

**Special Issue: Microfiltration and Ultrafiltration**  
**Membrane Science and Technology**

**Guest Editors:** Prof. Isabel C. Escobar (University of Toledo) and  
Prof. Bart Van der Bruggen (University of Leuven)

**EDITORIAL**

**Microfiltration and Ultrafiltration Membrane Science and Technology**

I. C. Escobar and B. Van der Bruggen, *J. Appl. Polym. Sci.* 2015,  
DOI: [10.1002/app.42002](https://doi.org/10.1002/app.42002)

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# Highly chlorine and oily fouling tolerant membrane surface modifications by *in situ* polymerization of dopamine and poly(ethylene glycol) diacrylate for water treatment

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**ABSTRACT:** Here we show a simple hydrophilic-membrane surface modification method using *in situ* polymerization of aqueous dopamine and poly(ethylene glycol) diacrylate (PEGDA) mixture to improve both oily fouling and chemical resistance of membranes for water treatment. Polydopamine (PD) induced from aqueous dopamine solution has been extensively studied for facile membrane surface modification but the PD layer is very susceptible to chemical attack (e.g., sodium hypochlorite [NaClO]). To overcome this disadvantage, in this study, crosslinked poly(ethylene glycol) (XLPEG) chains were successfully introduced with PD layer using PEGDA with a thermal free radical initiator. As a result, the XLPEG/PD-coated membranes showed excellent chemical stability against chlorine attack as well as much improved oily fouling tolerant behavior, without any sacrifice of original water permeance, as compared with only PD-coated membranes. This surface modification method will be readily used for many membranes for water treatment from flat sheet to hollow fiber membrane modules. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41661.

**KEYWORDS:** crosslinking; dopamine; membranes; poly(ethylene glycol); surface modifications; water treatment

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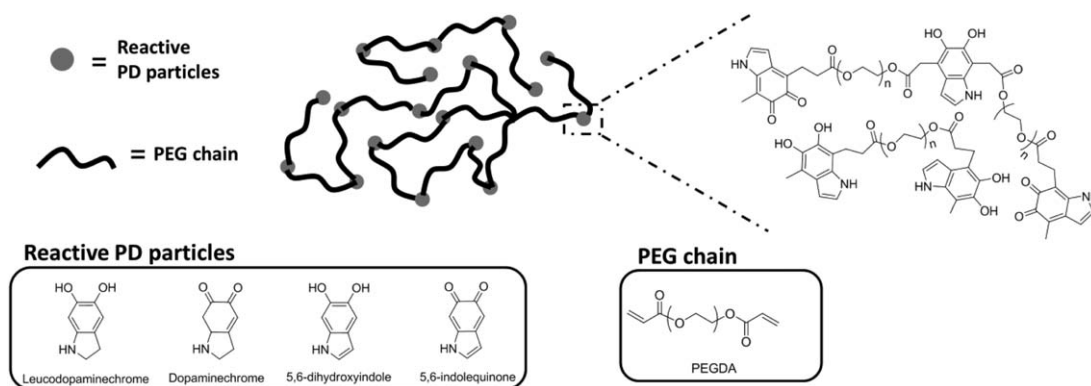
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## INTRODUCTION

As a member of catecholamine family, dopamine is a biological neurotransmitter, and is a precursor to other catecholamines, such as epinephrine and norepinephrine.<sup>1,2</sup> Recently, a novel and universal surface modification was first demonstrated by Lee *et al.*, using an aqueous dopamine solution at a certain pH level.<sup>3</sup> This surface modification method has gained a great interest owing to its simple and universal coating capability irrespective of material types and their surface properties. In general, it is believed that dopamine can be spontaneously oxidized under an aqueous basic solution, leading to *in situ* polymerization or surface deposit on almost all material surfaces ranging from organic to inorganic.<sup>4–10</sup> Also, the deposited polydopamine (PD) layers can make a material surface more hydrophilic.<sup>4,6</sup> Moreover, the PD layers offer a versatile platform for secondary chemical reactions, leading to useful coating designs with diverse functionality.<sup>7,8</sup> Accordingly, the PD surface modification method has been extensively studied in many promising applications, such as improved wettability of porous polymeric separator for lithium ion battery,<sup>4</sup> delayed release rates of heparin for anticoagulant,<sup>5</sup> enhanced dispersion for carbon nano-

tubes in aqueous solution,<sup>6</sup> and fouling-resistant membranes for water treatment.<sup>7–10</sup>

In particular, membrane community has been much more interested in the surface modification by PD because of its hydrophilic nature and simple coating processes.<sup>7–11</sup> Most of commercial membranes for water treatment are commonly fabricated using hydrophobic polymers such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethersulfone (PES), and polysulfone (PSF) owing to their outstanding mechanical properties and easy membrane formation, so hydrophobic solutes in the feed water, such as emulsified oils, can contaminate readily hydrophobic membrane surfaces and also plug external or internal pores due to strong hydrophobic interactions, thus usually leading to catastrophic membrane flux reduction.<sup>9,12</sup> Membrane separation technology for water treatment suffers from a serious problem, that is, membrane fouling.<sup>13–15</sup> Although numerous membrane surface treatments have been extensively studied for the improvement in fouling reduction, the surface modification of microfiltration (MF) or ultrafiltration (UF) membranes by PD has been considered as one of promising methods.<sup>7–9</sup> For instance, PD-coated PTFE MF



**Figure 1.** Illustration of the proposed reaction mechanism and structure of XLPEG/PD.

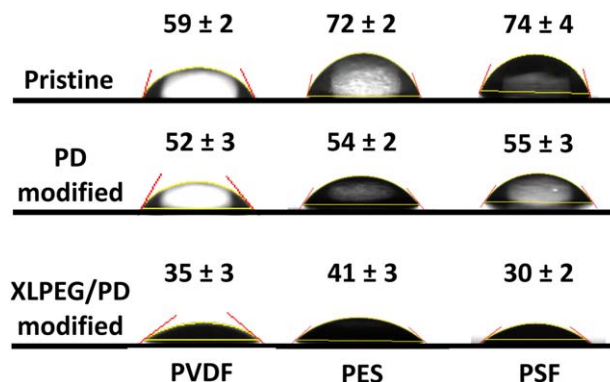
membranes exhibited a higher water permeance both during pure water filtration and emulsified oil filtration than unmodified PTFE MF membranes.<sup>8</sup> Also, PD-modified UF membranes showed much higher anti-fouling properties than the pristine membranes in oily water filtration experiment.<sup>8</sup>

The PD structures consisting of various catechol groups provide a versatile platform for further physical or chemical modification and functionalization.<sup>7,8,16–20</sup> For instance, the PD modified materials further coated with hydrophilic polymers via the multiple secondary forces such as hydrogen bonding.<sup>19</sup> These coating layers showed long-term stability and durability due to the strong noncovalent interactions.<sup>19</sup> Moreover, an oxidized quinone form of catechol groups can react with thiol- and amine-terminated bovine serum albumin (BSA) or poly(ethylene glycol) (PEG) by Michael addition or Schiff base reaction, in basic solutions.<sup>1,20</sup> Actually, PEG grafted to PD-modified microporous polymeric membranes (called PD-g-PEG modified membranes) presented higher fouling tolerance than pristine and only PD-modified membranes.<sup>7,8</sup> Interestingly, the water permeance of PD-g-PEG modified MF membranes was similar with that of only PD-modified MF membranes despite increased mass transport resistance caused by thicker PD-g-PEG layers.<sup>7</sup> Although the water permeances of PD-g-PEG modified UF membranes were decreased, as compared with those of pristine and PD modified UF membranes, that is, PEG-grafting also can lead to significantly improved fouling tolerance of PD-modified UF membranes.<sup>7</sup>

