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The Effect of Synthetic Silica on Ultrafiltration PSf Membrane

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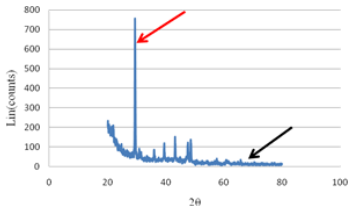
Graphical abstract



Abstract

This study investigates the effects of synthetic silica(SiO_2)with different weight percentage concentrations on the morphology and performance of the polysulfone (PSf) and polyethelene glycol (PEG) based membrane ultrafiltration (UF). Phase inversion method was used to prepare PSf/PEG ultrafiltration (UF) flatsheet membrane. SiO_2 and N-Methyl 2 Pyrrolidone (NMP) were used as an additive and solvent respectively. The fabricated membrane was characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and the performances of the membranes were measured in term of pure water flux by using distilled water and solute rejection at different wastewater concentration at 50%, 75% and 87.5%. The result showed that the addition of 2% silica in the dope solution increased the permeation in terms pure water flux and the best rejection with 62 Lm^{-2} h^{-1} and 89% (at 87.5 % waste water dilution) respectively

Keywords: Polysulfone (PSf); polyethelene glycol (PEG); silica (SiO_2)

1.0 INTRODUCTION

Enhancement of the membrane performance by increasing hydrophilic property to minimize the fouling problem is often used in polymer membrane fabrication. The common modification method that used to improve the performance is by incorporating additive into membrane formulation. The addition of small amount of additive into casting solution can lead to significant changes of membrane performance and characteristic.[1-7] The additives can affect the final membrane characteristic by changing the solvent mechanism in kinetic and thermodynamic of phase separation [4, 5]. Thus, additive have tendency to enlarge macrovoids formation which then improve the interconnectivity of the pores and resulting in higher porosities formation in the top layer and sub layer. [8] Furthermore, the addition of additive into solution may contribute to the changeable properties of membrane in term of pore distribution, physical properties and mechanical characteristics[9]. According to previous studies, by using silica, zeolite, titanium dioxide and silver as additives, membrane conductivity and mechanical properties were improved. [9, 10, 11, 12]. Other previous work that used graphite, polymer additive, inorganic additive, nano particles or carbon nanotube also proved that the membrane properties i.e permeability and fouling resistance increased by adding these additive.[9, 12, 14] Thus, by varying of this additive concentration or additive molecular weight, optimal membrane structure can be obtained through enlargement or suppression of macrovoids, antifouling mechanism, increase the flux permeation and higher rejection on the membrane performance [15].

Basically, silica is one of the inorganic materials that has capability to resist chemical attack and has high thermal stability. Besides that, silica that possesses strong hydrophilic properties can be used to prevent fouling mechanism by enhancing the permeability of the membrane. As reported by Suryani *et al*., the permeability of pure membrane polymer was less than the hybrid silica membrane polymer.[16] As proved by He *et al.* [17] that showed a remarkable enhancement in mixture vapor/gas selectivity of poly (4-methyl-2-pentyne) by introducing nanosized silica in the matrix of high-free-volume glassy polymers. They found that the gas permeability and the hydrocarbon, permanent-gas selectivity increased simultaneously with increasing this silica content. Another research by Arthanareeswaran *et al.*[18], reported that when increased silica content in the casting solution, the result showed that the reversible fouling resistance dominated the total fouling resistance thereby improving the fouling resistance ability of the blend or hybrid membranes. According Vatanpour *et al.*[19]also reported that many membranes fabricated from silica show a better performance in term of permeability, and fouling-resistance as well as permeate quality. In this present work, PSf mixed membrane with synthetic silica were prepared through

phase inversion method. Thus, the main objective of this work was to investigate the effects of the synthetic silica on the membrane performance and structural properties.

■2.0 EXPERIMENTAL

2.1 Material

Polysulfone (PSf UDEL P-1700) purchased from Solvay was used and dried at 100°C for one hour before used. N-methyl-2-pyrrolidone (NMP) was purchased from Merck as a solvent without further purification. Poly (ethylene glycol) with moleculer weight 400 was purchased from R& M chemical and the SiO_2 was purchased at Sigma Aldrich with S5130-0.007µm.

