

Fabrication of Nontoxic Filters from Regenerated Silk Fibroin and Polyacrylonitril Fibers

M.MOHAMMADIAN¹, A.K.HAGHI^{2*}

¹ Islamic Azad University, Department of Textile Engineering, Kashan Branch, Kashan, Iran

² University of Guilan, P.O. Box 3756, Rasht, Iran

The use of fine fiber has become an important design tool for filter media. Nanofibers-based filter media have some advantages such as lower energy consumption, longer filter life, high filtration capacity, easier maintenance, lower weight compared to other filter media. The nanofibers based filter media made up of fibers with diameters ranging from 100 to 1000 nm were conveniently produced by electrospinning technique. Typically filter media are produced with a layer of fine fibers that can be used lonely or as a component in a media structure. The fine fiber increases the efficiency of filtration by trapping small particles which increases the overall particulate filtration efficiency of the structure. Improved fine fiber structures have been developed in this study in which a controlled amount of fine fiber is placed on both sides of the media to result in an improvement in filter efficiency and a substantial improvement in lifetime. In this research, regenerated silk fibroin obtained from industrial silk wastes and polyacrylonitrile (PAN) fibers was used to produce filter. Characteristics such as fibers diameter and its distribution, porosity and thickness of nanofiber filters obtained in lab were examined by Scanning Electron Microscopy (SEM) and analysed using image processing algorithms.

Keywords: electrospinning, nanofilter, image processing, Fourier Transform, porosity

Electrospinning is a process that produces continuous polymer fibers with diameter in the submicron range. In the electrospinning process the electric body force acts on element of charged fluid. Electrospinning has emerged as a specialized processing technique for the formation of sub-micron fibers (typically between 100 nm and 1 μ m in diameter), with high specific surface areas. Due to their high specific surface area, high porosity, and small pore size, the unique fibers have been suggested as excellent candidate for use in filtration [1,2].

In the nonwoven industry one of the fastest growing segments is in filtration applications. Traditionally wet-laid, melt blown and spun nonwoven articles, containing micron size fibers are most popular for these applications because of the low cost, easy process ability and good filtration efficiency. Their applications in filtration can be divided into two major areas: air filtration and liquid filtration [3].

Air and water are the bulk transportation medium for transmission of particulate contaminants. The contaminants during air filtration are complex mixture of particles. Most of these particles are usually smaller than 1000 μ m in diameter. Chemical and biological aerosols are frequently in range of 1-10 μ m. The particulate matters may carry some gaseous contaminants. In water filtration removal of particulate and biological contaminants is an important step. Now the filtration industry is looking for energy efficient high performance filters for filtration of particles smaller than 0.3 μ m and adsorbed toxic gases [4].

Nanofibrous media have low basis weight, high permeability and small pore size that make them appropriate for a wide range of filtration applications. In addition, nanofiber membrane offers unique properties like high specific surface area (ranging from 1 to 35 m^2/g depending on the diameter of fibers), good inter-

connectivity of pores and potential to incorporate active chemistry or functionality on nanoscale [4,5].

Clearly, the properties of nanofibrous media will depend on its structural characteristics as well as the nature of the component fibers. Thus it is desirable to understand and determine these characteristics. The main objectives of this paper is to study the orientation distribution function (ODF) of nanofibers in nanofilter, the fiber thickness distribution and porosity of nanofibrous media by using image processing algorithms which was published recently [6-11]. Fourier methods are useful for extracting orientation information by transforming an intensity image into a frequency image where a higher rate of change in gray scale intensity will be reflected in higher amplitudes [12].

Effect of systematic parameters on electrospun nanofibers

It has been found that morphology such as fiber diameter and its uniformity of the electrospun nanofibers are dependent on many processing parameters. These parameters can be divided into three main groups: a) solution properties (viscosity of solution, solution concentration, molecular weight of solution, electrical conductivity, elasticity and surface tension), b) processing conditions (applied voltage and feed rate), c) ambient conditions (such as temperature and air turbulent). Each of the parameters has been found to affect the morphology of the electrospun fibers.

