Polymer Nanofibers Via Electrospinning: Factors Affecting Nanofiber Quality

ABSTRACT: Several methods have been developed to fabricate nanofibers, such as fibrillation, bicomponent, melt-blown and electrospinning. Electrospinning is a technique that can be used for fabricating micro and nanofibers has been developed to produce fibrous materials for a wide range of applications; such as filtration, catalysis, batteries/cells, sensors, nanofiber reinforcement, protective clothing, medical prostheses, wound dressing, controlled drug delivery, cosmetics and tissue engineering. Nanofibers can be produced from a wide range of polymers and they have extremely high specific surface area due to their small diameters. These unique characteristics over the functionalities from the polymers themselves impart nanofibers with many desirable properties for advanced applications.

Keywords: Electrospinning, Nanofiber Quality, Taylor Cone

1. INTRODUCTION

Electrostatic spinning or electrospinning is a process capable of producing polymer fibers in the nanometer diameter range. In order to understand the fundamental principle underlying the process of electrospinning, consider a spherically charged droplet of a low molecular weight conducting liquid that is held in vacuum. The droplet is under the influence of two forces, the electrostatic repulsive force and the surface tension that strives to hold the droplet within a spherical shape. The two forces completely balance each other, as is depicted by [1-3]:

\[
\frac{1}{8\pi\varepsilon_0} \frac{Q^2}{R^2} = 8\pi\sigma, R
\]

(1)

Where Q is the electrostatic charge on the surface of the droplet, R is the radius of the droplet, \(\varepsilon_0\) is the dielectric permeability of vacuum and \(\sigma\) is coefficient of surface tension. With increasing electric field strength, the charge on the surface of the droplet increases until it reaches a critical point when the electrostatic repulsive force overcomes the surface tension. When this happens the droplet repulsives and leads to the formation of smaller droplets. The small diameter provides a large surface to volume ratio that makes these electrospun fabrics interesting candidates for a number of applications including filtration, protective clothing, biomedical applications such as wound dressing, drug delivery systems, the design of solar sails, light sails and mirrors for use in space, the application of pesticides to plants, as structural elements in artificial organs and in reinforced composites [1].

In 1934, the first patent that described the operation of electrospinning appeared by Formhals who disclosed an apparatus for producing polymer filaments by taking advantage of electrostatic repulsions between surface charges. Despite these early discoveries, the procedure was not utilized commercially. In the 1970s, Simm patented the production of fibers with the diameters of less than 1 mm [4]. Utilizing a slightly different approach, Simm were able to fabricate a composite filter based on electrospun fibers.
The relationships between fiber diameter, jet length, solution viscosity, flow rate of the solution, and the electrospinning of acrylic nanofibers where fibers less than a micron in diameter were reported [1]. Larrondo and Manley not only studied the effect of some of the parameters on fiber formation but also conducted some characterization studies on fibers of polyethylene and polypropylene that were electrospun from the melt. The electrospun fibers were characterized by X-ray diffraction and mechanical testing. When the applied electric field was increased, the diffraction rings became arcs, thereby indicating the increasing alignment of the crystalline phase along the fiber axis. The fiber diameter was observed to decrease with increasing melt temperature and a qualitative correlation between the fiber diameter and viscosity was established [5].

In Vittoria’s study, he explained that Bornat conducted simultaneous electrospinning by using several nozzles/syringes to form fibers. The syringes were filled with the polymer solution and placed a certain distance from the collector that was in the form of a long metallic cylinder. However, this works which was followed by other patents, also remained unnoticed at that time.

Electrospun fibers were first commercialized for filter applications, as part of the nonwovens industry. Electrospinning gained substantial academic attention in the 1990s, which was partially initiated by the activities of the Reneker group. The effect of several process parameters on fiber formation was investigated in 1995. Ever since then, many polymers have been electrospun and various aspects that better characterize the electrospinning process have been studied in great detail. In the following sections, several of these aspects will be described [1,6-7].

In general, electrospinning method has some advantages such as very small diameters (40-2000 nm), environmentally friendly, large surface area, easy to install and inexpensive. Electrospun fibers can be charged as electrostatically or load can produce [8]. Although electrospinning method have advantages, there are many disadvantages such as low efficiency of the process, inadequate and low molecular orientation, non-uniform diameter distributions and poor mechanical properties.

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Electrospinning, first introduced by Formhals [1, 10] and later revived by Reneker [11, 12], uses high voltage to electrically charge the polymer solution for producing ultra-fine fibers [8]. The elements required for electrospinning include a polymer source, a high voltage supply, and a grounded collector.

