



Preparation of robust braid-reinforced poly(vinyl chloride) ultrafiltration hollow fiber membrane with antifouling surface and application to filtration of activated sludge solution



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ABSTRACT

Braid-reinforced hollow fiber membranes with high mechanical properties and considerable antifouling surface were prepared by blending poly(vinyl chloride) (PVC) with poly(vinyl chloride-co-poly(ethylene glycol) methyl ether methacrylate) (poly(VC-co-PEGMA)) copolymer via non-solvent induced phase separation (NIPS). The tensile strength of the braid-reinforced PVC hollow fiber membranes were significantly larger than those of previously reported various types of PVC hollow fiber membranes. The high interfacial bonding strength indicated the good compatibility between the coating materials and the surface of polyethylene terephthalate (PET)-braid. Owing to the surface segregation phenomena, the membrane surface PEGMA coverage increased upon increasing the poly(VC-co-PEGMA)/PVC blending ratio, resulting in higher hydrophilicities and bovine serum albumin (BSA) repulsion. To compare the fouling properties, membranes with similar PWPs were prepared by adjusting the dope solution composition to eliminate the effect of hydrodynamic conditions on the membrane fouling performance. The blend membranes surface exhibited considerable fouling resistance to the molecular adsorption from both BSA solution and activated sludge solution. In both cases, the flux recovered to almost 80% of the initial flux using only water backflush. Considering their great mechanical properties and antifouling resistance to activated sludge solution, these novel membranes show good potential for application in wastewater treatment.

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1. Introduction

Membrane separation is one of the most promising separation technologies and has been widely used for water treatment, such as in membrane bioreactors (MBRs) [1]. Several polymeric materials have been used for membrane fabrication, including polyvinylidene difluoride, polysulfone, polyacrylonitrile (PAN), and poly(ethersulfone) [2]. Poly(vinyl chloride) (PVC) is a promising alternative material for membrane preparation because of its excellent mechanical strength, high corrosion resistance, and low cost [3–5]. However, severe fouling problems can occur in PVC membranes because of their hydrophobic nature [6].

To endow PVC membranes with antifouling properties, the blending of an amphiphilic copolymer into the PVC dope solution has been investigated [7–10]. The hydrophilic segment of the amphiphilic copolymer segregates on the membrane surface, resulting in a membrane with good fouling resistance. The hydrophobic segment provides compatibility with the membrane matrix and improves copolymer retention in the

membrane matrix. Copolymers containing poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) chains can easily form a hydration layer, inhibiting the approach of foulant molecules to the membrane surface [11]. Liu et al. [12] prepared membranes with superior antifouling properties by blending a commercial PEO-based amphiphilic copolymer (Pluronic F-127) with a PVC matrix. Both the antifouling properties and pure water permeabilities (PWPs) of the prepared membranes were improved upon increasing the copolymer/PVC blend ratio. Jiang et al. [9] prepared poly(ether sulfone-g-poly(ethylene glycol)methyl ether methacrylate)/PVC blend membranes. The blend membranes exhibited considerable antifouling properties when the copolymer/PVC blend ratio was increased to 3:7. These studies suggest that PEG-based copolymer additives can effectively improve the hydrophilicity and antifouling properties of PVC membranes. However, PEG is well-known as a soft polymer [13]; thus, increasing the PEG-based copolymer content in PVC membranes can decrease the mechanical strength [14], which would limit the membrane application. For practical wastewater treatment, severe aeration or a backflush process can damage the membrane structure [15]. Therefore, PVC hollow fiber membranes with considerable mechanical strength and antifouling properties are desirable for practical application.

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Several methods have been proposed to improve the mechanical strength of PVC membranes. Some researchers have incorporated nano-size additives into the PVC matrix to improve the membrane mechanical strength, such as graphene oxide [16] or TiO₂ [17]. In other studies, dual-layer PVC hollow fiber membranes, where PVC dope solution was coated onto the microfiltration matrix membranes, have been developed [18–20]. However, these methods usually suffer from increased cost and altered membrane properties. As an alternative method, braid-reinforced hollow fiber membranes obtained by coating the dope solution onto low-cost tubular braids have attracted significant attention [21–23]. Different homopolymers have been used to coat the braid, and the effect of the compatibility between the coating material and braid on the interfacial bonding strength between the coating layer and braid has been investigated. In these works, the main target was to determine the optimal preparation conditions for fabrication of braid-reinforced membranes with good mechanical strength and membrane structures. Recently, Fan et al. [24] used the hydrophilic homopolymer cellulose acetate as the coating material to prepare braid-reinforced hollow fiber membranes with antifouling properties. The maximum tensile strength and bursting pressure of their membranes reached 63 and 0.7 MPa, respectively. However, without chemical cleaning, resistance to irreversible fouling of milk solution (protein foulant) was not observed. Therefore, a robust braid-reinforced hollow fiber membrane with better antifouling property is desired for practical use.

In the present study, we proposed an effective approach to obtain a robust ultrafiltration hollow fiber membrane with considerable antifouling surface using soft hydrophilic polymeric material. PVC was used as coating material to prepare braid-reinforced hollow fiber membrane with superior mechanical property, and an amphiphilic copolymer poly(vinyl chloride-co-poly(ethylene glycol)methyl ether methacrylate) (poly(VC-co-PEGMA)) was blended into the coating layer to endow the membrane surface with high antifouling property. To the best of our knowledge, the preparation of braid-reinforced PVC hollow fiber membranes with antifouling surface to effectively prevent actual foulants deposition, has not been studied yet. The mechanical strength and bursting strength of the braid-reinforced membranes were compared with those of a self-supporting membrane. The effects of the copolymer/PVC blend ratio on the structure, hydrophilicity, tensile strength, and especially the fouling propensity of bovine serum albumin (BSA) and activated sludge solution were evaluated. The braid-reinforced poly(VC-co-PEGMA)/PVC blend membranes exhibited advanced properties, such as the largest tensile strength among the reported PVC hollow fiber membranes, higher interfacial bonding strength between the coating layer and the surface of PET-braid compared to other reported coating materials, and considerable antifouling surface that can prevent molecular adsorption during filtration of activated sludge solution. Such superior properties strongly suggested the good application potential of these membranes for wastewater treatment.

