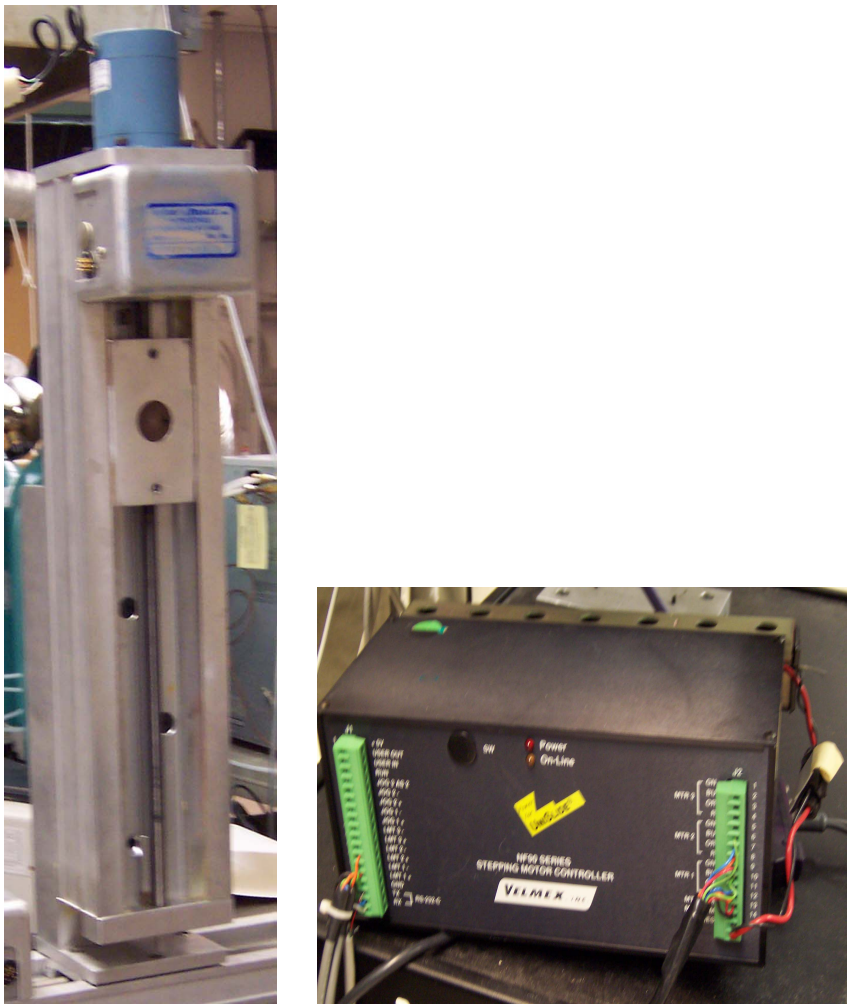
Figure 3.6: Detailed view of electrospinning setup.

of the syringe by use of a mouse. The device, called "Unislide", is shown in fig 3.7. It was manufactured by Velmex, inc. (model No. MB4015P40J-S4). An interface was necessary between the CPU and the Unislide. This device, called "Stepping Motor Controller", is also shown in fig 3.7. The interface is a NF90 Series Stepping Motor Controller manufactured by Velmex, Inc.

The syringe used in the experiments was driven by a syringe pump (see fig 3.8). The syringe pump allowed control of the flow rate and the volume of polymer ejected during each experiment. These are two important parameters that affect nanofiber production. These effects will be explained later. The syringe that was used had a capacity of 1-mL (see fig 3.9). There is a thin tube attached to the syringe that leads to a thin needle (0.8mm OD) that ejects the polymer. A high voltage generator with range of 0-20kV and limiting current of 100 mA was applied to the metal needle. The ground electrode was placed on a stand made of acrylic and was used for collection of both random and aligned nanofibers (see fig 3.10). The needle which is maintained at 0-20kV is located in a clamp that is attached to a rectangular bar of acrylic used to support the needle from the grounded electronic Unislide (fig 3.11). The typical ranges for the experimental operating parameters are given in Table 3.1.

