Preparation of PVDF/poly(tetrafluoroethylene-*co*-vinyl alcohol) blend membranes with antifouling propensities via nonsolvent induced phase separation method

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) was blended with a new amphiphilic copolymer, poly(tetrafluoroethylene-*co*-vinyl alcohol) [poly(TFE-VA)], via non-solvent induced phase separation (NIPS) method to make membranes with superior antifouling properties. The effects of the VA/TFE segment ratio of the copolymer and the copolymer/PVDF blend ratio on the properties of the prepared membranes were studied. Membranes with similar water permeabilities, surface pore sizes, and rejection properties were prepared and used in bovine serum albumin (BSA) filtrations with the same initial water flux and almost the same operating pressure, to evaluate the sole effect of membrane material on fouling propensity. While the VA/TFE segment ratio strongly affected the membrane antifouling properties, the effects of the copolymer/PVDF blending ratio were not so drastic. Membrane surface hydrophilicity increased, and BSA adsorption and fouling decreased upon blending a small amount of amphiphilic copolymer with a high VA/TFE segment ratio with PVDF (copolymer/PVDF blending ratio 1:5). © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43780.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is an outstanding polymer for fabricating membranes due to properties like high mechanical strength and resistance to harsh chemical conditions.[1] However, PVDF being hydrophobic, the application of PVDF membranes in water treatment is limited because of their strong fouling tendencies.[2] Foulants, such as proteins in the feed water, adsorb onto the membrane surface or block the membrane pores via hydrophobic–hydrophobic interaction, causing a sharp decrease in membrane flux,[3] which is undesirable as it indirectly raises the operation cost.

To inhibit fouling phenomena, an effective approach is to improve the hydrophilicity of the PVDF membrane. Several techniques have been developed to increase the hydrophilicity, such as grafting hydrophilic monomers,[4–6] surface coating,[7–9] blending with hydrophilic polymers,[10,11] and so on. Among them, blending with hydrophilic polymers is convenient for large-scale production,[1] because further modification processes are not required in the membrane preparation. In this method, the key issue is finding a suitable material with good hydrophilicity and good compatibility with PVDF. Although linear hydrophilic polymers, such as poly

(vinyl alcohol) (PVA),[10] poly(vinyl pyrrolidone) (PVP)[11,12] and poly(ethylene glycol) (PEG),[13] are cheap and easy to obtain, the major issue is their poor compatibility with the host polymer, PVDF. Furthermore, these linear polymers are soluble in water, which means that they leach out from the PVDF membrane during filtration, resulting in a gradual decrease in its hydrophilicity.[14] Therefore, amphiphilic copolymers have been developed as a preferable solution to overcome this stability problem. The hydrophobic segments in amphiphilic copolymers are highly compatible with the hydrophobic backbones of the PVDF membrane, and the hydrophilic segments migrate towards the membrane surface, resulting in an improvement in its hydrophilicity on the surface.

A preliminary application of the amphiphilic copolymer, poly (methyl methacrylate-*r*-poly(ethylene glycol) methyl ether methacrylate) [poly(MMA-*co*-PEGMA)] was reported by Mayes *et al.* in 1999.[15] Since then, several studies have been conducted into the applications of amphiphilic copolymers in membrane preparation.[16–19] Venault *et al.*[16] studied block copolymers of polystyrene and poly(ethylene glycol)methacrylate (PS-*b*-PEGMA) as a blending component in anti-biofouling PVDF membranes. The important role of PS-*b*-PEGMA in membrane formation was investigated, and they proved the satisfactory antifouling effect