2. Experimental

2.1. Materials

PVC ($M_w = 55,000$) and poly(VC-co-PEGMA) (with 6.1 mol% PEGMA and $M_w = 360,000$) were supplied by Sekisui Chemical Co., Ltd. (Japan). The chemical structure of this random copolymer is shown in Fig. 1. BSA, sodium dihydrogen phosphate, disodium hydrogen phosphate, and dimethylacetamide (DMAc) were purchased from Wako Pure Chemical Industries (Japan). The BSA solution was prepared by dissolving BSA in 0.1 M phosphate buffer solution (PBS). The monodispersed polystyrene latex particles (diameter = 20, 50, and 400 nm, size distribution < 3%) used for the rejection measurement were purchased from Duke Scientific Corporation (Thermo Fisher Scientific, Waltham, MA). Deionized water was produced by a Millipore Milli-

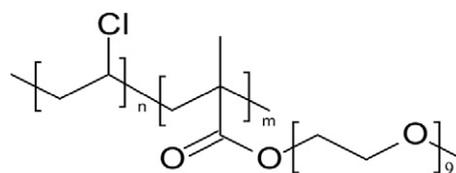


Fig. 1. Chemical structure of poly(VC-co-PEGMA).

Q unit. All the reagents were used as received. The activated sludge was obtained from Sekisui Chemical Co., Ltd., and the detailed compositions are listed in Table 1.

2.2. Fabrication of braid-reinforced hollow fiber membrane

The braid-reinforced pure PVC membrane and 3 blended membranes with various blend ratios of copolymer/PVC were prepared using NIPS. The compositions of the dope solutions used for the membrane casting are listed in Table 2, where the blend membranes are labeled as braid-reinforced blends 1:7, 1:3, and 1:1, corresponding to their copolymer/PVC blend ratios, respectively. For the prepared membranes, the dope compositions were adjusted to obtain similar PWP for a better comparison of the fouling properties. The polymers were dissolved in DMAc by stirring at 45 °C for 1 day to obtain homogeneous solutions and were degassed overnight at 25 °C. As shown in Fig. 2, the solution was loaded in a vessel tank. After removing air bubbles under vacuum at room temperature for 2 h, the dope solution was pressed out from the nozzle using a gear pump and coated on a tubular braid that was flowed through the nozzle and wound up by a take-up roller. The outer and inner diameters of the PET tubular braid were 2 and 1 mm, respectively. The braid was provided by Sekisui Corp. The dope extrusion rate, air gap, and take-up speed were set at 5 g/min, 5 mm, and 5 m/min, respectively. While the coated braid went through a coagulation bath of deionized water at 24 ± 1 °C, the NIPS process occurred, and the porous braid-reinforced hollow fiber membrane was formed. The prepared membranes were rinsed thoroughly with deionized water to remove residual solvent and were subsequently stored in deionized water until use.

The self-supporting hollow fiber membranes were prepared via NIPS using a batch-type extruder. The fabrication equipment and process were introduced in our previous work [25]. For the self-supporting hollow fiber membrane, the composition of the dope solution is also listed in Table 2, and this membrane was called self-supporting blend 1:1. The preparation process was the same as that for the braid-reinforced hollow fiber membrane except for the use of the tubular braid. The dope flow rate, bore flow rate, air gap, and take-up speed were set at 4 g/min, 4 g/min, 15 mm, and 4 m/min, respectively. After extracting the remaining solvent by immersing the prepared membranes in water, they were stored in deionized water until use.

2.3. BSA adsorption on polymer films surface

The amount of BSA adsorbed on the polymer film surface was measured using a quartz crystal microbalance with dissipation monitoring (QCM-D, Q-Sense E1, MEIWAFOFOSIS Co. Ltd., Japan). Piezoelectric quartz crystal sensors with a fundamental resonant frequency of 5 MHz and

Table 1
Water analysis of the activated sludge solution.

Sample	TOC [mg/L]	DOC [ppb]	Biopolymer [ppb]	Humics [ppb]	Building blocks [ppb]	Neutrals [ppb]
Activated sludge	88	9887	7138	1738	288	723

TOC: total organic carbon, DOC: dissolved organic carbon. The data were measured using a TOC analyzer (TOC-VCSN, Shimadzu Co., Japan) and size-exclusion liquid chromatography system equipped with an organic carbon detector (LC-OCD, DOC-LABOR, Germany).

Table 2
Dope solution compositions for preparing braid-reinforced and self-supporting hollow fiber membranes.

Membrane ID	Copolymer: PVC blend ratio	Copolymer [wt%]	PVC [wt%]	DMAc [wt%]	Total polymer conc. [wt%]	PWP [L/atm m ² h]	Rejection-20 [%]	Rejection-50 [%]
Braid-reinforced PVC control			15	86	14	290 ± 10	76 ± 0.4	100
Braid-reinforced blend 1:7	1:7	2.1	14.9	83	17	290 ± 15	76 ± 0.1	100
Braid-reinforced blend 1:3	1:3	4.8	14.3	81	19	300 ± 11	79 ± 0.5	100
Braid-reinforced blend 1:1	1:1	11.5	11.5	77	23	310 ± 10	76 ± 0.2	100
Self-supporting blend 1:1	1:1	9.5	9.5	81	19	300 ± 20	0	10

Rejection-20 and Rejection-50 refer to the results of the rejection measurements using polystyrene particles with average diameters of 20 and 50 nm, respectively. All the data in the table were filled by keeping to one decimal places.

diameter of 14 mm (Q SX 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., USA). After spin coating with a 1.0 wt% polymer solution at 3000 rpm for 1 min and drying on a hot stage (KATHERM C-MAG HP4' Kampmann GmbH, Germany) at 80 °C for 20 min, the sensor was placed in the QCM flow chamber. Then, the PBS solution was injected into the flow chamber at a flow rate of 50 µL/min for > 1 h to stabilize the sensor and obtain the baseline. Next, the PBS solution was replaced with a 1000 ppm BSA solution. The surface chemical compositions of the QCM-D samples were different from those of the prepared membranes because of the different preparation conditions. The QCM-D samples were prepared by solvent evaporation, whereas the membranes were obtained by phase separation in water. However, when the prepared QCM-D sample contacted PBS before the BSA solution, its surface reconstructed to minimize the interfacial free energy, resulting in a similar surface chemical composition to that of the membrane [32]. Therefore, the measured interaction between the BSA and QCM-D sample surface could be considered the interaction between the BSA and membrane surface. Using the Sauerbrey equation (Eq. (1)), the total amount of BSA adsorbed on the polymeric film surface was calculated by the changed sensor oscillation frequency during parallel flow of the BSA solution at a constant temperature of 25 °C [33]:

$$\Delta m = -C \frac{\Delta f}{n}, \quad (1)$$

where Δm is the adsorption amount (ng cm⁻²), C is the mass sensitivity constant (17.7 ng cm⁻² Hz⁻¹ at $f = 4.95$ MHz), Δf is the variation of frequency (Hz), and n is the overtone number ($n = 7$).

