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Investigation on the morphological characteristics of nanofiberous membrane as electrospun in the different processing parameters

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Abstract

In this study, polysulfone nanofibers were electrospun and effects of electrospinning parameters including applied voltage and tip-to-collector distance on the morphology of electrospun PSf nanofibers were investigated by SEM. SEM images of electrospun nanofibers showed that morphology and diameter of the nanofibers were mainly affected by applied voltage. Fourier transform infrared spectrometer and thermo-gravimetric/differential scanning calorimeter analysis were used to investigate the chemical and thermal properties of PSf nanofibers, respectively. The applied voltage and tip-to-collector distance were all shown to have varying effects on fiber diameter and fiber uniformity. Increasing the applied voltage results in increasing the surface charge of the jet and helps to reduce the frequency of occurrence of beads. It has shown that tip-to-collector distance directly affects spinnability and fiber diameter and at very low distance (5cm) droplets were formed due to the electro-spraying.

Keywords: Polysulfone, Electrospinning, Nanofiberous scaffold, Processing conditions

Background

Nanofibers have attracted interest and have been widely investigated for potential applications in electronics, mechanics, optoelectronics, and catalysis and for medical, biological, and environmental applications because of their several specific properties (e.g., high surface area to volume ratio, a very high aspect ratio, improved mechanical performance, relatively small pore size, and flexibility in surface functionalities) [1,2]. Nanofibers can be prepared by different processing techniques which include the following: (1) template synthesis [3], (2) self-assembly [4], (3) phase separation [5], (4) drawing [6], (5) melt-blowing [7], and (6) electrospinning [8]. Among them, electrospinning stands out as the most promising technique for fabrication of nanofibers. Although the electrostatic spinning processes have been discovered long time ago, electrospinning has gained much interest only by the end of the 20th century.

Electrospinning technique has attracted significant attention as a manufacturing process for producing nanofiber materials with diameters ranging from the micrometer to nanometer scales [9]. This technique provides a promising and straightforward way to fabricate infinite and continuous fibers applied as nanostructure and biomedical materials [10]. A wide range of materials such as engineered polymers, biological polymers, ceramics, and composites has been successfully electrospun into one-dimensional materials having many different microstructures [11]. Featuring the various outstanding properties such as very small fiber diameters, large surface area per mass ratio, high porosity along with small pore sizes [11], flexibility, and superior mechanical properties [12], nanofiber mats have found numerous applications in biomedicine (tissue engineering, drug delivery, and wound dressing), filtration, protective clothing, reinforcement in composite materials, and microelectronics (battery, transistors, supercapacitors, sensors, and display devices) [13-18].

The electrospinning process involves application of a high electric field to a polymer solution or polymer melt. A schematic of an electrospinning set-up is shown in

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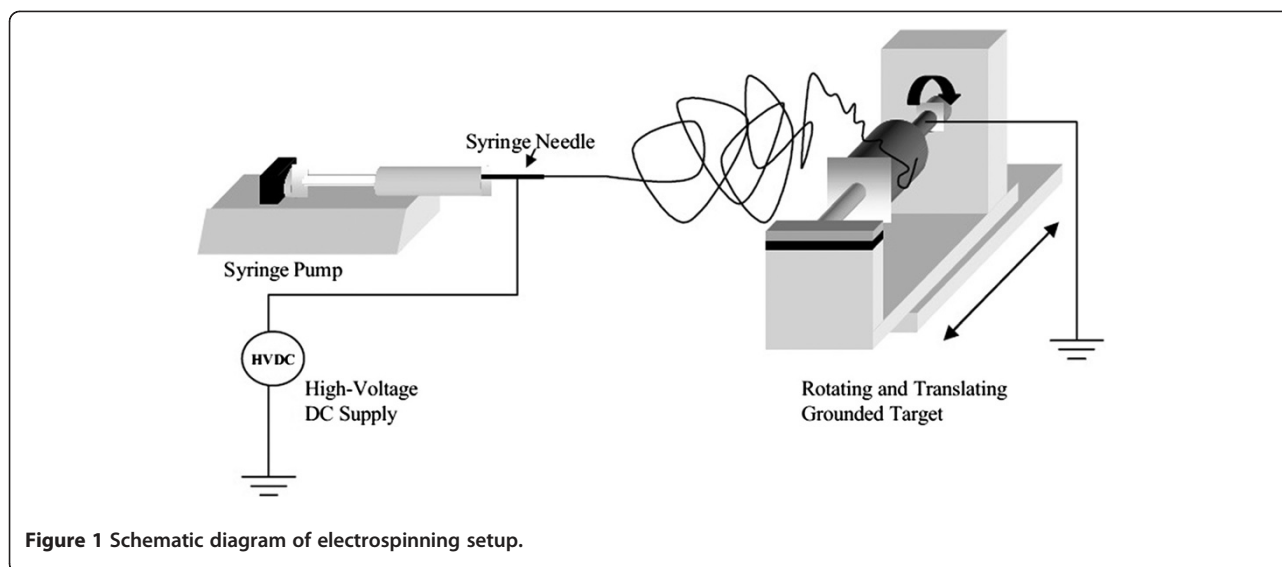


