Aligned Electrospun Nanofibers for Nanocomposite Applications

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ABSTRACT

Electrospinning is a rapidly developing technology that provides a unique way to produce novel polymer nanofibers with diameters ranging from 50 nm to 500 nm. Electrospinning was first patented in 1934 by Anton Formhals. Since then electrospun fibers have been used in the manufacture filtration media, ceramics, composites and other biomedical devices. In the electrospinning process the polymer solution or melt is usually contained in a syringe. A metering pump attached to the plunger of the syringe generates a constant pressure resulting in a flow of polymer through the syringe. The polymeric fluid being used is poly (vinyl alcohol) (PVA) in water and fumed silica particles have also been added to this solution as reinforcement. The driving force of the jet is provided by two high voltage sources. A combination of positive polarity at the syringe and negative polarity at the collector has proven to yield the most predictable fiber morphology. Adjusting the flow rate of the fluid and the magnitude of the electric field controls the spinning rate which influences fiber size. Through careful control of the experimental parameters, aligned fibers with a narrow width distribution can be obtained. Aligned nanofibers are essential for developing high strength nanocomposites. Morphological studies have been performed using an Electroscan 2020 Environmental Scanning Electron Microscope (ESEM) and a JEOL 2200 Transmission Electron Microscope (TEM).

Keywords: electrospinning, nanofiber, poly (vinyl alcohol), aligned

1 INTRODUCTION

Electrospinning is a method of producing nanoscale fibers from a solution using high voltage electric forces. This technique is capable of producing fibers having diameters in the micron to nanometer size range. This practice has been extensively investigated as a simple method to prepare fibers from polymer solutions or melts [1]. Fiber formation occurs in two stages. In the first stage, once the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is produced [2]. At the base of the needle a cone shaped structure is formed known as the Taylor Cone [3]. During the second stage, a bending instability is observed as the jet whips chaotically. This occurs at some point downstream from the needle tip when the jet has sufficiently thinned. The jet undergoes bending instabilities due to repulsive forces between the charges carried along the jet. The charged fiber decreases in diameter as it lengthens in this region until it finally lands on the collector [4]. The second stage of instability requires control in order to form aligned fibers. Electrospinning parameters fall under three general categories, geometric, solution or material and processing conditions.

Typical processing equipment allows for an electrical potential field to be developed between a droplet of polymer solution at the end of a capillary tube and a collector. The route of the charged jet is controlled by the applied electric field. In this experiment, two conductive strips separated by a void gap were used to collect the electrospun fibers. The use of the void gap allows fibers to be collected and harvested with minimal additional stresses. A schematic representation of the electrospinning setup is shown in Figure 1. This setup is similar to the split electrode apparatus used by Xia and Li [5]. The main advantage of this is that the fiber mat can easily be transferred without damaging the fibers.

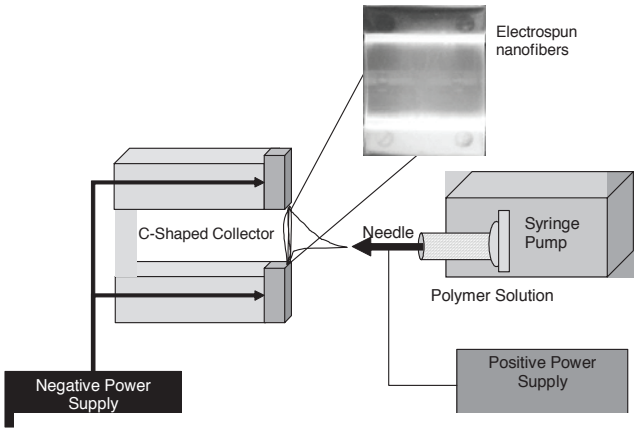

Figure 1: Electrospinning apparatus.

With this setup, the distance between the needle tip and the collector can be altered. When a constant voltage difference is applied between the collector and the needle tip, and the distance is altered, a variable electric field strength results. Electric field strength has been shown to alter fiber morphology [6]. Other parameters that can be changed include the syringe pump flow rate, the needle size and the solution viscosity. These parameters have been documented to cause changes in fiber morphology [7].