of this blend membrane. Protein and bacteria adsorptions were also largely inhibited, with >99% reduction for bacteria. Zhao et al.[17] studied three kinds of amphiphilic copolymers with different chemical structures. Based on their study, a copolymer consisting of a polysiloxane backbone and polyethylene oxide/polypropylene oxide side chains showed the best hydrophilicity in blended membranes, and bovine serum albumin (BSA) adsorption for this membrane was the lowest. The membrane regained most of its initial flux after cleaning with deionized water. Liu et al.[18] synthesized PVDF grafted with PEGMA by atom transfer radical polymerization (ATRP). By adding 10 or 15 wt % of PVDF-g-PEGMA to PVDF, a defect-free, high-performance ultrafiltration membrane could be fabricated. This membrane presented a periodic pillar-like or spherical structure on its surface and exhibited good performance in rejecting sodium alginate and Suwannee River humic acid. Sun et al.[19] synthesized a block copolymer with PMMA and poly[$N,N-2$-(dimethylamino)ethyl methacrylate] (PDMAEMA) via atom transfer radical polymerization method. Then PVDF/PMMA-b-PDMAEMA blend membrane was fabricated and evaluated. It was proven that by blending 15% of the synthesized copolymer, the water contact angle decreased from 98° (pure PVDF) to 76° (blend membrane), and adsorption of BSA molecules in the blend membranes was also largely inhibited, decreasing from 111 ± 3 g/cm^2 (pure PVDF membrane) to 46 ± 2 g/cm^2 (blend membrane). Newly prepared amphiphilic copolymers have successfully improved the hydrophilic properties of PVDF blend membranes. However, membrane performance was often evaluated in dead-end cells, or using membranes with different initial permeabilities and pore sizes in the cases described above. It is well known that the membrane initial water flux,[20] the operating water filtration pressure,[21] and selective layer pore size[22] have significant effects on the performance of membranes during filtration. Thus, it is difficult to discuss the sole effect of the membrane material on fouling propensity. In this study, membrane antifouling properties were evaluated by preparing membranes with similar pore size and water permeability by adjusting the dope solution composition to minimize the effect of membrane morphology and hydrodynamic factors on the fouling and mainly correlate the antifouling propertis to the membrane material properties.

To the best of our knowledge, only limited researches have been conducted on the application of amphiphilic copolymers with fluorinated backbones in preparing antifouling blend membranes. Considering that fluorinated copolymers have higher chemical stability than other reported copolymers, a novel fluorinated copolymer, poly(tetrafluoroethylene-co-vinyl alcohol) (poly(TFE-VA)), was used to fabricate PVDF blend membranes in this study. The PVDF and TFE segments of the copolymer are expected to show good compatibility, and the PVA segment of the copolymer would provide the appropriate hydrophilic properties. Therefore, both high stability and high hydrophilicity can be achieved by using poly(TFE-VA). The effects of the VA/TFE segment ratio strongly affected the hydrophilic properties, and subsequently the antifouling propensity of the prepared membranes. By selecting an appropriate VA/TFE segment ratio, a membrane with considerable antifouling properties obtained by blending copolymer with blending ratio as low as 1:5.
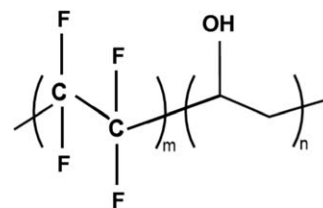

Figure 1. Chemical structure of poly(TFE-VA).

EXPERIMENTAL

Materials

PVDF ($M_w = 270,000$ g/mol) and two types of poly(TFE-VA) with different monomer segment ratios TFE:VA/mol:mol = 37:63, $M_w = 130,000$ g/mol, abbreviated as copolymer A and TFE:VA/mol:mol = 54:46, $M_w = 21,000$ g/mol, abbreviated as copolymer B were supplied by Daikin Industries Ltd. Figure 1 [TQ1]shows the chemical structure of the poly(TFE-VA) copolymer. N,N,-dimethylacetamide (DMAc), sodium dihydrogen phosphate (NaH$_2$PO$_4$), disodium hydrogen phosphate (Na$_2$HPO$_4$), and BSA were purchased from Wako Pure Chemical Industries. BSA solution was prepared by dissolving BSA in phosphate-buffered saline (PBS, 0.1 mol/L, pH = 7.4). Polystyrene latex particles with a 100 nm diameter, used for rejection experiments, were purchased from Duke Scientific Corporation (Thermo Fisher Scientific, Waltham, MA). Milli-Q water was produced in a Millipore Milli-Q unit (Millipore, Bedford, MA). All reagents were used as received.

