Literature Review on Electrospinning Process  
(A Fascinating Fiber Fabrication Technique)  

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Abstract: A literature review that discussed the early attempts at electrospinning, the process of fiber formation, were discussed in some detail. Here electrospinning process considerations were also discussed operating parameters and material properties which affect the electrospinning process and the resulting fibre morphology has also been discussed. Early Attempts on Electrospinning are mentioned here.

1. INTRODUCTION

Electrospinning is a unique technique of producing continuous polymer fibres. It has established a great deal of interest in recent times due to its flexibility in the spinning of a wide variety of polymeric fibres, and its consistency in producing polymer fibres with the fibre diameter on submicrometre to nanometre scales that depends on the kinds of polymer and processing conditions. The term “electrospinning” is technically derived from “electrostatic spinning”, in which electrical charges are employed in the process to produce polymer nanomembrane. Electrospinning represents an attractive approach for polymer biomaterials processing, with the opportunity for control over morphology, porosity and composition using simple equipment.

Formhals (1934) introduced electrospinning methods and described fibre formation during the spinning process. Vormegut et al (1952) were able to produce streams of highly electrified even droplets of about 0.1 mm in diameter. Simons (1966) patented an apparatus for the production of non-woven fabrics of ultra thin and very light in weight with dissimilar patterns using electrical spinning. He found that the fibres from low viscosity solutions tended to be shorter and finer whereas those from more viscous solutions were relatively continuous. Taylor (1969) fundamentally studied the form of the polymer droplet at the tip of the needle and demonstrated that it is a cone and the jet is ejected from the vertex of the cone, referred as the “Taylor Cone”. In the subsequent years, most research focused on the structural morphology and characterization of nanomembranes. Baumgarten (1971) produced electrospun acrylic fibers with diameters in the range of 500 - 1100 nm. The spinning drop was suspended from a stainless steel capillary tube and maintained constant in size by adjusting the feed rate of an infusion pump. A high-voltage current was connected to the capillary tube whereas the fibers were collected on a grounded metal screen.

Since 1980s and particularly in recent years, the electrospinning process has regained more attention probably due in part to a surging importance in nanotechnology, as ultrafine fibers or fibrous structures of various polymers with diameters down to submicrons or nanometers can be easily fabricated with this process. Electrospun nanofibers are being considered for a variety of applications where their unique properties contribute to product functionality. Those properties include high surface area, small fiber diameter, potential to incorporate active chemistry, filtration properties, layer thinness, high permeability, and low basis weight.

2. FUNDAMENTAL ASPECTS OF ELECTROSPINNING PROCESS

Figure 1 shows a typical electrospinning apparatus. There are basically three components to fulfill the process: a high voltage supplier, a capillary tube with a pipette or needle of small diameter, and a metal collecting screen.

Figure 1. Schematic diagram of electrospinning apparatus

In the electrospinning process a high voltage is used to produce an electrically charged jet of polymer solution out of the pipette. Before reaching the collecting screen, the solution jet
evaporates or solidifies, and is collected as an interconnected web of small fibers. One electrode is placed into the spinning solution and the other attached to the collector. In most cases, the collector is simply grounded. The electric field is subjected to the end of the capillary tube that contains the solution fluid held by its surface tension. This induces a charge on the surface of the liquid. Mutual charge repulsion and the contraction of the surface charges to the counter electrode cause a force directly opposite to the surface tension. As the voltage is increased the effect of the electric field becomes more prominent and as it approaches exerting a similar amount of force on the droplet as the surface tension does a cone (Taylor cone) as shown in Figure 2 shape begins to form with convex sides and a rounded tip. Further increasing the electric field, a critical value is attained with which the repulsive electrostatic force overcomes the surface tension and the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to become very long and thin. Meanwhile, the solvent evaporates, leaving behind a charged polymer fiber.

![Fig 2. Taylor cone](image)

3. PARAMETERS INVESTIGATION IN ELECTROSPINNING

It has been well established that both operating parameters and material properties affect the electrospinning process and the resulting fibre morphology. The operating parameters include the applied electrical field, the flow rate of the polymer solution, the distance between the tip and the collecting screen (spinning distance) and capillary tip diameter. A minute change in the operating parameters can lead to a considerable change in the fibre morphology. For example, finer nanofibres are electrospun from a nozzle of smaller diameter (Katti et al 2004); increasing the flow rate leads to larger fibre diameter; and a higher applied voltage results in the emergence of fibre beads, though reducing the fibre diameter (Deitzel et al 2001. Lee et al, 2004). The material properties that affect the electrospinning process and the fibre morphology include the polymer concentration, the solution viscosity, the solution conductivity, the surface tension and other properties concerning the solvent as well as the polymer itself. Among the material properties, the solution concentration plays a most important role in stabilizing the fibrous structure because it also affects other solution properties, such as the solution viscosity, the surface tension and the conductivity. The solvent used is another important factor because it mainly determines the surface tension and the evaporation process. The volatility of the solvent affects the fibre surface morphology and the nanomembrane structure.