This paper shows the results of altering the separation distance, and the morphological impacts of silica particles. When the separation distance is increased, it is expected that the fiber size will decrease [8]. This fiber diameter decreases due to more distance for whipping phenomena to occur, which has been shown to reduce the fiber diameter [9]. It was discovered that for this 10 wt% PVA in water system, the same general trends were observed, but large variations in the data do not indicate reliable trends.

The fiber morphology is controlled by the processing parameters and is dependent upon solution viscosity, solution conductivity, polymer molecular weight, surface tension, and applied voltage [8]. All of these parameters were maintained constant for this experiment. The importance of electrospinning is that it can provide continuous fibers with unusually large surface to volume ratios [10]. Electrospinning also allows for the creation of porous surface structures to be made easily [11]. These features are essential for the proper fabrication of high strength composite materials. Under most conditions, the chaotic oscillation of the electrospinning jet near the collector results in randomly oriented and isotropic structures. These fibers are generally in the form of non-woven nanofiber mats or webs. However, if processing conditions are tuned properly to control the charged fiber motion, fiber orientation can be achieved. Fiber orientation is a goal of this research since the fibers will be used in composite applications.

2 EXPERIMENTAL MATERIALS

Poly (vinyl alcohol) (PVA) was generously donated by the Celanese Corporation. 10 wt % solutions of Celvol 425 were prepared in deionized water by vigorous mixing for 12 hours at 90 °C. This PVA had 96.5 % degree of hydrolysis and 580 cps viscosity which was determined using a Brookfield viscometer. Pendant drop shape analysis yielded an average surface tension of 53.4 mN/m. Fumed silica from Cabot Corporation was used at 10 wt% of the PVA content.

2.2 Electrospinning Processing Conditions

The electrospinning equipment consisted of a negative high voltage power supply connected to the collector, a positive high voltage power supply connected to the syringe needle, a syringe pump fitted with a 20 ml syringe and a 2 inch stainless steel 20 gauge blunt tip needle. The syringe pump was operated at 0.2 ml/hr. The solution was electrospun horizontally using the setup shown schematically as Figure 1. The electric field strength employed was 0.7-1.4 kV/cm. It was found that maintaining the collector at a negative potential in reference to ground improved the collection efficiency. As shown in Figure 2, the amounts of stray fibers are minimal. The charged copper plates provide a large area for the charged fibers to collect. The needle tip is placed equidistant to the two copper plates. During the process, the electrospun fibers travel between the two collector strips which create the aligned fiber mat.

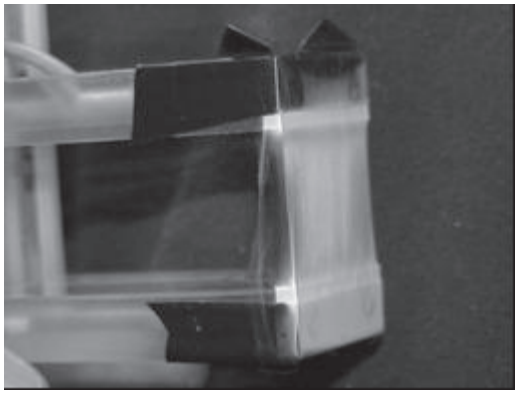

Figure 2: Digital image of the collector with electrospun nanofibers present.

The collection efficiency is a relative measure of how many fibers are collected across the void gap as compared to other areas of the collector. The conductive strips are made of copper which can easily be removed by unscrewing the copper plates from the collector. The collector is first removed from the electrospinning assembly, and then mounted in a lab vise. Once the collector is secure, a cardboard picture frame with adhesive is used to collect the fibers. This technique limits the stresses that the fibers incur. Forming fibers between the copper plates has proven to be the most advantageous harvesting technique. The cardboard picture frame can be easily transferred to a pedestal for ESEM characterization. The frame can also be mounted to other devices such as tensile testing grip fixtures for mechanical strength characterization.

A series of experiments were performed to understand the effects of altering the separation distance. Maintaining a constant applied voltage and varying the distance resulted in a matrix that compares the electric field strength with the fiber morphology. In this case, the morphological parameters of interest are fiber diameter and relative alignment. Separation distances were chosen to be 8 cm, 10 cm and 12 cm. ESEM and subsequent image analysis showed that the tightest diameter control is available at 10 cm, and the highest degree of alignment occurs at 8 cm. At longer separation distances, the chaotic motion of the fiber becomes more prevalent. Alignment generally becomes more difficult in this regime.

