


Surface modification of a PVDF membrane by co-grafting hydroxyl and zwitterionic polymers to enhance wettability and antifouling property

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Abstract

Polyvinylidene fluoride (PVDF) membranes have been widely applied in the separation of various organic matters owing to their excellent properties. However, they possess low wettability and undergo fouling because of the hydrophobic nature of PVDF. In this study, poly (2-hydroxyethyl methacrylate) (PHEMA) and poly (sulfobetaine methacrylate) (PSBMA) were co-introduced to modify the highly hydrophobic PVDF membrane surface via UV photo-irradiation. Facile UV photo-grafting was performed by irradiating the pristine PVDF membrane immersed in a PHEMA/PSBMA mixture solution with UV light for 5 min. The performance of the as-prepared PHEMA/PSBMA-grafted membrane was compared with that of membranes modified with solely PHEMA or PSBMA. The hydroxyl and zwitterionic groups of the grafted membranes enhanced wettability and increased flux. A tightly bound water layer was formed because of the enhanced wettability, significantly suppressing protein adsorption. The initial flux of bovine serum albumin (BSA) solution through the PHEMA/PSBMA-grafted membrane was 2861 LMH, which was 3.1 times higher than that obtained by the pristine PVDF membrane. Furthermore, the flux decline of the modified membrane caused by BSA fouling was 49% lower than that of the pristine PVDF membrane. Finally, the PHEMA/PSBMA-grafted PVDF membrane showed antifouling properties after three BSA filtration cycles.

KEYWORDS

coatings, membranes, surfaces and interfaces

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1 | INTRODUCTION

Membrane-based separation has been widely used for purification owing to its high separation efficiency, low energy consumption, and easy scaling-up.^{1,2} In particular, microfiltration and ultrafiltration membranes can remove bacteria, viruses, dyes, or organic materials through a size-exclusion mechanism.^{3–6} These membranes broadly utilize polymeric materials such as polyacrylonitrile,⁷ polyethersulfone,⁸ and polyvinylidene fluoride (PVDF).^{9,10} Among these polymeric membranes, PVDF membranes have garnered attention owing to their superior mechanical stability and chemical resistance. However, the intrinsic hydrophobicity of PVDF causes severe non-wetting and fouling^{11,12}; hydrophobic membranes inevitably require high filtration pressures, while fouling causes a decrease in flux over time.

Recent studies focus on novel approaches to modify hydrophobic PVDF membranes with hydrophilic or zwitterionic materials.^{13–19} This hydrophilic modification of membranes is frequently adopted to reduce fouling and enhance wettability. Hydrophilic membrane surfaces can bind with water molecules and form a hydration layer, which can effectively inhibit the adsorption of foulants, such as proteins.^{20,21}

Post-treatments, such as coating and grafting, are representative methods for modifying PVDF membranes. Hydrophilic, zwitterionic polymers, and metal oxides have been coated on PVDF membranes via various coating processes. The co-deposition of tannic acid and polyvinylpyrrolidone (PVP) was also conducted via one-step assembly coating for the hydrophilic modification of PVDF membranes, affording membranes with enhanced water flux and antifouling performance.²² Polydopamine (PDA) is another material that can be used to modify PVDF membranes owing to its effective adhesion properties and the simple coating method involved. PDA is frequently used in the co-deposition of hydrophilic materials or as a precursor layer between the PVDF membrane and hydrophilic layer. Jiang et al. co-deposited PDA and synthesized micromolecular zwitterions on PVDF membranes. The resulting modified membrane exhibited higher hydrophilicity than the pristine membrane and improved fouling resistance.²³ Zhao et al. coated PDA as a precursor layer between the PVDF membrane and sulfonated chitosan; the resulting membrane showed high flux and dynamic antifouling properties.²⁴ Among metal oxides, TiO₂ is actively used for modifying PVDF membranes because of its hydrophilicity and high stability.²⁵

Unlike the coating method, grafting has received significant attention for the modification of PVDF membranes because it introduces chemical bonding, which is

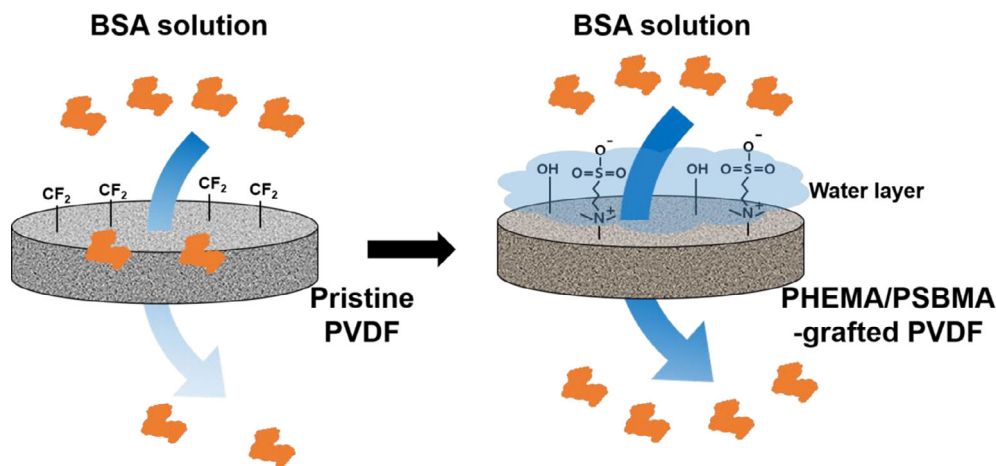
not achieved through coating.²⁶ This chemical bonding leads to high chemical and mechanical stability against foulants and contributes to long-term durability. Various hydrophilic monomers and inorganic materials have been grafted onto the surface of PVDF membranes. Yu et al. grafted hydrophilic hydroxyethyl acrylate monomers onto the PVDF membrane through high-energy γ irradiation.²⁷ Schulze et al. modified hydrophobic PVDF membranes to impart hydrophilicity by conducting electron-beam-induced grafting of hydrophilic polymers such as polyethylene glycol, polyvinyl alcohol, and PVP.²⁸ Atomic transfer radical polymerization was also performed for hydrophilic modification through zwitterionic polymer grafting.²⁹

