

Preparation and Properties of Electrospun Poly(Vinylidene Fluoride) Membranes

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) was electrospun into fibrous membranes from its solutions in a mixture of *N,N*-dimethylformamide (DMF) and acetone. The electrospun PVDF membranes were viewed under a scanning electron microscope. Effects of acetone amount, polymer concentration, and capillary-collector distance on the morphology of the membranes were studied. It was suggested that uniform fibrous membranes with fiber diameters ranging mainly from 50 nm to 300 nm were formed from a 15% (wt/v) PVDF solutions in 8 : 2 (v/v) DMF/acetone at 5-kV voltage, 0.3-mL/h flow rate, and 10 ~ 20-cm capillary-collector distance. After about 10 h of electrospinning, fi-

brous PVDF membranes with thickness of approximate 46 μm were obtained. The tensile moduli and the tensile strengths of the electrospun PVDF membranes were 100 ~ 170 MPa and 4 ~ 5 MPa, respectively, from the 13% PVDF solution. Analysis of differential scanning calorimeter and wide angle X-ray diffraction showed that the crystallization of PVDF in the electrospun membranes was weakened compared to the casting film and the raw material. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 466–474, 2005

Key words: electrospinning; poly(vinylidene fluoride); membrane; morphology; property

INTRODUCTION

Various applications of fibrous polymeric membranes with diameters in the range from several to hundreds of nanometers are of considerable interest, such as filters,¹ reinforcing components in nanocomposites,² and biomedical scaffolds for tissue regeneration.^{3,4} The electrospinning, also known as electrostatic spinning, is a straightforward way to produce this kind of ultrafine fibrous membranes. This method, patented first in 1934, has been known for almost 100 years, by which ultrafine polymeric fibers can be prepared from polymer solutions or melts under a high electric voltage.⁵ In typical solution electrospinning, a high voltage in the range of 5 kV to 30 kV is applied to the polymer solution, which is held in a syringe equipped with a capillary of about a millimeter in diameter. The droplet of the polymer solution at the capillary tip is distorted into a cone in the high voltage electric field, which is known as a Taylor cone.⁶ The charged droplet overcomes its own surface tension and viscoelasticity to form a jet when the voltage exceeds a critical value. The jet is stretched and accelerated in the electric field to split into ultrafine fluids.⁷ The fluids are solidified by the evaporation of solvents, and nonwoven fibrous membranes are directly prepared on the collector, that is, on stationary or revolving

grounded metallic targets.^{8,9} The diameter of the electrospun ultrafine fibers is influenced by the process and system parameters, such as applied voltage, polymer concentration, and capillary-collector distance, while the duration of the electrospinning determines the membrane thickness. Reneker and coworkers investigated electrospinning of many kinds of polymers and explained the reason why the jet undergoes a bending instability using a mathematical model.^{6,10–14} Shin and colleagues reported that a fluid jet underwent a whipping instability to form submicron fibers.^{7,15}

In the past 5 years, electrospinning has gained much more attention. More and more synthetic and natural polymers in solutions were electrospun into ultrafine fibers, such as poly(ethylene oxide) (PEO) in water,¹⁶ polyurethane in *N,N*-dimethylformamide (DMF),¹⁷ poly-L-lactide in dichloromethane,¹⁸ poly(ϵ -caprolactone) (PCL) in acetone,¹⁴ and regenerated cellulose in 2 : 1 (w/w) acetone/*N,N*-dimethylacetamide (DMAc).¹⁹ Many applications of the electrospun membranes were also studied. Norris and coworkers reported that electrospun polyaniline fibers could be developed into porous electrodes.²⁰ Lee and colleagues prepared nonwoven mats of PCL by electrospinning and tested their physical and mechanical properties.²¹ Wang and coworkers used the electrospun poly(acrylic acid)-poly(pyrene methanol) membrane as fluorescence quenching-based optical sensors for metal ions (Fe^{3+} and Hg^{2+}) and 2,4-dinitrotoluene.²² These sensors showed high sensitivity

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TABLE I
Solution Properties of PVDF in DMF/Acetone for Electrospinning

Sample number	Solution contents			Solution properties		
	PSF (g)	DMF (mL)	Acetone (mL)	Viscosity (Pa · s)	Surface tension (mN/m)	Conductivity ($\mu\text{S}/\text{cm}$)
1	15	100	0	4.10	38.32	42.8
2	15	90	10	3.98	36.99	40.2
3	15	80	20	3.82	35.50	37.7
4	15	70	30	3.39	33.51	36.2
A	10	80	20	0.28	35.12	31.7
B	13	80	20	0.61	35.25	35.2
C	15	80	20	3.82	35.50	37.8
D	17	80	20	5.52	35.56	40.3
E	20	80	20	6.48	35.82	42.7

due to the high surface/volume ratio of the nanofibrous structures. Zong and colleagues investigated morphology and degradation properties of electrospun poly(lactide-*co*-glycolide) membranes for tissue regeneration.^{8,23}

Poly(vinylidene fluoride) (PVDF) is a piezoelectric fluoro polymer with good mechanical properties and processability. PVDF can be applied as electronic devices and PVDF-based gel polymer electrolytes in lithium batteries.²⁴ In previous publications, Seoul and coworkers studied electrospinning of PVDF solutions in DMF with carbon nanotubes (CN) to obtain a conductive polymer/CN composite in the form of nanoscaled fibers.²⁵ PVDF with a 20 wt % concentration in 1 : 1 DMF/DMAc was also investigated in the formation of branched fibers by electrospinning.¹³

Considering the volatility of acetone, in this study, fibrous PVDF membranes were produced by electrospinning from its solution in a mixture of DMF and acetone. Effects of acetone amount, polymer concentration, and capillary-collector distance on the morphology of electrospun PVDF membranes were discussed in detail. Tensile properties and crystallization of the electrospun PVDF membranes were also studied.