2.4. Membrane characterization

2.4.1. Membrane morphology observation

A field-emission scanning electron microscope (FE-SEM; JSF-7500F, JEOL Co. Ltd., Japan) was used to examine the surface morphology of the membranes. The prepared membranes were freeze-dried using a freeze dryer (FD-1000, EYELA, Japan). After the samples were immersed into liquid nitrogen and removed using a razor blade, a 5-nm-thick osmium

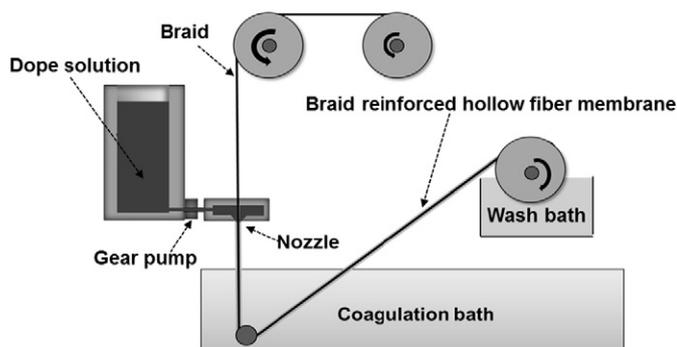


Fig. 2. Schematic diagram for preparing braid-reinforced hollow fiber membranes.

tetroxide (OsO₄) layer was sputtered on the samples using an osmium coater (Neoc-STB; MEIWAFOSSIS Co. Ltd., Japan). All the samples were examined at an accelerating voltage of 8 kV at different magnifications.

2.4.2. Tensile strength measurements

The tensile stresses of the prepared membranes were measured using a tensile testing apparatus (AG-X plus, Shimadzu Co., Japan). The membrane samples with lengths of 20 mm were placed vertically between a pair of pneumatic clamps, and a stretching rate of 20 mm/min was applied to the upper clamp. Finally, the maximum tensile stress of the sample was recorded until fracture. For each type of membrane, at least 7 measurements were averaged for reliability.

2.4.3. X-ray photoelectron spectroscopy 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 K α radiation source, the photoelectron take-off angle was set at 45°, and survey spectra were recorded over the range of 0 to 700 eV. The surface elemental composition was calculated from the peak area with a correction for atomic sensitivity.

2.4.4. Water permeability measurements

The PWP was evaluated using a homemade module containing a single hollow fiber membrane. The membrane set inside the module had a length of 240 mm. The Milli-Q water was forced to permeate from the outside to the inside of the hollow fiber membrane. The experimental apparatus is described in our previous paper [26]. The operating pressure during filtration was adjusted using a needle valve at the outlet. The average 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 1 L h⁻¹. Before the measurement, the membrane was compacted at 0.05 MPa until the water flux was stable. Then, the membrane permeability was measured at 0.02 MPa.

2.4.5. Polystyrene particle rejection measurement

The polystyrene particle rejection experiment was conducted using a 100 ppm solution of latex particles. The feed solution was prepared by adding monodisperse latex particles with diameters of 20 and 50 nm to an aqueous nonionic surfactant of 0.1 wt% (Triton X-100). The feed 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 concentrations of the feed and filtrate were measured using UV-vis spectrophotometry (U-2000, Hitachi Co., Tokyo, Japan) at a wavelength of 385 nm. The membrane rejection (R , %) was calculated using the following equation:

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

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

2.4.6. Interfacial bonding strength evaluation

The interfacial bonding strength between the coating layer and tubular braid was evaluated by measuring the bursting strength of the prepared membrane [21]. The test was performed using the same module described in Section 2.4.4. The bursting pressure was applied using pressurized Milli-Q water flowing through the inner surface of the prepared membrane to the outer surface. The PWP and rejection of 400-nm-diameter polystyrene particles were recorded for the prepared membrane for bursting pressures of 0.01 to 2.1 MPa. The tests were repeated at least 3 times.

2.4.7. Air bubble contact angle measurements

Contact angle measurements have been widely used to characterize the hydrophilicity of polymeric surfaces [27–29]. In this study, contact angle measurements were performed using the captive air bubble method rather than the sessile drop method because the membrane surface properties remain unchanged during the measurement [30]. The air bubble contact angle was measured by a contact angle goniometer (Drop Master 300, Kyowa Interface Science Co., Japan). A sample was randomly cut from the prepared membrane with a suitable size and then placed in a glass cell filled with deionized water. Using a special L-shaped syringe needle, an air bubble (5 μL) was released below the sample. The air bubble contact angle with the surface was measured automatically. To minimize experimental error, a minimum of 7 measurements were performed at different spots on the sample surface.

2.4.8. Membrane fouling experiments

The membrane fouling experiments were performed using the same apparatus as that used for the PWP evaluation. First, the membrane was compacted with Milli-Q water at a pressure of 0.05 MPa and a flow rate of 1 L/h for at least 15 min until the water flux was stabilized. Then, the initial water flux was set to 90 and 30 L/(m² h) for the BSA and activated sludge filtration experiments, respectively, by adjusting the filtration pressure. As described below, the prepared membranes had similar PWPs, and thus, all their adjusted transmembrane pressures were approximately 0.01 MPa. Subsequently, the fouling experiments were performed using a 1000 ppm BSA solution (pH 7.0) or the activated sludge solution. 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. After the filtration of the BSA solution or activated sludge for 2 or 1 h, respectively, backflushing was performed for 2 min at 0.01 MPa. This cycle of filtration for the activated sludge was performed continuously 4 times. All the fouling experiments were repeated at least 3 times for reproducibility.