UV photo-grafting is a facile and effective modification method, offering wide-scale applicability. It involves simple dipping and UV exposure processes with variables, such as intensity and UV exposure time, which are easy to control. Also, UV photo-grafting method has the advantages of low cost and easy continuous process compared to one of the conventional coating methods, plasma polymerization process, which usually includes the vacuum process. Moreover, numerous materials can be grafted through UV photo-grafting,^{30–33} with zwitterionic polymer grafting being a typical application. For instance, a polysulfobetaine methacrylate (PSBMA) brush was grafted onto a PVDF membrane to enhance its ultrafiltration performance.³⁴ PSBMA-grafted PVDF exhibited enhanced hydrophilicity and improved antifouling properties. However, the pristine PVDF membrane was only slightly hydrophobic with a contact angle of $\sim 75^\circ$. The modification of a more hydrophobic PVDF membrane with sulfobetaine methacrylate (SBMA) dissolved in deionized (DI) water remains unclear because uniform modification requires excellent wetting with the SBMA aqueous solution.

Numerous studies have focused on the modification of hydrophobic membranes to hydrophilic ones. However, most of these strategies used relatively less hydrophobic membranes, with water contact angles of 61.8° – 92.0° .^{23,27,28,35,36} Furthermore, highly hydrophobic membranes are difficult to convert to hydrophilic without chemical treatment or excessive modification because of their intrinsic considerably low surface energy.

In this study, poly(2-hydroxyethyl methacrylate) (PHEMA) and PSBMA were grafted simultaneously to modify the surface of the PVDF membrane via UV photo-irradiation. It was confirmed that both PHEMA and PSBMA were well-polymerized and grafted onto the hydrophobic PVDF membrane. Owing to the co-introduction of PHEMA and PSBMA in a water/EtOH mixture solution, a very hydrophobic PVDF membrane with a contact angle of 130° was successfully modified.

FIGURE 1 Schematic illustration of bovine serum albumin (BSA) solution filtration using pristine and PHEMA/PSBMA-grafted PVDF membranes. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54365)]



PHEMA and PSBMA improved the wettability of the membranes owing to their hydrophilic properties. Furthermore, the hydroxyl groups of PHEMA play an important role in absorbing water molecules, and the zwitterionic groups of PSBMA lead to electrostatic interactions between the polymer and water molecules.^{37,38} These interactions induce the formation of a water layer, which can effectively inhibit protein adsorption (Figure 1). Owing to these properties, the PHEMA/PSBMA-grafted PVDF membrane exhibits higher filtration performance than the pristine and solely PHEMA-grafted PVDF membranes.

2 | EXPERIMENTAL

2.1 | Modification of the PVDF membrane

The PVDF membrane (Durapore 0.1 μm , Millipore, United States) was consecutively immersed in ethanol and water. The wetted membrane was immersed in an 8 M monoethanolamine (MEA) ($\geq 98\%$, Sigma-Aldrich Co., United States) aqueous solution for 30 min, at 70°C to form double bonds in the PVDF chain. The modified membranes were dried in an oven at 60°C for 30 min. Next, the MEA-modified membrane was immersed in 20 wt% benzophenone (BP) (ReagentPlus[®] 99%, Sigma-Aldrich Co.) dissolved in methanol (MeOH) for 5 min. After 30 min of drying at 25°C, the membrane was immersed in a pre-mixed solution containing 2-hydroxyethyl methacrylate (HEMA $\geq 99\%$, Sigma-Aldrich Co.) and sulfobetaine methacrylate (SBMA $\geq 95\%$, Sigma-Aldrich Co.) for 30 min. The HEMA and SBMA mixtures were prepared by dissolving 10 wt% HEMA and 5 wt% SBMA into an ethanol (EtOH) and DI water mixture (weight ratio = 7:3). PHEMA-grafted PVDF membranes were also fabricated using 15 wt%

HEMA and a mixture with the same weight ratio of EtOH to DI water. The immersed membrane was treated with 365 nm and 1000 W UV light intensity for 1, 5, and 10 min. For future fabrications of UV-treated membranes, the UV treatment time was fixed at 5 min. The UV-treated PVDF membranes were washed with MeOH and sonicated with EtOH and DI water. The washed membranes were dried in an oven set at 60°C for 24 h. The PHEMA- and PSBMA-grafted membranes were fabricated using the same fabrication procedure as the PHEMA/PSBMA-grafted PVDF membrane.

