

ENHANCING HYDROPHILICITY OF POLYSULFONE MEMBRANE SURFACE BY UV IRRADIATION OF DIFFERENT WAVELENGTHS AND BY PEG GRAFTING

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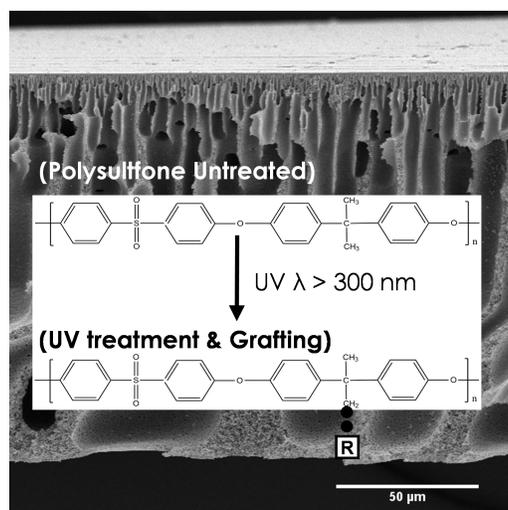
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Graphical abstract



Abstract

Polysulfone polymer (PSF) membrane has disadvantages due to its hydrophobicity, which may cause fouling and reduce separation performance. Therefore, this study aimed to enhance the hydrophilicity of PSF membranes by using irradiation at different ultraviolet (UV) wavelengths, followed by Poly(ethylene glycol) (PEG) grafting on the PSF surfaces. The hydrophilicity of the treated membrane surfaces was examined by measuring water contact angle (WCA), surface energy (SE), surface morphology, functional groups, salt rejection, and water flux in a filtration instrument. The results show that with long UV treatment for up to 72 h, the 312 nm wavelength gave lesser WCA than treatment at 254 nm. The treated PSF membrane irradiated at 312 nm for 72 h, followed by PEG grafting, was effectively improved and retained increased hydrophilicity for up to thirty days.

Keywords: UV treatment, PEG-grafting, Surface modification, hydrophilicity, polar component

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1.0 INTRODUCTION

Membrane technology is pervasive in the industry. Polysulfone (PSF) has been widely used as a polymer in the commercial production of microfiltration and ultrafiltration membranes, due to several advantages, such as good mechanical, chemical, and thermal properties, and easy film-forming [1, 2]. However, PSF membranes tend to have severe fouling during filtration due to natural hydrophobicity, low surface energy, and non-ionic character [3]. The membrane surface properties play a key role in the interactions

with atoms or molecules or other active particles. Many polymers that have been used in membranes are hydrophobic with a low surface energy, such as poly(ethylene terephthalate) (24.2 mN/m), poly(propylene) (29.5 mN/m), and poly(vinylidene fluoride) (42-47 mN/m) [4,5]. If the membrane surface is hydrophilic with a high surface energy, this reduces fouling due to electrostatic repulsion of other molecules from the membrane surface [6]. Several methods have been used in many studies to improve membrane surface energy, such as coating with a hydrophilic polymer for increased hydrophilicity of

the PSF membrane [7], or by blending in hydrophilic or organic materials or some minerals [8, 9]. Physical treatment with plasma is a popular technique due to its high efficiency. However, the weakness of this technique is that it still requires a low-pressure system for processing [10, 11]. Ultraviolet (UV) irradiation is another technique that is in widespread use to improve the surface properties, because it can work at atmospheric pressure and can change membrane surface properties without adverse influence on the bulk properties [12]. UV light can generate free radicals on the membrane surfaces by cutting chemical bonds of atoms or molecules. A PSF membrane surface irradiated with UV followed by Poly(ethylene glycol)(PEG) grafting was found to have enhanced charge density and pure water flux [13]. Many studies have used PEG as a membrane component to solve the problem of free radical disintegration on the membrane surfaces, which causes reversal back to hydrophobicity, because PEG is hydrophilic with flexible chains. However, it is difficult to put PEG on the membrane surfaces due to its poor mechanical and thermal properties. So, PEG grafting with UV light assistance has been studied to address these problems. The high-energy UV irradiated PSF membrane surfaces can struggle for balance between crosslinking and chain scission, causing a decreased water flux [14]. The membrane grafted with UV assistance was found to have improved antifouling performance [15]. The mechanism of polymer membrane improvement can be described as follows. In the first step, high-energy UV light generates free radical polymers. After that, the radical species will interact with other functional materials in the second step. The further interactions in the second step and the interactions between particles in the second step along with other functional materials continues until saturation [16].

