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The Development of New Composite Polymer Membrane : Polysulfone (PSf)/polyetherimide (PEI) coated membrane

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***Abstract*—In this research, the effect of coating composition (polyetherimide (PEI)) on the physical and mechanical characteristics as well as pure water flux (PWF) of the PSf/PEI composite membranes. The physical characteristics of membranes were analyzed based on the acquisition of surface and cross section morphology, porosity and pore size of PSf/PEI coated membranes, while the mechanical characteristics of membranes were analyzed based on the membrane's ability to maintain surface and internal pore size when applied to external loads (Young's modulus). Meanwhile, the PWF is obtained from the analysis using a "dead-end" membrane reactor with an operational pressure of 1 atm separation. The results of surface and cross-sectional morphology analysis showed that the level of PSf/PEI membrane pore density increased with increasing PEI contents in the coating solution. This finding is in line with the results of porosity and pore size analysis of the membrane using dry-wet weight method which shows a decrease in porosity and pore size along with the increase in polymer coating levels applied in the PSf/PEI coated membrane manufacturing process. The decrease in porosity and pore size is closely related to the increase in mechanical strength and a decrease in PWF of the PSf/PEI composite membrane.**

Keywords—Membrane, composite, polymer, polysulfone, polyetherimide

I. INTRODUCTION

Polysulfone (PSF) is one of the important polymer material in the production of synthetic membranes for several decades. This condition is induced by mechanical, thermal and chemical characteristics of excellent PSf. Regarding its chemical resistance, PSf has a wide pH range application [1] - [4]. These advantages have made PSf membranes have wide application areas, including gas and liquid separation [5], fuel cells [6], and ion exchange processes [7]. However, in subsequent developments, PSf membrane was known to have a total of weaknesses related to its physical characteristics. The dominance of symmetri pore structures with large mass transfer resistance has caused this membrane to have high fouling potential.

Fouling tends to cause a decrease in membrane fluxes and an increase in operating costs as a result of the need for a total of additional procedures for cleaning [8]. Symmetri pore structure dominated by sponge pore tends to be susceptible to deposition of dissolved particles, especially in the internal pore of the membrane, with a high level of cleaning difficulty [9]. Potential fouling on PSf membranes can be mitigated, one of which is through membrane surface modification using coating methods with other polymer materials that have the ability to form asymmetri structures, such as polyetherimide (PEI) [10].

Polyetherimide is a synthetic membrane forming polymer material with many advantages, such as asymmetry structure forming ability, mechanical strength and thermal resistance and excellent chemical [11]. Asymmetry structure with high porosity and low pore size and minimal macrovoid become surface morphology and the cross-section of PEI typical superior [12], which is able to present comparable permeability and selectivity, and excellent mechanical resistance. Meanwhile, the amount of binding energy possessed by the molecular structure of PEI has made this membrane have a thermal resistance of up to 500 ° C. Although attached to many advantages, PEI membranes are reported to have weaknesses related to their resistance in acidic and alkaline environments, which are generally lower compared to PSf and PVDF [13]. Thus, the PSf membrane surface coating by PEI material is predicted to be able to produce new composite membranes with outstanding characteristics and performance.

II. MATERIAL AND METHODS

A. *Material*

PSf (BM 35,000), PEI (melting point 9 g / 10 min, 337 ºC), and n-methyl pyrrolidone (NMP) (≥99.7%), each of which is used as the main polymer material and solvent in membrane preparation in this research was obtained from Sigma Aldrich Singapore. Ammonium chloride (NH_4Cl) (≥99.5%) used as a porogen additive in this research was obtained from Riedel de Haen China. To produce membranes with high mechanical resistance, in this research a gauze support layer was obtained from Kasa Husada Indonesia (254 mesh).

