

Fouling-Tolerant Nanofibrous Polymer Membranes for Water Treatment

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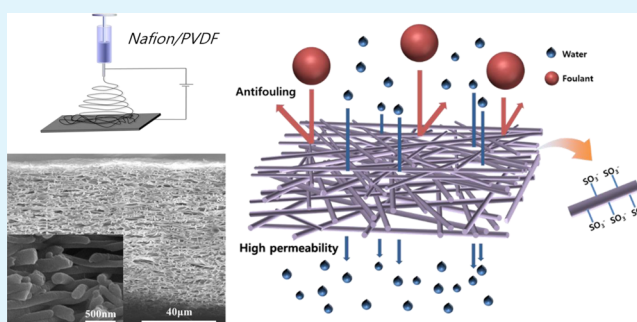
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ABSTRACT: Nafion/polyvinylidene fluoride (PVDF) nanofibrous membranes with electrostatically negative charges on the fiber surface were fabricated via electrospinning with superior water permeability and antifouling behaviors in comparison with the conventional microfiltration membranes. The fiber diameter and the resultant pore size in the nanofibrous membranes were easily controlled through tailoring the properties of the electrospinning solutions. The electrospun Nafion/PVDF nanofibrous membranes revealed high porosities (>80%) and high densities of sulfonate groups on the membrane surface, leading to praiseworthy water permeability. Unexpectedly, the water permeability was observed as proportional to the fiber diameter and pore size in the membrane. The presence of sulfonate groups on the membrane improved the antifouling performance against negatively charged oily foulants.

KEYWORDS: electrospinning, nanofibrous membrane, charged membrane, antifouling, Nafion, polyvinylidene fluoride, water treatment



INTRODUCTION

Polymeric nanofibrous membranes have gained tremendous attention for water treatment, because of their unique characteristics, such as high surface area, interconnected pore structure, high porosity (~80%), easy functionality, and high water permeability.^{1–4}

Electrospinning is a simple and versatile technique that produces continuous polymeric nanofibers with diameters in the submicrometer scale, which are used to make nanofibrous membranes. When a pertinent high voltage is applied to a polymer solution, the electrostatic force between the electrified polymer solution at the tip of metal spinnerette and the collector can overcome the surface tension of the solution, and thus the electrified polymer solution is electrospun into a cone (known as Taylor cone) from the tip of a spinnerette.^{5–7} The morphology of electrospun nanofibrous membranes can easily be manipulated through the alteration of various affecting factors, such as solution properties (concentration, viscosity, surface tension), processing conditions (applied voltage, feed rate, tip-to-collector distance, collection orientation), and ambient conditions (temperature, humidity).⁸

Despite many advantages of electrospinning technique, the electrospun nanofibrous membranes for water treatment are seriously vulnerable to fouling, the deposition of solutes or particles on the membrane surface and inner pores, because of their high porosity and surface roughness.⁹ The fouling

deteriorates the water permeability and rejection efficiency with operation time.^{10–12} Thus, many efforts have been devoted to develop fouling-tolerant membranes utilizing hydrophilic/hydrophobic interactions or electrostatic repulsions between foulants and membrane surfaces.^{13–16}

Surface-charged membranes are considered as promising alternatives to overcome the fouling problem in the membrane research community.^{13–17} In particular, negatively charged membranes were capable of minimizing the adsorption of negatively charged natural foulants, such as natural organic matters, accompanying a high water flux.¹⁷ One of the useful methods to fabricate the surface-charged membranes is to introduce a charged polymer into a neutral polymer matrix. Masuelli et al. prepared a charged membrane through blending sulfonated polycarbonate (SPC) and polyvinylidene fluoride (PVDF). They observed that the increase in SPC content increased the ion exchange capacity of the blend membrane and decreased the membrane fouling effect.¹³ Bowen et al. developed a charged membrane using a poly(ether imide) (PEI)/sulfonated polyether ether ketone (SPEEK) blend. They observed that the water permeability and the PEG rejection efficiency increased as the SPEEK concentration in the blend

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membrane increased, because of the electrostatic repulsion.¹⁴ Recently, Han et al. prepared a sulfonated PVDF microfiltration membrane through a direct sulfonation reaction on the surface of a PVDF microfiltration membrane. Fouling effect of the sulfonated PVDF membrane by charged polystyrene (PS) latex suspensions significantly decreased as the surface charge density of the membrane increased.¹⁵

Herein, we demonstrate that the negatively surface-charged membranes, fabricated via electrospinning with Nafion/PVDF blend solutions, have superior water permeability values and antifouling performances, compared with the conventional microfiltration membranes (Figure 1). Nafion was used as a

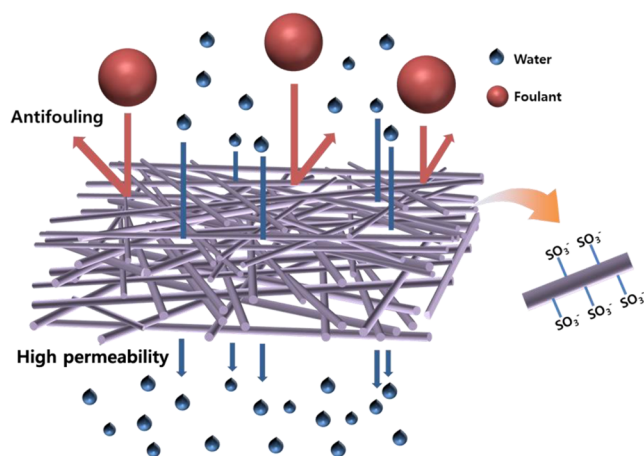


Figure 1. Schematic illustration of negatively charged Nafion/PVDF nanofibrous membrane with high water permeability and fouling tolerance.