2. ELECTROSPINNING THEORY

Electrospinning, first introduced by Formhals [1, 10] and later revived by Reneker [11, 12], uses high voltage to electrically charge the polymer solution for producing ultra-fine fibers [8]. The elements required for electrospinning include a polymer source, a high voltage supply, and a grounded collector.
When an electric potential is applied between the polymer source and collector, charge accumulates and is forced to the surface of an emerging polymeric droplet at the end of a metal needle. In electrospinning, the force of the electric field overcomes the cohesive force of the solution and an electrically charged jet of polymer-containing solution erupts. As the jet moves toward the collector plate, it is elongated by electrostatic interactions between charges on nearby segments of the same jet. Meanwhile, the solvent evaporates and finally the jet solidifies into a fiber.

Figure 2. Schematic illustration of electrospinning process [1]

When the critical voltage is reached, the equilibrium of the forces is disturbed and a charged jet emanates from the tip of the conical drop. The discharged jet diameter decreases in size with increase in length before being deposited on the collector. This process can be explained by the three types of physical instabilities experienced by the jet which influence the size and geometry of the fibers. The first instability is named Rayleigh instability and the others are bending and whipping instabilities, respectively [22, 23]. At high electric forces, the jet is dominated by bending (axisymmetric) and whipping instabilities.

Figure 4. Forces in the liquid cone [14]

2.2. The Jet

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Figure 5. Instabilities in the jet (A) Rayleigh instability, (B) Axisymmetric conducting instability, (C) Bending instability which results in whipping, (D) Whipping instability [20]

2.3. The Instability Region

As the jet is ejected from the bottom of the Taylor cone, it will remain stable for a certain distance which is specific to each solution and electrical configuration. Intensive electric relationships occur throughout the jet due to the number of fluid, equipment and operating variables that can alter any electrospinning
operation. No theory exists that can consider all variables and describe the process with quantitative accuracy.

These instabilities vary and increase with distance, electric field and fiber diameter at different rates depending on the fluid parameters and operating conditions. The first instability encountered is the Rayleigh instability at low electric fields and is most dependent on the surface tension of the material. Two other instabilities arise with an application of higher electric fields and are dependent on the conductivity of the solution. The model referenced realizes that the instabilities occur with wavelengths that are quite longer than the jet radius. This allows the jet to be modeled as a slender object of great length which simplifies the equations used to model a Newtonian fluid jet.

2.3.1. Rayleigh Instability

The first mode of instability for a droplet under an electric field is an increase in dripping regarding to small droplets being emitted from the capillary (Figure 5A). This instability is axisymmetric and suppressed when the applied electric field which is given by equation [25]:

\[ q^2 = 64\pi^2\Sigma_0\gamma^3 \alpha^3 \]  

\( q \) = charge on droplet  
\( \Sigma_0 \) = conductivity constant of free space  
\( \gamma \) = surface tension of droplet  
\( \alpha \) = diameter of droplet

The Rayleigh instability is generally referred to as a non-conducting mode instability because the conductivity of the medium does not play an important role. It is the surface tension which is important.

2.3.2. Axisymmetric Conducting Mode

This instability appears with an application of higher electric fields and depends on the conductivity of the solution. It can be visualized as a direct competition between the surface charges with the surface tension of the fiber, while the fiber is moving (Figure 5B) [26,27].

2.3.3. Whipping Conducting Mode

The whipping instability is non-axisymmetric and accounts for the small diameters of fibers which can be produced by electrospinning. This instability is a result of small bends in the initial uniformly charged straight fiber formation. As the fiber bends, the surface charges around the circumference of the jet are no longer uniform and a dipolar moment \( P(z) \) is induced perpendicular to the jet. These dipoles initiate a localized torque, in response to each other and the applied electric field. This torque bends the jet (Figure 5C). The bends are amplified as the jet moves further downstream thus becoming the whipping instability that causes the decreased diameter of the fibers (Figure 5D). The jet is further decreased in diameter by solvent evaporation [28]. The decrease in diameter due to the whipping instability is assumed to be a result of the increased path length that the jet travels as a result of the complex relationship between surface tension, viscosity and acceleration of jets surface charges and internal charges by the external electric field.

2.4. The Base

The base is the final region of the electrospinning apparatus. It must consist of an electrode of opposite charge for the fibers. Different electrodes and electrodes orientation have been utilized by numerous researchers such as a flat piece of metal, a screen, or even a rotating drum [29].

2.4.1. Flat Collector

It is the most widely used method of fiber collection which can be either a solid metal, foil, or screen. Other materials can also be placed in between the capillary and the collector [30].