3.2 Materials

Polycaprolactone (PCL) with M_w 42,500 was the polymer used in the electrospinning experiments. It was purchased from Sigma-Aldrich (Milwaukee,



(a) (b)

Figure 3.7: Equipment used to control syringe dispensing (a) Unislide and (b) Stepping Motor Controller.

Figure 3.8: Electronic syringe pump used to eject and control the flow rate of the liquid polymer.

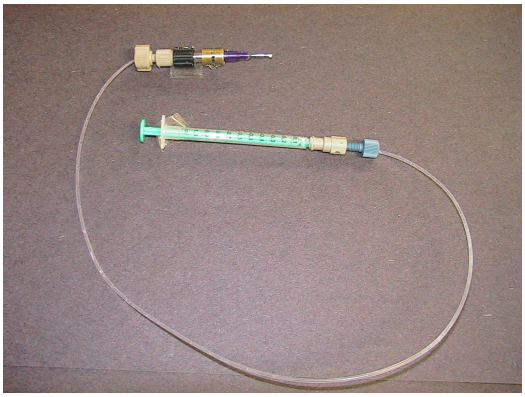


Figure 3.9: Syringe assembly used to hold the polymer solution.

Table 3.1: Typical range of operating parameters used for electrospinning experiments with PCL-Acetone solutions.

Flow Rate	1.0mL/h - 5.0mL/h
Syringe Capacity	1mL - 15mL
Electrode Spacing	7cm - 25cm
Capillary Diameter	0.1mm - 1.5mm
Voltage	10kV - 25kV
PCL Concentration	6%wt - 20%wt

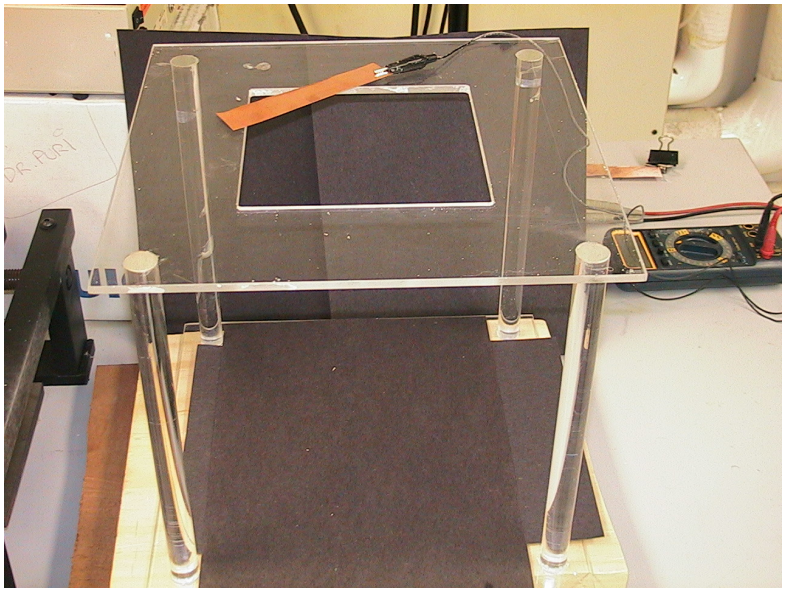


Figure 3.10: Acrylic insulating stand used to hold the ground electrode. A copper ground electrode used to collect nanofibers is shown on top of the stand.

WI). Tissue engineering requires scaffolds that will not inhibit but rather enable stem cell grow. PCL provides this with its non-toxic and biodegradable nature. In addition PCL is a good electrical conductor that is essential for electrospinning. PCL (pellet form) (see fig 3.12) was dissolved in Acetone with concentration ranging from 6 to 15 wt%.

3.3 Visualizing the electrospinning process

A high speed video camera was used to observe electrospinning phenomena. In addition to the precision obtained with the high-speed camera, the aperture, focal length, and the frame rates can be adjusted over a wide range. Frame rates are adjustable from 30fps (normal video speed) to 10000fps. Dynamic analysis over very short time periods (1/10000) sec allows the observer to see phenomena that cannot be seen using most other methods.

