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A comprehensive study on electrospinning of poly (vinyl alcohol): effects of the TCD, applied voltage, flow rate, and solution concentration

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Abstract: In the present work, the electrospun fibers of poly (vinyl alcohol) (PVA) are fabricated from its solution in water under ambient conditions, and the effect of altered working parameters used such as tip-to-collector distance (TCD), applied voltage, flow rate and solution concentration on the average diameter and frequency distribution of them is deeply discussed. The mean electrospun PVA fiber diameters and its distributions are estimated by a combination of the Scanning electron microscope (SEM) and the ImageJ analyzer program, which is extensively utilized in respective sciences. The achieved results from the experiments indicate that higher both TCD and applied voltage used decrease the average electrospun PVA fiber diameter. Conversely, when the flow rate or solution concentration is increased, diameters of achieved fibers are soared. It is anticipated that this comprehensive study will be beneficial to academia and industry working on potential PVA fiber applications.

Keywords: electrospinning; poly (vinyl alcohol); scanning electron microscope; working parameters.

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INTRODUCTION

To date, with the increasing global interest, considerable research efforts have been generated aiming at the production of fibers of both natural or synthetic polymers and inorganic materials for a remarkable range of application areas such as chemistry, medicine, material science, nanotechnology, textile, and so on (1-8). In this respect, the most well-known fiber production methods mentioned in the literature are mechanical drawing, self-assembly, hydrothermal processing, electrospinning, melt blowing, phase separation, template synthesis, extraction, vapor-phase polymerization, and solvent casting (7, 9). Among them, especially, electrospinning process, which can be applied as the spinning of the wet or dry solution, melt at elevated temperatures, gel, and emulsion has emerged as an efficient, affordable, and most extensively utilized method. A typical relatively simple electrospinning instrument setup consists of a metallic nozzle, syringe pump, voltage supply, and collector (screen or roller) apparatus for making fibers with diameters ranging from few nanometers to a few hundred nanometers. Generally, the setup is designed for feeding ranging from μL.h^{-1} to mL.min^{-1} and making 0–40 kV voltage value over distances of 0–40 cm between the nozzle and collector. During the experiments, after the voltage is imposed, the polymer droplet that emerged on the nozzle is transformed into a conical shape (known as Taylor cone) via potential difference formed. The continuously elongated polymeric jet that is ejected from the pendant droplet by overcoming the surface tension of the spinning solution reaches the collector while the solvent is evaporated. Many types of electrospinning parameters such as TCD distance, applied voltage, flow rate and needle diameter (process parameters), the solvent used, concentration, viscosity and conductivity of the solution, molecular weight, solubility, glass-transition temperature, chain entanglement density of polymer (molecular parameters), relative humidity, pressure and temperature of surrounding (ambient parameters) can strongly influence the various properties and structure of the final product (10). Producing the long lengths fibers, providing the higher surface area to volume ratio and superior mechanical properties, and allowing the functionalization and tunable surface morphologies are some of the advantages that it provides. Moreover, the electrospinning process offers many advantages due to its ease controllability, economic competitiveness, and versatility in broad range potential fields such as biosensor technology, enzyme immobilization, optoelectronics, filtration, tissue engineering, drug delivery, wound dressings, self-cleaning, environmental remediation, and etc (11).

PVA is biodegradable and biocompatible, semicrystalline and water-soluble industrial polymer, and is available as entirely (91-99%), moderately (92-96%) or partially (87-89%) hydrolyzed forms produced by sequential polymerization of vinyl acetate monomer and hydrolysis of achieved poly (vinyl acetate) (PVAc). Depending on its hydrolysis degree, the mechanical, chemical, and physical properties of PVA, such as rigidity, tensile strength, flexibility, solubility, crystallinity, and biodegradability are in a wide range (9, 12). As an FDA-approved material, PVA based products have been in use for advanced widespread industrial, commercial, food, and medical applications, including textile, paper, antimicrobial packaging, tissue engineering, wound dressing, contact lenses, and drug delivery on account of its excellent features (13-15). Hence, PVA has piqued the interest of industry and academia for many years due to the information mentioned above. Furthermore, PVA aqueous solution can be easily prepared and electrospun; thus, the present comprehensive study will be promising for the scientists working on different PVA fiber applications.