2.2 | Characterization

Chemical analysis was conducted through Fourier-transform infrared (FT-IR) spectroscopy (Nicolet 5700, Thermo Fisher Co., United States), x-ray photoelectron spectroscopy (XPS; Axis Supra, Kratos, United Kingdom), and energy dispersive x-ray spectroscopy (EDX; Quattro S, Thermo Fisher). The FT-IR spectra were measured in the wavelength range of 700–4000 cm^{-1} , and the atomic composition of the membrane surfaces was analyzed through XPS and EDX. Moreover, water contact angles were measured using a contact angle meter (DSA25S, Kruss, Germany) with 1 μL DI water. The surface and cross-sectional structures of the membranes were measured using field emission scanning electron microscopy (FE-SEM) (Quattro S, Thermo Fisher). The surface roughness was analyzed using atomic force microscopy (AFM) (Park systems, NX10 SPM System). The pore size was measured using a capillary flow porometer (POROLUX[™] 1000, Porometer, United States). Finally, the weight changes of the pristine, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes were calculated by measuring the weight difference after sonication in EtOH for 30 min for a

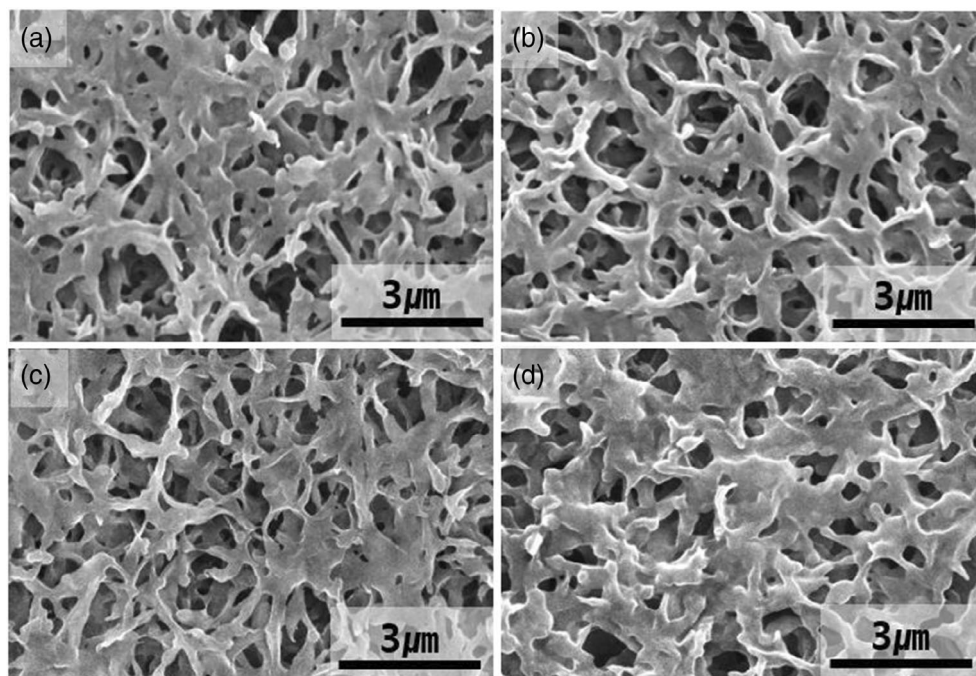


FIGURE 2 Surface morphologies of PHEMA/PSBMA-grafted PVDF membrane with respect to the UV treatment time: (a) Pristine PVDF membrane, (b) 1-min, (c) 5-min, and (d) 10-min UV-treated PHEMA/PSBMA-grafted PVDF membranes.

membrane area of 17.34 cm². The degree of grafting yield (D_g) was calculated using Equation (1).

$$D_g(\%) = \frac{(W_1 - W_0)}{W_0} \times 100 \quad (1)$$

where W_0 is the weight of the pristine membrane and W_1 is the weight of the grafted membrane.

2.3 | Filtration experiment

The DI water and BSA (BSA $\geq 96\%$, Sigma-Aldrich Co.) solution filtration tests were performed in the dead-end filtration mode. The membrane was installed in a test cell (HP4750, Sterlitech, United States), and pressure was applied for the test. The BSA solution was fabricated by dissolving 10,000 ppm BSA into 1 packet of an aqueous solution of phosphate-buffered saline (PBS, pH = 7.4, Sigma-Aldrich Co.). A 1000 ppm BSA solution was used for the cyclic filtration test. In the water and BSA flux test, the membranes were first wetted at 4 bars for comparison with a pristine PVDF membrane, followed by testing at 1 bar. The flux was calculated using Equation (2).

$$\text{Flux(LMH)} = \frac{1}{A} \times \frac{\Delta V}{\Delta t} \quad (2)$$

where A is the effective membrane area, ΔV is the volume of the collected permeate, and Δt is the permeation

time. The BSA rejection was measured using a UV-Vis spectrophotometer (SPECORD[®] 210 PLUS, Analytik Jena, Germany). For the cyclic filtration test, the modified membrane was tested repeatedly using the same procedure as the initial filtration test. Before each filtration cycle, the tested membrane was ultrasonicated with DI water.

