Some Aspects of Polyacrylonitrile (PAN) Electrospun Nanofibers Diameters Measurements

M.MOHAMMADIAN[1], A. K. HAGHI[2]*
Islamic Azad University, Department of Textile Engineering, Kashan Branch, Kashan, Iran
University of Guilan, P.O.Box 3756, Rasht, Iran

In this paper, some aspects of electrospun nanofiber diameter measurement has been presented. The method was tested by a simulated image with known characteristics and a real web. The results show that this approach is successful in making fast, accurate automated measurements of electrospun fiber diameters.

Keywords: transport properties, automated measurement, electrospinning, nanofiber diameter, image analysis

Nanofibers are considered as fibers with diameters in the range of one or two orders of magnitude smaller than those of conventional textile fibers. Electrospinning is a straightforward method for manufacturing nanofibers that combines the benefits of a controlled fiber diameter with the possibility for large scale automated production. In this process, a high electric field is applied between a target plate and nozzle of a cylinder containing a polymer / solvent dispersion. As the dispersion is pushed through the nozzle, an electrically charged jet of polymer is formed, which, on drying by means of evaporation of solvent, results in randomly oriented nanofibers collected on the target [1-4]. It has been found that morphology of nanofibers depends on many processing parameters. These parameters can be divided into 3 main groups as shown in table 1.

To date there has been no successful method developed for the automated measuring of electrospun fiber diameter which has hindered the uptake of this process for large-scale production. The objective of this investigation is to develop a new analysis for measuring electrospun nanofiber diameter.

Experimental part

Methodology

Our electrospinning apparatus consisted of a syringe pump, a 0–50 kV Dc power supply, an ammeter and various take up devices including metal screens, belts and other targets in an enclosed Faraday cage. Polyacrylonitrile (PAN) fibers (thickness =16 dtex ; length =150mm ; bright) were used to prepare solutions. This polymer was dissolved in dimethylformamide (DMF) solvent at 40-50°C and different concentrations.

Fiber diameter is usually determined from Scanning Electron Microscopy (SEM) images obtained of the electrospun webs (fug. 1). Due to the small fiber dimensions, high-quality images with appropriate magnifications are required.

Manual method

Routine measurement of fiber diameter and its distribution are carried out by manual method. First the scale is set. Then, pixels between two edges of a fiber perpendicular to the fiber axis are counted. The number of the pixels is then converted to *nm* using the scale and the resulting diameter is recorded. On a typical image, the diameter of 100 fibers are measured using this method and the histogram of fiber diameter distribution is plotted. This process is very much time-consuming and operator consistency and fatigue may reduce the accuracy. Identifying the edges of the fibers needs attention and the measurements are not exactly made perpendicular to the fiber axis. It cannot be used as on-line method for quality control, due to the need of an operator for measurement. Automating the fiber diameter measurement and eliminating the use of the human operator is a natural solution to this problem.

Image analysis

An image analysis based method was proposed [1-5] for measuring fiber diameter in nonwoven textiles. In this

Table 1
PROCESSING PARAMETERS IN ELECTROSPINNING

Solution properties	viscosity Polymer concentration * Molecular weight of polymer Molecular weight distribution Electrical conductivity Elasticity Topology (branched ,linear,etc) of the polymer Surface tension
Processing conditions	Applied voltage * Distance from needle to collector * Motion of target screen Volume feed rate Needle diameter
Ambient conditions	Temperature Humidity Atmospheric pressure

---

* *email: Haghi@Guilan.ac.ir*

method, a binary image of the textile is used to create a distance map and skeleton. The fiber diameter may be determined from the values of the distance map at any pixel location on the skeleton. However, the occurrence of a broken skeleton at intersection points is a main challenging area within the use of this method. Since two or more fibers cross each other at these intersections, the value of the center of the object in the distance map does not coincide with the fiber diameter at these points because it is not associated with a single fiber. The problem becomes more serious as fibers get thicker and for points where more fibers cross each other. Hence, the method fails in measuring fiber diameter at intersections.

New distance transform algorithm

We established a new method based on image analysis in which the problem associated with the intersections was solved. The method uses a binary image as an input. Then, the distance transformed image and the skeleton are created. It can be noted that the skeleton which is obtained by the process of *skeletonization* or *thinning* often contains short spurs which may be cleaned up through the use of a *pruning* procedure [1-6]. In order to solve the problems associated with measuring fiber diameter at the intersections, we first use a *sliding neighborhood* operation [1-6] to identify the location of these points. Then the thickness of each intersection is recorded from the distance transformed image. Finally the intersections are deleted from the skeleton image based on their measured thickness.

Figure 2 shows a simple simulated web and the resulting skeleton superimposed on the distance transformed image. The obtained skeleton is used as a guide for tracking the distance transformed image and the diameters are computed from the intensities of this image at all points along the skeleton. The data in pixels may then be converted to *nm* and the histogram of fiber diameter distribution is plotted.

