

Preparation of Porous PVDF Nanofiber from PVDF/PVP Blend by Electro spray Deposition

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(Received May 8, 2007; Accepted July 11, 2007; Published August 28, 2007)

ABSTRACT: Nanofiber with porous structures were prepared by electro spray deposition (ESD) from poly(vinylidene fluoride) (PVDF)/poly(vinylpyrrolidone) (PVP) blend and subsequent selective removal of PVP. In the present work, the effect of blending ratio of PVDF/PVP on formation of the pore and crystal structure of residual PVDF fiber was investigated. The residual PVDF nanofiber showed a higher specific surface area (the highest specific surface area was 28.54 m²/g from PVDF/PVP = 67/33 w/w). The Fourier transform infrared spectroscopy and wide angle X-ray diffraction measurement also showed that selective removal of PVP enhanced the formation of β -phase crystal structure in PVDF nanofiber (β -phase content > 90%). [[doi:10.1295/polymj.PJ2007037](https://doi.org/10.1295/polymj.PJ2007037)]

KEY WORDS Electro spray Deposition / Nanofiber / Poly(vinylidene fluoride) / Poly(vinylpyrrolidone) / Selective Extraction / Porous Structure / Crystalline Structure /

Recently, nanofiber and mat with high specific surface area have attracted much attention for the application such as filter media,¹ protective clothing,² aerospace,³ electronic device,⁴ tissue engineering,⁵ sensors,⁶ and biomedical uses.⁷ In addition, these applications could be greatly enhanced by the increasing the surface area and porosity of fibers.

Electro spray deposition (ESD) is the electric field induced spray processing and a versatile method for preparation of nano-microscaled fiber.⁸ Most of approaches for introducing porous structure into the bulk on a nanofiber relied on (i) the ESD of blends or composite followed by selective removal of one component,^{9,10} and (ii) phase separation based on evaporation of solvent or in the presence of vapor during ESD.^{11,12} Here, we attempt to prepare porous polymeric nanofiber from polymer blend by using a former approach.

Poly(vinylidene fluoride) (PVDF) is widely used for industrial applications because of its excellent chemical stability, mechanical strength, and ferroelectricity. PVDF has several crystalline structures: α , β , and γ -phase, based on the chain conformation as trans or gauche linkages.¹³ The α -phase is the most energetic stable state and β -phase has useful piezoelectric and pyroelectric properties.^{14,15} Our previous study showed that the addition of ionic surfactants remarkably enhanced the formation of β -phase structure of PVDF nanofiber during ESD process.¹⁶ Poly(vinyl

pyrrolidone) (PVP), which is amorphous and water soluble polymer, is commonly used as additive to control the pore structure in preparation of polymeric membranes.¹⁷ In the ESD process, PVP is also effective for controlling the pore structure.¹⁸ The electret fibers due to their polar structure can enhance the collection efficiency of aerosol for not only charged aerosol but also uncharged aerosol.¹⁹ In addition, the pore structure inside nanofiber increases the specific surface area. Therefore, porous PVDF nanofiber with high β -phase content is expected as material for high efficiency filter media.

The aim of present work is to investigate the effects of blending ratio of PVDF/PVP and selective removal of PVP on formation of pore and crystal structure of residual PVDF nanofiber.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVDF, $M_w = 141,000$, KF1100) was obtained from Kureha, Japan. Poly(vinyl pyrrolidone) (PVP, $M_w = 35,000$) and N, N-dimethyl acetamide (DMAc) were from Wako, Japan. Before use, PVDF was dissolved in N,N-dimethylformamide at 60 °C and the precipitated in methanol. Thereafter PVDF was washed with methanol and vacuum-dried for 24 h. Other reagents were used without further purification.

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A spray solution was prepared as follows: PVDF and PVP were dissolved in DMAc at various compositions: the total polymer concentration is fixed at 30 wt% and the blending ratio of PVDF/PVP is 83/17, 67/33, 50/50, 33/67 w/w. The PVDF/PVP solution was stirred at 60 °C for several hours and then cooled to room temperature.

Electrospray Deposition (ESD)

The ESD device consist of syringe-type infusion pump (MCIP-III, Minato Concept, Japan), a high voltage regulated DC power supply (HDV-20K 7.5Std, Pulse Engineering, Japan), and grounded collector (aluminium sheet).⁸ The polymer solution was contained in a syringe with stainless steel needle (1.0 mm internal diameter). The applied voltage was 15 kV, the distance from the tip of needle to collector was 12 cm, and the flow rate of solution was 2 μ l/min.

