

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Performance Improvement of Polysulfone Ultrafiltration Membranes Prepared with LiOH as Additive by UV Photo-grafting Technique.

Saputra B*, Suprihatin, and Noor E.

Department of Agroindustrial Technology, Faculty of Agricultural Engineering and Technology, Bogor Agricultural University, West Java, Indonesia.

ABSTRACT

Polysulfone (Psf) membrane was prepared via phase inversion with addition LiOH 2 % and modified by UV photo-grafting of hydrophilic monomers on the top membrane surface. This study aimed to modify and improve the performance of Psf membrane using LiOH and different concentrations of acrylic acid (AA) and irradiation times. LiOH as additive in dope solution acts as pore forming agent and hydrophilic modifier. The virgin and modified Psf membranes were characterized by cross-flow filtration, contact angle, degree of grafting, Fourier Transform Infrared (FTIR), and Scanning Electron Microscopy (SEM). The results showed that pure water flux of membrane decreases with the increase degree of grafting. The contact angle measurements demonstrated that the hydrophilicities of the membranes were significantly enhanced by grafting than virgin membranes without additives. The FTIR confirmed the occurrence of modification on Psf membrane by grafting and SEM confirmed membrane's pore reduction and formation of a thin grafted layer over the membrane surface. The flux of membranes was declined by grafting process but dyes rejection were slightly improved. The membrane prepared by UV photo-grafting in 10 % AA solution for 10 min demonstrated high Reactive Orange 84 (RO84) dye rejection (83.83 %) accompanied with high flux (25.08 L/m²h¹).

Keywords: Polysulfone membrane; phase inversion; UV photo-grafting; dyes rejection.

**Corresponding author*

INTRODUCTION

Polysulfone membranes (Psf) have been widely applied in water and wastewater treatment, particularly in the ultrafiltration and nanofiltration due to good chemical resistance, high strength, wide temperature tolerances, and high dimensional stability [1,2]. However, the nature of the hydrophobic polysulfone membrane causes particles, protein and other hydrophobic macromolecules can be adsorbed on the membrane surface [2,3]. This phenomenon causes the clogging of the membrane (membrane fouling) and decrease membrane performance during application. Fouling also contribute to the high cost of energy production and consumption [4,5].

Some surface modification techniques like graft polymerization monomer on the membrane surface widely applied to improve antifouling and hydrophilic properties [5-7,9]. The easy process, quick reaction, low investment costs, and applicable industry made grafting process with UV rays more studied [7]. More hydrophilic membrane surface proved to be effective in improving the performance and antifouling property [8].

High-yield photografting with a reaction without photoinitiator and controllable via various operating parameters appears to be industrially attractive. The photografting at fixed distances, which can be carried out within a few minutes, would be beneficial for industrial membrane preparation [9]. Grafting a short time (± 10 min) also recommended to obtaining a hydrophilic surface with increased membrane permeability [10].

Homayoonfal and Akbari was used acrylic acid concentration 3, 4.5, and 6 % with irradiation times from 1-3 h [11]. On the other hand, Piluharto *et al.* [12] successfully grafted Psf membrane on 15 min irradiation times and concentration of acrylic acid 5 %. Similar studies were carried out by Homayoongal and Akbari using short irradiation times (10-30 min) and AA 6 % [13]. This suggested graft condition can be set according to the desired objection and convenience in fabrication.

In this study, Psf membrane was prepared via immersion precipitation process using Psf as membrane material, LiOH 2 % as the additive, DMF as the solvent and tap water as the coagulation bath. The use of inorganic additives such as LiOH has not been reported well, such as additive polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) which has been assessed properly. Similarly with PEG, LiOH also easily prepared, soluble in water or organic solvents, and has a low toxicity [14].

Therefore, the first main objective of this work is to study the effect of LiOH during membrane formation and membrane performance. Secondly, these Psf UF membranes are modified by UV-photografting at different monomer concentrations and irradiation times in order to improve membrane performance. In this work, acrylic acid concentration was used 2.5, 5, and 10% with irradiation time 10, 20, and 30 minutes in absence of photoinitiator.

Membrane surface chemical composition, surface hydrophilicity and morphology were characterized by Fourier Transform Infrared Spectroscopy (FTIR) analysis, water contact angle measurement and Scanning Electron Microscope (SEM), respectively. Degree of grafting was measured by gravimetry. Pure water fluxes of the membranes were tested to reflect membrane permeability. Color Index Reactive Orange 84 (RO84) dyes were used to estimate flux and membrane rejection property in separation applications. Reactive Orange 84 is an azo dyes used in the textile industry, specifically in cotton clothing, which generates a highly colored residual water, because only 65% of this water is impregnated and the 35% remaining hydrolyses in water, generating a highly colored waste water [15].

METHODS

Materials

Polysulfone (Psf, MW = 35 kDa) purchased from Sigma-Aldrich Co. was used as the polymer. The solvent N-dimethylformamide (DMF) was purchased from Merck. Additive lithium hydroxide (LiOH) was purchased from Merck. Textile dyes reactive Index Color Orange 84 was purchased from Batik industry in Pekalongan, Indonesia. The monomers acrylic acid (AA) was purchased from engineering plastic factory in

Bogor. Tap water was used as non-solvent in the coagulation bath. All chemicals purchased in this study were used without any further purification.