Web simulation

In order to validate the method, test samples with known characteristics were required. Algorithms for simulation of nonwoven mats have been proposed [1-5]. Lately it has been discovered that the best way to simulate nonwoven mats of continuous fibers is through *μ-randomness* procedure which was used in this study for generating a simulated image with known characteristics.

Real web treatment

Fiber diameter determination by the use of image analysis requires the initial segmentation of the micrographs in order to produce binary images. The typical way of producing a binary image from a grayscale image is by global thresholding where a single constant threshold, usually selected by trial and error, is applied to segment the image. Global thresholding is very sensitive to any inhomogeneities in the gray-level distributions of the object and background pixels. This effect can be eliminated through the use of a local thresholding scheme. Automatic selection of the appropriate thresholds can be carried out based on the previously published method [1-5]. Note that, since the process is extremely sensitive to noise, before the segmentation, a procedure to clean the noise and enhance the contrast of the image is necessary.

Results and discussion

A simulated image with the diameter sampled from a normal distribution with the mean (M) of 15 and standard deviation (STD) of 4 pixels was used to test the validity of the method. It is noteworthy that the true M and STD of the simulated image (15.35 and 4.47) varies slightly with those used as simulation parameters.

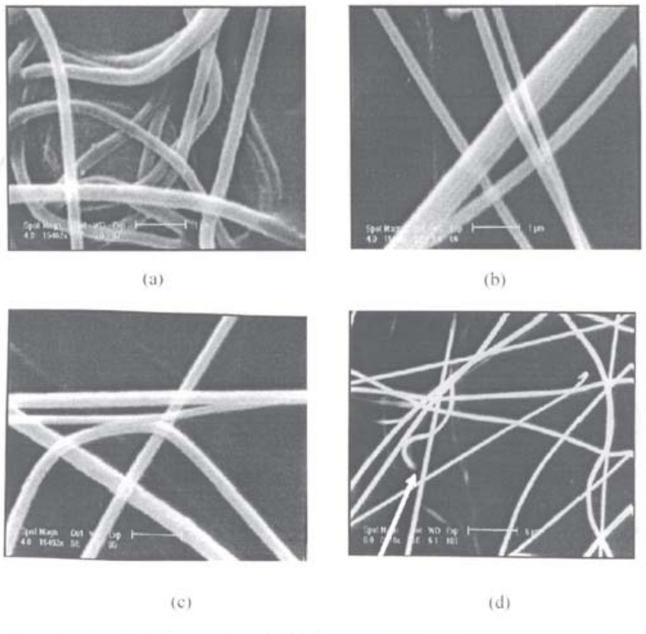

Fig. 1 SEM images of nanofibers studied

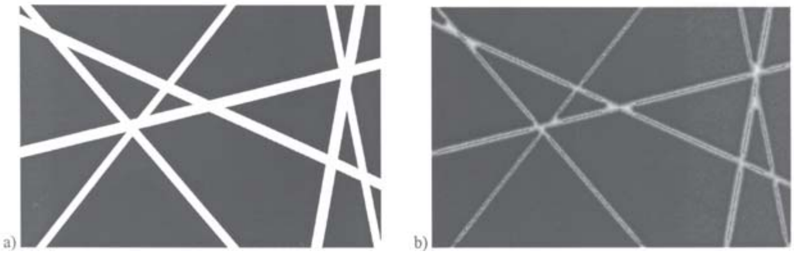

Fig. 2. a) A simple simulated image, b) Resulting skeleton overlaid on distance transformed image

