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Effect of Ethanol Composition in the Coagulation Bath on Membrane Performance

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Abstract: Ethanol, a coagulation medium, plays an important role in producing high performance asymmetric nanofiltration membrane. Thus, the effect of ethanol composition in coagulation bath on the performance, morphology and properties of Polyethersulfones (PES) flat sheet membrane was studied. The performances of the PES membrane were obtained from the Pure Water Flux (PWF) experiment and salt solution rejection experiment. The results showed that the permeability coefficient (Pm) in the pressure range of 0-10 bar for ET 0 (100% water), ET 50 (50% ethanol) and ET 100 (100% ethanol) were 11.971, 8.464 and 3.0823 (m^3 m^{-2} sec MPa), respectively, which showed that: Pm ET 0 > Pm ET 50 > Pm ET 100. The rejection range follows as ET 0 < ET 50 < ET 100, which were 0-10, 0-18 and 0-20%, respectively. The morphology of membranes were vary from finger-like to sponge-like with the increase of ethanol composition in coagulation bath. This shows that higher ethanol composition may create thick membrane layer and cause the water fluxes to be declined, thus enhancing the membrane rejection. It was found that ET 50 was the optimum ethanol composition for its high rejection with moderate flux and thus suitable for industrial application.

Key words: Nanofiltration, pes flat sheet membrane, ethanol, coagulation bath, sem

INTRODUCTION

Nanofiltration (NF) has become one of the major membrane separations technologies during the last decades. It is mostly being employed in water purification industry such as in water softening process and is recently used for the removal of disinfection by-product (DBP) (Mallevialle *et al*., 1996).

To date, the significant and effective membrane in membrane isolation is flat sheet NF membrane. Preparation of this membrane is fabricated by employing the phase inversion technique. As reported earlier by Mallevialle *et al*. (1996), the flat sheet membrane is controlled by many factors on morphology and performance. One of these controlling factors is the composition of coagulation bath. The addition composition in coagulation medium will affect the membrane formation in terms of their morphology and performance, which is caused by the exchange of solvent and non-solvent in coagulation bath. Others parameter that influenced the membrane formation are the inter-diffusion of solvent, ethanol and water system and the solubility parameter of the polymer solution components (Deshmukh and Li, 1998).

Thus, this study is conducted to investigate the effect of ethanol composition in coagulation bath on the morphology and performance of PES flat sheet membrane. Ethanol was employed as the addition composition in coagulation bath. The aim of this study is to produce the high performance asymmetric NF membrane (PES/NMP 21/79%) for industrial application.

APPROACH AND METHODS

Selection of material: In this study, Polyethersulfone (PES) manufactured by AMOCO and N-Methyl Pyrrolidone (NMP) supplied by Merck were used for fabricating membrane. PES was chosen due to its physical toughness, heat stability, excellent pH tolerance, low protein and drug binding and resistance to all but small number of organic chemicals. This additive was composed from 0, 50 and 100% (v/v) of ethanol contents in water bath. Water was used as a nonsolvent in the coagulation bath process.

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Preparation of dope solution: The Polyethersulfone (PES) was used as membrane material in 21% (w/w). N-Methyl Pyrrolidone (NMP) was use about 79% (w/w) to prepare a binary system solution. PES was dried for at least 24 h in vacuum oven at temperature about 80°C before used for the solution making. A motor driven stirrer, Model HS 30D Daihan was set up along with heating mantle, round bottom reaction flask, condenser with water tube and a stirrer were installed at fume chamber to prepare the dope solution. The solvent was poured into the round flask and was stirred at the temperature range at 60°C. After 10 min, the PES chips were slowly added over the time into the solvent until it finished. This process might take about 8 h and more to reach the homogeneous condition and completed. The homogeneous solution was then placed in an ultrasonic water bath for about 2 h for purpose of removing particles and gas bubbles that exist in the casting solution.