polymer component imparting the negative-charge character via its perfluorosulfonic acid functional groups. PVDF was blended with Nafion to endow Nafion with electrospinnability.^{18,19} Moreover, PVDF gives chemical stability and mechanical strength to the blend membrane.^{20,21} The resulting charged membranes possessed high densities of sulfonate groups on the surface and high porosities (>80%), thus revealed not only high water permeability but also good antifouling characteristics against oily foulants. Furthermore, this work promotes systematic understanding about the effects of fiber diameter and pore size in nanofibrous membranes on the water permeability, and the effects of surface charge of the nanofibrous membranes on the fouling behavior.

EXPERIMENTAL SECTION

Materials. A 20 wt % Nafion dispersion (DE-201), with a total acid capacity of 0.95 mequiv g⁻¹ (0.95 mmol H⁺ per 1 g polymer), was purchased from DuPont (Figure 2a). Polyvinylidene fluoride (PVDF) ($M_n = 153 \text{ kg mol}^{-1}$, $M_w = 352 \text{ kg mol}^{-1}$, Solef 1010) was purchased from Solvay Chemicals (Figure 2b). A chlorinated poly(vinyl chloride)

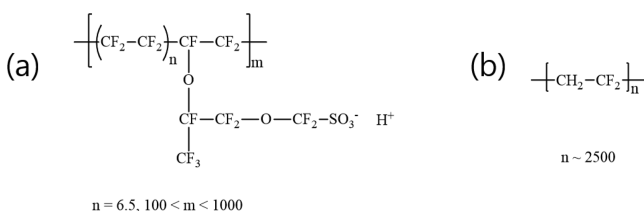


Figure 2. Chemical structures of (a) Nafion and (b) PVDF.

(CPVC) microfiltration membrane (average pore size = 450 nm) was supplied by Pure-Envitech Korea. Dimethylformamide (DMF) was purchased from J.T. Baker. All of the chemicals were used without further purification.

Preparation of Electrospun Nanofibrous Polymer Membranes. First, 10–30 wt % Nafion dispersions in DMF were prepared according to the following procedure. The solvents—water ($34 \pm 2 \text{ wt } \%$), 1-propanol ($44 \pm 2 \text{ wt } \%$), ethanol ($<2 \text{ wt } \%$), mixed ethers and other volatile organic compounds (VOCs, $<1 \text{ wt } \%$)—in the as-received 20 wt % Nafion dispersion were evaporated at 60 °C under vacuum until the residual solvent content remained at 5–10 wt %. The solution was then diluted with a sufficient amount of DMF and evaporated at 60 °C under vacuum, followed by diluting it with DMF again. This step was repeated three times. In the third step, the concentration of the dispersion was adjusted through addition of a predetermined amount of DMF to yield the 10–30 wt % Nafion dispersions in DMF. Blend solutions of Nafion and PVDF were prepared via mixing the Nafion dispersion in DMF and the powdered PVDF, stirring at 80 °C for 24 h, and then cooling at room temperature. The Nafion/PVDF blend solutions were prepared with various polymer compositions in the entire range of 0 to 100%. Electrospinning was carried out through an electrospinning setup (Model ESR-200R2D, NanoNC, Korea) at room temperature and a relative humidity of 18%–22%. The electrospinning process of polymer solutions was conducted under conditions of an applied voltage of $13 \pm 2 \text{ kV}$, a flow rate of $3 \mu\text{L min}^{-1}$, and a needle-to-collector distance of 10 cm. During electrospinning, the needle was scanned above an aluminum foil collector to form even membranes with a large-area quadrangle. The thicknesses of the nanofibrous membranes were controlled to 100 μm . The resulting membranes were heat-treated in a vacuum oven at 80 °C for 3 days to remove the residual solvent, followed by annealing at 130 °C for 1 h to develop the morphology of Nafion, giving enhanced mechanical properties and insolubility in most solvents.^{22,23} A representative sample code of N40P60_C20 denotes the electrospun Nafion/PVDF nanofibrous membrane produced from the Nafion/PVDF solution with a composition of Nafion (40 wt %):PVDF (60 wt %) in a solute and a total solid concentration of 20 wt % in DMF.