The solution bulk properties come from intermolecular interactions among the solvent molecules and the polymer macromolecules. Any factors that interfere with these interactions change the solution properties that affect the electrospinning process, and the fibre morphology is thus altered accordingly. For example, the solution viscosity is closely related to the entanglement of polymer macromolecules, in a good solvent, polymer chains with a higher molecular weight tangle with each other more easily, which leads to higher solution viscosity. Electrospinning such a polymer solution produces continuous and uniform fibres. However, when polymer of a low molecular weight is electrospun, even at the same polymer concentration, the resultant fibre could have a colloid bead or beaded fibre morphology (Koski et al 2003).

One of the most important quantities related with electrospinning is the fiber diameter. Since nanofibers are resulted from evaporation or solidification of polymer fluid jets, the fiber diameters will depend primarily on the jet sizes as well as on the polymer contents in the jets. It has been recognized that during the traveling of a solution jet from the pipette onto the metal collector, the primary jet may or may not be split into multiple jets, resulting in different fiber diameters (Figure. 3).
As long as no splitting is involved, one of the most significant parameters influencing the fiber diameter is the solution viscosity. A higher viscosity results in a larger fiber diameter. However, when a solid polymer is dissolved in a solvent, the solution viscosity is proportional to the polymer concentration. Thus, the higher the polymer concentration the larger the resulting nanofiber diameters will be. In fact, Deitzel et al (2001) pointed out that the fiber diameter increased with increasing polymer concentration according to a power law relationship. Demir et al (2002) found that the fiber diameter was proportional to the cube of the polymer concentration. Another parameter which affects the fiber diameter to a remarkable extent is the applied electrical voltage. In general, a higher applied voltage ejects more fluid in a jet, resulting in a larger fiber diameter.

Further challenge with current electrospinning lies in the fact that the fiber diameters obtained are seldom uniform. Not many reports have been given towards resolving this problem. Another problem encountered in electrospinning is that defects such as beads Figure 4, and pores Figure 3 may occur in polymer nanofibers. It has been found that the polymer concentration also affects the formation of the beads.

### 3.1 Polymer Solution Concentration

As the polymer solution concentration plays a major role in the electrospinning process, it is not surprising that the polymer solution concentration has been extensively exploited to change and control fibre morphology in electrospinning. Under the same electropinning conditions, increasing the polymer concentration will increase the diameter of the electrospun fibres. However, a non-linear relationship between the solution concentration and the fibre diameter usually forms (Deitzel et al 2001). The reason for this non-linear relationship can be attributed to the non-linear relationship between the polymer solution concentration and the solution viscosity. As the polymer solution concentration increases, the viscosity increases gradually until the concentration reaches a specific value, after which the viscosity increases considerably (Lin et al 2004).

In the electrospinning process, the solvent evaporates from the jet/filament continuously until the jet becomes dry. Stretching the jet increases the surface area, which accelerates the solvent evaporation. From the initial jet to dry fibres, the fibre stretching process is quick, taking only tens of milliseconds (Shin et al 2001). If the strength of the stretch filaments remains the same, electrospinning a polymer solution of higher velocity could be much harder than that with a lower viscosity, because the concentration has a larger influence on the viscosity when the concentration is high. On the other hand the polymer solution concentration affects the solution conductivity, which further influences the solution charge density. This could compensate to some extent for the difficulty in stretching a solution of high polymer solution concentration. In certain cases, the strength is improved to such an extent that it neutralizes the effect of the viscosity, which results in a similarly linear relationship between the concentration and the fibre diameter. The relationship between the solution viscosity and the polymer concentration is highly dependent on the nature of the polymer and the intermolecular interactions within the polymer solution. Although reducing the polymer concentration is a straightforward way to produce finer nanofibres, electrospinning a dilute polymer solution usually leads to the emergence of colloid beads. These defective even become the main products when the polymer concentration is very low. Because of this, the electrospinning of bead-free and uniform nanofibres particularly for the fibre diameters less than 100 nm still remains a great challenge.

