

## Enhanced Separation Performance of Cellulose Acetate Membrane For Brackish Water Separation Using Modification of Additives and Thermal Annealing

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### Abstract

Membrane is an alternative technology of water treatment with filtration principle that is being widely developed and used for water treatment. The main objective of this study was to make an asymmetric membrane using cellulose acetate polymer and study the effect of additive and annealing treatment on the morphology structure and performance of cellulose acetate membranes in brackish water treatment. Asymmetric membranes for brackish water treatment were casted using a casting machine process from dope solutions containing cellulose acetates and acetone as a solvent. Membranes were prepared by phase inversion method with variation of polyethylene glycol (PEG) concentration of 1, 3, and 5wt% and the annealing temperature at 60°C and 70°C for 5, 10, and 15 seconds. Membrane characterization consists of calculation of membrane flux and rejection with brackish water as a feed, SEM and FTIR analysis. The research concluded that asymmetric cellulose acetate membrane can be made by dry/wet phase inversion method. The more added concentration of PEG will be resulted the larger pore of membrane. Meanwhile the higher temperature and the longer time of annealing treatment, the skin layer of membrane become denser. Membrane with the composition of 18 wt% cellulose acetate, 5 wt% PEG, 1 wt% distilled water, with heat treatment at temperature of 70°C for 15 seconds is obtained optimal performance: flux 6.52 L.m<sup>-2</sup>.h<sup>-1</sup>.bar<sup>-1</sup>, 71% of total dissolved solid (TDS) rejection, 63.75% of turbidity rejection, 52.9% rejection of Ca<sup>2+</sup>, and 41.9% rejection of Mg<sup>2+</sup>.

**Keywords:** Asymmetric membrane; PEG; Cellulose acetate; Annealing; Brackish water

### Introduction

Membrane is an alternative technology to the water treatment with filtration principle that is being widely developed [1,2]. Membrane technology is considered to have more advantageous to be applied water treatment because it does not require any necessary chemical additives such as the existing conventional technologies [1]. Additionally, membrane technology does not require a lot of equipment because the membrane component is portable so that the investment costs are lower than conventional systems. Research related to the condition of making membrane is still interesting. This is because of the many parameters that affect characteristics of the resulting membrane [3,4]. The combination of various parameters allows obtaining tailor-made membranes that are specific to a particular separation purposes [1].

A common type of polymer used in production of membranes are cellulose acetate. Manufacture of cellulose acetate membranes is performed using dry/wet phase inversion technique which polymer is converted from liquid phase to solid phase with the precipitation in a evaporation and immersion. For certain purposes, additives are often added to the dope solution. Kind of additive that is often used is polyethylene glycol (PEG). The manufacture of membranes with addition of PEG additive has the effect of increasing rate membrane permeation because PEG is known as a pore-forming organic material on the membrane [5-7]. Increasing amount of PEG can increase the porosity of the chitosan-cellulose composite membrane, which is shown through an increase in flux of the membrane [6-8]. PEG is a biocompatible compound, highly hydrophilic and anti-fouling [6].

In the membrane separation process, success of the separation process can be affected by the morphological structure of the membrane [7]. An optimal condition of the membrane performance is generally expressed by the magnitude of membrane permeability

and selectivity of a particular chemical compound. The larger value of the permeability and selectivity of the membrane will have a better performance. But, in fact, on the membrane separation process will be found a common phenomenon that when the permeability of the membrane is high then selectivity will be low. Ismail et al. [5,8] stated that many factor affected the membrane performance such as: the type and concentration of polymer, solvent type, solvent evaporation time, additive concentration and shear rate. The membranes production with addition of PEG additive has the effect of increasing rate membrane permeation because PEG is known as a pore-forming organic material on the membrane [9].

The other important factor affected the membrane performance has heat treatment or annealing of membrane. A different of temperature of heat treatment can be resulted in different membrane performance. By the annealing processes, the resulting membrane will have a lower flux and higher selectivity than membrane without annealing [10]. Therefore, the main objective of the present study is to investigate the effect of PEG addition in dope solution and thermal annealing process on the performance of asymmetric cellulose acetate membranes for brackish water treatment. To our knowledge, there is no documentation on the use of PEG addition and thermal annealing

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process to increase the performance of asymmetric cellulose acetate membrane for brackish water treatment.