Characterization. The viscosities of the Nafion/PVDF blend solutions were measured using a Brookfield DV-II+ viscometer (Brookfield Engineering Laboratories, Inc.) with a spindle (No. 6) at a rotating speed of 10 rpm. The morphology of the electrospun Nafion/PVDF nanofibrous membranes was observed via field-emission scanning electron microscopy (FE-SEM) (Inspect F50, FEI). The average diameter of nanofibers in the membranes was determined through analyzing 30 fibers in an FE-SEM micrograph using UTHSCSA Image Tool 3.0 software. The pore size of the membranes was determined as the longest void length in FE-SEM micrograph. The porosity of the Nafion/PVDF nanofibrous membrane was calculated using the following equation:²⁴

$$\text{porosity (\%)} = \frac{\rho_{\text{true}} - \rho_{\text{app}}}{\rho_{\text{true}}} \times 100 \quad (1)$$

where ρ_{app} and ρ_{true} are the apparent and true densities of the nanofibrous membrane, respectively, which were calculated using the following equations:

$$\rho_{\text{app}} = \frac{w}{At} \quad (2)$$

$$\rho_{\text{true}} = \rho_{\text{Nafion}} \times f_{\text{Nafion}} + \rho_{\text{PVDF}} \times (1 - f_{\text{Nafion}}) \quad (3)$$

where w , A , and t are the weight, area, and thickness of the nanofibrous membrane, respectively, and ρ_{Nafion} and ρ_{PVDF} are the densities of Nafion and PVDF (1.97 g cm^{-3} for Nafion, 1.78 g cm^{-3} for PVDF), respectively. f_{Nafion} is the fraction of Nafion in the Nafion/PVDF nanofibrous membranes.

The chemical structures and compositions of the Nafion/PVDF nanofibrous membranes were examined using X-ray photoelectron spectroscopy technique (XPS, K-Alpha, Thermo Scientific) with Al K α

(1486.6 eV) as the X-ray source and a power of 72 W. Narrow scans were performed with steps of 0.1 eV. To determine the water permeability in the membranes, a dead-end filtration apparatus was used. The membrane was immersed in deionized water (DIW) for at least 30 min, then it was put in a stirred cell (Amicon Model 8050, Millipore Corp.; effective membrane area: 13.4 cm²) with a nonwoven polyester support. The water permeability was measured after a stabilization period (3 h) with continuous feeding of DIW into the stirred cell. The measurement was carried out at 25 °C with an applied pressure of 0.5 bar. The water permeability values (J_w , L m⁻² h⁻¹ bar⁻¹) were calculated using the following equation:

$$J_w = \frac{\Delta m}{\rho A \Delta t \Delta P} \quad (4)$$

where Δm is the permeate weight during the filtration time of Δt , ρ the density of water under the test conditions, A the membrane area, and ΔP the applied pressure. For the fouling test, an oily emulsion with a negative charge at pH 7 was prepared via mixing a commercial soybean oil of 2000 ppm in DIW with a surfactant (Dabco DC193, Air Products and Chemicals, USA) of 200 ppm using a blender (CB15, Waring Commercial, USA) at a constant speed of 1200 rpm for 5 min. The oily emulsion was flowed through a stirred cell assembled with a membrane specimen at 0.5 bar for 50 min after flowing DIW for 3 min. After the fouling step, the oily cake deposited on the membrane was removed through back-flushing with DIW for 10 min, followed by flowing DIW to determine the recovered water permeability percentage ($R\%$), which was calculated as follows.²⁵

$$R\% = \frac{J_{w,x}}{J_{w,0}} \times 100 \quad (5)$$

where $J_{w,0}$ is the pure water permeability in the membrane before fouling and $J_{w,x}$ is the recovered pure water permeability after fouling and membrane cleaning.

RESULTS AND DISCUSSION

Preparation of Electrospun Nafion/PVDF Nanofibers and Their Nanofibrous Membranes. Figure 3 shows the

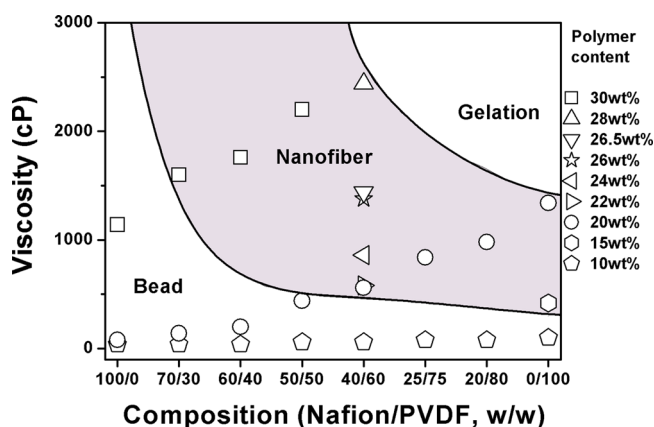


Figure 3. Viscosity and electrospinnability of Nafion/PVDF blend solutions at various Nafion/PVDF compositions and contents.

viscosity and electrospinnability of Nafion/PVDF blend solutions for electrospinning, depending on the blend composition and content. The viscosity was affected by the polymer content and composition of the blend solution. At a constant composition, the viscosity of blend solution increased with an increase in the polymer blend content. At a constant polymer content, the viscosity of blend solution increased with an increase in PVDF fraction of the Nafion/PVDF blend solution, and the viscosity increased more rapidly at larger

polymer contents. Especially, at large polymer contents, the Nafion/PVDF blend showed a gelation behavior; therefore, the viscosity of the gel could not be measured using a Brookfield viscometer. The gelation threshold concentration decreased with an increase in PVDF fraction in the polymer blend solution. These rheological behaviors of the Nafion/PVDF blend solutions are attributed to the fact that the high-molecular-weight PVDF, responsible for the chain entanglement, increases the viscosity of the polymer blend solution and a high fraction of PVDF in DMF makes strong secondary interactions such as hydrogen bond.