Preparation of asymmetric flat sheet membrane: Flat sheet membranes were prepared according to the dry/wet phase separation processes. The polymer solution was cast on the clean glass plate using the electric casting machine fabricated in-house. The casting knife from steel blade was arranged to form an adjustable gap between the blade and glass plate. The selected thickness of casting blade was adjusted for 200 μm and the solution was cast with the speed of 15 sec to produce about 13 in of membrane. The membrane was immersed in the quench medium consists of 0, 50 and 100% of ethanol compositions in water coagulation bath for 24 h to form a thin film of membrane and then dried under the room conditions for a day. The summaries of membrane casting condition are specified in Table 1.

Membrane testing: The membranes prepared were performed using Dead-end Cell Filtration supplied from Sterlitech HP4750 Stirred Cell, to determine the PWF and rejection (%) of the produced membrane through the separation process. PWF experiment was conducted using distilled water as the feed solution in order to determine the permeability coefficient of the membrane. The operation pressures applied were various from 0-10 bars.

Membrane sheet was cut into round shape and put on the Membrane sheet was cut into round shape and put on the metal (stainless alloy). The area of the membrane module in thin sheet was 1.46×10^{-3} m^2. The volume needed for permeable product was as much as 3 mL. Flux can be determined using the following formula:

Table 1: Flat sheet membrane casting conditions

Conditions	Value
Casting solution composition	PES : 21 wt %
	NMP : 79 wt %
Casting knife gap distance	200 μm
Casting temperature	Ambient temperature, 29°C
Casting time	15 sec
Casting speed	0.0213 ms^{-1}
Shear rate	106.7 sec^{-1}
Coagulation bath compositions	a) Ethanol : Water
	= 0 : 100%
	b) Ethanol : Water
	= 50 : 50%
	c) Ethanol : Water
	= 100 : 0%
Coagulation temperature	27°C
Room humidity	70-80% RH
Drying procedure	Ethanol : Water/1 day/27°C
	Atmosphere/1day/ambient temperature

$$J = \frac{V}{At} \quad (1)$$

Where:
J = Flux (m/s),
A = The area of membrane (m^2),
V = The volume of permeable solution (m^3) at time, t (s).

The pure water permeability can be expressed as P_m and can be obtained as the water flux at various pressures. The unit for flux is expressed by m^3 m^{-2} sec.

$$J_V = P_m \Delta P \quad (2)$$

Rejection: The steps of rejection measurement were the same as the determination of Pure Water Flux (PWF). But the difference was using 0.01 M NaCl solutions as the feed solution. The concentration of feed, permeate and retentate are expressed as C_f, C_p and C_y, respectively. The concentration of permeate was collected in cylinder and the conductivity readings of each, C_f, C_p and C_y with different pressures were measured using the conductivity meter, Model Cyber Scan CON 150. The percentage of rejection is usually expressed as selectivity of membrane. It defined concentration of solute in permeate phase, C_p, relative to the concentration of wall, C_w.

$$\text{Percentages of rejection, R (\%)} = \left[1 - \frac{C_p}{C_w}\right] \times 100\% \quad (3)$$

The characteristics that influenced in rate of rejection are the size, shapes and charge and the pore sizes of membranes relative to membrane configuration. Apart from that, the chemical properties and interaction between membrane and solutes, for instance adsorption, concentration polarization, fouling and ion exclusion effects (Alborzfar *et al*., 1998).

Membrane structure characterization: In this study, membrane structure characterization was performed using

Scanning Electron Microscope (SEM) model JSM-630LA for showing the structure and morphology of the cross-section of membrane. Before the membrane was put in the SEM, the membrane sample was cut into small pieces and pasted on stub. Then, the membrane was covered with gold using auto-coater machine model JFC1600.

RESULTS

The membranes prepared were cast from a polymer solution of 21% PES and 79% NMP and coagulated in water coagulation bath consists of 0, 50 and 100% of ethanol compositions. Table 2 showed the produced membranes and their coding.

