A simplified method for preparation of hydrophilic PVDF membranes from an amphiphilic graft copolymer

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Abstract

An attempt to reduce the number of steps and hence the overall costs involved in the preparation of hydrophilic flat sheet poly(vinylidene fluoride) (PVDF) membranes was made by adding PVDF polymer powders directly to an amphiphilic copolymer mixture containing PVDF grafted with poly(ethylene glycol) methyl ether methacrylate (PEGMA) (PVDF-g-PEGMA), solvent and unreacted PEGMA from the atom transfer radical polymerisation (ATRP) method. The membrane was characterised by Fourier transform infra-red attenuated reflection spectroscopy (FTIR-ATR), atomic force microscopy (AFM), scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM), pure water flux, contact angle measurement and protein filtration experiments. The presence of ester and ether groups attributable to the PEGMA in the resultant membrane was observed from FTIR-ATR spectra. From SEM and FESEM observations, an asymmetric membrane was formed with a thin skin layer accompanied by short finger-like and macrovoid structures, but the membrane morphology changed when the copolymer content was increased. AFM reveals that the roughness of the membranes becomes greater with higher amount of PVDF-g-PEGMA. The pure water permeation flux of the prepared membrane increased significantly to 116 L/m² h compared to pure PVDF membranes, while contact angle measurements show a moderate value of between 57° and 67°. The percentage of fouling recovered using water cleaning after protein filtration was found to be 100% for all membranes prepared from this method. The results suggested that hydrophilic and low-fouling PVDF membranes were formed from the newly developed method. Since membrane hydrophilicity has a pronounced effect on the fouling properties, hydrophilic PVDF membranes developed from this process are anticipated to be suitable not only for bio-separation, but also for wastewater treatment.

Keywords:
Poly(vinylidene fluoride)
Poly(ethylene glycol) methyl ether methacrylate
Atom transfer radical polymerisation
Graft copolymer
Hydrophilic
Phase inversion

1. Introduction

Surface modification of membranes prepared from hydrophobic polymers such as poly(vinylidene fluoride) (PVDF), polysulfone (PS) and polypropylene (PP) is often desirable so as to increase membrane hydrophilicity and fouling resistance properties, while retaining the bulk membrane properties. Membranes made from these hydrophobic materials are often susceptible to fouling when applied in water filtration. Membrane fouling is an undesirable phenomenon because it causes a sharp decline in permeation flux, which leads to a decrease in the efficiency of the membrane process. Nevertheless, PVDF membranes remain popular in many applications due to their excellent chemical resistance and good thermal and mechanical properties [1–5]. Since an ideal membrane for industrial water or wastewater treatment should combine the excellent bulk properties of the hydrophobic material with the surface chemistry of the hydrophilic materials, surface modification of PVDF membranes has attracted much interest among researchers [6–10].

Considerable effort is being devoted to developing suitable techniques for surface modification of PVDF membranes, which in general, can be classified into coating [11], surface graft polymerisation [8,12–14], adsorption [15], and hydrophilic chemical modification of bulk membrane materials [16]. Another method that has been recently reported to have improved the hydrophilicity of PVDF membranes is the blending amphiphilic graft copolymers with the casting solution during membrane preparation [10,17,18]. This type of copolymer has good compatibility with the PVDF matrix and provides engineered surface properties such as fouling resistance, when blended with the polymer solution. The hydrophilic side chains of amphiphilic copolymer self-segregate towards the membrane surface upon immersion of the polymer casting solution into the coagulation bath, while the hydrophobic backbone provides compatibility with the matrix material and water insolubility during the phase inversion process. PVDF polymer itself could also be a good candidate for the
hydrophobic component in producing amphiphilic copolymers with hydrophilic side chains. One of the methods recently used for synthesising amphiphilic copolymers with PVDF as a hydrophobic backbone is the atom transfer radical polymerisation (ATRP) method [19]. Examples of copolymers prepared using this method include graft copolymers of PVDF with poly(methyl methacrylate) (PVDF-g-PMMA) and poly(ethylene glycol) methyl ether methacrylate (PVDF-g-PEGMA), which have been successfully employed in improving the hydrophilicity and anti-fouling properties of PVDF membranes [20].