Figure 1. There are three basic components including a high voltage supply device, a reservoir with a capillary tip for the spinning solution, and a metallic collector [19]. The polymer solution or melt is delivered through the capillary by means of an appropriate pump. One electrode lead of a high voltage power supply is immersed into the polymer solution or connected to the capillary tip of the reservoir, and the other one is connected to the collector. Applying high voltage (between 10 and 50 kV) on the solution induces electric charges. The mutual charge repulsion creates force acting oppositely to the solution surface tension. As the applied field strength is increased, the hemispherical solution surface at the tip of the capillary deforms into a conical shape (Taylor cone) [20]. When the applied field strength exceeds a threshold value, the repulsive electrostatic force overcomes the surface tension, and the charged jet is ejected from the tip of the Taylor cone. The small jet diameter permits rapid mass exchange, and the solvent usually evaporates during its travel from the capillary to the collector acting as a counter electrode. As a result, charged polymer fiber is deposited on the collector. The electrospun fiber charges are gradually neutralized in the environment. The end product of the process usually consists of randomly deposited fibers (mat) with diameters ranging from micrometers to nanometers.

Morphological characteristics of electrospun nanofibers, such as fiber diameter and uniformity, depend on many parameters which are mainly divided into the three categories: solution properties (solution concentration, solution viscosity, polymer molecular weight, and surface tension), processing conditions (applied voltage, volume flow rate, spinning distance, and needle diameter), and ambient conditions (temperature,

humidity, and atmosphere pressure). It should be noted that among them, processing conditions are the most affecting parameter on the morphology of electrospun fibers [21]. In this study, electrospun polysulfone (PSf) nanofibers were fabricated by electrospinning 15% (w/v) PSf in *N,N*-dimethyl formamide (DMF) as solvent. Also, the effect of processing conditions (applied voltage and tip-to-collector distance (TCD)) on the fiber properties such as diameter and uniformity was analyzed, and the optimum conditions to make the best nanofiber mat were investigated.

Methods

Electrospinning of PSf nanofibers

PSf ($M_w = 70,000$, Sigma-Aldrich Corporation, St. Louis, MO, USA) and DMF as solvent (Merck Co., Germany) were used as received without further purification. It has been shown that electrospun PSf fibers can be produced using various solvent systems, and among them, DMF was found to be the most favorable solvent for producing uniform round fibers with smooth surfaces due to its high boiling point, high solution conductivity, and high dielectric constant compared to other solvents [22].

The electrospinning of the PSf solution was conducted using 15% (w/v) PSf (Scheme 1) solution in DMF. The complete electrospinning apparatus consisted of a syringe

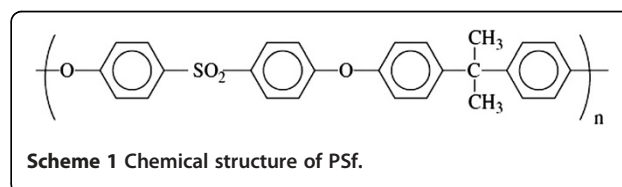


Table 1 Processing parameters of electrospinning

Trial number	V (kv)	D (cm)	C (w/v)	F (ml/min)	S (rpm)	Average fiber diameter (nm)
1	10	5	15	0.5	1,000	320
2	10	10	15	0.5	1,000	300
3	10	15	15	0.5	1,000	270
4	15	5	15	0.5	1,000	500
5	15	10	15	0.5	1,000	430
6	15	15	15	0.5	1,000	350
7	25	5	15	0.5	1,000	370
8	25	10	15	0.5	1,000	330
9	25	15	15	0.5	1,000	305

