

EFFECTS OF FABRICATION CONDITIONS ON THE MICROSTRUCTURE AND PERFORMANCE PES MEMBRANE

Nik Shamimi Nazma Nik Mohamed Kamal, Nurhidayati Othman

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract—Phase inversion is a flexible technique that can be used to prepare membrane with various microstructure / morphologies targeted for fluid separation. Effects of membrane preparation parameter towards the morphology of polyethersulfone (PES) membrane was investigated by varying the polymer compositions from 15 wt% to 25 wt% where Dimethyl acetamide (DMAc) was used as a solvent while polyvinylpyrrolidone (PVP) was used as a pore forming additive during the membrane preparation. The prepared membranes were immersed into three types of coagulation bath (water, water + 37.5 % ethanol and water + 75% ethanol) at various evaporation times ranging 0s to 60s. The PES membranes targeted for reverse osmosis application were characterized using FTIR to indicate the existence of hydrophilic carbonyl and hydroxyl group, Contact angle measurement was conducted to investigate the hydrophilicity of the PES membranes and water flux for performance PES membrane. It is found that fabrication condition affect the microstructure and performance PES membrane in reverse osmosis application is achieved.

Keywords—polyethersulfone, dimethyl acetamide, membrane, phase inversion, fabrication conditions

INTRODUCTION

The pure drinking water would be a more serious problem cause form the global population that excess 7 billion by directly developing nations in the world. This problem had forced scientist to look for alternative sources of water [1]. To overcome this issue, different membrane techniques is applied for water treatment, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and membrane distillation (MD). In water treatment, the UF and MF are being used while RO is applied in water desalination and purification. MD is a new evolution technique and it has potential for rising saline water in desalination. By the mixture of interfacial polymerization (IP) and phase inversion technique with fabricate using RO composite membrane is produce higher water flux compared to the asymmetric membranes prepared by the phase inversion technique alone. This improvement is outstanding to the low-water transport resistance of ultrathin polyamide (PA) selective layer which is on the top of a porous support [2].

Polyethersulfone (PES) membrane is the one of polymeric material that commonly used to prepare ultrafiltration membrane. The advantages of commercial PES membrane is thermally stable polymer that used in high-performance application. Based from the application,

it is toughness, good thermal resistance and chemical inertness[3]. By casting the polymer solution using phase inversion technique, many factors like membrane morphology, water permeability, membrane hydrophobicity, thermal stability and pore size distribution are studied.

The choice of membrane polymer is depending on fabrication techniques which are included phase inversion, interfacial polymerization, stretching, track-etching and electrospinning [1]. For separation process, usually the phase inversion technique is used in membrane fabrication methods. Development of phase inversion method for membrane technology through immersion precipitation is the consistent way to preparation of the most polymeric microfiltration and ultrafiltration and a few of nanofiltration membranes which used for separation processes [3] such as ultrafiltration membrane and nanofiltration membrane [4].

In this phase inversion technique, the flat sheet polymer membrane was prepared and need to immerse in liquid external coagulant to take place phase inversion process. Normally, the water is used as external coagulant as it is a very cheap and safe liquid. The flat sheet membrane is controlled by many factors on morphology and performance. The composition of coagulations bath is the one of the factor. The addition composition in coagulation medium will affect the membrane formation in terms of their morphology and performance, which is according to exchange of solvent and non-solvent in coagulation bath [4] Another factors that affecting membrane on morphology and performance is to measure the permeate water flux and rejection of salt. The membrane structure and performance also depends on polymer choice, composition, types of coagulation bath and dope solution. Furthermore, by exchanging of these variables, the quite significantly can give effect to the dependent on membrane structure [5].

However, PES membrane had been used widely prepared using phase inversion technique. Among one main issues faces by PES membrane hydrophobicity although they offers good chemical resistance, wide pH range toleration, and thermal and mechanical properties [6]. These hydrophobicity issues of PES membrane contributed to lower of membrane performance, reduced anti-fouling properties, and lower membrane permeability [7] Therefore, by modifying the structure of PES membrane, the performance of PES membrane can be improved.

Fabrication parameters play an important role in fabrication PES membrane using phase inversion technique. The effect of solvent type and concentration and effect of coagulation bath and concentration that used in this study are investigated using different concentration

of PES concentration. PES membrane was prepared using DMAc, and DMF as solvent in polymer solution in the casting solution. During casting, the upper layer of the membrane is thin and porosity of the support layer is improved [8]. Then, after the polymer is casting, it immersed in coagulation bath type which are ethanol and methanol.