Membranes morphology: Figure 1(a-c) showed the morphology of PES membranes for ET 0, ET 50 and ET 100 by SEM micrographs. For ET 0, it is clearly seen that long finger-like structure are presented at the active layer to porous support layer.

For ET50, It is shown that the active layer of membrane is formed by sponge-like structure, whereas the support layer formed a finger-like structure with macrovoids. While for ET100, It is clearly viewed that the formation is fully composed of sponge-like structure. Thus, addition of ethanol composition would change the membrane morphology from finger like to spongy structure in the following sequence: ET 0 > ET 50 > ET 100.

Table 2: Membrane coding of membranes at various compositions of ethanol in coagulation bath

Membrane code	Ethanol compositions in coagulation bath (%)
ET 0	Ethanol : Water = 0 : 100
ET 50	Ethanol : Water = 50 : 50
ET 100	Ethanol : Water = 100 : 0

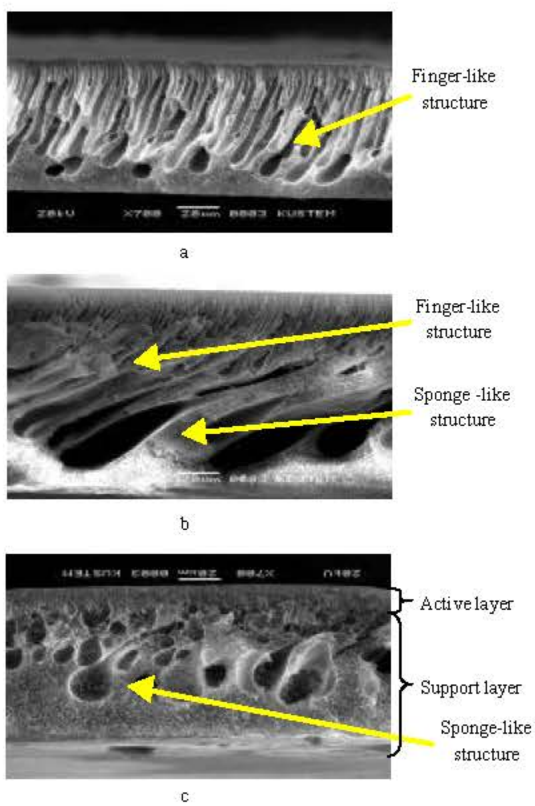

Fig. 1: Scanning electron photomicrograph of membrane at different ethanol composition in coagulation bath (a) ET 0, (b) ET 50 and (c) ET 100, respectively

MEMBRANE PERFORMANCES

Water flux experiment of PES membrane: Table 3 showed the results of permeability coefficient (Pm) in the pressure range of 0-10 bar according to the various ethanol compositions employed. It shows that: Pm ET 0 (11.971) > Pm ET 50 (8.464) > Pm ET 100 (3.082).

Rejection of NaCl by PES membrane: Table 4 showed the rejection values by various ethanol compositions in coagulation bath in the pressure range of 0-10 bar. The rejections ranges showed that ET 100 > ET 50 > ET 0, which were 0-20, 0-18 and 0-10%, respectively.

Figure 2 shows the NaCl flux (permeability) versus pressure for ET 0, ET 50 and ET 100. It showed that the NaCl flux decreased with the increase of ethanol composition in coagulation bath.

From, Fig. 3 it can be seen that the composition of ethanol in coagulant bath influenced the rate of rejections in most condition. At the low pressure of 2 bars, the rejection rates of all membranes were being affected after long periods of rejection and thus their value is closed to each other.