C, concentration; D, spinning distance; F, flow rate of solution; S, speed of rotating collector; V, voltage.

and stainless needle, ground electrode, copper plate covered by aluminum foil as a collector, and adjustable high voltage supply (FNM Co., Tehran, Iran). The prepared solution was placed into the syringe, and a positive lead from the power supply was attached to the external surface of the metal needle. When high voltage was applied across the solution and the grounded collector, the solutions in the syringe would be ejected from the tip of the needle to generate fibers, which would be collected on the grounded collector. In this study, the resulting solutions were electrospun at 10- to 25-kV applied positive voltage, 5- to 15-cm working distance (the distance between the needle tip and the collector), and 1 ml/h solution flow rate controlled by a syringe pump (Table 1).

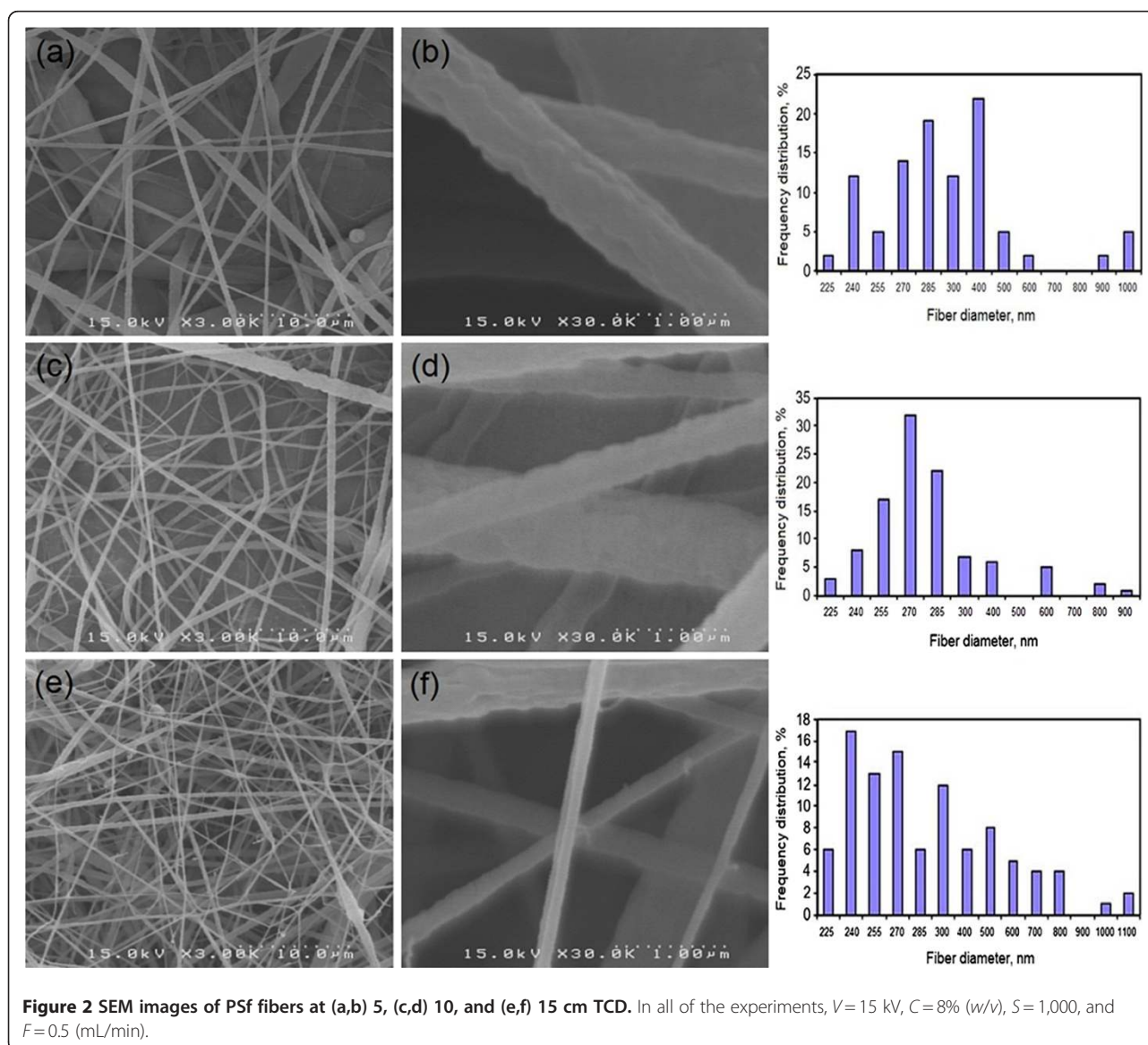


Figure 2 SEM images of PSf fibers at (a,b) 5, (c,d) 10, and (e,f) 15 cm TCD. In all of the experiments, V = 15 kV, C = 8% (w/v), S = 1,000, and F = 0.5 (mL/min).