BSA Adsorption on Polymer Films

The amount of BSA adsorbed on the polymer films was measured using a quartz crystal microbalance with a dissipation monitoring apparatus (QCM-D, Q-Sense E1; MEIWAFOSIS Co. Ltd, Japan). Piezoelectric quartz crystal sensors with a fundamental resonant frequency of around 5 MHz and a diameter of 14 mm (QSX 301; Q-Sense Co., Sweden) were used. Before each measurement, the sensor was cleaned using an ultraviolet/ozone cleaner (Pro Cleaner 110; BioForce Nanosciences Co.). After spin coating the sensor (QSX 301) with a 1.0 wt % polymer or copolymer solution at 3000 rpm for 1 min and drying at 80 °C for 20 min, it was placed in the QCM flow chamber. The PBS solution was injected into the flow chamber at a flow rate of 50 µL/min. After the baseline stabilized, the solution was replaced by 1000 ppm BSA solution to measure the BSA absorption. After measuring the BSA adsorption, the solution was changed again back to PBS to measure the desorption of BSA from the polymer surface. In accordance with the Sauerbrey equation [eq. (1)], the total amount of BSA adsorbed on the polymeric film surface was calculated by varying the sensor oscillation frequency during parallel flow of BSA solution at a constant temperature of 25 °C[23]:

$$\Delta m = -C \frac{\Delta f}{n} \tag{1}$$

In eq. (1), Δm is the adsorption amount (ng cm^{-2}), C is the mass sensitivity constant (17.7 ng/cm^2 Hz at $f = 4.95$ MHz), Δf is the variation of frequency (Hz), and n is the overtone number ($n = 7$).

Flat-Sheet Membrane Fabrication

Flat-sheet membranes were prepared by a non-solvent induced phase separation (NIPS) method as follows. Polymers were dissolved in

Table I. Dope Solution Composition of the Membranes Prepared

Membrane	Copolymer/PVDF (blend ratio)	Copolymer (wt %)	PVDF (wt %)	DMAc (wt %)	Total polymer concentration (wt %)
PVDF	—	—	14.0	86.0	14.0
A(1:9)	1:9	1.7	15.3	83.0	17.0
A(1:5)	1:5	3.7	18.3	78.0	22.0
B(1:5)	1:5	3.0	15.0	82.0	18.0

PVDF, Poly(vinylidene fluoride); DMAc, N,N,-dimethylacetamide.

DMAc by stirring at 60 °C for 24 h to obtain homogeneous solutions, and, degassed overnight at 25 °C. Then, the solution was cast onto a glass plate with a nonwoven support using a steel knife with a thickness of 200 μm to obtain the nascent polymer film. After allowing to expose in air for 10 seconds, the plate and film were subsequently immersed in a bath of Milli-Q water at room temperature, leading to phase separation and formation of a porous membrane. All membranes were washed thoroughly with Milli-Q water to remove residual solvent and stored in Milli-Q water until use. The pure PVDF membrane and three blended membranes using two types of copolymers with different VA segment percentage and various copolymer/PVDF blend ratios were prepared. The compositions of the dope solutions used for membrane casting are shown in Table I, where membranes prepared with copolymer A with blending ratios of 1:9 and 1:5, and copolymer B with a blending ratio of 1:5 are abbreviated as A(1:9), A(1:5), and B(1:5), respectively. Different total polymer concentrations were applied in order to set similar permeability and pore size for all membranes.

It is well known that the membrane initial water flux,[20] the operating water filtration pressure,[21] and skin layer pore size[22] strongly affect the fouling propensity of membranes. For the prepared membranes in this study, the total polymer concentrations of the dope solutions were adjusted so that the prepared membranes had similar pure water permeabilities and surface pore sizes to enable a better comparison of the fouling properties, without the effects of different water permeabilities and surface pore sizes.

Membrane Characterization

X-ray Photoelectron Spectroscopic Analysis. X-ray photoelectron spectroscopy (XPS, PHI X-tool; ULVAC-PHI, Japan) was used to evaluate the surface chemical composition of the polymeric membranes. The system was equipped with an Al Kα radiation source (280 eV). Survey spectra were recorded over the range of 0–700 eV. The surface elemental composition was calculated from the peak area with a correction for atomic sensitivity. The photoelectron take-off angle was set at 45°.

Membrane Morphology Observation. A field emission scanning electronic microscope (FE-SEM; JSF-7500F, JEOL Co. Ltd., Japan) was used to observe the surface morphology of the membranes. The prepared flat membranes were freeze-dried using a freeze dryer (FD-1000; EYELA, Japan) and then sputter coated with a 5 nm osmium layer using an osmium coater (Neoc-STB; MEIWAFOSIS Co. Ltd., Japan). The coated samples were examined at an accelerating voltage of 7 kV at different magnifications.

