The Effect of Polyethelene Glycol on The Performance of Polysulfone Membrane Blend with Silica From Rice Husk

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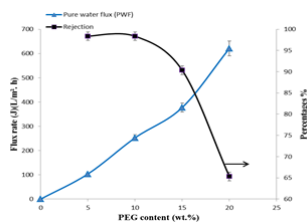
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Graphical abstract

Abstract

In the present work, the effect of rice husk silica (RHS) on the performance of polysulfone (PSf) blended with polyethylene glycol (PEG) membranes were investigated. The hybrid ultrafiltration membranes were prepared by phase inversion technique. The membrane performance was analyzed by using pure water flux, humic acid for the rejection test and followed by the membrane characterization. Results showed that PEG increased membrane pure water flux to 621.212 LMH and rejection humic acid at and 98%. The analysis of SEM revealed that PEG obviously changed the microstructure of the membrane especially at the top and sub layer.

Keywords: PSf; PEG; rice husk silica

■1.0 INTRODUCTION

Phase inversion is a common technique for the preparation of polymer membrane with the asymmetric structure where a thin layer of polymer dissolved in an appropriate solvent is casted on a suitable support and phase separation is introduced by a non-solvent.[1] The morphology of asymmetric membranes generally shows a characteristic of a dense top layer and microporous sublayer. These membranes are widely used today in various applications such as microfiltration, ultrafiltration and reverse osmosis because the thin top layer plays a role as a selective barrier film while the porous sublayer with macrovoids and microporous structure were not only excellent in mechanical strength property but also ease the permeation mechanism. [2] Basically, membrane structure and properties prepared by phase inversion method depend on many factors. As reported in previous literature, an additive can affect the final membrane characteristics either by changing solvent capacity or by changing phase separation kinetic and also thermodynamic properties.[3-5] As proved previously, by varying of additive

concentration or additive molecular weight (MW), optimal membrane structure can be obtained through enlargement or suppression of macrovoids in the membrane.[6-8]

Polymer additive or non-solvent additive is a play vital role in the formation of membrane structure by enhancing or preventing the microvoid formation, enlarging pore formation, improving pore inter connectivity and introducing hydrophilicity.[9-10] According to Luo et. al, by adding the polymer additive such as Polyvinylpyrrolidone (PVP), polyethelene glycol (PEG), polyetherimide (PEI) and polyvinyl chloride (PVC) in membrane formulation can produce the high porous membrane, well interconnectivity pores and well surface properties.[11] Furthermore, the advantages of using polymeric additives is that they are miscible with membrane polymer and also soluble in both aqueous and many organic media.[5,12] In fact, the addition of polymeric additive result in for the formation of micro pores and porosity with at the time the disappearance of macrovoid formation as reported in several papers.[5,9,13]

PEG has an excellent non-toxic and non-immunogenic nature which makes it extensively useful in various biological, pharmaceutical and chemical applications. In membrane fabrication, PEG is used to control the thermodynamics and kinetics in casting system to enhance the pore size of membrane.[5] Other study by Ehsan Saljoughi et. al, found that PEG can increase the porosity and thickness of membrane. The increasing of PEG concentration in membrane formulation with reduction of coagulation bath temperature had enhanced the thermal chemical stability of the prepared membranes.[9] In addition, the presence of PEG at low MW in the casting solution film increased the porosity, permeability and simultaneously thermal/chemical stability of the prepared membranes.[5] In phase inversion process, non-solvent acts as a pore forming agent to improve membrane permeability and alter the membrane structure.[12] Theoretically, increase in MW of PEG, the pore number as well as pore size in membranes will increase while also membranes with PEG at higher MW have higher permeation water flux (PWF) and higher hydraulic permeability due to higher porosity.[14-16] However, Arthanareeswaran et. al, reported that by increasing PEG MW enhance the viscosity in casting solution.[17] The higher viscosity may result in difficulty of PEG molecules mobility to diffuse from casting solution into coagulation bath [5,18,19] As a consequence, the delayed phase separation occurred in all the immersion cases and therefore the top surface that relatively dense with a great deal of aggregated residual PEG was formed.[20]