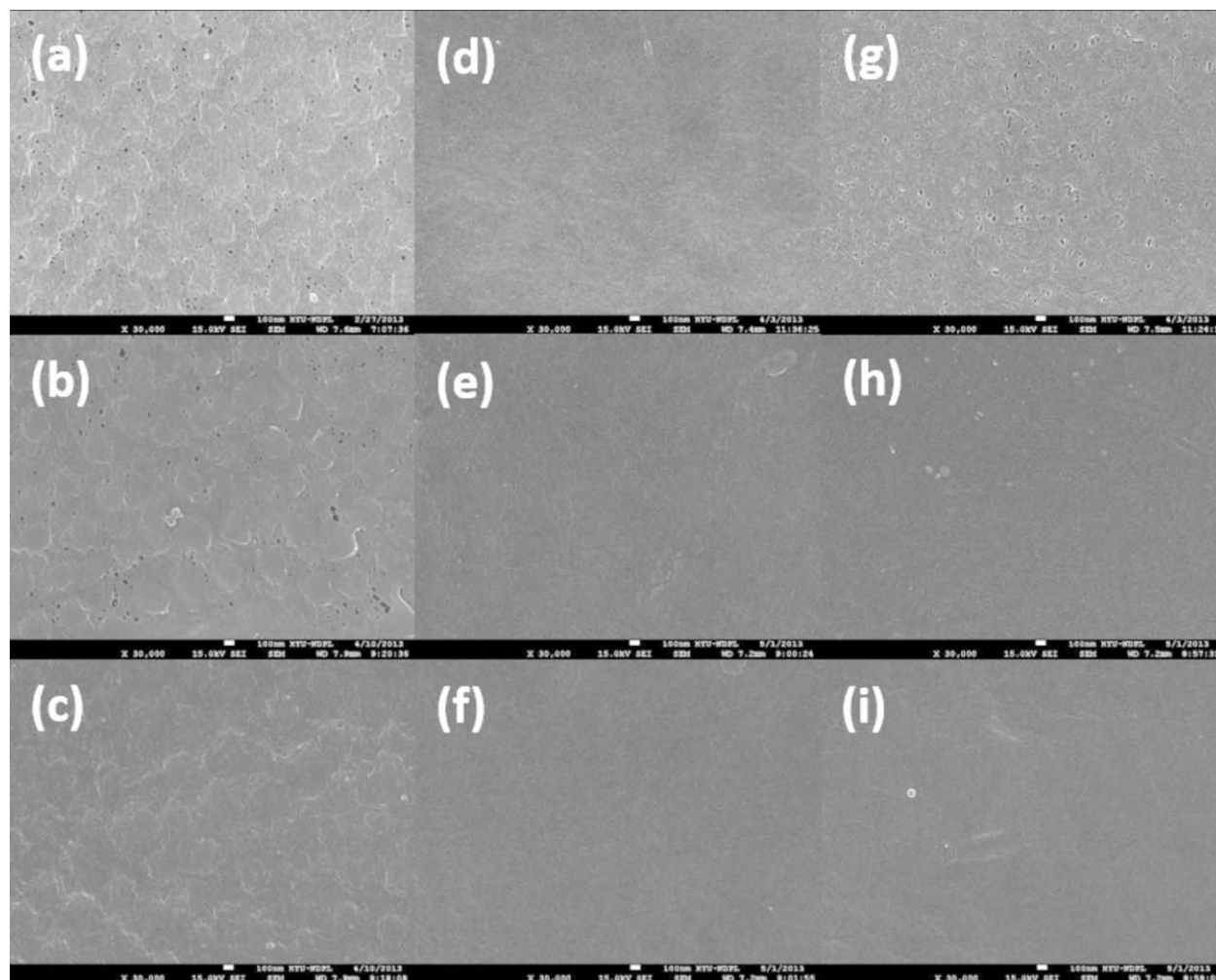
Several studies described the kinetics of PD formation by changing initial dopamine concentration or reaction time.<sup>3,16–18</sup> In many cases, the thickness of PD layer coated on membrane surfaces tends to reach a constant value at around 50 nm, of course, which can be slightly changed, depending on the type of membranes.<sup>3</sup> In other words, the coating thickness of PD deposition layer was increased with the reaction time, but it reaches a plateau after about almost several hours. However, a recent study reported that the maximal thickness of PD layer become gradually thicker with increasing the dopamine solution concentration between 0.1 and 5.0 g L<sup>-1</sup>.<sup>16</sup> More recently, our group systematically studied the effect of oxygen concentration on the dopamine oxidation reaction kinetics, and found the oxygen concentration in aqueous dopamine solution is a crucial factor to achieve more homogeneous PD coating.<sup>17</sup> Namely, a higher

oxygen concentration in the dopamine solution can speed up the reaction kinetics, resulting in more homogeneous, smoother, and thinner PD coating on any membrane substrates, giving rise to both much improved water permeance and anti-fouling properties.<sup>17</sup>

Although PD-modified membranes showed outstanding fouling-tolerant behaviors, unfortunately, the PD thin layer has low chemical stability against typical chemical cleaning reagents, such as sodium hypochlorite (NaClO).<sup>21–24</sup> In general, it is assumed that the chemical structure of PD is made up of various compounds, including leucodopaminechrome (LDC), dopaminechrome (DC), 5,6-dihydroxyindole (DHI), and 5,6-indolequinone (IDQ), and the PD structure is also kept by both hydrogen bonding and strong hydrophobic interaction, although there is still argument about exact chemical structure of PD.<sup>17,18,21</sup> The LDC and DHI molecules act as proton donors while the DC and IDQ molecules serve as proton acceptors.<sup>17,21</sup> Particularly, the LDC and DHI molecules can be oxidized under a certain oxidation condition whereas the DC and IDQ molecules can be deoxidized under a reduction condition.<sup>17</sup> Accordingly, the PD deposition layers would be decomposed when they are exposed to strong acid or base solutions for a while.<sup>21,22</sup> For instance, the PD coating layer is spontaneously peeled off during the chemical cleaning process using NaClO solution, thus resulting in the significant loss of their excellent



**Figure 2.** Water contact angles of pristine, PD, and XLPEG/PD modified UF membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** SEM images of unmodified and modified membranes. (a) Pristine PVDF membrane, (b) PD modified PVDF membrane, (c) XLPEG/PD modified PVDF membrane, (d) pristine PES membrane, (e) PD modified PES membrane, (f) XLPEG/PD modified PES membrane, (g) pristine PSF membrane, (h) PD modified PSF membrane, (i) XLPEG/PD modified PSF membrane.

antifouling properties caused by their hydrophilicity. Therefore, the chemical stability of PD coating layer should be further improved for membranes for water treatment.

In this study, we proposed a new surface modification based on aqueous dopamine solution by adding poly(ethylene glycol) diacrylate (PEGDA) as a cross-linker to improve the chemical stability against chlorine-containing cleaning reagents frequently used in membrane industry fields. *In situ* crosslinking reaction of PEDGA with PD formation on commercial UF membrane surfaces (e.g., PSF, PES, and PVDF) was performed to protect PD coating layer against chlorine attack and simultaneously to reduce the fouling.