## Experimental

### Materials

Materials used in the making of membranes are cellulose acetate from MKR Chemicals, 99.75% acetone from Mallinckrodt Chemicals, distilled water, PEG 4000 and brackish water from Demak.

### Fabrication of asymmetric cellulose acetates

In this study, the dope solution consists of 18 wt % cellulose acetates, acetone, distilled water and PEG as additives with various concentration of 1% wt, 3% wt, 5% wt. The homogeneous dope solutions were prepared according to the following procedure; the cellulose acetate polymers were dispersed in to the solvent and stirred for 6 hours followed by the addition of a desired amount of PEG. The dope solution was agitated with a stirrer at least 6 hours to ensure complete dissolution of the polymer. A desired amount of distilled water was added to the homogenous solution. This dope solution was than agitated at high speed for at least 12 hours. After all the ingredients mix completely fit variable, then the dope solution allowed to stand for 1 hour to remove bubbles. Casting membrane using the method of phase inversion that is scored on a glass plate using a casting knife and allowed to correspond with the time variation of evaporation and then dipped into a coagulation bath containing distilled water in place for 1 day at room temperature. Defect on the membrane surface were repaired by a heat treatment method. Asymmetric membranes module after the air drying were dried in an oven at different temperatures (60 and 70°C). Furthermore, heat treatment for different durations (5, 10, and 15 seconds) at 60 and 70°C was also carried out. After the treatment the membranes were cooled down slowly to room temperature. The treated membrane after being subjected to different heat treatment methods were tested using a dead-end nanofiltration testing system. Subsequently membrane filtration cell is cut to size for the characterization of the flux and rejection.

### Characterization of cellulose acetates membranes

In this study, the cellulose acetate membranes were tested in a brackish water from Demak using a dead-end filtration system. Figure 1 illustrated the schematic diagram of a testing apparatus to measure the flux and rejection values. Permeation experiments were carried out at room temperature. Before the permeability test, membrane first did compaction using distilled water for 30-45 minutes, hence the polymer

chains could arrange themselves. After the compaction process, distilled water was replaced with brackish water. Brackish water flux values was measured by measuring the volume of brackish water every 5 minutes. Determination of membrane rejection was performed by determining the concentration of total dissolved solid (TDS),  $Ca^{2+}$ ,  $Mg^{2+}$ , and brackish water turbidity before and after passing through the membrane. Determination of brackish water TDS was performed using a TDS meter, the analysis of brackish water turbidity was determined by turbidimeter, while the determination of  $Ca^{2+}$  and  $Mg^{2+}$  ion is using substitution and hardness titration. The flux was calculated using the equation as stated by Dasilva [11]:

$$J = V / (A \cdot t \cdot p) \quad (1)$$

$$J = \text{Flux, L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$$

$$V = \text{Volume of Permeate, litre}$$

$$A = \text{Membrane Surface Area, m}^2$$

$$t = \text{Time, hour}$$

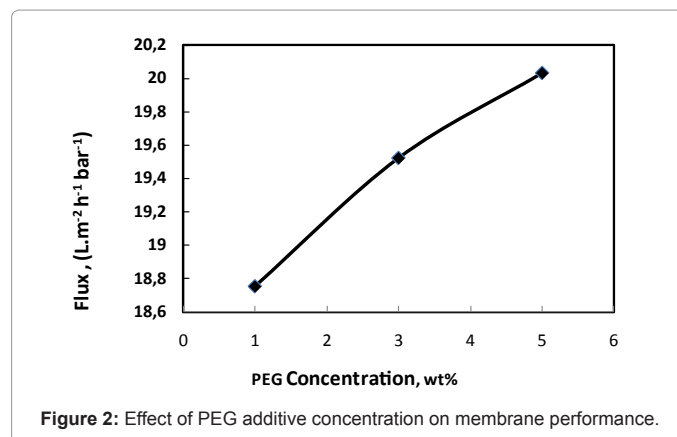
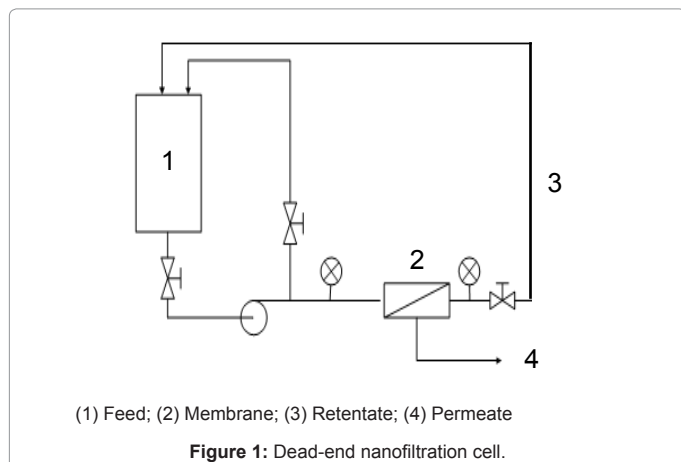
$$p = \text{Pressure, bar}$$