In general, the synthesis of copolymers using ATRP method involves three major steps, i.e. polymerisation, precipitation and purification. After drying under vacuum, the copolymers will then be added into a polymer casting solution as a polymer blend. The overall process, starting from the synthesis of the graft copolymer up to the preparation of the membrane casting solution is schematically illustrated in Fig. 1a. Previous publications have detailed the synthesis of amphiphilic copolymer PVDF-g-PEGMA in a solvent, 1-methyl-2-pyrrolidinone (NMP) [20,21]. The copolymer was then precipitated and purified with a methanol/petroleum ether mixture so as to get rid of the catalyst, copper (I) chloride (CuCl), ligand 4,4′-dimethyl-2,2′-dipyridyl (DMDP), and excess PEGMA. Subsequently, the copolymer was dried under vacuum in order to remove the solvent (NMP) and was then added to the membrane casting solutions containing PVDF, and dimethylacetamide (DMAc) as a solvent.

In principle, these steps are performed in order to isolate the synthesised copolymer and to remove the catalyst, ligand and unreacted monomers from the copolymer. However, we found that the copolymer solution (including the reaction mixture) could be added directly to the membrane casting solution. This is because, although DMAc was found to be the preferable solvent for PVDF, NMP is still capable of dissolving the PVDF[22], thus, direct addition of copolymer and reaction mixture into a PVDF casting solution is feasible. In addition, the amounts of CuCl and DMDP present in bulk polymerisation solution are relatively small, i.e. 0.04 wt% and 0.23 wt%, respectively. When the copolymer solution is added to the membrane casting solution according to the desired composition, the percentages of CuCl and DMDP in the final casting solution are expected to be much smaller. Therefore, it is assumed that this would have a negligible effect on the ultimate membrane morphology and overall performance. Additionally, it should also be noted that during polymerisation, some of the CuCl have been converted to copper (II) chloride (CuCl₂) and since CuCl₂ is a water-soluble salt, CuCl₂ is expected to be easily washed out upon immersion of polymer solution into the water bath. Finally, the excess or unreacted PEGMA can act as a pore forming agent in the membrane. Since PEGMA is hydrophilic in nature [6,23], the unreacted PEGMA present after polymerisation is expected to be washed out during the phase inversion process.

In this study, we propose a simplified and economical method for the preparation of surface modified PVDF membranes with amphiphilic graft copolymer PVDF-g-PEGMA. Hydrophilic PVDF membranes from graft copolymer PVDF-g-PEGMA could be prepared directly by adding copolymer solution from polymerisation into the membrane casting solution based on the specific amount required for membrane fabrication as shown in Fig. 1b. The proposed method appears to be easier and more economical, as the time required for precipitation, purification and drying of copolymer could be saved. Since quite a large amount of chemicals are required in the precipitation and purification of copolymer during the conventional method, the newly simplified method is expected to provide significant cost reduction.

2. Experimental

2.1. Materials

Commercially available poly(vinylidene fluoride)(PVDF, Kynar® K-761) powder was obtained from Elf Atochem, UK. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, Mn = 475 g/mol), copper (I) chloride (CuCl), 4,4′-dimethyl-2,2′-dipyridyl (DMDP), silicone oil, bovine serum albumin (BSA, Fraction V) and phosphate-buffered saline (PBS) were purchased from Sigma–Aldrich, UK. 1-Methyl-2-pyrrolidinone (NMP) was purchased from Rathburn Chemicals Ltd., UK. All solvents and chemicals were reagent grade, and all reagents were used as received. The PBS solution (pH 7.4) was prepared by the addition of pre-packaged buffered salts to deionised water.

2.2. Synthesis of graft copolymer PVDF-g-PEGMA and preparation of hydrophilic PVDF membranes

PVDF (5 g) was dissolved in NMP (40 mL) in a conical flask at 50 °C. The solution was cooled to room temperature, after which PEGMA (50 mL), CuCl (0.04 g), and initiator DMDP (0.23 g) were added and the flask was sealed with a rubber septum. Nitrogen gas was bubbled through the reaction mixture for 30 min while stirring. The reaction vessel was then placed in a silicon oil bath preheated to 90 °C, and the reaction was allowed to proceed for 19 h. After cooling the copolymer mixture at room temperature, the copolymer mixture was transferred to a bottle. NMP and PVDF were added directly to the bottle containing the copolymer mixture to form PVDF casting solutions according to the desired compositions. The copolymer concentrations were estimated based on an actual weight of copolymer could be precipitated from an amount of poly-

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Fig. 1. Simplified diagram for the preparation of membrane from copolymer; (a) conventional method and (b) simplified method.