Pure Water Permeability Measurement. Water permeability was evaluated using a two-parallel-plate cross-flow module (C10-T; Nitto Denko Co. Ltd., Japan). The module channel had a clearance of 2.5 mm, a width of 45 mm, and a length of 180 mm. The flat membrane was installed on a permeable support. The effective membrane area inside the footprint of the O-ring was 6×10^{-2} m^2. Mili-Q water was pumped into the module using a peristaltic pump. The operating pressure at filtration was adjusted by a needle valve at the outlet. The mean pressure at the inlet and outlet of the membrane module was taken as the operating pressure. The feed water flow rate at the entrance of the membrane module was maintained at 160 mL/min. Before starting the measurements, the membrane was compacted at 0.1 MPa until the water flux became stable. Then, the membrane permeability was measured at 0.05 MPa for three times.

Polystyrene Particle Rejection Measurement. The polystyrene particle rejection experiment was conducted in a cross-flow stainless steel cell with an effective filtration area of 8×10^{-4} m^2 using 300 ppm latex particle solution. The feed solution was prepared by adding the monodisperse latex particles, which had a diameter of 100 nm, in an aqueous nonionic surfactant (mass fraction 0.1%, Triton X-100). This solution was then forced to permeate through the membrane under a pressure of 0.05 MPa. The filtrate was collected after 15 min of feed circulation. The concentration of both the feed and the filtrate were measured via UV-vis spectrophotometry (U-2000; Hitachi Co., Tokyo, Japan) at a wavelength of 385 nm. The membrane rejection was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (2)$$

where R, C_p, and C_f are the rejection, latex particle concentration of permeate, and feed solution concentration, respectively.

Air Bubble Contact Angle Measurement. The air-bubble contact angle of each membrane was measured with a contact angle goniometer (Drop Master 300; Kyowa Interface Science Co., Japan) to evaluate their surface hydrophilicities. A sample was prepared by cutting off a random part of the membrane of a suitable size and then fixing this sample upside-down in a glass cell filled with Milli-Q water. By using a special J-shaped syringe needle, an air bubble (5 μL) was released below the sample. The air-bubble contact angle with the surface was measured automatically upon contact of the bubble with the membrane. At least 10 times measurements was carried out at different sample
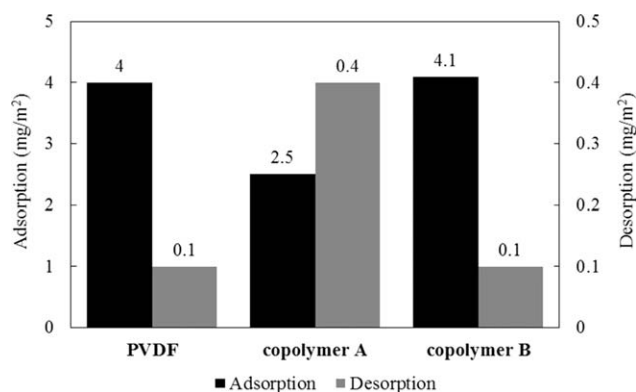
Figure 2. BSA adsorption and desorption amounts of PVDF and copolymers A and B, measured by QCM.

locations. In this experiment, when the membrane surface was hydrophilic, the air bubble contact angle became larger because air is hydrophobic.

Membrane Fouling Experiments. The membrane fouling experiments were carried out using the same apparatus as that used for the membrane water permeability measurements. First, the membrane was compacted with Milli-Q water at a pressure of 0.1 MPa and a flow rate of 160 mL/min for at least 15 min until the water flux stabilized. Then, the initial water flux was set to around 230 L/(m^2 h) by adjusting the filtration pressure. As described below, the prepared membranes had similar water permeabilities, and thus, their adjusted pressures did not differ significantly. Subsequently, the BSA fouling experiments were performed by replacing Milli-Q water with a 50 ppm BSA solution (pH 7.0 in PBS), and the flux was measured over the 2 h filtration period. After 60 min of filtration, the back-flushing was carried out using Milli-Q water at 0.01 MPa for 2 min. The retentate was recycled into the feed tank, while the permeate was collected and weighed. The collected permeate was returned to the feed tank every 10 min to maintain a constant concentration of the feed solution.