Viscosity

The viscosity range of a different nanofiber solution which is spinnable is different. One of the most significant parameters influencing the fiber diameter is the solution viscosity. A higher viscosity results in a large fiber diameter. Beads and beaded fibers are less likely to be formed for the more viscous solutions. The diameter of the beads

* email: Haghi@Guilan.ac.ir

becomes bigger and the average distance between beads on the fibers longer as the viscosity increases.

Solution concentration

In electrospinning process, for fiber formation to occur, a minimum solution concentration is required. As the solution concentration increases, a mixture of beads and fibers is obtained. The shape of the beads changes from spherical to spindle-like when the solution concentration varies from low to high levels. It should be noted that the fiber diameter increases with increasing solution concentration because of the higher viscosity resistance. Nevertheless, at higher concentration, viscoelastic force which usually resists rapid changes in fiber shape may result in uniform fiber formation. However, it is impossible to electrospin if the solution concentration or the corresponding viscosity become too high due to the difficulty in liquid jet formation.

Molecular weight

Molecular weight also has a significant effect on the rheological and electrical properties such as viscosity, surface tension, conductivity and dielectric strength. It has been observed that too low molecular weight solution tends to form beads rather than fibers and high molecular weight nanofiber solution gives fibers with larger average diameter.

Surface tension

The surface tension of a liquid is often defined as the force acting at right angles to any line of unit length on the liquid surface. By reducing surface tension of a nanofiber solution, fibers could be obtained without beads. The surface tension seems more likely to be a function of solvent compositions, but is negligibly dependent on the solution concentration. Different solvents may contribute to different surface tensions. However, not necessarily a lower surface tension of a solvent will always be more suitable for electrospinning. Generally, surface tension determines the upper and lower boundaries of electrospinning window if all other variables are held constant.

The formation of droplets, bead and fibers can be driven by the surface tension of solution and lower surface tension of the spinning solution helps electrospinning to occur at lower electric field.

Solution conductivity

There is a significant drop in the diameter of the electrospun nanofibers when the electrical conductivity of the solution increases. Beads may also be observed due to low conductivity of the solution, which results in insufficient elongation of a jet by electrical force to produce uniform fiber. In general, electrospun nanofibers with the smallest fiber diameter can be obtained with the highest electrical conductivity. This means that the drop in the size of the fibers is due to the increased electrical conductivity.

Applied voltage

In the case of electrospinning, the electric current due to the ionic conduction of charge in the nanofiber solution is usually assumed small enough to be negligible. The only mechanism of charge transport is the flow of solution from the tip to the target. Thus, an increase in the electrospinning current generally reflects an increase in the mass flow rate from the capillary tip to the grounded target when all other variables (conductivity, dielectric constant, and flow rate of solution to the capillary tip) are held constant. Increasing the applied voltage (*i.e.*, increasing the electric field

strength) will increase the electrostatic repulsive force on the fluid jet which favours the thinner fiber formation. On the other hand, the solution will be removed from the capillary tip more quickly as jet is ejected from Taylor cone. This results in the increase of the fiber diameter.

Feed Rate

The morphological structure can be slightly changed by changing the solution flow rate. When the flow rate exceeded a critical value, the delivery rate of the solution jet to the capillary tip exceeds the rate at which the solution was removed from the tip by the electric forces. This shift in the mass-balance resulted in sustained but unstable jet and fibers with big beads formation.

Experimental part

Electrospinning and Preparation of Nanofibrous Media

Silk fiber wastes was degummed in an aqueous 0.5 wt % NaHCO_3 and rinsed with water to extract sericin and gain silk fibroin (SF). The degummed silk was then dissolved in ternary $\text{CaCl}_2/\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (1:2:8 in molar ratio) at 70°C for 6 h and then dialyzed with cellulose tubular membrane (pore size=250 nm) to carry out dialysis against 1000 mL of deionized water for 3 days at room temperature. Dialyzed SF was lyophilized since SF became sponge.