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merisation mixture. The PVDF polymer, solvent and copolymer mixtures were mixed for 24 h at 60 °C to ensure complete dissolution of polymers. The polymer dopes with copolymer mixture were then cast on a glass plate and the flat sheet membranes were immediately immersed in coagulation bath containing deionised water. Pure flat sheet PVDF membrane was also prepared to compare the performance in terms of contact angle and pure water flux, with the membranes prepared using the simplified method. The membranes were immersed in deionised water for 3 days prior to characterization. The membrane casting conditions and compositions of the casting solutions are shown in Tables 1 and 2, respectively.

### Table 1

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting knife gap distance</td>
<td>150 μm</td>
</tr>
<tr>
<td>Casting temperature</td>
<td>20 °C</td>
</tr>
<tr>
<td>Coagulation bath temperature</td>
<td>20 °C</td>
</tr>
<tr>
<td>Casting speed</td>
<td>3.9 cm s⁻¹</td>
</tr>
<tr>
<td>Evaporation time</td>
<td>10 s</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Membrane</th>
<th>PVDF(copolymer* NMP, CuCl, DMDP and unreacted PEGMA (wt%)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVDF</td>
<td>20/0/80</td>
<td>4500.0</td>
</tr>
<tr>
<td>A1</td>
<td>20/1/79</td>
<td>6440.0</td>
</tr>
<tr>
<td>A2</td>
<td>20/2/78</td>
<td>21100.0</td>
</tr>
<tr>
<td>A3</td>
<td>20/3/77</td>
<td>38900.0</td>
</tr>
</tbody>
</table>

* Based on estimation data obtained through actual experiments.

These membrane samples were then positioned on a metal holder, and sputter coated with gold (for SEM) and chromium (for FESEM) under vacuum for 3 min and 1 min, respectively. The micrographs of the surface and cross-section of the membranes were taken at various magnifications.

#### 2.3.4. Pure water permeation

Pure water permeation measurements for membranes were conducted in a stainless-steel, SEPA-ST (Osmotics, USA) dead-end nanofiltration cell. Membrane discs with an effective membrane area of 0.0015 m² (diameter = 0.044 m) were cut and placed on a sintered metal plate. An O-ring was used to seal the feed solution from the permeate side. Nitrogen gas was used as the driving force for water filtration using deionised water at different operating pressures. Pure water permeation flux of the membrane was calculated by the following equation:

\[ J_w = \frac{V}{A \Delta t} \]

where V is the volume of water or solution permeated through membrane (L), A is the membrane effective surface area (m²) and \( \Delta t \) is the permeation time (h).

#### 2.3.5. BSA filtration studies

BSA was used as a model protein to evaluate the protein contamination of the prepared membrane. Filtration experiments were carried out at 20 °C similar to the filtration protocol carried out previously by Liu et al. [8]. The membrane was first pre-compacted at a transmembrane pressure of 5 bar for 30 min and the pure water flux was recorded every 5 min at transmembrane pressure of 1 bar. Then the deionised water was replaced with 0.1 wt% BSA in PBS solution for the fouling resistance test. After the protein ultrafiltration experiment (total filtration time of 1 h), the membrane was dismounted from the cell and cleaned with deionised water in ultrasonic bath for 5 min, three times, then the water flux was measured again.

The rejection rate (R) of the membrane was calculated by the following equation:

\[ R (\%) = \left( 1 - \frac{C_p}{C_b} \right) \times 100 \]

where \( C_p \) and \( C_b \) were protein concentrations in permeate and feed (mg/mL), respectively. The values were determined using a UV–vis spectrophotometer (UV-2101PC, Shimadzu, UK) at a fixed wavelength of 280 nm.