Almost as imperative as selecting a good camera, a proper cleaning process must be undertaken on each substrate before conducting each experiment. Impurities on the experimental substrate such as dirt, oil from a

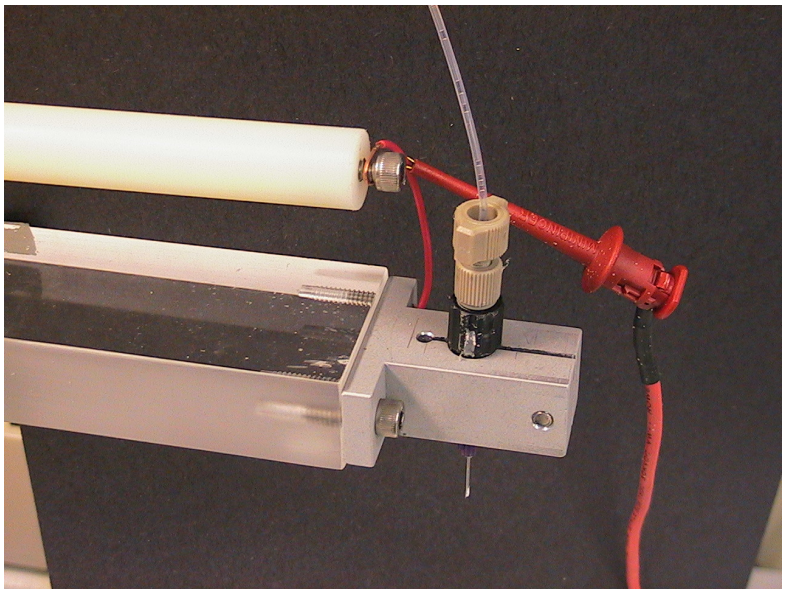


Figure 3.11: Detail showing connection of positive electrode and high voltage source. The top rod provides an isolated connection of the high voltage source and positive electrode. The bottom bar made of acrylic holds the clamp that contains the needle that ejects the polymer solution.

Figure 3.12: Polycaprolactone (PCL) with M_w 42,500 in pellet form.

human hand, etc. can adversely affect the quality of the nanofiber samples. This is especially prevalent with low energy surfaces. Each substrate was first cleaned with Boric acid. This was followed by an application of acetone (the solvent) and dried using pressurized air.

An electronic caliper was used to find the diameter of the syringe. All of the photos collected with the high-speed camera were analyzed using Adobe Photo Shop along with VideoMach. Calibration measurements were used to convert the measurements from pixels to nanometers.

Chapter 4

Results and Discussion

There are several parameters that affect size and defects associated with nanofibers produced by electrospinning. The parameters that were studied include concentration and electrode spacing. The main defect that is common and problematic to eliminate is called beading (see fig 4.1). Each parameter studied indicated that there is some trade-off between beading defects and size of the produced nanofibers. In other words, the beading defects become more prevalent as fiber diameter is reduced. In order to observe the morphology and diameter size of the fibers, Scanning Electronic Microscopy (SEM) and Transmission Electron Microscopy (TEM) were utilized.

4.1 Concentration Effects

Changing the concentration of the polymer adversely affected the resulting nanofibers produced. As mentioned earlier, it is important to reduce the nanofiber diameter as much as possible. The mechanical properties become better as fiber diameter is reduced. The reduction of nanofiber diameter was achieved by lowering the concentration of the PCL. The problem that arose by lowering the concentration of PCL was the resulting beading defects.

An important parameter to consider when electrospinning is the concentration. Both diameter and beading defects were investigated for 6%, 10%, and 15% PCL dissolved in acetone. Figure 4.2 shows the SEM images for the concentration variations at a magnification of 1k. The image shows that as the concentration is increased, the beading defects are decreased and the diameter of the fibers is increased. The effect of concentration on diameter