EXPERIMENTAL

Materials

PVDF with melt index of 20 ~ 24 was provided by Chenguang Chemical Engineering Institute (Sichuan, China) and used without further purification. Its intrinsic viscosity $[\eta]$ is 1.094 dL/g measured at 25°C in a diluted polymer/DMF solution (0.1g/dL) using an Ubbelohde viscometer with 0.47-mm capillary diameter. DMF and acetone were chemical reagents.

Preparation and properties of electrospun solutions

PVDF solutions for electrospinning were prepared by dissolving the polymer in a mixture of DMF and ace-

tone in a given ratio at room temperature. The polymer concentration was determined by the percentage of PVDF mass (g) in the solvent volume (mL). Two series of PVDF solutions were prepared as shown in Table I. One series was referred to PVDF solutions in 15% concentration with different DMF/acetone ratios

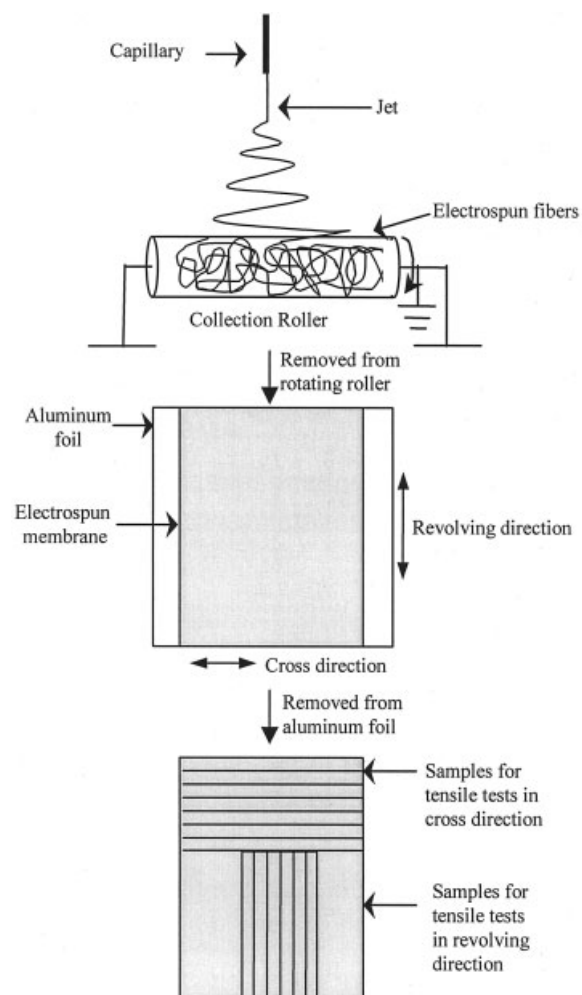


Figure 1 The schematic setup of electrospinning and the sample preparation for tensile tests.

TABLE II
Comparison of Solvent Properties

Solvent	Electron Donating Index	Dielectric constant	Dipole moment (D)	Boiling point (°C)
Acetone	17.0	20.9	2.84	56.2
DMF	26.6	36.7	3.80	153.0

in volume (Samples 1–4), that is, DMF, 9 : 1 DMF/acetone, and 8 : 2 DMF/acetone. The other series was assigned to PVDF solutions with 10–20% concentrations in 8 : 2 (v/v) DMF/acetone (Samples A–E).

The surface tension of electrospun PVDF solutions was tested at room temperature in the Wilhelmy plate method with a tensiometer (DCAT 21, Dataphysics, Germany). The clear platinum plate was used. The viscosity of polymer solutions was measured at room temperature in a rotating viscometer (Model NDJ-79, Shanghai, China). The largest rotating cylinder was used and the shear rate was controlled at 2028 s^{-1} . The electric conductivity of polymer solutions was determined in a conductivity instrument (Model DDS-11A, Shanghai, China).

Electrospinning

The electrospinning setup included syringe, pump, capillary, high-voltage power supply, and collector, as depicted in our previous article.²⁶ A hypodermic stainless steel needle with inner diameter of 0.8 mm and 3 cm in length was fixed to the syringe as a capillary, the tip of which has been cut flat. The metal capillary was connected to the high-voltage power supply (Tianjin University, China), which can generate DC voltages up to 60 kV. A microinfusion pump (WZ-50C2, Hangzhou, China) was used to control the flow rate of the PVDF solution at a certain value from 0.1 to 99.9 mL/h. Generally, the electrospun PVDF membranes were prepared from 13% or 15% solutions in 8 : 2 (v/v) DMF/acetone at 5-kV voltage, 0.3-mL/h flow rate, and 10-cm capillary-collector distance.

