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Polyethylene Oxide Nanofiber Production by Electrospinning

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Running title: Electrospun Polyethlyene Oxide Nanofibers

Abstract

Electrospinning is an inexpensive technique that is used to produce nanofibers for a variety of applications. In electrospinning, a polymer solution is dispensed from a hypodermic-like syringe where an intense electric field attracts the solution to a collector while drawing the polymer into a very thin fiber. The diameter of the fiber can be controlled by tuning the process parameters such as the applied electric field, solution flow rate, distance between syringe tip and collector, and the collector geometry. In this paper we describe results from electrospinning poly(ethylene oxide) (PEO), a likely candidate for applications involving scaffolding for tissue engineering. The PEO nanofibers were fabricated from different polymer solution concentrations ranging from 14% - 22% (by weight). Each sample was then imaged using a scanning electron microscope. The morphology of the fibers produced from varying solution concentrations is discussed.

Introduction

Electrospinning is an inexpensive technique that can be used to produce nanofibers from a variety of different material systems. With the nanofibers' high surface area to volume ratio, they have shown great promise in applications ranging from filtration systems (Kosmider and Scott 2002), catalysis (Demir et al. 2004), energy harvesting (Chang et al. 2012), and biomedical engineering (Fang et al. 2008). One exciting example is the potential to use electrospun nanofibers as scaffolding for tissue engineering applications. In order for these nanofibers to be used as scaffolding they must meet several requirements; namely, they must be porous to promote the growth of living cell tissue, exhibit adequate structural integrity, and they should be biocompatible so that it is not toxic to living cells (Ma 2004). Poly(ethylene oxide) (PEO) is a biocompatible, porous material that is an excellent candidate for enzymes as chemical catalysts (Xie and Hsieh 2003) and scaffolding for tissue engineering applications (Subramanian et al. 2012).

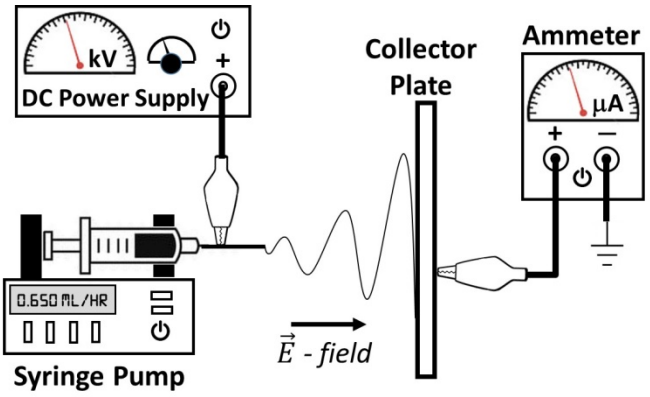

Figure 1. An illustration an electrospinning apparatus consisting of a solution dispensing system, high voltage power supply and collector plate.

Electrospinning is a technique that can be used to produce fibers ranging in diameter from tens of nanometers to several microns (Beachley and Wen 2009). Although electrospinning systems can vary depending on the application, all systems contain the same fundamental components. Figure 1 is an illustration of an electrospinning apparatus consisting of three integral parts: a solution dispensing system, high voltage power supply, and a grounded collector. The solution dispensing part of the electrospinning apparatus is composed of a syringe filled with the polymer solution of interest. Connected to the syringe is a metallic hypodermic needle, often referred to as a spinneret. The spinneret serves two purposes: one is to provide a surface from which the solution will form a drop that will eventually be pulled out into a fiber, and secondly the spinneret provides an electrical connection which is used to transfer charge to the

surface of the solution. For most applications the spinneret has a simple uniaxial geometry, however it is possible to use coaxial or even triaxial spinnerets to produce nanofibers that have core-sheath structures (Sun et al. 2003). The syringe-spinneret assembly is loaded into a syringe pumping system that allows for precise control of the flow of the solution out of the spinneret. Connected to the spinneret is a high voltage DC power supply. The power supply is used to impart charge to the solution and orient the electric field which is required for the electrospinning process. The final component of the system is a collector plate. The collector plate is used to collect the randomly oriented nanofiber samples as well as providing an electrical connection to ground. In Figure 1, a simple flat plate collector is shown, however it is possible to use more complicated collector geometries in order to produce aligned nanofibers (Li et al. 2003). One of the most common examples is a rotating drum geometry that consists of a metal cylinder that is rotating about its axis (Katta et al. 2004). By translating the drum or the spinneret back and forth while the drum is rotating it is possible to form nanofibers that exhibit a high degree of alignment. Connected in series to the collector plate is a digital ammeter that is used to measure the collector current. Under standard electrospinning conditions, the collector current typically measures in the tens of micro-amps, however the magnitude of the current is not as useful as the stability of the measurement. When the current measurement is relatively stable this indicates that the apparatus is producing fibers at a steady rate.

In this paper, our objective is to study fiber formation and morphology as it relates to the PEO solution concentration.