Membrane Preparations

Flat sheet membrane was prepared by phase inversion via immersion precipitation technique. Polysulfone (15 wt %) was dissolved in DMF at room temperature mixed with LiOH (2 wt %) as additives. The membrane solution was stirred for 3 h. The casting solution was kept at room temperature for at least 2 h in order to remove air bubbles. The membrane solution was casted on glass plate with 200 μm thickness, and then evaporated for 30 seconds. The nascent membrane was immersed in tap water until all of the solvent was completely evaporated. The obtained membrane was thoroughly washed with water to remove the residual DMF. Finally, the membranes sheet were cut in circular form with 5 cm diameter and were kept in aqueous solution.

Membrane Surface Modification

Psf membranes were modified by dip coating technique which was followed by UV irradiating. Dip coating of membrane was carried out by dipped the membranes in monomer solutions (2.5, 5 and 10 wt % of AA). Then, the soaked membranes irradiated with UV light radiation intensity 10, 20 and 30 min at room temperature. After photo-grafting, the membrane was sufficiently washed with deionized water to remove the residual monomer and the homopolymers. The membranes were stored in deionized water before analyses [16].

Membrane Characterization

Degree of Grafting

The degree of grafting was calculated according to the weight difference between the original membrane and membrane after grafting process [16]. The degree of grafting was calculated as follows:

$$DG = \frac{W_g - W_o}{A} \text{ mg/cm}^2 \quad (1)$$

where W_o and W_g was the weight of the sample before and after the grafting, respectively. A was surface area of the sample.

Pure Water Flux and Permeability

The pure water flux (PWF) of the membrane with an effective area of 12.56 cm^2 was tested using a cross-flow UF experimental apparatus. Initially, membrane compaction study was carried out for 40 min. The pure water flux was measured at 3 transmembrane pressures (TMP) 0.79, 1.27, and 1.82 bar by collecting the filtrate per time unit. The pure water flux was calculated by the following equation:

$$Jw = \frac{V}{A \times \Delta t} \quad (2)$$

where Jw ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) is the pure water flux, V (L) is the volume of permeated water, A (m^2) is the effective membrane area and Δt (h) is the permeation time.

The permeability values were obtained by measuring the PWF (Jw) at different TMP. The slope of the line obtained by plotting the permeate PWF vs. TMP corresponds to the membrane intrinsic permeability (L_p), according to Darcy's law (Eq. (3)).

$$Jw = L_p \cdot \text{TMP} \quad (3)$$

Water Contact Angles

Membrane hydrophobicity was quantified by measuring the contact angle that was formed between the membrane surface and water. A constant drop volume of 1 μ L of de-ionized water was deposited with a micro syringe onto a dry membrane in air [17]. At least three water contact angles at different locations on one membrane surface were averaged to get a reliable value.

Membrane Performance in Dye Separation

The dyes permeation flux and rejection of membrane were measured based on the ultrafiltration experimental set-up, which used RO84 dye at concentration of 300 mg/L at TMP 2 bar. Before the filtration process, membrane was compacted with distilled water. Dyes flux and rejection were determined with respect to experimental dyes after the steady conditions of flow were obtained. Dye flux was calculated as in equation (2).

The dyes concentration in the feed and permeate were measured with UV-Vis spectrophotometer at the wavelength corresponding to maximum absorbance. The separation efficiency was calculated using Eq. (4):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (4)$$

where R is rejection percentage (%), C_p and C_f are solute concentration in permeate and feed, respectively.

Chemical and Morphological Characterization

Fourier Transform Infrared (FTIR) Bruker Tensor 27 was employed to detect and analysis the functional groups within the molecules of the polymer based structure in the prepared membrane with resolution between wave number 400 and 4000 cm^{-1} . Scanning Electron Microscope (SEM) JEOL JED-2300 was used to examine the morphology of membrane (cross section and top layer). The membrane was immersed in liquid nitrogen and fractured carefully. The fractured samples were then gold sputtered prior to the scanning with voltage 15-20 kV.

RESULTS AND DISCUSSION

Effect of Grafting Conditions on Degree of Grafting

The degree of grafting increases both with monomer concentration and with irradiation time. In Figure 1, the degree of grafting increased with irradiation times to 30 min at a concentration of AA 5 and 10 %. At longer irradiation times, the number of active sites available on the chain membrane increased. Therefore, the level of initiation and propagation of photografting copolymerization increased with longer irradiation.

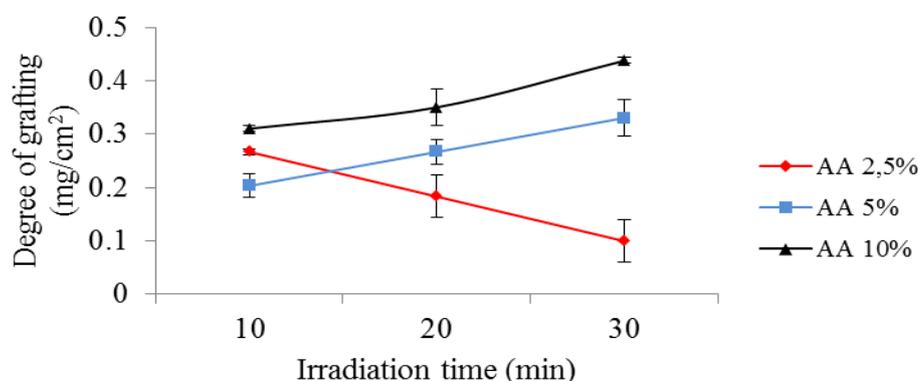


Figure 1: The effect of AA concentration and irradiation time on degree of grafting

Moreover, over-irradiation caused crosslinking monomers which reduces the available sites and could break the monomers that had already been grafted on the membranes. As a result, lower degree of grafting values obtained as seen on AA concentration of 2.5 % with long radiation 20 min and 30 min. It was found that time radiation for 10 min suitable to make AA grafted to the membrane completely.