RESULTS AND DISCUSSION

BSA Adsorption on Polymer Films

The BSA adsorption amount on films prepared using different copolymers were measured using QCM and results are shown in Figure 2. QCM results show that while the BSA interaction with copolymer B was similar to that of PVDF, copolymer A showed a weaker interaction with BSA. Not only was the BSA adsorption amount on copolymer A lower, but also the desorption amount was four times higher than that of the PVDF film. The different interactions of these copolymers with BSA can be explained by considering the chemical structures of the copolymers. While the VA segment of the copolymer is hydrophilic and shows weak interactions with BSA, the TFE segment is completely hydrophobic and strongly interacts with the BSA molecules through hydrophobic-hydrophobic interactions. The copolymers used in this study were linear with different VA/TFE segment ratios. Essentially, it was expected that both copolymers would show lower BSA adsorption amounts, due to the presence of the OH groups in the VA segments of the copolymers.

However, it should be noted that the TFE segments would also partially appear on the film surface as well as the VA segments, because both copolymers used in this study were linear and moving the VA segment to the membrane surface would move the TFE segment, especially when considering that QCM sensors were spin-coated and heated in air. Perfluoro structure of the TFE makes it more hydrophobic than PVDF and it showed a stronger interaction with BSA. Thus, only the film prepared using a copolymer with a higher VA content (copolymer A), more VA segments and fewer TFE segments could appear on the film and make the BSA interaction weak. However, copolymer B with lower VA content, showed a stronger BSA interaction. Although QCM results cannot reflect the real interaction between membrane surface and BSA molecules, we can still consider QCM analysis as a helpful procedure in the evaluation of material performance. Based on these results, we expected to obtain membranes with good BSA adsorption resistance when copolymer A was blended with PVDF.

XPS Measurements

The surface chemical compositions of PVDF and blend membranes with the same blend ratio (1:5) were examined using XPS wide scans, and the results are shown in Table II. The presence of oxygen on the membrane surface is considered representative of the VA segment of the copolymer because there is no oxygen in the PVDF chemical structure. It is worth mentioning here that the presence of the oxygen in PVDF membrane is related to surface oxidation by environmental oxygen[24] or O$_2$ adsorption on the surface, and we believe that this surface oxidation occurred in all of the prepared membranes. The surface chemical compositions of the prepared membranes were evaluated by considering the O/C ratios.

From XPS results, shown in Table II, it is clear that the blend membranes with copolymer A showed higher oxygen contents on the membrane surfaces, than the membrane with copolymer B. It is well studied that during the phase separation process, the hydrophilic part of the amphiphilic copolymer segregates to the membrane surface[25] and the membrane surface becomes more hydrophilic. Therefore, it was expected that during phase separation, the VA segment of the copolymer would segregate to the membrane surface, which would increase its hydrophilicity. Considering the higher VA/TFE segment ratio of copolymer A, during the phase separation of blend membrane with copolymer A, more oxygen atoms segregated to the membrane surface than in that of the membrane with copolymer B. Although the different M_w of copolymer A and B could be another possible

Table II. Membrane Surface Chemical Compositions Measured by XPS

| Membrane | Element (mol %) | | | O/C ratio |
	C	O	F	
PVDF	51.5	3.0	45.5	0.058
A(1:9)	50.0	6.7	43.3	0.134
A(1:5)	50.2	8.3	41.5	0.165
B(1:5)	49.8	6.2	44.0	0.124

XPS, X-ray photoelectron spectroscopy; PVDF, Poly(vinylidene fluoride).
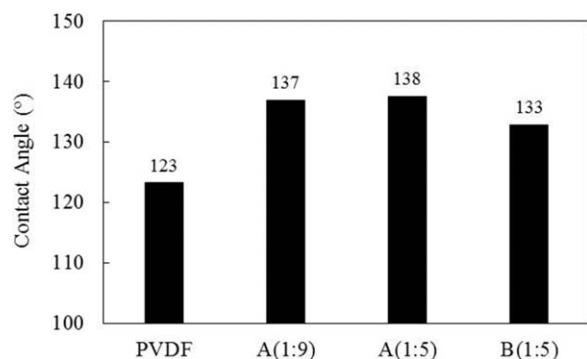
Figure 3. Air bubble contact angle results for the membranes.

factor affecting the hydrophilicity of the membrane prepared, we were not able to evaluate this point systematically, as M_w is not a controllable factor in the syntheic procedure. We also noticed that the solidification rate of the membrane with copolymer A was much slower than that of the membrane with copolymer B; however, it is not studied in detail here and further evaluation is needed. The slower solidification rate of the membrane with copolymer A gives more chances for the VA segments of the copolymer to move to the membrane surface (water side). This process would also increase the oxygen content and hydrophilicity of the membrane surface.