B. *Instrumentation*

The instruments used in this research include membrane reactors (homemade) with dead-end flow systems and pressure thrust (max. 6 bar) used to evaluate permeability, Zeiss EVO MA10 Scanning Electron Microscopy (SEM) which is used to ensure the formation of asymmetry structures and RCT / 10KN / AF Toyo Seiki Strograph used to analyze mechanical resistance

C. Psf / PEI composite membrane preparation

PSf membrane (PSf / NMP / NH_4Cl) (% b / b) 16/84/0 was prepared by dissolving 16 g PSf in 84 g of NMP solvent. To obtain a homogeneous PSf casting solution, the stirring is done using a magnetic stirrer at 60 ° C for 420 minutes. In a different place, PEI casting solution is prepared with the composition of PEI / NMP / NH_4Cl (% b / b) 2/84/14; which will be used as a coating. Homogenization of PEI polymer solution was also carried out using a magnetic stirrer at a temperature of 60 ° C for 420 minutes. To ensure the absence of air bubbles in both casting solutions, the homogeneous PSf casting solution and PEI coatings were allowed to stand for 1.080 minutes at room temperature.

The casting and coating process is carried out using an automatic casting knife with a temperature of 40 ° C and a casting thickness of 0,8 mm. PEI polymer coating is carried out with the same procedure and 0,2 mm thickness. Subsequent casting solution allowed to stand 30 minutes ($t_{pra\text{-}immersion}$ = 30 minutes) at 40 ° C ($T_{pra\text{-}immersion}$ 40 ° C). Solid composite membranes were obtained after immersion in a coagulation medium using a non-solvent 100% H_2O which was conditioned at a temperature of 40 ° C for 120 minutes. PSf / PEI membrane washing is formed using water flow. The membrane drying process is carried out in air for 1.440 minutes. The dry PSf / PEI composite membrane is put in a closed place and only removed just before analysis.

To obtain the membrane with the best characteristics and performance, in this research variations were made, including: (1) composition of coating solution (PEI): PEI / NMP / NH4Cl (% b / b) 2/84/14; 4/84/12; 6/84/10; 8/84/8; 10/84/6; 12/84/4; 14/84/2; and 16/84/0, (2) pre-immersion time: 0 minutes, 30 minutes, 60 minutes, 90 minutes, and 120 minutes; (3) pre-immersion temperature: 40 ºC, 50 ºC, 60 ºC, 70 ºC, and 80 ºC.

D. Characterization of PSf / PEI composite membranes

In this research characterization of PSf / PEI composite membranes carried out included physical characterization (surface morphology and cross-section) using SEM with a magnification of 20.000x, mechanical characterization (Young's modulus) using strograph with an external load of 30 kN, and chemical characterization (functional group) using FTIR with a wave number of 400-4.000 cm^{-1}. To obtain a more accurate and precise effect of the three independent variables studied the physical characteristics of the membrane, porosity analysis and pore size were analyzed using dry wet weight method.

E. PSf / PEI composite membrane permeability test

A circular composite membrane with a diameter of ± 6 cm is placed at the bottom of the test equipment which was previously coated with filter paper. In the next stage, a total of 250 mL of 100 ppm feed is passed through a membrane with the thrust pressure of 1 kg / cm^2. The time required for all the feed to pass through the membrane is recorded, to be used in the calculation of flux based on the following equation.

$$J = \frac{V}{A \times t} \tag{1}$$

Where J is the flux, which is stated in L / m^2. Hour; V is the permeate volume, which is expressed in liters (L); A is the membrane surface area, which is expressed in m^2; and t is the time needed until the entire feed is passed through the membrane, which is stated in hours.

III. RESULT AND DISCUSSION

A. Physical and mechanical characteristics of PSf / PEI composite membranes

In this research, has been engineered membrane PSf coating by PEI with a combination of phase inversion method / immersion-precipitation and wet coating include the composition of the coating solution PEI / NMP / NH_4Cl (% w/w) 8/84/8; 10/84/6; 12/84/4; 14/84/2; and 16/84/0. Increased contents of PEI in the coating solution appear to increase the potential for pore asymmetry structure (sponge and finger pore) which are known to be more resistant to fouling. Increased contents of PEI also increase the potential for porous layers with a high total of pores on the membrane, creating a composite membrane that not only has high permeability but also high mechanical strength and selectivity.