## EXPERIMENTAL

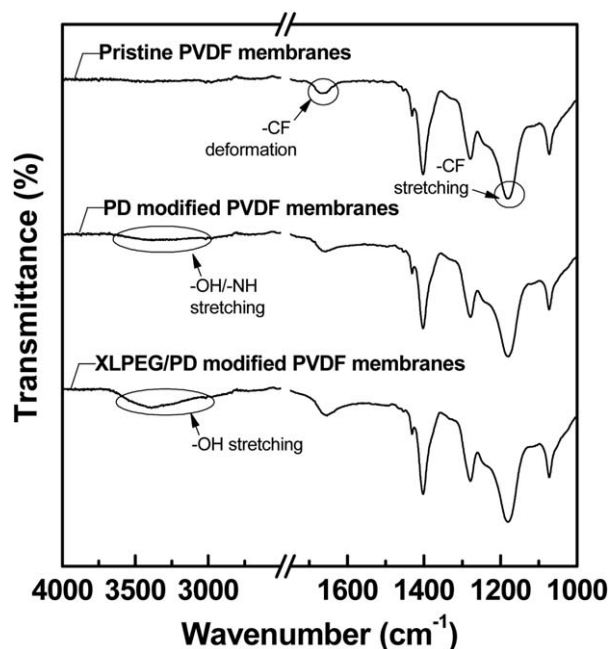
### Materials

Dopamine hydrochloride, trizma hydrochloride (Tris-HCl), potassium persulfate (KPS), poly(ethylene glycol) diacrylate (PEGDA) (number average molecular weight [ $M_n$ ] = 700), and 1-hydroxy cyclohexyl phenyl ketone (HCPK) were purchased from Sigma Aldrich (St. Louis, MO). Hydrochloric acid (HCl)

and sodium hydroxide (NaOH) were purchased from Dae Jung Chemical (Duksan, Gyeonggi-do, South Korea) for pH control. Soybean oil and non-ionic surfactant DC193 were purchased from a local supermarket and Air Products and Chemicals (Allentown, PA), respectively, for oily fouling experiments. NaClO was purchased from Sigma Aldrich for membrane cleaning process. Commercial UF flat-sheet membranes such as PSF (~20 kDa PEG molecular weight cut-off [MWCO]), PES (~20 kDa PEG MWCO), and PVDF (~75 kDa PVA MWCO) were purchased from Sepro Membranes (Oceanside, CA).

### PD and XLPEG/PD Coating on UF Membrane Surfaces

Before surface treatment, all UF membranes used in this study were immersed in isopropyl alcohol (IPA) solution for 10 min, and then the membrane coupons were rinsed with deionized water (DI) for 30 min. For a surface modification, the membranes were taped to the bottom of a glass reactor. For PD coating, dopamine hydrochloride solution ( $2.0 \text{ mg mL}^{-1}$ ) was added into a buffer solution (15 mM Tris-HCl, pH 8.8 buffer). Ultra-high pure  $\text{O}_2$  (purity: 99.995%, injection rate:  $1.0 \text{ L min}^{-1}$ ) was continuously purged into dopamine solution for



**Figure 4.** ATR-FTIR spectroscopy of unmodified and modified PVDF membranes.

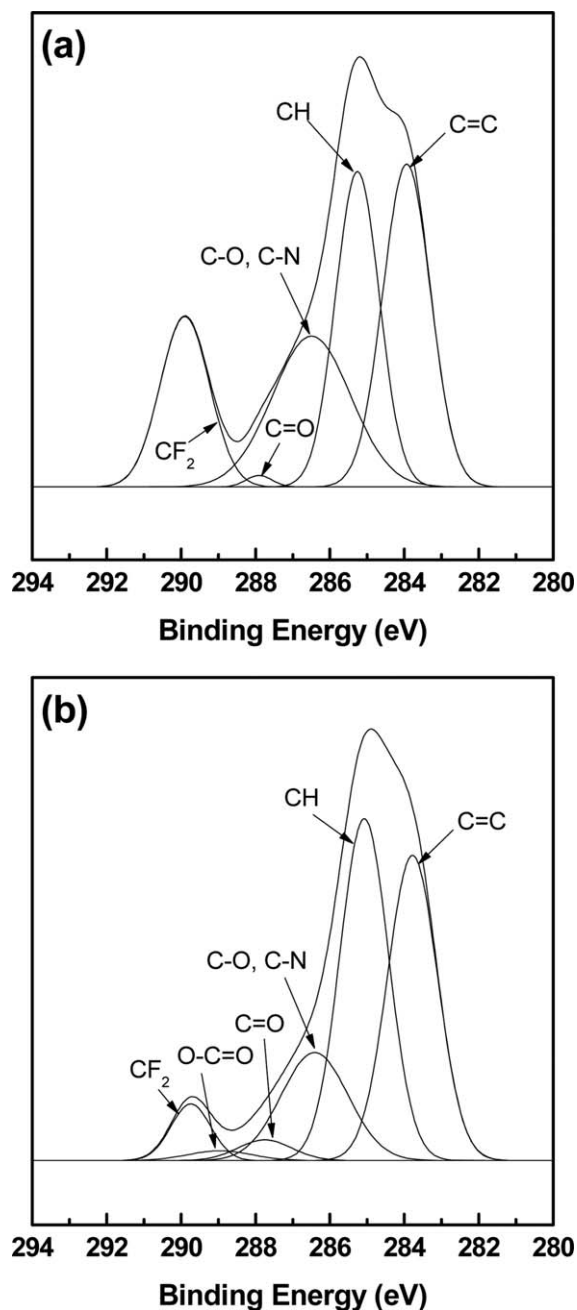
homogeneous and rapid reaction. The solution was slowly stirred at an ambient temperature for 30 min. For XLPEG/PD coating, the membranes in a glass reactor were placed in a heating bath. Before adding dopamine ( $1.0 \text{ mg mL}^{-1}$ ) into buffer solution ( $15 \text{ mM Tris-HCl}$ , pH 8.8 buffer), PEGDA ( $1.0 \text{ mg mL}^{-1}$ ) was dissolved into buffer solution and continuously stirred for 1 h. When the solution placed in a bath was heated to  $70^\circ\text{C}$  for free radical initiation, the dopamine and KPS were immediately dissolved in the heated solution. The mixture solution was slowly stirred for 30 min.

### Membrane Characterizations

**Membrane Surface Characterizations.** For the wettability of modified membrane surfaces, the water contact angle was measured using a Phoenix 300 contact angle analyzer (Surface Electro Optics, Suwon, South Korea). To avoid spreading water quickly, a tip of syringe was fixed as closely as possible to the measuring membrane surface. The values reported in this study are the average and standard deviation of at least five times measurements. To observe the surface-morphological change before and after surface treatment, we primarily used a field emission-scanning electron microscope (FE-SEM) (JEOL, Tokyo, Japan). The membrane coupons were previously coated with platinum for 100 s to avoid electron charging. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet 6700, Thermo Fisher Scientific, MA) equipped with a Smart ARK horizontal ATR was used to analyze the chemical structure of PD and XLPEG/PD coating layers on membrane surfaces. The Smart ARK is an advanced multi-bounce horizontal attenuated reflectance (HATR) accessory, producing 12 reflections with a penetration depth (infrared beam) of  $2.0 \mu\text{m}$ . The spectra were obtained in the range from  $4000$  to  $600 \text{ cm}^{-1}$ , using 64 scans at  $4 \text{ cm}^{-1}$ . Also, the atomic compositions of the modified membrane surfaces were identi-

fied using an X-ray photoelectron spectroscopy (XPS) with a monochromatized Al  $K\alpha$  X-ray source (Quantum2000, Physical electronics, Chanhassen, MN).

