Assessment of the Distribution of Nanofibers in Membranes Based on Microstructure Photos

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Abstract. This paper presents a methodology for estimation of fibers distribution in fibrous mat. Distribution of fibers is important for the mechanical and electrical properties of created new materials. For this study, membranes of polyvinylidene fluoride and polyvinyl pyrrolidone nanofibers with different sizes and random orientation are prepared via electrospinning. The fiber distribution evaluation of the membranes was based on microstructure photos. The developed method can be used as a practical tool to estimate the distribution of fibers.

1. Introduction

Electrospinning is a simple method to produce polymer fibers by charging high voltage to polymer solutions or melts. Over the past two decades, this technique has attracted considerable attention among the research community due to its low cost, versatility and simplicity for the fabrication of fibers with a wide variety of materials. Additionally, electrospinning allows the preparation of fibrous mats with different morphologies by the modification of the polymer solutions and processing parameters used during the electrospinning.

Due to the high surface area and porosity, electrospun nanofibers are excellent materials for several applications as filtration membranes [1], triboelectric sensors [2, 3] and advanced composite materials [4, 5]. For these applications, the morphology and the distribution of the fibers are important for the performance and properties of the created nanomaterials. Therefore, it is urgent to develop methods to measure accurately the diameter and distribution of the fibers.

The fiber diameters and its distribution are usually measured from scanning electron microscope (SEM) images using a ruler (manual analysis). The mentioned method is very time-consuming and can only be used for relative small size samples because the area of analysis is very small as compared to the total size of the fibrous material. Furthermore, manual analysis is not suitable for automated measurements during higher production rate of nanofibers [6]. In this work, we suggest an alternative method to estimate the distribution of the fibers based on digital image analysis. The developed method is automatized, versatile and more time-efficient method than the manual analysis used for most of researchers.

In this paper, membranes of polyvinylide fluoride (PVDF) and polyvinyl pyrrolidone (PVP) fibers are prepared using the technique of electrospinning. The aim of this work is to investigate the

distribution of the fibers in the fabricated membranes using image analysis processing. The main advantages of digital image analysis respect to conventional manual analysis is that it can be used for large size materials and saves considerable time. To the best of our knowledge, very little research has been published about this method and the majority the studies utilized manual analysis to measure the distribution of the fibers in electrospun membranes. Therefore, there is a need to propose alternative measurement methods as digital image analysis.

2. Preparation of nanofiber membranes

The aim of the section is to describe the procedure used to fabricate the membranes of PVDF and PVP nanofibers using the technique of electrospinning.

In the preparation of polyvinylidene fluoride nanofibers, PVDF with a molecular weight of 275,000 g mol^{-1}, N, N- dimethylformamide (DMF) and acetone solvents are purchased from Sigma Aldrich. Initially, PVDF in form of pellets is dissolved in a solvent mixture of DMF and acetone (40/60) to prepare chemical solutions at three different polymer concentrations of 16 %, 20 % and 24 % w/v respectively. Subsequently, the homogeneous PVDF solutions are transferred to an electrospinning machine (Nanon-01A) to be spun under the following conditions: applied voltage 15 kV, feed rate 1 ml/h, distance between the collector and needle tip 15 cm, static collector and room temperature. As a results, membranes of random PVDF nanofibers with three different sizes are obtained as illustrated in section 4.

During the preparation of polyvinyl pyrrolidone electrospun fibers, PVP with a molecular weight of 360,000 g mol^{-1} and ethanol solvent are acquired from Sigma Aldrich as well. First, PVP in form of powder is dissolved in ethanol to prepare a 10% w/v polymer solution. Then, the same laboratory electrospinning apparatus is used to spun the polymer solution using the following conditions: applied voltage 18 kV, feed rate 0.5 ml/h, distance between the collector and needle tip 12 cm, static collector and room temperature. Finally, membranes of PVP nanofibers with random morphology and microscale size are prepared as reported above.

3.   Analysis of the fibre diameter distribution

This section introduces the methodology used to determinate the distribution of the fibers. The investigation is organized as follows: First, membranes of PVDF and PVP submicron fibers are produced via electrospinnning (section 2). Second, photos of the nanofibers are obtained using a scanning electron microscope (SEM). Finally, the SEM images are processed by manual and automatic analysis with the aim to measure the distribution of the fibers.