The natural UV-rays have a wide wavelengths range (200-400 nm) and each wavelength has a different quantum energy [17]. So, irradiation by different UV wavelengths for different treatment times can provide different surface properties. Such factors may affect PEG grafting on the membrane surface with UV assistance. So, this investigation studied the effects of different UV-ray wavelengths and treatment times for improving hydrophilicity properties of PSF membranes by grafting with PEG, and studied the permanence or longevity of the hydrophilicity improvement.

2.0 METHODOLOGY

Polysulfone (PSF) Udel P-1700 as pellets was supplied by Solvay (China). Polyvinylpyrrolidone (PVP, K30) and Poly (ethylene glycol) (Mw 8,000) (PEG) were purchased from Sigma-Aldrich, while N-Methyl-2-Pyrrolidone (NMP) was supplied by ACI Lab-scan (Thailand). Sodium chloride (NaCl) was purchased from Ajax Finechem.

The dope solution for this work was prepared by mixing 17.5 wt% PSF, 0.5 wt% PVP and 82 wt% NMP. The PSF pellets were dried at 80 °C for 24 h in a vacuum oven (BINDER, VD53) before use. To prepare the dope solution, PVP and NMP were mixed in a beaker before stirred for 10 min with a magnetic stirrer. Then, PSF pellets were added into the solution under vigorous stirring for 24 h. After that, the solution was ultra-sonicated in an ultrasonic cleaner (GT SONIC, VGT-1620T) for 30 min to remove any bubbles. Subsequently, the free bubble dope solution was cast on a smooth clear glass plate followed by instantaneous immersion in reverse osmosis (RO) water coagulation bath at room temperature (23 °C) for wet phase inversion, to form a wet thin membrane. After peeling off from the glass plate, the membrane was placed in a second RO water bath and was soaked for 24 h to remove the solvent. Afterwards, the membrane was desiccated in ambient conditions for 24 h and dried in a vacuum oven at 70°C for 24 h before use.

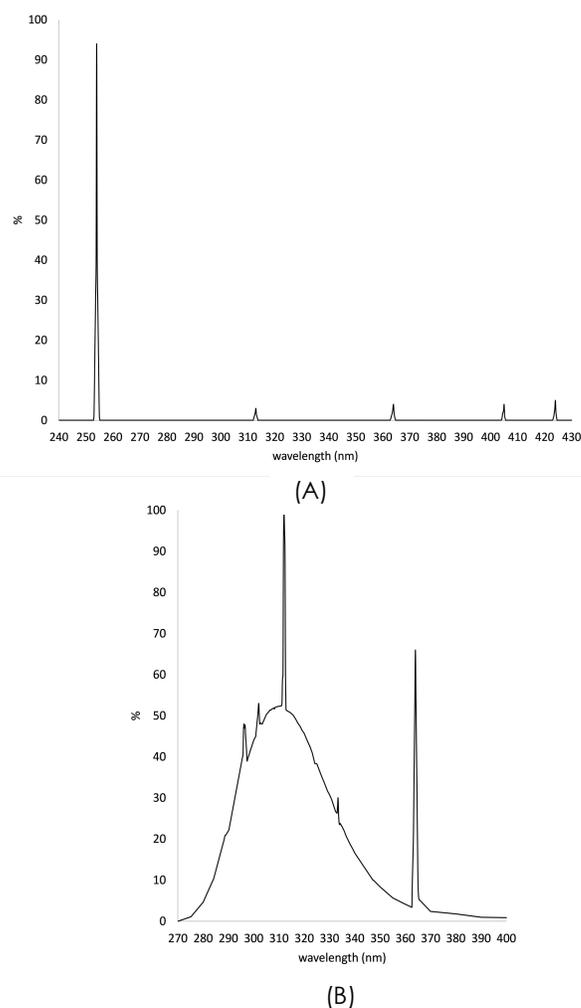


Figure 1 The spectra of UV sources for (A) 254 nm, and (B) 312 nm nominal wavelengths