The fabrication membrane is studied because to improved water flux. However, in some situation, the decreasing water flux is reported. During casting, the speed of cast will affect the membrane morphology, porosity and pore size. Membrane film that has a molecular orientation will affect shear rate induced during casting in which random molecular orientation will be transformed to more aligned structures that will subsequently improve the membrane's selectivity. The alteration of PES membrane structure is depending on casting speed where the arrangement of the structure is varying with the shear rates induced. Even if, the casting method were done by many researchers, only a few of shear rate of casting speed can be achieved [9].

In this work, it is to prepare a micro-structured polyethersulfone (PES) membrane using phase inversion technique targeted for fluid separation. In order to achieve that, the effects of preparation methods towards the morphology membrane was studied and the application of the PES membrane in reverse osmosis application was investigated by varying polymer concentration using Dmac solution and difference type of coagulation bath and evaporation time. The performance were characterizes using Scanning Electron Microscopy (SEM), contact angle measurement, Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), pure water flux and rejection of Sodium Chloride (NaCl).

METHODOLOGY

Materials

PES (Mw= 22,000 g/mol) powder form was obtained from Veradel and used as a polymer to prepare polymeric membrane. Dimethylactamide (Dmac) from Merk (Germany) were used as a solvent for preparation of dope solutions mainly because of good miscibility with PES membrane. PVP (Mw=40,000 g/mol) from Merk (Germany) was employed as additive. Ethanol (96%, Fisher Chemical) was used as coagulation agents. Sodium Chloride (Mw=58.44 g/mol, Avantor) was used for salt rejection at 2000ppm under 1 bar.

Membrane Fabrication

Dope solutions were prepared by dissolving pre-determined amounts of PES powder in the respective solvents as shown in Table 1. Polyvinylpyrrolidone (PVP) of 1.0 wt% is added in the prescribed amounts to the dope solution as additives. The solutions were stirred at least 24 hrs at room temperature to ensure complete dissolution. After the solution was homogenously dissolved, the dope solution was sonicated for 1 hrs to remove air bubbles which were trapped inside the dope solution. Then, the solutions was cast onto glass plate using glass rod. The casted membrane was left in air for pre- determined time

(0 s, 30s and 60 s) as shown in Table 1 before immersed into coagulation bath and remained for 24 hrs to allow residual solvent to leach out. Finally, the wet membranes were dried at room temperature for another 24 hrs and were cut into round shape with diameter of 5cm as shown on figure 1 below.

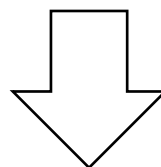
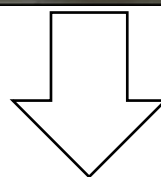


Figure 1: Polymeric Membrane Preparation

Table 1: Fabrication conditions of PES membrane.

Sample
15P-0T-OB
15P-60T-OB
15P-0T-37.5B
15P-0T-75B
15P-60T-75B
20P-30T-OB
20P-0T-37.5B
20P-60T-37.5B
20P-60T-75B
25P-0T-OB
25P-60T-OB
25P-0T-37.5B
25P-0T-75B
25P-60T-75B

P-polymer, T-evaporation time, B-Bath

Membrane Characteristics

Contact Angle Measurement

In order to evaluate membrane surface properties, contact angles were measured at a room temperature (30⁰ C) using the sessile drop method with a goniometer (VCA 3000, Water Surface Analysis System). Deionized water was used as the probe liquid in all measurement. To minimize the experimental error, the measurement was carried out at five random locations for each sample and then the average value was reported.

Fourier Transform Infrared (FTIR) Spectroscopy

The surface functional groups of the PES membrane's was using Perkin Elmer fourier transform infrared (FTIR) Spectroscopy. The dried membranes were scanned from 4000 cm⁻¹ to 515 cm⁻¹.

Water Flux Study

The pure water flux study of the fabricated membranes were performed using permeation set up as shown in figure 2 manufacture from in house system. Experiment was conducted using distilled water as the feed solution to determine permeability coefficient of the membrane. The operation pressure was applied at 1bar.



Figure 2: Experiment set up

The prepared membrane sheet was cut into round shape and put on the metal (stainless alloy). The area of the membrane module in thin sheet was 0.02 m². The volume needed for permeable product was as much as 100 mL. Flux can be determined using the formula;

$$J = \frac{V_p}{A \times t} \quad (1)$$

where J is the water flux (L/m² h), V is the permeate volume (L), A is the membrane area (m²) and t is the treatment time (h).

RESULT AND DISCUSSION

Contact Angle Analysis

The contact angle, θ is an angle between water and the surface of membrane. Generally, hydrophilic membrane surface have a contact angle in the range of $0^\circ < \theta < 90^\circ$, while hydrophobic membrane surface have a contact angle in the range of $90^\circ < \theta < 180^\circ$ [10].

Figure 1 displays the effects of membrane fabrication parameter such as compositions of PES, ethanol and types of coagulation bath towards contact angle measurements.