In Figure 1 and Figure 2, each of them shows the surface morphology and cross-section of PSf coating by PEI membrane with the composition of PEI / NMP / NH4Cl (% b / b) 8/84/8; 10/84/6; 12/84/4; 14/84/2; and 16/84/0. Surface morphology data showed that membranes with contents PEI 8% (w / w) had the most tenuous pore structure compared to membranes with other PEI compositions. Increased contents of PEI in the coating solution have increased the pore density in the PSf / PEI composite membrane. The natural characteristics of PEI membranes which tend to have high porosity with tight pore size have dominated the membrane surface along with increased contents of PEI. However, an increase in PEI contents that exceed the optimum results in serious shrinkage of the membrane. This condition has caused the PSf / PEI membrane to have lower porosity with smaller pore size.

The increasing level of pore density causes an increase in the mechanical strength and selectivity of the composite membrane. However, to get a composite membrane with comparable permeability and selectivity, pore structure must be formed asymmetry on the membrane. Therefore, it becomes important to evaluate the cross-section morphology of the membrane resulting from variations in the composition of the coating solution. Based on the cross-section morphology data in Figure 2, it can be seen that the asymmetry pore structure which is one of the achievement targets in this research has been formed on all types of PSf / PEI composite membranes obtained from the variation of the coating solution composition. However, it is clear that the coating with increasing PEI levels in PSf membranes has led to a lowering of the quantity and volume of the macrovoid that accompanies the decrease in pore size.

SEM image analysis using computers has become a standard and widely used for porous material research.

However, morphological parameters such as size and total pore are difficult to measure using SEM images because almost all pores are in the same range [14] - [15]. Such a method only gives a rough estimate of the size of the pores by overestimating the smallest pores on the surface and also by considering clogged pores and open pores [16]. The dry-wet weight method (measurement of porosity) and the Guerout-Elford-Ferry equation (pore size measurement) have been used to compare the morphology of a total different membranes.

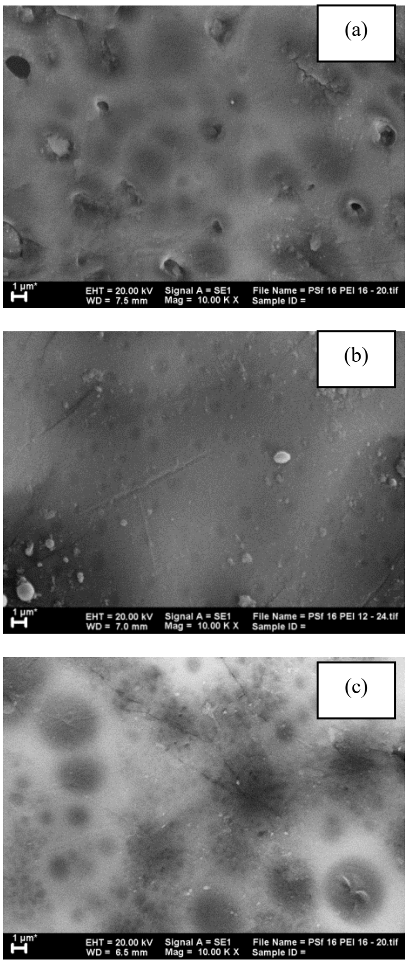

Fig. 1. PSf / PEI composite membrane surface morphology with coating solution composition (PEI / NMP / NH4Cl) (% b / b): (a) 8/84/8; (b) 12/84/4; and (c) 16/84/0

In addition to influencing the surface morphology and cross-section, the increase in PEI contents in the coating solution is also closely related to the PSf / PEI composite membrane porosity. Regarding this, membrane porosity can be determined by the dry-wet weight method. In table 1, the data of PSf coating by PEI membrane porosity is obtained from variations in the composition of the coating solution. Increased contents of PEI in the coating solution have caused a decrease in porosity, which will often increase with decreasing porogen contents of NH_4Cl in the coating solution.