2.2 Membrane Preparation

PSF membranes were prepared using composition as shown Table 1 via phase-inversion process from 18 wt.% solution in NMP with stirring for 4 h. Then, SiO_2 at different concentration was subsequently added with continuous stirring and heating at 60 °C until the solution was completely homogeneous. After that, the casting solution is poured into bottle and ultrasonicated for 1 hour to release the bubbles. After the bubbles completely released, the solution with essential concentration was cast on the glass plate (support) with a knife and, after that, place in coagulation bath (filled with 2.5 litters of distilled water). Then, the flat sheet membrane was removing from the coagulation bath and was dried in temperature room for 24 h.

Table 1 Composition of membrane preparation solution

Dope formulation	PSf(%)	PEG(%)	SiO_2(%)	NMP (%)
1	18	8	1	73
2	18	8	2	72
3	18	8	3	71
4	18	8	4	70
5	18	8	5	69

2.3 Membranes Characterization

2.3.1 X-ray Diffractometer Analysis

The peak of SiO_2 in PSf membrane was obtained by using XRD Bruker D8 advance with a 40kV scaled copper tube as source and a graphite crystal as monochromator. The 1 x 1 cm of membrane was used to record the XRD patterns with diffraction angles of 20˚- 90˚ at 2θ. The X-ray diffraction pattern is shown in Figure 1.

2.3.2 Scanning Electron microscopy (SEM) examination

Membrane morphology was examined using a JEOL JSM-6380LA scanning electron microscope (SEM). The cross section area of the membrane was prepared by immersed and fracturing the membrane at the temperature of liquid nitrogen manufactured by MOX. All the specimens were coated with thin layer of gold before SEM analysis.

2.4 Membrane Performance

2.4.1 Permeation Flux (PWF) and Rejection (R)

The permeation flux and rejection was measured by using the ultrafiltration cross flow water permeability testing unit. The experiment was conducted at a trans membrane pressure of 2 bar for every 10 minutes. The permeation flux was carried out by using distilled water and rejection was carried out by using humic acid. The membrane was cut into 5.5 cm diameter before testing. The permeation flux was defined as the formula (1).

$$PWF = Q/(Ax\ \Delta t) \quad (1)$$

where PWF is the pure water flux (LMH), Q is the permeate volume, A is the membrane area (m^2), and Δt is the time (h). Rejection was measured with wastewater. The wastewater was prepared based on ASTM D5905-98 with different concentration dilution (50%, 75%, and 87.5%). The concentration of wastewater was measured by using a Perkin-Elmer Lamda 25 UV-Vis spectrophotometer at the wave length of 254 nm.

The rejection was defined as the formulation (2).

$$R\ (\%) – [1- (C_p/C_f)]\ x\ 100 \quad (2)$$

where, C_p - permeate solute concentration, C_F - feed solute concentration

■3.0 RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD)

Figure 1 shows the the XRD diffraction patterns of PSf/PEG/SiO_2 membrane were obtained from 2θ range of 20˚ to 80˚ at 40 kVp and 20 mA. PSf exhibited a broad peak which corresponds to amorphous structure (shown by black arrows). Meanwhile, SiO_2 with sharp peak is observed at about 30˚ at 2θ which attributed to the highcrystallinity (shown by red arrows). This is showed that the silica still existed in polysulfone membrane even after mixing and the phase inversion method. It also proves that SiO_2 distributed homogenously across membrane even the percentage used is quite small.

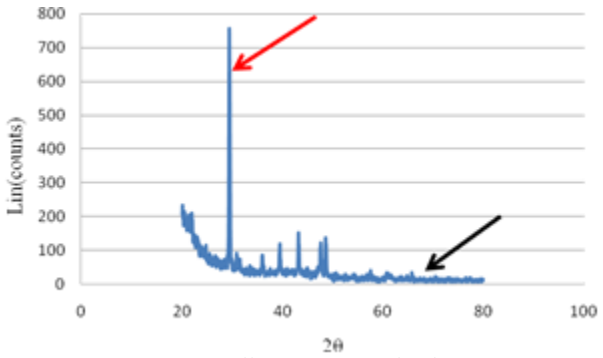


Figure 1 X-ray diffraction pattern of PSf/SiO_2membrane

3.2 Morphology Properties

Figure 2 shows the SEM images of the cross section of PSf/PEG/SiO_2 membrane. Observation of the microstructure