**Water Permeance Measurement.** Water permeances through membranes were measured using a cross-flow filtration system equipped with a filtration cell (effective area:  $19.0 \text{ cm}^2$ ) and a Masterflex diaphragm Pump (Cole-Parmer International, East Bunker Court Vernon Hills, IL). The water permeance data were obtained at a feed flow rate of  $1.0 \text{ L min}^{-1}$  ( $Re \sim 1327$ ),



**Figure 5.** XPS spectroscopy of PD and XLPEG/PD modified PVDF membranes. (a) XPS spectra of PD modified PVDF membrane, (b) XPS spectra of XLPEG/PD modified PVDF membrane.

**Table I.** Pure Water Permeances for Unmodified, PD Modified, and XLPEG/PD Modified Membranes

Membranes	Water permeance ( $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ )		
	Pristine	PD modified	XLPEG/PD modified
PVDF	$260 \pm 35$	$280 \pm 30$	$210 \pm 40$
PES	$290 \pm 30$	$340 \pm 35$	$210 \pm 20$
PSF	$650 \pm 55$	$700 \pm 55$	$610 \pm 55$

Membranes were coated using an aqueous dopamine solution for 30 min at 25°C and an aqueous dopamine and PEGDA mixture for 30 min at 70°C.

at applied feed pressure of 1.0 bar, and at 25°C. The water permeance ( $J_w$ :  $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ ) was calculated as follows:

$$J_w = \frac{\Delta m}{\rho \cdot A \cdot \Delta t \cdot \Delta P}, \quad (1)$$

where  $\Delta m$  is the permeate weight during the filtration time  $\Delta t$ ,  $\rho$  is the density of water at 25°C,  $A$  is the membrane area ( $19.0 \text{ cm}^2$ ), and  $\Delta P$  is the applied feed pressure (1.0 bar).

For fouling experiment, emulsified oil was prepared by blending 0.50 g DC193 (as a surfactant) and 4.5 g soybean oil in 3 L of DI, using a laboratory blender at a high speed (3000 rpm) for 10 min. Also, the oily water fouling test was performed using a cross-flow filtration equipment. Organic rejection was calculated as follows:

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

where  $R$  is rejection (%),  $C_p$  is the organic concentration in the permeate, and  $C_f$  is organic concentration in the feed.  $C_p$  and  $C_f$  were measured using a total organic carbon analyzer (TOC multi N/C 3100, Analytik JENA, Germany). For chlorine resistance evaluation, the membrane fouling experiments (for 10 min) and chemical cleaning processes (for 1 min) were repeated in a certain period. NaClO (1.0 wt %) was used for a chemical cleaning reagent.

#### Analysis of PD and XLPEG/PD Particles

To check the chemical stability of PD and XLPEG/PD, Fourier transform infrared (FTIR) spectra were measured using a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, MA) in the range  $4000\text{--}750 \text{ cm}^{-1}$ . PD and XLPEG/PD particles in the reacted solution were collected by vacuum filtration method. PD and XLPEG/PD particles were treated by 5.0 wt % NaClO solution for 30 min.

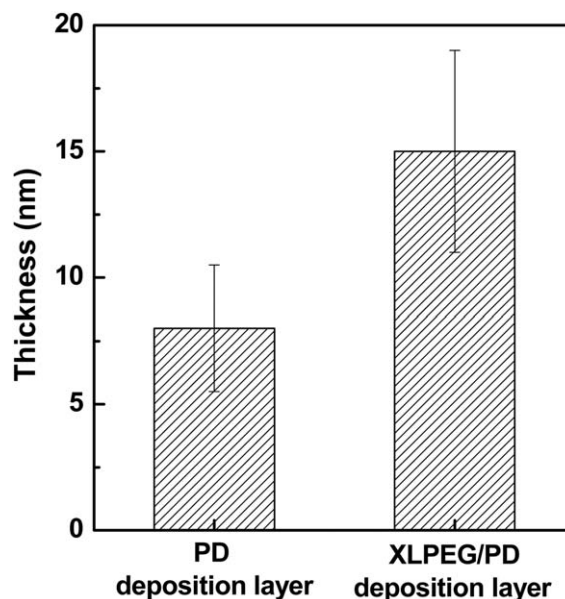
## RESULTS AND DISCUSSION

### Surface Properties of Unmodified and Modified UF Membranes

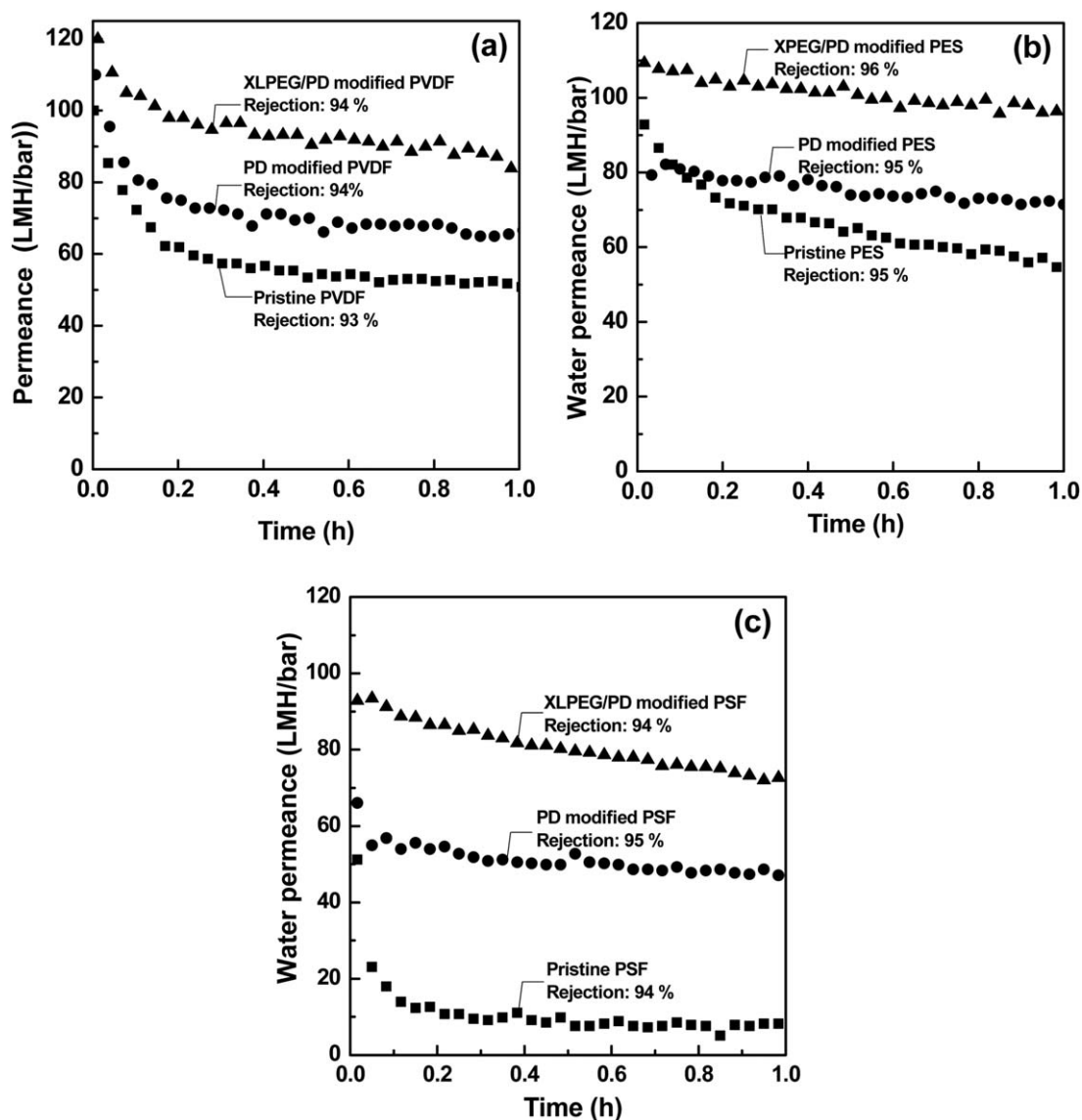
Using dopamine solution and PEGDA/dopamine mixture solution, respectively, the surface modification was performed on the UF membrane surfaces. Figure 1 illustrates the proposed chemical structure of crosslinked PEG (XLPEG)/PD obtained from PEGDA/dopamine solution. After the surface treatment, we measured the water contact angle of unmodified and modified membranes to evaluate the change of surface wettability. As shown in Figure 2, the water contact angles of PD modified