3 | RESULTS AND DISCUSSION

The pristine PVDF membrane was treated with an MEA solution to introduce double bonds in the PVDF chain. The MEA alkaline treatment leads to the deprotonation of the $-\text{CH}_2$ groups in the PVDF chain and the elimination of F^- by a chain reaction.^{39,40} In addition, EDX results showed decreased F1s and increased C1s intensities, indicating the elimination of F^- (Table S1). After the MEA treatment, the membrane was simultaneously modified with PHEMA and PSBMA via UV photo-irradiation.

To identify the change in the PVDF membrane after the PHEMA/PSBMA modification with UV treatment, the surface structure was observed with respect to the treatment time (Figure 2). As the UV treatment time increased, more PHEMA/PSBMA was deposited onto the membrane surface. The 1- and 5-min UV-treated PHEMA/PSBMA-grafted PVDF membranes exhibited highly porous structures, while the 10-min UV-treated membrane consisted of partially clogged pores. After 20 min of UV irradiation, the membrane exhibited completely blocked pores with the polymer covering its

FIGURE 3 (a) Water contact angles and (b) water flux of the pristine and 1-min, 5-min, and 10-min UV-treated PHEMA/PSBMA-grafted PVDF membranes. [Color figure can be viewed at wileyonlinelibrary.com]

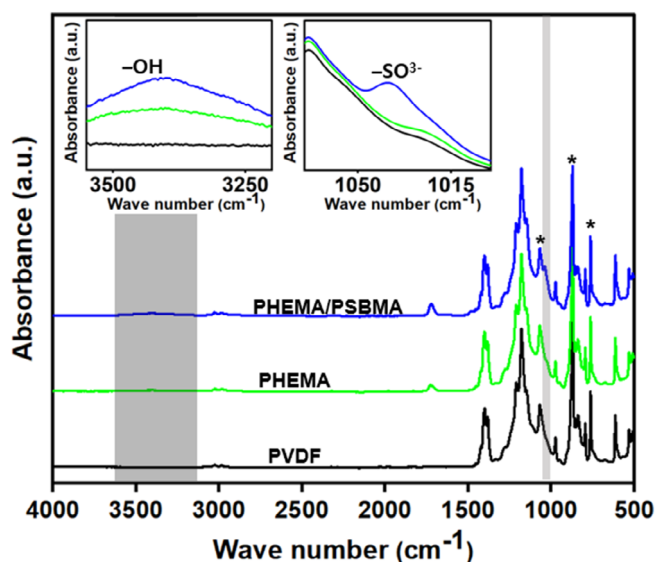
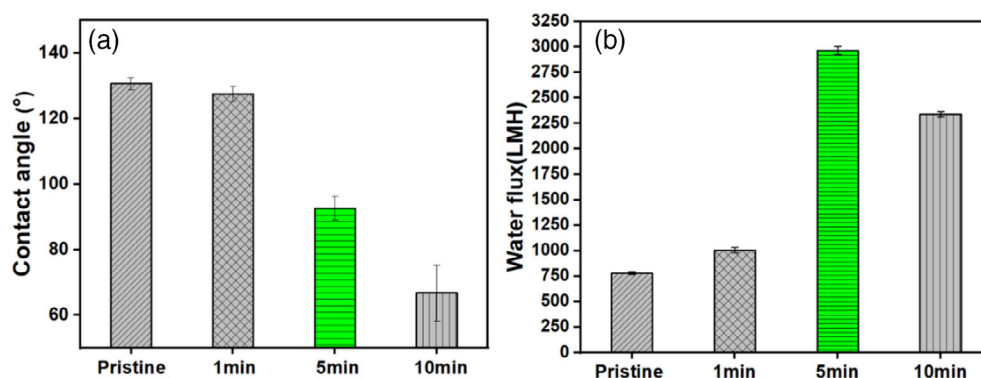


FIGURE 4 Fourier-transform infrared (FT-IR) spectra of the pristine PVDF, PHEMA, and PHEMA/PSBMA-grafted PVDF membranes. [Color figure can be viewed at wileyonlinelibrary.com]

entire surface, which implied the formation of a polymer coating (Figure S1). The mean pore sizes of the pristine PVDF membrane and the 1-, 5-, and 10-min UV-treated PHEMA/PSBMA-grafted membranes were 0.267, 0.236, 0.237, and 0.211 μm , respectively (Figure S2). The decreased pore size of the 10-min UV-treated PHEMA/PSBMA-grafted PVDF membrane coincided with its surface morphology. The exposure to the UV lamp increased the temperature, resulting in evaporation of the DI water and EtOH solvents of the HEMA/SBMA solution and therefore increasing the concentration of the polymer. The concentration of the polymer solution during the UV treatment directly affected the pore size and surface morphology of the samples. In contrast, the 1- and 5-min UV-treated PHEMA/PSBMA-grafted PVDF membranes exhibited smaller pore size reduction.

The water contact angles and fluxes of the pristine and 1-, 5-, and 10-min UV-treated PHEMA/PSBMA-

TABLE 1 Atomic percentages of pristine PVDF, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes.