The electrospun membranes for the measurement by scanning electron microscopy (SEM) were collected on a stationary flat aluminum foil (collector) connected to ground under the syringe. For measurements of mechanical properties, by differential scanning calorimeter (DSC) and wide angle X-ray diffraction (WAXD), the membranes were collected on a rotating cylindrical roller with 6.8-cm diameter wrapped by flat aluminum foil, as shown in Figure 1. The rotating speed of the cylinder was controlled constantly at 43 rpm, that is, the collection speed was 9.2 m/min. After about 10 h of electrospinning, the electrospun PVDF membrane was removed from the aluminum foil and vacuum-dried for further use.

Characterization

The morphology of the electrospun ultrafine fibers was observed under a scanning electron microscope (Philips XL-30, the Netherlands) after gold coating. The diameter of the electrospun fibers was measured in Adobe Photoshop 5.0 software from SEM pictures in original magnification of $10 \text{ k} \times$ or $20 \text{ k} \times$.

The mechanical properties of the electrospun PVDF membranes were tested in a tensile machine (Testo-

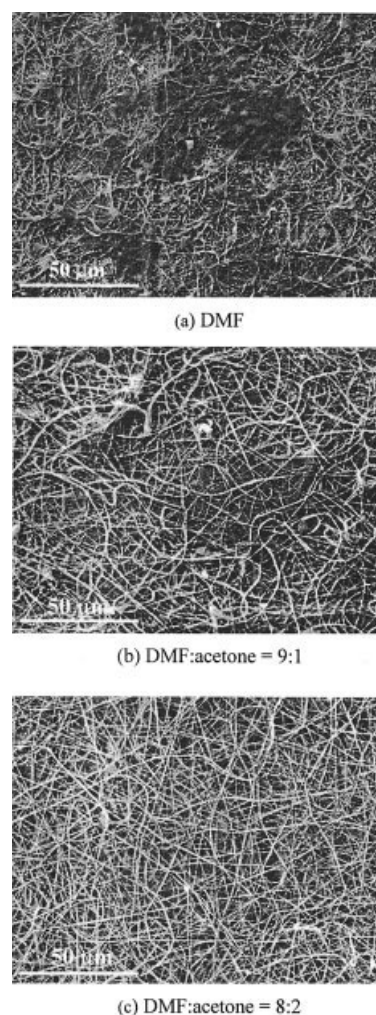


Figure 2 SEM micrographs of electrospun PVDF membranes with different DMF/acetone ratios. Original magnification $500 \times$. Voltage: 5 kV; concentration: 15%; flow rate: 0.3 mL/h; distance: 10 cm. (a) DMF, (b) DMF : acetone = 9 : 1, (c) DMF : acetone = 8 : 2.