cross section shows that membrane has a dense skin layer, porous finger-like structure and sponge-like structure at the bottom. As can be seen in this Figure 1, the increased of SiO_2 content, will change the finger like structure become smaller and slightly extended. The extensions of finger-like structure cause the suppression of macrovoid structure at bottom layer. This was obviously shown by addition higher percentage of SiO_2 (3-5 wt.%) decreased sponges like structure at the sub layer of membranes. As reported by others researcher that show the addition of SiO_2 can reduce the pore size formation at the top separation layer and this caused the better rejection mechanism. [2, 10] Observation of SEM at higher magnification shows that there is a small white particle that revealed the presence of SiO_2. In fact, higher concentration of SiO_2 will cause agglomeration and create non-homogeneous structure. The presence of agglomeration lead to weak interaction between silica and polysulfone and will result in leaching of silica especially at high pressure.[10]

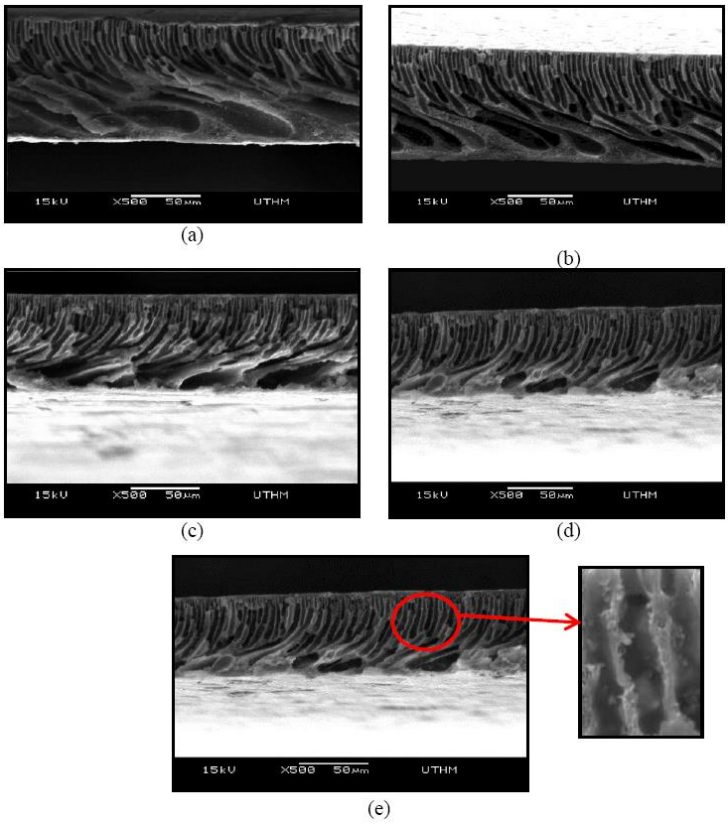


Figure 2 SEM cross-section of PSf membrane with different SiO_2 content. a) 1 wt.%, b) 2 wt.%, c) 3 wt.%, d) 4 wt.% and e) 5 wt.%

3.3 Pure Water Fluxes (PWF)

Figure 3 demonstrates the performance of PSf/SiO_2 membrane in term of Pure Water Flux (PWF) permeation. According to the graph, the flux increase when the amounts of SiO_2 increase up to 2 wt.%. However, the flux decrease drastically when the amounts of SiO_2 increases up to 5 wt.%. The PWF 2 wt.% is 62 LMH meanwhile for 5 wt.% is 24 LMH.These phenomena might be due to the incorporation small amount of SiO_2 particles into membrane provide good morphology in term of surface and cross sectional area as mentioned in SEM result. This condition indirectly affect the membrane Pure Water Flux where the membrane have better structure will produce high permeation especially for pure water flux. This explanation also agreed by others previous studies. [20] In addition, the presence of polyethylene glycol as macromolecular additives into PSf/SiO_2 casting solution also assists increase membrane PWF. The PEG acting as pore former agent to produce membrane with big pore size and fine skin layer.[20] to bring better performance of membrane for pure water permeation. Thus, based on this condition, the ideal permeation flux can be considered at membrane which contains 2 wt.% amount of SiO_2.