From the result obtained, at 15% PES Membrane the highest contact angle is at 0% of ethanol which is distilled water as a coagulation bath. While the lowest contact angle is at 37.5% ethanol. Lower contact angle shows that the membrane is more hydrophilic. The result can be seen that the contact angle decreased from 56.59 ° to 48.99° when the composition of ethanol was added in the coagulation bath to immerse the prepared PES membrane. But at 75% of ethanol, the contact angle was increased from 48.99° to 53.43°.

For 25% PES membrane, the highest contact angle is at 0% of ethanol. The result also shows that, the contact angle become more decreases when the addition of percentage of ethanol in coagulation bath was increases. As seen from figure 3, the contact angle was decreases from 63.96 ° to 54.12°.

By comparing the composition of PES membrane, 25% PES membrane was found to have the highest contact angle than 15 % PES compositions which is 63.96°. This show that the effect of contact angle is depends on polymer concentration. When the polymer concentration is higher, the contact angle is also higher. This result also agree by [11] studies that effect of polymer concentration on the hydrophilicity of the membrane is depends on the membrane pore size.

Table 2: Effect of membrane fabrication parameters towards the surface properties/ contact angle

Sample	Contact angle Measurement	
	15 wt% PES	25% wt% PES
0T-OB	56.49 ⁰	63.96 ⁰
0T-37.5B	48.99 ⁰	55.47 ⁰
0T-75B	53.43 ⁰	54.12 ⁰

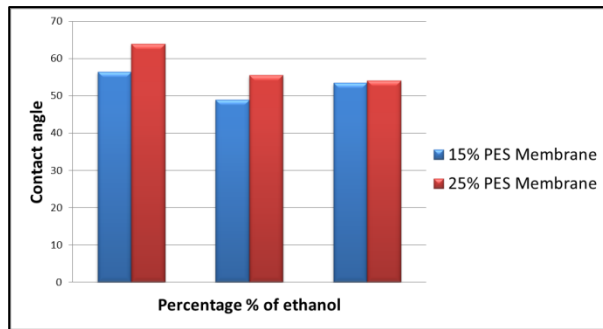


Figure 3: Effect of membrane fabrication parameters towards the surface properties/ contact angle.

FTIR Analysis

Figure 4 shows FTIR spectra for PES membrane prepared using 15 wt% polymer. This analysis was conducted to observe the effects of evaporation time and coagulation bath type and in the functional groups of PES membrane. From figure 4, it shows that 75% ethanol has the highest peak of hydroxyl (R-O-H) at 0s with 3610 cm^{-1} when compared with 0s of evaporation time, which is confirmed that coagulation bath effect the porosity and pore size of the membrane. For evaporation time at 0s, the highest peak of hydroxyl (R-O-H) is at 37.5% Ethanol with 3610 cm^{-1} when compared with 75% of ethanol and distilled water. For coagulation bath type, 37.5% Ethanol has the highest peak of carbonyl (C=O) which is at 0s of evaporation time with 1661.59 cm^{-1} when compared with distilled water of coagulation bath. After the analysis effect of PES membrane on coagulation bath and evaporation time, it confirms that pore size of membrane which responsible hydrophilic characteristic of coagulation bath and evaporation time.

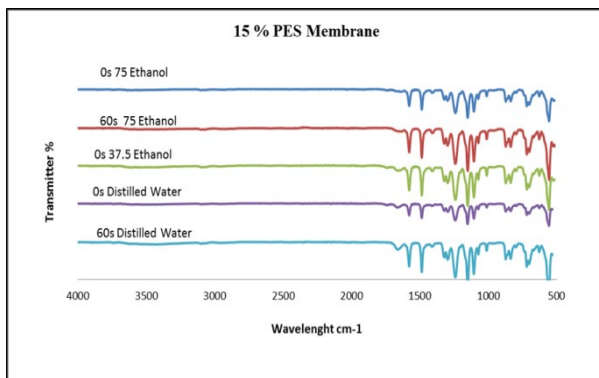


Figure 4: FTIR of 15% PES membrane at 0s 75% ET, 60s 75% ET, 0s 37.5% ET, 0s Distilled Water and 60s Distilled Water.

From figure 5 for 30s of evaporation time, 75% of Ethanol has the highest peak of hydroxyl (R-O-H) with 3610.57 cm^{-1} compared to distilled water. This shows that the highest peak of hydroxyl it shows that it is more hydrophilic characteristics. For 30s of evaporation time, 75% of ethanol has the highest peak of carbonyl (C=O) with 1662.20 cm^{-1} compared to distilled water.