This study aims to demonstrate the influence of a variety of electrospinning parameters on the average diameter and frequency distribution of electrospun PVA fibers to create a detailed database for scientists and industry workers. The morphological analysis of PVA fibers was studied through scanning electron microscopy and accurate image processing.

EXPERIMENTAL SECTION

Materials

During the experiments, the utilized commercially available fully hydrolyzed Poly (vinyl alcohol) (PVA, M_w =60,000 g.mol^{-1}) was purchased from Merck (Darmstadt, Germany). To prepare the PVA electrospinning solutions, water (H_2O, ultrapure grade) procured from Merck (Steinheim, Germany) was used. Rectangular microscope cover glasses used as fiber accumulated substrate (3×1 inch) were supplied from ISOLAB (Istanbul, Turkey). No necessary purification and distillation procedures were implemented for all chemicals and solvents used.

Preparation of electrospinning solutions

Commercially available, fully hydrolyzed PVA was dissolved in distilled H_2O by vigorously stirring on a magnetic stirrer at 60 °C for 3 h to obtain 11, 13, and 15% (w/w) solutions to be used in the electrospinning process for determining the effect of solution concentration.

Electrospinning procedure of PVA

To fabricate the electrospun fibers of PVA achieved previously from its solutions at different concentrations, a transparent chamber of electrospinning setup equipped with a syringe pump (NE-500, New Era Pump Systems Inc., Turkey), a high voltage power source (Electrosis, PW1010, Turkey). A 5 mL plastic syringe with metal needle and rectangular microscope cover glasses, which are cleaned two times with chromic acid solution-distilled water cycle, having 3×1 inch dimensions stuck aluminum plate collector was utilized. To conduct the detailed investigation on the effect of different parameters on electrospinning, 15, 20 and 25 kV are applied on PVA solutions at 11, 13 and 15% concentrations when they are fed by 0.6, 1.0 and 1.4 mL.h^{-1} rates fixed to 7, 10 and 13 cm TCDs, separately. During the experiments, relative humidity and temperature were 41% and 24.1 °C and almost constant. After conducting the electrospinning experiments, electrospun fiber coated glasses were kept in a desiccator to remove the residual H_2O for 72 h at room temperature to be used for SEM analysis. Electrospinning time was 5 min for all experiments.

Characterizations

Surface morphologies and characteristics of each PVA fibers obtained by using different electrospinning parameters were examined with the help of scanning electron microscopy (SEM, at 10.0 kV, JEOL JSM-6335F, Tokyo, Japan, after coating with Pt (Platin) by sputter coater device (Polaron SC7620, East Sussex, United Kingdom). The average diameters and histograms of fibers were determined to utilize Image J processing software application (National Institutes of Health; USA).

RESULTS AND DISCUSSION

The electrospinning variables influencing the full range of features of the fibers have motivated the investigators in many types of research for use in diverse applications (16, 17). In our study, electrospinning parameters mentioned elsewhere in the literature were changed; a variety of optimum spinning conditions were utilized to achieve the smooth and uniform PVA fibers without the free beads. Some SEM images selected were presented in Figures (a)-(e) to provide seeing the micrometer scale, unimodal, cylindrical, and beadless structure and smooth surface of the achieved PVA fibers to readers. As can be easily seen from the ×2,500 and 10,000 zoomed SEM images, while the flow rate and solution concentration fixed, if the applied voltage or TCD is increased to higher values, it is visibly evident that average diameter of the obtained fibers decreases to lower, as expected. Moreover, the obtained PVA fiber structures were almost the same in these conditions.

The primary purpose of this study was to provide researchers with a comprehensive overview of how several electrospinning parameters would affect the average fiber diameters of PVA fibers and their distribution. In this respect, the detailed Table 1 and some selected histograms (Figures 2(a)–(e) were presented.