Roughly, the rejection rate of ET 0 and ET 50 followed the same pattern at the applied pressure of 4, 6,

Table 3: Permeability coefficient at various ethanol compositions at different pressures applied

Compositions in coagulation bath	Permeability coefficient ($\times 10^{-6}$ m^3 m^{-2} sec MPa)
ET 0	11.9710
ET 50	8.4640
ET 100	3.0823

Table 4: Rejection values at various ethanol compositions in coagulation bath

Composition	Flux NaCl (m^3 m^{-2} sec)	Rejection (%)
ET 0	0-5.931	0-10
ET 50	0-3.039	0-18
ET 100	0-1.048	0-20

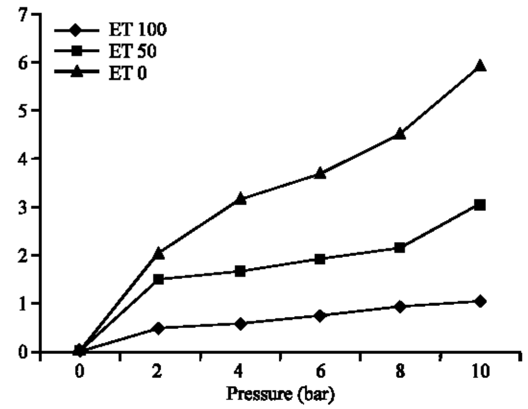

Fig. 2: NaCl fluxes at different operation pressure for ET 0, ET 50 and ET 100

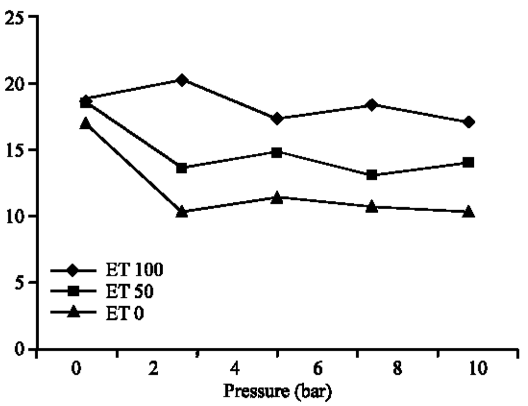

Fig. 3: Rejections versus pressures for ET 0, ET 50 and ET 100

8 and 10 bars. Meanwhile the ET 100 showed an obvious higher rejection rate than ET 50. Generally, the increase of ethanol contents in coagulation bath resulted in higher rejection rate of membranes.

Figure 4 showed the graph of rejections versus fluxes of the membranes prepared using NaCl solution. It showed the correlation between the rejections and fluxes in between these membranes with different composition. The 100% of ethanol composition in coagulation bath (ET 100) resulted the highest rejection rate with the lowest flux value. While for the membrane that coagulated in 100% of water (ET 0), it had produced the lowest rejection rates but the highest flux rate. Yet, the membrane produced by 50% of both ethanol and water composition in coagulation bath was showing intermediate values of both rejection rates and fluxes. Thus, the flux rate of membranes were summarized as these following sequence, ET 0 > ET 50 > ET100 whereas the rejection rates results were ET 100 > ET 50 > ET 0.

Table 5: Relationship between permeability coefficient, NaCl flux and rejection at various ethanol compositions in coagulation bath

Composition	P_m ($\times10^{-6}$ m^3 m^{-2} sec MPa)	NaCl flux (m^3 m^{-2} sec)	Rejection (%)
ET 0	11.971	5.931	0-10
ET 50	8.464	3.039	0-17
ET 100	3.082	1.048	0-20

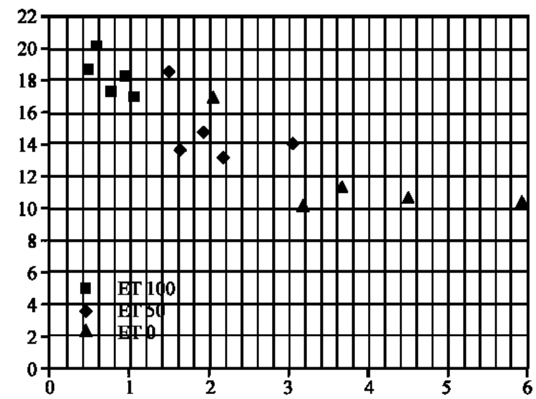

Fig. 4: Rejections (%) versus flux ($\times10^{-6}$) (m^3 m^{-2} sec). The optimum composition of ethanol in coagulation bath and the best membrane performance

In this study, three formulations of ethanol composition were applied in coagulation bath. The various ethanol percentages applied in coagulation bath caused differentiation on its rejection and flux. The optimum ethanol composition in coagulation bath was determined by the intersection between the rejection and flux curves of ET 0, ET 50 and ET 100 membranes. The best membrane performance in between three fabricated membranes was selected on its selectivity and productivity, which produced the higher rejection rate and moderate flux.