Characterizations

The surface morphology of the electrospun fibers was observed on a JEOL JSM-5600LV scanning electron microscope (JEOL Ltd., Akishima, Tokyo, Japan) at an acceleration voltage of 10 to 25 kV. The samples for scanning electron microscopy (SEM) were dried under vacuum, mounted on metal stubs, and sputter-coated with gold. The mean PSf fiber diameters were estimated using image analysis J software and calculated by selecting 100 fibers randomly observed on the SEM image.

The samples used for Fourier transform infrared (FTIR) analysis were cast to be thin enough to ensure that the observed absorption was within the linearity range of the detector. FTIR spectra of the electrospun PSf mat were recorded using attenuated total reflection in an IR

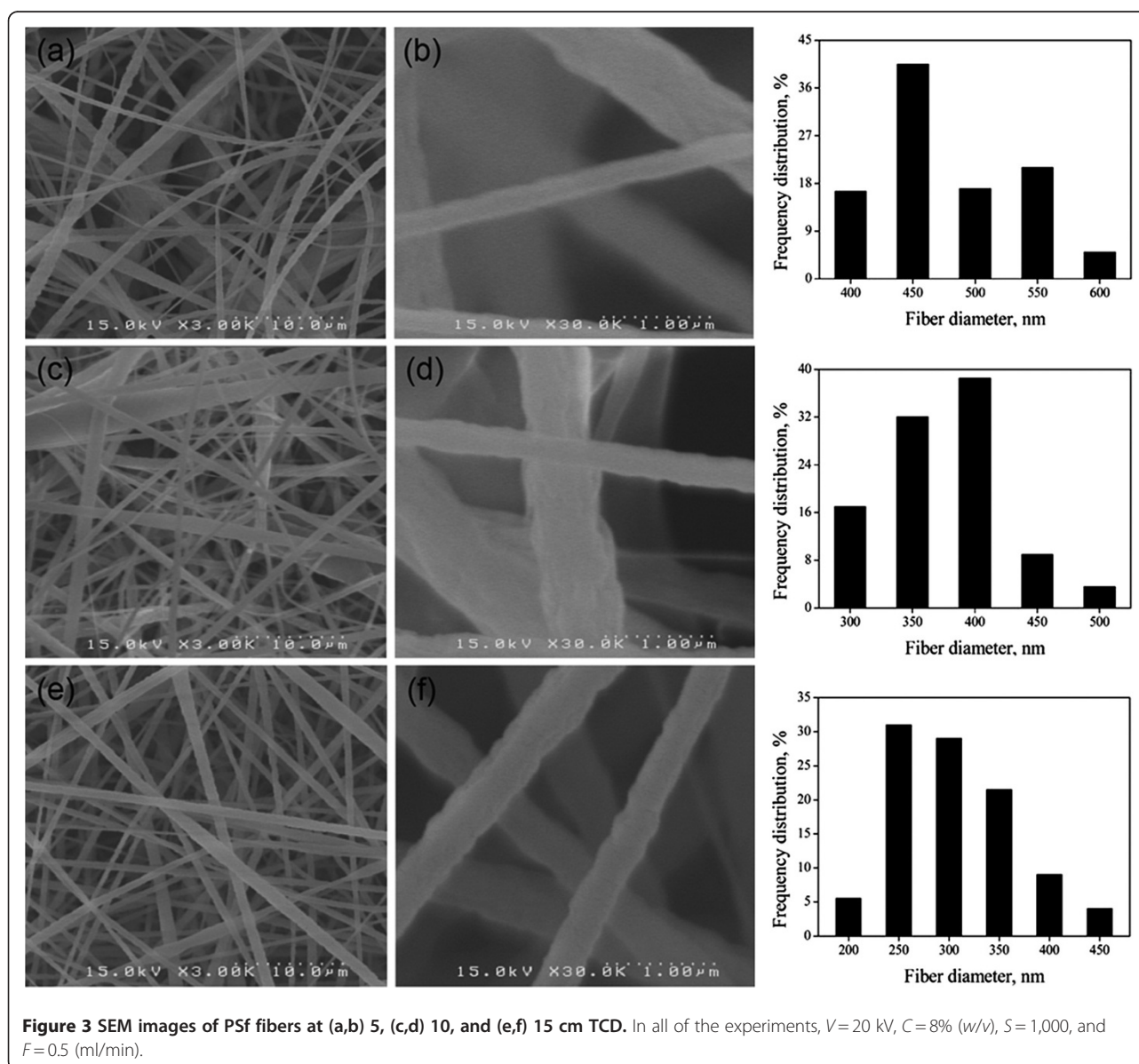
spectrometer (Nicolet Avatar 360, Madison, WI, USA.). The transmission infrared spectra of all samples exhibited broad peaks in a range from 4,000/cm to 400/cm.