In this study, 8 wt and 12 wt % SF solution in formic acid was obtained for producing silk nanofibrous filter media. The 8 wt % and 13 wt % polyacrylonitrile solution for electrospinning was prepared by dissolving the pre-determined quantity of polyacrylonitrile (Polyacryle co., MW 150000) in *n,n*-dimethyl formamide(DMF).

The electrospinning apparatus consisted of 5.0 mL syringe, a high voltage power supply(able to produce 0-30 kV), syringe pump and a rotating collector (stainless steel drum) with diameter 6.75 cm and 13 cm length (schematic diagram of electrospinning process is shown in fig. 1).

Electrospinning parameters for silk were as follows: voltage=15 kV, needle distance=7cm, collector drum speed=100 r.p.m and for polyacrylonitrile were voltage=12 kV, needle distance=10 cm, collector drum speed= 100 r.p.m.

Image analysis using image processing algorithms

The morphologies of nanofibers were observed by scanning electron microscopy (Philips XL-30 ESEM).

The SEM photos converted to gray scale forms. Fourier transform was performed on all gray scale images. Figures 2 and 3 illustrate the application of Fourier transform on a sample image with known orientation angles, 0, 20 and 90°. For the porosity analysis, SEM micrographs were converted to binary format and then used (the picture pixels have only two values, 0 and 255).

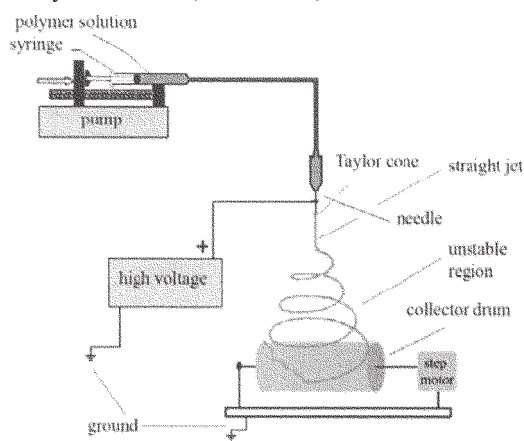


Fig. 1 Schematic of electrospinning set up.

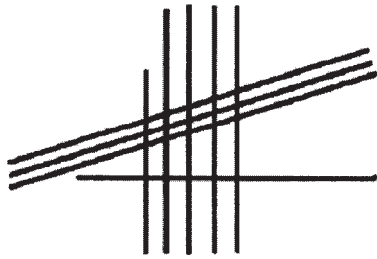


Fig. 2 Sample of image with known orientation angles, 0°, 20° and 90°

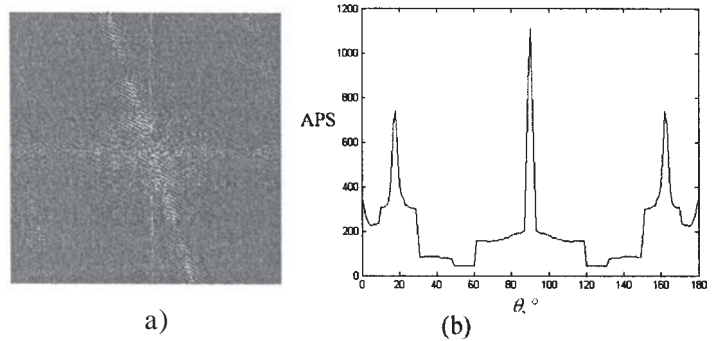


Fig. 3 (a): Fast Fourier Transform (FFT), (b): Angular Power Spectrum (APS) of samples