A Scanning Electron Microscopy (SEM) was used to determine the asymmetric structure and the dimension of the asymmetric membranes. Membrane samples were fractured in liquid nitrogen. The membranes were mounted on an aluminium disk with double surface tape and then the sample holder was placed and evacuated in a sputter-coater with gold. Through this analysis, it can be seen the cross-sectional and the surface morphology of the membrane with a certain magnification. The changes in the chemical structure during the blending were identified using Fourier transform infrared spectroscopy (FTIR). The IR absorption spectra were measured at room temperature from 4000 to 500  $\text{cm}^{-1}$  with a spectral resolution of 8  $\text{cm}^{-1}$  and averaged over 16 scans. This test is done to ensure the presence of cellulose acetate and PEG on the membrane.

## Results and Discussions

### Effect of PEG additive concentration on the membrane performance

The permeation flux of the membranes was measured by dead-end filtration cell for measuring the membrane permeate flow rate per unit area per unit time. The effect of PEG additive is presented in Figures 2 and 3. Figure 2 shows that the more PEG additive added to the dope solution, the greater the flux membranes obtained. This increase in flux due to membrane pore formed by the addition of greater concentrations



of PEG. PEG is an additive that has hydrophilic characteristic, thus increasing PEG concentration will lead to the formation of larger macrovoid in the pore structure of the membrane [8]. The larger the pore size of the membrane will increase the flux value.

Performance of the membrane can also be determined by the value of membrane rejection. Membrane rejection was performed using a dead-end filtration cell, together with measurements of membrane flux. On rejection measurement, the indicators are based on the values of total dissolved solid (TDS), turbidity degree and level of  $Ca^{2+}$  and  $Mg^{2+}$  concentration before and after passing through the membrane. The effect of PEG additive on the performance of membrane rejection is shown in Figure 3. Based on Figure 3, it can be concluded that increasing the concentration of PEG additive will decrease membrane rejection values for TDS, turbidity (NTU),  $Ca^{2+}$  and  $Mg^{2+}$ . This phenomenon was because the more concentration of PEG is added to dope solution increases the number of pores or pore size that formed in membranes. PEG serves as porogen or pore-forming that are soluble in water, moreover, the PEG molecules will be diffused into the coagulation bath containing water and leaving pores in the matrix of cellulose acetate [12]. As a result, the increasing of the concentration of PEG will be increased the macrovoid in the membrane and will be caused a lot of species qualify and are not filtered as it passes through the membrane. Therefore, the membrane rejection will be decreased.

### Effect of annealing treatment on the membrane performance

Before applied in brackish water treatment, cellulose acetate membrane were given annealing treatment first at temperature of 60°C and 70°C with annealing time for 5, 10, and 15 seconds. Then, the membrane flux measurements were performed using dead end cell filtration. The results of membrane flux measurements for the brackish water treatment with annealing treatment at temperature of 60°C and 70°C during 5, 10, and 15 seconds are presented in Table 1.