In those cases, AA can be homopolymerized under UV irradiation. AA has strong absorption of the UV irradiation leads to the decrease in the UV intensity at the grafting sites with increasing AA concentration and hence less grafting reactions occurred. In addition, Suka and Simanjuntak found that monomer solvent like water caused homopolymer higher than polar solvent like metanol or etanol [18]. Homopolymerization limited the diffusion to active sites of Psf membrane and increased the viscosity of monomer solution, thus slowing the grafting polymerization [17].

Same results also reported by Suka, the type of solvent for monomer is crucial in degree of grafting. Degree of grafting increased with the increasing concentration of organic solvent in the solution and reached a maximum at a certain concentration depends on the type solvent used. At higher concentration of organic solvent, degree of grafting decreased because of transfer chain between solvent with polymer chains [19]. These results showed that the photografting reaction is obtained directly with the UV irradiation, in the presence of AA monomer without any photo-initiator. However, the degree of grafting is not directly proportional to the water flux measurement results. In fact, PWF of grafted membrane decreases with an increase in degree of grafting, which indicated that the hydrophilic of membranes was improved.

Effect of LiOH and Grafting Conditions on PWF and Permeability

Effect of additive LiOH and graft condition on PWF showed in Table 1. In this work, a low concentration of LiOH (2 wt %) was used as additive in membranes preparation. As shown in the Table 1, the membrane was formed by Psf-DMF solution without additive produced extremely low pure water flux. However, the addition of LiOH on dope solution induced formation a porous structure and these properties resulted in high PWF. During the phase inversion, LiOH 2 % acts as pore forming agent which favors the instantaneous demixing and formation of a porous layer on the membrane surface.

Table 1: Pure water flux (PWF) and permeability of the original and modified membranes

Membrane	PWF (L.m ⁻² .h ⁻¹)			Permeability (L m ⁻² .h ⁻¹ .bar ⁻¹)
	0.79 bar	1.27 bar	1.82 bar	
Psf (LiOH 0 %)	3.18 ± 1.38	4.78 ± 0.00	6.37 ± 0.00	3.09
Psf-LiOH (LiOH 2 %)	29.46 ± 1.38	38.22 ± 0.00	46.97 ± 1.38	16.98
Psf-g1 (AA 2.5 % 10 minutes)	2.39 ± 0.00	9.55 ± 0.00	17.91 ± 1.69	0.78
Psf-g2 (AA 2.5 % 20 minutes)	5.97 ± 1.69	14.33 ± 0.00	23.89 ± 0.00	0.90
Psf-g3 (AA 2.5 % 30 minutes)	7.17 ± 3.38	17.91 ± 1.69	26.27 ± 3.38	0.96
Psf-g4 (AA 5 % 10 minutes)	9.55 ± 0.00	16.72 ± 3.38	23.89 ± 0.00	0.72
Psf-g5 (AA 5 % 20 minutes)	10.75 ± 1.69	17.91 ± 1.69	21.50 ± 3.38	0.54
Psf-g6 (AA 5 % 30 minutes)	9.55 ± 0.00	17.91 ± 1.69	19.11 ± 0.00	0.48
Psf-g7 (AA 10 % 10 minutes)	14.33 ± 0.00	22.69 ± 1.69	27.47 ± 1.69	0.66
Psf-g8 (AA 10 % 20 minutes)	8.36 ± 1.69	15.53 ± 1.69	19.11 ± 0.00	0.54
Psf-g9 (AA 10 % 30 minutes)	4.78 ± 3.38	16.72 ± 3.38	17.91 ± 1.69	0.66

The effect of AA concentration and irradiation times on PWF also showed in Table 1. Result of grafting AA on membrane surface caused formation of PAA around the pores. This phenomenon causes pore blocking, reduces pore size and consequently declined PWF. Similar result was also reported in other study [12].

All grafted membranes showed a lower permeability when compared with non-grafting membrane (Table 1). It was also reported in other studies [5,20,21]. Interaction between AA monomer with the membrane surface during the grafting process produced a thin layer on membrane surface, as revealed by the

SEM imaging which causes blockage of pores and therefore adding an additional hydraulic resistance to the filtration process. Thus, it was explained that the permeability of grafted membranes lower.

Meanwhile, the higher permeability on membrane Psf-LiOH can be elucidated by the interaction between solvent and additive, which leads to a DMF-LiOH complex. This complex caused a reduction in solvent strength, which means the polymer is less soluble in the solvent. When a little amount of LiOH was blended and easy to be dissolved in water, the lost LiOH played a role in the formation of membrane pore as a porogen. Because of this, the number of through pores can be effectively increased, resulting in a high porosity and an increased water flux.