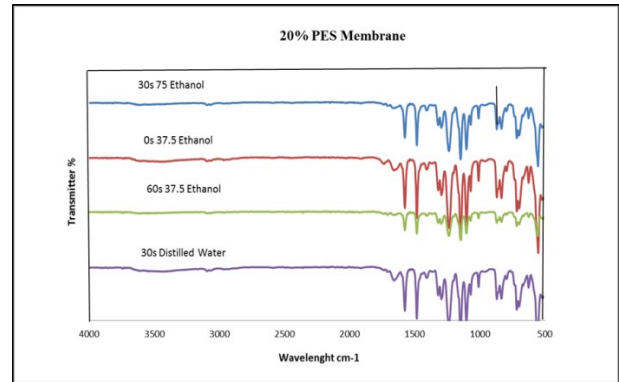


Figure 3: : FTIR of 20% PES membrane on 30s 75% ET, 60s, 0s 37.5% ET, 60s 37.5% Ethanol and 30s Distilled Water.

Figure 5 shows that 0s of evaporation time, distilled water has the highest peak of hydroxyl (R-O-H) with 3422.16 cm^{-1} compared with 37.5 % of ethanol. For coagulation bath of distilled water, 0s of evaporation time has the highest peak of hydroxyl (R-O-H) with 3422.16 cm^{-1} compared with 60s of evaporation time. By comparing for 75% of ethanol, 0s of evaporation time has the highest peak of hydroxyl (R-O-H) with 3545.72 cm^{-1} compared with 60s of evaporation time. By comparing for distilled water, 60s of evaporation time has the highest peak of carbonyl (C=O) with 1661.57 cm^{-1} compared with 0s of evaporation time. In term of time at 0s of evaporation time, distilled water has the highest peak of carbonyl (C=O) with 1659.08 cm^{-1} compared with 75% of ethanol and 37.5% of ethanol.

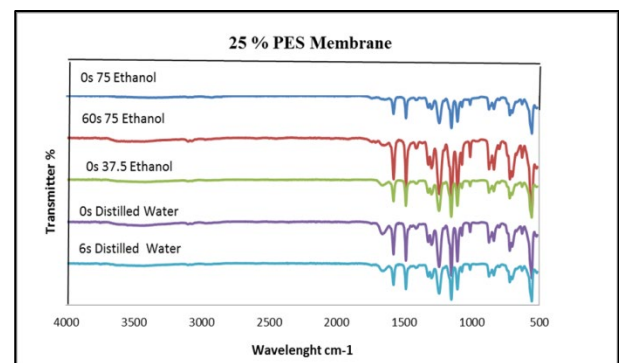


Figure 5: FTIR of 25% PES membrane at 0s 75% ET, 60s 75% ET, 0s 37.5% ET, 0s Distilled Water and 60s Distilled Water.

Water flux Analysis

Figure 5 below shows the stability of pure water flux for 1 hour. From figure 5 shows that the pure water flux on effect of coagulation bath. The figure shows that water flux increase from 8.22 ($\text{L}/\text{m}^2\cdot\text{h}$) to 16.49 ($\text{L}/\text{m}^2\cdot\text{h}$) when the percentage of ethanol was added in coagulation bath. But the water flux is decrease from 16.49 ($\text{L}/\text{m}^2\cdot\text{h}$) to 2 ($\text{L}/\text{m}^2\cdot\text{h}$) when the percentage of ethanol is added. As seen result from figure 5, the water flux is higher at 37.5% ethanol at 15 wt% PES. Studies from Madaeni., (2009), he proved that higher addition of coagulation bath, higher

water flux. However, from the result at figure 5, it showed that when more addition of coagulation bath, the water flux is low.

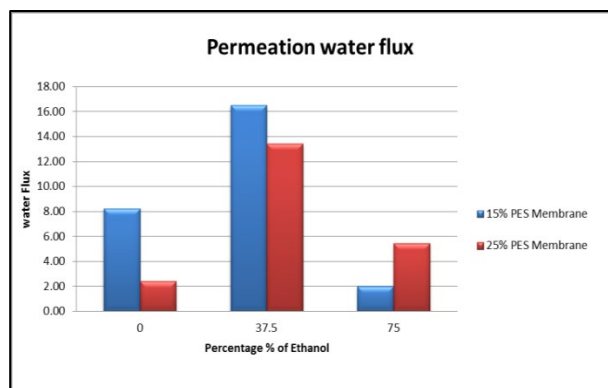


Figure 5: Pure water flux test

CONCLUSION

In this work, polyethersulfone (PES) membrane targeted for fluid separation was achieved. The effect of preparation methods towards the morphology membrane by varying the polymer compositions which are 15 wt%, 20wt% and 25wt% and by using different type of coagulation bath (addition ethanol) and evaporation times investigated using FTIR, contact angle, and water flux. The structure of membrane was observed to depend to type of coagulation bath and evaporation time. In all cases, the higher PES concentration provides higher contact angle, and lower flux. The lower evaporation time and coagulation addition, the lower measurement of contact angle as well water flux permeability.

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