Preparation and Characterization of Antifouling Poly(vinylidene fluoride) Blended Membranes

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) membranes have been widely used in microfiltration and ultrafiltration because of their excellent chemical resistance and thermal properties. However, PVDF membranes have exhibited severe membrane fouling because of their hydrophobic properties. In this study, we investigated the antifouling properties of PVDF blended membranes. Antifouling PVDF blended membranes were prepared with a PVDF-g-poly(ethylene glycol) methyl ether methacrylate (POEM) graft copolymer. The PVDF-g-POEM graft copolymer was synthesized by the atom transfer radical polymerization (ATRP) method. The chemical structure and properties of the synthesized PVDF-g-POEM graft copolymer were determined by NMR, Fourier transform infrared spectroscopy, and gel permeation chromatography. To investigate the antifouling properties of the membranes, we prepared microfiltration membranes by using the phase-inversion method, which uses various PVDF/PVDF-g-POEM concentrations in dope solutions. The pure water permeabilities were obtained at various pressures. The PVDF/PVDF-g-POEM blended membranes exhibited no irreversible fouling in the dead-end filtration of foulants, including bovine serum albumin, sodium alginate, and *Escherichia coli* broth. However, the hydrophobic PVDF membrane exhibited severe fouling in comparison with the PVDF/PVDF-g-POEM blended membranes. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 286–291, 2012

Key words: atom transfer radical polymerization (ATRP); membranes; phase separation

INTRODUCTION

Membrane filtration processes have been applied to many fields, especially drinking water treatment and wastewater treatment. In recent years, poly(vinylidene fluoride) (PVDF) has come into the spotlight in the field of membrane materials. PVDF is well known its excellent thermal and chemical resistances and good mechanical properties. However, PVDF membranes undergo severe membrane fouling because they are hydrophobic.[1–3]

When they are used in wastewater treatment and drinking-water treatment processes, hydrophobic adsorption causes microbial products, such as extracellular polymeric substances (EPSs), to attach to the membrane surfaces. Therefore, the durability of the membranes is reduced, and the process costs increase.[2,4]

To improve the hydrophilicity and/or antifouling properties of PVDF membranes, many approaches have been investigated; these include blending with metal oxide materials,[5,6] surface grafting with hydrophilic materials,[7,8] and modification of PVDF bulk material with atom transfer radical polymerization (ATRP).[2,9,10]

In this study, we synthesized a PVDF-g-poly(ethyleneglycol) methyl ether methacrylate (POEM) graft copolymer containing hydrophilic poly(ethylene glycol) (PEG) side chains by ATRP and used it to blend the PVDF bulk materials in various ratios to prepare microfiltration membranes.[2] The chemical structure and properties of the graft copolymer were evaluated by NMR, Fourier transform infrared (FTIR) spectroscopy, and gel permeation chromatography. The aim of this study was to investigate the antifouling properties of the microfiltration membranes with respect to EPS. The permeation characteristics of the prepared membranes were examined with a dead-end cell unit, and the fouling resistances (R_f's) were estimated.

EXPERIMENTAL

Materials

PVDF powders with a molecular weight of 180 kg/mol were used in this study and were obtained from Solvay (Seoul, Korea). POEM (number-average molecular weight $\sim$ 475 g/mol), copper(I) chloride, 4,4'-dimethyl-2,2'-dipyridyl, and bovine serum albumin (BSA) were purchased from Sigma-Aldrich (Yongin, Gyenggi-do, Korea). N,N-Dimethylformamide (DMF), petroleum ether, methanol, and sodium alginate were purchased from Samchun Chemicals (Seoul, Korea). Polyvinylpyrrolidone (PVP; number-average molecular weight = 30,000–35,000 g/mol) was purchased from BASF. All of the solvents were reagent grade, and all of the reagents were used as received.

