Polymer Nanofibers from Multiple Jets Produced on a Porous Surface by Electrospinning

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ABSTRACT

A novel method for the electrospinning of polymer solution into nanofibers is presented. The objective of this work is to demonstrate the production of suitable multiple jets on a porous surface for electrospinning, without a multi-needle arrangement. In this experiment, a cylindrical nozzle made from porous polypropylene (e=0.44) with pore sizes ranging between 10-20 microns served as the porous matrix. A 20 wt% Nylon 6 solution flowed at 5 psig through the porous matrix. Several stable jets that formed on the surface spun fibers of nanoscale. The production was 250 times the rate of production from a single spinneret, on a mass basis. The Nylon 6 fibers collected were similarly analyzed and fitted to the log-normal distribution. Consequently, we have a method for the mass production nanofibers that has many advantages over other known methods.

Keywords: electrospinning, nanofibers, multiple jets, porous plastics.

1 INTRODUCTION

Production of one-dimensional nanostructures by electrospinning from polymeric materials has attracted much attention during the last few years. Remarkable large length to diameter ratios, drive the interest and advantages offered by the nanostructures, for instance, nanofibers provide significant increases in filtration efficiency at relatively modest decreases in permeability[1]. Nanofibers have also been shown to improve significantly separation efficiency in coalescence filtration of oil/water emulsions and aerosol coalescence[2,3]. Electrospinning is a simple and straightforward method of producing nanostructures.

The nanostructures produced ranged from simple unstructured fiber mats, wires, rods, belts, spirals and rings to carefully aligned tubes. The materials also vary from biomaterials to synthetic polymers. The applications of the nanostructures themselves are quite diverse. They include filter media, composite materials, biomedical applications (tissue engineering, scaffolds, bandages and drug release systems), protective clothing, micro- and optoelectronic devices, photonic crystals and flexible photocells. Li and Xia[4] recently made an extensive survey of advances to date in electrospinning of nanofibers and potential applications.

Electrospinning, being contactless, has proven superior to mechanical drawing, generating much thinner fibers. Although, electrospinning was introduced by Formhals in 1934[5], interest in the method was revived in the 1990s. Renneker[6] and his research group have demonstrated the fabrication of ultra thin fibers from a broad range of organic polymers.

The electrospinning method is a uniaxial stretching of a viscoelastic jet derived from a polymer solution or melt. Up to 1993 the method was known as electrostatic spinning. The process uses an electric field to draw a polymer solution from the tip of a capillary to a collector. A very high voltage is applied to the polymer solution (or melt), which causes a jet of the solution to be drawn toward a grounded collector. The jet is unstable due to an electrically induced bending instability which results in strong looping and stretching of the jet elements [7, 8, 9]. The fine jet dries as the solvent evaporates, to form nanofibers with diameters in the submicron range.

To date, the viscoeslatic jets are derived from drops that are suspended at the tip of a needle, which is attached to a vessel filled with polymer solution, from where the supply to the tip of the needle is maintained. This arrangement typically produces a single jet and the mass rate of fiber deposition from a single jet is relatively slow (hundredths or tenths of grams per hour). To significantly increase the production rate of this design multiple jets from many needles are required. A multi-needle arrangement can be most inconvenient due to its complexity and high probability of clogging. A novel attempt [10] to produce multiple jets using a layer of ferromagnetic suspension, under a magnetic field, beneath a layer of polymer solution in order to perturb the inter layer surface and consequently produce multiple jets on the surface, was reported recently. Yarin and Zussman reported a potential of 12 fold increase in production rate over a comparable multi-needle arrangement.

The objective of this work is to produce multiple jets on the surface of a porous matrix. If such a goal could be achieved, electrospinning from multiple jets could be realized without a multi-needle arrangements and its attendant complexity.

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2 THEORY

2.1 Electrospinning

When a high voltage is applied, the pendent or sessile drop of polymer solution will become highly electrified and the induced charges are evenly distributed over the surface. Consequently, the drop will experience two major types of electrostatic forces: the electrostatic repulsion between the surface charges; and the Coulombic force exerted by the external electric field. Under the action of these electrostatic interactions, the liquid drop will be distorted into a conical object often referred to as the Taylor cone. Once the strength of electric field has surpassed a threshold value, the electrostatic forces can overcome the surface tension of the polymer solution and thus force the ejection of a liquid jet. This electrified jet then undergoes a stretching and whipping process, leading to the formation of a long and thin thread. As the liquid jet is continuously elongated and the solvent is evaporated, its diameter can be greatly reduced from hundreds of micrometers to as small as tens of nanometers.

3 EXPERIMENTAL

3.1 Porous Plastic

At this time, we used a cylindrical nozzle constructed from porous polypropylene rod (GenPore, Reading, Pennsylvania, USA) with pore sizes around 10 microns and porosity of 0.44. The cylinder has an internal diameter of ½" and external diameter of 1", with one end sealed. The small pore size aids in controlling the flow rate of the polymer through the walls to give time for the jets to form on the drops.