Membrane Surface Hydrophilicity

The water contact angle is often used to evaluate the hydrophilic of the membranes. Original Psf membrane is hydrophobic, which has a contact angle 72.33°. In a practical application, the surface Psf membrane has no hydrogen-bond interaction with water. Hydrophobic solutes approaching membrane surface were easy to be absorbed and deposited on the membrane surface caused severe membrane fouling and decreased membrane performance. The addition of additive LiOH 2 % in dope solution decreased contact angle of membrane to 50.17°. The smaller of contact angle shows hydrophilic of membrane surface increases. As explained previously, LiOH was role as pore-forming during membrane preparation. Since LiOH is soluble in DMF and less soluble in water, a substantial amount of LiOH was diffuse out with DMF from the membrane matrix in the coagulation bath (water). But the rest amounts of LiOH were still remain in the membrane and contributing as modifiers hydrophilic properties, since LiOH has a polar group (-OH). The effect of LiOH additive in membrane formation is illustrated in Fig. 2.

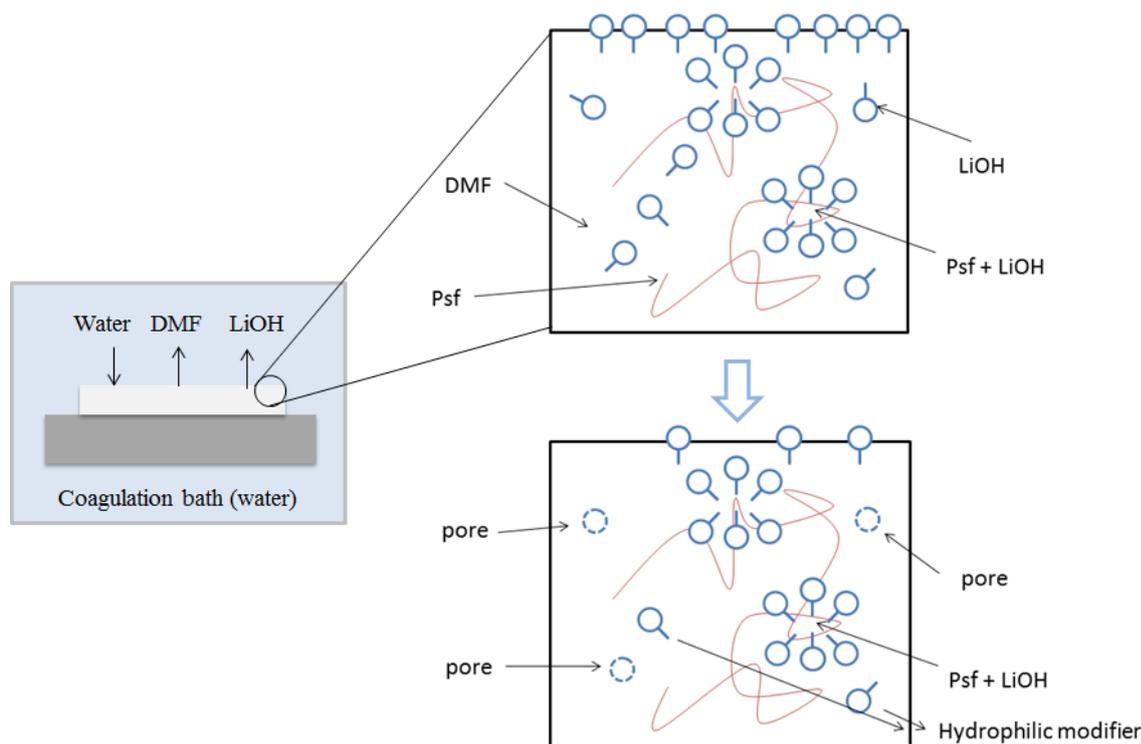


Figure 2: The effect of LiOH additive during Psf membrane formation by phase inversion

The contact angles after modified with UV photografting presented in Fig. 3. As expected, all the grafted membranes have lower contact angles than the original Psf membrane without additives. A decrease in the contact angle can be caused by: (1) increased hydrophilic properties on the membrane surface or due to (2) increased pore size so as to facilitate the diffusion of water [22]. Based on the PWF result, pore size is not increased so the decrease in contact angle possibility due to the increased of hydrophilic properties on

membrane surface. Meanwhile, grafted membranes showed larger contact angles than Psf-LiOH membrane. This may probably happen because hydrogen bond after grafting process become weaker.