	PVDF	PHEMA	PHEMA/PSBMA
C 1s	55.0	56.4	56.0
F 1s	45.0	41.4	39.3
O 1s		2.2	3.1
N 1s			1.1
S 2s			0.5

grafted PVDF membranes were measured to identify the hydrophilicity changes after the PHEMA/PSBMA modification (Figure 3). The pristine PVDF membrane demonstrated a water contact angle of $130.0 \pm 1.8^\circ$ owing to the hydrophobic nature of the $-\text{CF}_2$ groups in PVDF. After the UV treatment of the PHEMA/PSBMA, the water contact angle decreased as the UV treatment time increased. The 1-min UV-treated membrane showed a water contact angle value similar to that of the pristine PVDF (within the error margin), indicating insufficient modification time. The 5- and 10-min UV-treated membrane exhibited water contact angles of $92.6 \pm 3.6^\circ$ and $66.7 \pm 8.6^\circ$, respectively. These results imply that a UV treatment time over 5 min is required to obtain enhanced wettability. Unlike previously reported modified PVDF membranes, the pristine PVDF membrane used in this work was highly hydrophobic. The enhanced hydrophobicity led to improved PVDF properties, however, it hampered the transformation to a hydrophilic membrane. Notably, PHEMA/PSBMA UV photo-grafting significantly decreased the water contact angle while maintaining the porous structure of the membrane (Figure 2).

The water flux results also support the improved wettability results. The dried pristine PVDF membrane could not be permeated by water because of its extremely high hydrophobicity. The PHEMA/PSBMA-grafted PVDF membrane demonstrated water permeation due to the improved wettability; the 5-min UV-treated membrane

had the highest water flux. Although the 10-min UV-treated membrane exhibited the lowest water contact angle, the decreased pore size of the membrane disrupted the water flow. Based on these results, the UV treatment time was fixed at 5 min for further modification.

The pristine PVDF, PHEMA-grafted PVDF, and PHEMA/PSBMA-grafted PVDF membranes were fabricated to compare their properties and filtration performance. FT-IR spectroscopy was conducted to confirm the successful PHEMA/PSBMA modification (Figure 4). The representative $-\text{CF}_2$ -assigned peaks for the PVDF membranes were observed at 763, 871, and 1068 cm^{-1}

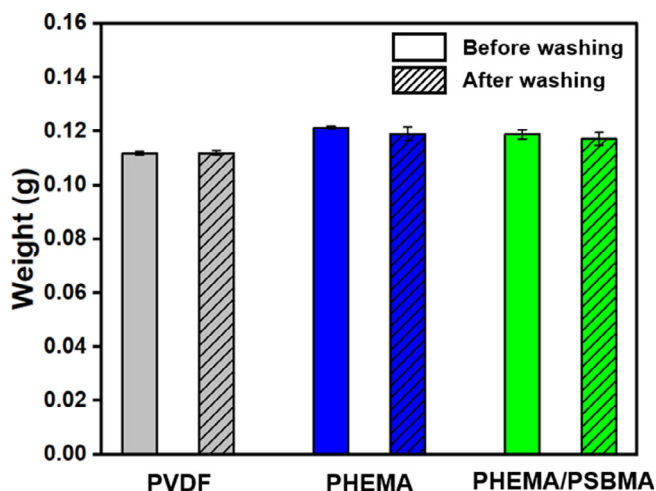


FIGURE 5 Weights of the pristine PVDF, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes before and after EtOH sonication washing. [Color figure can be viewed at wileyonlinelibrary.com]

(marked by asterisks), and were present throughout the all tested membrane samples.⁴¹ These results indicate that there was no damage to PVDF during UV photo-grafting. The PHEMA/PSBMA-grafted PVDF membrane exhibited a broad $-\text{OH}$ peak (shaded in dark gray) around 3408 cm^{-1} and a $-\text{SO}_3^-$ peak (shaded in light gray) at 1038 cm^{-1} , suggesting that PHEMA/PSBMA was successfully grafted onto the PVDF membrane. Compared to the PHEMA-grafted PVDF membrane, the SO_3^- peak from the zwitterionic functional group in the PHEMA/PSBMA-grafted PVDF membrane was clearly observed (Figure 4 inset).^{42,43}

Table 1 and Figure S3 show the results of the XPS analysis that was performed to identify the PHEMA/PSBMA modification. Compared to the pristine membrane, the atomic percentage of C increased slightly, while that of F decreased in the PHEMA- and PHEMA/PSBMA-grafted membranes, owing to F^- elimination during MEA treatment followed by the introduction of hydroxyl and zwitterionic functional groups. O was observed in both the PHEMA- and PHEMA/PSBMA-grafted PVDF membranes, originating from the $-\text{OH}$ group of HEMA and the $-\text{SO}_3^-$ group of PSBMA. Unlike the PHEMA-grafted PVDF membrane, N and S were detected in the PHEMA/PSBMA-grafted PVDF membrane, which directly indicates the presence of zwitterionic groups from SBMA. Corroborating with the XPS results, the EDX results confirmed that the PVDF membrane was successfully chemically modified (Table S2). All chemical analyses were performed using the modified membranes ultrasonicated with DI water and EtOH to confirm that the functional groups were entirely