Synthesis of the PVDF-g-POEM copolymer

Twenty-five grams of PVDF was dissolved in 200 mL of DMF in a 1000-mL, round-bottom flask at 50°C. The solution was cooled to room temperature, after which POEM (250 g), copper(I) chloride (0.2 g), and 4,4'-dimethyl-2,2'-dipyridyl (1.15 g) were added to the reaction vessel. The solution was degassed by the infusion of bubbling nitrogen through it for 20 min; this was followed by refluxing at 90°C for 19 h. The resulting graft copolymer was purified by several precipitations in a methanol/petroleum ether/HCl mixture solution and dried in vacuo at 25°C for 24 h.[2]

Analysis of the graft copolymer

The graft copolymer was characterized by ^{1}H-NMR in dimethyl sulfoxide with a 600-MHz high-resolution NMR spectrometer (AVANCE 600 FT-NMR, Bruker, Karlsruhe, Germany). Attenuated total reflection (ATR)–FTIR spectra of the PVDF and PVDF-g-POEM graft copolymer films were examined with a Midac Nicolet

TABLE I
Various Dope Compositions for the Preparation of the PVDF Blended Membranes

| Code | Composition(wt %) | | PVP | DMF |
	PVDF	PVDF-g-POEM copolymer		
100/0	14.0	0	3.85	82.15
90/10	12.6	1.4		
80/20	11.2	2.8		
50/50	7.0	7.0		
0/100	0	14.0		

Magna 550 series II FTIR apparatus (MIDAC Corp., Costa Mesa, CA, USA).

Preparation of the antifouling PVDF blended membranes

Various concentrations of the PVDF, PVDF-g-POEM copolymer, and PVP were dissolved in DMF as a solvent for 24 h at 60°C. In this study, PVP was used as an additive in dope solutions to improve the pore size of the membranes. Table I shows various dope compositions for preparing the PVDF blended membranes in this study. The homogeneous polymer solution was cast onto a polyethylene nonwoven fabric with a doctors knife gap of 200 μm. The membrane was precipitated by immersion in deionized water just after casting at 25 ± 1°C and 65 ± 5% relative humidity. The prepared membranes were then washed several times with deionized water and stored at 4°C in deionized water until use.

Membrane characterization and membrane fouling analysis

Membrane performance was tested with an Amicon stirred, dead-end filtration cell (Millipore, Seoul, Korea) with a cell volume of 200 mL and an effective
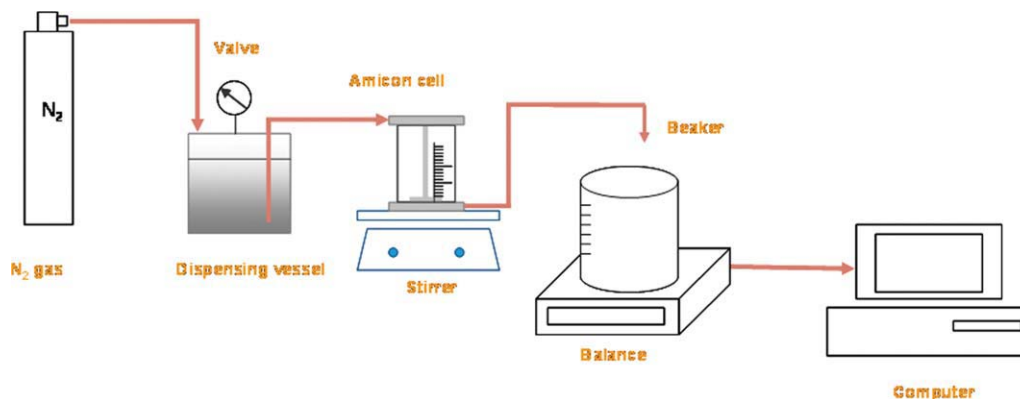
Figure 1 Schematic diagram of the filtration system used in this study. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

area of 27.4 cm^2; the cell was attached to a 4-L stainless pressure vessel. In this study, we adjusted the initial flux of the membranes to 100 L m^{-2} h^{-1} during the fouling test. A schematic diagram of the filtration system used in this study is shown in Figure 1. The filtration cell was stirred at 400 rpm with a stir plate to minimize concentration polarization. The pure water flux was measured under various transmembrane pressures at 25 ± 1°C after the flux reached steady state. The molecular weight cutoff was characterized by the rejection performance of 1000 mg/L PEG or poly
(ethylene oxide) aqueous solution.[11] The rejection (R) was calculated with the following equation:

$$R(\%) = (1 - \frac{C_{per}}{C_{feed}}) \times 100$$

where C_{per} is the concentration of the permeate and C_{feed} is the feed concentration.