Generally, when a polymer of higher molecular
weight is dissolved in a solvent, its viscosity will be higher than solution of the same polymer but of a lower molecular weight. One of the conditions necessary for electrospinning to occur where fibers are formed is that the solution must consists of polymer of sufficient molecular weight and the solution must be of sufficient viscosity. As the jet leaves the needle tip during electrosprining, the polymer solution is stretched as it travels towards the collection plate. 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, monomeric polymer solution does not form fibers when electrospun (Buchko et al 1999).

The polymer chain entanglements were found to have a significant impact on whether the electrospinning jet breaks up into small droplets or whether resultant electrospun fibers contain beads (Shenoy et al 2005). Although a minimum amount of polymer chain entanglements and thus, viscosity is necessary for electrospinning, a viscosity that is too high will make it very difficult to pump the solution through the syringe needle (Kameoka et al 2003). Moreover, when the viscosity is too high, the solution may dries at the tip of the needle before electrosprinning can be initiated (Zhong et al 2002). Many experiments have shown that a minimum viscosity for each polymer solution is required to yield fibers without beads (Fong et al 1999). At a low viscosity, it is common to find beads along the fibers deposited on the collection plate. At a lower viscosity, the higher amount of solvent molecules and fewer chain entanglements will mean that surface tension has a dominant influence on the jet causing beads to form along the fiber. When the viscosity is increased which means that there is a higher amount of polymer chains entanglement in the solution, the charges on the electrosprinning jet will be able to fully stretch the solution with the solvent molecules distributed among the polymer chains. With increased viscosity, the diameter of the fiber also increases (Jarusuwannapoom et al 2005). This is probably due to the greater resistance of the solution to be stretched by the charges on the jet.

3.2 Applied Voltage

A crucial element in electrospinning is the application of a high voltage to the polymer solution. The high voltage will induce the necessary charges to the solution and together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution. Generally, both high negative or positive voltage of more than 6kV is able to cause the solution drop at the tip of the needle to distort into the shape of a Taylor Cone during jet initiation (Taylor 1964). Depending on the feedrate of the solution, a higher voltage may be required so that the Taylor Cone is stable. The columnic repulsive force in the jet will then stretch the viscoelastic solution. If the applied voltage is higher, the greater amount of charges will cause the jet to accelerate faster and more volume of solution will be drawn from the tip of the needle. This may result in a smaller and less stable Taylor Cone (Zhong et al 2002). When the drawing of the solution to the collection plate is faster than the supply from the source, the Taylor Cone may recede into the needle (Deitzel et al 2001).

As both the voltage supplied and the resultant electric field have an influence in the stretching and the acceleration of the jet, they will have an influence on the morphology of the fibers obtained. In most cases, a higher voltage will lead to greater stretching of the solution due to the greater columnic forces in the jet as well as the stronger electric field. These have the effect of reducing the diameter of the fibers (Lee et al 2004) and also encourage faster solvent evaporation to yield drier fibers (Pawlowski et al 2005). When a solution of lower viscosity is used, a higher voltage may favor the formation of secondary jets during electrospinning. This has the effect of reducing the fiber diameter (Demir et al 2002). Another factor that may influence the diameter of the fiber is the flight time of the electrosprinning jet. A longer flight time will allow more time for the fibers to stretch and elongate before it is deposited on the collection plate. Thus, at a lower voltage, the reduced acceleration of the jet and the weaker electric field may increase the flight time of the electrosprinning jet which may favor the formation of finer fibers. In this case, a voltage close to the critical voltage for electrospinning may be favorable to obtain finer fibers (Zhao et al 2004). At a higher voltage, it was found that there is a greater tendency for beads formation (Zhong et al 2002). The increased in beads density due to increased voltage may be the result of increased instability of the jet as the Taylor Cone recedes into the syringe needle. In an interesting observation, Krishnappa et al (2002) reported that increasing voltage will increased the beads density, which at an even higher voltage; the beads will join to form a thicker diameter fiber. The effect of high voltage is not only on the physical appearance of the fiber, it also affects the crystallility of the polymer fiber.
The electrostatic field may cause the polymer molecules to be more ordered during electrospinning thus induces a greater crystallinity in the fiber. However, above a certain voltage, the crystallinity of the fiber is reduced. With increased voltage, the acceleration of the fibers also increases. This reduces the flight time of the electrospinning jet. Since the orientation of the polymer molecules will take some time, the reduced flight time means that the fibers will be deposited before the polymer molecules have sufficient time to align itself. Thus, given sufficient flight time, the crystallinity of the fiber will improve with higher voltage (Zhao et al 2004).