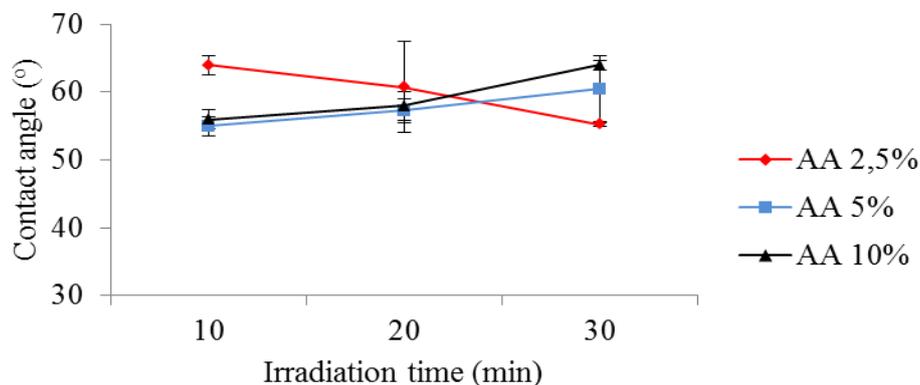


Figure 3: The effect of AA concentration and irradiation time on contact angle

The energy generated from UV rays broke the sulfur (S) or carbon (C) bond of polysulfone backbone to form free radicals. This free radical then grafted with monomers resulting hydroxyl groups (OH) at the end. Hydroxyl groups could bind with water through hydrogen and polar bond, which is likely to affect the hydrophilic of grafted membranes on contact angle measurements. In summary, the increased hydrophilicity of all grafted membranes confirmed that AA was significantly polymerized onto the membrane surface and the hydrophobic Psf membrane was effectively hydrophilized via photografting of hydrophilic monomers onto the membrane surface.

Membrane Performance in Separation Dyes

The dye flux performance of the membranes is shown in Figure 4, where 300 mg/L aqueous solution of RO84 dye was used as feed. The performances of the grafted membranes were compared to the performances of the original Psf membrane and Psf-LiOH membrane. As shown in Fig. 4, the dye fluxes of grafted membranes were slightly lower than Psf membrane, but still higher than original Psf membrane. The addition of LiOH into the matrix of polysulfone not only increased the hydrophilicity which greatly influenced the permeation of dye. The highest dye flux was Psf-g7 membrane with 25.08 L.m⁻².h⁻¹.

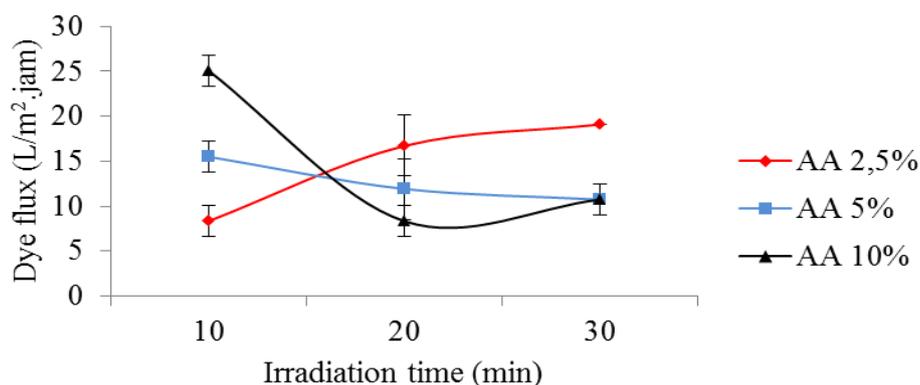


Figure 4: The effect of AA concentration and irradiation time on flux

The rejection of dye for grafted membrane was higher than dye rejection of Psf-LiOH (57.19 %), except Psf-g6 membrane which was equal to 52 %. Furthermore, all grafted membrane showed 2-3 times higher rejection when compared with original membrane Psf. This indicated that the membrane pore sizes decreased by the monomer, which made the organic macromolecules difficultly pass through, and caused higher dye rejection. The highest dye rejection as shown in Figure 5 was Psf-g7 membrane with 83.83 % rejection. According to the result of membrane performances (dye flux and rejection), the optimal conditions in this grafting process would be AA 10 % with 10 min irradiation times.

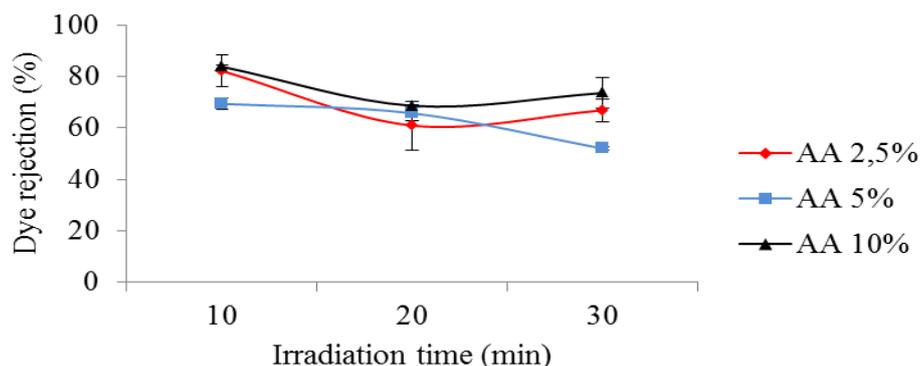
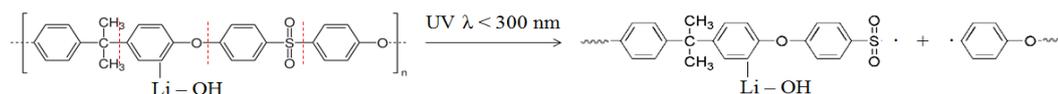


Figure 5: The effect of AA concentration and irradiation time on dye rejection

Additionally, grafting AA monomer may also promote antifouling properties in grafted membrane. According to literatures, AA has been used as antifouling monomer [23-25]. As shown in Fig. 6, grafted (Psf-g7) membranes showed clean surface membrane after dye filtration. In contrast, original Psf and Psf-LiOH membrane changed to colour orange due to dye adsorption. This may be attributed to the presence of AA in grafted polymer chains, which resulted in decrease of membrane pore size, more hydrophilicity surface, and improved the antifouling property of the membranes effectively. Generally, cleaning of membranes fouled with dyes was very difficult because the strong interaction between the dye and membrane [26].