2.4.2. Rotating drum collector

The schematic of the electrospinning setup with a rotating drum collector is shown in Fig. 6. This method is commonly used to collect aligned arrays of fibers. Furthermore, the diameter of the fiber can be controlled and tailored based on the rotational speed of the drum [31–33]. The cylindrical drum is capable of rotating at high speeds (a few 1000 rpm) and of orienting the fibers circularly. Ideally, the linear rate of the rotating drum should match the evaporation rate of the solvent, such that the fibers are deposited and taken up on the surface of the drum. The alignment of the fibers is induced by the rotating drum and the degree of alignment improves with the rotational speed [31,33]. At rotational speeds slower than the fiber take-up speed, randomly oriented fibers are obtained on the drum. At higher speeds, a centrifugal force is developed near the vicinity of the circumference of the rotating drum, which elongates the fibers before being collected on the drum [34–37]. However, at much higher speeds, the take-up velocity breaks the depositing fiber jet and continuous fibers are not collected.
2.4.3. Parallel electrodes

There has already been several groups produced well-aligned nanofibers by using two grounded parallel electrode, such as aluminum strips with a 1 cm gap used [38] and the metal frame [39]. The observed orientation is believed to be due to the polymer jet jumping back and forth from one side of the frame to the other because of electrostatic charging effects. The same as the rotating drum method, it works by modifying the collectors. The drawbacks of both these two methods are that they can only produce aligned fiber in a small area and fibers fabricated by this method cannot be conveniently transferred to different types of substrates.

2.4.4. Rotating disk collector

The rotating disk collector is a variation setup of the rotating drum collector and is used to obtain uniaxially aligned fibers. The advantage of this collector is that most of the fibers are deposited on the sharp-edged disk and are collected as aligned patterned nanofibers [41–44]. The jet travels in a conical and inverse conical path with the use of the rotating disk collector as opposed to a conical path obtained when using a drum collector. During the first stage, the jet follows the usual envelope cone path which is due to the instabilities influencing the jet. At a point above the disk, the diameter of the loop decreases as the conical shape of the jet starts to shrink which results in the inverted cone appearance, with the apex of the cone resting on the disk.

3. FACTORS AFFECTING ELECTROSPINNING PROCESS AND NANOFIBER PROPERTIES

3.1. Solution Parameters

The properties of the polymer solution have the most significant influence on the electrospinning process and fiber morphology. The shapes and dimensions of the fibers formed depend on a large set of parameters, such as molecular weight, molecular weight distribution, glass transition temperature, viscosity, viscoelasticity, concentration, surface tension, and electrical conductivity.
3.1.1. Molecular Weight and Viscosity

Generally, when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than solution of the same polymer having a lower molecular weight. As the jet leaves the needle tip during electrospinning, the polymer solution is stretched as it travels towards the collector. During the stretching of the polymer solution, it is the entanglement of the molecule chains that prevents the electrically driven jet from breaking up thus maintaining a continuous solution jet. As a result, polymer solution does not form fibers when electrospun.

The molecular weight of the polymer presents the length of the polymer chain, which in turn have an effect on the viscosity of the solution since the polymer length will determine the amount of entanglement of the polymer chains in the solvent. Another way to increase the viscosity of the solution is to increase the polymer concentration. Similar to increasing the molecular weight, an increased in the concentration will result in greater polymer chain entanglements within the solution which is necessary to maintain the continuity of the jet during electrospinning [1].

In electrospinning, the polymer solution must consists of sufficient molecular weight and viscosity. The studies by this time, it shows the fiber diameter increased with solution concentration. When concentration is too low, polymer fibers before they become that falling electro-spray droplets on surface. When concentration is too high, electrical forces don’t beat surface tension and viscosity. Therefore, the polymer flow don’t ensured. As the concentration (and the viscosity) was increased, the fiber diameter was larger and the shape of the beads changed from spherical to spindle-like [40].

3.1.2. Surface Tension

Surface tension has the effect of decreasing the surface area per unit mass of a fluid. In this case, when there is a high concentration of free solvent molecules, there is a greater tendency for the solvent molecules to congregate and adopt a spherical shape due to surface tension[45]. A higher viscosity means that there is greater interaction between the solvent and polymer molecules thus when the solution is stretched under the influence of the charges, the solvent molecules will tend to spread over the entangled polymer molecules thus reducing the tendency for the solvent molecules to come together under the influence of surface tension. While surface tension directly proportional with solution viscosity, it is opposite proportional with concentration.

3.1.3. Solution Conductivity

Electrospinning involves stretching of the solution caused by repulsion of the charges on its surface. Thus if the conductivity of the solution is increased, more charges can be carried by the electrospinning jet. The conductivity of the solution can be increased by the addition of ions. Smaller diameter ions have higher charge capacities. However, extra low or extra high solution conductivity could cause disorders in electrospun fiber production [45].