The electrospinning characteristic of the Nafion/PVDF blend solution was greatly affected by the polymer content and composition and the resulting viscosity, as shown in Figure 3. The shadow region indicates the electrospinnable conditions of the blend solution in terms of polymer composition and viscosity, whereas the white region indicates the bead-forming conditions or the gelation conditions. Initially, Nafion solutions were just sprayed to form beads, not electrospun to form nanofibers at any Nafion contents through an electrospinning technique due to strong electrostatic interactions between the ionic groups and hydrophobic interactions between the fluorocarbon backbones.¹⁸ It was reported that these interactions form Nafion aggregates in the solvents. The Nafion aggregates were categorized as (i) the primary rodlike aggregates (~500 nm) formed by the hydrophobic interaction of fluorocarbon backbones, and (ii) the secondary larger aggregate particles (>1 μm) formed by the ionic interaction of the primary aggregates. These aggregates would undoubtedly prevent the Nafion chains from being entangled. The polymer chain entanglement is a prime requirement for electrospinnability.¹⁸ When PVDF was added to the Nafion solution, the blend solution began to be electrospun to form nanofibers in proper concentration ranges. At a fixed Nafion/PVDF blend composition, the blend solution was electrospun at low concentrations and electrospun at medium concentrations. To give electrospinnability to the blend solution, the viscosity above 400 cP seemed to be required. At high concentrations, some solutions revealed a gelation behavior. The gel did not be discharged through the nozzle because the electrostatic force between the electrified gel at the tip of metal spinnerette and the collector could not overcome a high surface tension of the gel.

Representative SEM micrographs of the Nafion/PVDF nanofibrous membranes electrospun from the blend solutions of various polymer contents are shown in Figure 4. The composition of Nafion/PVDF was fixed to 40/60 (w/w). Electrospinning of the Nafion/PVDF blend solution formed many submicrometer beads up to a polymer content of 10 wt %, and a nanofiber morphology in a medium polymer content range from 20 wt % to 28 wt %. The diameter of electrospun nanofibers increased as the polymer content increased. At higher polymer contents of over 30 wt %, the blend solution did not permit electrospinning again, because of a strong gelation behavior. Figure 4e shows a cross-sectional SEM micrograph of the Nafion/PVDF (40/60, w/w) membrane with a 20 wt % polymer content. A SEM micrograph of a commercial CPVC microfiltration membrane surface, produced through a vapor-induced phase separation (VIPS) method, was also prepared, shown in Figure 4f. The morphology of the CPVC membrane was observed largely different from those of the electrospun nanofibrous membranes, indicating that the

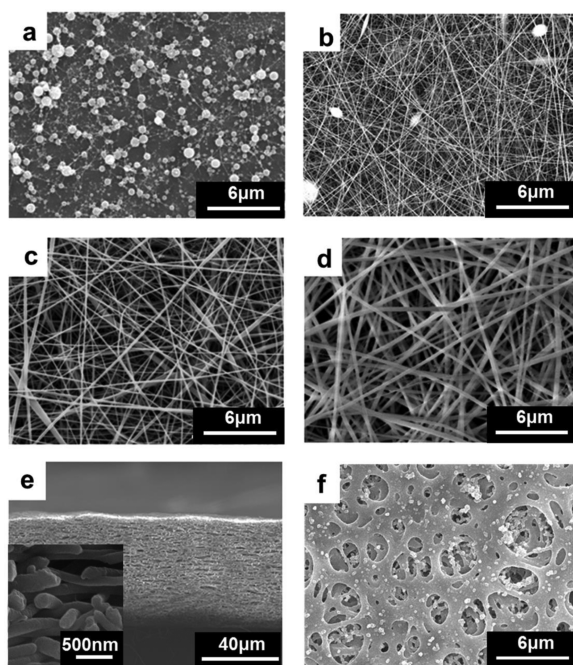


Figure 4. SEM images of Nafion/PVDF (40/60, w/w) nanofibrous membranes surface electrospun with the blend solutions of various polymer contents: (a) 10, (b) 20, (c) 26, and (d) 28 wt %. (e) A cross-sectional SEM image of the Nafion/PVDF (40/60, w/w) membrane with a 20 wt % polymer content and the inset is the magnified image. (f) SEM image of a commercial CPVC membrane surface.

CPVC had circular pores with an average size of 450 nm and a porosity of 40%.