Comparing the XPS (Table II) and QCM (Figure 2) results for the membrane and film prepared using copolymer B, it appears that there are some discrepancies. While the XPS results show that a considerable amount of oxygen, originating from the VA segment of copolymer, was available on the membrane surface, the QCM results of the membrane with copolymer B were almost the same as that of PVDF. This difference might be explained as follows: although QCM analysis is very accurate and helpful in evaluating the interactions of the BSA molecules with the prepared films, the procedure for the preparation of the film for QCM analysis was completely different from that of the porous membrane. During the membrane preparation, the dope solution came into contact with water, which induced a movement of the VA segments at the membrane surface to move to the water side. However, in the case of the preparation of films for QCM, the prepared polymeric solution came into contact with air during spin coating, which induced a segregation of the TFE segments to the film surface, because air is hydrophobic. Thus, it is reasonable that the XPS and QCM results were not in good agreement with each other.

Air Bubble Contact Angle
To evaluate the hydrophilicity of the prepared membrane surface, air-bubble contact angles were measured and the results are illustrated in Figure 3. The membrane contact angles increased by blending both copolymers, indicating that the hydrophilic part of the copolymer, the VA segment, was present on the membrane surface. This increase in hydrophilicity by adding the copolymer agreed well with the XPS results showing the oxygen content originated from the VA segment increase on the membrane surface. The addition of copolymer A was more effective in improving the membrane surface hydrophilicity than copolymer B. The higher hydrophilicity of blending PVDF

with copolymer A, rather than B, was expected due to the higher VA/TFE segment ratio. As explained before in "XPS Measurements," the slower solidification rate of dope solution containing copolymer A, might be another reason for the higher hydrophilic properties of this blend membrane. When the copolymer A blending ratio increased from 1:9 to 1:5, no significant change was observed in the contact angle. A possible reason for this inconsistency is that the contact angle of a porous surface not only depends on its surface hydrophilicity but also the surface roughness and pore sizes.[26,27] However, detailed evaluation of roughness on a microfiltration membrane is omitted because relatively large pores exist on the surface, making the measurement of a typical surface roughness very difficult.

Membrane Surface Morphology
FE-SEM images (Figure 4) show the surface morphology of the obtained membranes. Although it appears that pore sizes and densities are not exactly same, there's no significant difference and we can consider that pore sizes at the surface of the prepared membranes are similar. It is very well studied, and has been proven, that the higher the copolymer content in the dope solution, the higher the hydrophilicity of the dope solution, the faster the influx of water into the dope solution during membrane formation, the faster the demixing process, and the larger the pore size at the selective-membrane surface.[28] In this study, by changing the total polymer concentration in the dope solution composition (Table II), membranes with not much different surface pore sizes were obtained. Thus, the total polymer concentration was the lowest (14%) for the preparation of PVDF membrane, while the total polymer concentration was the highest (22%) in the preparation of A(1:5) membrane, because A(1:5) has the highest hydrophilicity.

Pure Water Permeability and Polystyrene Particle Rejection
The pure water permeabilities of the prepared membranes are presented in Figure 5. The pure water permeabilities of the prepared membranes were similar, at 240 ± 35 L/(m^2 atm h). With difference within such range, it can be considered that no obvious effect on filtration property will be caused. As mentioned in "Pure Water Permeability Measurement," membranes with similar water permeabilities were prepared by adjusting the total polymer concentration in the dope solution to eliminate the effect of hydrodynamic conditions (i.e., initial water flux and operating pressure) and to evaluate the effects of material on the membrane fouling performance.