Thermal stability of the electrospun PSf mats was examined by thermogravimetric/differential scanning calorimeter (TGA/DTA) experiments using SII model EXTAR TG 6200 (Seiko Instruments Inc., Chiba, Japan). All the samples were pre-weighed and allowed to undergo programmed heating in the temperature range of 50°C to 700°C at a rate of 10°C/min.

Results and discussion

Morphological properties: effect of processing conditions

Fiber formation using electrospinning technique is a complex process affected by a great number of



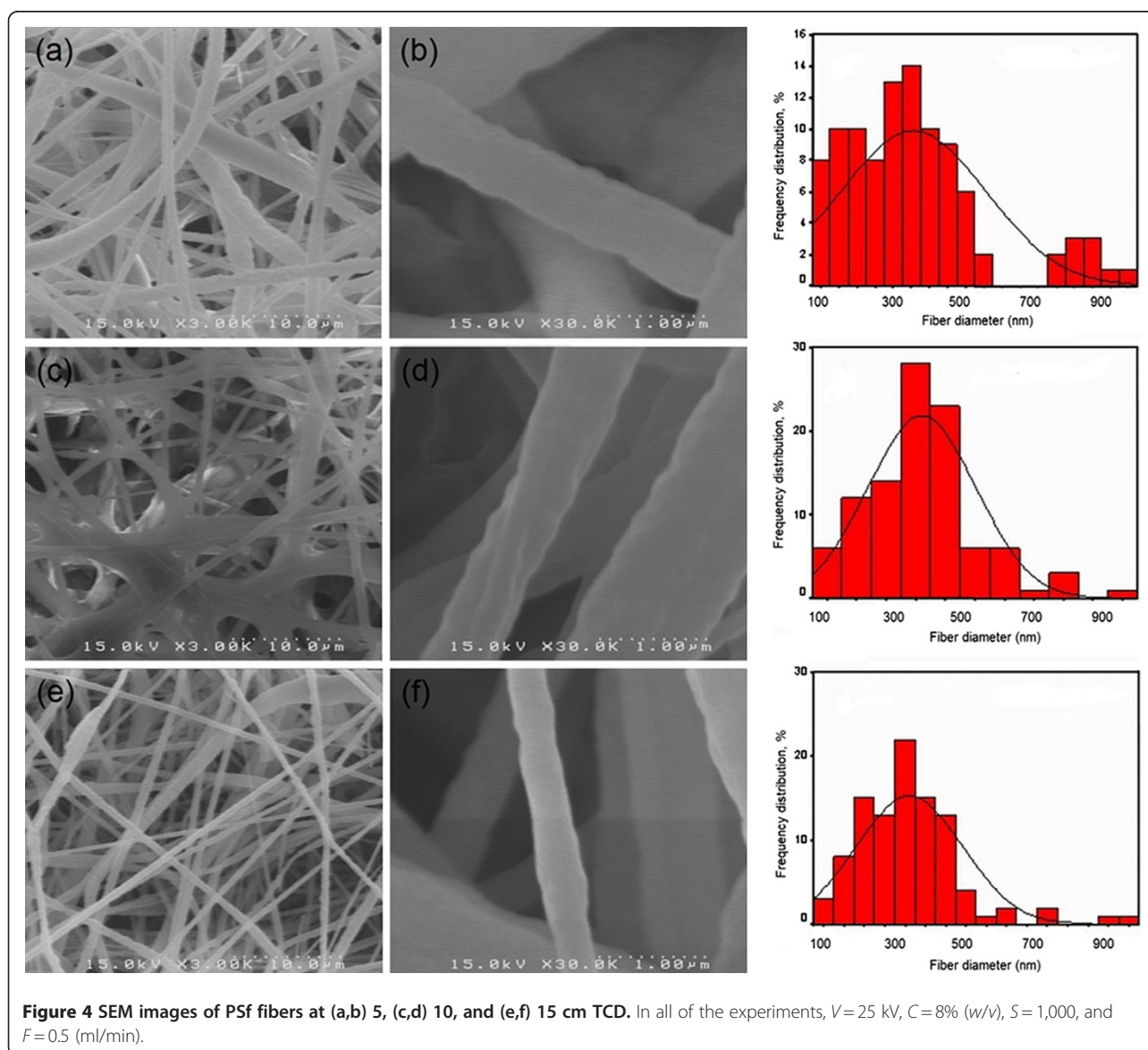
parameters that generally include the following: (1) solution parameters, (2) process variables, and (3) ambient parameters.

Solution parameters include polymer type (natural or synthetic, organic or inorganic, monogenic or non-monogenic, linear or branched), polymer molar mass, solution characteristics (viscosity, volatility, dielectric constant), absence or presence of a low molecular weight organic or inorganic salt, conductivity of spinning solution, and solution surface tension. Process variables include electric potential at the capillary tip, the gap (distance between the tip and the collector (TCD)), and feed rate. Ambient parameters include air pressure, temperature, and humidity. Knowledge and control of these parameters are of great importance for successful preparation of micro- and nanofibers of polymers with a desired morphology.

Among these parameters, the process variables have more effect on the morphological characteristics of fibers. In this study, effect of applied voltage (10 to 25 kV) and TCD (5 to 15 cm) on the fiber diameter and morphology were investigated and discussed with the results tabulated in Table 1.

Applied voltage

Figure 2 shows the morphology and average diameter of electrospun fibers fabricated at various levels of voltage applied to 15 wt.% PSf. Electrospinning was done at a solution flow rate of 100 ml/min and TCD of 5, 10, and 15 cm. It was shown that as the applied voltage was increased from 10 to 15 kV, the fiber diameter was increased, and after that with more increases of voltage, fiber diameters were decreased. At higher applied