membranes were in the range of 40–55°, which are similar values of other PD-modified membranes in the literature.<sup>3,8</sup> That is, all membrane surfaces in this work were successfully modified by aqueous dopamine solution. Conversely, the water contact angles of XLPEG/PD modified membranes were slightly lower than those of only PD modified membranes (below 40°). According to previous study, the water contact angle of dense XLPEG membrane (i.e., hydrogel state) can be affected by the prepolymerization water content of PEGDA.<sup>15</sup> For example, the water contact angles of dense XLPEG membranes were decreased from 60 to 40° as the prepolymerization water content of PEGDA solution was increased from 0 to 80 wt %. That is, the water contact angle was gradually decreased with increasing prepolymerization water content,<sup>15</sup> because the existing water molecules in prepolymerization solution act as a hindrance for effective formation of crosslinking network.<sup>15,25</sup> Based on these results, a low water contact angle of XLPEG/PD modified membranes might be mainly due to the incorporation of less-crosslinked hydrophilic PEG chains in PD structure and the existence of water molecules and various dopamine derivatives in mixed solution, this leading to more hydrophilic surface properties than both pristine PD modified membrane surface and only dense XLPEG dense membrane.

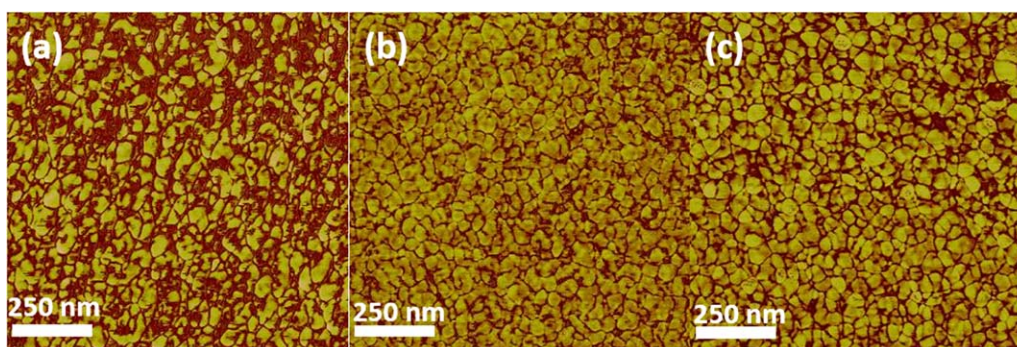
Morphological changes in membrane surface can give a clue to decide whether the membrane surfaces were successfully modified or not. Figure 3 presents the membrane surface images of modified and unmodified membranes. Pristine membranes exhibited the typical surface images of UF membranes, indicating that the pores of about 50 nm are dispersed through the entire membranes surface. However, the pores disappeared after the surface modifications, meaning that the membrane surfaces were well-covered with PD or XLPEG/PD layers. As expected, the PD modified membranes showed more homogeneous surface morphologies as a high oxygen concentration supplied in dopamine solution led to much smoother surface morphologies



**Figure 6.** Coating layer thickness of PD and XLPEG/PD-coated PSF membrane measured by ellipsometry.

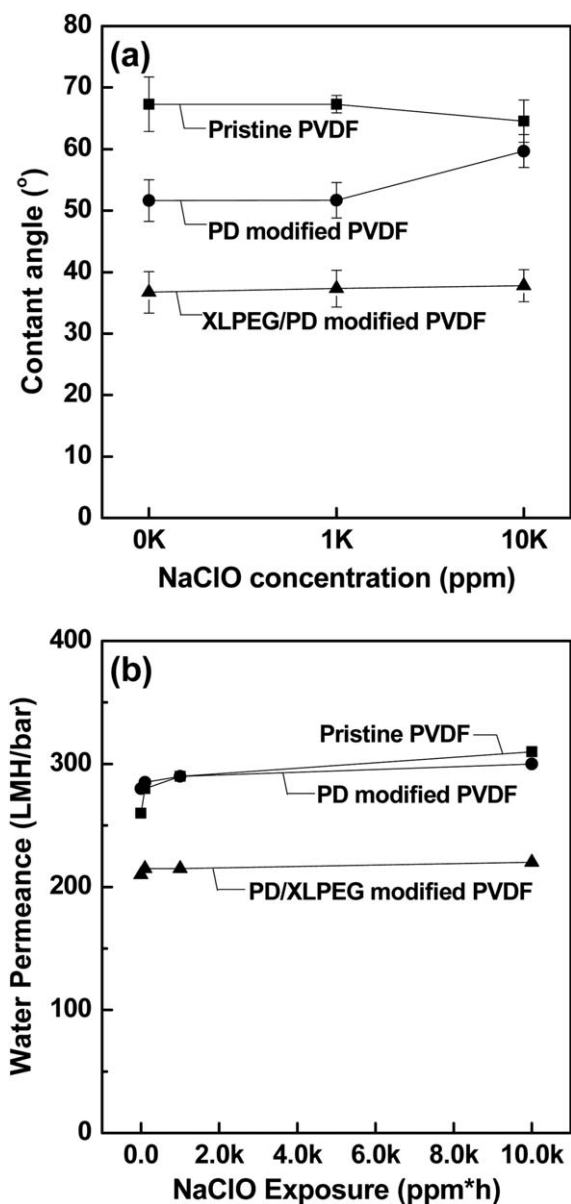


**Figure 7.** Oily emulsion separation performance on pristine and modified UF membranes. (a) Pristine and modified PVDF membranes, (b) pristine and modified PES membranes, (c) pristine and modified PSF membranes. Experimental conditions: applied pressure, 1.0 bar; temperature, 25°C; soybean oil concentration, 1000 ppm; flow rate, 1.0 L min<sup>-1</sup> ( $Re \sim 1327$ ).



