

## A Study of Electrospun PVDF on PET Sheet

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**Abstract:** PVDF (Kynar<sup>®</sup> 761) nanofibers were made by electrospinning with an external voltage of 6-10 kV, a traveling distance of 7-15 cm and a flow rate of 0.4-1 mL/h. Although the mean diameter of the fibers has not changed significantly, the conditions affected the change in diameter distribution. This was attributed to interactions, both attraction and repulsion, between the positive charges on the polymer solutions and the electrically grounded collector. Higher voltages and traveling distance increased the level of attraction between the positive charge on the polymer solution and the electrically grounded collector, resulting in a narrow diameter distribution. In addition, a high flow rate allowed a high population of uniformly charged solutions to travel to the grounded collector, which resulted in a narrow diameter distribution. The optimum conditions for electrospinning of PVDF in DMAc/acetone (3/7 by wt) were a collector voltage of 6 kV, a syringe tip to collector of 7 cm, a flux rate of 0.4 mL/h and 10 kV, 10 cm, 1 mL/h. Since PVDF is widely used as a filtration membrane, it was electrospun on a PET support with a rotating drum as a grounded collector. Surprisingly, some straight nanofibers were separated from the randomly deposited nanofibers. The straight nanofiber area was transparent, while the randomly deposited nanofiber area was opaque. Both straight nanofibers and aligned nanofibers could be obtained by manipulating the PET drum collector. These phenomena were not observed when the support was changed to an Al sheet. This suggests that a pseudo dual collector was generated on the PET sheet. No negative charge was created because the PET sheet was not a conductive material. However, less charge was created when the sheet was not perfectly attached to the metal drum. Hence, the nanofibers jumped from one grounded site to the nearest one, yielding a straight nanofiber.

*Keywords:* PVDF, electrospinning, alignment.

### Introduction

Electrospinning is a fiber spinning technique that produces materials with sub-micrometer to nanometer size and high surface area. Current research efforts are focused on using electrospun fibers for filtration, chemical/biological resistant protective clothing, tissue engineering, and electronic applications.<sup>1-5</sup> In electrospinning, a polymer solution is ejected from a capillary by a strong electrostatic force and deposited as a non-woven fibrous mat on an electrically grounded target. As this jet travels through the air, the solvent evaporates, leaving behind ultrafine polymer fibers.

Electrospinning is derived from electrospraying, and hence unexpected morphologies such as beads, necklaces, etc. can be formed.<sup>6,7</sup> However, with optimum conditions, a nice non-woven fibrous mat is obtained.

Because of its outstanding properties: good electrical insulation and chemical resistance, good thermal properties, and biocompatibility, poly(vinylidene fluoride) (PVDF) has been extensively investigated for its application as membrane materials.<sup>8,9</sup> PVDF membranes have been used for proton conduction,<sup>10-12</sup> gas removal and separation, and biological applications.<sup>13-18</sup> The disadvantage of using PVDF as a membrane is its tendency to foul. Hence a variety of techniques (e.g. chemical treatment, chemical or radiochemical grafting, plasma treatment, dip coating) have been developed to make

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the membrane surface hydrophilic.<sup>19-24</sup> Most membranes are currently produced by a phase inversion of polymer solutions. However, pore and pore size distribution are difficult to control. As a result, electrospinning, an easy and convenient technique can be a new method for making fibrous mat membranes.

The goal of this study was to produce electrospun PVDF fibers, to determine the effect of processing parameters on their morphology, and to attempt to electrospin PVDF fibers onto PET sheet to make filtration membranes.