3.3 Capillary Tip Collector Distance

The gap distance between the capillary tip and the collector influences the fiber deposition time, the evaporation rate, and the whipping or instability interval, which subsequently affect the fiber characteristics. In several cases, the flight time as well as the electric field strength will affect the electrospinning process and the resultant fibers. Varying the distance between the tip and the collector will have a direct influence in both the flight time and the electric field strength. For independent fibers to form, the electrospinning jet must be allowed time for most of the solvents to be evaporated. When the distance between the tip and the collector is reduced, the jet will have a shorter distance to travel before it reaches the collector plate. Moreover, the electric field strength will also increase at the same time and this will increase the acceleration of the jet to the collector. As a result, there may not have enough time for the solvents to evaporate when it hits the collector. When the distance is too low, excess solvent may cause the fibers to merge where they contact to form junctions resulting in inter and intra layer bonding (Buchko et al 1999). Depending on the solution property, the effect of varying the distance may or may not have a significant effect on the fiber morphology. In some cases, changing the distance has no significant effect on the fiber diameter.

However, beads were observed to form when distance was too low (Megelski et al 2002). The formation of beads may be the result of increased field strength between the needle tip and the collector. Decreasing the distance has the same effect as increasing the voltage supplied and this will cause an increased in the field strength. As mentioned earlier, if the field strength is too high, the increased instability of the jet may encourage beads formation. However, if the distance is such that the field strength is at an optimal value, there is less beads formed as the electrostatic field provides sufficient stretching force to the jet (Jarusuwannapoom et al 2005). In other circumstances, increasing the distance results in a decrease in the average fiber diameter (Ayutsede et al 2005). The longer distance means that there is a longer flight time for the solution to be stretched before it is deposited on the collector. However, there are cases where at a longer distance, the fiber diameter increases. This is due to the decrease in the electrostatic field strength resulting in less stretching of the fibers (Lee et al 2004). When the distance is too large, no fibers are deposited on the collector. Therefore, it seems that there is an optimal electrostatic field strength below which the stretching of the solution will decrease resulting in increased fiber diameters.

3.4 Flow Rate

Megelski et al (2002) found that the flow rate of polymer solution affects the jet velocity and the material transfer rate with enhanced pore, fiber sizes and beaded structures, as well with an increase in the polymer flow rate in case of polystyrene fibers. For a given voltage, there is a corresponding flow rate if a stable Taylor cone is to be maintained. When the flow rate is increased, there is a corresponding increase in the fiber diameter or beads size. This is apparent as there is a greater volume of solution that is drawn away from the needle tip (Rutledge et al 2000).

If the flow rate is at the same rate which the solution is carried away by the electrospinning jet, there must be a corresponding increased in charges when the flow rate is increased. Thus there is a corresponding increased in the stretching of the solution which counters the increased diameter due to increased volume. Due to the greater volume of solution drawn from the needle tip, the jet will takes a longer time to dry. As a result, the solvents in the deposited fibers may not have enough time to evaporate given the same flight time. The residual solvents may cause the fibers to fuse together where they make contact forming webs. A lower flow rate is more desirable as the solvent will have more time for evaporation (Yuan et. al. 2004).

3.5 Diameter of Pipette Orifice Needle

The internal diameter of the needle or the pipette orifice has a certain effect on the electrospinning process. A smaller internal diameter was found to reduce the clogging as well as the amount of beads on the electrospun fibers (Mao et al 2004). The
reduction in the clogging could be due to less exposure of the solution to the atmosphere during electrospinning. Decrease in the internal diameter of the orifice was also found to cause a reduction in the diameter of the electrospun fibers. When the size of the droplet at the tip of the orifice is decreased, such as in the case of a smaller internal diameter of the orifice, the surface tension of the droplet increases. For the same voltage supplied, a greater cumbic force is required to cause jet initiation. As a result, the acceleration of the jet decreases and this allows more time for the solution to be stretched and elongated before it is collected. However, if the diameter of the orifice is too small, it may not be possible to extrude a droplet of solution at the tip of the orifice (Zhao et al 2004).