3.1.4. Dielectric Constant of Solvent

The dielectric constant of a solvent has a significant effect on electrospinning. In general, a solution with a greater dielectric property reduces the beads formation and the diameter of the electrospun fiber. The bending instability of the electrospinning jet also increases with higher dielectric constant. If a solvent having higher dielectric constant it will simplify the reduction of the fiber diameter due to the increased jet path of the solution. The interaction between the mixtures such as the solubility of the polymer will also have an impact on the morphology of the resultant fibers.

When DMF is added to polystyrene (PS) solution, beads are formed even though electrospinnability should improve due to the higher dielectric constant of DMF [45]. The diameter of the nanofiber (D) is determined by the function of surface tension, electric current and surface charge repulsion. The equation of the nanofiber diameter is [47]:

\[ D = \left( \frac{\gamma \xi}{I^2} \frac{2}{\pi(2\ln(\frac{l}{d}) - 3)} \right)^{\frac{1}{3}} \]  

where \( \gamma \) is surface tension of the solution, \( \xi \) dielectric constant, \( Q \) flow rate of the solution, \( I \) current carried by the jet, \( l \) initial jet length and \( d \) diameter of the nozzle. As a result of this equation; flow rate, electric current and surface tension of the solution control the whipping jet diameter.

3.2. Process Parameters

The morphology and diameter of electrospun fibers are dependent on a number of processing parameters that affects the electrospun fibers which includes the voltage supplied, the feed rate, temperature of the solution, type of collector, diameter of needle and distance between the needle tip and collector. They have a certain influence in the fiber morphology although they are less significant than the solution parameters.
3.2.1. Diameter of Needle

At the beginning of electrospinning, a pendent droplet of the polymer solution was supported by the surface tension at the tip of the needle. When a high voltage was applied to the needle, the competition between electrical forces and the surface tension resulted in the formation of a liquid cone, which is commonly referred to as “Taylor cone,” at the tip of the needle.

The base of the Taylor cone is the inner diameter of the needle while the apex angle of the cone has the same value of about 50° for all liquids [48]. Therefore, a larger needle diameter would result in a larger Taylor cone, which facilitated the formation of a larger initial jet of the polymer solution (Figure 9). As the solvent in the initial jet evaporated and the jet solidified over the course of its trajectory, the resulting fiber was over five orders of magnitude smaller than the initiating jet [49].

Recently, many studies were conducted to understand the effect of the diameter of the needle. As a result of these studies by using different injection needles while other parameters were kept constant, it was found that the fiber diameter increased linearly with the needle diameter (inner diameter).

Figure 9. Shape of initiating droplet and initiating jet: (a) from a small inner diameter needle, and (b) from a large inner diameter needle [49]

3.2.2. Applied Voltage

Applied voltage (kV) provides the surface charge on the electrospinning jet. Instability and stretching of the jet therefore increases with the applied voltage leading generally to smaller fiber diameters [51].

Within the range of voltages that allows the formation of uniform fibers, the effect of applied voltage on the diameter of electrospun fibers is a controversial issue. Some researchers showed that the fiber diameter increased with applied voltage [52-55]. While some others suggested that the diameter of electrospun fibers was not significantly affected by the applied voltage [56-58]. A few other research groups even reported that the fiber diameter decreased with increasing applied voltage [59-63]. The seemingly opposite observations made by different researchers could be explained as follows: The applied voltage may affect the fiber diameter in two different ways during the same electrospinning. On the one hand, a higher applied voltage pushes more polymer solution from the needle and causes the formation of a larger diameter initial jet, which in turn facilitates the formation of larger diameter of fibers (see effect 1 in Fig. 11).

On the other hand, a higher applied voltage renders a higher density of surface charges on the initial jet and hence promotes the jet to split into smaller jets (see Effect 2 in Fig. 11), resulting in small diameter fibers.

Both effects can occur at the same time. If the first effect dominates, the large diameter fibers are obtained, but if the second effect dominates, small diameter fibers are formed.

The polarity of the applied voltage may also affect the fiber size. It was found that the fiber diameter increased with voltage when the polymer jet was
positively charged while the fiber diameter decreased with increasing voltage when the jet was pseudo-negatively charged.

### 3.2.3. Working Distance

The effect of working distance on fiber diameter could be explained by considering the jet path during electrospinning. At the beginning, inside the applied electric field, the jet was bent back and forth with a growing amplitude for a short distance. Then, the jet followed a spiraling path in three dimensions, which is commonly known as “bending instability.”