The effect of polymer solution concentration on the diameter of electrospun fibers has been studied in the literature by several groups. Indeed, the uniaxial stretching of a charged jet, which can strongly be affected by the solution concentration mentioned in the Introduction part, is the essential phenomenon in the electrospinning technique. Based on the literature results, it is well-known that the increasing solution concentration caused to an increase in solution viscosity and formation of uniform fibers after the critical chain entanglement value, and increasing average diameter of fibers as well (18, 19). Firstly the effect of solution concentration on the average diameter of electrospun PVA fibers was investigated, and PVA solution concentration was varied from 11 to 15% (w/w). After the solution concentration was increased from 11 to 13 or 15%, the mean diameter of PVA fibers gradually was increased. The obtained results were in good agreement with the literature, as tabulated in Table 1 (20).

As stated in previous information, feeding or flow rate is another parameter that affected the resulted average diameter of fibers in the electrospinning process. Higher flow rate produces fibers with relatively larger diameter or vice versa due to the formation of a higher accumulated amount of suspended droplet on the spinneret that can lead to insufficient time to elongation of polymer chains (21). In our study, the flow rate was varied in the range of 0.6 and 1.4 $mL.h^{-1}$. One can see in Table 1, after the used flow rate was increased, the mean diameter of electrospun PVA fibers was increased, supporting the above-stated results achieved from concentration changes.

The reverse influences solution concentration and flow rate effects were obtained by altering both TCD and applied voltage parameters. The prevention of bead formation and adjusting the fiber diameter can be taken control by selecting the optimal TCD providing adequate time to complete solvent evaporation from the fibers before reaching the collector (19). As can be seen in Figures 1(a)-(e) and 2(a)-(e), and Table 1 as well, while the electrospinning TCD changed from 7 to 13 cm, the mean PVA fiber diameter decreased probably due to the reason mentioned above. On the other hand, the applied voltage that is known as driving force to jet initiation during electrospinning was the other examined parameter for solution electrospinning of PVA. In this respect, in our present study, PVA solution having different either concentrations and feed rates or varied TCD was electrospun with 15, 20, or 25 kV applied voltage. The average diameter of all the electrospun fibers achieved as uniform without bead formation decreased gradually with the increasing applied voltage from 15 to 25 kV, supporting the trend of mean diameter change when the TCD increased from 7 to 13 cm. These applied voltage changing results combined with the TCD alteration results were attributable to producing ultrafine or nanofibers resulting from higher electrostatic force to stretch the jet during electrospinning. Also, the observed results were in good agreement with the literature, as expected (22).