Electrospinnability of the polymers blend solution was also significantly influenced by the Nafion/PVDF composition. At a constant polymer content of 20 wt %, the electrospinnability improved with an increase in PVDF fraction in the Nafion/PVDF blend solution. The blend solution with a low fraction of PVDF formed lots of beads; however, as the PVDF content increased, a fibrous feature began to appear. Figure 5 shows representative SEM micrographs of the Nafion/PVDF nanofibrous membranes electrospun from the blend solutions with

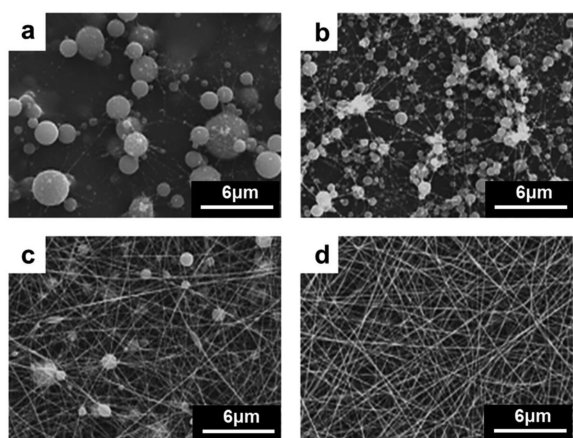


Figure 5. SEM images of electrospun nanofibrous membranes surface with various Nafion/PVDF compositions: (a) 100/0, (b) 60/40, (c) 50/50, and (d) 25/75 (w/w). Blend solutions with constant polymer content of 20 wt % were electrospun for the fabrication of the nanofibrous membranes.

various Nafion/PVDF compositions at a constant polymer content of 20 wt %. Electrospinning with the Nafion/PVDF blend solution formed beads up to a PVDF fraction of 50 wt % and neat nanofibers at higher PVDF fractions of >60 wt %. In addition, the increase in PVDF fraction led to a slight increase in fiber diameter. Meanwhile, the morphology of Nafion electrospun with a Nafion solution (Figure 5a) showed Nafion beads with the size of 0.1–4.0 μm . The size of beads matched well with those of the two types of Nafion aggregates mentioned earlier. This may indicate that the Nafion aggregates in the Nafion solution were just sprayed under the applied electric potential, because of the absence of chain entanglement.

The viscosities of the Nafion/PVDF blend solutions, the diameters of the electrospun nanofibers, the porosities, and pore sizes of the resulting nanofibrous membranes are summarized in Table 1. Figure 6 shows the relationship between the viscosity of the blend solutions and the diameter of the resultant electrospun nanofibers. It clearly shows that the nanofiber diameter is almost linearly proportional to the viscosity of the blend solution, regardless of the ratio of Nafion to PVDF.

Figure 7 shows the relationships between fiber diameter, pore size, and porosity in the electrospun nanofibrous membranes. The pore size of the membranes was proportional to the fiber diameter, regardless of the blend composition. The pore size increased from 106 nm to 395 nm with the increase of the fiber diameter in the range of 31–240 nm. In the meantime, the porosity was almost constant in the overall range of fiber diameter. These results are in good agreement with the previous literature reports.^{26,27}

Figure 8a shows the XPS survey scan spectra of Nafion/PVDF nanofibrous membranes. F 1s, O 1s, C 1s, and S 2p spectra were observed in the ranges of 680–690 eV, 530–540 eV, 280–295 eV, and 165–175 eV, respectively. The Nafion/PVDF nanofibrous membranes contained sulfur and oxygen, whereas the two elements were absent from the surface of the pristine PVDF fibrous membrane. Moreover, the intensities for the two elements increased as the fraction of Nafion in the blend increased. Figure 8b shows a representative oxygen narrow scan spectrum of a Nafion/PVDF nanofibrous membrane. The O 1s XPS spectrum was composed of two types of oxygen: –O–S– (oxygen bound in sulfonic acid group, 535.8 eV) and –O–C– (oxygen in ether configuration, 532.7 eV), both of which are originated from Nafion.²⁸ The atomic compositions of the blend membranes determined by XPS technique are summarized in Table 2. The composition of sulfur on the surface of the Nafion/PVDF membrane, attributed to the presence of Nafion, approximately matched with the respective Nafion contents. This result may indicate that sulfonate groups, responsible for the negative charge, were evenly distributed on the membrane surface, suggesting that Nafion and PVDF should have a good compatibility and miscibility in the compositional range of this work. The density of sulfonate groups on the membrane surface was easily controlled by means of Nafion content.

Herein, Nafion/PVDF nanofibrous membranes were fabricated using an electrospinning method. Electrospinnability of the Nafion/PVDF blend solution was affected by the polymer content and composition, and viscosity of the blend solution. The electrospinnability was improved when the PVDF fraction increased, because it formed a polymer chain entanglement inside the electrospinning blend solution, which is essential for