Selective removal of PVP

To remove PVP, the as-deposited PVDF/PVP fiber was immersed in distilled water at 60 °C for 1 d and then vacuum-dried for 1 d.

Characterization of fibers

The surface morphologies of as-deposited PVDF/PVP fiber and the residual PVDF fiber were observed by using a scanning electron microscope (SEM, SM-200, Topcon, Japan) operated at 10 kV. All the SEM samples were sputtered-coated with Au. The average fiber diameter was analyzed from the SEM image using Adobe Photoshop 7.0 Software (Adobe, USA). The crystallinity of the nanofiber was measured by differential scanning calorimeter (DSC 6100, Seiko Instruments, Japan). Crystalline structure of the nanofiber was analyzed by a Fourier transform infrared spectrometer (FI-IR-410, Jasco, Japan) and X-ray diffraction (MiniFlex, Rigaku, Japan). Adsorption isotherm and the Brunauer-Emmet-Teller (BET) specific surface area¹⁸ of the as-deposited PVDF/PVP fiber and the residual PVDF fiber were determined using an adsorption apparatus (ASAP 2010, micrometrics, USA). Nitrogen was selected as probe molecule. To specify the pore size on the residual PVDF fiber, mercury porosimetry measurement was carried by an instrument (AutoPore IV 9520, Micrometrics, USA).

RESULT AND DISCUSSION

Morphology of nanofiber

Figures 1 and 2 show the morphologies and fiber diameter of PVDF/PVP fiber before and after selective removal of PVP, respectively. Diameter of fiber is in the range of 200–800 nm. Removal of PVP influenced on morphology and fiber diameter: average

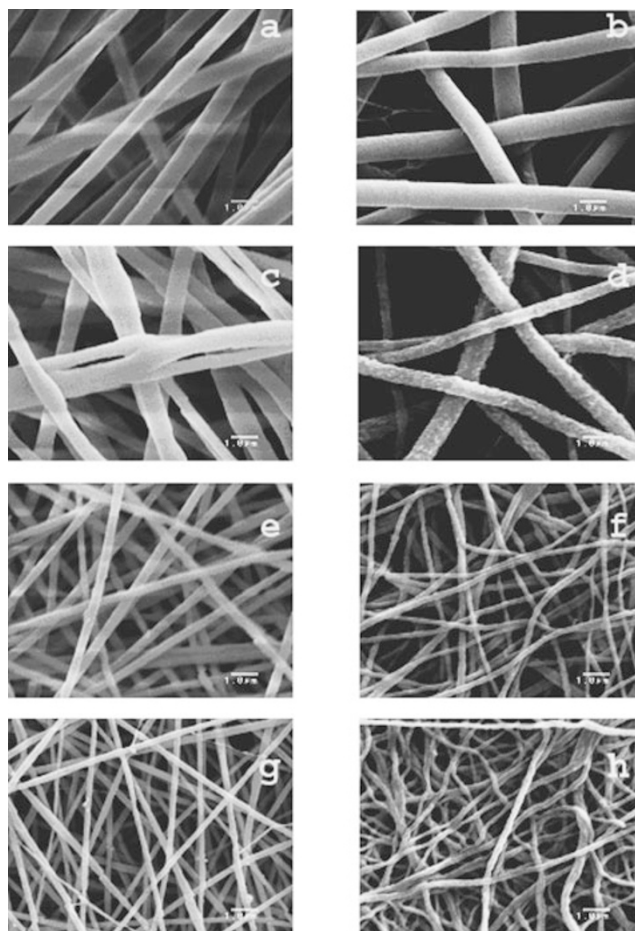


Figure 1. Surface SEM images of as-deposited PVDF/PVP fibers with various blending ratios and their residual PVDF fibers after removal of PVP. (a) PVDF/PVP = 83/17, (b) PVDF from PVDF/PVP = 83/17, (c) PVDF/PVP = 67/33, (d) PVDF from PVDF/PVP = 67/33, (e) PVDF/PVP = 50/50, (f) PVDF from PVDF/PVP = 50/50, (g) PVDF/PVP = 33/67, and (h) PVDF from PVDF/PVP = 33/67.