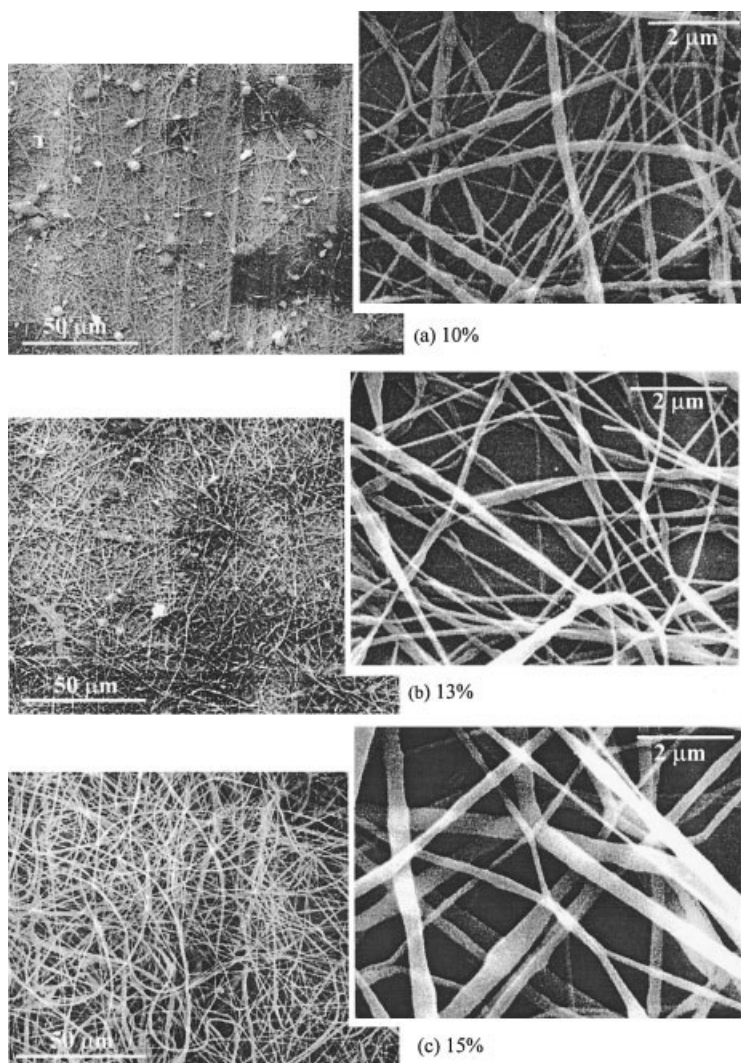


Figure 3 Variation of electrospun membrane morphology with polymer concentration. Original magnification: $500\times$ (left) and $10\text{ k}\times$ (right). Voltage: 5 kV; flow rate: 0.3 mL/h; distance: 10 cm; DMF : acetone = 8 : 2. (a) 10%, (b) 13%, (c) 15%, (d) 17%, (e) 20%.

metric M350–20kN, UK) equipped with a 100N load-cell. The membranes were cut into $70\text{ mm}\times 10\text{ mm}$, with tensile direction along the revolving or cross direction of the collection roller, as shown in Figure 1. Specimens with a gauge length of 40 mm were carefully mounted. The tests were conducted at a cross-head speed of 5 mm/min at room temperature. The reported tensile moduli, tensile strengths, and elongations represented average results of three or five tests.

DSC measurements were performed in a Perkin–Elmer DSC 7 machine at $10^\circ\text{C}/\text{min}$ heating rate in flushing nitrogen. Each sample of the electrospun PVDF membranes and raw PVDF powders was approximately 10 mg. The casting PVDF film, prepared from the 15% solution, was also tested. The melting temperature (T_m) was noted as the temperature at the maximum value of the melting peak. The melting enthalpy (ΔH_m) was referred to as the corresponding energy (J/g), that is, the peak area above the baseline.

WAXD spectra were obtained by a Rigaku D/max 500V/PC diffractometer at a 2θ scanning rate of $3^\circ/\text{min}$ in the range of $5^\circ\sim 50^\circ$. Cu $K\alpha$ radiation was used for the diffraction with a voltage of 40 kV and a current of 100 mA.

RESULTS AND DISCUSSION

Generally, it was more feasible to generate ultrafine fibers by electrospinning from polymer solutions than from polymer melts. Furthermore, the solvent used in polymer solutions for electrospinning was the most important factor determining the morphology of the electrospun fibers. From the data shown in Table II, DMF shows strong polarity for it holds a higher electron donating index, dielectric constant, and dipole moment than acetone. However, DMF possesses a higher boiling temperature, 153.0°C . The polarity of DMF could facilitate the formation of ultrafine fibers,

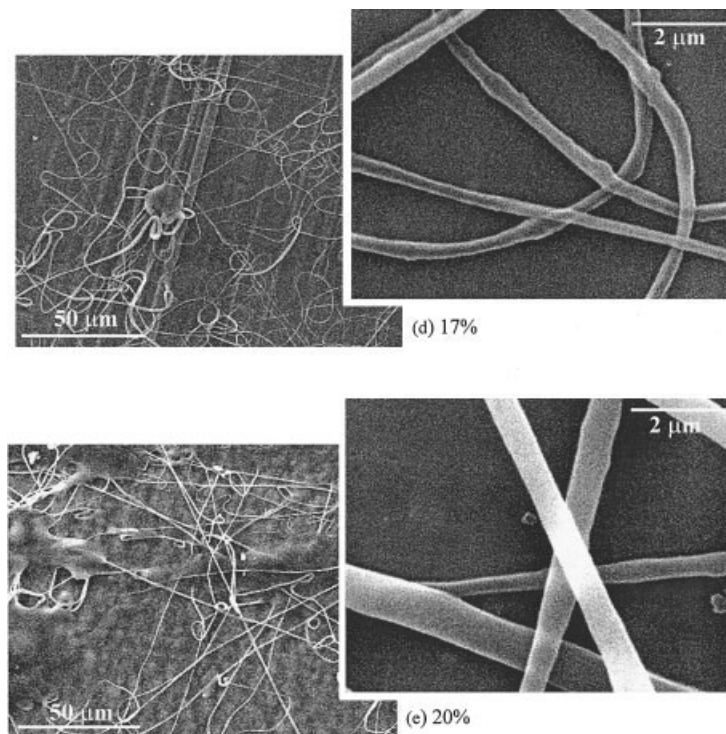


Figure 3 (Continued from the previous page)

but the lower volatility could make the ultrafine fiber generation difficult from polymer/DMF solutions. Considering the higher volatility of acetone, which has a lower boiling temperature of 56.2°C, electrospinning of PVDF in a mixture of DMF and acetone was studied for this article.