3.1. Manual analysis

The software Image J 1.45s is used to measure the fibers diameters from the SEM images. The average fiber diameter value and standard deviation is calculated based on the measurements of 100 fibers.

3.2. Automatic analysis

Figure 1 shows the processing algorithm used to analyze the nanostructured membranes. The scanning electron microscope images show fibers with disordered weave, variable diameter and uneven exposure conditions. Different SEM image areas are characterized by different brightness and sharpness. Therefore, image processing and measurement was conducted on square slices with a side of 200 pixels as shown in Figure 1a. Firstly, the image slices were processed with a Canny filter to emphasize the edges of the fibers (Figure1b). The edge detection in the supplied binary image contained errors due to uneven illumination of the cylindrical surface of wide fibers. As a result,

additional edges were formed on the areas of the fiber surface. Figure 1 (c) shows a detailed image of the multiple edges. Secondly, geometric edge detection was performed using a Hough filter as indicated in Figure 1d. The direction of the gradient was defined perpendicular to the line as observed in the figure. Next, the lines were joined in pairs surrounding the fibers. In this way, a geometric image of the SEM view was obtained (Figure 1e).
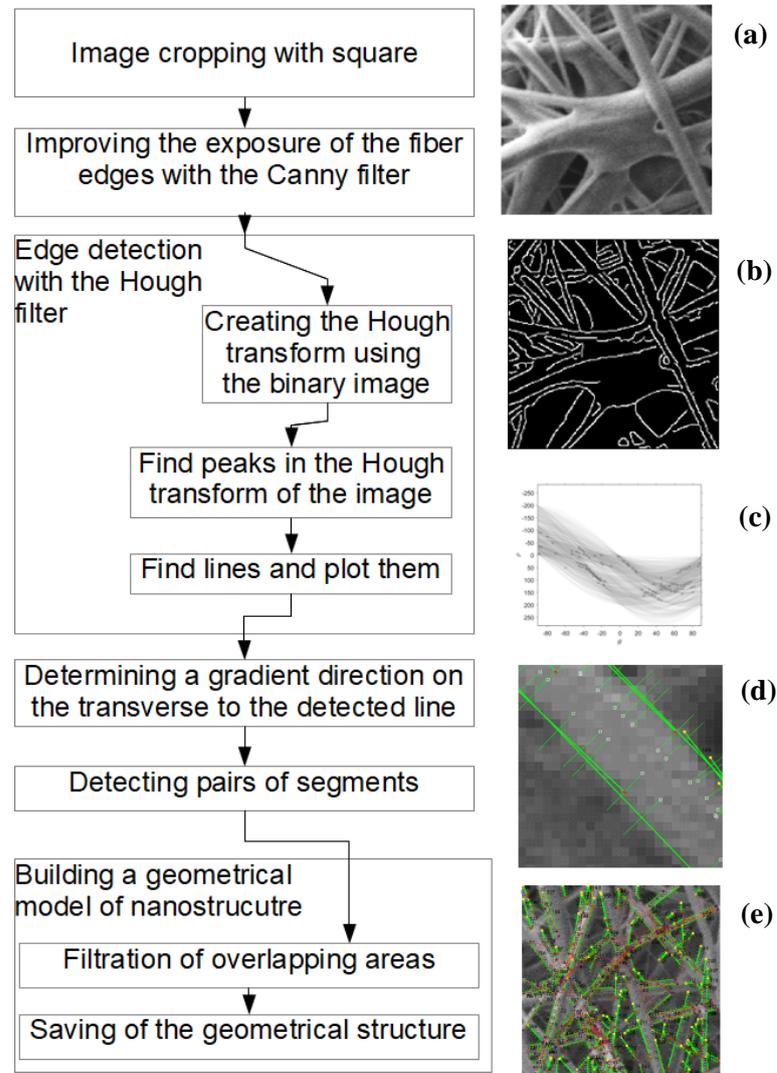
Figure 1. Stages of the SEM automatic image processing algorithm using Canny and Hough filters.