In this study, PEG at MW 400 KDa was used in membrane fabrication. According to Chakrabarty et. al., PSf membrane formulation was kept at 12 wt.% with PEG of 3 different MW 400, 6000 and 20,000 were studied result showed that membrane flux and porosity increased when MW increased rejection seem to decrease.[12] Obviously, PEG is an important additive in controlling membranes structure. It has been concluded that by adding polymeric additive in the membrane formation micropores and porosity will be increased and the macrovoids will be disappeared.[21] In fact, PEG is miscible with most of the membrane materials and are soluble in both aqueous and many organic media.[5]

Table 1 Composition of casting solution

Membrane	PSf (wt.%)	NMP (wt.%)	RHS (wt.%)	PEG (wt.%)
1	18	82	3	0
2	18	82	3	5
3	18	82	3	10
4	18	82	3	15
5	18	82	3	20

■2.0 EXPERIMENTAL

2.1 Materials

Polysulfone (PSf UDEL P-1700) purchased from Solvay was dried at 100 °C for 1h before use. N-methyl-2-pyrrolidone (NMP) from Merck was used as a solvent without further purification. Poly (ethylene glycol) (PEG) with MW 400 was purchased from R& M chemical.

2.2 Membrane Preparation

PSf was first mixed with NMP under mechanism stirring for 4h. Then, RHS and PEG additive at different concentration (Table 1) was subsequently added with continuous stirring and heating at 60 °C until the solution was completely homogeneous. RHS was prepared by burning rice husk in a furnace at 600 ^{0}C for 1h. RHS was burnt for 24 h, cooled and sieved until the size is less than 25μm. After that, the casting solution was ultrasonicated for 1 h to release the bubbles. The membrane solution was cast on the glass plate (support) with a knife and placed in coagulation bath (filled with 2.5 litters of distilled water). Then, the flat sheet membrane was removed and dried at room temperature for 24 h.

2.3 Characterizations

2.3.1 SEM Analysis

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

2.3.2 Membrane Porosity

The porosity was estimated using the Guerot-Elford-Ferry equation. Membrane densit (p_w), volume (v), weight in wet (w_w) and dried (w_d) were measured. Firstly, the membrane was immersed into distilled water about 24 h at 25˚C. After that, membrane was weighed before drying in oven for 24 hour at 50˚C. Next, the membrane was weighed again (w_w). The Guerot-Elfort- Ferry Equation (1) was used to calculate the membrane surface porosity and membrane porosity.

$$\text{Porosity} = (w_{w-w_d}) / (p_{w \times v}) \tag{1}$$

where, (p_w) is pure water density at room temperature (g/cm³) and v is the volume of membrane in wet state (cm³).

2.3.3 Tensile Strength Analysis

Tensile strength was determined by using the Universal Tensile Machine (AG-I, Shimadzu). The standard tensile test referred from American Society of Testing Method (ASTM) designation code of D882-12 at the strain rate of 5 mm min^{-1}. In order to measure membrane tensile strength, each type was cut into strips 5 cm long and 1 cm wide. The vernier calliper was used to measure the thickness of samples and all measurement was carried out at room temperature.

2.4 Membrane Performance

2.4.1 Pure Water Flux (PWF) and rejection (%R)

Membrane PWF 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 and permeate was collected for every 10 minutes. The PWF 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 Equation (2).

$$\text{PWF} = Q/(Ax \, \Delta t) \tag{2}$$

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 200 mg/L humic acid aqueous solution. The concentration of humic acid was measured by using a Perkin-Elmer Lamda 25 UV-Vis spectrophotometer at the wave length of 254 nm. The rejection was defined as Equation (3).

$$R\ (\%) - [1 - (C_p/C_f)] \times 100 \tag{3}$$

where C_p is solute concentration in permeate stream, C_f is solute concentration in feed stream