4. Working principle

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. As shown in Figure 1.1a), the droplet is under the influence of two forces, viz. 1) the disintegrative electrostatic repulsive force and 2) the surface tension that strives to hold the droplet within a spherical shape. At equilibrium, the two forces completely balance each other, as is depicted by:

\[
\frac{1}{\varepsilon \sigma_0} \frac{Q^2}{R^2} = 8 \pi \sigma
\]

(1.1)

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 the surface tension coefficient. 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 then the droplet disintegrates and leads to the formation of smaller droplets [Fig. 5b]. This process is termed as electrospraying and has been utilized extensively for automotive spray painting.

If this concept is extended to a solution of high molecular weight polymer solution that has sufficient chain entanglements, then instead of the formation of the droplets, a steady jet is formed that later solidifies in a polymer filament. Thus, the fundamental principle underlying the fiber formation by electrospinning can be stated as follows: a high electric potential is applied to a polymer solution (or melt) suspended from the end of the spinneret that imparts an electrostatic charge to the polymer solution. At low electric potentials, the disintegrative electrostatic repulsive forces that primarily reside on the liquid surface are balanced by the surface tension. At high electric potentials, the electrostatic repulsive force at the surface of the fluid overcomes the surface tension that results in the ejection of a charged jet. The jet extends in a straight line for a certain distance, and then bends and follows a looping and spiraling path. The electrostatic repulsion forces can elongate the jet to several thousand times leading to the formation of very thin jet. When the solvent evaporates, solidified polymer filaments are collected on a grounded target (or a winder) in the form of a non-woven fabric. The small diameter provides a large surface to volume ratio that makes these electrospun fabrics interesting candidates for a number of applications including membranes, tissue scaffolding and other biomedical applications, reinforcement in composites and nanoelectronics. In the following sections, a review of the literature will be provided that will discuss the early attempts at electrospinning, the process of fiber formation.

Literature Review

The electrical forces on free charges residing on the surface of a polymeric liquid are primarily
responsible for driving the electrospinning process. In conventional spinning processes like melt or solution spinning, the fiber is subjected to tensile, rheological, gravitational, inertial and aerodynamic forces. The action of these forces has been described in detail by Ziabicki. In electrospinning, the tensile force is provided by the repulsion of like charges on the surface of the polymer jet. The principle of electrospinning finds similarities to electrostatic spraying. In fact, the electrostatic spray literature provides many insights into the electrospinning process and will be discussed in the next section.

Historical Background

The behavior of electrically driven jets and the stability of electrically charged liquid drops have been of interest for many years. In 1745, Bose created an aerosol spray by applying a high potential to a liquid at the end of a glass capillary tube. Lord Raleigh also studied the instabilities that occur in electrically charged liquid droplets. He calculated the maximum amount of charge that a drop of liquid can maintain before the electrical forces overcame the surface tension of the drop and led to the creation of a jet. Zeleny studied the role of the surface instability in electrical discharges from charged droplets. His findings showed that the theoretical relations for instability were satisfied when the discharge of the jet began.

Vonnegut and Neubauer generated uniform streams of highly charged droplets with diameters around 0.1 mm. Their experiments proved that monodisperse aerosols with a particle radius of a micron or less could be produced from the pendant droplet at the end of a pipette. In the 1960s, Taylor analyzed the conditions at the point of a droplet that was deformed by an electric field in a conical geometry. He identified the critical electrical potential for an electrostatic formation of a cone of liquid (now known as a Taylor cone) at the end of a capillary tube. The conducting drop was supposed to be surrounded by air and suspended in a stable position from the capillary tube. By examining a range of low molecular weight fluids, Taylor concluded that the conical interface between air and the fluid was stable at the semi-angle conical angle of 49.3°. However, it was shown that conductivity and viscosity both play an important role in the electrostatic atomization process which then influence the equilibrium angle and other aspects of the process. Taylor cones are considered to be important to electrospinning as they define the onset of extensional velocity gradients in the fiber formation process.

Review of the Early Attempts on Electrospinning

There is a precedent for the application of electrostatic atomization or spraying to polymeric solutions in the patent and academic literature. The electrospinning of fibers dates back to 1938 when Formhals invented the electrostatic apparatus. As shown in Figure 6, the spinning solution was discharged using a high electric field from an electrode of negative polarity. The fine filaments were attracted towards the movable electrode that was at a positive polarity. A stripping device facilitated the removal of fibers in the form of a fibrous sliver. A major drawback of such a setup was the difficulty to remove the fine fibers that adhered to the moving parts of the collecting belts, drums, wheels etc. Formhals formed fibers from a solution of cellulose acetate in ethylene glycol at a potential difference of 57kV.