Our observation that the prepared membranes have similar surface pore sizes by SEM studies (Figure 4) was confirmed by performing a polystyrene particle rejection experiment. The results are summarized in Figure 6. The rejection properties of the prepared membranes were not much different and varied between 79 and 93% for 100 nm polystyrene particles. Similar polystyrene particle rejection results suggested that the selective layer pore sizes for all membranes were similar. Thus, we succeeded in preparing membranes with similar water permeabilities and pore sizes. We believe that these kinds of adjustments were essential to relate the fouling tendencies to the membrane material properties (membrane surface hydrophilicity), rather than to initial water flux, operating pressure, or membrane surface pore size.
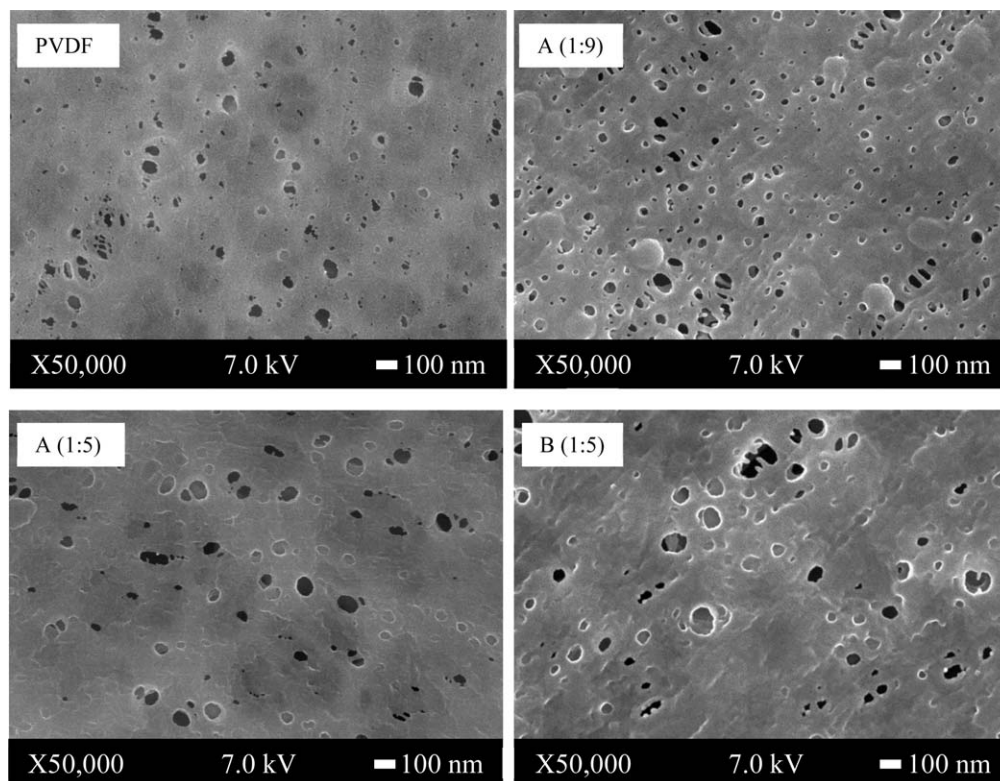
Figure 4. SEM images of the membranes surfaces (top surfaces).

Antifouling Property Evaluation

The antifouling properties of the prepared membranes were evaluated by filtration experiments using 50 ppm BSA solution. The water fluxes observed during the filtration time and results are shown in Figure 7. By adjusting the filtration pressure, the initial water fluxes for membranes were set to around 230 L/(m^2 h). After 60-min filtration, back-flushing was carried out using Milli-Q. From Figure 7, it is clear that the PVDF membrane flux decreased sharply within just a few minutes, and reached less than 20% of its initial flux within one hour of BSA filtration. Back-flushing the fouled PVDF membrane showed only a marginal recovery in permeation flux. This marginal recovery meant that the BSA interaction with the PVDF membrane surface was very strong and, as a result, irreversible fouling occurred. This agreed well with our QCM results that the BSA adsorbed amount on PVDF was high and desorption was low, thus confirming a strong interaction between the BSA and PVDF. When PVDF was blended

with copolymer B (low VA/TFE segment ratio) with a 1:5 blending ratio, only a slight improvement in membrane antifouling was observed. This meant that although the fouling occurred slower, after 60 min of BSA filtration, the same decrease in water flux was observed. In this case, back-flushing the fouled blend membrane showed partly recovery in permeation flux. Although not shown here, even when the blending ratio was increased to 3:1, no improvement of any kind could be reserved. Thus, using copolymer B as a blending agent for the preparation of antifouling membrane was not appropriate. These results agreed well with QCM analysis that showed the BSA interaction with copolymer B was similar to that of the PVDF. The antifouling results of these two membranes [PVDF and B(1:5)] did not agree well with the contact angle results, which showed a higher hydrophilicity for the blend membrane B(1:5). Although the reason for this discrepancy
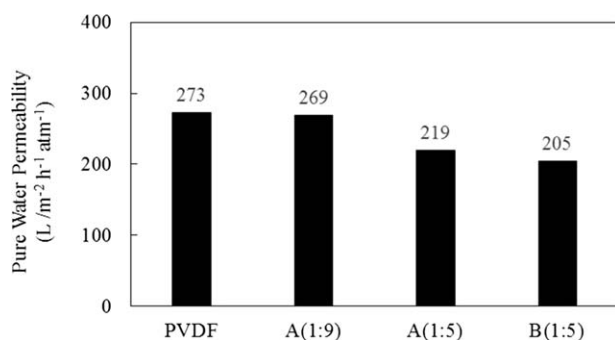