UV Irradiation:



Graft Polymerization:

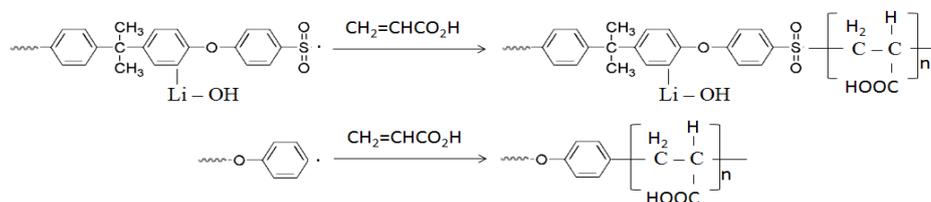


Figure 6: Schematic mechanism of graft polymerization on Psf membranes

Chemical and Morphological Characterization of The Membrane Surface

The proposed mechanism for UV-initiated grafting PSF ultrafiltration membranes is illustrated in Fig. 7. In this study, photo-initiator like benzophenone (BP) is not used in photografting process. In general, the photo-initiator is required for a significant grafting of hydrophilic monomers onto the membrane surface. BP could abstract primary H from methyl groups of Psf chains and created active sites when excited by UV irradiation [24]. According to literature, Psf is a photo-sensitive polymer on which a radical grafting can be performed without using a photo-initiator [17].



Figure 7: Changes in appearance of (a) Psf-LiOH, and (b) Psf-g7 membrane after filtration process

Fig. 8 shows the FTIR spectra of Psf ultrafiltration membranes before (original Psf membrane and Psf membrane with additive LiOH) and after UV photografting (membran Psf-g7). As seen in the Fig. 8a, Psf membrane has characteristic absorption peak such as: an aromatic bond of benzene ring (1584 cm^{-1}) and C=C bond (1485 cm^{-1}), an aromatic ether bond O=S=O (1240 cm^{-1}) and aromatic sulfone chromophore bond around 1151 cm^{-1} [27]. The intensity of aromatic C-H bend at wavenumber 943 cm^{-1} decreased on Psf-LiOH membrane indicated interaction Li^+ ion with Psf functional groups (substituted aromatic) through crosslinking or overlapping.

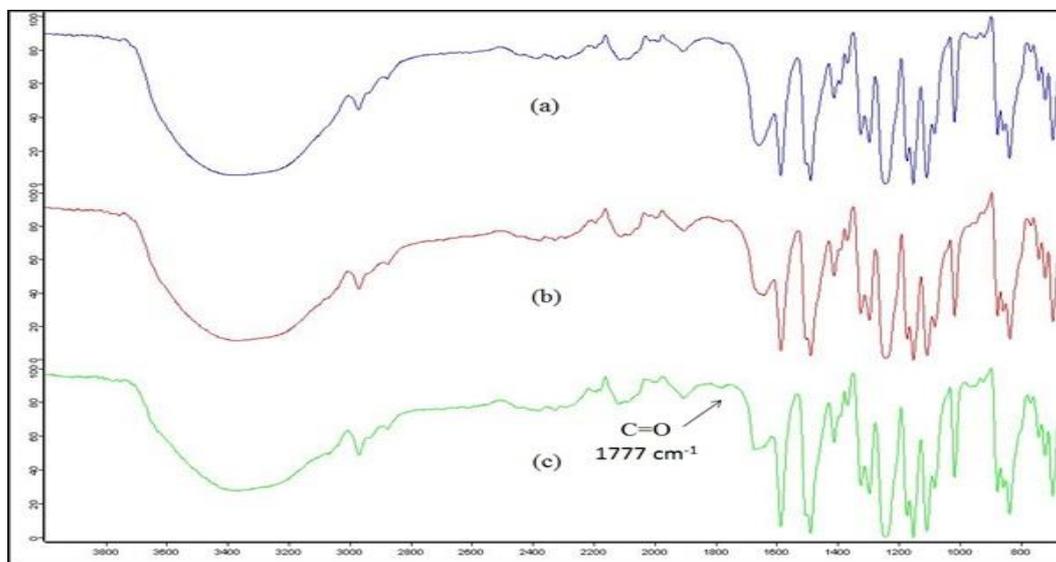


Figure 8: FTIR spectra of (a) Psf, (b) Psf-LiOH, and (c) Psf-g7 membrane

After photografting process, a new absorption peak at 1777 cm^{-1} appeared (Fig. 8c). Moreover, the intensity of these characteristic peaks became stronger with the increase of grafting degree. This peak is assigned to the characteristic C=O stretching vibrations of the carbonyl group in AA [28]. The presence carbonyl group and increased intensity of C-H stretching vibrations (2967 cm^{-1}) indicated the success of photografting on the membranes surface.