The optimized membrane surface was irradiated by UV radiation in the ambient atmosphere ($25 \pm 2^\circ\text{C}$ and 60–65% relative humidity, measured by Traceable Digital Thermohygrometer, Cole-Palmer (Thailand)). The sample membranes were exposed to UV source (15W-254 nm or 15W-312 nm, Vilber Lourmal, VI-215. MC (France)) for different conditions shown in Table 1 while the distance between the membrane sample and the UV source was kept fixed at 20 cm. The spectrum of UV source for this experiment was characterized by using a laser power meter, Coherent Inc.; GES-UM2, shown in Figure 1A and 1B [18]. After the UV treatment, the membrane was immersed in PEG solution (1.0 wt%) for 3 h. After that, the treated membrane was soaked in RO water for 24 h before drying in ambient air at room temperature for 12 h before testing. After treatment process was complete, the first set of the treated membrane was verified by measuring WCA and the other set of dry membranes was retained in ambient air at temperature of 23–25 °C and relative humidity of 66 – 68 % for 30 days before testing

Table 1 The conditions of UV treatment membrane

| Condition | | 5 h | 10 h | 24 h | 48 h | 72 h |
|-----------|--------|-----|------|------|------|------|
| UV 254 nm | No PEG | A5 | A10 | A24 | A48 | A72 |
| | PEG | B5 | B10 | B24 | B48 | B72 |
| UV 312 nm | No PEG | C5 | C10 | C24 | C48 | C72 |
| | PEG | D5 | D10 | D24 | D48 | D72 |

The morphology of the treated membrane was investigated on top side, bottom side and in a cross-section by using a Scanning Electron Microscope (SEM, JSM-5800 LV). The hydrophilicity of the treated membrane was examined by measuring the water contact angle (WCA) and the surface energy (SE). The measurement of contact angle was done with three types of liquid: water, Formamide and Ethylene glycol with known γ^p (polar component) and γ^d (dispersive component). The SE was calculated with Equation (1) [19, 20].

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_L^d \cdot \gamma_S^d)^{1/2} + 2(\gamma_L^p \cdot \gamma_S^p)^{1/2} \quad (1)$$

The functional groups on the PSF membrane surface were assessed by using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Bruker, Hyperion 3000).

Before membrane testing, the membrane was immersed in water for 1 hour. After that, the reverse osmosis water was forced through each treated membrane in a cross-flow process at 0.1 MPa to characterize the water flux ($\text{L m}^{-2} \text{h}^{-1}$) using Equation (2) [9, 21].

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

Here V is the volume of the filtrate (L or dm^3), A is the practicable area of the membrane (m^2) and t is the testing time (h).

The rejection rate was also used to assess the treated membrane properties after 30 min of filtration. The conductivities of permeate and feed solution were measured by using Eutech Instruments, Syberscan PC300 (Singapore). The rejection ratio (R) was calculated according to Equation (3).

$$R(\%) = 1 - \frac{C_p}{C_f} \times 100\% \quad (3)$$

Here C_f and C_p are the Sodium chloride (NaCl) concentrations of permeate and feed solution (1 molar), respectively.

3.0 RESULTS AND DISCUSSION

The hydrophilicity properties of the variously treated PSF membranes were examined by measuring WCA and SE, with results shown in Figure 2. For the treatment times from 0 to 10 h, WCA after treatment at UV wavelength 254 nm (UV254) was lower than after treatment at 312 nm (UV312), as shown in Figure 2(A). This means that for treatment times shorter than 10 h, the hydrophilicity with UV254 was better than with UV312. However, for treatment times exceeding 10 h, the WCA with UV312 was less than that with UV254: for comparatively long treatments up to 72 h, the hydrophilicity with UV312 was better than with UV254, as shown in Figure 2(A).

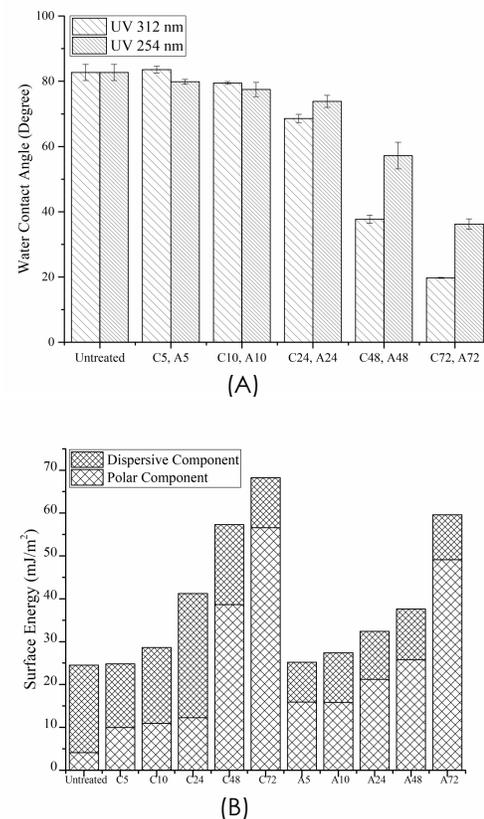


Figure 2 The water contact angles (A), and surface energies (B) of membranes treated with UV254 and UV312 for various treatment times (without PEG grafting)