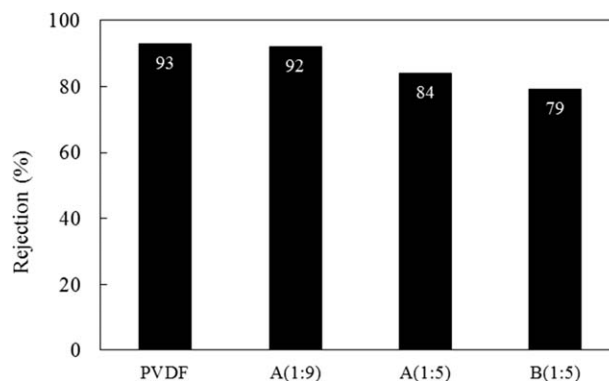**Figure 5.** Pure water permeabilites of the prepared membranes.

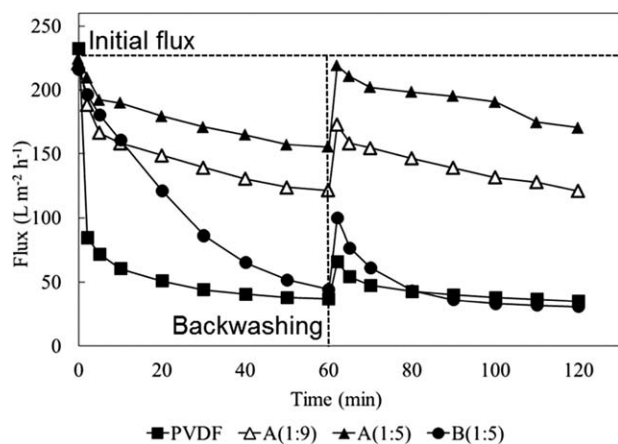**Figure 6.** Rejections of the prepared membranes (100 nm PS particles).

Figure 7. Flux declining tendencies in BSA filtration for the membranes.

was not clear and further detail studies are needed, we hypothesize that the contact angle of a porous surface not only depended on its surface hydrophilicity but also on the surface roughness and pore sizes.[26,27] While the antifouling properties of the blend membrane A(1:5) were higher than that of A(1:9), air bubble contact angle results for these two membranes were similar. Considering the XPS analysis (Table II) of these two membranes showing that the oxygen concentration was higher at the outer surface of membrane A(1:5) than that of membrane A(1:9), this meant that more VA segments were available at the outer surface of the membrane A(1:5), which decreased the BSA interaction with the membrane surface and increased the antifouling properties.

The blend membrane prepared using copolymer A with a 1:5 blending ratio maintained 70% of its initial water flux within 60 min and after back-flushing, flux recovered almost completely, which meant its fouling propensity was much lower and reversible. When the copolymer/PVDF blending ratio decreased to 1:9, the membrane maintained 50% of its initial water flux within 60 min, and back-flushing was not able to recover the flux completely. This meant that the antifouling properties were affected by the copolymer/PVDF blending ratio, even when copolymer A was used.

CONCLUSIONS

Novel amphiphilic copolymers, poly(TFE-VA) with different VA/TFE segment ratios, were used to prepare PVDF blend membranes with superior antifouling properties. BSA filtration was performed for PVDF and blend membranes with similar water permeabilities, selective layer pore sizes and rejection properties. The initial water fluxes were set to be the same to evaluate only the effect of membrane material on fouling propensity. When blending PVDF with a copolymer with a high VA/TFE segment ratio, BSA interactions decreased, and the membrane surface hydrophilicity increased. The prepared membrane showed an improved antifouling property and complete reversible fouling when the copolymer/PVDF blending ratio was increased from 1:9 to 1:5. In contrast, when the copolymer with a low VA/TFE segment ratio was used, antifouling properties were marginal, even when the copolymer/PVDF ratio increased to 3:1. Thus, it was concluded that the effect of the VA/TFE segment ratio was much more significant than the copolymer/PVDF blend-

ing ratio to the antifouling properties of the prepared blend membranes.

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