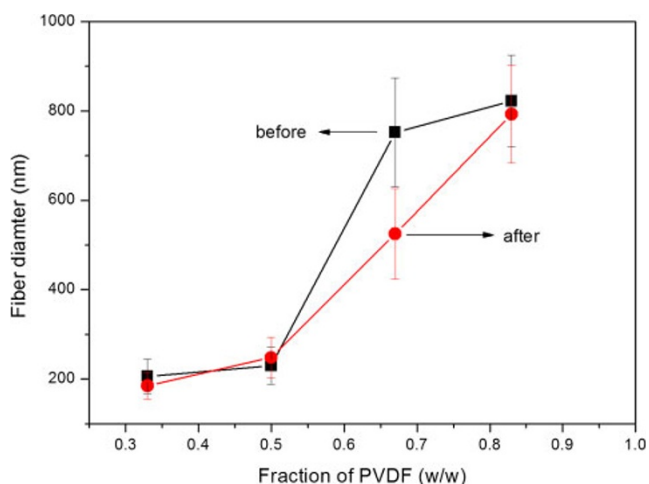
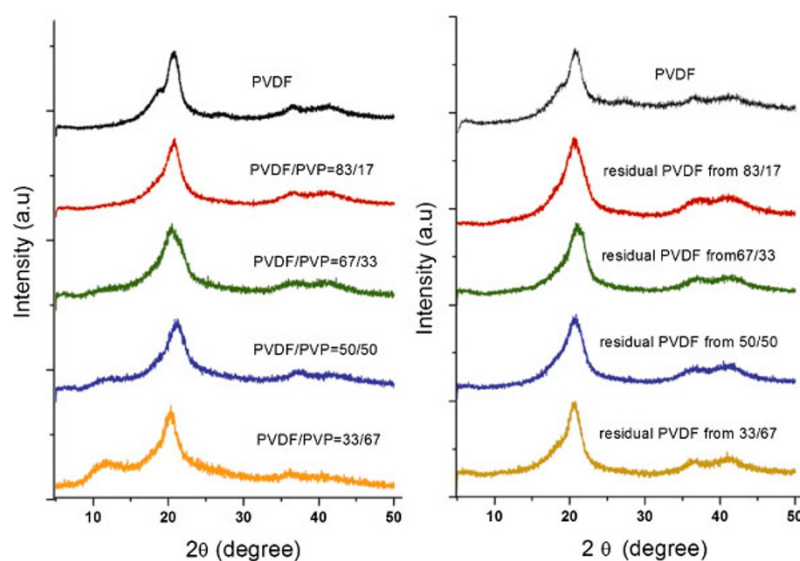


Figure 2. Effect of blending ratio of PVDF/PVP on fiber diameter of as-deposited PVDF/PVP fiber and residual PVDF fiber.

Table I. The melting point and total crystallinity of nanofiber

Samples	T _m (°C)	Crystallinity (%)
As-deposited PVDF	172.0	65
As-deposited PVDF/PVP = 83/17	163.0	47
As-deposited PVDF/PVP = 67/33	164.5	17
As-deposited PVDF/PVP = 50/50	154.1	12
As-deposited PVDF/PVP = 67/33	153.4	6
Residual PVDF from PVDF/PVP = 83/17	172.6	52
Residual PVDF from PVDF/PVP = 67/33	171.8	48
Residual PVDF from PVDF/PVP = 50/50	171.9	54
Residual PVDF from PVDF/PVP = 33/67	172.6	49

**Figure 3.** WAXD diagram of as-deposited PVDF/PVP fibers with various blending ratios and their residual PVDF fibers after removal of PVP.

fiber diameter of as-deposited PVDF/PVP fiber from PVDF/PVP = 67/33 blend decreased from 752 to 525 nm by removal of PVP. This decrease may be caused by formation of porous structure in fiber and shrinking of fiber during immersion in water.

The BET specific surface areas of residual PVDF fiber were 4.49 m²/g (from PVDF/PVP = 83/16), 28.54 m²/g (from PVDF/PVP = 67/33), 15.21 m²/g (from PVDF/PVP = 50/50), and 8.25 m²/g (from PVDF/PVP = 33/67), respectively. The mercury porosimetry measurements supported that the surface of residual PVDF fiber contains pore around 30 nm in diameter.

Characterization of Crystalline Structure

The melting point and crystallinity of nanofiber determined by DSC measurements are summarized in Table I. The increase in PVP blending ratio decreased the melting point and crystallinity of as-deposited PVDF/PVP fiber (melting point of PVP and PVDF are 96.7 and 172 °C, respectively). After removing of PVP, the melting point and crystallinity of residual

PVDF nanofiber shifted to those of PVDF. These results indicate that the presence of PVP inhibited the crystallization of PVDF in the blends during ESD. The same trend was reported by Alfonso *et al.* for the PVDF/PVP cast film.²⁰

Figure 3 shows the WAXD diagram of as-deposited PVDF/PVP fiber with various blending ratios and their residual PVDF fiber after removal of PVP. The as-deposited PVDF contains a mixture of α -phase and β -phase crystal. The 2 theta peaks around 19.3° and 20.3° correspond to α -phase and β -phase crystals, respectively. Removal of PVP enhanced the formation of β -phase crystal structure.