When spectra on Fig. 8b compared to spectra on Fig. 8a, the OH stretching peak slightly shifted (3362.54 cm^{-1}) and became apparently wide. Hydrogen bond causes adsorption peak widened and shift toward shorter wavenumber. This indicated that hydrogen bonds were strong formed between hydroxyl group (OH) of additive and oxygen atom in ether or sulphone groups of Psf. As seen on Fig. 8c, OH group (3380.59 cm^{-1}) re-narrowing toward maximum wavenumber on original Psf membrane (3380.03 cm^{-1}). This indicated that hydrogen bond become weak after grafting process, resulted in lower PWF and lower hydrophilicity of grafted membrane rather than Psf-LiOH membrane as reported previously.

FTIR spectra of Psf-LiOH and Psf-g7 membrane have very similar infra-red absorption band in the characteristic absorption peak of original Psf membrane. The similarity of the infrared spectra over this range confirmed that the membranes had the same basic structure of Psf and grafting process didn't change the chemical structure of membrane Psf.

Membrane surface and cross-sectional morphologies were observed by SEM. The surface images of the membranes prepared via phase inversion are depicted in Fig. 9. Visually, the surface of Psf membrane was porous but completely blocked with polymer aggregation. Cross section of Psf membrane showed a selective layer thickness with large pores, which caused a low flux and rejection. The addition of LiOH as additive led to increasing of pores number and prevalent pore distribution in the sub layer. As a result from increased pores number, a higher flux but low rejection were obtained as reported previously. However, pores size was not uniformly on Psf-LiOH membrane surface shown in Fig. 10b.

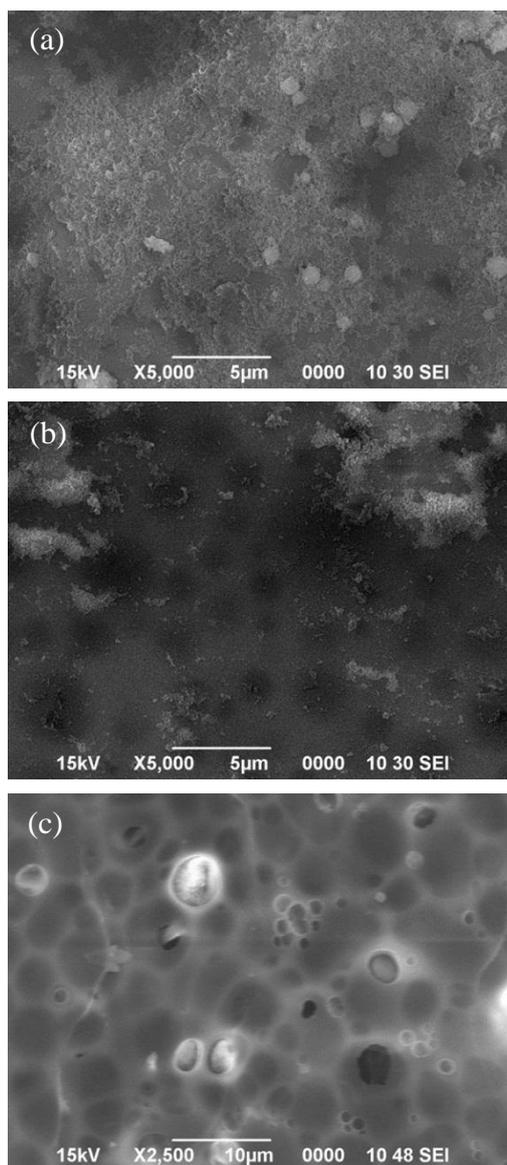
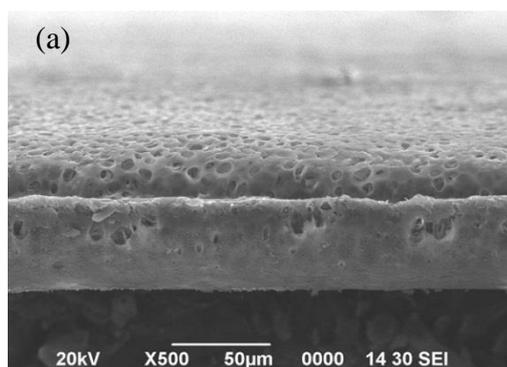


Figure 9: SEM image on surface of (a) Psf, (b) Psf-LiOH, and (c) Psf-g7 membrane

As shown in Fig. 10, all of the membranes exhibit typical asymmetrical structure of ultrafiltration membrane including a dense top layer and a porous sub layer. Differently, surface of Psf-g7 membrane showed a thin grafted layer which is formed by AA monomers bonding after the grafting process as shown in Fig. 9c. Deposition of AA monomer on the surface of the membrane caused adsorption or closed pore resulting in smaller pore size. Similar effect also reported in other studies [29]. In fact, this supported the results of dye rejection which provides conclusions regarding the reduction in membrane pores size.