For fouling experiments, we used BSA, alginate, and *Escherichia coli* broth. The size of the alginate was measured by an electrophoretic light scattering spectrophotometer (ELS-8000, OTSUKA Electronics, Japan). The size distribution of the alginate ranged from 400 to 700 nm, and the mean particle diameter was approximately 500 nm. The *E. coli* was grown in Luria–Bertani medium (10 g of tryptone/L, 5 g of yeast extract/L, and 5 g of NaCl/L), which was used for the flask cultures. The *E. coli* was cultured in a 1-L flask containing 250 mL of Luria–Bertani medium in a shaking incubator at 37°C and 200 rpm for 24 h.

The fouling performance was measured with 50 mg/L BSA, 50 mg/L alginate, and an *E. coli* broth with an optical density of 0.34 at 100 L m^{-2} h^{-1}. It was calculated with the following equation:

$$J_w = \frac{V}{A * t}$$

where J_w is the pure water flux (L/m^{2}h), V is the permeate volume (L), A_t is the membrane area (m^2), and t is the time (h).

The degree of membrane fouling was quantitatively calculated with the resistance in series model:[12]

$$R_t = \frac{\Delta P_T}{\eta J}$$

$$R_t = R_m + R_c + R_f$$

where J is the permeation flux (m^3/m^2·s), ΔP_T is the transmembrane pressure (Pa), η is the viscosity of the permeate (Pa s), R_t is the total filtration resistance (m^{-1}), R_m is the membrane resistance (m^{-1}), R_c

is the cake layer resistance (m^{-1}), and R_f is the fouling resistance (m^{-1}).

The intrinsic R_m value, the R_c value on the membrane surface, and the R_f value caused by pore plugging and the irreversible adsorption of foulants onto the membrane pore wall or surface could be calculated with the following equations:

$$R_m = \frac{\Delta P_T}{\eta J_w}$$

$$R_f = \frac{\Delta P_T}{\eta J'_w} - R_m$$

$$R_c = \frac{\Delta P_T}{\eta J_S} - R_m - R_f$$

where J_S is the flux of various foulants, J_w is the initial water flux, and J'_w is the final water flux after the removal of the cake layer by its washing with an ultrasound sonicator.