Silica nanoparticles were added to the solution to understand morphological and mechanical strength effects of nanoscale reinforcing agents. This preliminary work will provide the basis for continuing experiments in functionalization and reinforcement of electrospun materials. Addition of silica particles was also examined at the 10 cm distance to compare morphology.

2.3 Microscopy

An Electroscan 2020 ESEM was used to obtain sample images. The samples were first mounted on ESEM pedestals, then sputter coated with gold. The samples were imaged at 15 kV from 500 to 10,000 magnifications to obtain alignment and size distribution information. A JEOL 2200 TEM was used to determine the location of the silica particles within the polymeric fibers. TEM images were recorded at 200 kV from 5,000 to 50,000 magnifications from clamshell grids.

2.4 Image Analysis

ImagePro software was utilized to aid in the fiber diameter and alignment analysis. The classical method of viewing the samples from the top down was chosen and it was assumed that the fibers were circular in cross section [7]. The purpose of the top down method is for easy alignment characterization and fiber size estimation. A typical ESEM micrograph is shown below as Figure 3. This picture shows that using the experimental setup shown can provide aligned fibers with narrow width distribution.

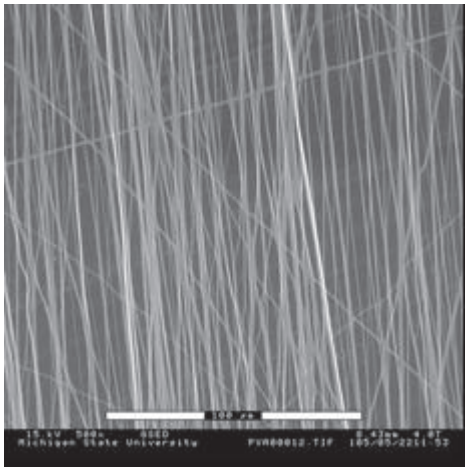

Figure 3: ESEM micrograph electrospun 10 wt% PVA fibers, 10 cm separation distance, 500 X magnification, 15 kV accelerating voltage, scale bar is 100 μm.

3 RESULTS

3.1 Diameter Distribution

The average fiber diameter of electrospun 10 wt % PVA ranges from 177 to 599 nm. A series of high magnification images were required to obtain statistically significant.

For the fibers spun from a separation distance of 8 cm, the data shows more variability. The standard deviation for this distance is 115.7 nm, which is significantly higher than the others. This distance also shows the largest range in the data from 448 nm to 897 nm, with an average of 599 nm. Only 63% of the fibers are within 100 nm of the average fiber size with this setup. The electric field strength for this setup was 1.0 kV/cm, the syringe pump flow rate was 0.1 ml/hr through a 2 inch 20 gauge blunt tip needle.

Increasing the separation distance to 10 cm shows the tightest width distribution. This setup seems to work the best for obtaining fibers that are most similar in size, 355 nm on average, with a range 297 nm to 420 nm. The smallest average fibers are found from the 10 cm placement.. The electric field strength was 0.8 kV/cm. These parameters produce fibers that are very uniform in diameter, with 97 % within 100 nm of the average fiber size.

A separation distance of 12 cm yields slightly larger fibers, with more variation in the data. The range of diameters is quite large from 188 nm to 572 nm, with an average of 380 nm. The electric field strength was 0.67 kV/cm. This setup also produces uniform fiber sizes, with 88 % of the diameters being within 100 nm of the average.

The silica loaded samples showed an average diameter of 177 nm, with a tight range from 110 nm to 265 nm. The electric field strength was 1.4 kV/cm, which may account for the decrease in fiber diameter. 97% of the fibers were within 100 nm of the average fiber size.

According to the National Science Foundation (NSF), a nanomaterial must be less than 100 nm in at least one dimension [12]. This definition is not universally agreed upon, but is a good reference. Since the average fiber diameters are at least 177 nm, these cannot be labeled as true nanofibers, only nanoscale materials.