To analyze the effect of polymer solutions on the formation of ultrafine fibers, the properties of the PVDF solution, including viscosity, conductivity, and surface tension, were measured as shown in Table I. The results showed that these properties varied with the acetone amount in the solution and the polymer concentration. In detail, the viscosity of the polymer solutions decreased while the acetone amount was rising, but increased significantly from 0.28 Pa s to 6.48 Pa s with the polymer concentration increasing from 10 to 20% (Samples A ~ E). It is a typical phenomenon that the solution viscosity increases with the polymer concentration. The weak solubility of PVDF in acetone could be the reason for a slight drop of viscosity with increasing acetone amount. While the acetone amount increased in the PVDF solutions, the surface tension and the conductivity also exhibited significant decreases. On the other hand, when the polymer concentration increased, the surface tension increased slightly, but the conductivity increased remarkably, as shown in Table I. The change tendency of solution viscosity, conductivity, and surface tension were similar to our previous study of poly(D,L-lactide) (PDLLA) solutions in DMF/acetone.²⁷

Effect of acetone amount

SEM micrographs of electrospun PVDF membranes prepared by electrospinning from 15% PVDF solutions in DMF/acetone with different volume ratios are shown in Figure 2. From Figure 2a, bead-fibers were found when DMF was used as the solvent without acetone. Dark patches could also be observed in this picture, which were assumed to be the remnant of solution droplets deposited directly on the collector during the process of electrospinning. When 9 : 1 DMF/acetone was used as the solvent in the polymer solution, that is, 10% acetone was added (Sample 2 in Table I), beads in the electrospun membrane almost disappeared (Fig. 2b). Furthermore, the ultrafine fibers without beads (Fig. 2c) demonstrated clearly when the acetone amount in the solution increased to 20%, that is, DMF/acetone volume ratio was 8 : 2 (Sample 3 in Table I). In other words, uniform ultrafine fibers could be formed when a certain amount of acetone was added in the electrospun PVDF solution.

Acetone is more volatile than DMF. Furthermore, the changes of solution properties by the addition of acetone (Table I) could probably improve the electrospun membrane morphology and decrease the possibility of bead formation. The electrospun fibers become more and more uniform with the acetone amount increasing (Figs. 2b,c). Similar results have been gained in our previous study about electrospin-

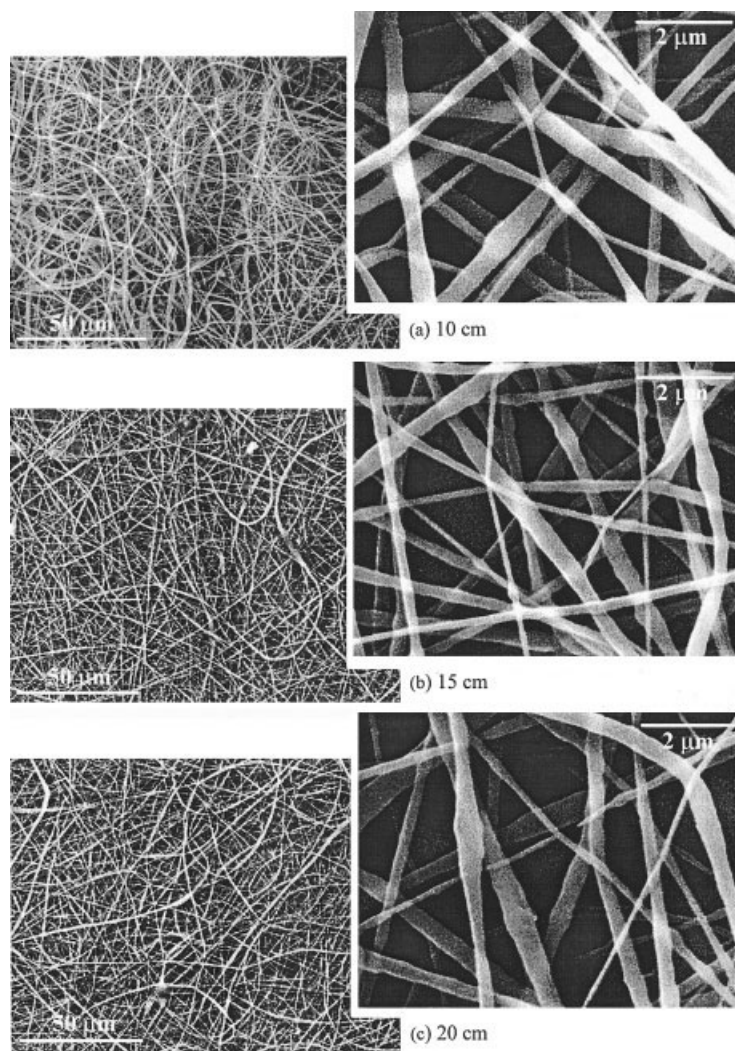


Figure 4 Variation of electrospun membrane morphology with the capillary-collector distance. Original magnification $500\times$ (left) and $10\text{ k}\times$ (right). Voltage: 5 kV; concentration: 15%; flow rate: 0.3 mL/h; DMF : acetone = 8 : 2. (a) 10 cm, (b) 15 cm, (c) 20 cm.

ning of PDLLA solutions in DMF/acetone and polysulfone (PSF) in DMAc/acetone.^{27,28}

Effect of polymer concentration

The polymer concentration is one of the most effective variables to control the electrospun fiber morphology because of the large fluctuation of the solution viscosity caused by the concentration increasing. Figure 3 shows SEM micrographs of electrospun membranes prepared from PVDF solutions with different concentrations in 8 : 2 DMF/acetone. For the lower polymer concentration of 10%, there were a large number of beads and bead-fibers in the picture (Fig. 3a). Similar to Figure 2a, there were some dark patches in Figure 3a (left) in magnification of $500\times$. The low viscosity of the 10% PVDF solution was the reason for formation of beads and beaded fibers. The phenomenon of bead-

fibers also was reported in electrospinning of PEO/water.²⁹ With the concentration increasing from 10 to 15%, the density of beads and bead-fibers decreased, and the ultrafine fibers became much more visible. Beads disappeared at 15% concentration, as shown in Figure 3c. When the concentration increased to 17 and 20%, a few ultrafine fibers were obtained with solution remnants (Fig. 3d,e). The viscosity (Table I) of these two solutions was too high to form fluid jets smoothly.

