Effect of Processing Parameters on the Morphology of PVDF Electrospun Nanofiber

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Abstract. Electrospinning is a process that produces continuous polymer fibers with diameters in the submicron range through the action of an external electric field imposed on a polymer solution or melt. Because of the tiny diameter in several hundreds of nanometers and the high porosity, electrospun membranes show potential applications in extensive areas such as filtration systems, biomedical tissue templates, drug delivery membranes, and so on. In the electrospinning process, some parameters such as polymer concentration, feeding rate of the polymer solution, additives, humidity, viscosity, surface tension, applied voltage, and nozzle-to-ground collector distance will affect the fiber diameter and morphology. In this work, we have evaluated the effects of two processing parameters including the flow rate of the polymer solution and nozzle-to-ground collector distance, on the morphology of the fibers formed. The solutions used in the electrospinning experiments were prepared using Poly(vinylidene fluoride) (PVDF). This material was dissolved in N,N-dimethylformamide (DMF) to make solutions with concentrations of 20 wt%. These solutions was electrospun using a 5 mL plastic syringe with an 8 gauge stainless needle at an applied voltage of 20.0 kV, a flow rate of 0.02-0.04 mL/min and nozzle-to-ground collector distance of 12 and 15 cm. Electrospinning of PVDF polymer solution was performed in horizontal alignment having a grounded aluminum foil which serves as a collector. The nanofibers obtained were characterized by polarizing optical microscope. We find that the low flow rate of the polymer solution and nozzle-to-ground collector distance are strongly correlated with the formation of bead defects in the fibers.

1. Introduction
Polymer nanofibers are an important class of nano-materials, which have attracted increasing attention in the last decade because of their high surface-to-mass (or volume) ratio and special characteristics attractive for advanced application, such as filtration and water treatment [1,2], catalyst and catalyst support [3,4], adsorbents [5-9], polymer electrolyte membrane [10], membrane distillation [11], hydrogen generator [12] and sensors [13]. Traditional methods of obtaining polymer fibers include melt spinning, spinning from solution or liquid crystalline state, and forming fibers from a gel state [14]. Nowadays, there has been increased interest in another method of fiber production, namely electrospinning, which can consistently produce fibers that are sub-micron in diameter [14].
The electrospinning process consists of the following steps: (i) a strong electric field is applied between a polymer solution contained in a nozzle and a conductive substrate; (ii) when the voltage reaches a critical value, electrostatic forces overcome the surface tension of the solution; (iii) charged droplets or jets are sprayed from the tip of the nozzle, in a dry atmosphere; and (iv) the dried droplets or jets are finally collected on the substrate to form a thin film [15]. In the electrospinning process, some parameters such as polymer concentration, flow rate of the polymer solution, additives, humidity, viscosity, surface tension, applied voltage, and nozzle-to-ground collector distance will affect the fiber diameter and morphology [15].

Polyvinylidene fluoride (PVDF) is a thermoplastic polymer built on \((\text{CH}_2\text{CF}_2)_n\) monomer and usually contain 59.4% fluorin and 3% hydrogen [16]. PVDF possesses excellent thermal and chemical stability, excellent mechanical strength [17-19], resistance towards UV radiation and corrosion, high dielectric permittivity and characteristic pyroelectric and piezoelectric properties [20]. PVDF is a non-flammable material with a good sliding property and high abrasion capacity. Its soluble in several polar organic solvent namely N,N-Dimethylacetamide (DMAc), N,N-Dimethylformamide (DMF) and N-Methyl-2-pyrrolidone (NMP) [17]. PVDF is an electro active polymer due to high polarizability of the C-F moiety. It has at least four main crystalline structure (\(\alpha\), \(\beta\), \(\gamma\), \(\delta\)) with different polarity, i.e. \(\alpha\)-phase is a non-polar whilst \(\beta\)-phase has polar properties. Each phase of PVDF can be used for specific application [15,16]. Owing to its properties, PVDF is developed as high performance membrane for application in distillation, membrane contactor and wastewater treatment [16,17].