RESULTS AND DISCUSSION

Composition and molecular weight of the graft copolymer

Figure 2 shows an example of the ^{1}H-NMR spectrum of the PVDF and PVDF-*g*-POEM graft copolymer. The spectrum of the PVDF films exhibited well-known peaks, specifically, head-to-tail and head-to-head bonding at 2.3 and 2.9 ppm, respectively. The PVDF-*g*-POEM graft copolymer spectrum was dominated by methacrylate protons and poly(ethylene oxide)
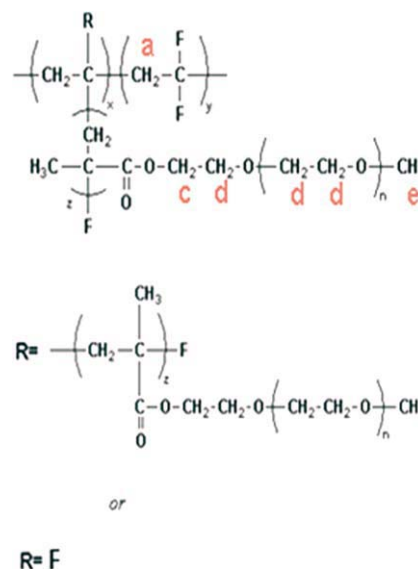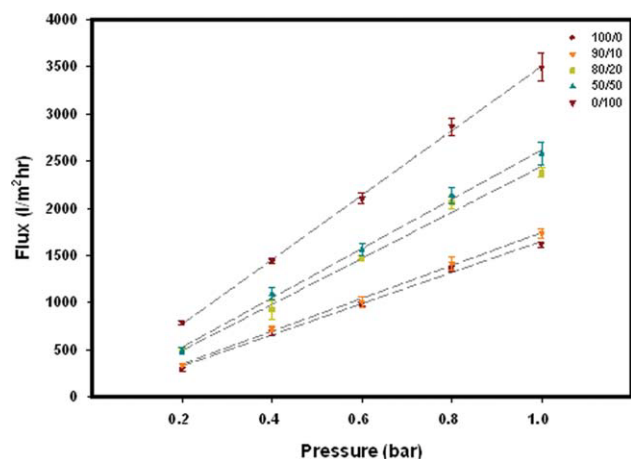

Figure 2 Example of the ^{1}H-NMR spectra of the PVDF and PVDF-*g*-POEM graft copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
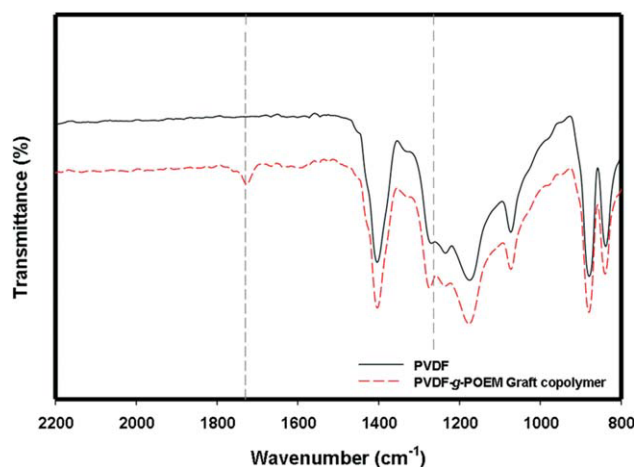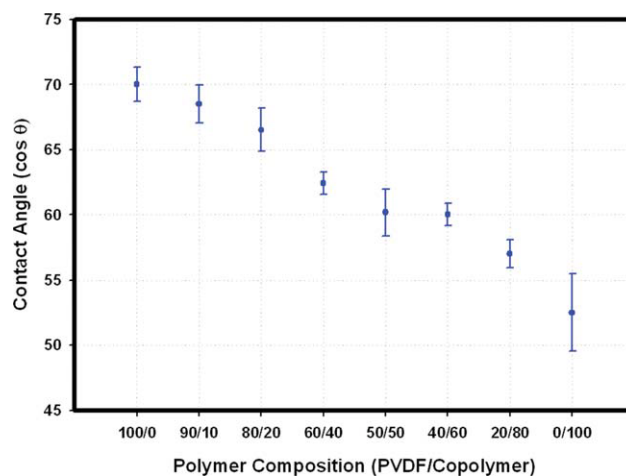
Figure 3 ATR–FTIR spectra of the PVDF and graft copolymer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 Contact angle data of the PVDF and PVDF/PVDF-*g*-POEM blended membranes. [Color figure can be viewed in the online issue, which is available at wiley onlinelibrary.com.]

protons at 3.4–4.4 ppm. The molar ratio of POEM to PVDF was calculated to be 0.06 : 1 on the basis of the intensities of a, c, d, and e (shown in Fig. 2). The strong signals at 2.5 and 3.3 ppm were from the DMSO. The graft copolymer had a number-average molecular weight of 140,000, a weight-average molecular weight of 310,000, and a polydispersity index of 2.2, as determined by gel permeation chromatography. The ATR–FTIR spectra of the PVDF and graft copolymer films are shown in Figure 3. The absorption peaks from the C=O of the ester carbonyl group and C—O stretches of the PEG chain in the graft copolymer were present in the spectra of the graft copolymer film at 1730 and 1270 cm^{-1}, respectively; this indicated that the PVDF-*g*-POEM graft copolymer was successfully synthesized.