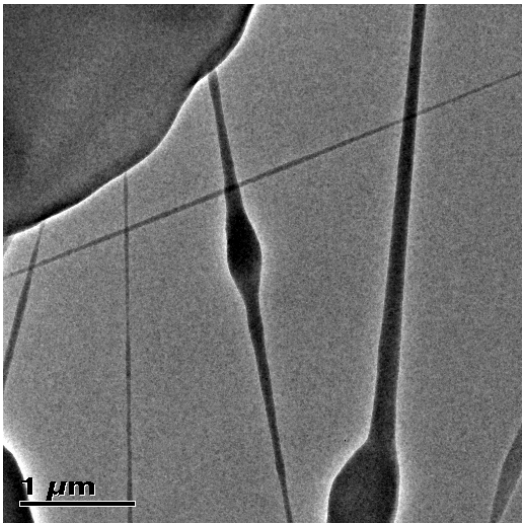
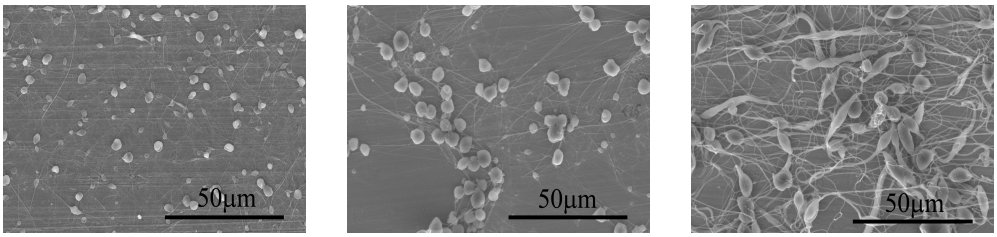


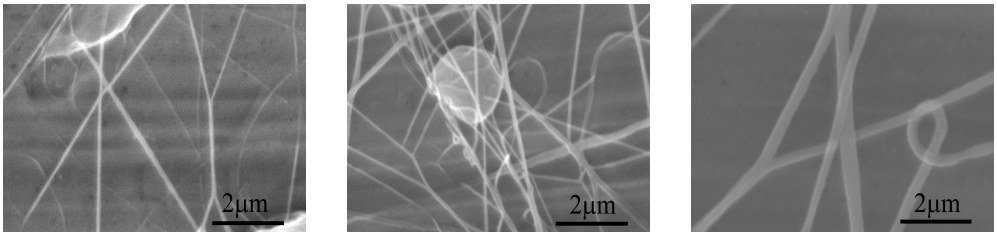
Figure 4.1: Beading defects were very common when using low PCL concentrations.

is easiest to see in fig 4.3. These are the same SEM images in fig 4.2 but at 15k magnification. Diameter measurements of the nanofibers were made on these images using Adobe Photo Shop 7.0. The average diameter for 6% concentration was 77nm ± 47nm, 131nm ± 47nm for 10%, and 375nm ± 47nm for 15%. This indicates quantitatively that the diameter does indeed increase with higher concentrations.



(a) (b) (c)

Figure 4.2: Nanofiber scaffolds electrospun at a constant 21kV with an electrode spacing of 15cm with varying concentration. a) 6% b) 10% c) 15%.



(a) (b) (c)

Figure 4.3: Nanofiber scaffolds electrospun at a constant 21kV with an electrode spacing of 15cm with varying concentration. a) 6% b) 10% c) 15%.