Some of the methods to characterize the microstructure require the identification of fiber edges on microscopic images of sample cross-sections. Others are based on quantitative measurements of the areas occupied by the components of the composite [7-11]. They consist on counting the cases where the characteristics of lower level, such as the values of color components of the pixel in fig.1a have a value lower than the threshold. The advantage of using a geometrical model of the microstructure is that allows the calculation of almost all kinds of measures and indicators. In this work, the fiber diameters were obtained using the geometric images of the studied structures as indicated in fig.1e. It consisted of measuring the distance between the paired lines. During the research, the efficiency of the algorithm was improved by adjusting the processing parameters to the images of various structures. The accuracy of the results was proved by measuring the degree of coverage of the SEM image with

measurements. Areas defined by overlapping pairs of fibers with similar angles and spacing were discarded in the analysis.

4. Results and discussion

In this study, membranes of PVDF and PVP electrospun fibers with different sizes are produced using the electrospinning procedure detailed in Section 2. The SEM images of the fibrous mats are shown in figure 2. The SEM images show good quality nanofibers distributed randomly in the membrane with different fiber diameter sizes. The distribution of nanofibers from the SEM images was determined by manual and digital image analysis with the aim to test the accuracy of the automatic method. The experimental results of the analysis are given in figure 3.
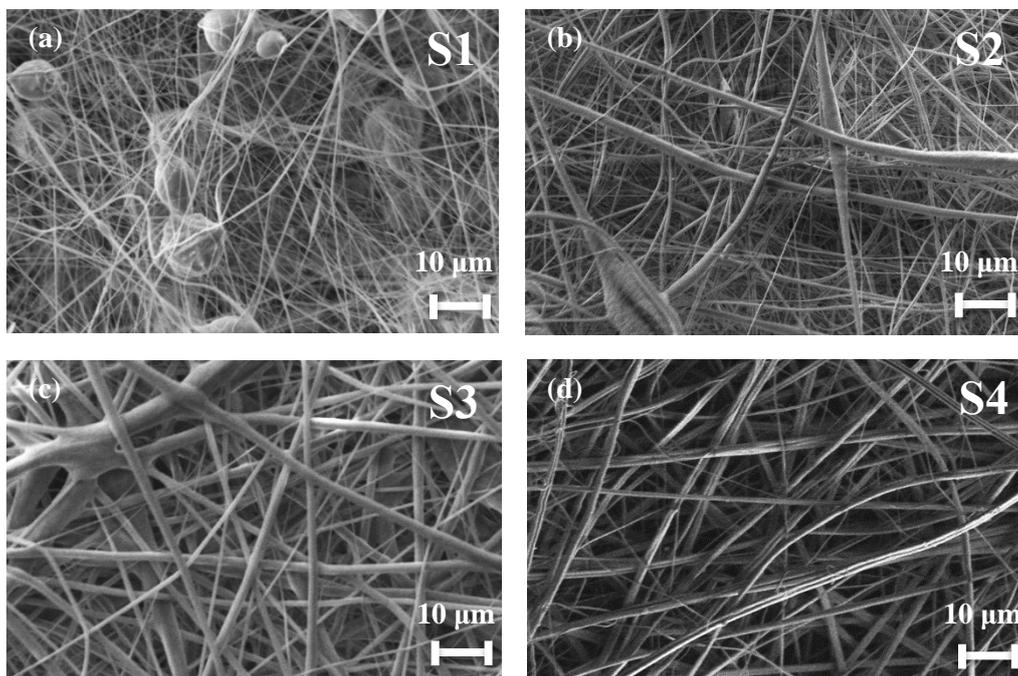
Figure 2. SEM images of nanofibers with different fiber diameters and random orientations used in the digital image analysis: (a) PVDF spun at 16% w/v, (b) PVDF spun at 20% w/v, (c) PVDF spun at 24 % w/v and (d) PVP spun at 10 % w/v.

4.1. Comparison between manual analysis and automatic analysis

Figure 3 shows the results of measurements made manually and automatically. The manual measurements were made using the ruler tool in the software for image analysis. The location of the measured sections and measuring points were decided by the operator. The authomatic measurements were made using the algorithm presented in the article. The Processing parameters were chosen adjusted to a series of representative images. It can be assumed that the geometric images obtained using the automated method are burdened with defects consisting in detecting ostensible edges. These defects lead to the formation of systematic errors of measurements of fiber diameters.