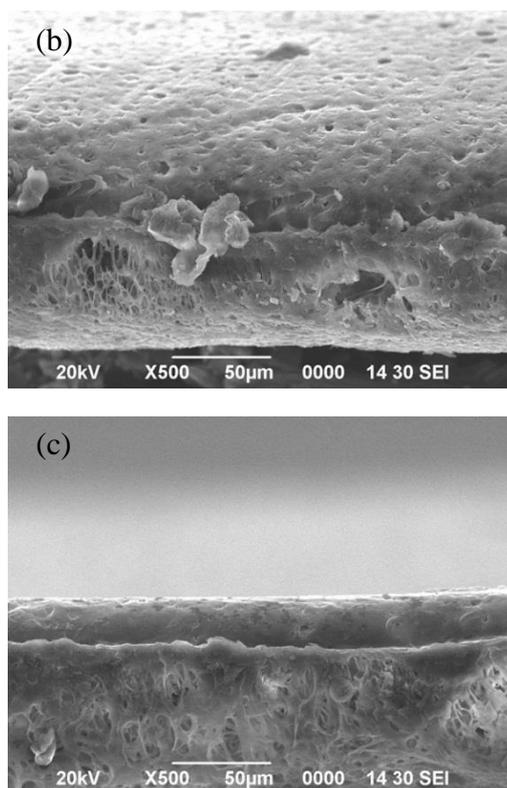


Figure 10: SEM image on cross-section of (a) Psf, (b) Psf-LiOH, and (c) Psf-g7 membrane

CONCLUSION

Polysulfone (Psf) membranes were prepared via phase inversion method and surface modified by UV photo-grafting of AA monomers. During membrane formation, LiOH 2% wt% performed as both pore forming agent and hydrophilic modifier. The surface modification can be easily carried out on prepared membranes by graft polymerization of monomer under UV irradiation. Monomer concentration and irradiation times affect in the characteristic of membranes. The result showed that pure water flux (PWF) and permeability of grafted membranes were declined. Degree of grafting was inversely proportional to the PWF values. Contact angle measurements indicated that the hydrophilicity of grafted membranes can be enhanced actually with the increase degree of grafting.

FTIR spectroscopy confirmed that carbonyl group from AA monomer was introduced onto membrane surface after polymerization. SEM images showed that grafting of acrylic acid on membrane surface made a formation of a thin layer which leads to decrease size of pores. After the surface modified, membrane showed performance improved at RO84 dyes rejection despite a decline in the dyes flux.

REFERENCES

- [1] J Li, Z Xu, H Yang. *Poly Adv Technol* 2008;19:251-257.
- [2] R Du, B Gao, Y Li. *App Surf Sci* 2013;274:288-294.
- [3] J Wang, Y Xu, L Zhu, J Li, B Zhu. *Polymer* 2008;49:3256-3264.
- [4] P Qu, H Tang, Y Gao, L Zhang, S Wang. *Bio Res* 2010;5:2323-2336.
- [5] MN Abu Seman, M Khayet, N Hilal. *J Membr Sci* 2010;348:109-116.
- [6] H Susanto, H Arafat, EML Janssen, M Ulbricht. *Sep Purif Technol* 2008;63:558-565.
- [7] C Qiu, QT Nguyena, L Zhang, Z Ping. *Sep Purif Technol* 2006;51:325-331.
- [8] H Yu, et al. *J Appl Polym Sci* 2015;132.
- [9] C Qiu, F Xu, QT Nguyen, Z. Ping. *J Membr Sci* 2004;255:107-115.
- [10] Z Xu, X Huang, L Wang. *Surface Engineering of Polymer Membranes*, Zhejiang University Pr, Hangzhou, 2009.
- [11] M Homayoonfal, A Akbari. *Iran J Environ Health Sci Eng* 2010;7:407-412.

- [12] B Piluharto, A Sjaifullah, I Rahmawati, Maryanto. *Jurnal ILMU DASAR* 2013;14:36-41.
- [13] M Homayoonfal, A Akbari. *IJNN* 2009;45:43-52.
- [14] Y Ma, F Shi, J Ma, M Wu, J Zhang, C Gao. *Desalination* 2011;272:51-58.
- [15] LFG Giraldo, GP Mesa. *Revista Lasallista De Investigación* 2007;4:17-23.
- [16] M Zhang, QT Nguyen, Z Ping. *J Membr Sci* 2009;327:77-86.
- [17] H Deng, Y Xu, Q Chen, X Wei, B Zhu. *J Membr Sci* 2011;366:363-372.
- [18] IG Suka, W Simanjuntak. *J Sains Tek* 2006;12:192-198.
- [19] IG Suka Kopolimerisasi cangkok (graft copolymerization) N-isopropilakrilamida pada film selulosa yang diinduksi oleh sinar ultraviolet dan karakterisasinya, *Makara, Sains* 14 (2010) 1-6.
- [20] A Rahimpour, SS Madaeni, S Zereshki, Y Mansourpanah. *App Surf Sci* 2009; 255:7455-7461.
- [21] A Rahimpour. *Desalination* 2011;93:93-101.
- [22] S Bequet, T Abenoza, P Aptel, JM Espenan, JC Remigy, A Ricard. *Desalination* 2000;131:299-305.
- [23] S Bequet, J Remigy, J Rouch, J Espenan. *Desalination* 2002;144:9-14.
- [24] M Ulbricht, et al. *J Membr Sci* 1996;120:239-259.
- [25] M Ulbricht, M Riedel. *Biomaterials* 1998;19:1229-1237.
- [26] N Tahri, G Masmoudi, E Ellouze, A Jrad, P Drogui, RB Amar. *J Cleaner Prod* 2012;33:226-235.
- [27] X Wei, Z Wang, J Wang, S Wang. *Membrane Water Treatment* 2012;3:35-49.
- [28] J Wang, H Sun, X Gao, C. Gao. *App Surf Sci* 2014;317:210-219.
- [29] H Hua, et al. *J Environ Sci* 2008;20:565-570.