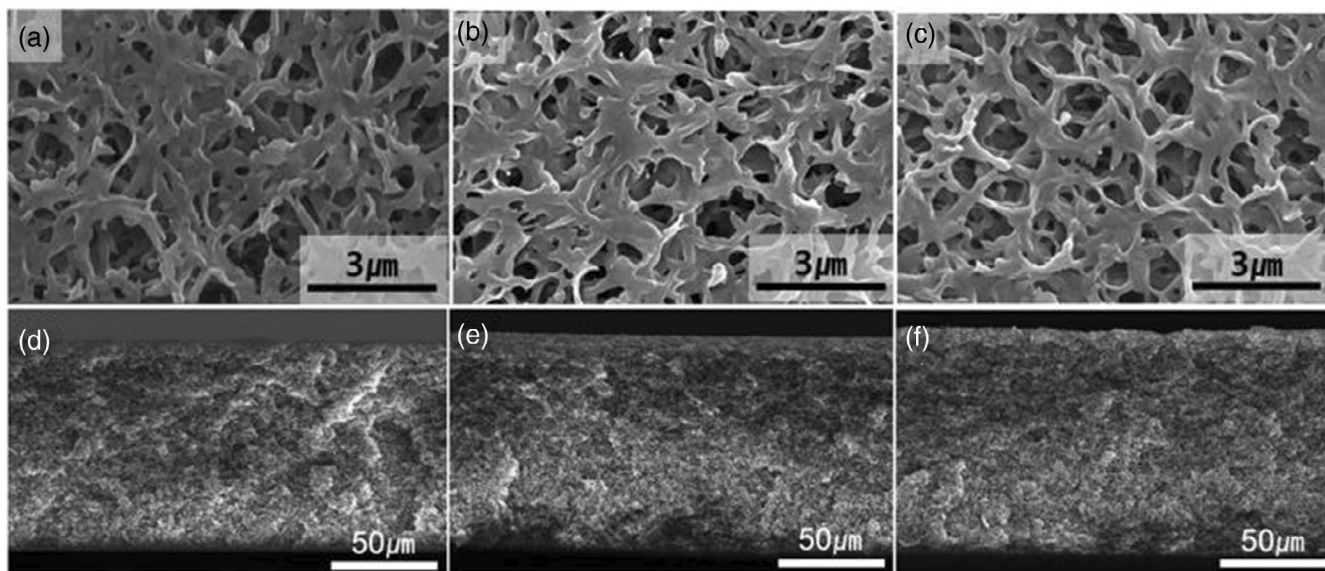


FIGURE 6 Surface and cross-sectional morphologies of the (a, d) pristine, (b, e) PHEMA-grafted, and (c, f) PHEMA/PSBMA-grafted PVDF membranes.

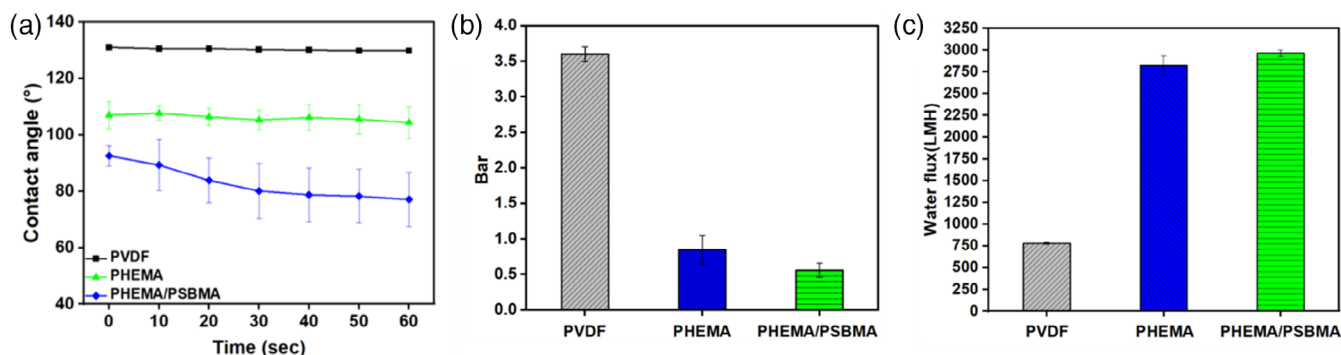


FIGURE 7 (a) Water contact angles according to time, (b) water intrusion pressure, and (c) water flux of the pristine PVDF, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54365)]