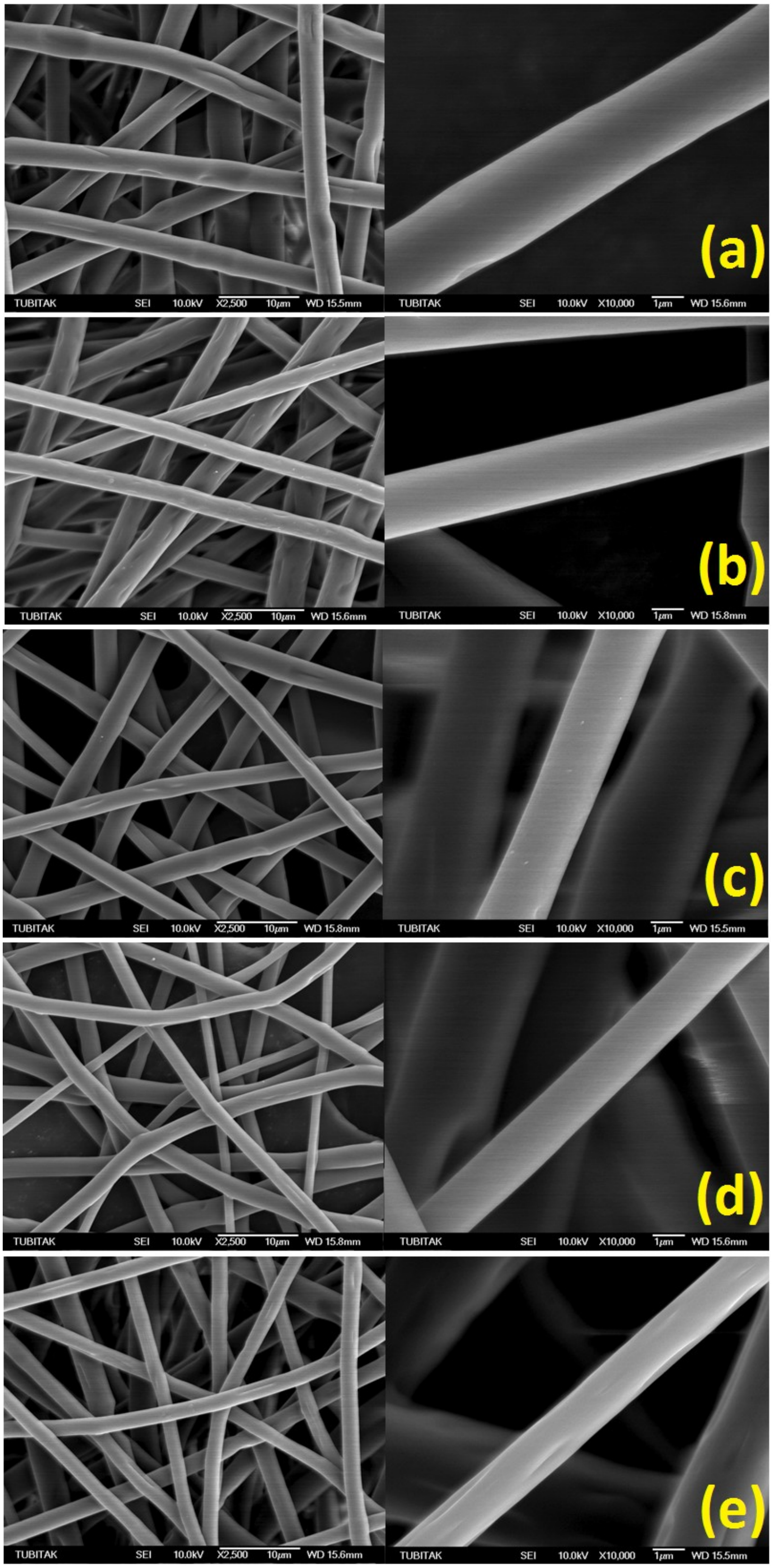

Figure 1. The SEM images (left, ×2,500) and their magnified micrographs (right, ×10,000) of electrospun PVA fibers obtained from 1 mL .h^{-1} flow rate, 13% (w/w) solution concentration, (a) 15 kV (7 cm TCD) (b) 20 kV (7 cm TCD) (c) 25 kV (7 cm TCD) (d) 25 kV (10 cm TCD) (e) 25 kV (13 cm TCD) applied voltages.