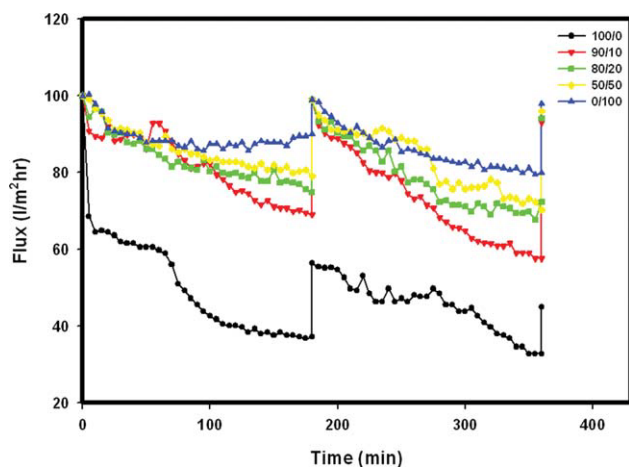## Pure water permeability and contact angle measurements

The pure water fluxes of the PVDF blended membranes are shown in Figure 4. The membrane fluxes were affected by the graft copolymer ratio. Figure 4 shows that increased PVDF-*g*-POEM graft copolymer concentrations led to increased fluxes. Because the synthesized graft copolymer was an amphiphilic polymer with hydrophilic and hydrophobic segments, as more graft copolymer was added to the dope solution, higher water fluxes resulted because of hydrophilicity. As shown in Figure 4, the water fluxes improved when the pressure increased for all of the membranes.

The static water contact angles of the membrane surfaces were measured by the sessile drop method with a contact angle goniometer(Erma G-1, Japan). The contact angle data of the PVDF and PVDF/PVDF-*g*-POEM blended membranes are shown in Figure 5. Also, the contact angles of the membrane surface decreased when more graft copolymer was added to the dope solution.

Flux behavior during the dead-end flow filtration processes

In this study, various foulants were used to evaluate the antifouling performance of the PVDF blended membranes. The membrane performance decreased when EPSs were attached to the membrane surface.
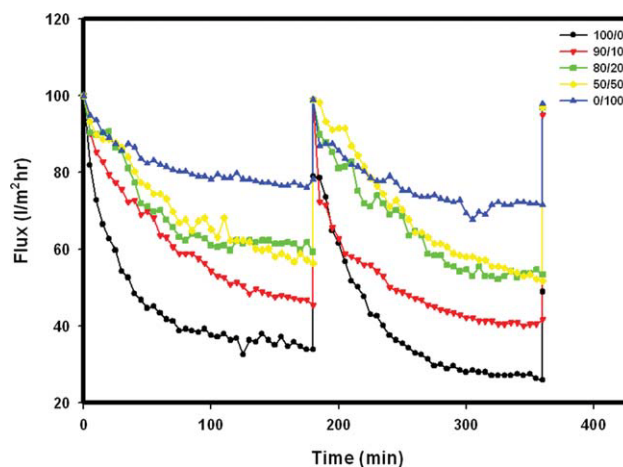
We estimated the antifouling properties of the PVDF blended membranes with various foulants (BSA, alginate, and *E. coli* broth) and adjusted the initial flux to 100 L/m²h. The permeate flux decline with BSA (50 mg/L solution) for 3 h is shown in Figure 6. The flux decline ratio of the PVDF

Figure 4 Pure water fluxes of PVDF blended membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Permeate flux decline with BSA (50 mg/L solution) for 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 Flux behaviors during alginate solution filtration for 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membrane was 65% during the filtration time. However, in the case of membranes containing PVDF-*g*-POEM copolymer, the flux decline ratios were 10–30%. Generally, graft copolymers change the surface hydrophilicity of a membrane, as PEG side chains lead to a steric hindrance effect. Thus, the higher graft copolymer concentration in the dope solution led to an increased permeate flux. The flux recovery of the PVDF membranes and graft copolymer blended membranes were 56% and around 100%, respectively.