**Figure 8.** AFM phase images of unmodified and modified PES membranes. (a) Pristine PES membrane, (b) PD modified PES membrane, and (c) XLPEG/PD modified PES membrane. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 9.** Chlorine stability experiments. (a) Water contact angle of unmodified and modified membranes as a function of NaClO concentration, (b) water permeances of unmodified and modified membranes as a function of NaClO concentration.

by aid of the accelerated dopamine reaction kinetics.<sup>17</sup> By considering that the less-crosslinked PEG chains are intermingled in the PD structure, we expected that the addition of these PEG chains might influence the surface morphologies of the XLPEG/PD-coated membranes. However, unexpectedly, the surface morphologies of the XLPEG/PD modified membranes were similar to that of only PD modified membrane. As a result, XLPEG/PD layers were also homogeneously coated on the UF membranes. Also, this effective coating of XLPEG/PD is mainly attributed to the instinct adhesion of hydrophilic PD. Namely, PDs are a primary coating material in XLPEG/PD coating on the membrane surfaces, and PEG chains act as a more stable coating layer by covalent bonding between PD molecules and

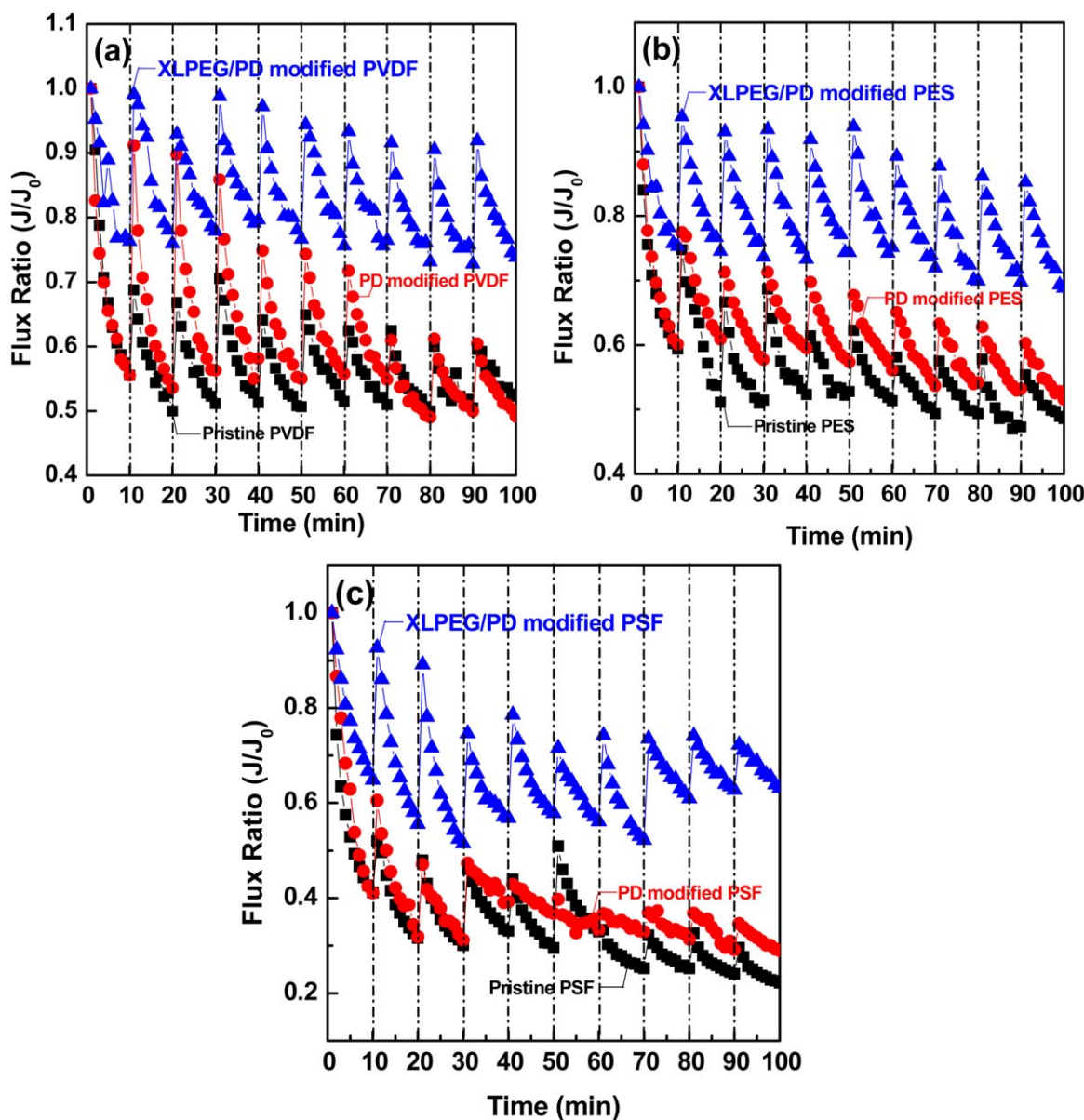
PEG chains. It should be noted that XLPEG coating did not occur on hydrophobic UF membrane surface in the absence of dopamine in the solution state because of the repulsive force between hydrophilicity of XLPEG and hydrophobic membrane surfaces.

To see the evidence of the covalent bonding between PD and PEG chains, we performed the ATR-IR and XPS measurements. For these measurements, we used PVDF membrane as a substrate rather than PSF and PES membranes because PVDF consists of C, F, and H, so it was easy to distinct the characteristic peaks from the bonding between PD and XLPEG from those of substrates. Figure 4 shows characteristic absorption bands of modified and unmodified PVDF membranes in an ATR-FTIR mode. For pristine PVDF membranes, there are characteristic absorption bands corresponding to  $-\text{CF}_2$  deformation and stretching vibration at 1400 and 1182  $\text{cm}^{-1}$ , respectively. After PD coating on PVDF membranes, the weak and broad absorption bands of  $-\text{OH}$  and  $-\text{NH}$  stretching vibration appear at 3000–3500  $\text{cm}^{-1}$ .<sup>17</sup> Conversely, for XLPEG/PD modified PVDF membranes, the markedly strong and broad absorption band of  $-\text{OH}$  stretching appears at 3000–3500  $\text{cm}^{-1}$ , indicating that PEG moieties are well-incorporated into PD structure.

Figure 5 represents the XPS C1s core-level spectra of PD and XLPEG/PD modified PVDF membranes. The XPS C1s core-level spectrum of PD modified PVDF membranes can be classified into five peaks components with binding energies at 284.0, 285.5, 286.5, 288.0, and 290.0 eV attributed to  $\text{C}=\text{C}$ ,  $\text{C}-\text{C}$ ,  $\text{C}-\text{N}$ ,  $\text{C}=\text{O}$ , and  $\text{C}-\text{F}$ , respectively.<sup>9,26</sup> For XLPEG/PD modified PVDF membranes, the C1s spectra signal at 289.0 eV corresponding to the carbon in  $\text{O}-\text{C}=\text{O}$  newly appears due to the presence of XLPEG chain in a mixed coating layer.<sup>27</sup> Also, the intensity of  $\text{C}=\text{C}$  peak for XLPEG/PD-coated PVDF membranes slightly decreases as compared with that of the pristine PD-coated PVDF membranes. Hence, XLPEG chains in XLPEG/PD coating layers might be covalently linked with aromatic carbon in PD molecules.