Table 1 shows that the longer the heating time the membrane

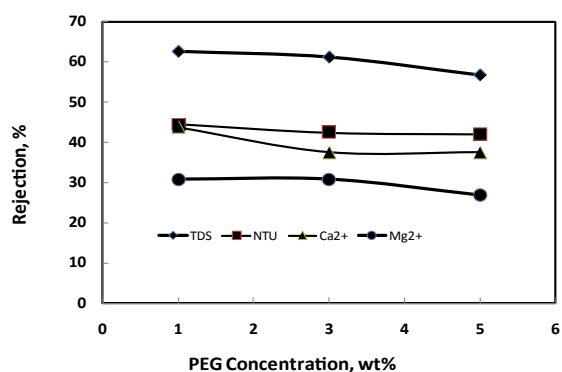


Figure 3: Effect of PEG additive concentration on the membrane rejection.

Temperature (°C)	Time (s)	Average flux (L.m <sup>-2</sup> .h <sup>-1</sup> .bar <sup>-1</sup> )
60	5	18.17
	10	16.13
	15	12.05
70	5	14.15
	10	7.45
	15	6.52

Table 1: Effect of temperature and time of annealing treatment on the membrane performance.

flux decreased. This is because the heat treatment on the membrane will cause some membrane molecules that are more stable and more meetings and will be the narrowing of the pore membrane [13,14]. Therefore, the flux is decreased. As shown in Table 1, it appears that the increasing of the heating time and heating temperature was also affected the membrane flux, i.e the higher the heating temperature will decrease the value of the membrane flux. The higher the heating temperature of the membrane that forms the lining will be tight and smooth. Formed pore size also will be smaller, hence the flux value has decreased.

Rejection value of cellulose acetate membrane modified with annealing treatment at temperature 60°C and 70°C for annealing time of 5, 10, and 15 seconds is determined by comparing the value of TDS brackish water, the degree of turbidity, and concentration of  $Ca^{2+}$  and  $Mg^{2+}$  ion before and after passing through the membrane. The results of cellulose acetate membrane rejection are presented in Figure 4. Figure 4 indicated that the higher temperature of annealing treatment given to membrane, the rejection value for TDS, turbidity,  $Ca^{2+}$  and  $Mg^{2+}$  ions increased. Increasing the value of this rejection also applies along with the length time of annealing treatment given. The annealing treatment given to the membrane will be improved the membrane performance because the arrangement of molecules on the membrane are more stable. The higher annealing temperature and the longer annealing treatment time on membrane, the membrane pores will shrinkage moreover the membrane surface layer becomes denser [13-15]. As a result, the membrane pore is narrowed which then increases the value of the membrane rejection.

### Effect of PEG additive concentration on the characterization of membrane by FTIR analysis

Figures 5 and 6 were presented the FTIR spectra of asymmetric cellulose acetate membranes. Analysis of FTIR (Fourier Transform Infrared) on the membrane is used to determine the functional groups present in membrane. The effect of PEG concentration on the spectra of FTIR is depicted in Figure 5. Figure 5 illustrates that cellulose acetate membranes having functional groups of chemical compounds with wavelengths shown in Table 2.

Figure 5 showed that the cellulose acetate membrane has a group of -OH, -C=O, -CH<sub>3</sub>, -COOH, C - C, and -CH. In Table 2 it can be seen the shift of the wavelength from chemical compounds in cellulose acetate membranes with PEG concentration of 1% and 5 wt%. The wavelength shift indicated that the PEG concentration in dope solution affects the membrane morphology structure. PEG as additive in cellulose acetate membrane is indicated by the presence of functional groups C=O and the re-unit -CH<sub>2</sub>-CH<sub>2</sub>O-. In cellulose acetate membrane with PEG concentration of 5 wt%, for wave numbers 1381.03 and 1435.04 cm<sup>-1</sup> showed greater extents than cellulose acetate membrane with PEG concentration of 1 wt% for the same functional group, in this case for the wave number 1381.03 cm<sup>-1</sup>. The wider absorption area showed that increasing addition of PEG concentration, the more the re-unit of -CH<sub>2</sub>-CH<sub>2</sub>O- in membrane.

### Effect of annealing treatment on the characterization of membrane by FTIR analysis

Figure 6 shows the FTIR characterization results on the cellulose acetate membrane with annealing treatment at temperature of 60°C and 70°C and annealing time for 5 seconds and 15 seconds. The functional group of chemical compounds with wavelength is presented Table 3.