Because the transmembrane pressures were very low during BSA solution filtration, the cake layer was composed by weak compaction, and then, BSA

particles were easily detached from the membrane surface by ultrasound treatment.

We also observed that irreversible R_f was severe during BSA filtration with the 100/0 membrane, as shown in Figure 7. In this case, the surface of the PVDF membrane was hydrophobic, so BSA particles easily attached to the membrane surface and pores because of hydrophobic–hydrophobic interactions. Irreversible R_f was observed to make the highest contribution to flux decline in 100/0 membranes. However, R_c was observed to have an effect smaller than irreversible fouling because of low transmembrane pressure and rapid stirring speed on the membrane surfaces.
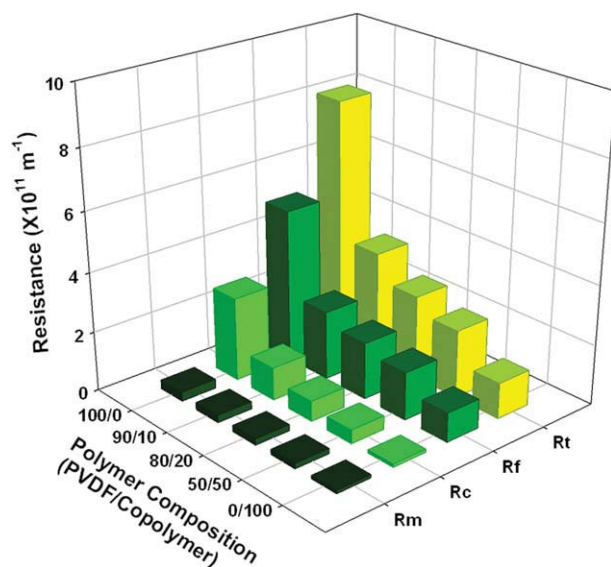
Figure 7 Irreversible R_f during BSA filtration with the 100/0 membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
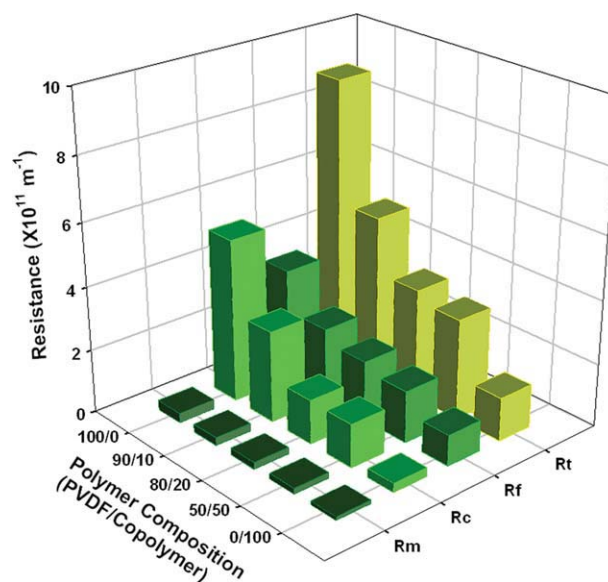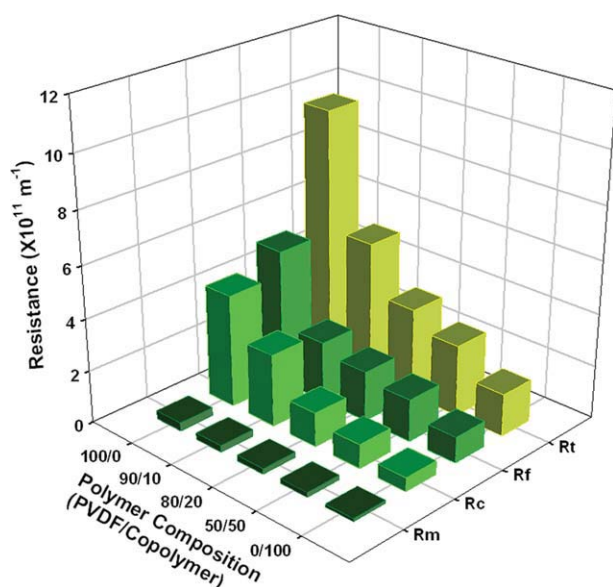