Table 1. Characterization of Nafion/PVDF Nanofibrous Membranes^a

sample	polymer content (wt %)	Composition		viscosity (cP)	bead diameter (nm)	fiber diameter (nm)	porosity (%)	pore size (nm)
		Nafion	PVDF					
N100P0_C30	30	100	0	1140	1200			
N70P30_C30	30	70	30	1600		103	86	199
N60P40_C30	30	60	40	1760		156	87	293
N50P50_C30	30	50	50	2200		178	85	395
N40P60_C30	30	40	60	Gel		solution was not jetted		
N25P75_C30	30	25	75	Gel		solution was not jetted		
N20P80_C30	30	20	80	Gel		solution was not jetted		
N0P100_C30	30	0	100	Gel		solution was not jetted		
N100P0_C20	20	100	0	80	1094			
N70P30_C20	20	70	30	140	665			
N60P40_C20	20	60	40	200	687			
N50P50_C20	20	50	50	440	748			
N40P60_C20	20	40	60	560		31	86	106
N25P75_C20	20	25	75	840		73	85	221
N20P80_C20	20	20	80	980		78	87	264
N0P100_C20	20	0	100	1340		777	78	1231
N100P0_C10	10	100	0	40	1253			
N70P30_C10	10	70	30	40	597			
N60P40_C10	10	60	40	40	442			
N50P50_C10	10	50	50	60	441			
N40P60_C10	10	40	60	60	482			
N25P75_C10	10	25	75	80	575			
N20P80_C10	10	20	80	80	655			
N0P100_C10	10	0	100	100	647			
N40P60_C22	22	40	60	580		60	88	124
N40P60_C24	24	40	60	860		64	90	150
N40P60_C26	26	40	60	1380		71	88	184
N40P60_C26.5	26.5	40	60	1440		156	88	256
N40P60_C28	28	40	60	2440		240	88	390
N0P100_C15	15	0	100	420		85	85	177
CPVC							40	450

^aNote: Porosity and pore size were measured just for the nanofibrous membranes. For comparison, a commercial CPVC (chlorinated polyvinyl chloride) membrane was engaged in this study.

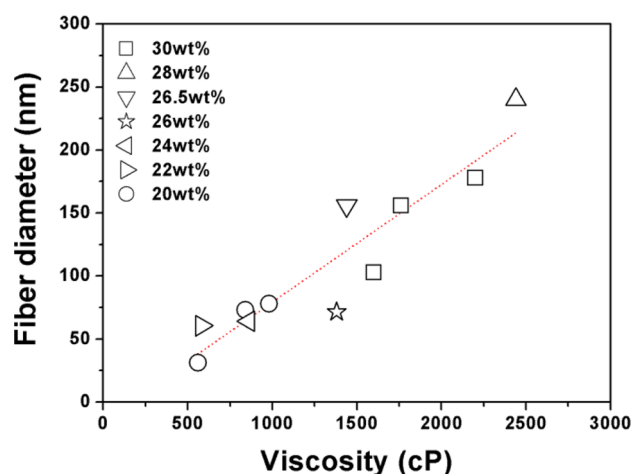


Figure 6. Plot showing the relationship between the viscosity of electrospinning solution and the diameter of electrospun nanofiber. The legend indicates the polymer content of electrospinning solution.

the electrospinning process. The viscosity of the blend solution also increased for the same reason. The diameter of nanofibers in the membrane increased as the solution viscosity increased. On the other hand, the porosity of the membrane was almost constant, regardless of the polymer content and composition of

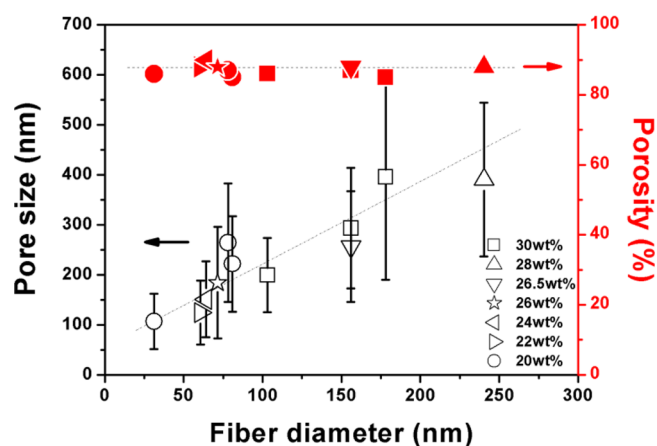


Figure 7. Plot showing the relationship between fiber diameter, pore size, and porosity in the electrospun Nafion/PVDF nanofibrous membranes.

the blend solution. Therefore, the pore size of the membrane increased as the fiber diameter in the membrane increased. Nafion and PVDF formed a miscible blend in DMF. The density of sulfonate group on the electrospun Nafion/PVDF nanofibrous membrane was proportional to the Nafion fraction in the membrane.