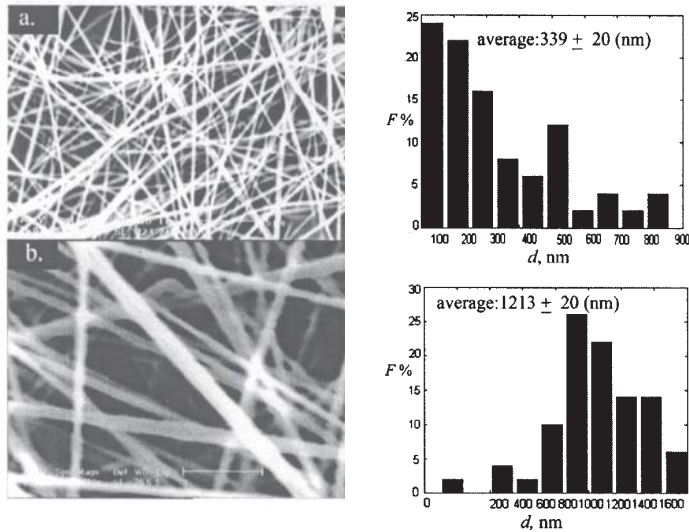


Fig. 4. The Distribution of fiber diameters and morphology of silk nanofibers at concentrations (a) 8 wt % and (b) 12 wt % , constant tip-to-collector distance of 7 cm and applied voltage= 15 kV . Collector speed= 100 r.p.m.

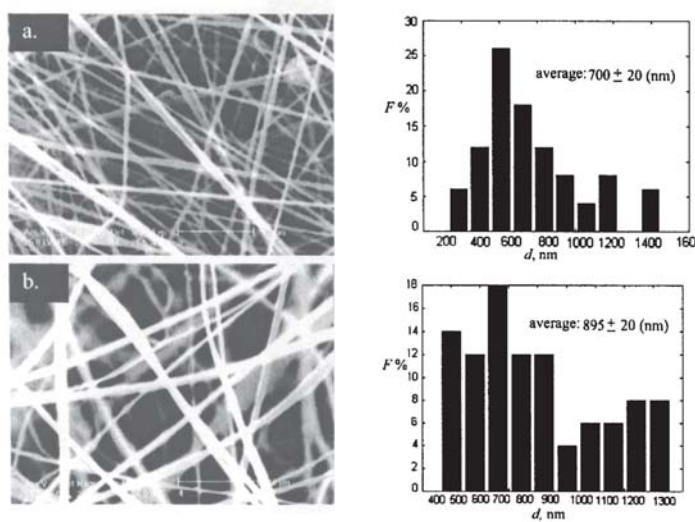


Fig. 5. The Distribution of fiber diameters and morphology of PAN nanofibers at concentrations (a) 8 wt % and (b) 13 wt % constant tip-to-collector distance of 10 cm and applied voltage= 12 kV. Collector speed= 100 r.p.m

Results and discussions

Diameter distribution of nanofibers

Diameter distribution of nanofibers and its average was extracted by using of Image analysis [7-9]. Figure.4 shows nanofibrous Media obtained from solutions of 8 and 12 silk/ (formic acid) at the concentration of 12 wt. %, the average fiber diameter is much larger than that of fibers spun at 8% concentration. The distribution of fiber diameters at 8 and 12 wt. % concentrations is shown in figure. 4. The fiber distribution becomes broader with increasing of concentration. Figure 5 shows the same results for polyacrylonitrile (PAN) nanomats.

Nanofiber orientation distribution

As shown in figure 6 Fourier transform can detect the angular orientation (depicts orientation as a pick) of fibers with approximation.

For all samples of nanofiber-based nanomats produced at low concentration solutions were more uniform and arbitrary rather than sample from high concentration solutions.