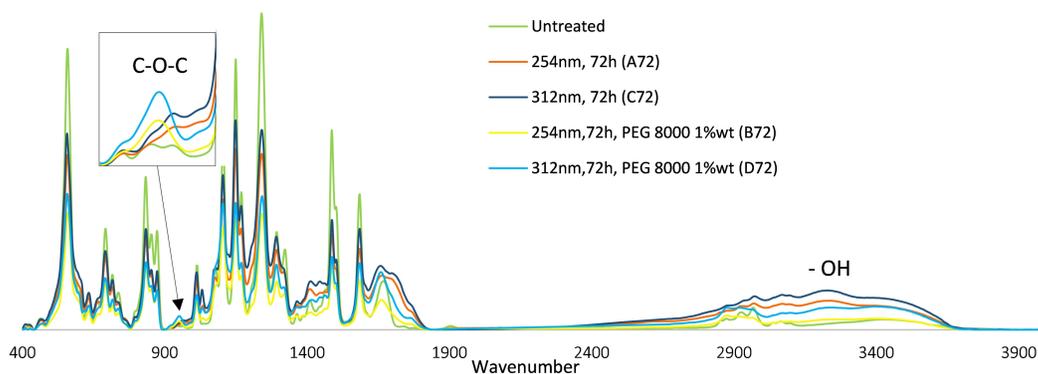


Figure 3 The FTIR spectra of membranes treated for 72 h with UV254 or UV312, with or without grafted

Furthermore, the membrane surface energies matched the WCA results. After UV treatment for 72 h, the SE with UV254 and UV312 treatments had increased from 27.7 mJ/m² for untreated membrane to 68.2 and 59.9 mJ/m², respectively. In addition, the surface energy consists of a dispersive component that represents non-polar forces between non-polar molecules and of a polar component related to the bonding forces between polar molecules. An increased polar component for the treated membrane can indicate improved membrane surface wettability [22, 23].

After UV treatment for 72 h, the polar component of the membrane surface increased from 4.1 mJ/m² for untreated to 49.1 mJ/m² and 56.6 mJ/m² for UV254 and UV312 treated membranes, respectively, shown in Figure 2B. So, for a long treatment time of up to 72 h, the hydrophilicity and surface energy of membranes treated with UV312 were better when treated with UV254. However, for short treatment times of less than 10 h, the hydrophilicity and surface energy with UV254 were better than with UV312. The hydrophilicity of PSF membrane surface may come from the hydroxyl groups that were confirmed by FTIR, as shown in Figure 3. The intensity of the hydroxyl (-OH) groups in FTIR results (3,100 – 3,600 cm⁻¹) was higher after UV312 treatment (dark blue line) than after UV254 treatment (orange line). The high-energy UV254 radiation may have destroyed formed -OH groups after 10 h of treatment. So, the membrane treated by UV254 has less OH on membrane surfaces than the membrane treated by UV312. The amount of polar functional groups on membrane surfaces contributed to hydrophilicity [1, 24]. So, the PSF membrane that was treated for 72 h with UV312 had the lowest WCA and the highest SE, and this matches the results from FTIR.

Although WCA of the treated membrane surface strongly decreased after treatment with UV, the WCA of so treated membrane gradually increased in a few hours, in other words the hydrophilicity of the membrane decreased. The membrane was reverting back to hydrophobic after the UV treatment. This behavior may be caused by the decay of free radicals or of free charges on the membrane surfaces, leading to a rearrangement of