Figure 4 shows the typical FT-IR spectra of as-deposited PVDF/PVP fiber and its residual PVDF fiber after removal of PVP. The peaks around 766, 840, and 1667 cm⁻¹ correspond to α - and β -phase PVDF and carbonyl group of PVP, respectively. After removal of PVP, the peak from carbonyl group of PVP shifted to lower wavelength. This indicates that the hydrogen bonding between PVDF and PVP molecule is weakened by removal PVP. Here, the ratio of

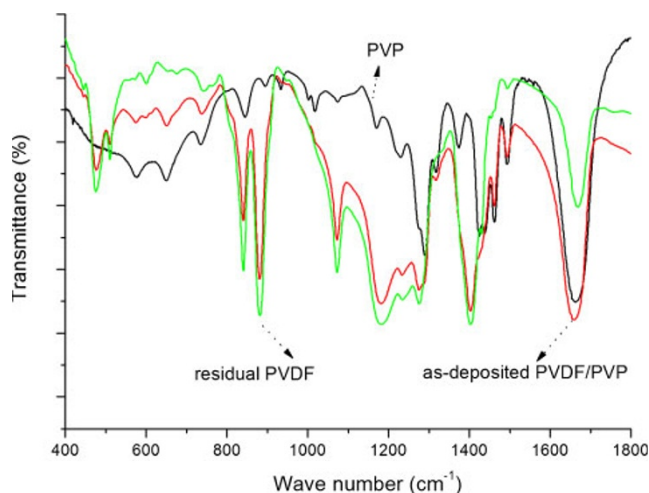


Figure 4. FT-IR spectra of as-deposited PVDF/PVP fibers with the blending ratio PVDF/PVP = 67/33 and its residual PVDF fibers after removal of PVP.

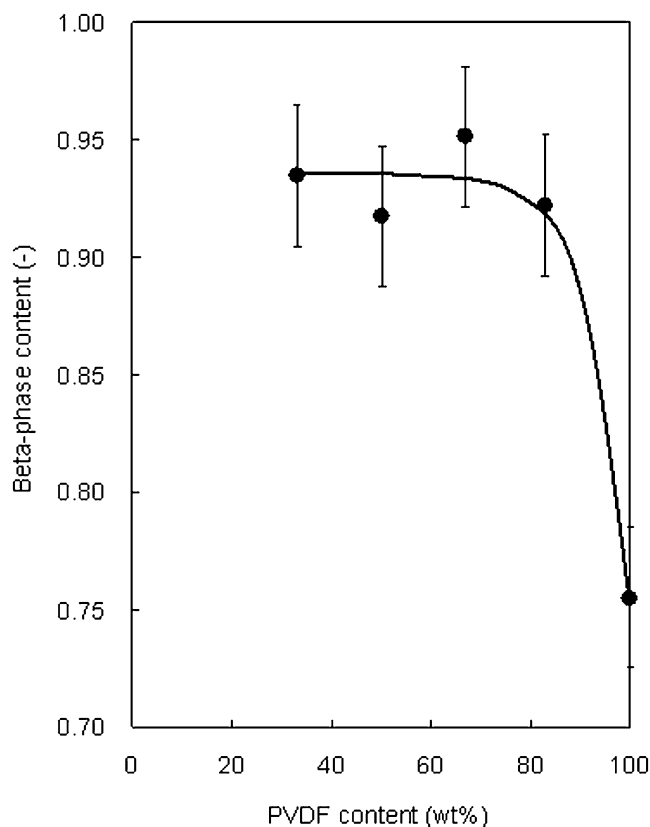


Figure 5. β -phase crystal fraction of residual PVDF from PVDF/PVP blend with various compositions.

the β -phase to α -phase is calculated from the absorbance of the respective vibration band peaks FT-IR spectra (β -phase: 840 cm^{-1} and α -phase: 766 cm^{-1}).⁸

Figure 5 shows β -phase crystal content of the residual PVDF fiber from PVDF/PVP blend with various blend compositions. All residual PVDF nanofiber showed high content of β -phase crystal structure

(>90%). Hanada *et al.* reported that the Flory-Huggins interaction parameter χ_{12} for the PVDF/PVP showing very huge value *ca.* -0.36 at 160°C below the PVDF content of 80 wt%, compared with the one for PVDF/PMMA of -0.30 . On the other hand, it showed anomaly *ca.* 0.8 at the PVDF content of 90 wt%.²¹ Therefore, the addition of the small amount of PVP decreased the χ_{12} drastically, and such strong compatible interaction prevents the formation of TGTG-conformational segments which grow up to the nucleus of the α -phase crystalline and the TT-conformation for β -crystalline forms preferably. In addition, the formation of high (but incomplete) β -phase crystal structure would be explained by the remained of PVP. The peak from carbonyl group remained in PVP was observed at 1675 cm^{-1} for all residual PVDF nanofiber.