In 1966, Simons invented a process to produce a patterned non-woven fabric by electrospinning that was collected on a segmented receiver. The segmented receiver had two sets of segments such that one of the sets was at a different potential than the other causing the preferential deposition of fibers leading to a patterned fabric that had regions of low and high fiber density. Filaments were electrospun from a solution of polyurethane in methyl ethyl ketone having a viscosity in the range of 100 to 3000 centipoise. In a different process, Isakoff devised a process to prepare fibrous sheets of organic synthetic polymers in which a filamentary web of fibers were electrostatically charged before being collected on a grounded movable surface. Fibers were electrically charged after they were formed by conventional solution spinning to facilitate their passage in a controlled trajectory.
Utilizing a different geometry of the electrospinning apparatus, Fine et al. electrospun a thermoplastic elastomer where a cup-like apparatus contained the charged polymer solution that rotated about its vertical axis. The centrifugal forces pushed the polymer solution to the edge of the cup and into the ambient air. The presence of an electrical field caused the formation of a jet that was attracted to a grounded movable aluminum screen that was driven slowly around the rollers in the form of a belt. The combined action of electrostatic and centrifugal forces led to the formation of high strength fibrous sheets. Instead of placing the polymer solution in a cup, Guignard utilized another movable belt that carried the charged molten polymer. Here, two movable belts were used, as shown in Figure 7. As one of the belts, which carried the charged molten polymer, approached the grounded belt, formation of several jets from the surface of the exposed melt took place. These jets traveled towards the grounded collector belt and got deposited in the form of short filaments on the grounded belt.

In a different study, in 1977 Martin et al. extended the concepts of single component electrospinning to electrospin a mat of organic fibers from a liquid containing a ‘plurality of components’ from a single nozzle/syringe. They were also able to electrospin polymeric solutions having different compositions (blends) simultaneously from multiple nozzles/syringes. Collectors were either a stationary metal screen or a movable belt. The patent claimed the mat to be composed of fibers of a high molecular weight thermoplastic polymer based either on a fluorinated hydrocarbon, a silicone or an urea/formaldehyde. The resulting mats were flexible, non-absorbent, porous, and hydrophobic. These were suggested to be used as a wound dressing and as a lining for a prosthetic device.
In 1982, Bornat conducted simultaneous electrospinning by using several nozzles/syringes to form fibers. As shown in Figure 8, 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. The syringes were kept at a ground potential whereas an electrical potential of \(-50\) kV was applied to the collector. The electrostatic forces caused the formation of jets that were attracted towards the rotating collector. Solidified polymer filaments of poly(tetrafluoroethylene) and poly(ethylene oxide) (electrospun simultaneously) were wound on the rotating collector in this fashion to form a tubular product. The tubular products were suggested to find applications as synthetic blood vessels and urinary ducts.

Utilizing a slightly different approach, Simm et al. were able to fabricate a composite filter based on electrospun fibers. They invented a process for the production of fiber filters in which a solution of polystyrene in methylene chloride was electrospun from an annular electrode onto two equidistant collector electrodes in the form of movable belts. The collector electrodes were already covered with a layer of cellulose fibers produced by conventional spinning methods. Thus, a composite filter that had electrospun polystyrene fibers on top of a layer of cellulose fleece was fabricated.

More recently, in 2000, Scardino et al. have patented a process to make a hybrid/composite yarn. The electrospun fibers having diameters ranging from 0.4 nm to 1 nm were suctioned into an air vortex and then combined with a carrier filament(s) (obtained from conventional spinning techniques) to form nonwoven or linear (yarns) assemblies. The yarns were later utilized for weaving, braiding or knitting fabrics. Utilizing the similar approach to make composite fibrous mats, Zarkoob et al. patented a process to produce silk nanofibers and silk nanofiber composites utilizing electrospinning. The electrospinning principles utilized were very similar to those mentioned above with some differences in the engineering details of the apparatus.

In a detailed study in 1971, Baumgarten studied the relationships between fiber diameter, jet length, solution viscosity, flow rate of the solution and the composition of the surrounding gas. He investigated the electrospinning of acrylic nanofibers where fibers less than a micron in diameter were reported. In 1981, Lorondo and Manley not only studied the effect of some of the parameters on fiber formation but also conducted some characterization studies on fibers of poly(ethylene) and poly(propylene) 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.

After a brief gap of a decade and a half, Reneker and his coworkers revived interest in electrospinning. In 1995, Doshi and Reneker studied the effect of several process parameters on fiber formation of poly(ethylene oxide) (PEO) fibers. 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.