## Experimental

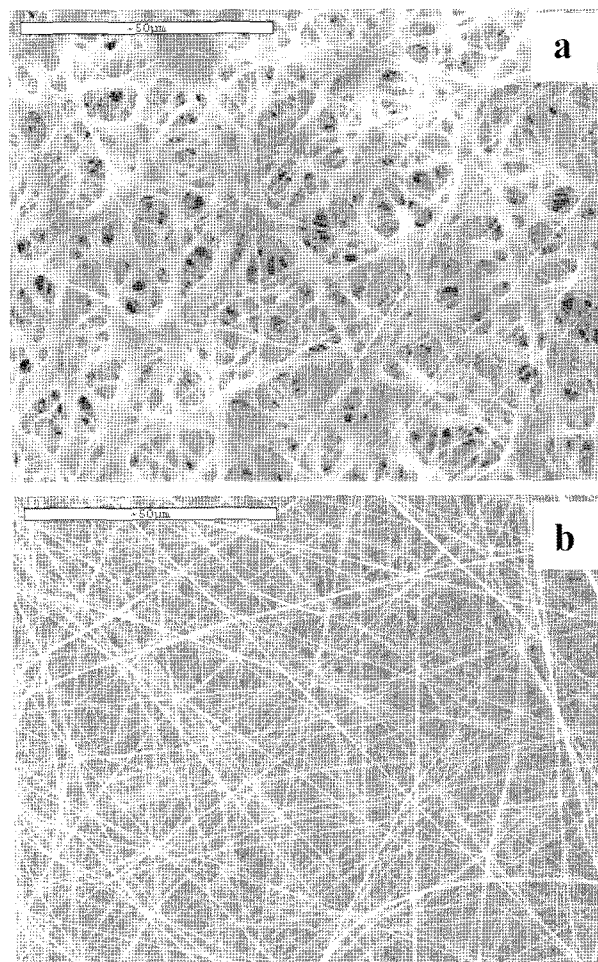
**Chemicals and Preparation of Solutions.** Polyvinylidene fluoride (Kynar<sup>®</sup> 761) with a  $M_w$  of 441,000 was obtained from Arkema Ltd., Korea. Acetone and *N,N*-dimethylacetamide (DMAc) were purchased from Duksan Chemical Co. Ltd. The polymer was dissolved in a mixed solvent of acetone/DMAc with the ratio of 7/3 by weight to obtain a concentration of 19% by weight. The polymer was dissolved at 35 °C.

**Electrospinning.** The electrospinning setup consisted of a plastic syringe (5 mL) and a steel needle (0.41 mm i.d.). The needle was connected to a high voltage power supply (Chungpa EMT Co., Korea). An automatic voltage regulator (Hyo Sung Electric Eng. Co.) was attached to the power supply to produce uniform voltages. The fiber was deposited on an Al sheet or PET sheet on the grounded electrodes, both as a flat sheet and on a rotating drum. Typically, electrospinning was performed at voltage of 6-15 kV and a distance between the needle tip and the grounded collector (so-called traveling distance) of 7-15 cm. The flow rate of the solution was controlled by a syringe pump (Kd Scientific series 100, USA) and maintained at 0.4-1 mL/h from the needle outlet. All the experiments were carried out at 19-24 °C and 15-25% humidity.

**Scanning Electron Microscope (SEM).** Electrospun fibers were coated with gold using sputter coating and their morphology was observed under SEM (model: JSM-5410, JEOL) with an accelerating voltage of 20 kV and a magnification of 1,000-10,000. An optical microscope was also used for morphological scans. The size of nanofiber was measured on 10,000 magnification SEM images using a vernier. The distribution of fiber diameters was evaluated from 65-90 measurements.