### Oily Fouling Behaviors Through Unmodified and Modified UF Membranes

Generally, water transport through the modified UF membranes is strongly affected by the coating thickness.<sup>7</sup> Most approaches for hydrophilic surface treatments suffer from severe water flux decline mainly due to its thick coating layer,<sup>15,25</sup> although the surface modified membranes exhibit the improved fouling resistances. For instance, XLPEG-coated PSF UF membranes represented significantly improved fouling resistance against oily feed water while the membranes showed relatively low water permeance due to micrometric coating thickness. That is, the water permeance of XLPEG-coated PSF membranes (coated by Knife casting) was significantly decreased at about 75% as compared with that of pristine PSF membranes.<sup>25</sup> The water permeance of PD modified membranes also was gradually decreased as the thickness of PD coating was increased.<sup>7</sup> Therefore, it should be necessary to control the surface coating time to avoid the severe decline of original high water flux and also to obtain the



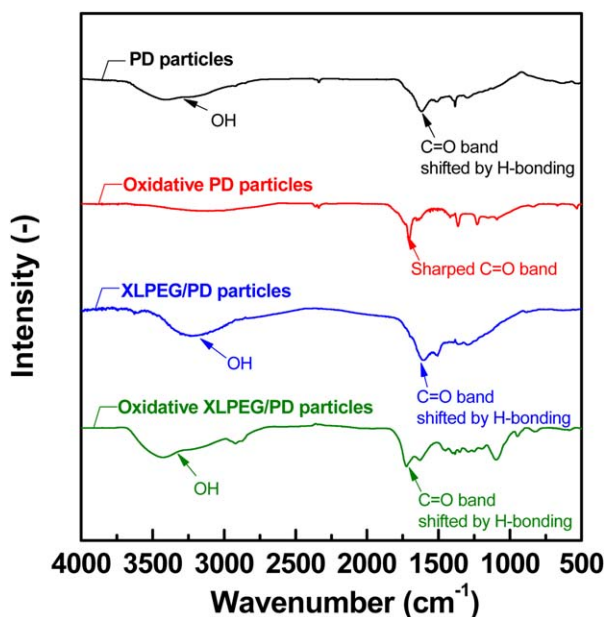
**Figure 10.** Repetitive oily emulsion separation and NaClO cleaning processes on pristine, PD, and XLPEG/PD-coated membranes. (a) PVDF membranes, (b) PES membranes, and (c) PSF membranes. Experimental conditions: applied pressure, 1.0 bar; temperature, 25°C; soybean oil concentration, 1000 ppm; flow rate, 1.0 L min<sup>-1</sup> (Re ~ 1327), NaClO concentration, 1000 ppm; soaking time, 1 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

improved fouling tolerant properties for surface modified UF membranes.

As listed in Table I, the water permeance of PD-modified UF membranes was much higher than that of the pristine UF membranes, if the coating time can be properly controlled. This phenomenon was also observed in the PD-modified MF membranes having relatively larger pore sizes than UF membranes.<sup>8</sup> For example, after the surface treatment by PD coating, even highly hydrophobic MF membrane (e.g., PTFE) showed much increased water permeances than the pristine membranes due to the increased wettability and more pore opening. That is, the enhanced wettability of PD modified membranes can overcome the mass transfer resistance due to

the increase of PD coating thickness. Owing to relatively large pore size of MF membranes, it is difficult to be fully covered with PD coating, which leads to negligible mass transfer resistance. However, the pore sizes of UF membranes are relatively lower than those of MF membranes. Moreover, the PD-modified UF membranes show more homogeneous membrane surface due to the accelerated PD reaction kinetics.<sup>7,8</sup> Therefore, the enhanced water permeances of modified membranes are caused by ultrathin PD coating layer as well as increased hydrophilicity.

XLPEG/PD modified membranes showed slightly lower water permeance than pristine and PD modified membranes. However, the reduction ratio of water permeance in XLPEG/PD



**Figure 11.** FTIR spectroscopy of pristine PD, oxidative PD, pristine XLPEG/PD, and oxidative XLPEG/PD particles. Oxidation process is followed that PD and XLPEG/PD particles are dissolved for 1 min under 5000 ppm of NaClO solution and then the oxidative PD and XLPEG/PD particles are dried at 80°C under vacuum oven for 24 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

modified membranes is significantly low, as compared with that of conventional XLPEG-coated membrane.<sup>15,25</sup> For instance, the pure water permeances in the XLPEG coated and uncoated PSF membranes were 36 and 141 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, respectively.<sup>15</sup> The significant reduction of pure water permeance in the XLPEG-coated membranes was largely due to micron-thick XLPEG coating layer.<sup>15</sup> Conversely, the water permeances of XLPEG/PD modified PSF membranes were decreased to approximately 15% as compared with that of pristine PSF membranes (Table I). The relatively low water permeance decline in such membranes is mainly caused by the nano-thick XLPEG/PD deposition layer. These ultrathin characters in XLPEG/PD deposition are attributed to surface modification properties based on the PD deposition. To estimate the coating thickness, we measured the thickness of PD and XLPEG/PD coated on silicon wafer using an ellipsometry. The thickness of PD coating is about 5–10 nm, which is good agreement with literature,<sup>7</sup> and XLPEG/PD becomes slightly thicker, as shown in Figure 6. As such, the effective thickness of XLPEG/PD coating is at around 15 nm, indicating that lower water permeances of XLPEG/PD-coated membranes are primarily caused by increasing coating thickness, as compared with PD-coated membranes.

In general, PD or XLPEG surface modifications are an easy technique for improved anti-fouling properties owing to their hydrophilic properties.<sup>15,17</sup> To estimate the membrane fouling, we studied the separation performance of oil/water emulsion (1500 ppm) for uncoated and coated UF membranes using cross-flow filtration. As shown in Figure 7, the pristine membranes are more susceptible to fouling while the PD-coated UF

membranes exhibited the outstanding fouling resistant properties, maintaining their excellent rejections for oil/water emulsion. Particularly, XLPEG/PD-coated UF membranes also showed much higher fouling tolerance for oily water than PD-coated UF membranes. For example, the water permeances of XLPEG/PD-coated PSF membranes are approximately improved by 160 and 800%, as compared with PD coated and pristine PSF membranes, respectively. This enhancement of water permeance in XLPEG/PD-coated UF membranes in the oily feed water comes from excellent fouling tolerance due to the improved surface hydrophilicity, as compared with PD coated and pristine PSF membranes. Interestingly, the water permeances of XLPEG/PD-coated UF membranes showed the highest values among the membranes used in this study, although the pure water permeance of XLPEG/PD-coated UF membranes had the lowest values of all the membranes used in this work.

We measured the surface roughness of the uncoated and coated membranes using AFM. As shown in Figure 8, the PD-coated PSF membrane shows much smoother surface, as previously reported,<sup>17</sup> while the XLPEG/PD-coated PSF membrane has relatively rougher surface. That is, root mean squared roughness ( $R_q$ ) and average roughness ( $R_a$ ) in PD coating layer are about 2.46 and 1.96 nm, respectively, while the  $R_q$  and  $R_a$  in XLPEG/PD coating layer are about 5.29 and 3.39 nm, respectively, which are similar to the surface roughness of pristine PSF membranes. From these results, the improvement of water permeance in XLPEG/PD-coated membranes is mainly caused by loose network structure due to the incorporation PEG chains into PD structure and enhanced wettability over the membrane surfaces.