5. Electrospinning Process Considerations

5.1 Schematic of the Electrospinning Process

Most of the studies conducted to date have electrospun polymer solutions or melts in air (ambient conditions), although a study where electrospinning was conducted in vacuum has also been reported. As shown in Figure 9, a typical experimental setup of the electrospinning process consists of a syringe-like apparatus that contains the polymer solution. The narrow end of the syringe is connected to a capillary, e.g. glass or Teflon. A platinum electrode dipped in the polymer solution is connected to a high voltage DC supply. When the high voltage DC supply is turned on, the electrode imparts an electrical charge to the polymer solution. As mentioned previously, a jet is ejected from the suspended liquid meniscus at the capillary-end when the applied electric field strength overcomes the surface tension of the liquid. Near the critical point, where the electric field strength is about to overcome the surface tension of the fluid, the free surface of the suspended drop changes to a Taylor cone, as described earlier. The jet is ejected from the tip of this Taylor cone as the electric field strength is increased. When this idea is extended to polymer solutions or melts, solidified polymer filaments are obtained on the grounded target as the jet dries. Typical operating conditions are: internal diameter of the capillary-end is usually 0.7 – 1mm, flow rates of 3-10 ml/h are commonly employed at a potential drop of 5 – 20 KV and distances of 10 – 30 cm between the capillary-end and target. The target or the collector screen can be at a ground potential or be kept at a polarity opposite to that of the polymer solution. Different types, shapes and sizes of target have been utilized. Also, the target could be kept stationary or be movable. It can also be rotated about its axis to produce a mat that has a preferential alignment of fibers along a specific direction. However, the degree of molecular orientation in a fiber spun from a solution of a polymer (in particular an amorphous system) is not generally high. This is due to the high molecular mobility in fibers containing solvents (chain relaxation is often faster than the time it takes for the solvent to evaporate completely from the fiber before the onset of Tg restricts any further orientation loss).

5.2 Process of Fiber Formation

The electrospinning process has three stages: a) initiation of the jet and the extension of the jet along a straight line; b) the growth of a bending instability and further elongation or drawing of the
jet that allows it to move in a looping and spiraling path; c) solidification of the jet into nanofibers. In the next three sections, these three stages will be described following which various mathematical models that have offered to quantify the jet behavior will be briefly outlined.

5.2.1 Initiation of the jet

In a typical electrospinning apparatus, the polymer solution is contained in a syringe or a glass capillary. One of the electrodes is dipped in the polymer solution whereas the other acts as the collector target that is kept at a certain distance from the syringe (hence, not immersed in the solution). When an electric field is applied to a polymer solution, ions in the solution aggregate around the electrode of opposite polarity. This results in the build-up of an excess of ions of oppositely charged polarity near an electrode. For instance, if a positive electrode is dipped in the polymer solution, then the negative ions migrate towards the anode but the positive ions aggregate at the tip of the capillary leading to a charge build-up. Thus, the region of interest is the solution near the tip of the capillary where these excess charges aggregate at the surface of the suspended liquid/solution drop. The shape of the meniscus of the suspended polymer droplet is defined by the balance of hydrostatic pressure, electrical forces and, surface tension. In weak fields, the polymer solution is held at the end of the capillary by surface tension. When the electric field increases, the meniscus elongates to form a conical configuration (Taylor Cone), until at some critical value of the electric field, surface tension can no longer balance the hydrostatic and electric forces and a thin jet is ejected from the meniscus. This ejected jet travels toward the nearest electrode of opposite polarity, or electrical ground. It is believed that excess charge is essentially static with respect to the moving coordinate system of the jet. This means that the electrospinning jet can be essentially thought of as a string of charged elements connected by a viscoelastic medium, with one end fixed at a point of origin and the other end free.

Doshi and Reneker were able to measure the jet diameter as a function of distance from the apex of the cone by laser light diffraction. For a 4wt % PEO solution in water electrospun at a electric field strength of 0.4 kV/cm, the jet diameter was observed to decrease with increasing distance. The jet diameter decreased by a factor of 5 (from 90 µm to about 18 µm) at a distance of 10 mm from the tip of the cone. Taking the solvent (water) evaporation into account, this indicated a large amount of stretching of polymer chains in the jet. With the aid of high-speed photography, Fong and Reneker measured jet diameters in the range of 20 – 100 µm for a 3wt% PEO solution in water electrospun at electric field strength of 0.5kV/cm. The polymer solution was electrospun through a hole of 300 µm in the bottom of a metal spoon. It was found that when the semi-vertex conical angle was 22.5°, the electric force was high enough to overcome both the surface tension and viscoelastic forces and as a result, a jet was ejected. After the initiation of the jet, the conical protrusion relaxed to a steady rounded shape in a few milliseconds. At times, the shape of the conical protrusion and jet current pulsed even though the applied field strength was constant. A steady current was associated with the cone that had a constant shape.