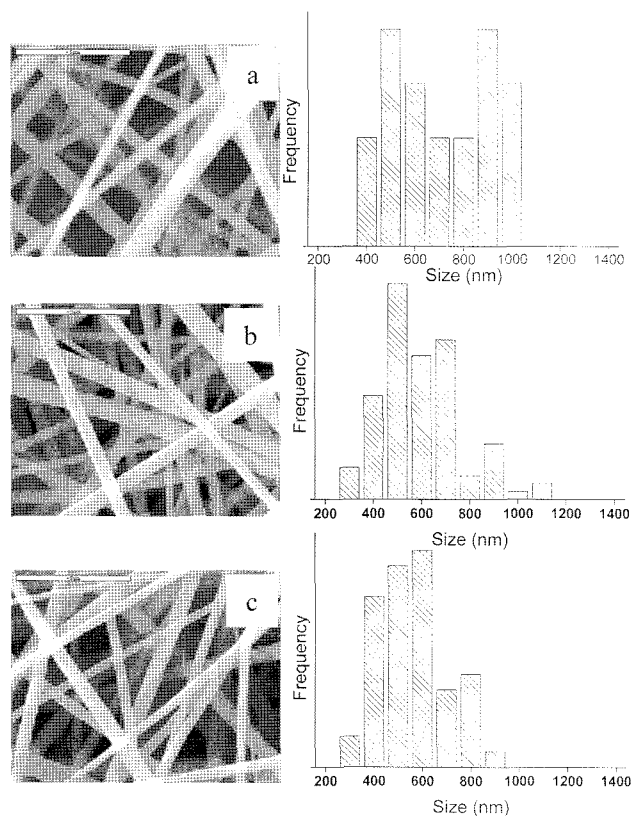
## Results and Discussion

**Conditions for Electrospinning.** PVDF has been electrospun<sup>25-28</sup> with a variety of solvents and concentrations. As a matter of fact, the morphology of the electrospun polymer fibers is dependent on many parameters – solution properties, processing conditions, and ambient conditions.<sup>29,30</sup> However, solution properties are one of the most important parameters



**Figure 1.** SEM images of 19% PVDF (DMAc/acetone : 3/7 by wt.) at traveling distance of 7 cm; (a) 7 kV, 0.25 mL/h and (b) 6 kV, 0.4 mL/h.

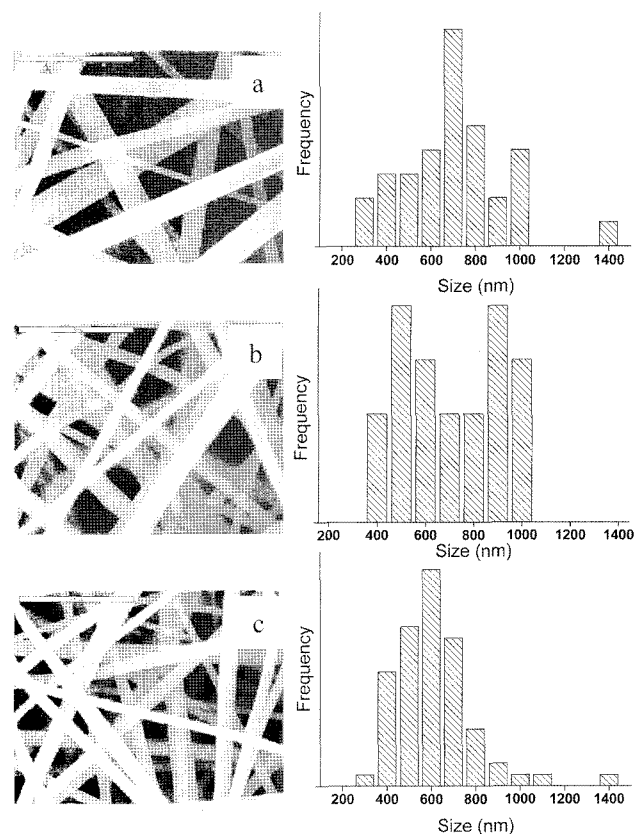
in electrospinning technique. The molecular weight of the polymer is the first issue to be considered. The molecules of the polymer should be long enough to entangle. The concentration of the polymer solution is the next consideration. Although the polymer molecules are entangled, low concentrations cause molecular chains to separate from each other. As a result, fibers are not formed but only droplets are produced due to the jet breaking up into droplets known as beads. On the other hand, electrospinning is suppressed at too high polymer concentrations, clearly seen as highly viscous solutions, because it prohibits flow of a polymer solution continuously to the capillary tip.<sup>6</sup> In this work, initial attempts to electrospin with 16% PVDF in DMAc/acetone gave beaded, defected fibers under all conditions, suggesting that the entanglement of molecules was not strong enough to overcome the repulsion of positive charge arising from external voltage. Therefore, 19% PVDF was electrospun on aluminized flat plates with a voltage of 6-10 kV, and a traveling distance of 7-15 cm. Perfect fibers were