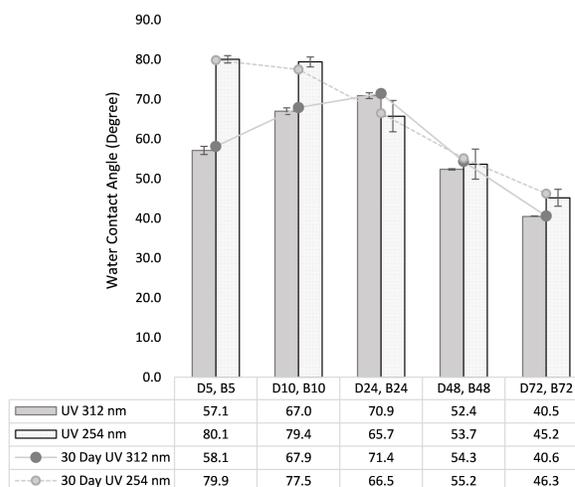


Figure 4 The water contact angles immediately after of PEG-UV treatment (bars) and 30 days later (lines)

the polar groups into the bulk material, or of nonpolar groups from the bulk to the surface, and migration of low molecular-weight oxidized materials (LMWOMs) from the surface to the bulk [25, 27]. The rapid return of the membrane surface to hydrophobic status becomes an important issue that devalues the UV-treatment. However, this drawback can be solved by PEG-grafting. PEG was grafted on an active membrane surface after the UV irradiation treatment (PEG-UV). The results in Figure 4 show that as treatment time was increased, the WCA of the treated membrane (PEG-UV) decreased. For PEG-UV254 (B5, B10, B24, B48, and B72) cases the WCA continued to decrease with treatment time, while for PEG-UV312 (D5, D10, D24, D48 and D72) cases the WCA pattern was different. With treatment times from 5 to 24 h (D5, D10, D24), the WCA increased, but with treatment times longer than 24 hours (D48, D72) the WCA decreased. This behavior may be caused by the broad wavelength spread of the UV light, as shown in Figure 1B. Although UV-254 provided lower WCA than UV-312 for treatment in a short period (less than 10 h), but for long period of treatment time (more than 10 h) UV-312 provided lower WCA than

UV-254. These results may cause by the prominent intensity of UV source. UV-254 has only one prominent peak while UV-312 has two prominent peaks (312 nm

and 360 - 370 nm) which shown the better results than UV-254 after treatment for more than 10 h shown in Figure 4.

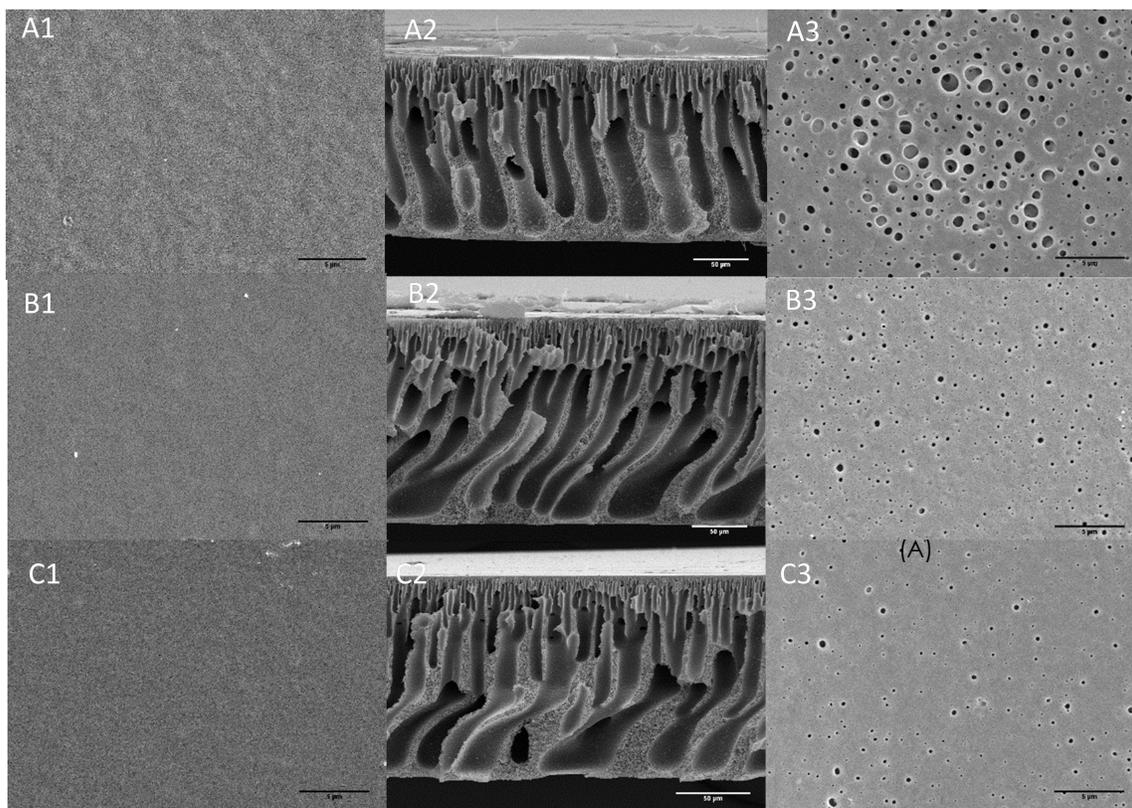


Figure 5 SEM images A1, B1, and C1 are of the top; A2, B2, and C2 of the cross section; and A3, B3, and C3 of the bottom of the membrane. Here A, B, and C are the D5, D24 and D72 conditions, respectively