CONCLUSION

In the present study, porous nanofibers were prepared by ESD from PVDF/PVP blends and subsequent selective removal of PVP. The effects of blending ratio of PVDF/PVP and selective removal of PVP on formation of the pore and crystal structures of residual PVDF fibers were investigated. Specific surface area of residual PVDF fiber depended on the blending ratio of PVDF/PVP (The highest BET surface area of residual PVDF fiber was $28.54\text{ m}^2/\text{g}$). All residual PVDF nanofibers, on the other hand, showed a high content of β -phase crystal structure (> 90%). The high β -phase content and porous PVDF is a promising material for high efficiency filter media.

REFERENCES

1. P. Gibson, H. Schreuder-Gibson, and D. Rivin, *Colloids Surf., A*, **187–188**, 469 (2001).
2. V. Z. Mordkovich, *Theor. Found. Chem. Eng.*, **37**, 429 (2003).
3. G. Zhang, W. Kataphinan, R. Teye-Mensah, P. Katta, L. Khatri, E. A. Evans, G. G. Chase, R. D. Ramsier, and D. H. Reneker, *Mater. Sci. Eng., B*, **116**, 353 (2005).
4. R. J. Tseng, J. Huang, J. Ouyang, R. B. Kaner, and Y. Yang, *Nano Lett.*, **5**, 1077 (2005).
5. S. Zhang, *Nat. Biotechnol.*, **21**, 1171 (2003).
6. S. Virji, R. B. Kaner, and B. H. Weiller, *J. Phys. Chem. B*, **110**, 22266 (2006).
7. Z. Ma, M. Kotaki, R. Inai, and S. Ramakrishna, *Tissue Eng.*, **11**, 101 (2005).
8. M. Nasir, H. Matsumoto, T. Danno, M. Minagawa, T. Irisawa, M. Shioya, and A. Tanioka, *J. Polym. Sci., Part B: Polym. Phys.*, **44**, 779 (2006).
9. L. Zhang and Y.-L. Hsieh, *Nanotechnology*, **17**, 4414 (2006).
10. Y. Z. Zhang, Y. Feng, Z.-M. Huang, S. Ramakrishna, and C. T. Lim, *Nanotechnology*, **17**, 901 (2006).

11. S. Megelski, J. S. Stephens, D. B. Chase, and J. F. Rabolt, *Macromolecules*, **35**, 8456 (2002).
12. J. T. McCann, M. Marquez, and Y. Xia, *J. Am. Chem. Soc.*, **128**, 1436 (2006).
13. H. Kawai, *Jpn. J. Appl. Phys.*, **8**, 975 (1969).
14. B. Mohammadi, A. A. Yousefi, and S. M. Bellah, *Polym. Test.*, **26**, 42 (2007).
15. Y. Ye, Y. Jiang, Z. Wu, and H. Zeng, *Integrated Ferroelectrics*, **80**, 245 (2006).
16. M. Nasir, H. Matsumoto, M. Minagawa, A. Tanioka, T. Danno, and H. Horibe, *Polym. J.*, **39**, 670 (2007).
17. M. Khayet, C. Y. Feng, K. C. Khulbeeb, and T. Matsuura, *Polymer*, **43**, 3879 (2002).
18. K. Ishizaki, S. Komarneni, and M. Nanko, in "Porous Material: Process Technology and applications," Kluwer Academic Publisher, London, 1998, pp 204–214.
19. W. Sae-lim, W. Tanthapanichakoon, and C. Kanaoka, *J. Aerosol Sci.*, **37**, 228 (2006).
20. G. C. Alfonso, A. Turturro, M. Pizzoli, M. Scandola, and G. Ceccorulli, *J. Polym. Sci., Part B: Polym. Phys.*, **27**, 1195 (1989).
21. T. Hanada and Y. Ando, in "the series of the natural science and engineering," The Bulletin of Tokyo Kasei Gakuin University, 41, 2001, p 77.