Porosity

The porosity of samples (the pixels of empty spaces ratio to total pixel of the picture) are given in table 1. As shown in table 1 the degree of porosity for nanofibers

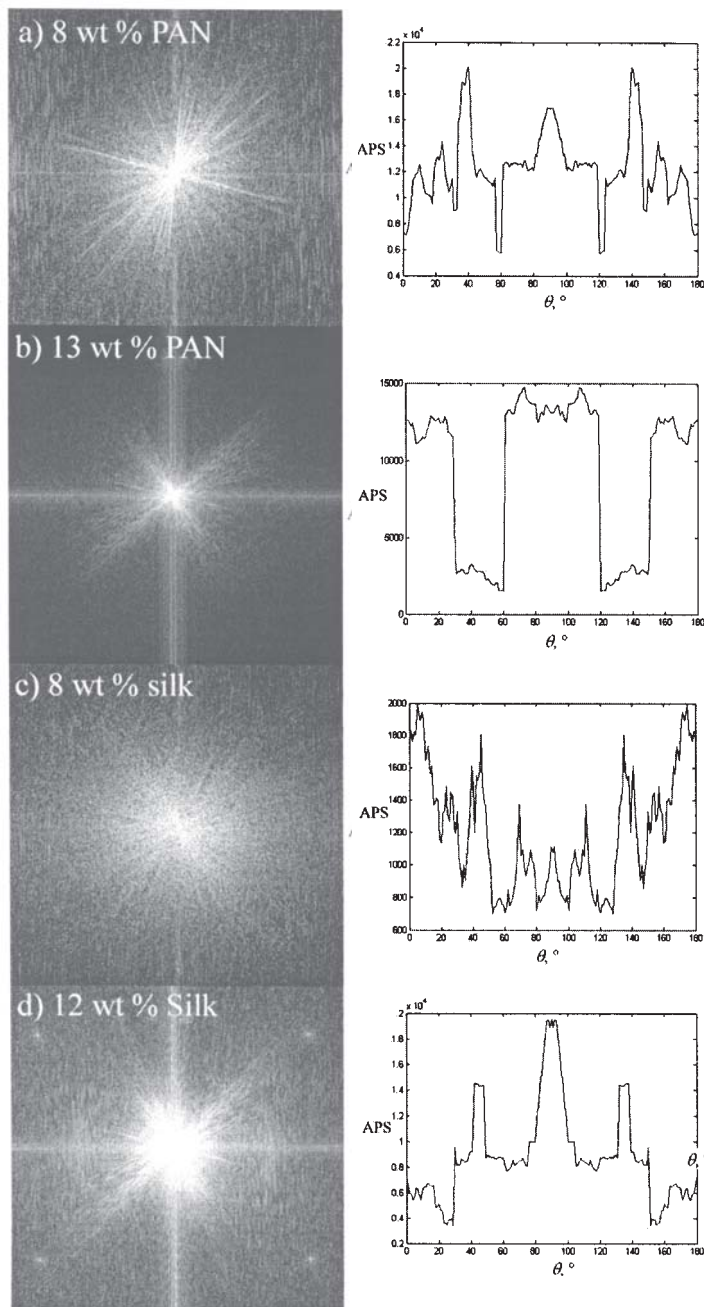


Fig. 6. Fast Fourier Transform (FFT) and angular power spectrum (APS) of (a) 8 wt % PAN in pure DMF, (b) 13 wt % PAN in pure DMF, (c) 8 wt % silk in pure formic acid, (d) 12 wt % silk in pure formic acid

Figure number	Figure size (pixels)	Fiber pixels (white)	Porosity
Fig. 4a (silk 8 wt %)	1056×732	428792	0.446
Fig. 4b (silk 12 wt %)	2202×1686	2051467	0.492
Fig. 5a (PAN 8 wt %)	2203×1640	1886830	0.432
Fig. 5b (PAN 13 wt %)	2200×737	1539663	0.572

Table 1
POROSITY OF ELECTROSPUN NANOMATS

electrospun from higher concentration solutions is higher than the electrospun from low concentration solutions. It is clear that by increasing solution concentration the fiber diameter increases. Subsequently by increasing the diameter, surface to volume ratio of fibers decreases and the pore size between fibers become larger.