3. Results and discussion

3.1. Membrane morphology

FE-SEM images were obtained to examine the membrane morphology. The surface and cross-sectional structures of the prepared membrane are shown in Figs. 3 and 4, respectively. Although the braid-reinforced membranes were prepared with different copolymer/PVC blend ratios, the outer surface structures are similar (Fig. 3). Note that PEG or PEG-based copolymers exhibit strong pore forming ability, generally leading to enlarged pore size or increased surface porosity [12,14,31]. Increasing the copolymer content in the dope solution results in improved hydrophilicity of the dope solution. This improvement leads to a faster influx of water into the dope solution during membrane formation and a faster demixing process, resulting in a larger pore size at the selective-membrane layer surface [32]. However, increasing the total polymer concentration can effectively decrease the porosity of the membrane surface because of the effect of delayed demixing [2]. Therefore, the contrary effects of the increase of the copolymer content and the total polymer concentration on the surface morphology

resulted in the similar surface structure of the braid-reinforced hollow fiber membranes. The similar pore structure of the 4 types of membranes is critical to verify the effect of the membrane materials on the fouling property because the effect of the pore structure can be disregarded in this situation. Moreover, the pores on the inner and outer surface of the self-supporting blend 1:1 membrane were larger than those on the surface structure of the braid-reinforced blend 1:1 membranes, which is mainly attributed to the lower total polymer concentration in the dope solution (Table 2) and the different fabrication processes.

The cross-sectional structures of the prepared hollow fiber membrane are shown in Fig. 4. For the braid-reinforced hollow fiber membranes, porous coating layers with narrow finger-like macrovoids formed on the top surface of the tubular braid, where a small amount of the coating solution penetrated into the substrate. The thickness of the coating layer and length of the macrovoids for the copolymer/PVC blend membranes were larger than those of the PVC control membrane, indicating the strong pore-forming ability of the hydrophilic poly(VCCo-PEGMA). In addition, 2 skin layers were observed in the cross-section of the self-supporting membrane, whereas only 1 skin layer was observed for the braid-reinforced membranes. The coating layer thickness of the braid-reinforced membranes was approximately 1/3 of the membrane thickness of the self-supporting membrane. In general, a thinner membrane thickness and reduced number of skin layers can reduce the membrane filtration resistance, resulting in improvement of the membrane permeability [2].

3.2. Mechanical strength and interfacial bonding strength

To evaluate the mechanical strength, the tensile stress and elongation of the membranes and tubular braid were measured, and the data are plotted in Fig. 5. The braid-reinforced membranes exhibited super-high tensile stress at break (higher than 170 MPa), which was much higher than that of the self-supporting membrane and previously reported PVC hollow fiber membranes (Table 3). The tensile strength of the braid-reinforced PVC hollow fiber membranes was nearly 34 and 9 times higher than that of the self-supporting and the dual-layer reinforced PVC hollow fiber membranes, respectively [36–43]. Considering that the membrane mechanical strength is an important factor limiting the application of hollow fiber membranes in the wastewater treatment [1–2], the robust braid-reinforced PVC hollow fiber membranes could be expected as a promising alternative to wastewater treatment. Note that the increase of the PEG-based copolymer content in the dope solution can decrease the membrane mechanical strength [14] because of the softness of PEG [13]. In Fig. 4, the braid-reinforced blend membrane, PVC control membrane, and tubular braid exhibited similar maximum forces of approximately 170 MPa, indicating that the mechanical strength of the braid-reinforced membranes was determined by the properties of the selected braid rather than those of the coating layer. Furthermore, it can be observed that the elongations of the braid-reinforced membranes were lower than that of the braid itself because the formed coating layer on the braid limited the deformation of the braid, which can inhibit the straining of the braid membranes [33].

Although braid-reinforced membranes exhibit extremely high tensile strength at break, many researchers have noted that the interfacial bonding strength between the coating layer and braid is more crucial for reinforced hollow fiber membranes, which could restrict the application and operating life of the membranes [22,24]. The interfacial bonding strength of reinforced hollow fiber membranes was investigated by testing the membrane bursting pressure [22,24]. The changes of the PWP and rejection with the backflush pressure for the self-supporting and braid-reinforced blend membranes are plotted in Fig. 6(a) and (b), respectively. The rejection tests for the self-supporting and braid-reinforced membranes were performed using polystyrene particles with average diameters of 400 and 50 nm, respectively. Fig. 6 demonstrates that even though the coating material of the both types of membranes was the same, the PWP increased and the rejection decreased sharply for the self-supporting membrane when