Figure 9 Flux recovery results of the PVDF membrane and graft copolymer blended membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
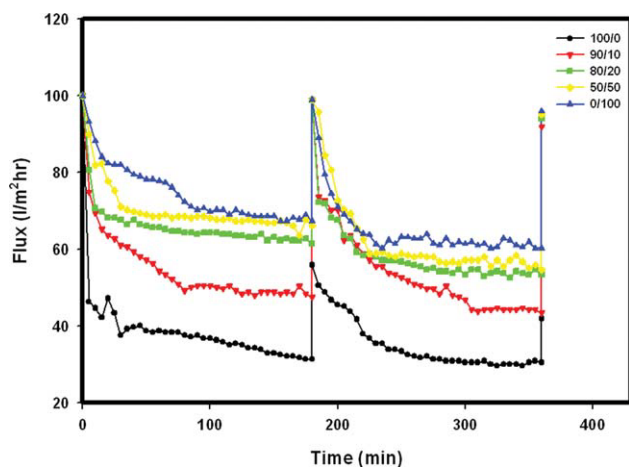
Figure 10 Flux decline of membranes with *E. coli* broth. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 shows flux behaviors during alginate solution filtration for 3 h. The 100/0 PVDF membrane showed an 80% flux recovery of alginate, whereas the graft copolymer blended membranes had about a 100% flux recovery of alginate; the results are shown in Figure 9. In this case, R_c was observed to affect the total resistance. The higher R_c was the result of the physicochemical adsorption of the alginate due to its higher molecular weight compared to BSA.

Finally, to prove the biofouling effect during the filtration process, the filtration of *E. coli* broth was tested with actual microbial cells and their EPS material. Figure 10 shows the flux decline of mem-

branes with *E. coli* broth. As shown in Figure 10, the PVDF-*g*-POEM copolymer membranes, 90/10, 80/20, 50/50, and 0/100, allowed for a much higher flux of *E. coli* broth than the 100/0 PVDF membrane (Fig. 11). The flux recovery of the 100/0 membrane was 56%, and those of the 90/10 to 0/100 membranes were almost 100%. In this process, both R_c and irreversible R_f were higher than the total resistance found in the BSA and alginate filtration processes. Irreversible and strong adsorption of *E. coli* broth onto the membrane surfaces could be expected, so the flux recovery of the 100/0 membrane was very low. In contrast, the high flux recovery results from the PVDF/PVDF-*g*-POEM blended membranes were due to the increased hydrophilicity and the flexible movements of PEG side chains on the membrane surface into the water.

CONCLUSIONS

In this study, we prepared graft copolymers by the ATRP polymerization of PVDF and POEM. Microfiltration membranes from various concentrations of PVDF/PVDF-*g*-POEM copolymer in casting solution were prepared by the phase-inversion method, and their fouling characteristics were investigated with biomaterials, such as proteins, polysaccharides, and microbial cells at feed concentrations of 50 mg/L and above. The permeate flux increase and R_f's of the PVDF-*g*-POEM copolymer blend membranes were attributed to increases in the surface hydrophilicity and the PEG side chains on the membrane surface. Thus, the antifouling properties of the graft copolymer blend membranes were improved.

Figure 11 Flux of *E. coli* broth of the 100/0 PVDF membrane (Fig. 11). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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