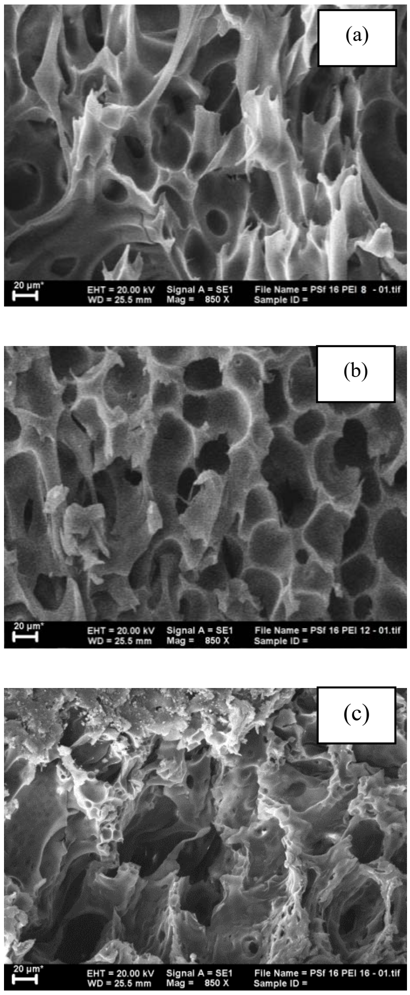

Fig. 2. Morphology of cross section of PSf coating by PEI membrane with coating solution composition (PEI / NMP / NH4Cl) (% b / b): (a) 8/84/8; (b) 12/84/4; and (c) 16/84/0

TABLE 1. DATA OF PSF COATING BY PEI MEMBRANE POROSITY WITH VARIATION IN COATING SOLUTION COMPOSITION

No	Coating Solution Composition (%b/b)			Porosity (%)
	PEI	*NMP*	*NH_4Cl*	
1	8	84	8	28,43
2	10	84	6	33,11
3	12	84	4	41,69
4	14	84	2	71,37
5	16	84	0	46,59

Figure 3 shows the effect of increasing contents of PEI in the coating solution on decreasing membrane pore size, where the pore size of the PSf coating by PEI membrane prepared with the composition of PEI / NMP / NH4Cl (% b / b) 8/84/8 coating solution was 1,99 nm. Membrane pore size will continue to decreasing and reach its peak when PSf membrane coating is carried out using the composition of PEI / NMP / NH4Cl (% b / b) 14/84/2, where the pore size obtained is 0,46 nm. However, when the PSf membrane matrix coating by PEI composition of 16% b / b, a pore size was increased to 0,75 nm.

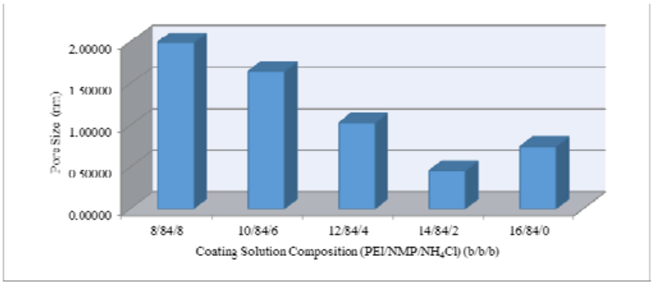

Figure 3. The pore size of PSf / PEI composite membrane prepared with variations in the composition of the coating solution

Tensile strength and elongation of membranes when broken are two important parameters for describing the mechanical characteristics of membranes. The effect of the coating solution composition on the mechanical strength of the PSf coating by PEI membrane is shown in Table 2. Increased PEI contents in the coating solution have resulted in a modulus young membrane decrease from 2,257 N/m^2 for the composition of PEI / NMP / NH_4Cl (% b / b) 8/84 / 8; to 604 N/m^2 for the composition of PEI / NMP / NH_4Cl (% b / b) 14/84/2. The increase in membrane porosity that occurs along with the decrease in pore size in the use of coating solutions with increasing PEI contents indicates that in this case, the increase in porosity has a more significant effect than the decrease in pore size in determining the mechanical strength of the membrane concerned. However, a decrease in membrane porosity was observed when the coating solution used contained PEI (16% w / w). This decrease shows that PEI contents in the coating solution has exceeded the optimum to cause optimum membrane shrinkage there depress the amount and size pore of the membrane. This condition has triggered an increase in mechanical strength (Young's modulus) PSf coating by PEI membrane up to 1,806 N/m^2.