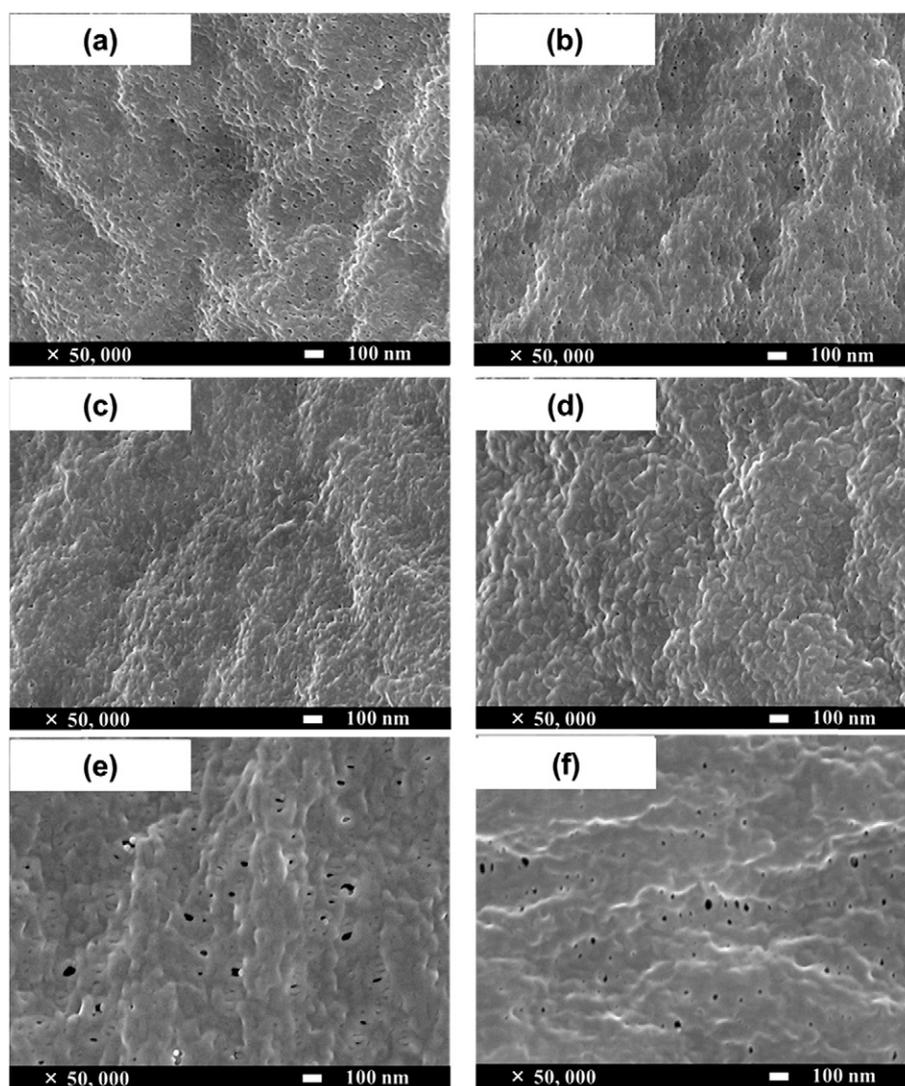


Fig. 3. FE-SEM images of the membrane surfaces: (a) braid-reinforced PVC control, (b) braid-reinforced blend 1:7, (c) braid-reinforced blend 1:3, (d) braid-reinforced blend 1:1, (e) self-supporting blend 1:1 inner surface, (f) self-supporting blend 1:1 outer surface.

the backflush pressure was over 0.3 MPa, whereas those of the braid-reinforced membrane remained stable even for a backflush pressure of 2.0 MPa. The bonding strength of the braid-reinforced membranes was at least 3 times larger than that of the PAN-braid-reinforced CA membrane [21], indicating the better interfacial bonding strength between the poly(VC-co-PEGMA)/PVC coating layer and the PET-braid. Thus, considering the super-high mechanical properties, braid-reinforced membranes are expected to be useful for long-term application for the frequent backwashing process in wastewater treatment [34,35].

3.3. XPS measurements

The surface chemical compositions of the prepared membranes were examined using XPS, and the results are presented in Fig. 7. The prepared membranes exhibited 4 major emission peaks at 201, 270, 284, and 530 eV, which were attributed to Cl 2p, Cl 2 s, C 1 s, and O 1 s emissions, respectively. The O 1 s peak at the membrane surface is considered representative of the poly(VC-co-PEGMA) component because of the lack of oxygen atom in PVC.

The surface chemical compositions of the prepared membranes were evaluated by considering the O/C ratios. The O/C ratios from XPS measurements and the theoretical calculations are presented in Fig. 8. The calculation method for the theoretical values of the O/C ratio is same as that

described in our previous report [14]. The experimental results indicated that the O/C ratios increased as the copolymer/PVC blending ratio increased. In addition, the measured O/C ratios were 2 times larger than the theoretical values for all the prepared blend membranes. This finding indicates that the copolymer poly(VC-co-PEGMA) was localized at the membrane surface during the membrane fabrication process because of the strong interactions between the PEGMA chains and water in the coagulation bath [44]. The small O/C ratio of 0.02 for the PVC control membrane can be attributed to surface oxidation by environmental oxygen [45], and this surface oxidation may occur in all the prepared membranes.

3.4. PWP and polystyrene particle rejection

The PWPs for the prepared membranes are listed in Table 2. All the prepared membranes including the self-supporting membrane have similar PWPs of approximately 300 ± 10 L/(m² atm h). Note that the preparation of membranes with similar PWPs can be used to evaluate the effect of the membrane material properties alone (i.e., hydrophilicity in this study) on membrane fouling and avoids the effect of hydrodynamic conditions on fouling tendency (i.e., initial water flux and operating pressure) [46–48].

The rejection properties of the prepared membranes were investigated using polystyrene latex particles with diameters of 20 and 50 nm. As indicated in Table 2, all the braid-reinforced hollow fiber