The jet in each loop grew thinner as the loop circumference increased. At some point, segments of the loop suddenly developed a second cycle of bending instability, which was similar to but at a smaller scale than the first cycle [64-65].

Since the new cycle of instability must occur at a smaller scale than the previous cycle, the jet diameter further decreased with working distance. Therefore, fibers with small diameters would be formed when the working distance was increased. However, the ultrafine fiber morphology could not be further maintained when beads would be formed on fibers at a long working distance. Because a long working distance would allow the jet to have a long time to contract, thus giving more opportunities for the remaining polymer solution jet to form beads, provided that the solvent had not evaporated. A long distance would not permit a long time for contraction if the solvent had already evaporated.

**Figure 12.** Schematic diagram of the trajectory of the polymer jet during electrospinning [49]

When the increase in the distance between the two charged poles, parabolic decrease is shown in electric field forces. A decrease in distance between two charged poles increases the electric field which causes electrospinning of coarser, semi solidified, bead defected fibers [67].

### 3.2.4. Feed Rate

By the time the studies reported that the effects of solution feed rate on fiber diameter were not significant. The cross-section of the initiating jet of different polymer solutions was not significantly affected by the feed rate. However, a sufficient solution feeding rate must be maintained in order to produce electrospun fibers. The residual solvents may cause the fibers to fuse together where they make contact forming webs. A lower feed rate is more desirable as the solvent will have more time for evaporation [68-71].

### 3.2.5. Temperature

The increasing of solution temperature affects the evaporation rate and viscosity of the polymer solution. If a polymer solution is heated up at the constant concentration, the polymer chains opens up, interactions between polymer chains decrease, thus viscosity declines. This may be due to the lower viscosity of the solution and greater solubility of the polymer in the solvent which allows more even stretching of the solution. With a lower viscosity, the columatic forces are able to exert a greater stretching force on the solution thus resulting in fibers of smaller diameter. Increased polymer molecules mobility due to increased temperature also allows the columatic force to stretch the solution further [72].
3.3. Ambient Parameters

3.3.1. Humidity

The humidity of the electrospinning environment affects the polymer solution during electrospinning. At high humidity, it is likely that water condenses on the surface of the fiber when electrospinning is carried out under normal atmosphere. As a result, this may have an influence on the fiber morphology especially polymer dissolved in volatile solvents.

Experiments using polysulfone (PS) dissolved in tetrahydrofuran (THF) shows that at humidity of less than 50%, the fiber surfaces are smooth. However, an increased in the humidity during electrospinning will cause circular pores to form on the fiber surfaces. The sizes of the circular pores increases with increasing humidity until they coalesce to form large, non-uniform shaped structures [70].

3.3.2. Ambient Temperature

When the ambient temperature is low, evaporation rate of solvent slows regarding the polymer jets do not completely solidify when they arrive at the collector, so diameter of nanofibers gets higher. If ambient temperature is high, time that is needed for polymer jet splaying and jet elongation can not be completed because of higher solidification rates resulting nanofiber diameter distributions become higher. As a result of, fibers can be made thinner with optimum temperature ranges, which adjusted for evaporation of solvent on the jet and getting thinner of fiber [9].

4. CONCLUSIONS

Many polymers have been successfully electrospun into nanofibers. In 1934, the first patent that described the operation of electrospinning appeared by Formhals who disclosed an apparatus for producing polymer filaments by taking advantage of electrostatic repulsions between surface charges. The conical formation occurs from a combination of charge repulsion and surface tension mechanisms. Researchers have mostly focused on optimizing the processing parameters to obtain fibers of desired shapes and forms with little understanding of the parameters that control the enhanced microstructures. Nanofiber materials produced by electrospinning method are preferable with their high surface area to volume ratio and high porosity properties. Despite the fact that the electrospinning process is an easily applicable and reproducible nanofiber production method at laboratory scale, the process is affected by numerous parameters which may be easily observed on large scale electrospinning set-ups. The properties of the polymer solution have the most significant effect in the electrospinning process and fiber morphology. The morphology and dimensions of the nanofibers depend on a large set of parameters: properties of the polymers (such as molecular weight, molecular-weight distribution, glass-transition temperature and solubility), as well the properties of the polymer solution (such as viscosity, viscoelasticity, concentration, surface tension, and electrical conductivity). In addition, the morphology and diameter of electrospun fibers depend on a number
of process parameters which includes the voltage supplied, the feed rate, temperature of the solution, type of collector, diameter of needle and distance between the needle tip and collector. These parameters have a certain influence in the fiber morphology although they are less significant than the solution parameters.

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