TABLE 2. DATA OF THE TENSILE STRENGTH AND ELONGATION MEMBRANE OF PSF COATING BY PEI ON THE COMPOSITION OF THE COATING SOLUTION

No	Coating Solution Composition /*Coating*(%b/b)			Mechanical Strength		
	PEI	*NMP*	*NH_4Cl*	*Tensile strength* (N/m^2)	*Elongation* (%)	*Modulus Young* (N/m^2)
1	8	84	8	217	10	2.257
2	10	84	6	342	21	1.604
3	12	84	4	300	19	1.619
4	14	84	2	150	25	604
5	16	84	0	133	7	1.806

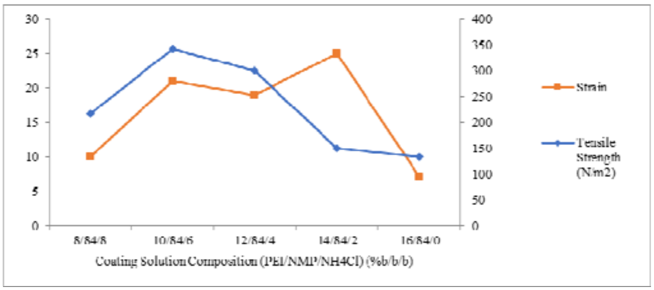

Figure 4. Tensile strength and elongation of membranes prepared of PSf coating by PEI with the variation coating solution composition

F. Pure water permeability of PSf / PEI composite membranes

Pure water permeability and pore size are key specification factors for porous membranes, where the permeability of pure water has a direct relationship to the total and size of pores on the surface and internal pores of the membrane (uplayer porosity). The effect of coating solution composition on the pure water permeability of PSf / PEI composite membranes is shown in Figure 5. The data in Figure 5 shows a decrease in the pure water permeability of PSf coating by PEI membrane along with an increase in PEI contents in the coating solution composition. Based on porosity data and pore size previously obtained, it can be seen that the increase in porosity that occurs along with the decrease in membrane pore size does not have a significant effect on increasing the permeability of pure water. Thus, the decrease in permeability of pure water produced in this case is caused or influenced by pore size compared to porosity. Specifically, for PSf coating by PEI membranes produced by the coating process using PEI 16% b / b, an increase in pure water permeability has been detected. This condition is the opposite of what happened before, where in theory, increasing contents of PEI in the PSf coating solution will increase the pore density and decrease the porosity of the membrane which then leads to the low permeability of pure water. However, the results of the observations during the experiment showed that the high viscosity of the resulting coating solution had increased the barriers to coating PEI using a casting knife in PSf casting solution. This has a direct effect on the perfection of the low coating process and leads to a pattern of changes in permeability of the PSf / PEI membrane pure water.

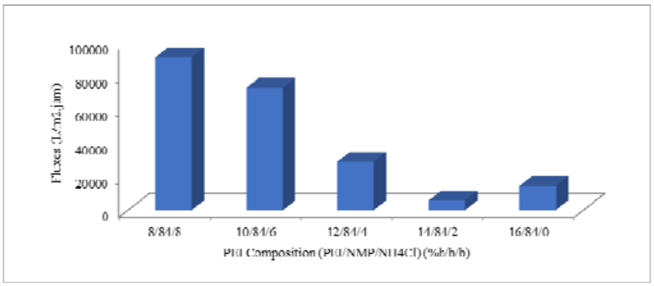

Figure 5. The permeability of the pure water membrane of PSf coating by PEI prepared with variation in coating solution composition (PEI)

IV. CONCLUSION

Based on the results of data analysis it can be concluded that the composition of the coating solution (PEI) has an effect on the surface morphology and cross-section of PSf / PEI membranes, where an increase in the composition of PEI has increased porosity and decreased pores membrane to certain compositions. Correspondingly, the composition of the coating solution has an effect on the mechanical strength and permeability of the PSf / PEI membrane, where an increase in the composition of PEI has decrease the mechanical strength of the membrane to a certain composition and induced a decrease in permeability of membrane pure water. Overall, the resulting PSf / PEI composite membrane has a structure of asymmetry with the porosity of 28,43% -71,37%; pore size 0.75 nm - 1.99 nm; mechanical strength 604-2,257 N / m^2; and pure water permeability of 5,773-91,398 L / m^2. hours.

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