#### 3. Results and discussion

##### 3.1. FTIR-ATR characterisation

The structures of the pure PVDF membranes and the membranes containing the PVDF-g-PEGMA copolymers fabricated from the simplified method were studied by FTIR. Fig. 2 shows the respective FTIR-ATR spectra for the top surface (air surface) of the pure PVDF membrane (a), and membranes with an estimated copolymer concentration of 1 wt% (b), 2 wt% (c) and 3 wt% (d) addressed herein as A1, A2 and A3, respectively. Comparing the IR spectra of these membranes, new peaks at 1109 cm⁻¹ and 1728 cm⁻¹ appeared in the spectra of the grafted ones. These peaks represent the characteristic bands for C=O stretching and C=O-C stretching attributed to the carbonyl and ester groups, respectively [6], which indicates that the presence of graft PEGMA in the resultant membranes. This result is consistent with the results of previous studies on grafting of poly(ethylene glycol) methyl ether methacrylate onto PVDF membranes [6,8], hence suggesting that the membrane containing the graft copolymer, PVDF-g-PEGMA has been successfully
formed. Furthermore, from the spectra, there are no significant peaks observed at 1641 cm$^{-1}$ attributable to carbon–carbon double bond stretch, indicating that no more unreacted monomer PEGMA remains on the membrane surface [8], which means that the unreacted PEGMA from polymerisation might have been completely removed from the resultant membrane after immersion in water for several days.

### 3.2. Contact angle measurement

Hydrophilicity of the membranes including pure PVDF was characterised through the water contact angle measurement. The static contact angle and dynamic contact angle were measured in order to determine the hydrophilicity of the membranes, and the data is reported in Table 3 and Fig. 3. The values from Table 3 clearly show that the static contact angle of PVDF membranes fabricated using this method decrease significantly, suggesting that the membranes containing the grafted polymer exhibit higher surface wettability when compared with the pure ones. Among all, the greatest surface wettability is exhibited by A3 membrane, followed by A2 and A1 membranes. Since the contact angles of A1–A3 membranes are in ascending order, the higher the amount of PVDF-g-PEGMA in the casting solution, the greater the surface hydrophilicity of the membrane is. PVDF membranes containing final composition of 4.7–13 wt% PVDF-g-PEGMA developed in this study has shown a comparable contact angle of 57–67$^\circ$ with the ones containing 5–10 wt% PVDF-g-PEGMA prepared from a conventional method [20].

Through visual observations, the water droplets on membrane surfaces containing PVDF-g-PEGMA disappear and ultimately wet through the membranes after 5 min for A1 membrane and about 7–10 min for A2 and A3 membranes, respectively, whilst for pure PVDF membrane, the water droplet does not ultimately wet through after 10 min. As seen in Fig. 3, the contact angle does not decrease drastically over time as expected, however the membrane morphology observed from SEM and FESEM analyses could be employed to explain this phenomenon, as will be discussed further in the next section (Section 3.3). Nevertheless, the result strongly indicates that the hydrophilic side chains of the graft copolymer attributed to the PEGMA component have self-segregated on the membrane outer surface, resulting in improved hydrophilic properties of the PVDF membrane.

### 3.3. Membrane structure and morphology

The cross-section and surface morphology of fabricated membranes were studied using SEM and FESEM. Cross-sectional SEM micrographs of PVDF membranes prepared with the simplified method are shown in Fig. 4. The membrane prepared from 1 wt% copolymer (based on estimation) exhibits a typical asymmetric structure consisting of a thin skin layer of approximately 10 μm thickness accompanied by relatively short finger-like structures. Some large macrovoids beyond these structures are also observed. As reported by Kesting [24], this kind of morphology generally suggests the occurrence of a fast coagulation process when the polymer solution is brought into contact with water. Since the membrane casting solution consists of graft copolymer PVDF-g-PEGMA, unreacted PEGMA, catalyst CuCl, ligand DMDP and PVDF polymer itself, the hydrophilic side chains of the PEGMA from the graft copolymer might have quickly moved towards water upon immersing the casting polymer solution in the water coagulation bath and might have self-segregated towards the membrane surface; thus further facilitating the precipitation process. The presence of an amphiphilic polymer in the casting solution is expected to have enhanced the solvent–non-solvent exchange by increasing the affinity of the casting solution and water; therefore creating favourable conditions for instantaneous liquid–liquid demixing. The overall morphology seems to be similar with the previous report on surface modified PVDF membranes with amphiphilic graft copolymer PVDF-g-PEGMA using a typical membrane preparation method [20].