Table 5 showed the permeability coefficient, NaCl flux and percentage of NaCl rejection. It showed that the addition of higher ethanol composition in coagulation bath has caused the decrease of both membrane permeability coefficient and NaCl flux rate, which resulted in the increase of rejection rate of NaCl.

Figure 5 showed the difference of permeability coefficients of each membrane. It showed that the higher ethanol composition in coagulation bath would decrease the membrane's permeability coefficients.

For Fig. 6, it showed the relationship between the rejection and the flux at various ethanol compositions in coagulation bath. The range of rejection was around 10-20%, whereas the flux was in the range of 1.048-5.931 (m^3 m^{-2} sec). It was obviously demonstrated that the flux

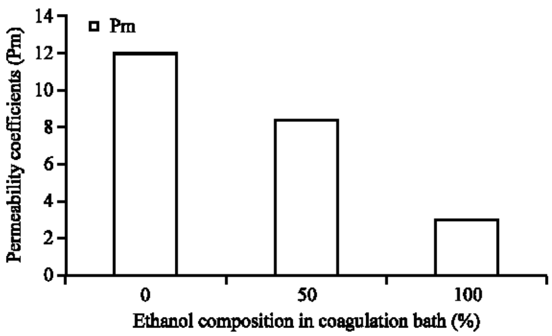

Fig. 5: Differentiation of permeability coefficients for ET 0, ET 50 and ET100

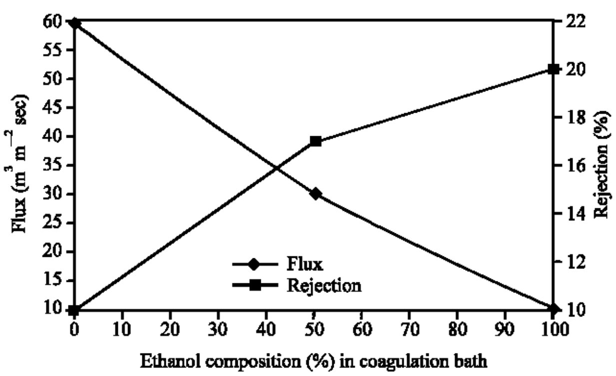

Fig. 6: Relationship between the rejection and the flux value according to the composition of ethanol in coagulation bath

is inversely proportional to the membrane rejection. This graph would point out the optimum NF membrane as the intersection of the lines. It was shown from this graph that the intersection fell in the range of 40-50% of ethanol composition. Thus, this showed that the optimum ethanol composition in coagulation bath was almost closed to membrane produced by 50% ethanol in the coagulation bath, which is ET 50 in this study. Based on this factor, ET 50 was selected as the best composition of ethanol in coagulation bath.