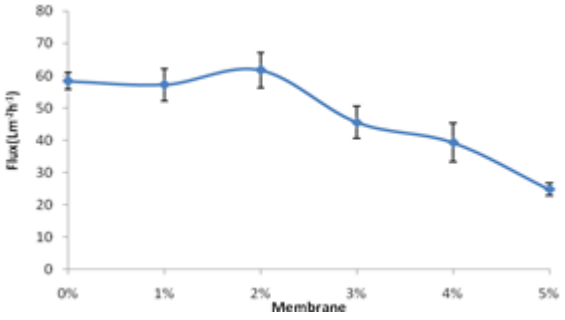


Figure 3 Permeation of pure water flux with different addition of SiO_2 percentage

3.4 Wastewater Rejection

Figure 4 illustrated the effect of wastewater with different concentration where is 50%, 75% and 87.5% dilution in percentage rejection and flux rate after filtration by PSf/SiO_2 membrane. Based on the plot, the membrane containing 2 wt.%

SiO_2 shows highest value percentage rejection and flux rate for all different wastewater concentration compared to the others membrane. Rejection at different wastewater concentration shows that the highest rejection is given by 2 wt.% of silica membrane by using 87.5% wastewater dilution with rejection approximately 90%. This also indicates that the wastewaters with low concentration easy to filtrate by membrane compared to high concentration. This condition also revealed that the wastewater concentration affect the performance of membrane rejection. This finding can be interpreted as follows that PSf is a hydrophobic polymer.[21-22] The presence of SiO_2 particles would improve the membrane hydrophilicity that leads to the attraction of wastewater molecules towards the membrane, that result in the increased of rejection percentage and flux rate.[23-24] However, the increase amount of SiO_2 particles from 3 wt.% until 5 wt.% shows decrease value in percentage rejection and flux rate possibility due to agglomeration occur between SiO_2 and polymer at the membrane structure. In addition, the cryatalline structure of SiO_2 has low compatibility when mixed with polymer amorphous structure. This situation indirectly affects membrane rejection performance.

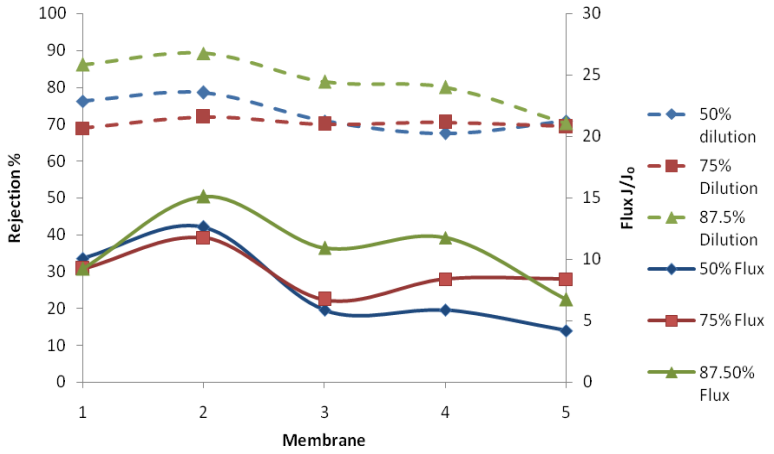


Figure 4 The effect of silica percentage based on rejection and permeation water concentration

4.0 CONCLUSION

In this study, flat sheet PSf/SiO_2 ultrafiltation membranes were successfully prepared using casting technique containing additive 1 wt.% until 5 wt.% silica with N-methyl-2-pyrrolidone (NMP) as a solvent. The presences of SiO_2/PEG in casting formulation were influence of membrane structure permeability and rejection. As the observation, all the membranes have asymmetric structure as can be seen from SEM image. The SEM image shows that membrane morphology change after the addition of silica at different weight percentage (wt.%) in the casting solution. In addition, by increasing small amount of SiO_2 in casting solution will increased the permeability, rejection and hydrophilicity of membrane. As the conclusion, the best composition was at the membrane content 2 wt.% SiO_2 where produces high pure water flux and give the best rejection at 62 LMH and 89% respectively.

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