5.2.2 Growth of the Bending Instability and Further Elongation of the Jet

In a detailed study, Reneker and coworkers observed the path of the jet. After initiation, the jet traveled in a straight line for some distance (typically 2-3 cm). It was hypothesized that an electrically driven instability triggered by the perturbations of the lateral position and lateral velocity of the jet caused it to follow a bending, winding, spiraling and looping path in three dimensions. As shown in Figure 10, high-speed photographs taken at 2000 frames per second demonstrated that the jet in each loop became longer and thinner as the loop diameter and circumference increased. After some time, the segments of the thinner smoothly curved loop developed a new instability similar to, but at a comparatively smaller
Figure 10. High speed photography results on electrospun 6 wt % PEO (400,000 MW) in 60 % Water & 40 % Ethanol & 1kV/cm. The jet initiation is at the bottom right of every frame.

Scale, than the first. The new bending instabilities continued to grow in a similar fashion that caused the jet to spiral around the path of the first loop. The process of promoting the bending instability repeated in a self-similar manner as the polymer jet dried into a solidified filament. These were collected on the target that was kept at an attractive potential. Rutledge et al. also confirmed these observations by utilizing similar high-speed photography experiments. The bending instability of the rapidly moving jet was referred to as the ‘whipping jet’, where each self-similar repetition of bending instability, as described by Reneker and coworkers has been termed as a ‘whipping’ process. The spatial dimensions of the whipping periodicity was found to be significantly greater than the radius of the jet, so that when the jet is observed with a naked eye (30-40 frames/second) the jet appears to be splaying into multiple filaments, a hypothesis that was widely accepted.

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5.2.3 Solidification of the Jet into a Polymer Filament

As the rapidly ‘whipping’ jet moved towards the target maintained at an attractive potential, it continued to expand into a spiraling and looping path. This process continued until the jet became fairly thin and was intercepted by the target. As can be premised, the greater the distance the jet travels, the thinner it becomes. Thus, the distance between the capillary-end and the target is one process parameter that has direct implications on the fiber diameter. In fact, other process parameters include the flow rate, concentration, and electric field strength, to name a few.

5.3 Effect of System and Process Parameters on Electrospun Fiber Diameter

The following system and process parameters have been noted to affect the fiber diameter:

System Parameters:

- Viscosity
- Concentration
• Net charge density (conductivity)
• Surface tension of the polymer fluid.
• Molecular weight
• Molecular weight distribution
• Topology (branched, linear etc.) of the polymer.

Process Parameters:
• Electric potential
• Flow rate of the polymer solution
• Distance between the capillary-end and target/collection screen
• Ambient parameters (temperature, humidity and air velocity in the chamber)
• Motion of target screen
• Internal diameter of the nozzle/capillary

As discussed earlier, an electrically driven jet of low molecular weight liquid would form droplets, a phenomenon more commonly referred as electrospraying. The formation of such droplets was reported to be due to the capillary breakup of the jet by surface tension. In the case of polymer solutions, the pattern of capillary breakup is quite different. Instead of a complete breakup of the jet in response to the capillary instability, the jet between the droplets forms a nanofiber and the contraction of the radius of the jet, which is driven by surface tension, causes the remaining solution to form a bead.

6. Concluding remarks
In the preceding sections a brief introduction to the underlying principles of electrospinning were provided. In addition, a literature review that discussed the early attempts at electrospinning, the process of fiber formation, were discussed in some detail. The ability to produce high specific surface fibers by electrospinning has generated significant interest in the scientific community in the last ten years. As a result, researchers have been working in making novel structures based on electrospun fibers that find applications in numerous areas, viz., membranes, filtration, protective clothing, optical and electronic devices biomedical applications including tissue scaffolds and reinforcement in composites. Electrospun nanomembrane is a good wound dressing candidate because of its unique properties. Various types of polymers are produced into electrospun nanomembranes for wound care dressings applications. Drug can also incorporated in the electrospun nanomembrane for sustain delivery on the wound, several drug deliver electrospun nanomembrane wound care were also developed.

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