DISCUSSION

The appearance of the structure for ET 0 can be attributed to the rapid precipitation or instantaneous precipitation occurred that resulted in many long finger-like pores. According to Kesting (1985), the formation of large finger-like macrovoids and cavities structure were resulted from the fast coagulation rate. Meanwhile, the porous-sponge like structure was due to the slow precipitation rate. From the previous study, when no addition of ethanol in coagulation bath, it could resulted large finger-like macrovoid and cavities presented near the inner and outer of skin layers of hollow fiber. The inner skin surface macrovoid size reported is larger than the outer skin (Deshmukh and Li, 1998). For ET50, the long finger like structure was slowly changed through a short finger-like structure to a little spongy structure when the ethanol concentration increased from 0 to 50%. According to Deshmukh and Li (1998), the existence of ethanol in water bath led to slow diffusion of nonsolvent into the forming structure and thus, the rate of precipitation was decreased. Moreover, the addition of solvent in coagulation bath will also influence the morphology of membrane, where the solubility parameter of solvent, nonsolvent will become smaller due to the occurrence of delayed demixing caused by the strong interaction between solvent and nonsolvent. While for ET100, the short finger-like structure was fully substituted by sponge-like structure and few circular void. This present result was respected due to previous researches focusing on membrane structure of 100% ethanol. According to Mulder (1996), formation of dense membrane structure were caused by smaller demixing gap. Deshmukh and Li (1998) also revealed that the increased of ethanol concentration in coagulation bath would decreased the effective porosity (open-end pores). Thus, this concludes that ethanol addition in coagulation bath influences the membrane morphology in the formation of macrovoid or microvoid that is presented by the finger-like and sponge-like structure, which is influenced by delay demixing.

Generally, the results from water flux experiment indicated the permeability coefficients were decreased with the increase of ethanol composition in coagulation bath, which obey the findings in previous research (Tsui and Cheryan, 2004; Mulder, 1996) and thus caused the formation of denser membrane structure. According to Mohammad *et al.* (2003), the permeability of NF membrane was in the range of 10^{-11}-10^{-12} m^3 m^{-2} sec Pa. Thus, the PES flat sheet membranes produced in this study falls in the range of NF membranes based on their obtaining permeability coefficient.

The NaCl rejection shown by PES membrane revealed that the increase of ethanol contents in coagulation medium would increase the rejection of NaCl solution but decrease the NaCl flux rate. Addition of ethanol composition in coagulation bath resulted a slow precipitation rate that caused delay demixing occupance in precipitation (Deshmukh and Li, 1998). According to Fan *et al.* (2002), when the selectivity increases from the water to ethanol in coagulation bath, the permeation rate decreases drastically. This fact can be explained due to the theory stated that the location of binodal curve far from the solvent-polymer axis resulted by the slow liquid-liquid demixing when applying ethanol in coagulation medium. In addition, the higher alcohol molar volume in coagulation bath caused a delayed mechanism of liquid-liquid phase separation.

Comparisons were made between ET 50 with ET 0 and ET 100 in order to select the best membrane performance among them. The best performance is judged in this study as the membrane that produced high rejection rates with moderate flux. ET 0 had produced membrane with higher NaCl flux value but with the lowest rejection rate (%). This showed that ET 0 is not effective enough compare to ET 50 and ET 100 because of its low rejection rate.

For the membrane produced by ET 100, it yielded the highest rejection rate but with the lowest NaCl flux and membrane permeability coefficient. Therefore, ET 100 is also not effective enough because its spongy structure required the higher pressure applied to achieve the higher rejection but with the poor membrane permeability.

Hence, ET 50 is the selected membrane with the best membrane performance. It can be explained due to its moderate permeability coefficient and NaCl flux rate yet high rejection rate. It almost reached to the optimum value of ethanol composition in coagulation bath, which is in the range of 40-50%.

CONCLUSION

The results showed that the permeability coefficient (Pm) in the pressure range of 0-10 bar for ET 0 (100% water), ET 50 (50% ethanol) and ET 100 (100% ethanol) were 11.971, 8.464 and 3.0823 (m^3 m^{-2} sec MPa), respectively, which showed that: Pm ET 0 > Pm ET 50 > Pm ET 100. The rejections ranges showed that ET 0 < ET 50 < ET 100, which were 0-10, 0-18 and 0-20%, respectively. The morphology of membranes were varied from finger-like to sponge-like with the increase of ethanol composition in coagulation bath. This shows that higher ethanol composition may create thick membrane layer and causes the water fluxes to be declined, thus enhancing the membrane rejection. It was found that ET 50 was the optimum ethanol composition for its high rejection with moderate flux and thus suitable for industrial application.

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