The diameters of electrospun PVDF fibers prepared from 13% or 15% PVDF solutions in 8 : 2 DMF/acetone were mostly among 50 ~ 300 nm but for a small amount of fibers, which were thicker. The average fiber diameter was 172 ± 89 nm from the 15% PVDF solution.

Compared to the morphology of the electrospun PSF fibers,²⁸ the electrospun PVDF membranes exhibited more irregular and more random fiber shapes, as

shown in the larger magnification (Fig. 3 right)]. The fiber showed uneven surfaces and a larger diameter difference between the thin and the thick fibers. The special shape of electrospun PVDF fibers was probably formed from axisymmetric instability of a fluid jet during electrospinning caused by the strong polarity of the polymer.⁷

Effect of capillary-collector distance

Figure 4 shows SEM micrographs of the electrospun PVDF fibers prepared at capillary-collector distances of 10 cm, 15 cm, and 20 cm, respectively, from a 15% PVDF solution in 8 : 2 DMF/acetone. It can be seen that there were almost no visible differences between these pictures (500 ×). Increasing the distance between capillary and collector could give a longer time for the solvent to evaporate and the charged fluid to slit more times, but weak electric force during electrospinning at longer distance could also cause fluids to split less times. Results in Figure 4 suggested that the distance range from 10 cm to 20 cm was suitable for PVDF/DMF/acetone solutions to be electrospun. From the pictures in larger magnification, the ultrafine fibers obtained at 15-cm distance were most uniform among the three pictures. The fiber diameters mostly centralized in 50 ~ 300 nm, 100 ~ 400 nm, and 50 ~ 350 nm, respectively, at 10-cm, 15-cm, and 20-cm distances, except for smaller amounts happening outside these ranges.

Tensile properties of the electrospun PVDF membranes

To prepare electrospun membranes for mechanical study, a rotating grounded metallic cylinder wrapped with a piece of aluminum foil was used as the collector. After about 10 h of electrospinning, the ultrafine fibrous PVDF membranes with $46 \pm 2 \mu\text{m}$ in thickness were formed from a 13% PVDF solution in 8 : 2 (v/v) DMF/acetone at 5-kV voltage, 0.3-mL/h flow rate, and 10-cm distance. Two tensile tests were measured. One tensile direction was along the revolving direction, and the other was in the cross direction, as shown in Figure 1. Typical stress-strain curves along with the tensile results of the electrospun PVDF membranes are shown in Figure 5. Results suggested that the tensile moduli, tensile strengths, and elongations showed no significant differences ($p > 0.4$) between the data in the revolving direction and the cross direction, and their values were in 100 ~ 170 MPa, 4 ~ 5 MPa, and 9 ~ 12%, respectively. In the present study, tensile properties of electrospun PVDF membranes showed no relationships to the collection directions. It could be assigned to the random fiber shape and the broad fiber diameter distribution of electrospun PVDF membranes. This result did not coincide with Lee's conclu-

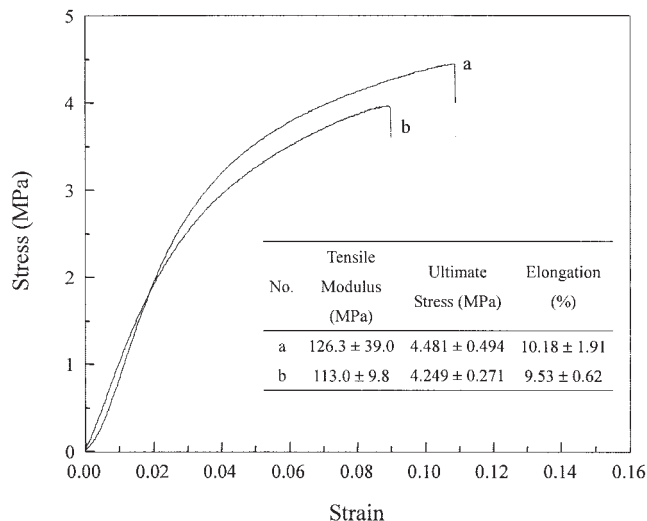


Figure 5 Typical tensile stress-strain curves of electrospun PVDF membranes prepared from a 13% PVDF solution in 8 : 2 (v/v) DMF/acetone at 5-kV voltage, 0.3-mL/h flow rate and 10-cm capillary-collector distance. (a) revolving direction; (b) cross direction.