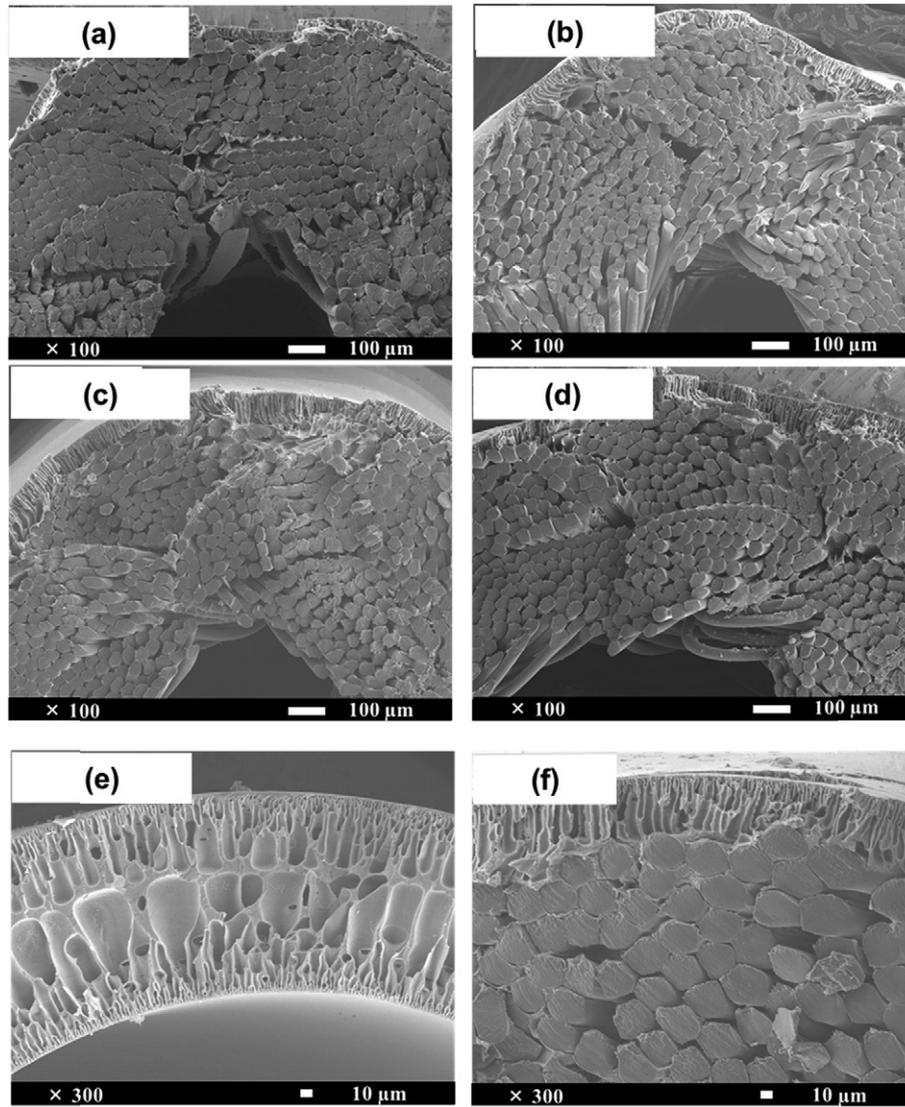


Fig. 4. FE-SEM images of the membrane cross-sections: (a) braid-reinforced PVC control, (b) braid-reinforced blend 1:7, (c) braid-reinforced blend 1:3, (d) braid-reinforced blend 1:1, (e) self-supporting blend 1:1, (f) braid-reinforced blend 1:1 with same magnification as that for self-supporting blend 1:1 to compare the coating layer thickness.

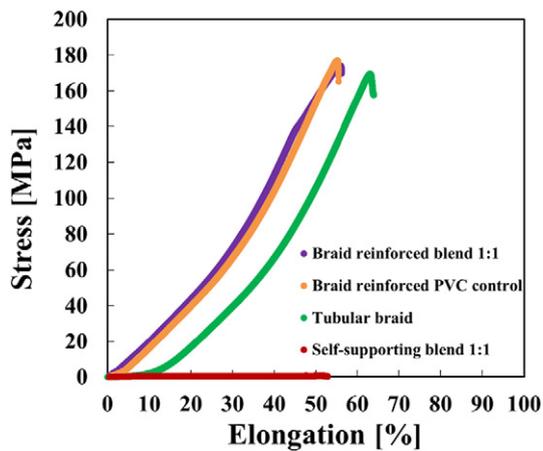


Fig. 5. Mechanical strength of self-supporting and braid-reinforced hollow fiber membranes and tubular braid.

Table 3

Mechanical properties of previously reported PVC hollow fiber membranes and our braid-reinforced PVC hollow fiber membranes.

Dope solution material	Membrane type	Tensile strength at break [MPa]	Elongation at break [%]	Ref	Publication year
PDMAE-BC/PVC	Self-supporting	2.3	62	[36]	2016
TEOS/PVC	Self-supporting	1.5–3.8	56–80	[37]	2015
PVP/PVC	Dual-layer reinforced	9.0–10.6	95–120	[20]	2015
PEG or PVP/PVC	Dual-layer reinforced	12–21	32–49	[18]	2014
PEG/PVC	Dual-layer reinforced	19–22	93–102	[38]	2013
Polystyrene/PVC	Self-supporting	2.4–4.1	37–54	[39]	2012
PAN/PVC	Self-supporting	2.8–5	–	[40]	2012
PAN/SiO ₂ /PVC	Self-supporting	4–4.8	18–42	[41]	2011
PVC	Self-supporting	2–4	58–84	[42]	2011
PEG or PEG/PVC	Self-supporting	1.8–4.3	9–47	[43]	2002
Present work	Braid-reinforced	170 ± 0.5	50 ± 0.8		

PDMAE-BC, poly(methacryloxyethyl benzyl dimethyl ammonium chloride); TEOS, tetraethoxysilane.

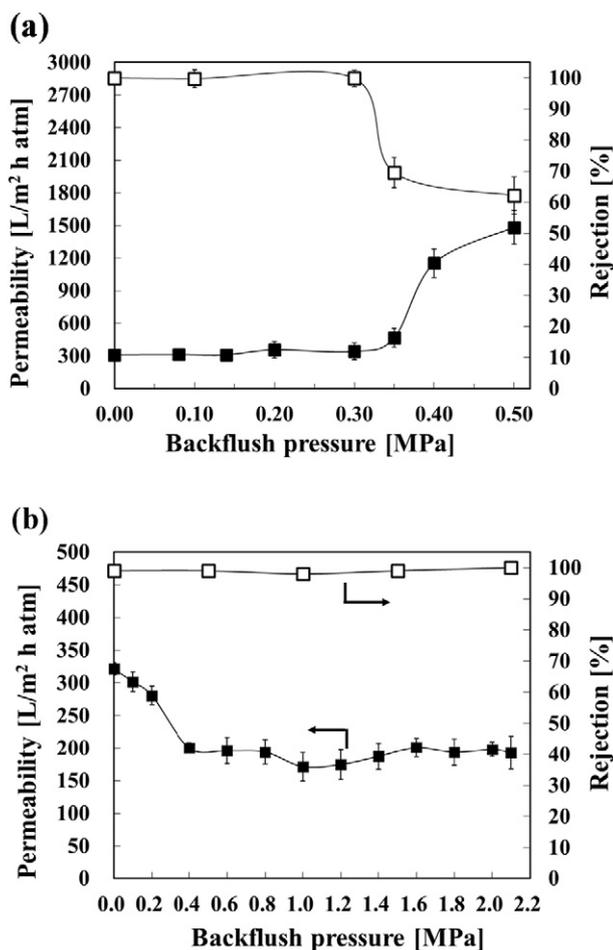


Fig. 6. PWP and rejection for various backflush pressures for (a) self-supporting blend 1:1 and (b) braid-reinforced blend 1:1. The rejection measurements were performed using polystyrene particles with average diameters of 400 and 50 nm, respectively.

membranes had similar 76% rejections of the 20-nm particles and 100% rejections of the 50-nm particles, whereas the self-supporting blend 1:1 exhibited no rejection of the 20-nm particles and only 10% rejection of the 50-nm particles. The rejection results agree well with the surface structures (Fig. 3), where the pore size of the self-supporting membrane

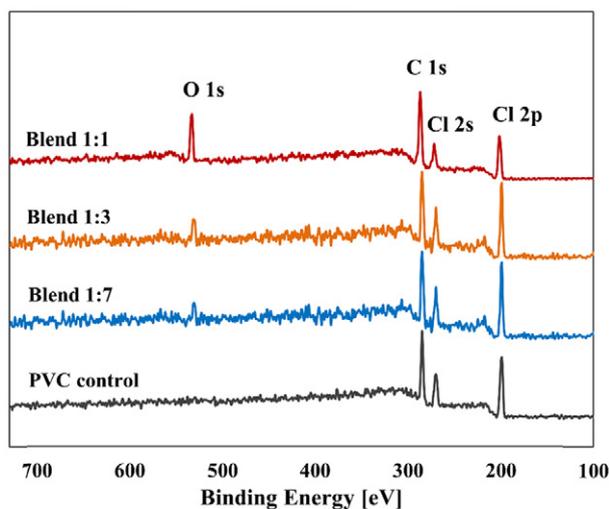


Fig. 7. XPS spectra for the prepared braid-reinforced membranes with different copolymer/PVC blend ratios.