Materials and Methods

Electrospun poly(ethylene oxide) (PEO) fibers were produced by first dissolving PEO powder (having a molecular weight of 100,000 g/mol) purchased from Sigma-Aldrich in distilled water. Aqueous solutions ranging in concentration from 1% to 22% (by weight) were prepared. Each solution was then stirred overnight at room temperature using a magnetic stirring plate to ensure a homogenous solution. The solution being tested was then poured into a 10 mL syringe that was attached to a 21 gauge (diameter of 0.8 mm) stainless steel needle via a standard 1/8" polyvinyllidene fluoride (PVDF) tubing. The syringe was then loaded into a model NE-1000 Multi-Phaser™ programmable syringe pump. The pumping rate was programmed to be between 0.55 – 0.65 ml/hr. This pumping speed was such that when a small droplet would form at the tip of the syringe and wiped away, it was quickly replaced with a new droplet as a result of the pumping speed. An Acopian High Voltage power supply was used to provide positive DC power, ranging from 2-20 kV, to the syringe. The high voltage power supply was current limited to around 2mA. To accurately measure the syringe voltage, a Vitrek 4700 precision high voltage meter (accurate to within 0.35% of voltage reading) was incorporated into the experimental setup by attaching a metal alligator style clip directly to the syringe and then connecting the clip to the voltage meter via high voltage wire. Randomly oriented fibers were collected using an electrically grounded stainless steel flat collector plate (145 mm × 230 mm × 1 mm). For each experiment, the collector plate was wrapped with a single layer of aluminum foil in order to easily collect and transport samples for microscopy as well as ensuring an electrical connection to ground.

In order to study the effect of PEO solution concentration on fiber formation, desired solutions were loaded into the syringe and placed into the syringe pump and an appropriate pumping speed was set corresponding to 0.55 – 0.65 mL/hr. The collector plate was then placed 10-12 cm from the end of the syringe. To observe the initiation of jet formation, a Hovercam Solo 8 high magnification, 4k resolution, long working-distance CCD based document camera was placed over the tip of the syringe. Care was taken to ensure that the distance the camera was located relative to the syringe was great enough to not disturb the electric field generated at the syringe tip. Next, high voltage DC power was supplied to the syringe and slowly increased until a stable jet was observed. After stability was established by monitoring the collector current, the high voltage power supply was turned off and a fresh layer of aluminum foil was placed on the collector plate. The power was then turned on and samples were collected for 5 minutes. Each solution was tested under ambient conditions. In order to ensure similar conditions the room temperature and humidity levels were recorded for each sample and the ambient temperatures were within ± 2 ºC and humidity levels were within ± 5% of each process run.

Each sample was stored in a climate controlled environment for at least 24 hours to ensure adequate drying of the fibers. The samples were then imaged using a Phenom Scanning Electron Microscope (SEM) at the University of Arkansas – Pine Bluff Advanced Physics Lab facility. Multiple images were taken for

each sample. The samples were imaged without adding a metallic sputter coating.

Results

Characteristic SEM images for three successively higher solution concentrations (14%, 18%, and 22% respectively) are shown in Figures 2a, 2b and 2c. Each of these images measures 45μm × 45μm and are cropped from debris free areas. Fibers were spun for concentrations ranging from 14% to 22%. Attempts were made to produce fibers from concentrations below 14% however, fibers formation was not observed for these samples. Also, attempts were made to spin fibers from concentrations above 22% however, above this concentration the solution was too viscous to stir to ensure a homogenous solution. The 14% concentration image in Figure 2a shows the onset of fiber formation. The image also reveals several small spherical polymer beads. Figures 2b and 2c show significant fiber formation with the density of fibers being larger in 2b and smaller in 2c. Additionally the fibers shown in figure 2c are larger in diameter when compared to those shown in Figures 2a and 2b.