sion about electrospun PCL membranes with 4.5 m/min of collection speed.²¹

Crystallinity of the electrospun PVDF membranes

Figure 6 shows the DSC curves and the data of T_m and ΔH_m of the raw PVDF material, casting PVDF film, and the electrospun PVDF membranes. Results showed that the electrospun PVDF membranes prepared from 13 and 15% PVDF solutions shifted their melting temperatures to 161.4°C and 163.0°C, respectively, from 160.6°C of the raw PVDF. In addition, the thermal enthalpies of the electrospun PVDF membranes prepared from 13 and 15% PVDF solutions were 54.1 J/g and 59.6 J/g, respectively, also higher than 50.0 J/g, the value of the raw PVDF. However, compared to the casting PVDF film with 162.4°C of melting temperature and 64.3 J/g of thermal enthalpy, the electrospun PVDF membranes exhibited a lower tendency of crystallization.

To examine the crystalline structure of PVDF in the electrospun membranes, WAXD diffraction patterns of the electrospun PVDF membranes from 13 and 15% polymer solutions, along with the raw PVDF material and the casting PVDF film, are shown in Figure 7. The raw PVDF material showed clear diffraction peaks at 18.3°, 20.0°, 26.4°, 33.1°, 36.4°, and 38.6° of 2θ (Fig. 7a), and the casting PVDF film also exhibited clear diffraction peaks at 20.0° of 2θ and apparent diffraction peaks at 18.3°, 26.4°, 36.4°, and 38.6° of 2θ (Fig. 7b). However, both electrospun PVDF membranes only exhibited two clear diffraction peaks at 20.0° and 22.4° of 2θ (Figs. 7c,d). The clear diffractions could represent

the perfection of α and β crystalline forms appearing in the raw PVDF material and the casting PVDF film rather than in the electrospun PVDF membranes. Results from both DSC and WAXD suggested that the crystallization of PVDF was weakened by electrospinning, compared with the raw material and the casting PVDF film.

CONCLUSIONS

Electrospinning of PVDF can be carried out from a 15% PVDF solution in 8 : 2 (v/v) DMF/acetone at 5-kV voltage, 0.3-mL/h flow rate, and 10 ~ 20-cm capillary-collector distances to obtain uniform fibrous PVDF membranes. The electrospun PVDF fibers exhibited a diameter distribution from 50 nm to 300 nm, and the average fiber diameter was 172 ± 89 nm. DMF/acetone ratio and polymer concentration were the main factors influencing morphology of the electrospun PVDF membranes. The tensile moduli and the tensile strengths of the electrospun PVDF membranes from the 13% PVDF solution were 100 ~ 170 MPa and 4 ~ 5 MPa, respectively. Analysis of DSC and WAXD showed that the crystallization of PVDF was weakened by electrospinning.

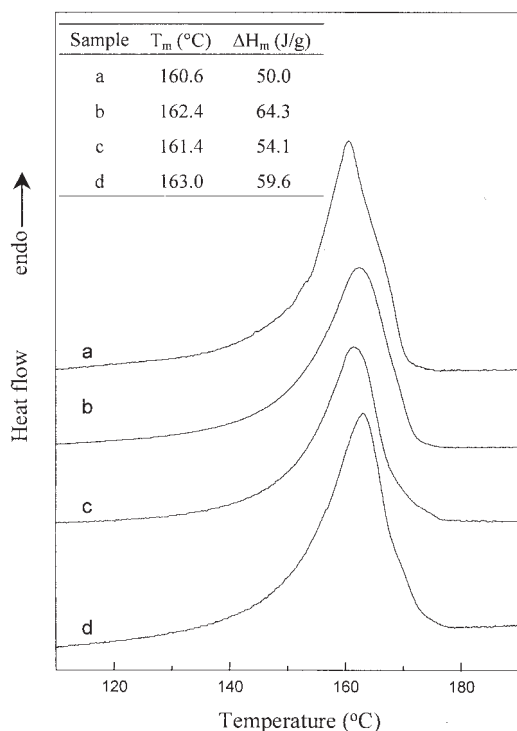


Figure 6 DSC curves of raw PVDF material (a), casting PVDF film (b), and electrospun PVDF membranes prepared from 13% (c) and 15% PVDF (d) solutions in 8 : 2 (v/v) DMF/acetone at 5-kV voltage, 0.3-mL/h flow rate, and 10-cm capillary-collector distance.