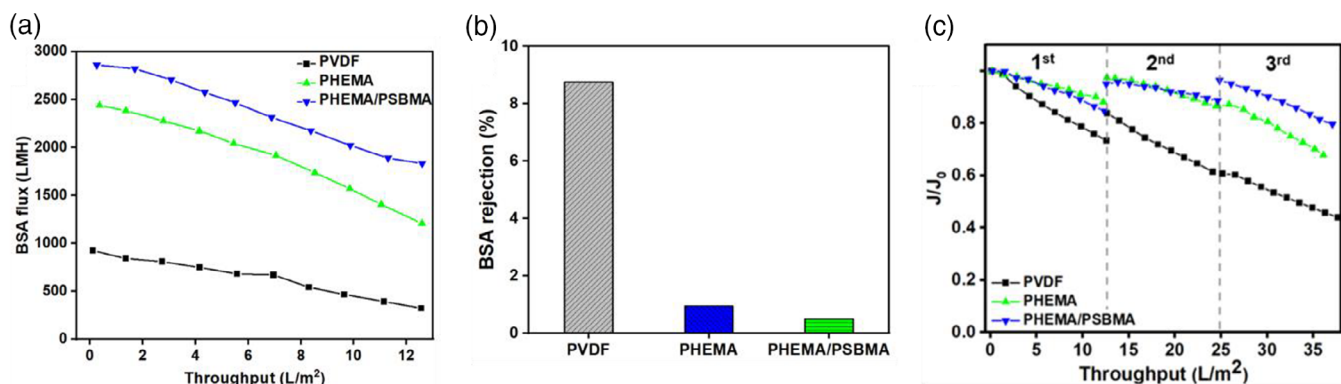


FIGURE 8 (a) Bovine serum albumin (BSA) flux and (b) BSA rejection with a 10,000 ppm BSA solution, (c) BSA relative flux for three cycles of the pristine, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes with 1,000 ppm BSA solution. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54365)]

preserved and that the change in the surface structure was maintained even after intensive cleaning following the chemical grafting.

The degree of grafting yield and grafting stability was calculated by measuring the weight difference of the membranes. The weights of the membranes before and after EtOH sonication washing are shown in Figure 5. Before sonication washing, the weight of the pristine PVDF membrane was 0.1118 g, while those of the PHEMA- and PHEMA/PSBMA-grafted PVDF membranes were 0.1213 and 0.1189 g, corresponding to D_g values of 8.5% and 6.4%, respectively. After EtOH sonication washing, the weight of each membrane was measured to investigate the grafting stability. No significant weight changes were observed after EtOH sonication washing, which indirectly confirmed the stability of the grafted polymer. Furthermore, no significant changes were observed in the contact angle after EtOH sonication washing, which further confirmed the grafting stability (Figure S4).

The structural changes that occurred after grafting were confirmed through SEM analysis (Figure 6). The

pristine PVDF membrane exhibited a porous structure, with rough branches (Figure 6a). Even after grafting PHEMA and PHEMA/PSBMA onto the PVDF membranes, the porous structure was well-maintained (Figure 6b,c). As shown in the cross-sectional SEM images, no significant differences were observed in the thickness or inner porous structure between the pristine and grafted membranes (Figure 6d-f). The pore size distribution in each membrane was measured to identify changes in the pore size (Figure S5). The mean pore sizes of the pristine PVDF, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes were 0.267, 0.214, and 0.215 μm , respectively. After UV treatment, the pore size of the modified membrane decreased slightly, whereas the porous structure was sufficiently maintained. Even though the membrane surfaces had similar porous structures, the roughness of the branch of the modified membranes was distinctly reduced (average roughness, S_a values of pristine PVDF: 0.3466 μm , PHEMA: 0.1251 μm , PHEMA/PSBMA: 0.1527 μm), implying that the polymer layer was deposited onto the original structure of each branch (Figure S6).

The SEM images and pore size distribution of the PSBMA-grafted PVDF membrane were analyzed and compared with the PSBMA-grafted PVDF membrane (Figure S7). Unlike the PHEMA- and PHEMA/PSBMA-grafted membranes, severe pore clogging was observed on the SEM image of the PSBMA-grafted PVDF membrane surface. The PSBMA solution was fabricated with 15 wt% SBMA in an EtOH and DI water mixture; EtOH was added because pristine PVDF could not be wetted when only DI water was used. However, since SBMA is dissolved solely in water, which has low wettability to PVDF, non-uniform deposition of PSBMA is expected to occur when using the water/EtOH solvent mixture. This decrease in the pore size was also confirmed by the pore size distribution results. The mean pore size of the PSBMA-grafted PVDF membrane was 0.188 μm , which is considerably smaller than those of the PHEMA- and PHEMA/PSBMA-grafted PVDF membranes.

To identify the wettability and water flux after modification, the water contact angle and water flux of the pristine PVDF-, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes were measured (Figure 7). The pristine PVDF membrane exhibited a high water contact angle of $130.5 \pm 0.7^\circ$, owing to the hydrophobic nature of PVDF, whereas the PHEMA-grafted PVDF membrane, influenced by the hydrophilic and water-absorbing properties of PHEMA, had a lower water contact angle of $107.7 \pm 2.5^\circ$. The water contact angles of the pristine and PHEMA-grafted PVDF membranes did not change significantly during 60 s after water dropping. Unlike these membranes, the PHEMA/PSBMA-grafted PVDF membrane exhibited a more hydrophilic behavior with an $89.3 \pm 9.1^\circ$ water contact angle. Furthermore, a change in the water contact angle ($\sim 77.1^\circ$) was observed over time, which directly indicated that the wettability enhanced with time. The addition of the zwitterionic polymer, PSBMA, is expected to bind more water molecules compared to the introduction of PHEMA alone.⁴⁴

Although membrane modification did not change the water contact angle to values that are characteristics of superhydrophilic surfaces, it reduced the water intrusion pressure of the membrane (Figure 7b). This led to a more wettable environment at a specific pressure. While the pristine PVDF membrane exhibited a water intrusion pressure of over 3.5 bar, the water intrusion pressures of the PHEMA- and PHEMA/PSBMA-grafted PVDF membranes were reduced to 0.95 and 0.56 bar, respectively. The water flux results confirmed the relationship between membrane wettability and water flux (Figure 7c). While the pristine PVDF membrane exhibited a water flux of only 778 LMH, the PHEMA- and PHEMA/PSBMA-grafted PVDF membranes showed enhanced water fluxes of 2,823 and 2964 LMH,

respectively, because the co-introduced PHEMA and PSBMA altered the membrane to become more hydrophilic and easily-wettable.