**Figure 2.** Morphology and diameter distribution of PVDF nanofiber at traveling distance of 10 cm, flow rate 0.5 mL, and voltage of (a) 6 kV, (b) 7 kV, and (c) 10 kV.

formed. At 13 kV and higher, fiber at the capillary tip always formed, suggesting that the high voltage caused the solvent to evaporate faster, especially the low-boiling acetone component. This effect was deleterious to the fibrous mat. Moreover, the shorter the traveling distance, the faster the jet traveled to the grounded target due to charge attraction, yielding wet fibers. This problem was solved by reducing the charge interaction by lowering the voltage. Figure 1 shows wet fibers at 7 kV with the traveling distance of 7 cm, while nice dry fibers were formed at a voltage of 6 kV and the same traveling distance.

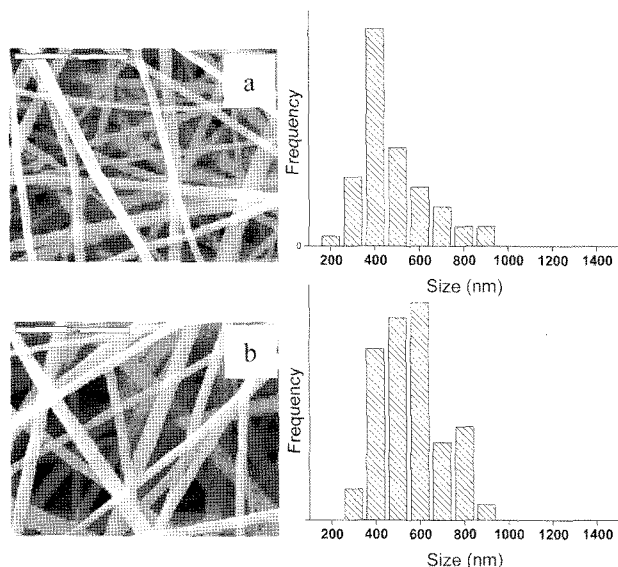
In addition, it is found that the diameter of the PVDF fibers did not significantly change with the processing conditions, consistent with the work of Son *et al.*,<sup>31</sup> and Morota *et al.*<sup>32</sup> The diameters of the PVDF fibers were in the range of 200 nm to 1 micron. However, the distribution of diameters was affected by processing conditions. Apparently the diameter distribution depends both on attractive charge interactions between positive charge on polymer solution and electrically grounded collector, and repulsion of charges on polymer molecules. The stronger interactions cause a high elongation force, resulting in a smaller diameter and a narrower diameter distribution. Figure 2 shows how the diameter distribution gradually broadens with decreasing external



**Figure 3.** Morphology and diameter distribution of PVDF nanofiber at voltage of 6 kV, flow rate of 0.5 mL/h and distance of (a) 15 cm, (b) 10 cm, and (c) 7 cm.

voltage. A large diameter distribution was found at low voltage (Figure 2(a)). It seems there are two populations of fibers, one in the range of 500 nm and a second in the range of 900 nm. When a voltage was increased to 7 kV (Figure 2(b)), the large diameter population decreased. With a voltage of 10 kV (Figure 2(c)), a narrower size distribution was formed. This suggested that the charge density was low at low voltage, thus less repulsion of charge on all molecules. But when the voltage increased, the charge density in the molecules increased, inducing high charge repulsion, and thus only suitable molecules that can tolerate the repulsion jetted to the grounded collector. Moreover, the population shifted to smaller diameters, suggesting that higher elongation forces due to greater repulsion at high voltages were imposed to the jet, resulting in smaller fiber diameters.