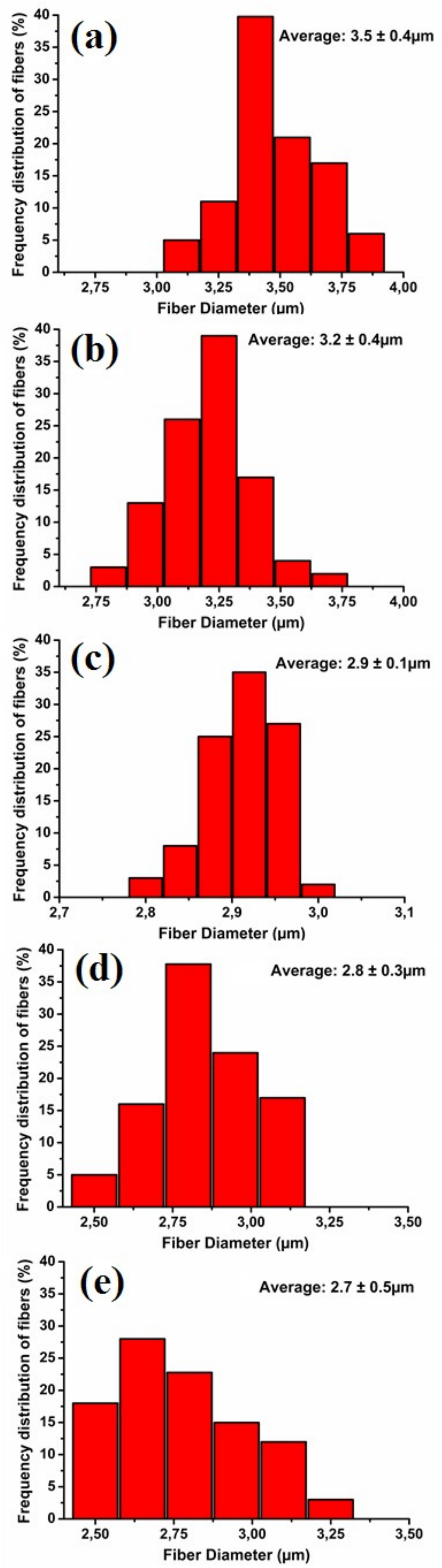

Figure 2. Frequency distribution and average diameter histograms of electrospun PVA fibers obtained from 1 mL.h^{-1} flow rate, 13% (w/w) solution concentration, (a) 15 kV (7 cm TCD) (b) 20 kV (7 cm TCD) (c) 25 kV (7 cm TCD) (d) 25 kV (10 cm TCD) (e) 25 kV (13 cm TCD) applied voltages.

Table 1. The data of experiments carried out at each variable of tip-to-collector distance, solution concentration, applied voltage, and solution flow rate.

Experiment No	Tip-to-Collector Distance, x= 7, 10 and 13 (cm)			Average Fiber Diameter ±std dev. (μm)		
	Solution Conc. (%w/w)	Applied Voltage (kV)	Solution Flow Rate ($mL.h^{-1}$)	x=7cm	x=10cm	x=13cm
1	11	15	0.6	3.1±0.3	3.0±0.1	2.9±0.7
2	11	15	1.0	3.1±0.5	3.0±0.5	3.0±0.1
3	11	15	1.4	3.1±0.9	3.1±0.4	3.0±0.9
4	11	20	0.6	2.9±0.4	2.7±0.1	2.6±0.8
5	11	20	1.0	2.9±0.9	2.9±0.2	2.8±0.8
6	11	20	1.4	3.0±1.0	3.0±0.6	2.9±0.9
7	11	25	0.6	2.7±0.5	2.6±0.9	2.4±0.2
8	11	25	1.0	2.8±0.1	2.7±0.7	2.6±0.7
9	11	25	1.4	2.8±0.5	2.9±0.5	2.9±0.1
10	13	15	0.6	3.4±0.3	3.2±0.3	3.1±0.1
11	13	15	1.0	3.5±0.4	3.4±0.6	3.2±0.4
12	13	15	1.4	3.6±0.3	3.4±0.2	3.3±0.3
13	13	20	0.6	3.0±0.4	2.9±0.3	2.8±0.3
14	13	20	1.0	3.2±0.4	3.1±0.5	2.9±0.4
15	13	20	1.4	3.3±0.4	3.2±0.3	3.1±0.6
16	13	25	0.6	2.8±0.2	2.7±0.3	2.5±0.3
17	13	25	1.0	2.9±0.1	2.8±0.3	2.7±0.5
18	13	25	1.4	3.0±0.5	2.9±0.1	2.8±0.7
19	15	15	0.6	3.6±0.5	3.5±0.4	3.3±0.5
20	15	15	1.0	3.7±0.4	3.6±0.3	3.5±0.3
21	15	15	1.4	3.8±0.3	3.6±0.7	3.6±0.1
22	15	20	0.6	3.4±0.5	3.2±0.5	3.1±0.3
23	15	20	1.0	3.4±0.8	3.3±0.7	3.2±0.1
24	15	20	1.4	3.6±0.4	3.6±0.8	3.5±0.9
25	15	25	0.6	3.1±0.3	2.9±0.3	2.8±0.1
26	15	25	1.0	3.2±0.5	3.1±0.7	3.1±0.2
27	15	25	1.4	3.2±0.8	3.2±0.2	3.1±0.9

CONCLUSION

In this study, the influence of electrospinning parameters such as polymer solution concentration, solution flow rate, tip-to-collector distance, and applied voltage was investigated deeply for the electrospun PVA fiber morphology, frequency distribution, and average diameter by conducting 27 separate experiments. Fiber properties such as fiber mean diameter, morphology, frequency distribution, etc. can be fully controlled with an appropriate combination of process, solution, and environmental parameters in the electrospinning process for the desired functions. The effect of these different variables on the resulted PVA fibers was tried to be explained logically by correlating with the previously published electrospinning literature papers. Depending on the attained results from the present comprehensive study, PVA fibers thus offer many attributions to scientists working on PVA fiber applications.

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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