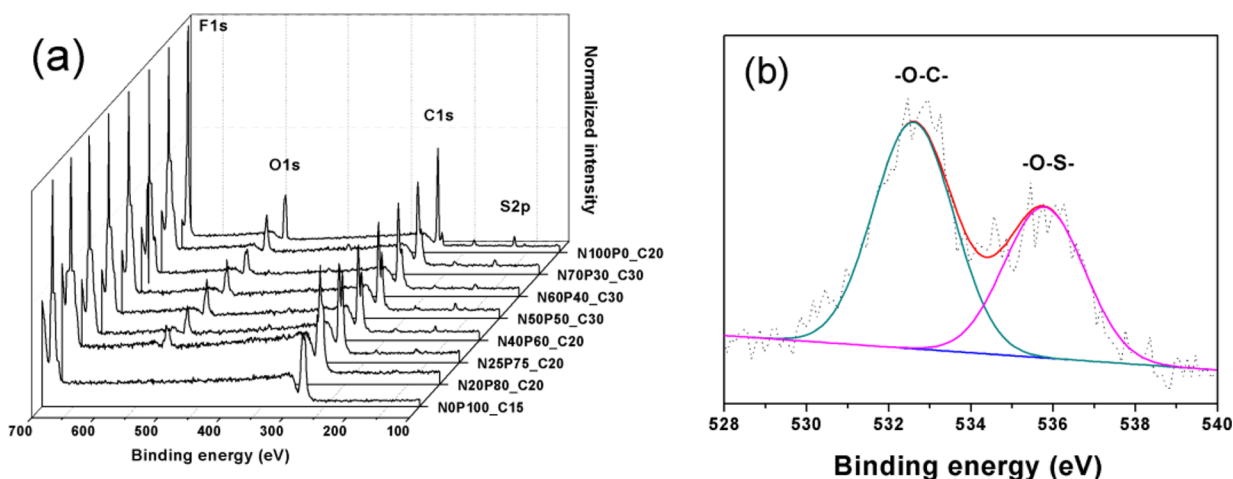


Figure 8. XPS spectra of electrospun Nafion/PVDF nanofibrous membranes: (a) survey scan spectra of the membranes and (b) narrow scan spectrum of N40P60_C20 in the range of O 1s.

Table 2. Composition of Nafion/PVDF Nanofibrous Membranes Determined by XPS

sample	Atomic Content (at.%)			
	C	F	O	S
N100P0_C20	38.5	51.0	8.3	2.2
N70P30_C30	40.1	52.8	5.7	1.5
N60P40_C30	40.8	53.1	4.8	1.4
N50P50_C30	42.9	51.3	4.7	1.2
N40P60_C20	44.3	49.5	5.3	0.9
N25P75_C20	46.2	49.2	4.0	0.6
N20P80_C20	44.9	51.8	2.7	0.6
NOP100_C15	50.3	49.7	0	0

Water Filtration and Fouling Behaviors of Membranes. Figure 9a shows the water permeability values in the electrospun Nafion/PVDF nanofibrous membranes with various nanofiber diameters (31–240 nm). All the membranes tested had a constant Nafion/PVDF composition (40/60, w/w). The water permeability increased with the increase in fiber diameter. Figure 9b shows a plot of water permeability versus pore size for the nanofibrous membranes. The water permeability was dominantly affected by the pore size, regardless of the Nafion/PVDF composition. The water permeability increased from 5000 L m⁻² h⁻¹ bar⁻¹ to 20 000 L m⁻² h⁻¹ bar⁻¹ when the pore size increased from 100 nm to 400 nm. For comparison, a commercial CPVC microfiltration membrane (average pore size = 450 nm, porosity = 40%; refer to Figure 4f for the morphology), produced through a VIPS method, was also examined. The water permeability of the electrospun Nafion/PVDF nanofibrous membrane with the identical pore size (water permeability: >20 000 L m⁻² h⁻¹ bar⁻¹) was substantially greater than that of the commercial CPVC membrane (water permeability: 8000 L m⁻² h⁻¹ bar⁻¹). The larger water permeability of the nanofibrous membrane was attributed to the high porosity (>80%).

The relationship between the water permeability and the pore size can be expressed by the Hagen–Poiseuille equation:^{29,30}

$$J = \frac{\varepsilon r^2 \Delta P}{8\eta\tau\Delta x} \quad (6)$$

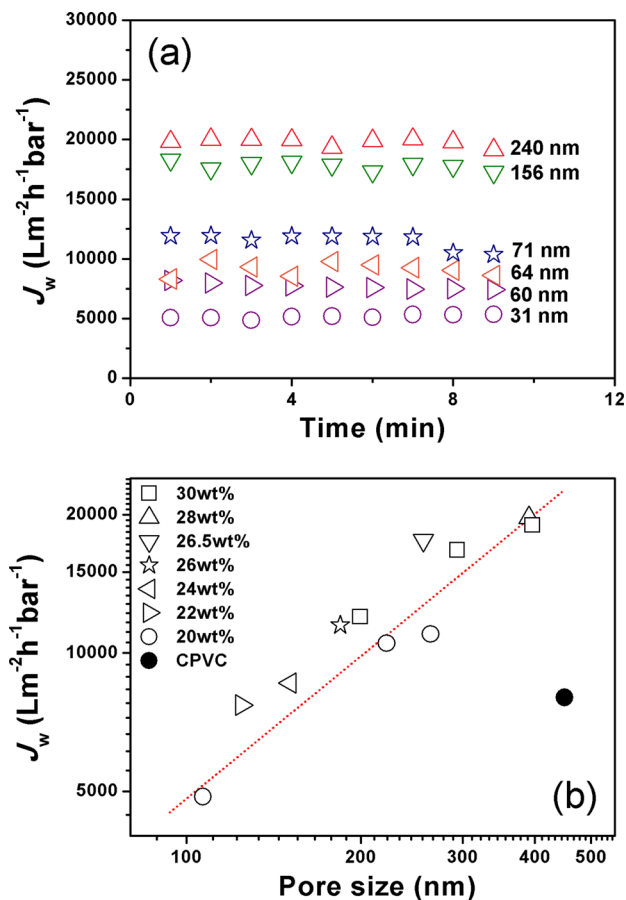


Figure 9. (a) Water permeability versus time profiles in electrospun Nafion/PVDF nanofibrous membranes with different fiber diameters; the legend indicates the fiber diameter. A constant Nafion/PVDF composition (40/60, w/w) was engaged in this experiment. (b) Water permeability versus pore size plot for the nanofibrous membranes; the water permeability of a commercial chlorinated poly(vinyl chloride) (CPVC) microfiltration membrane was measured for comparison.

where J is the solvent permeability, ε the porosity, r the pore radius, ΔP the pressure difference across the membrane, η the solvent viscosity, τ the tortuosity factor, and Δx the membrane thickness. In the equation, which describes the permeability behavior for pressure-driven viscous flow in porous material, it

is assumed that the pore of the material is regular and straight cylindrical. According to eq 6, the water permeability is proportional to the square of pore radius under the ideal condition.