■3.0 RESULTS AND DISCUSSION

3.1 Morphology Properties

Figure 1 shows the SEM image of different membranes cross section prepared with various content of PEG. All prepared membrane shows asymmetric structure consisting of a dense top–layer, a porous sub layer and a small portion of sponge-like bottom surface layer. The addition of PEG into the casting solution clearly plays a significant role on morphology of the membranes prepared. Figure 1(a-e) depicts SEM micrographs of prepared membranes with various content of PEG. Results showed that the pore-sizes, number of finger-like pores and porosity of the top-layer in the prepared membranes increased with PEG content. Similar results were demonstrated by Ma et. al., where the number of finger-like pores increase with the dosage of PEG 400 in membrane formulation.[5] In fact, by increasing the PEG content, the length of finger–like cavities become shorter and large macrovoids were formed at the bottom layer as can be seen in Figure 1 (d-e).[5] In addition, the finger-like structures were enlarged and tend to possess a sponge shape. It is also noticed that the thickness of top-layer and the sub–layer structure also depend on solubility and diffusivity of the PEG.[12] As clearly shown by SEM images, the thickness of the top layer become thinner (dense) with the increment of PEG content. It is also obvious that the thickness of membrane top-layer strongly influences the membrane performances in terms of pure water flux (to be discussed in section 3.3).[4] From the previous studies on RHS and PEG, it is obvious that the membrane microstructure was changed in term of finger-like, interconnectivity and pore size especially at top and bottom layers.[4,7,8]
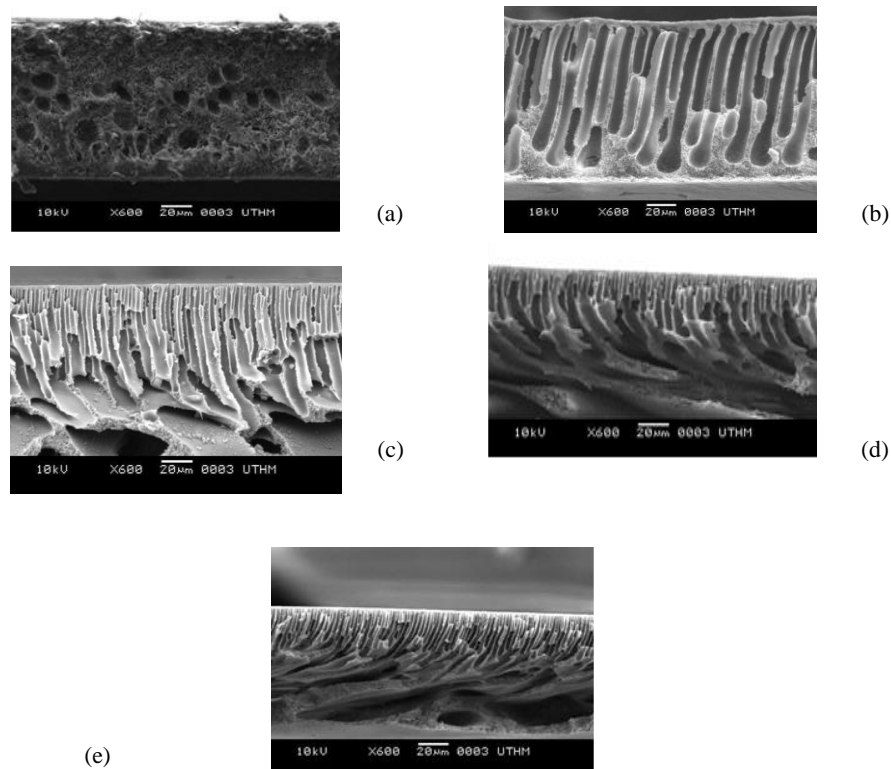

(a)

(b)

(c)

(d)

(e)

Figure 1 SEM cross-section of PSf membrane with different PEG content. a) 0 wt.% b) 5 wt%. c) 10 wt%. d) 15wt%. e) 20 wt.%

3.2 Porosity and Tensile Properties

In general, membrane porosity can be defined as weight of water trapped in 1 m^3 of membrane structure. It is an important parameter in membrane separation area PWF, rejection and mechanical strength of membrane. Figure 2 shows the porosity and tensile strength data for prepared membrane at various content of PEG. The results demonstrated that, the porosity increased significantly with PEG content. Figure 2 clearly shows the increased porosity from 5% to 30% as PEG increased. Meanwhile, the tensile strength for different content of PEG is illustrated in Figure 2. Figure 2 revealed that membrane tensile decreased from 5.1477 MPa to 2.6278 MPa as the PEG content increased from 0 wt. % to 20 wt. %. According to Ma et. al., the decrease in tensile could be owing to the rupture of weak structure of membrane resulting from the increased porosity.[5]
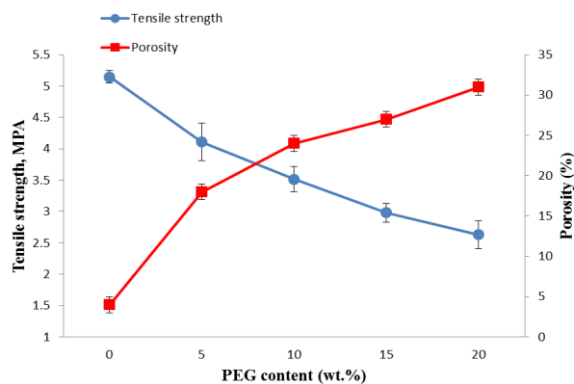
Figure 2 Tensile strength and porosity of PSf membrane with different PEG content