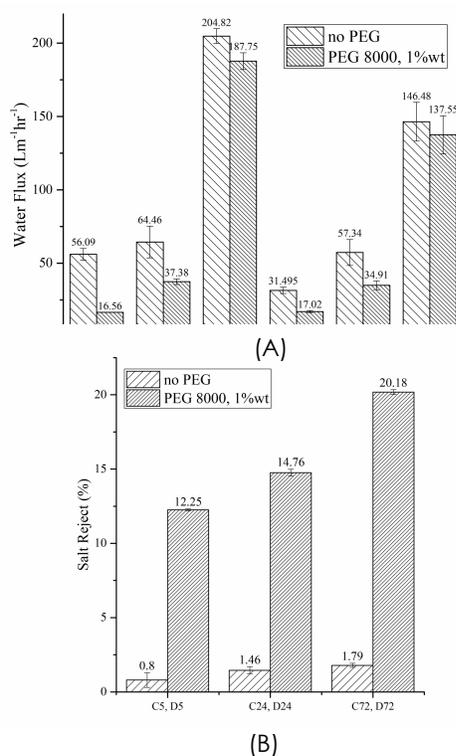


Figure 6 Water flux (A), and salt rejection (B) of PEG-UV treated membranes

However, both UV 254 nm and UV 312 nm treatments gave the lowest WCA with 72 h treatment, and PEG-UV312 (D72) case had a lower WCA than the PEG-UV254 (B72) case. Furthermore, the WCA of each treated membrane remained constant after 30 days from the completed membrane treatment. This means that PEG-UV combination can provide prolonged hydrophilicity to treated membranes, for at least 30 days after completion of the treatment. The PEG-UV312 approach uses high energy from UV light to cut hydrogen bonding (H-) from methyl side groups in the PSF membrane and reconstructs chemical bonds by grafting with PEG. On the other hand, the excess energy of UV 254 nm irradiation can destroy the structure of membrane surface, causing pore etching or polymer chain scission (B) the membrane [28, 29]. So, PEG grafting after UV 312 nm treatment was better than after UV 254 nm treatment. The FTIR spectra in Figure 3 show the C-O-C ether stretch peaks [1,30,31] at 1,100 – 1,300 cm⁻¹, and intensity of the light blue line (PEG-UV312 treatment, D72) is higher than that of the yellow line (PEG-UV254 treatment, B72). The intensity of C-O-C relates to the PEG functional groups. This means that the intensity of C-O-C can indicate the amount of

PEG on PSF membrane surface. The results in Figure 4 reveal that WCA after PEG-UV312 treatment was lower than after PEG-UV254 treatment, matching the FTIR results in Figure 3.

The morphologies of PEG-UV312 treated membranes after treatments for 5h, 24 h and 72 h (D5, D24, and D72) are shown in Figure 5. These show small pores on membrane surfaces due to the PEG adhered on the polymer component, and show similar morphologies for both top surface (A1, B1, and C1) and cross-section (A2, B2, and C2).

Although the pores are small, the water flux and salt rejection results improved with treatment time, as shown in Figure 6. This may be caused by improved hydrophilicity of the treated membrane surfaces, due to PEG grafting.

4.0 CONCLUSION

Hydrophilicity of a PSF membrane can be improved by UV irradiation, which can beneficially be followed by PEG grafting. The energy of UV light can break down chemical bonds on the PSF polymer membrane, so that polar functional groups are created on the membrane surface. Different UV wavelengths provide different photon energy levels, which affects the mechanisms and reactions on the membrane surfaces, leading to different surface wettability responses to treatment time. In addition, PEG grafting after the UV treatment was found to prolong hydrophilicity to last for at least 30 days after treatment. Furthermore, membrane improved by PEG-UV treatment provided high permeability and selectivity at the same time, which is attributed to the polar functional groups of PEG on the treated membrane surfaces.

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