Membranes prepared with an estimated copolymer concentration of 2 wt% (A2 membrane) and 3 wt% (A3 membrane) revealed remarkably different morphologies from the previously mentioned 1 wt% (A1 membrane). The structure seems to be quite complicated, with the size of finger–like structures becoming thinner and kind of “compressed”, while the overall thickness and membrane skin layer...
As a consequence, the phase separation may be kinetically hindered and this can result in delayed onset of liquid–liquid demixing [25,26]. As can be seen from Table 2, the viscosity of solutions with 2 wt% and 3 wt% estimated copolymer concentration is dramatically increased in comparison with pure PVDF and 1 wt% estimated copolymer solutions. Due to an increase of unreacted monomer in line with the increase of copolymer concentration in the solution, the relationship between the solution viscosity and copolymer concentration does not rise proportionally as expected. Therefore, the phase inversion process in kinetically hindered resulting in delayed onset of liquid–liquid demixing.

Another factor contributing to the ultimate morphology of A2 and A3 membranes could be explained in terms of thermodynamic incompatibility induced between hydrophilic and hydrophobic components. By increasing the copolymer concentration, repulsions between hydrophilic segments of copolymer and the naturally hydrophobic PVDF polymer might have been induced during the immersion precipitation process. There exists some experimental evidence for the formation of aggregates and/or micelles occurring in the amphiphilic diblock copolymer, as well as amphiphilic graft copolymer due to repulsions between hydrophilic and hydrophobic segments in solution [27–30]. Depending on the type of solution, whether aqueous solution or organic solvent, amphiphilic copolymers show complex behaviour in solution depending on their ability to associate and change conformation in the medium. It is believed that in our study, the repulsions between hydrophobic PVDF polymer and hydrophilic copolymer might have occurred during immersion of the casting solution in the water coagulation bath, resulting in the morphology as seen in A2 and A3 membranes. Zhang and Eisenberg reported that various morphologies including spheres, rods, and vesicles of amphiphilic diblock copolymer aggregates could be obtained depending on the copolymer composition and the length of the hydrophobic backbone and hydrophilic side chains in low molecular weight solvents [31]. It is of interest to study the effects of amphiphilic graft copolymer aggregation or micelles on the membrane morphology developed in our studies.

While membranes prepared with a higher amount of copolymer exhibit a slightly wavy and uneven structure at the top surface (air side), the membrane with the lowest amount of copolymer shows a relatively smoother surface morphology, as can be observed from FESEM images represented by Fig. 5(a), (c) and (e). Nodule-like structure becomes apparent at the membrane bottom surfaces (Fig. 5(b), (d) and (f)) when the contents of copolymer PVDF-g-PEGMA were raised. Morphology of the membranes top surfaces were further characterised by AFM analysis and the three-dimensional AFM images are presented in Fig. 6 with 10 μm × 10 μm scanning area. The AFM images reveal that the surfaces of the membranes are not smooth, where these membranes consist mass of peaks and valleys, which are shown by bright region and dark region, respectively. It can also be seen from these images that the membrane top surfaces become rougher with the increase in PVDF-g-PEGMA content. With increasing copolymer contents in casting solution, more PEGMA is expected to self-segregate at the top of the membrane, thereby could be promoting a higher degree of surface roughness [21]. As a result, the surface roughness of the membrane becomes greater with the higher amount of amphiphilic copolymer. Further evidence supporting the roughness of the membrane surfaces are in terms of mean roughness, $R_a$ and mean square roughness, $R_q$, which are summarised in Table 4. Both $R_a$ and $R_q$ values are gradually increased when the PVDF-g-PEGMA contents are raised from 1 wt% to 3 wt% in polymer solutions.