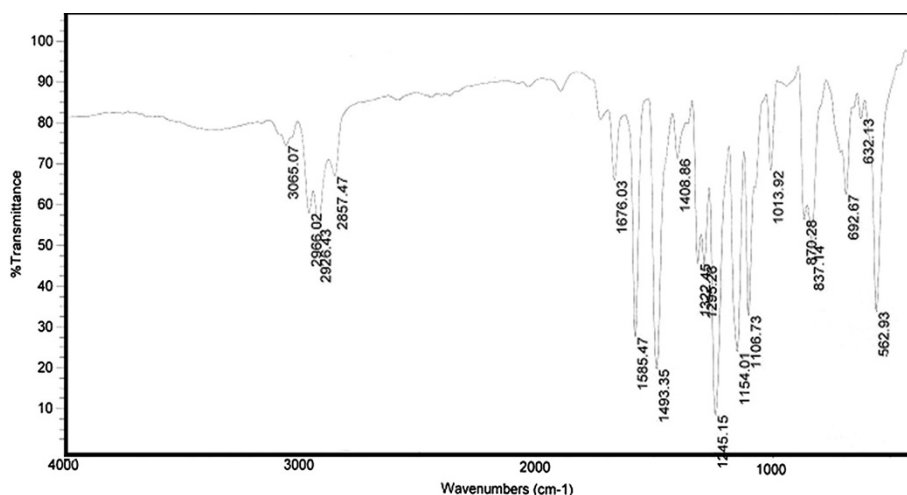


Figure 5 FTIR spectra of PSf.

voltages, the charge could be accelerated so that there is not enough time for the spinning solution to be developed, and thus, the fiber diameter increased as it was observed for the 20-kV applied voltage [23]. However, in most cases, a higher voltage will lead to greater stretching of the solution due to the greater columbic forces in the jet as well as the stronger electric field. These have the effect of reducing the diameter of the fibers as observed for 25-kV applied voltage [24].

In general, when high voltage is applied during the electrospinning process, Taylor cone formation becomes stable, and then, the columbic repulsive force within the jet of spinning solution makes the viscoelastic solution extended. If the applied voltage is higher than the critical point, wherein more charge will drop from the end of

the needle due to the acceleration of charge, the Taylor cone becomes unstable [25].

Distance between tip and collector

Bead formation is the most common type of defect encountered in electrospun fibers and occurs primarily as a result of the instability of the jet under different process conditions [26]. Qualitatively, beads may be expected at times during the electrospinning whenever the surface tension forces tend to overcome the forces (including charge repulsion and viscoelastic forces) that favor the elongation of the continuous jet [27]. This process occurs intermittently, as fiber formation still remains a dominant process and consequently leads to the typical 'beads on a string' morphology described for a variety of different polymer-solvent systems (Figure 3) [28].

Table 2 FTIR assignments of electrospun PSf nanofiber mat

Frequency (cm ⁻¹)	Assignments
3,065	O-H stretching vibrations
2,966; 2,926; 2,857	Asymmetric and symmetric C-H stretching vibrations involving entire methyl group
1,585; 1,493	Aromatic C=C stretching
1,408	Asymmetric C-H bending deformation of methyl group
1,365	Symmetric C-H bending deformation of methyl group
1,322; 1,295	Doublet resulting from asymmetric O = S = O stretching of sulfone group
1,245	Asymmetric C-O-C stretching of aryl ether group
1,154	Asymmetric O = S = O stretching of sulfonate group
1,106	Symmetric O = S = O stretching of sulfone group
1,013	Aromatic ring vibrations

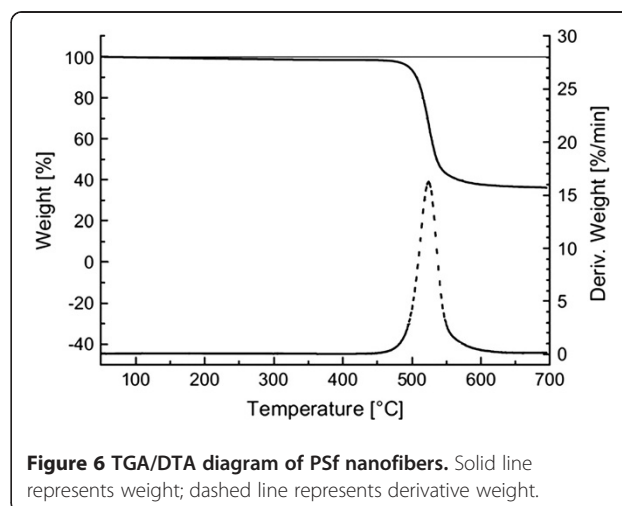


Figure 6 TGA/DTA diagram of PSf nanofibers. Solid line represents weight; dashed line represents derivative weight.