A BSA flux test was conducted to identify the effect of PHEMA/PSBMA grafting on the PVDF membranes with 10,000 ppm BSA (Figure 8a). A concentration of 10,000 ppm was chosen to observe the differences in the antifouling properties of each membrane clearly. Unlike the water flux test, to compare the performance of each membrane, the membranes were tested after wetting with forced pressure, particularly for the pristine PVDF membrane. The initial fluxes of the pristine PVDF, PHEMA-, and PHEMA/PSBMA-grafted PVDF membranes were 925, 2439, and 2861 LMH, respectively. Compared to the pristine and PHEMA-grafted PVDF membranes and similarly to the water flux results, the PHEMA/PSBMA-grafted PVDF membrane exhibited a higher initial flux. As the throughput increased, the BSA flux decreased because of protein fouling. However, the flux decline of the PHEMA/PSBMA-grafted PVDF membrane was 35.9%, indicating reduced protein fouling compared to that observed for the pristine and PHEMA-grafted PVDF membranes, 72.9% and 50.5%, respectively. The pristine PVDF membrane showed a relatively high BSA rejection value of 8.6% owing to the large amount of BSA adsorbed on the PVDF membrane, whereas the modified membranes showed a decreased BSA rejection value owing to their antifouling property (Figure 8b). The enhanced performance of the PHEMA/PSBMA-grafted PVDF membrane can be attributed to the effect of the zwitterionic group. While each hydroxyl group can bind one molecule of water, the zwitterionic group can bind eight molecules of water, owing to its electrostatic interactions.⁴⁵ Furthermore, the water molecules are bound more tightly to the zwitterionic group than to the hydroxyl group. These phenomena might be the reason for the better antifouling property of the zwitterionic group.⁴⁶ The bound water molecules formed a water layer that significantly inhibited the adsorption of protein molecules.⁴⁷ The fouling tendency was confirmed by observing the surface structure of the membranes after the BSA filtration test (Figure S8). A significant amount of BSA was adsorbed onto the surface of the pristine PVDF membrane and the pores were considerably clogged due to hydrophobic interactions between PVDF and BSA.⁴⁸ The PHEMA-grafted membrane also showed partially clogged pores due to BSA adsorption, which was less than the pristine PVDF. Among the three membranes, the PHEMA/PSBMA-grafted PVDF membrane showed the most porous structure, even after the 10,000 ppm BSA filtration test. Further, antifouling properties were confirmed through the cyclic BSA filtration test with a 1,000 ppm BSA concentration (Figure 8c).

After each cycle, the BSA flux of the pristine PVDF membrane decreased because the adsorbed protein remained and clogged the pores even after the washing process. The relative flux of the PHEMA/PSBMA-grafted PVDF membrane did not change significantly during cyclic filtration, indicating that the foulant was removed by washing. The hydrophilicity and antifouling properties of PHEMA/PSBMA led to low adhesion of proteins, which were easily detached after applying a washing force.

4 | CONCLUSIONS

Both PHEMA (with hydroxyl groups) and PSBMA (with zwitterionic groups) were co-grafted onto a hydrophobic PVDF membrane via UV photo-irradiation. The modification was conducted concisely by immersing the membrane in the two mixtures of monomer solutions for 5-min under UV irradiation. The PHEMA/PSBMA-grafted PVDF membrane showed improved wettability and antifouling properties in relation to the pristine and PHEMA-grafted PVDF membranes. The hydrophilic and electrostatic interactions between the polymer and water molecules effectively induced the formation of a water layer, which inhibited protein adsorption on the membrane. Compared to the hydroxyl group, the zwitterionic group could bind more water molecules in a tighter manner. In addition, only zwitterionic modification was performed in a water-based solvent, which made the modification of the non-wettable hydrophobic surface difficult. The modified membrane exhibited further antifouling properties upon cycling. This simple and efficient modification of PVDF membranes, which incorporates antifouling properties, has promising applications for the separation and purification of organic compounds, particularly proteins.

AUTHOR CONTRIBUTIONS

Jin Yeon Lee: Data curation (lead); formal analysis (lead); investigation (lead); writing – original draft (equal). **Young Hoon Cho:** Data curation (equal); methodology (equal). **Seung-Eun Nam:** Funding acquisition (equal); investigation (equal). **In-Chul Kim:** Investigation (equal). **Ho Bum Park:** Investigation (equal). **You-In Park:** Funding acquisition (equal); investigation (equal). **Sun Ho Bae:** Data curation (equal). **Youngmin Yoo:** Conceptualization (lead); methodology (lead); supervision (lead); writing – review and editing (lead).

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CONFLICT OF INTEREST STATEMENT

The authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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