   The trend of average fiber diameters in measurements made by hand and automatically are similar as shown in figure 3a. The fiber diameters increase with increasing polymer concentration. The results are characterized by a high value of the standard deviation (figure 3.b), which is caused by the occurrence of high outliers values. This is also evidenced by average values that are higher than median values.
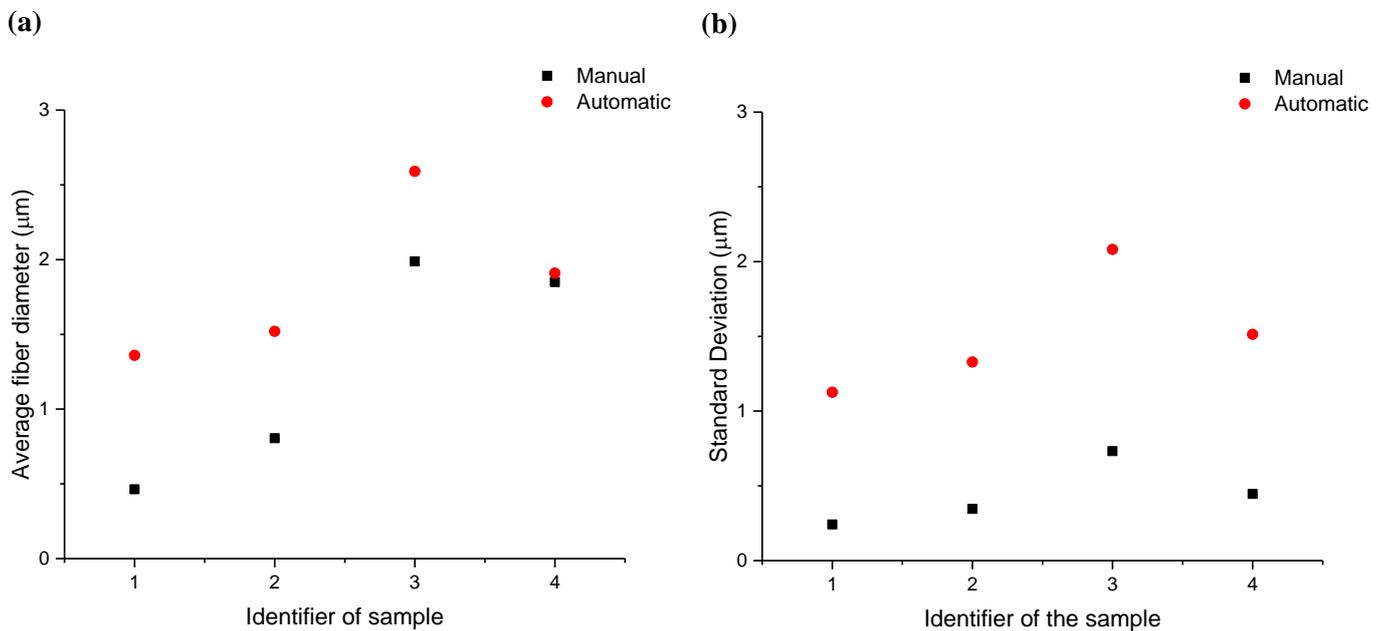
Figure 3. Results of fiber diameters measurements made manually and automatically using digital image analysis: (a) average fiber diameters and (b) standard deviations.

5. Conclusions

The processing of SEM images with random nanofibers and multiple fibre diameters, is a complicated task. By the digital image analysis (automatic measurement), edges and positions of fibers are recorded, while manual analysis allow for measurement of diameters or quantitative measurements with the use of image elements. Digital image analysis provides a geometric model of the structure and multiple measurements, including randomly or systematically arranged testing elements like lines or cycloids.

The article compares manual and automatic measurements carried out by digital image analysis. Manual measurements are subjective, because an operator chooses the number and localization of measurements. However, in the automatic method systematic errors are present. Due to the inability of the possibility of direct measurement it is difficult to estimate measurement error. The accuracy of measurements in the automatic method consist in verification by the operator, based on the distinguished geometrical features.

During the manual and automatic measurements observed similar differences between the average values characterizing the different types of samples. Assuming that the values of the systematic errors caused by the automated method are constant (having its source in the parameters of the algorithm of automatic process), it can be used in comparative studies of various structures.

6. References

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