Theoretical analyses of the mechanism of the bead formation have been attempted by several groups. The rapidly elongating jet could undergo several different modes of instability. Analysis, for instance, predicted three modes of instability that can develop in extending the jet, of which two are axisymmetric. One of these is the Rayleigh instability, which is primarily governed by the surface tension, and the other is the conducting instability governed mainly by the electrical conductivity of the fluid. In axisymmetric instability, the axis of the electrospun fiber remains undisturbed, but its radius is modulated, yielding the wave-like deformations of the fiber that are the precursors of beads. Therefore, the processing conditions that favor axisymmetric instabilities also favor bead formation, whereas increased whipping instability discourages bead formation. Higher surface charge densities favor whipping instability over axisymmetric modes, therefore generally suppressing bead formation (Figure 4).

In general, depending on the solution property, the effect of varying the distance may or may not have a significant effect on the electrospun fiber morphology. In some cases, changing this distance has no significant effect on the fiber diameter. However, beads were observed to form when the distance was too low (Figure 3) [28]. The formation of beads may be the result of the increased field strength between the needle tip and the collector. Decreasing the distance has the same effect as increasing the applied voltage, and this will cause an increase in the field strength. As the field strength becomes too high, increased instability of the jet may encourage bead formation [29]. However, if the distance being such that the field strength is at an optimal value, there are less beads formed as the electrostatic field provides sufficient stretching force to the electrospun jet [30].

In other circumstances, increasing the distance results in a decrease in average fiber diameter (Figure 4) [31]. A longer distance means that there is a longer flight time for the polymer solution to be stretched before it is deposited on the collector [32]. However, there are some cases where at a longer distance, the fiber diameter increases. This is due to the decrease in the electrostatic field strength, resulting in less stretching of the resultant fibers [33]. When this distance is too large, no fibers are deposited on the collector. Therefore, it seems that there is an optimal electrostatic field strength; below which, the stretching of the PSf solution will decrease, resulting in increased fiber diameters.

Structural properties

FTIR spectroscopy

The FTIR spectra of the electrospun PSf nanofiber mat are shown in Figure 5, and the chemical assignments of PSf were illustrated in Table 2. The main peaks of PSf were characterized by the peaks at 1,585, 1,245, 1,322,

1,154, 1,106, and 1,013 cm^{-1} that correspond to the stretching of aromatic C = C, C-O-C (ether group), and O = S = O, respectively.

Thermal properties

The thermal decomposition of the PSf nanofiber mat has been studied using thermal analyses. Figure 6 shows the TGA/DTA diagram for the electrospun fibers. TGA of PSf nanofibers showed two different stages of weight loss. The first stage ranges between 100°C and 520°C that may correspond to the loss of adsorbed and bound water and other organics. The second stage of weight loss starts at around 520°C, in which there was 90% weight loss, due to the degradation of PSf. The DTA of PSf shows a broad endothermic peak around 520°C. This peak is attributed to the decomposition of the PSf nanofiber mat.

Experimental

Polysulfone (PSf) ($M_w = 70,000$, Aldrich Co., St. Louis, 104Q6 MO, USA) and N,N-dimethyl formamide (DMF) as solvent (Merck Co., Germany) were used as received without further purification. It has been shown that electrospun PSf fibers can be produced by using various solvent systems, and among them, DMF was found to be the most favorable solvent for producing uniform round fibers with smooth surfaces due to its high boiling point, high solution conductivity and high dielectric constant compared to other solvents [22].

Conclusion

This study deals with the effects of processing variables including applied voltage and TCD on the morphological properties of electrospun PSf fibers that were investigated quantitatively as well as qualitatively. The appropriate range of parameters including dry, bead-free, and continuous fibers without breaking up to droplets was formed. It was observed that TCD has a direct influence on jet flight time and electric field strength. A decrease in this distance shortens flight times and solvent evaporation time and also increases the electric field strength, which results in more bead formation. Longer spinning distance resulted in more uniform PSf fibers. The effect of the spinning distances was more pronounced at higher applied voltages. Increasing the applied voltage increases the surface charge of the jet and helps to reduce the frequency of occurrence of beads.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

All authors read and approved the final manuscript.

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