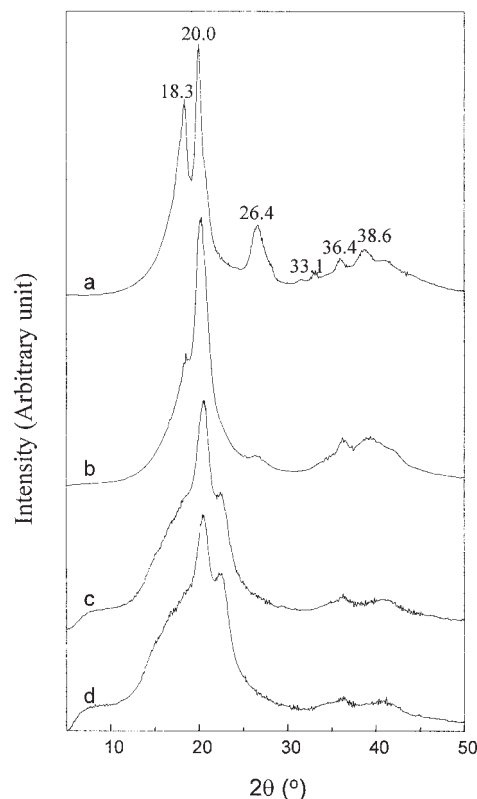


Figure 7 WAXD diffraction patterns of raw PVDF material (a), casting PVDF film (b), and electrospun PVDF membranes prepared from 13% (c) and 15% PVDF (d) solutions in 8 : 2 (v/v) DMF/acetone at 5-kV voltage, 0.3-mL/h flow rate, and 10-cm capillary-collector distance.

References

- Gibson, P.; Schreuder-Gibson, H.; Rivin, D. *Colloids Surf A* 2001, 469, 187.
- Fong, H.; Liu, W. D.; Wang, C. S.; Vaia, R. A. *Polymer* 2002, 43, 775.
- Li, W. J.; Laurencin, C. T.; Catterson, E. J.; Tuan, R. S.; Ko, F. K. *J Biomed Mater Res* 2002, 60, 613.
- Yoshimoto, H.; Shin, Y. M.; Terai, H.; Vacanti, J. P. *Biomaterials* 2003, 24, 2077.
- Formhals, A. U.S. Pat. 1,975,504 (1934).
- Doshi, J.; Reneker, D. H. *J Electrostatics* 1995, 35, 151.
- Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. *Polymer* 2001, 42, 9955.
- Zong, X. H.; Kim, K.; Fang, D. F.; Ran, S. F.; Hsiao, B. S.; Chu, B. *Polymer* 2002, 43, 4403.
- Buchko, C. J.; Chen, L. C.; Shen, Y.; Martin, D. C. *Polymer* 1999, 40, 7397.
- Reneker, D. H.; Chun, I. *Nanotechnology* 1996, 7, 216.
- Reneker, D. H.; Yarin, A. L.; Fong, H. *J Appl Phys* 2000, 87, 4531.
- Yarin, A. L.; Koombhongse, S.; Reneker, D. H. *J Appl Phys* 2000, 89, 3018.
- Koombhongse, S.; Liu, W. X.; Reneker, D. H. *J Polym Sci Polym Phys* 2001, 39, 2598.
- Reneker, D. H.; Kataphinan, W.; Theron, A.; Zussman, E.; Yarin, A. L. *Polymer* 2002, 43, 6785.
- Shin, Y. M.; Hohman, M. M.; Rutledge, G. C. *Appl Phys Lett* 2001, 78, 1149.
- Deitzel, J. M.; Kleinmeyer, J. D.; Hirvonen, J. K.; Beck Tan, N. C. *Polymer* 2001, 42, 8163.

17. Demir, M. M.; Yilgor, I.; Yilgor, E.; Erman, B. *Polymer* 2002, 43, 3303.
18. Zeng, J.; Hou, H. Q.; Schaper, A.; Wendorff, J. H.; Greiner, A. *e-Polymer HomePage*. <http://www.e-polymers.org/index.cfm>, 2003, 009.
19. Liu, H. Q.; Hsieh, Y. L. *J Polym Sci Polym Phys* 2003, 41, 953.
20. Norris, I. D.; Shaker, M. M.; Ko, F. K.; MacDiarmid, A. G. *Synth Met* 2000, 114, 109.
21. Lee, K. H.; Kim, H. Y.; Khil, M. S.; La, Y. M.; Lee, D. R. *Polymer* 2003, 44, 1287.
22. Wang, X. Y.; Drew, C.; Lee, S. H.; Senecal, K. J.; Kumar, J.; Samuelson, L. A. *Nano Lett* 2002, 2, 1273.
23. Zong, X. Y.; Ran, S. F.; Kim, K. S.; Fang, D. F.; Hsiao, B. S.; Chu, B. *Biomacromolecules* 2003, 4, 416.
24. Periasamy, P.; Tatsumi, K.; Shikano, M.; Fujieda, T.; Sakai, T.; Saito, Y.; Mizuhata, M.; Kajinami, A.; Deki, S. *Solid State Ionics* 1999, 126, 285.
25. Seoul, C.; Kim, Y. T.; Baek, C. K. *J Polym Sci Polym Phys* 2003, 41, 1572.
26. Duan, B.; Dong, C. H.; Yuan, X. Y.; Yao, K. D. *J Biomat Sci-Polym E* 2004, 15, 797.
27. Dong, C. H.; Duan, B.; Yuan, X. Y.; Yao, K. D. *Shengwu Yixue Gongchengxue Zazhi/J Biomed Eng* 2004, to appear.
28. Yuan, X. Y.; Zhang, Y. Y.; Dong, C. H.; Sheng, J. *Polym Int* 2004, 53, 1704.
29. Fong, H.; Chun, I.; Reneker, D. H. *Polymer* 1999, 40, 4585.