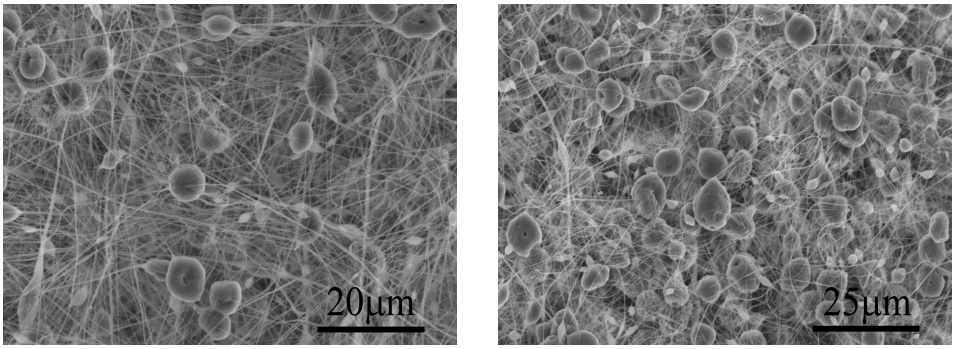
4.2 Electrode spacing effects

An important parameter to consider in electrospinning is the spacing between the high-voltage electrode and the ground plate electrode. As mentioned earlier, there are at least two aspects of nanofibers that are affected by electrode spacing –diameter and beading. Since it is important to reduce the size of the fibers as much as possible, the electrode spacing is a good parameter to investigate. It is evident from fig 4.4 that nanofibers can be made smaller by increasing the electrode spacing. To get a clearer understanding of this fact it is important to quantify the results. This was done by investigating the diameters of about 50 nanofibers from each SEM photograph in fig 4.4. The resulting histogram for each SEM photo is given in fig 4.5. The diameter measurements were made using Adobe Photo Shop 7.0. Due to the low resolution of the SEM photos, the accuracy of the diameter was only good to approximately ± 66.67nm. It appears from the histogram that the diameter distribution shifts to a lower value for larger electrode spacing. Unfortunately, due to the low resolution, a conclusion cannot be drawn about the effect of electrode spacing on nanofiber diameter.

Another important detail that is suggested from the data obtained is that the uniformity of the nanofiber diameter becomes better with increased electrode spacing. This is evident by observing the distribution of the histogram in fig 4.5. For far electrode spacing (21.6cm) there are 18 occurrences in the 115nm-140nm range. This accounts for nearly half (39%) of the samples that were taken. For close electrode spacing (11.4cm) the largest range 140-165nm has the largest number of occurrences with 12 (24%). The majority

of the data for close electrode spacing is distributed evenly. This information suggests that higher precision can be obtained for a larger electrode separation. Uniformity of the electrospun nanofibers is an important aspect to tissue engineering.

Also evident from fig 4.4 is the fact that a trade off is made between the diameter and the beading defects. The amount of beading for the 11.4cm spacing is approximately 3.7 beads/μm^2 and the amount of beading for the 21.6cm spacing is approximately 10.3 beads/μm^2. This fact indicates that beading increased when the electrode spacing was increased.

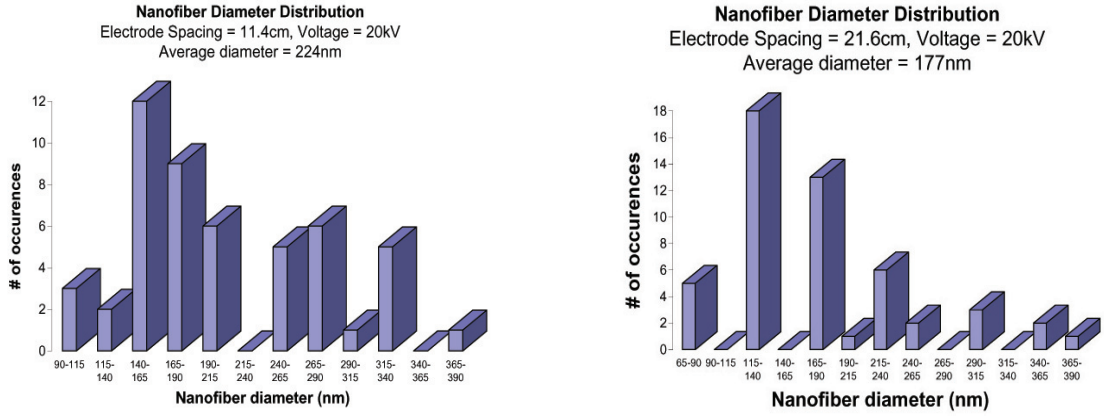


(a) (b)

Figure 4.4: Nanofiber scaffolds electrospun at a constant 20kV with varying electrode spacing. a) 11.4 cm b) 21.6 cm.

4.3 Future Work

It is important to understand that the work presented in this paper was performed over a short ten-week period. The majority of this time was spent learning about electrospinning, designing the experimental setup and obtaining equipment and materials. Only a few weeks were left to spend obtaining experimental data. There is data from other engineers that have spent long periods of time investigating some of the aspects of electrospinning. There are many experiments that still need to be performed at UIC in order to draw solid conclusions about nanofiber production. The effects of concentration, voltage, and environmental variations are important to the understanding on



(a) (b)

Figure 4.5: Nanofiber scaffolds electrospun at a constant 20kV with varying electrode spacing. a) 11.4 cm b) 21.6 cm

how to control the electrospun nanofibers. This will allow scientists to have the ability to produce fibers optimal for their specific use.

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