Although porous plastic are rarely classified by pore sizes, it quite possible to use material of much smaller pore sizes. We expect that, as the pore sizes reduce the diameter of the fiber formed may be much smaller. Presently, we are investigating other porous materials as alternatives for constructing the nozzle.

3.2 Polymer solution

Polymer solution concentration of 20wt.% were prepared by dissolving Nylon 6 (Aldrich, Germany), as received, in 88% formic acid (FisherChemicals, New Jersey, USA).

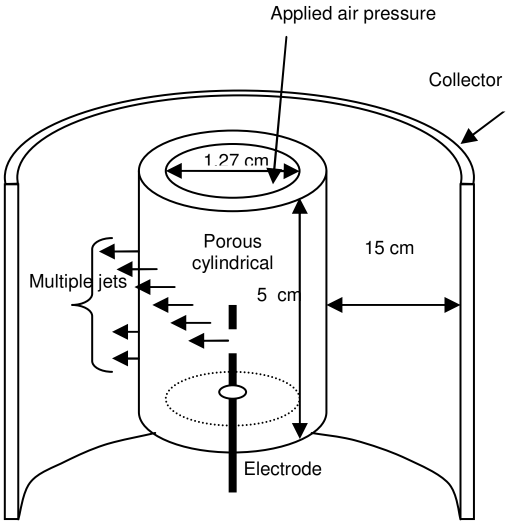

Figure 1: Cutaway view showing the cylindrical porous nozzle with cylindrical collector

4 RESULTS AND DISCUSSION

Several jets that lasted for a period (many minutes) and many intermittent jets that lasted for much shorter periods formed all over the surface of the nozzle as seen in Figures 2(A-D). The fiber formation is very simple and fast. The fibers formed were collected on a cylindrical wire mesh surrounding the nozzle. Figure 2D became fuzzy due to the presence of the fibers on the mesh blocking the view of the camera.

Figure 3 is the SEM image of a sample of the collected fibers. The image shows clearly that the fibers produced are of nanofibers dimensions. Fibers in this size range are suitable for many purposes. An image analysis tool, IMAGEJ[11] was subsequently used to determine the dimension of the fibers.

In order to determine the characteristic property that best describe a population, it is usual to compare observations with known statistical distributions. The Gaussian distribution (Equation 2) is known as the normal distribution because of its prevalence in nature.

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$$\frac{dF}{dx} = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{\left(x-\bar{x}\right)^2}{2\sigma^2}\right) \tag{1}$$

where F is the cumulative undersize fraction of particles, x is the particle size, σ is the standard deviation, and $\bar{x}$ is the mean particle size.

However, when one extreme is more prevalent in the population (skewness), then a better description must be used. When the lower-end dominate the population (left skewed) the log-normal distribution (Equation 3), a modified form the Gaussian's offer a better description.

$$\frac{xdF}{dx} = \frac{1}{\ln\sigma_g\sqrt{2\pi}}\exp\left(-\frac{\left(\ln x - \ln\overline{x_g}\right)^2}{2\ln^2\sigma_g}\right) \tag{2}$$

where $\overline{x_g}$ is the geometric mean and is equal to the median size (where 50% of the particles are greater in size and 50% are smaller in size).

In this case, the fibers with smaller diameter are more prevalent, suggesting a log-normal distribution. Regression analysis showed that coefficient of regression, R^2 are close (Gaussian [0.998], log-normal [0.999]). However, the area between the data and each distribution show clearly that log-normal distribution offer a better fit (Gaussian [110.95]; log-normal [10.64]). Also, as shown in Figure 4, the data visually fits the log-normal distribution better than the Gaussian.

For comparison, a single spinneret (needle) was mounted in place of the porous surface of Figure 1. The Nylon 6 fibers collected were similarly analyzed and the log-normal distribution gave a better fit. Figure 5 illustrates the frequency distribution of the fiber diameters obtained from the two processes. This shows that the two distributions have about the same mean and mode, but the distribution from the multiple jets is broader than the distribution from the single jet. These two curves are appropriate for comparison because the areas under the curves are normalized to equal 1.

Also, the production rate of nanofibers was found to be very large in the electrospinning from the porous surface compared to single needle arrangement. A typical needle produces nanofibers at a rate of about 0.02 g/hr. The porous nozzle used in this experiment produced nanofibers at a rate greater than 5 g/hr or about 250 times. It may be possible to assemble 250 needles together in the same volume as the porous nozzle but the close proximity of the needles will affect the geometry of the electric field and cause jets to form from some needles and not others, hence many more needles are needed to achieve the same production rate. The porous nozzle is much simpler for construction, operation and control.

In addition, the pores in porous materials can be smaller than the diameters of needles often used for electrospinning. Smaller diameter pores may make it possible to make smaller diameter fibers. It should be possible to use materials having pores of sizes much smaller than those used for this experiment.