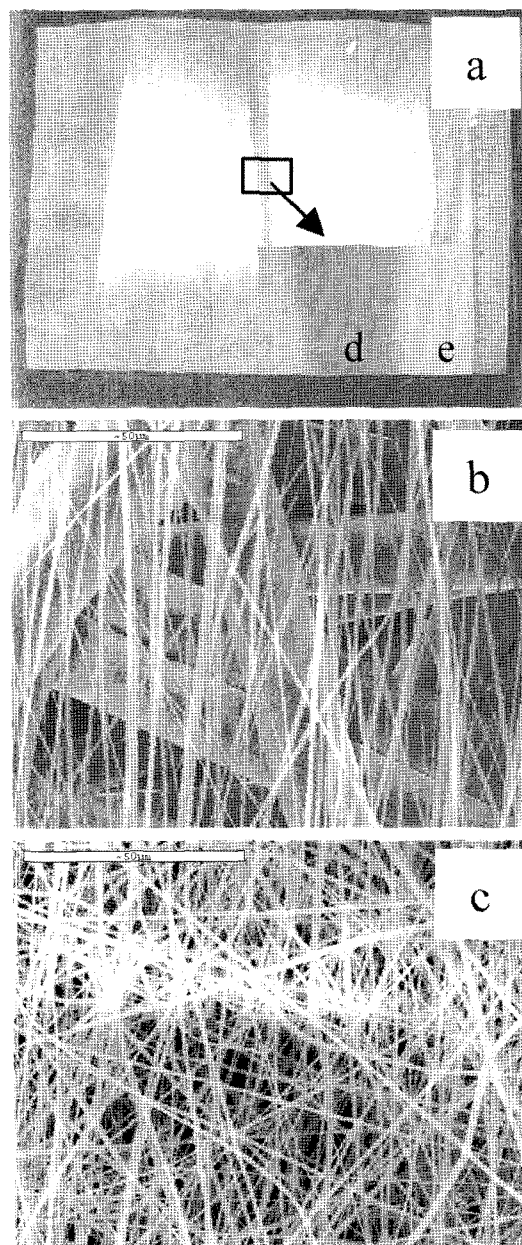
Other changes in diameter distribution due to the charge interactions when the traveling distance and flow rate were varied are shown in Figure 3 and Figure 4. At a longer traveling distance, less interaction between positive charge and grounded collector reduced the elongation force. As a result, the main population exhibited a large diameter, as shown in Figure 3(a). The distribution of diameters was also broad because the reduced interaction allowed a wider distribution of charged molecules to travel to the grounded collector. In



**Figure 4.** Morphology and diameter distribution of PVDF nanofiber at voltage of 10 kV, traveling distance of 10 cm and flow rate of (a) 1 mL/h and (b) 0.5 mL/h.

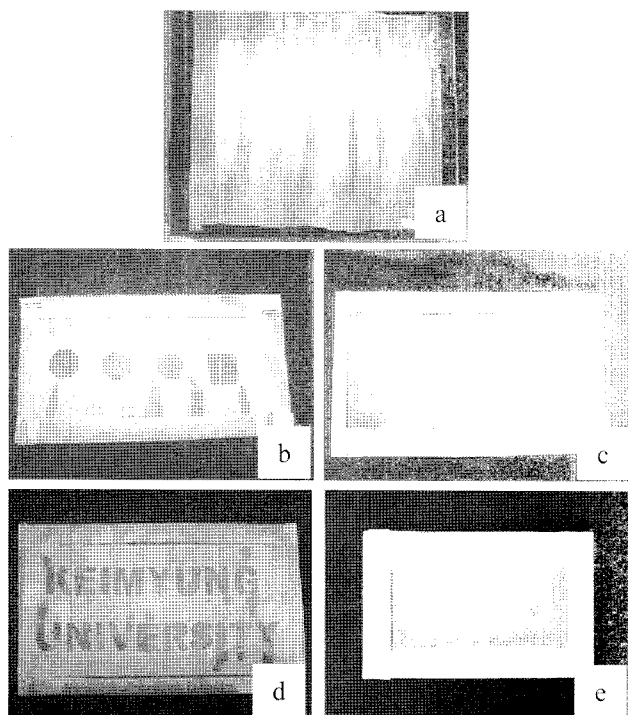
contrast, high interactions due to a shortened traveling distance in Figure 3(c) showed that only molecules that have a high charge density traveled to the grounded collector, yielding a narrow diameter distribution and a shift to smaller average diameter. It can be concluded that at high flow rate a high population of molecules with the same charge density are deposited on the grounded collector. However, at a lower flow rate, probably there was more charge repulsion and the fiber jet produces a larger distribution of diameters, as shown in Figure 4. Therefore, it can be summarized that charge interactions affect the diameter distribution of nanofibrous mats. PVDF electrospun fibers with smaller diameter population and narrower diameter distribution can be produced at a voltage, traveling distance, and flow rate of 6 kV, 7 cm, 0.5 mL/h or 10 kV, 10 cm, 1 mL/h, respectively. This showed that there was an optimum condition for each voltage which was related to the optimum charge interaction.