Figure 3 Effect of PEG 400 content on the pure water flux and humic acid rejection of PSf membrane

3.3 Pure Water Fluxes (PWF) and Rejection (%R)

Figure 3 shows the membrane performance and membrane capability to resist their permeability by water permeation flux testing unit. As shown in Figure 3, membrane fluxes have significantly improved by the addition of PEG in the range of 5 wt. % to 20 wt.% percent. PWF increases constantly from 0 to 621.212 LMH as PEG dosage content increased to 20 wt.%. According to previous researchers, by adding PEG, the number of pore at the membrane top surface can be increased and this definitely will affect the PWF value.[5,12] The PWF results also agreed well with the increment of the pore number in SEM observation. The porosity enhancement at the top-layer on the membrane prepared as the concentration of PEG increased is also an interesting finding in this study. Ma et. al. and Kim *et al*., reported that PEG functioned as a pore-forming agent, therefore increasing PEG content in dope solution is a way to increase membrane porosity, which then leading to the enhancement of PWF and decrease solute rejection.[2,5] In addition, previous studies on membrane mixed RHS reported that the PEG strongly may also affect the pore number, even with the mixed inorganic particles and incompatibility of hybrid RHS membrane structure, the pore formation significantly increased as PEG added.[4,7] The addition of PEG in the hybrid PSf membrane with the aid of RHS may increases the hydrophilic property of membrane by supporting more RHS particles to the permeate medium.[4,8] Figure 3 shows the effect of PEG content on humic acid rejection of PSf membrane. From the plot, the rejection is increased with the addition of PEG content from 5 wt.% until 20 wt.%. Based on the rejection plot, it is noticed that the addition of 5 wt.% and 10 wt.% PEG both give the highest rejection at 98%. The result also indicates that the increasing of PEG content reduce membrane rejection on humic acid at 65%. This may be due to the high porosity especially at the membrane bottom layer which then reduces rejection value.[12] Similar results were observed by Sotto *et al*. that the declining in rejection potential was owing to formation of membrane pores with larger porosity.[21] Hamid et. al. reported that to prevent humic acid from entering the pore length, the pore size of membrane must be small enough to block the solute particles.[22-23] According to Z. Harun et. al., even RHS can reduce the pore size formation at the separation layer but by adding the 10 wt.% PEG the flux and rejection of this membrane was improved .[4] According to C. Bath et. al., porous membrane surface and give better interconnectivity inside membrane indirectly enhanced pure water flux and reduced solute rejection.[20]
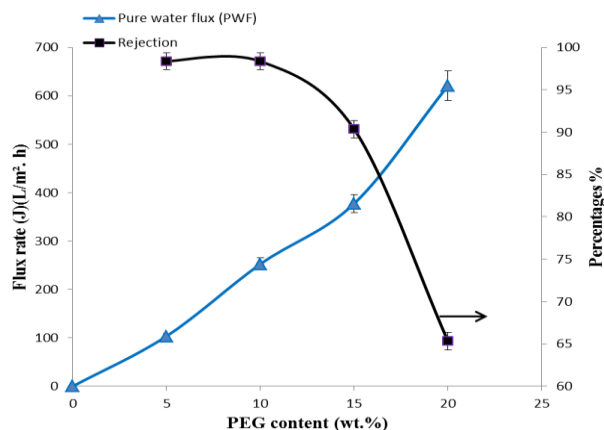
■4.0 CONCLUSION

In this work, addition PEG with PSf/RHS membrane was successfully prepared by phase inversion method containing 18 wt.% of PSf, 82 wt.% of N-methyl-2-pyrrolidone (NMP) and 3% RHS. The effect of PEG content on the morphology and properties in term porosity and tensile strength were studied and observed. The performance of prepared membrane was evaluated in terms of PWF and rejection of humic acid. The results can be summarized as follows:
- The SEM images indicated that the increment of PEG content has resulted in the increase of size and finger-like pore number at the separation layer.
- PEG has functioned as forming agent by creating bigger pore at bottom layer.

Due to the promising results, PSf/RHS/PEG membrane is potential in separating humic acid from environmental sample.

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