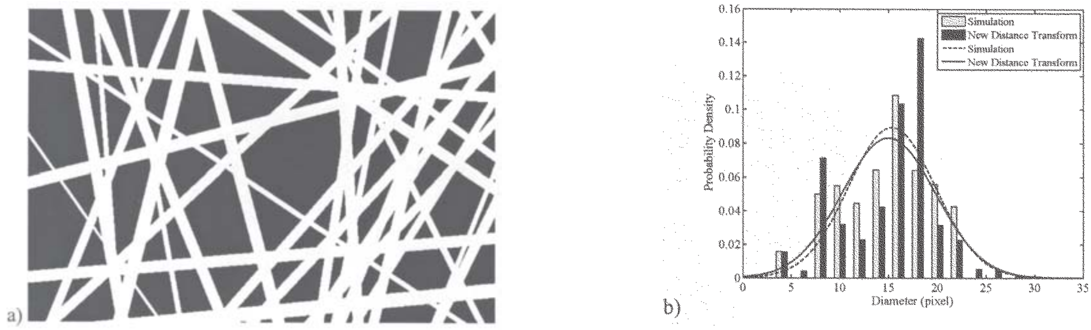

Fig. 3. a) simulated image, b) diameter distribution

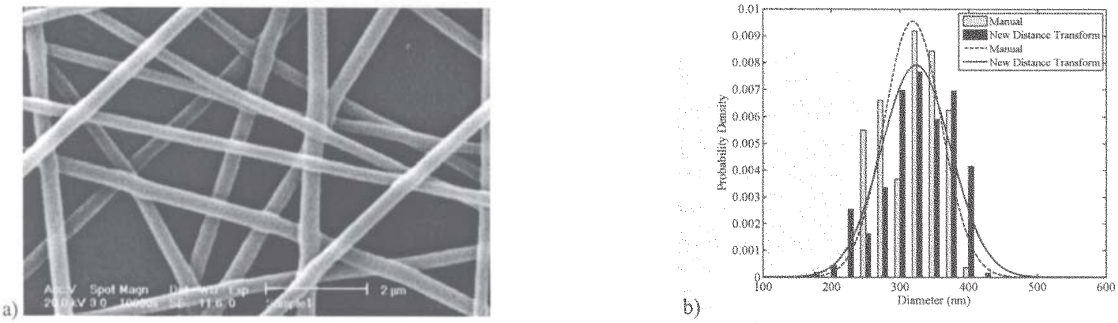

Fig. 4 a) Micrographs of an electrospun web, b) diameter distribution

Figure 3 shows the simulated image and its diameter distribution obtained from the new distance transform method. The M and STD of fiber diameter obtained by this method were 15.02 and 4.80 respectively, showing a good correlation between the calculated and true M and STD of the simulated image.

Using this method, there can be up to half a pixel error in either direction when measuring the fiber diameter, resulting in a total measurement error of up to 1-pixel. The slight differences observed between the calculated and true values could be attributed to this 1-pixel measurement error, some parts of branches remaining after pruning and other slight variations in the skeleton adjacent to the deleted intersections. Furthermore, the fiber diameters at the deleted intersections were not counted within the measurement and may contribute slightly to the variation observed.

To prove that this process is suitable for determination of fiber diameter on real samples, a real nanofiber web was obtained from electrospinning of polyvinyl alcohol (PVA) with average molecular weight of 72000 g/mol (MERCK). The micrograph of the electrospun web (Fig. 4a), was taken using a Philips (XL-30) Environmental Scanning Electron Microscope after gold sputter coating.

Figure 4b shows the diameter distribution for the real web. The respective M and STD of the fiber diameter obtained by this new method were 24.74 and 3.85 in terms of pixel and 323.7 and 50.4 in term of *nm* which are in good agreement with the values 24.36 and 3.19 pixels and 318.7 and 41.8 *nm* obtained from manual methods. The differences here can also be attributed to the different number of measurements taken between the methods used (over 2000 for our method versus 100 for the manual method). Nevertheless, in each case presented, the difference observed was within 1-pixel measurement error suggesting the main limitation with the process is with the resolution of the taken image.

Conclusion

In this study, a new image analysis based method for assessing nanofibers diameters was successfully developed. The validity of the method was tested using a simulated image as well as an image of a real electrospun nanofiber web. In the case of the real web, local thresholding was applied on the micrograph of the web taken from SEM to attain the necessary binary image. The M and STD of fiber diameter which were obtained using this new method were extremely close to true values on the simulated image. For the real web, M and STD of fiber diameter measured by the method were also in good agreement with those obtained from the manual method. The results show the effectiveness of the method for diameter measurement. The method is automated, accurate, and much faster than manual method and has the capability of being used as an on-line technique for quality control.

References

1 ZIABARI, M., MOTTAGHITALAB, V., MCGOVERN, S.T., HAGHI, A.K, Measuring Electrospun Nanofibre Diameter: A Novel Approach, Chin.Phys.Lett., 2008, vol.25, no. 8 , p. 3071.

2. ZIABARI, M., MOTTAGHITALAB, V., MCGOVERN, S.T., HAGHI, A.K., A new image analysis based method for measuring electrospun nanofiber diameter, Nanoscale Research Letter 2007, , vol. 2, p. 297

3. ZIABARI, M., MOTTAGHITALAB, V., HAGHI,A.K, 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 ,2008.

4. ZIABARI, M., MOTTAGHITALAB, V., HAGHI,A.K, Evaluation of electrospun nanofiber pore structure parameters, Korean Journal of Chemical engng ,2008, vol, 25, no. 4, p.923.

5. ZIABARI, M., MOTTAGHITALAB, V., HAGHI,A.K. Distance Transform Algoritm for Measuring Nanofiber Diameter, Korean Journal of Chemical engng ,2008, vol, 25, no. 4, p.. 905.

6. HAGHI, A.K., AKBARI, M., Trends in electrospinning of natural nanofibers, Physica Status Solidi , 2007, vol.204, no. 6, p.1830

Manuscript received: 6.02.2012