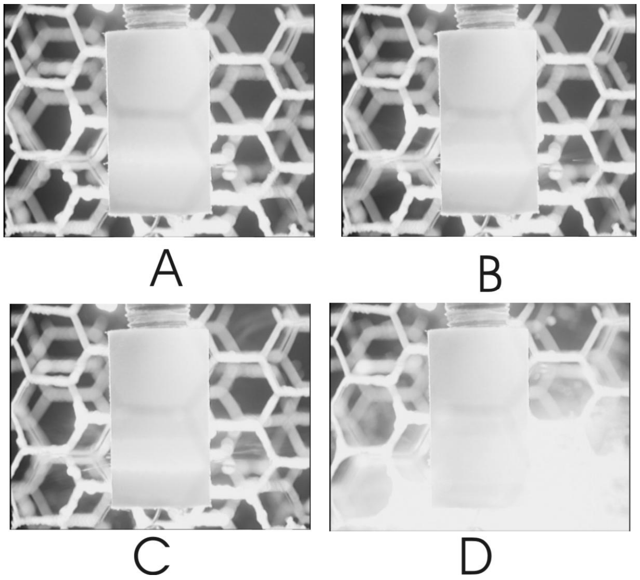

Figure 2: (A)The porous nozzle in the center of a cylindrical wire mesh, the electrode enters the nozzle from the bottom. (B & C) Jets protrude from the walls of the nozzle (D) Image of nozzle became fuzzy because of mat of unwoven fiber on the collector

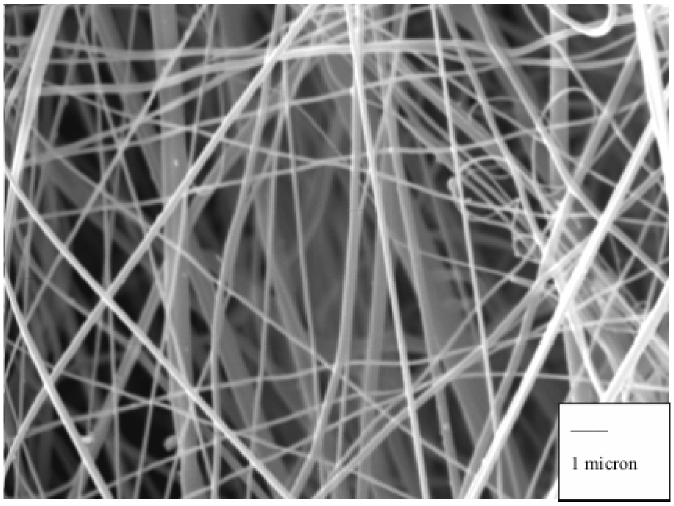

Figure 3: SEM image of Nylon 6 fibers made from multiple jet electrospinning.

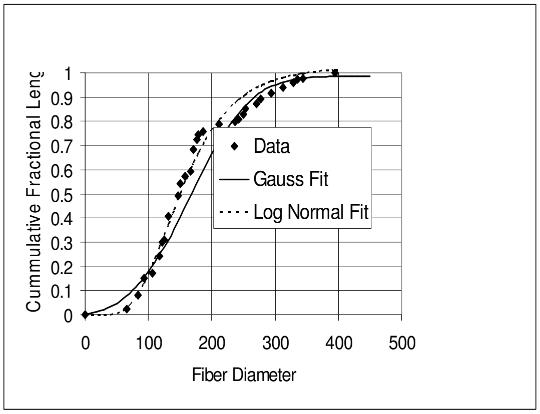

Figure 4: Fiber diameter distribution of Nylon 6 made from multiple jet electrospinning

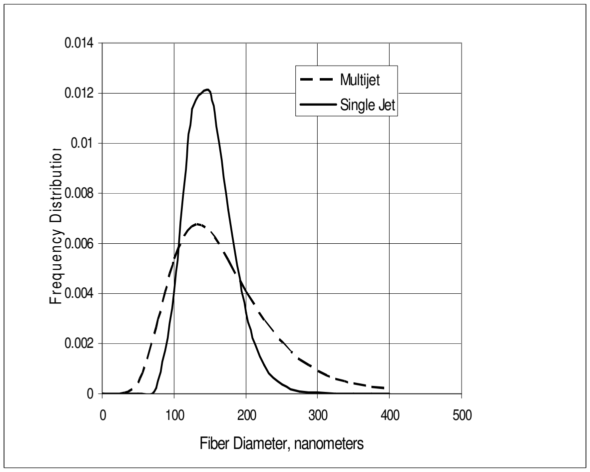

Figure 5: Frequency distribution of fiber diameter of Nylon 6 from electrospinning.

5 CONCLUSION

Therefore, we have demonstrated the production of suitable multiple jets on a porous surface for electrospinning, without a multi-needle. In addition to increase in the rate of fiber production, the method can produce fibers of much smaller dimensions than from needles. Consequently, we have a method that has many advantages over the conventional. However, further studies are required to investigate the relationship between fiber size and pore size. In addition, a theoretical model is required to predict the non-Newtonian flow of the polymer solution in the pores of the matrix. The model will be very useful in predicting the conditions of the jets delivered to the surface of the porous matrix.

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