2. Materials and method

2.1. Materials
PVDF polymer (Scientific Polymer Products, USA), N,N-dimethylformamide (DMF; Aldrich, Milwaukee, WI, USA), Electrospinning apparatus, optic microscopy (Nikon Eclips E400, Japan).

2.2. Method
The PVDF polymer was dissolved in N,N-dimethylformamide to form a 20 wt% solution. The polymer solution was transferred to a spin pack containing spinnerets (capillary tip = 0.5 mm diameter). Electrospinning was carried out by applying a high positive voltage (20 kV) to the polymer solution via the spinneret tip with flow rate ranging from 0.02 to 0.04 mL/min and nozzle-to-ground collector distance of 12 and 15 cm. The electrospun fibers were collected as a thin web on a current collector plate with a suction collector. The electrospun nanofiber web was then passed under rollers at 140 \(^\circ\)C to fabricate a dense PVDF nanofiber membrane. The morphology and structure of the PVDF nanofiber membrane were characterized by optic microscopy.

3. Results and Discussion

3.1. Effect of flow rate
The effect of flow rate on morphology of the nanofibers formed can be seen at Figure 1. The nanofibers produced under 0.02 mL/min conditions have a cylindrical morphology with many bead defects present and not uniform (Figure 1a).

As flow rate is increased, the electrospun fibers produced still have essentially a cylindrical morphology, but there is a distinct decrease in number of bead defects present in the fiber mat. At 0.04 mL/min, the morphology of the fibers produced becomes more uniform and the bead defects are lost. Formation of beads can occur when the wet polymer fibers were collected on the grounded collector with the self-repulsion force by the electric field. Without strain force, this condition caused the fibers to melt and solidify, hence formation of beads [21]. When the flow rate was increased the fibers are formed faster hence more strain force on the grounded collector and the beads do not has sufficient time to form.
The flow rate of the PVDF solution also affects the surface charge density and the electrical current of the polymer solution [22]. Increasing the flow rate will cause an increase in electrical current due to the electroactive nature of PVDF polymer. On the contrary, the surface charge density decreases as the flow rate increases, thus preventing the formation of beads defects on the fiber mat. The wavy morphology caused by the presence of beads will reduce the membrane porosity hence the ability to minimize its formation will be preferred.

![Optical micrographs of nanofiber by electrospinning from PVDF solution at different flow rate](image1)

(a) 0.02 mL/min (b) 0.03 mL/min, and (c) 0.04 mL/min.

**Figure 1.** Optical micrographs of nanofiber by electrospinning from PVDF solution at different flow rate (a) 0.02 mL/min (b) 0.03 mL/min, and (c) 0.04 mL/min.

### 3.2. Effect of nozzle to ground collector distance

Figure 2 shows that higher nozzle to ground collector distance produce uniform fibers. This effect is common for electrospun polymers [21,23]. Nozzle to ground collector distance will affect the jet pathway and electric field strength hence the morphology of the nanofibers. Narrow nozzle and ground collector distance cause the formation of wavy fiber mat (Figure 2a). Higher distance will form more uniform fibers (Figure 2b).

The nozzle-to-ground collector distance affects the solvent evaporation and the continuous stretching due to the electrical force [24]. As the distance increases, the electrical field strength at constant applied voltage decreases; however, the evaporation time of the polymer jet to reach the ground collector increases.

![Optical micrographs of nanofiber by electrospinning from PVDF solution at different nozzle to ground collector distance](image2)

(a) 12 cm (b) 15 cm.

**Figure 2.** Optical micrographs of nanofiber by electrospinning from PVDF solution at different nozzle to ground collector distance (a) 12 cm (b) 15 cm.
4. Conclusion
In the present study, the determining factors on the beads formation on fibers mat were investigated. Lower flow rate (0.02 mL/min) induces the formation of beads defects and produce fibers with cylindrical morphology. As the flow rate was increased to 0.04 ml/min, the beads defects are lost. Another parameter that influences the formation of beads defects is nozzle-to-ground collector distance. A clear difference was observed when the fibers are formed at 12 and 15 cm nozzle-to-ground collector distance. At higher nozzle to ground collector distance the fibers are more uniform with little beads formation observed on the optical micrographs images. These results provide information for preparation of high-performance PVDF nanofiber by electrospinning method.

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