As seen from SEM and FESEM analyses, the morphology of membranes fabricated from simplified method exhibit dense top surfaces. A membrane with a dense top surface often results in a lower water permeation rate; therefore the contact angle does not

![Fig. 4. SEM cross-sectional images of membranes (a) membrane A1, (b) membrane A2 and (c) membrane A3.](image-url)
3.4. Pure water flux and protein filtration studies

The effects of copolymer compositions on PVDF membrane performance were investigated by pure water permeation and protein filtration studies. According to Table 3, it can be seen that the pure water flux, \( J_0 \) of PVDF membranes prepared from the simplified method increases significantly compared to pure PVDF membrane. Approximately 20-fold increase in pure water flux to 116 L/m² h was observed from membrane prepared with copolymer composition of 1 wt%, compared to the pure ones. The water permeation flux of membranes prepared with higher copolymer concentration of 2 wt% and 3 wt% are lower than that for A1 membrane, for which the flux decreases with increasing copolymer amount. The result is as expected, which is based on the SEM structural observations in the preceding section. Since the former membranes reveal a more compact structure, higher thickness and less macrovoids, the transport properties across the membranes might be hindered resulting in lower water permeation flux. Yang et al. discovered that at a relatively higher concentration of non-solvent additive such as polyvinylpyrrolidone (PVP), can swell in the membrane pores when it is entrapped in the polymer matrix, where this can result in lower permeability of the membrane [32]. Therefore, it is believed that the higher concentration of PVDF-g-PEGMA in the casting solution may also cause the copolymer to be entrapped in the PVDF matrix, resulting in a reduction in water flux.
Nevertheless, the performance of all the modified membranes in terms of water flux have shown a substantial improvement, in comparison with the pure PVDF.

A comparison between membranes of pure water flux recovery after water cleaning is shown in Table 3 and is extended in Fig. 7, where $J_p$ represents the permeate flux during BSA filtration and $J_c$ is the permeate flux after cleaning the membrane with deionised water in an ultrasonic bath. The values of $J_p$ and $J_c$ for pure PVDF membrane could not be obtained through this experiment due to the drastic drop in permeate flux and severe membrane fouling, as it is well known that PVDF membrane is highly hydrophobic. While no significant trends could be observed from the percentage of total fouling on the modified membranes, all membranes exhibit excellent pure water flux recovery, which is 100% after water cleaning.

The excellent pure water flux recovery finding is similar to the ones reported by Asatekin et al. [33]. The values of $J_p$ and $J_c$ are found to be the same for all membranes prepared in this study except for pure PVDF membrane, indicating that the membranes exhibit reversible fouling characteristics, where initial water flux could be easily recovered by simple cleaning method using deionised water. In other words, no other type of physical cleaning methods or the use of chemicals is necessary to clean these membranes.

Although the pure water flux becomes lower with the increment of copolymer PVDF-g-PEGMA in polymer solution, the BSA filtration profile shows improvement in the BSA rejection rate from 2% to 66%. It is well known that the membrane performance could be governed by many factors including casting condition and membrane morphology. By increasing polymer concentration in casting solution, the coagulation process of the membrane tend to be slower allowing the surface morphology to evolve further [34]. In this study, higher copolymer concentration could have lowered the rate of coagulation, thus promoting the surface morphology of the resulting membrane to become relatively denser than the membrane containing low copolymer concentration. As a result, membranes with a denser surface layer would have relatively higher protein rejection rate but with a lower pure water flux.

4. Conclusions

The newly developed simplified method for the preparation of hydrophilic PVDF membranes from amphiphilic copolymer, PVDF-g-PEGMA is proven to be useful. Verification on the presence of copolymer in the membrane prepared through the direct addition of copolymer mixture into the polymer solution is made by FTIR-ATR spectra. PVDF membrane has shown significant improvement in terms of hydrophilicity and pure water flux with this method. By increasing the copolymer concentration in the casting solution, the contact angle of the membrane can be greatly reduced, though the pure water permeation flux is decreased. A typical asymmetric membrane structure could be observed in the prepared membranes, mainly for membranes developed using the least amount of copolymer solution, though these membranes exhibit some macrovoids formation. With increasing copolymer concentration,
the macrovoid formation could be suppressed and the surface roughness becomes greater. The initial water permeation flux of the membranes could be completely recovered by using simple water cleaning, after filtration experiments with protein. This indicates that the membranes exhibit reversible fouling properties, which is one of the critical considerations in industrial applications. Although further studies are required to improve the protein rejection properties of membrane, the simplified method for the preparation of hydrophilic PVDF membranes from amphiphilic copolymer PVDF-g-PEGMA developed in this study is anticipated to result in considerable reductions on membrane production cost.

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