Conclusions

The porosity of nanofilters and the nanofiber diameter and its statistical parameters (average & distribution) were computed by analyzing of SEM pictures. The results indicated that increasing solution concentration leads to

larger fiber diameter and broader diameter distribution in both silk and PAN nanofibers. Image analysis of porosity illustrated that in nanofiberous media with larger fiber diameter, the porosity and empty spaces are in a large measure than nanomats with finer nanofibers. It is clear that Fourier methods can provide good approximated values for the Orientation Distribution Function (ODF) and can be a useful tool for the characterization of nanofiberous media.

Nomenclature

d – fiber diameter, nm
 θ – orientation angle, °

APS – Angular Power Spectrum
F % – frequency percent
FFT – Fast Fourier Transform
ODF – Orientation Distribution Function

References

1. A. K. HAGHI, M. AKBARI, Trends in electrospinning of natural nanofibers, *Physica Status Solidi*, 2007, vol. 204, no. 6, pp. 1830–1834.
2. B. DING, E. KIMURA, T. SATO, S. FUJITA, S. Shiratori, Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning, *Polymer*, 2004, vol. 45, p. 1895-1902.
3. K.YOON, K.KIM, X.WANG, D.FANG, B. S.HSIAO, B. CHU, High flux ultrafiltration membranes based on electrospun nanofibrous PAN scaffolds and chitosan coating, *Polymer*, 2006, vol. 47, p. 2434-2441.
4. R.S. BARHATE, SEERAM RAMAKRISHNA, Nanofibrous filtering media: Filtration problems and solutions from tiny materials, *Journal of Membrane Science*, 2007, vol. 296, p. 1-8.
5. P. GIBSON, H. SCHREUDER-GIBSON, D. RIVIN, Transport properties of porous membranes based on electrospun nanofibers, *Colloids and Surfaces A : Physicochem. Eng. Aspects*, 2001, vol. 187–188, p. 469
6. M. ZIABARI, V. MOTTAGHITALAB, A. K. HAGHI, Application of direct tracking method for measuring electrospun nanofiber diameter. *Braz. J. Chem. Eng.*, 2009, vol. 26, no. 1, p. 53-62.
7. M. ZIABARI, V. MOTTAGHITALAB, S. T. MCGOVERN, A. K. HAGHI, Measuring Electrospun Nanofibre Diameter: A Novel Approach, *Chin.Phys.Lett.*, 2008, vol. 25, no. 8 , p. 3071-3074.
8. M. ZIABARI, V. MOTTAGHITALAB, S. T. MCGOVERN, A. K. HAGHI, A new image analysis based method for measuring electrospun nanofiber diameter, *Nanoscale Research Letter*, 2007, vol. 2, p. 297
9. M. ZIABARI, V. MOTTAGHITALAB, A. K. HAGHI, Simulated image of electrospun nonwoven web of PVA and corresponding nanofiber diameter distribution, *Korean Journal of Chemical engng*, 2008, vol. 25, no. 4, p. 919-922.
10. M. ZIABARI, V. MOTTAGHITALAB, A. K. HAGHI, Distance transform algorithm for measuring nanofiber diameter, *Korean Journal of Chemical engng*, 2008, vol. 25, no. 4, p. 905-918.
11. M. ZIABARI, V. MOTTAGHITALAB, A. K. HAGHI, Evaluation of electrospun nanofiber pore structure parameters, *Korean Journal of Chemical engng*, 2008, vol. 25, no. 4, p. 923-932.
12. B. POURDEYHIMI, R. DENT, H. DAVIS, Measuring fiber orientation in nonwovens, part III: Fourier transform, *Textile Research Journal*, 1997, vol. 67, no. 2, p.143-151

Manuscript received: 3.02.2012