The expected trend of higher electric field strength producing narrower fibers is not fully supported in this data. The large amount of variability in the 8 cm separation distance, (1.0 kV/cm) data is the reason for the inconsistencies. The trend is slightly present when comparing the 10 cm (0.8 kV/cm) and 12 cm (0.67 kV/cm) data. The decreased electric field strength resulted in larger diameter fibers. The images show that uniform fiber shape is available through the use of this experimental setup. The goal of creating uniform fibers is for the intended application of composite materials, and to aid in estimating individual fiber properties based on bulk sample data.

3.2 Alignment Distribution

Previous research has shown that not using the proper setup, and in our case the negative potential collector, results in poor fiber alignment. An accurate numerical description of well aligned fibers is difficult to find. The number of fibers that are within 10 degrees of the average fiber angle has been chosen as a standard for comparison. AN (10) has been chosen to represent the number of angles within 10 degrees of the average fiber angle. These fiber angles have been calculated using the ImagePro software.

The 1 kV/cm data has the lowest range and the least amount of standard deviation. 92% of the fibers from this sample were within 10 degrees of the average. Decreasing

the electric field strength, broadened the range and lowered the AN (10) number. At 12 cm (0.67 kV/cm), only 69% of the fibers are within 10 degrees of the average fiber, at 10 cm (0.8 kV/cm), it increases to 80%. The silica loaded samples at 10 cm (1.4 kV/cm) have AN (10) of 89%. AN (10) numbers larger than 80% should be considered aligned. These fibers appear nearly parallel in most regions examined with the ESEM.

The alignment distribution proves that closer distances result in less stray fibers. In this chart, the majority of the fibers in all electric field strength scenarios are within 5 degrees from the average fiber angle. This can also be interpreted as the increased field strength forces the charged fibers to go towards the collector rather than going astray. It has been shown that the void gap plays a significant role in how the charged fiber behaves near the collector [13].

Collection of aligned fibers is important for composite applications. Aligned electrospun fibers can significantly improve the mechanical properties of the composite. The importance of a high degree of alignment is essential to fully realize the reinforcing effect of the materials [14].

3.3 Silica Particle Distribution

Ideally the silica particles will be well dispersed, be contained within the fiber and be less than the fiber width, to eliminate stress producing defects. This dispersion should result in optimal mechanical properties. Ultrasonic mixing was used in conjunction with magnetic stir bar mixing to blend the silica in water. Once the solution was sufficiently clear, it was added to the solid PVA pellets and magnetic stir bar mixing continued until the polymer was dissolved. This method allows the silica agglomerates to be disrupted without damaging the polymer with ultrasonic treatment. Figure 4 shows the TEM image of silica reinforced electrospun PVA. The silica is clearly present as small agglomerates contained within the fiber structure. It should be noted that the dispersion is not ideal, since there are long sections of fiber with little or no silica present. The silica loading ratio has not been optimized in this case.

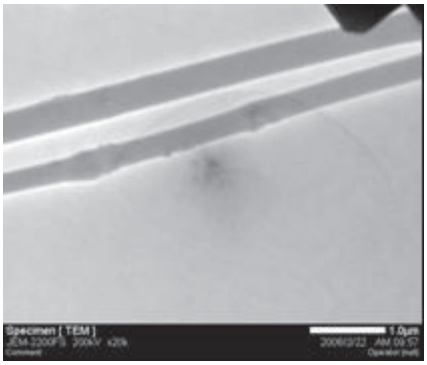

Figure 4: TEM image of silica reinforced PVA, 1 μm scale bar, 20,000 X magnification.

4 FUTURE CONSIDERATIONS

Through surfactant chemistry, the dispersion may be greatly improved, which would lead to better fiber morphology and ultimately higher strength electrospun nanocomposites. Mechanical testing of the fiber mats will also be explored. Careful selection of materials has allowed for the facile harvesting of fiber mats with minimal damage. These fiber mats will be transferred to a tensile testing machine for the correlation of strength to fiber size and filler content.

5 CONCLUSIONS

Through careful control of the experimental parameters, aligned fibers with a narrow width distribution can be obtained. Aligned nanofibers are essential for developing high strength nanocomposites. Aligned fibers were demonstrated by harvesting the fibers that spanned the gap of a C-shaped collector. This experimental apparatus used both positive voltage at the needle tip and negative voltage at the collector. Maintaining the collector at negative potential aids the fiber collection efficiency; fewer stray fibers are produced. Collecting the fibers across a void gap enables the fibers to be easily gathered for future processing and evaluation.

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