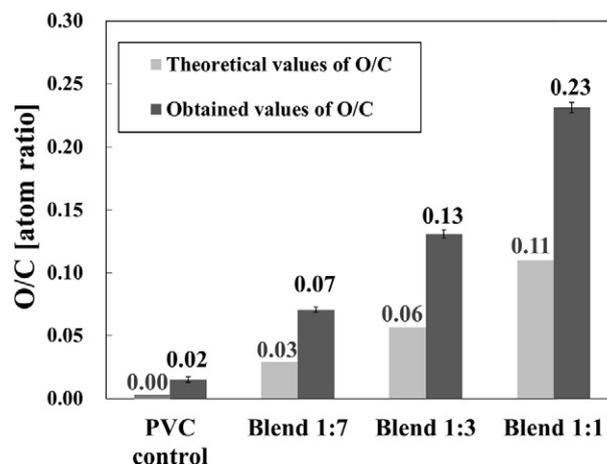


Fig. 8. Surface O/C atom ratios of the prepared braid-reinforced membranes with different copolymer/PVC blend ratios.

was much larger than those of the braid-reinforced membranes. Note that although the PWP and materials of the braid-reinforced and self-supporting membranes were almost the same, a much higher rejection property and smaller surface pore size were obtained for the braid-reinforced membrane, which can lead to reduced fouling propensity during the filtration process [26].

3.5. Hydrophilicity of the membranes

Air bubble contact angle measurements were performed to evaluate the surface hydrophilicity of the braid-reinforced membranes, and the results are presented in Fig. 9. The air bubble contact angles of the prepared membranes increased with increasing copolymer/PVC blend ratio, indicating an increase of the surface hydrophilicity [30]. Compared with the air bubble contact angle for the PVC control membrane, those of the blend membranes increased to 138° and 142° for copolymer/PVC blend ratios of 1:7 and 1:3, respectively; in addition, the air bubble contact angle increased slightly upon further increasing the blend ratio over 1:3. The increase in contact angle is consistent with the increased copolymer concentration at the membrane surfaces, as observed by XPS and illustrated in Fig. 8. Where enrichment of the copolymer on the surface of braid-reinforced blend 1:1 membrane was observed, we expected the surface hydrophilicity and air bubble contact angle to be larger than that of the blend 1:3 membrane. However, the blend 1:3 and blend 1:1 membranes exhibited similar contact angles, suggesting that the hydrophilicity of the blend membrane was unchanged as the blend ratio increased over 1:3. Considering that some factors (such as surface roughness and membrane pore distribution) could affect the contact angle results [27], we hypothesized that the small contact angle difference of the blend 1:3 and blend 1:1 membranes could be

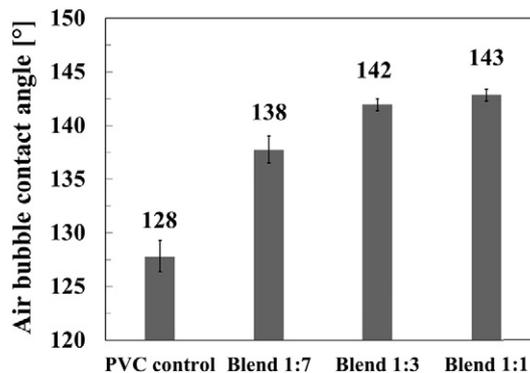


Fig. 9. Air bubble contact angles for the braid-reinforced membranes.

attributed to the multiple effects of the hydrophilicity and surface morphologies.

3.6. Fouling resistance to BSA and activated sludge solutions

3.6.1. BSA adsorption on polymeric films

QCM-D analysis was performed to evaluate the interaction between the BSA molecule and surface of the polymer films. Fig. 10 demonstrates that the BSA adsorption amount decreased as the copolymer content in the copolymer/PVC blends increased from 0 to 50 wt% and remained constant upon further increasing the copolymer content. These results indicate that blending poly(VC-co-PEGMA) into PVC film can significantly weaken the interaction with BSA molecules, enhancing the resistance to BSA adsorption. Therefore, good resistance to BSA fouling can be expected when using an appropriate blend ratio.

3.6.2. BSA fouling property

Protein fouling experiments were performed on the membranes using a 1000 ppm BSA solution. The initial water flux through the membranes was set to 90 L/(m² h) by adjusting the transmembrane pressure. The transmembrane pressures for the prepared membranes in the filtration experiments were almost the same because of the similar membrane PWPs, as observed in Table 2. Therefore, the net effect of the membrane material on BSA fouling could be evaluated by removing the effects of the initial flux and transmembrane pressure. The water flux values of the prepared membranes as a function of filtration time are plotted in Fig. 11. The permeation flux of the blend 1:7 and 1:3 membranes and the PVC control membrane decreased to approximately 30% because of the fouling. However, the flux of the blend 1:1 membrane remained at approximately 70% after 120 min of BSA filtration. After backflushing, the water fluxes of the blend 1:7, 1:3, and 1:1 membranes notably recovered to 75%, 80%, and 90% of the initial fluxes, respectively, whereas that of the PVC control membrane only recovered to 50%. The blend 1:1 membrane exhibited the best antifouling performance during the filtration of the BSA solution. However, even though the total BSA fouling performances of the blend 1:7 and 1:3 membranes and PVC control membrane were similar, the blend membranes exhibited improved flux recovery abilities and decreased irreversible fouling, indicating their better antifouling properties [49]. This result is consistent with the increased resistance of protein adsorption observed in the QCM-D characterization. Thus, we can conclude that the improved antifouling properties of the blend membranes resulted from their fouling-resistant surfaces.