**Electrospinning of PVDF on PET Sheet Using an Electrically Grounded Drum.** As it acquires increased scientific attention and industrial importance because of its outstanding properties,<sup>24</sup> PVDF is ever widely used as a filtration membrane for microfiltration, ultrafiltration and nanofiltration. For this reason, we targeted PET sheet as a supported material for the PVDF fibrous mat. Recently, we found alignment of electrospun PS on an aluminized flat collector.<sup>30</sup> This result stemmed from the interaction of the aromatic ring of PS molecules with the external voltage, yielding dipoles. Presumably this dipole makes the chain elongation, and then the aromatic rings are aligned and frozen during travel to the grounded collector. Although PVDF can be polarized,<sup>33</sup> it was not aligned on the aluminized flat and grounded drum collector, probably because the alignment



**Figure 5.** (a) PVDF nanofibrous mat, (b) SEM image of alignment nanofibers, and (c) SEM image of randomly deposited nanofibers.

was along the polymer chain which was quite flexible. Surprisingly, when PET sheet replaced the Al sheet, we found straight nanofibers separated from the randomly deposited nanofibers, as shown in Figure 5(a). The aligned nanofiber area was transparent (Figure 5(d)), while the randomly deposited nanofiber area was opaque (Figure 5(e)). The SEM images of the both areas were shown in Figure 5(b) and 5(c), respectively (The large fiber under the aligned fiber was PET fiber). It is apparent that when voltage was applied to the PET drum, some parts of PET were static to



**Figure 6.** Manipulating of straight nanofibers and randomly deposited nanofibers.

the electrically grounded drum and left the rest ungrounded. The aligned nanofibers were formed in an ungrounded area. Thus it can be postulated that pseudo dual collectors were generated on the PET sheet. Since PET sheet was not a conductive material, there will be no negative charge. However less charge was created when the sheet was not perfectly attached to the grounded drum. Hence, the nanofibers jump from the one grounded area of the collector to the next nearest one, yielding a straight line of nanofiber. This evident was clearly shown when other figures were manipulated, as shown in Figure 6. In Figure 6(a) the transparent area was aligned fiber. The geometric shapes in Figure 6(b) were straight lines to the nearest ground. However, the geometric shapes in Figure 6(c) displayed in contrast to randomly deposited nanofibrous mat. Figure 6(d)-(e) nanofibers was prepared using the certain letters which were grounded.

## Conclusions

PVDF (Kynar® 761) nanofibers were successfully electrospun within certain parameters of external voltage, traveling distance, flow rate, and polymer concentration. The diameter of the fibers varied from 200 nanometers to 1 micron, but the diameter distributions varied with voltage and flow rate. The appearance of electrospun PVDF fiber mats differed markedly with PET vs Al collector sheets due to different charge distributions. By manipulating on a

PET drum, not only straight lines of nanofibers, but also aligned nanofibers were obtained. However, these phenomena were not seen on an aluminized collector. This suggested that pseudo dual collectors were generated on the PET sheet.

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