The pore size of the nanofibrous membrane was observed to be proportional to the fiber diameter in the membrane (Figure 7). The water permeability was improved as the pore size increased (Figure 9b). In this study, however, it was observed that the water permeability (water flux per applied pressure) was linearly proportional to the pore size, which did not match with the Hagen–Poiseuille equation. This mismatch between the experimental result and the Hagen–Poiseuille relationship seems to originate from the broad pore-size distribution and high tortuosity.

The fouling properties of the negatively charged Nafion/PVDF nanofibrous membranes were investigated with an oily water sample. Figure 10 displays the fouling behaviors of

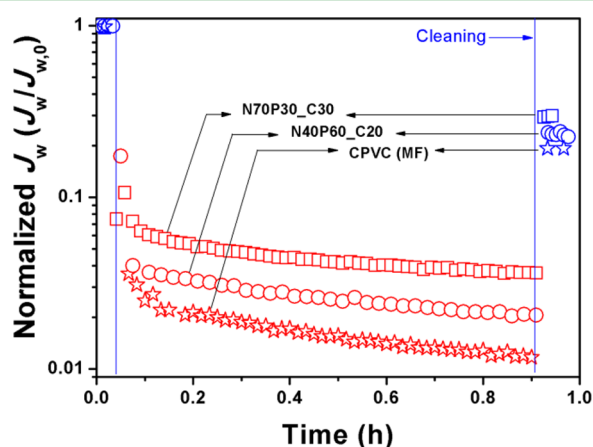


Figure 10. Fouling behaviors of electrospun Nafion/PVDF nanofibrous membranes. Blue symbols represent the pure water permeability, and red symbols represent the water permeability with an oily water feed. The fouling behavior of a commercial CPVC microfiltration membrane was assessed for comparison.

N70P30_C30 (pore size = 199 nm and water permeability = $12\,000\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$) and N40P60_C20 (pore size = 106 nm and water permeability = $4900\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$) nanofibrous membranes. A conventional CPVC microfiltration membrane with much larger pore size of 450 nm and intermediate water permeability of $8000\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}^{-1}$ was also examined, for comparison. The oily emulsion with a negative charge at pH 7 was flowed through a stirred cell assembled with a membrane specimen at 0.5 bar for 50 min after flowing DIW for 3 min. During the flow of the oily emulsion, a thick oily cake was deposited on the membrane surface. After the fouling step, the cake on the membrane was removed through back-flushing with DIW for 10 min, followed by flowing of DIW to determine the recovered water permeability percentage. The electrospun Nafion/PVDF nanofibrous membranes revealed much larger water permeability values with feeding an oily water and recovered water permeability percentages than the commercial CPVC membrane, despite much smaller pore sizes in the nanofibrous membranes. The recovery percentage increased with the increase in Nafion fraction in the nanofibrous membrane. The recovered water permeability percentages for N70P30_C30 and N40P60_C20 samples were 30% and 24%, respectively, whereas that for the CPVC membrane was 19%.

From this study, it was evidenced that the electrospun Nafion/PVDF nanofibrous membranes reveal a remarkable antifouling behavior against negatively charged foulants, such as emulsion of oil in water, accompanying a high water permeability. This good antifouling performance is attributed to the strong electrostatic repulsion between the membrane surface and the oily foulant.^{31–34}

CONCLUSIONS

In this study, high-permeability and fouling-tolerant Nafion/PVDF nanofibrous membranes were successfully fabricated through electrospinning process and the relationships between structure of nanofibrous membrane and properties, such as water permeability and antifouling property, were investigated. The electrospinnability of the Nafion/PVDF blend solution and the morphology of the resulting nanofibrous membrane were affected by the polymer content and composition, and viscosity of the blend solution for electrospinning. The fiber diameter and pore size in the Nafion/PVDF nanofibrous membrane could easily be tuned through controlling the viscosity of the electrospinning solution. Unexpectedly, the water permeability of the nanofibrous membrane was proportional to the pore size. The electrospun Nafion/PVDF nanofibrous membranes showed superior water permeability values and antifouling performances against negatively charged oily foulants compared with a conventional CPVC microfiltration membrane due to the strong electrostatic repulsion between the negatively charged natural foulant and the negatively charged membrane surface. Our observation in this work demonstrates that the Nafion/PVDF nanofibrous membranes deserve to be considered as a promising candidate to overcome the problems of conventional microfiltration membranes, such as low permeability and severe fouling behavior.

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Notes

The authors declare no competing financial interest.

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