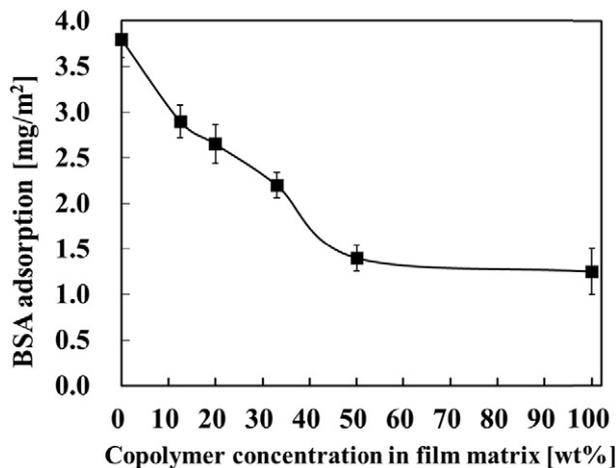


Fig. 10. BSA adsorption on polymeric films for copolymer/PVC blends with various copolymer contents.

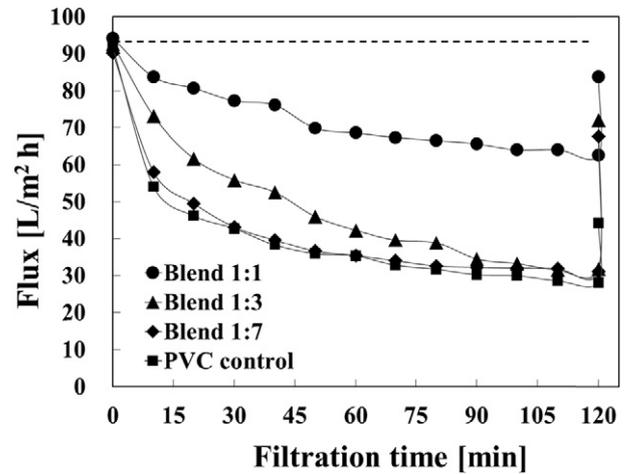


Fig. 11. BSA fouling performance of the braid-reinforced hollow fiber membranes.

3.6.3. Activated sludge fouling property

The performance of the membranes in filtrating activated sludge solution is shown in Fig. 12. During the filtration experiment, the initial water flux was set to approximately 30 L/(m² h) by adjusting the transmembrane pressure. The backflush was performed every 30 min during the filtration process, which is close to the backflush conditions in a practical MBR [50]. As depicted in Fig. 12, the blend membrane also exhibited considerable antifouling property compared with that of the PVC control membrane for the filtration of activated sludge solution; however, the fouling tendency of the activated sludge solution was much more severe than that of the 1000 ppm BSA solution (Fig. 11). The permeation flux of the blend membrane decreased to nearly 45% of the initial flux after just over 30-min filtration of the activated sludge solution, whereas that of the PVC control membrane dramatically dropped to 25%. After the first backflush, the water flux of the blend membrane recovered to almost 77% of the initial flux, whereas that of the PVC control membrane only recovered to approximately 35%. The blend membrane exhibited much lower fouling propensity and higher resistance to irreversible fouling. All 4 filtration circles exhibited similar flux decline tendencies and flux recoveries, suggesting the unchanged antifouling performance. Thus, the blend membrane could be expected to be used in practical MBR processes with stable antifouling properties, which will be examined in our future work.

The good antifouling performance of the copolymer/PVC braid-reinforced membrane can be attributed to the existence of a PEG layer at the outer surface of the membrane and pores [51]. Because the

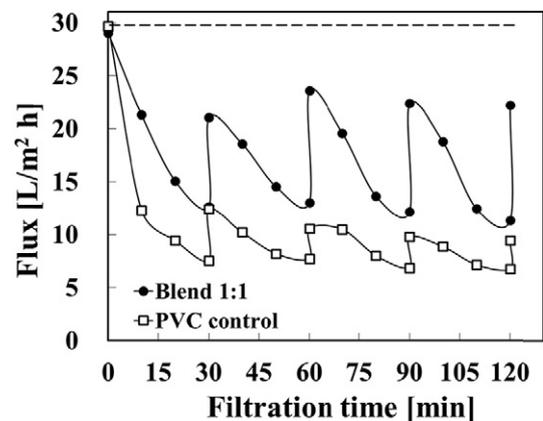


Fig. 12. Activated sludge fouling performance of braid-reinforced 1:1 blend and PVC control hollow fiber membranes.

hydrated PEG chains have a large excluded volume in an aqueous environment, the PEG layer tends to repel the foulant molecules approaching the membrane surface, serving as a steric barrier to foulant adsorption [11,49]. However, as observed in Table 1, the major component in the activated sludge is a biopolymer substance (72%), which can lead to more severe membrane fouling [50,52]. Nevertheless, the considerable antifouling performance of the copolymer/PVC blend membranes was apparent even in the filtration of such activated sludge solution.

In summary, considering the super-high mechanical strength and good fouling resistance to activated sludge solution, braid-reinforced poly(VC-co-PEGMA)/PVC hollow fiber membranes show great potential for application in wastewater treatment, including MBR treatment [35, 53,54]

4. Conclusion

Braid-reinforced poly(VC-co-PEGMA)/PVC hollow fiber membranes were successfully prepared via NIPS. These membranes exhibited thinner polymer coating layer thicknesses and smaller surface pore sizes than those of a self-supporting hollow fiber membrane (same membrane material and PWP). The tensile strength and bursting strength of the braid-reinforced hollow fiber membranes were higher than 170 and 2.1 MPa, respectively, which were significantly larger than those of the self-supporting hollow fiber membrane and the various reported PVC hollow fiber membranes. Owing to the copolymer surface segregation, the copolymer incorporated membrane surface showed the improved hydrophilicity and antifouling properties. When the copolymer/PVC blending ratio reached 1:1, considerable improvement of the antifouling propensity and flux recovery after water backflush were observed for the filtration of BSA solution and activated sludge solution. In conclusion, the newly prepared braid-reinforced poly(VC-co-PEGMA)/PVC hollow fiber membranes exhibited great mechanical properties and surface antifouling resistance to activated sludge solution, suggesting their potential for application in practical wastewater treatment. According to this work, the fabrication of braid-reinforced hollow fiber membrane can be suggested, when the soft amphiphilic copolymers is used to prepare robust hollow fiber membrane.

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