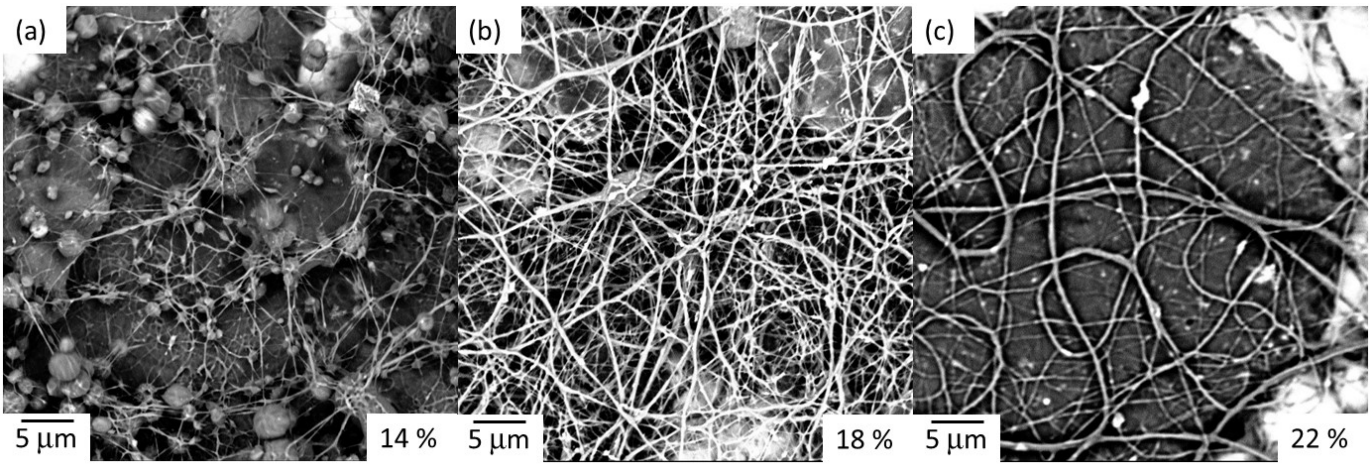

Figure 2. SEM images (45μm × 45 μm) of electrospun fibers produced from three different PEO solution concentrations (a) 14%, (b) 18%, and (c) 22%. For each concentration, the fibers were produced using an 18 kV tip potential, 15 cm tip-collector separation, and a 0.65 mL/hr solution pumping speed.

Discussion

The morphology of nanofibers formed by electrospinning is a result of several process parameters. These parameters can be classified into two categories. In the first category the parameters are a result of the hardware setup. These include the syringe pumping speed, spinneret type (uniaxial, coaxial, etc.), applied voltage, distance between the spinneret and collector, and the collector type and geometry. The second category of process parameters are those due to the solution chemistry. These parameters include solvent type, solute molecular weight, solution temperature, and solution concentration. Each of the process parameters (both hardware and chemistry) can have an effect on the resultant morphology of the nanofibers.

During the electrospinning process, a small droplet of solution is subjected to an intense electrostatic force resulting from the applied electric field. The magnitude of the electrostatic force is directly proportional to the electric field and the total charge on the droplet, via Coulomb's Law ($F = qE$, where F is the magnitude of the electrostatic force, q is the total charge on the drop and E is the intensity of the electric field). The electric field intensity is determined by the ratio of the applied voltage to the syringe tip-collector separation distance ($E = V/d$, where E is the electric field intensity, V is the voltage applied to the syringe, and d is the tip-collector separation). When the electrostatic forces are strong enough the droplet becomes elongated and can form what is known as a Taylor cone. The Taylor cone is the result of hydrodynamic forces (resulting from the solution pumping rate), electrostatic forces (resulting from the applied electric field), and viscoelastic forces (resulting from the surface tension and viscosity of the solution). If the electrostatic forces are strong enough to overcome the surface tension of the Taylor cone the solution will develop a jet whereby either microscopic droplets or strings of solution are ejected from the

cone. If droplets are formed, this is known as electrospraying, whereas if strings are ejected it is termed electrospinning. To produce nanofibers the jet must eject string like structures. When this happens the string experiences an acceleration towards the collector plate. As the string traverses the gap between the Taylor cone and collector plate it is elongated and this elongation causes the string to experience axial thinning, so that by the time the jet has reached the collector, the size can be on the order of magnitude of several tens-hundreds of nanometers. The thinning process is not only an artifact of the stretching of the string as it reaches towards the collector, but it is also a result of the evaporation of the solvent due to the increasing surface area of the string structure.

One of the most important process parameters at play during the electrospinning process is the solution concentration. The solution concentration effects the viscosity of the polymer, as the solution concentration increases the solution becomes more viscous. In the limit of extremely high viscosities (resulting from a very high solute concentration) the electrostatic force on the solution is not strong enough to initiate a jet from the tip of the syringe. In this limit the applied electric field needed to initiate a jet would be on the same order of magnitude as the electric breakdown voltage of the polymer. If the viscosity is reduced (but maintained relatively high) by decreasing the solution concentration, it has been shown that large helix shaped fibers will form (Yang et al. 2004). Further reduction in the solution viscosity will result in smooth, continuous fibers (Eda and Shivkumar 2007, Fong et al. 1999, Lee et al. 2003). In general it has been shown that within this process window of intermediate concentration that larger diameter fibers form with higher concentrations and the diameter tends to decrease with decreasing concentration. As the concentration is decreased further there is a mixture of fibers and beads formed. As the concentration becomes lower the surface tension of the solution becomes the dominant factor and fiber formation no longer occurs (Deitzel et al. 2001). At these low concentrations the viscosity is low relative to the solution's surface tension leading to the formation of spheres as a result of minimizing the Gibb's surface free energy.

Conclusions

In conclusion, we present results of the electrospinning process that produces PEO nanofibers. In order for nanofibers to form a critical concentration must be reached. Below this concentration beads are formed. Further increasing the concentration results in a mixture of beads and fibers. As the concentration becomes higher uniform, continuous fibers are formed. In general, in this fiber formation regime, as the concentration increases so does the diameter of the fibers.

Acknowledgements

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