#### Chlorine Tolerance of PD and XLPEG/PD Layers

Although the PD and XLPEG/PD-coated membranes represent the outstanding fouling tolerant properties, these membranes also suffer from reversible and irreversible fouling during the long-term permeation experiments. To remove the reversible and irreversible foulants, membrane industry widely uses physical and chemical cleaning processes.<sup>13,24</sup> For chemical cleaning processes, sodium hypochlorite (NaClO) is the most widely used chemical cleaning agent as it is relatively inexpensive and highly effective.<sup>23,24,28</sup> Unfortunately, the PD coating layer tends to be continuously decomposed when it exposes to NaClO solution.<sup>22</sup> This situation might be due to its nature of network structures based on secondary forces such as hydrophobic interaction and hydrogen bonding.<sup>11,21</sup> Hence, only PD coating on membrane surface may not be proper for practical applications despite many advantages. Conversely, only XLPEG modified membranes generally show outstanding fouling-tolerant and chlorine-resistant properties.<sup>15</sup> However, this method suffers from considerable flux decline due to its thick coating layer,<sup>15</sup> which is a main hurdle for practical application for membrane-based water treatments.

Owing to the presence of covalent bonding on XLPEG/PD deposition layer, we considered that the XLPEG/PD deposition layers might be stronger against chemical attack as compared with PD deposition layers. The chemical cleaning experiments were also performed by immersing the modified membranes in

aqueous buffer solutions of NaClO at the concentrations of 10, 100, and 1000 ppm, respectively. Then, the water contact angle and pure water permeances were measured.<sup>29</sup> For PD-coated membranes, the water contact angle was gradually increased up to 50–65° with increasing the exposure time of NaClO cleaning solution, meaning that the PD coating layer was continuously detached from membrane surface, as shown in Figure 9(a). In contrast, the water contact angle of XLPEG/PD-coated membranes was still constant even with increasing exposure time of cleaning solution. Also, the water permeances through PD-coated membranes started to change after NaClO treatment while the water permeances through XLPEG/PD-coated membranes were kept constant even to high exposure to NaClO concentration, as shown in Figure 9(b).

We also performed oil/water emulsion fouling experiment with repetitive NaClO cleaning process in a period. Oily water fouling experiment was maintained for 10 min, and then immediately chemical cleaning process using 1000 ppm NaClO solution was performed for 1 min. This process was repeated several times. After cleaning treatment, the recovery ratio of original water permeance was measured in the case of both the pristine and modified membranes, as shown in Figure 10. The recovery ratio of pristine and PD-coated membranes was gradually decreased as the number of chemical cleaning processes were increased, reflecting that PD coating was detached or decomposed on membrane surfaces. Oppositely, XLPEG/PD-coated membranes maintained their water permeance, although the recovery ratio of water permeance in XLPEG/PD-coated membranes was slightly decreased with repeated chemical cleaning treatment. For instance, PD-coated PVDF membranes show a large reduction of water permeance with repeated cleaning treatment, while the XLPEG/PD modified PVDF membranes keep their water permeance trace even with repeated chemical cleaning treatment. This outstanding chemical resistance of XLPEG/PD coating layers is primarily due to the chemical bonding between PD and PEG chains, which was also supported by XPS results.

We also conducted XLPEG/PD modification by changing the concentration ratio of these materials to find optimal conditions. As the PD coating provides the ultrathin and versatile coating properties and the XLPEG modification contributes to the improved chlorine resistance, the membrane performances including water flux and chlorine resistance strongly depended on surface modification conditions such as the dopamine/PEGDA concentration ratio. For example, increasing PEGDA concentration ratio leads to low water flux while decreasing PEGDA concentration ratio results in poor chlorine resistance. Thus, we found that the concentration of dopamine (1.0 g L<sup>-1</sup>) and PEGDA (1.0 g L<sup>-1</sup>) is the optimal conditions to show the improved chlorine tolerant properties and reasonable water flux reduction.

Recently, Frari group investigated on the decomposition mechanism of PD coating layer using strong oxidizing agents such as NaClO by means of cyclic voltammetry.<sup>22</sup> They concluded that the degradation of PD deposition in the presence of NaClO is mainly caused by the transition of oxidative materials such as dopaminochrome and 5,6-indolequinone, confirmed by XPS. Based on this result, we also evaluated the chemical resistance

of PD and XLPEG/PD materials using 5000 ppm of NaClO solution. Figure 11 represents the FTIR spectra of both PD and NaClO treated PD particles. For PD particles, there are characteristic absorption bands of —OH vibration at 3211 cm<sup>-1</sup> with broad band, C=O vibration at 1604 cm<sup>-1</sup>, which is slightly shifted by hydrogen bonding (interactions between primary alcohol and carbonyl).<sup>9</sup> Also, the weak absorbance peaks appear at 3616 cm<sup>-1</sup> and 1515 cm<sup>-1</sup> for N—H stretching vibration.<sup>9</sup>

In PD particles treated by NaClO solution, the strong absorption band of C=O stretching at around 1705 cm<sup>-1</sup> appears while the absorption bands of —O—H vibration at 3211 cm<sup>-1</sup> are significantly reduced. Also, the carbonyl peak is shifted from 1612 to 1705 cm<sup>-1</sup> which implies that hydrogen bonding is cleaved by the oxidative reaction of PD.<sup>22</sup> The reaction between hypochlorite ions and PD particles changes from proton-donating compounds such as LDC and DHI to proton-accepting compounds such as DC and IDQ.<sup>17,30</sup> As a result, an increase in oxidative molecules leads to looser PD network structures by breaking hydrogen bonding due to the lack of hydrogen donor groups.<sup>11,21</sup>

For XLPEG/PD sample, the characteristic absorption bands of typical PD and PEGDA are observed, such as —O—H vibration at 3339 cm<sup>-1</sup>, C=O stretching at 1721 cm<sup>-1</sup>, N—H vibration at 1592 cm<sup>-1</sup> for PD particles, and C—O bending at 1080 cm<sup>-1</sup>, C—H stretching at 2863 cm<sup>-1</sup>, C—H bending or scissoring at 1475 cm<sup>-1</sup>, and C=C bending at 946 and 836 cm<sup>-1</sup> for XLPEG material, respectively.<sup>31,32</sup> Interestingly, XLPEG/PD samples maintained its characteristic absorption bands after NaClO treatment, indicating that XLPEG/PD structures have stronger chemical resistance than pristine PD particles. Such structural stability leads to enhanced chemical resistance against strong cleaning agents.

## CONCLUSIONS

We developed a facile and universal membrane surface modification method showing both excellent antifouling behavior and chemical stability against chlorine attack. The PD and XLPEG/PD modified UF membranes showed outstanding water permeances and fouling tolerance during oil emulsion filtrations. Also, the XLPEG/PD coating layers are highly robust and stable structures, as well as improved hydrophilic properties than the PD coating layers, owing to the incorporation of less crosslinked PEG chains into PD structure. The surface treatment using ultrathin XLPEG/PD coating will be promising for membranes for water treatment.

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