Figure 6 indicated that the cellulose acetate membrane has a group

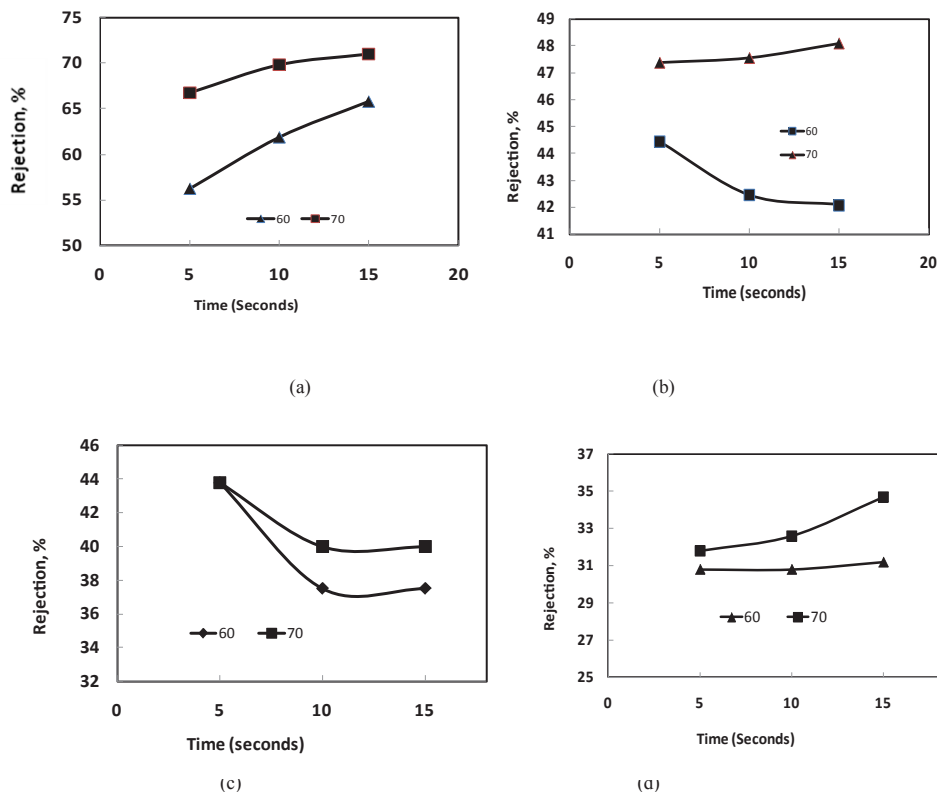


Figure 4: Effect of annealing time and temperature on the membrane rejection for: (a) TDS (b) turbidity (c) Ca<sup>2+</sup> (d) Mg<sup>2+</sup>.

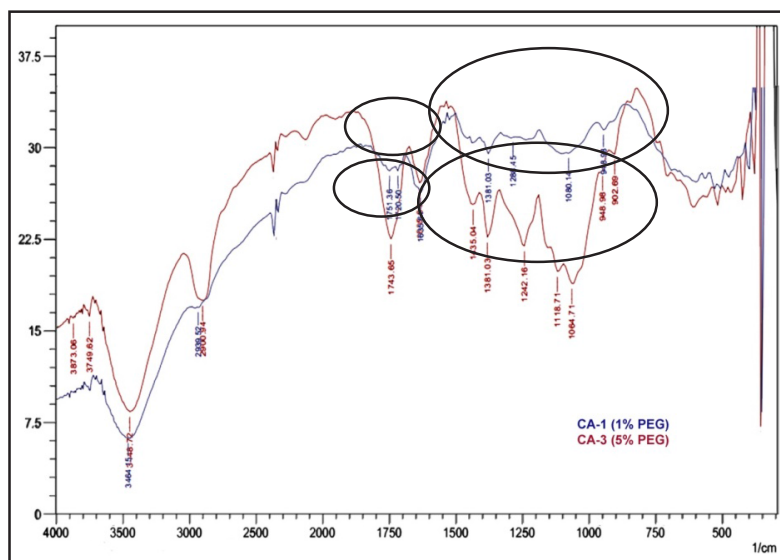


Figure 5: FTIR result for cellulose acetate membrane with PEG concentration of 1% and 5%wt.

-OH, -C=O, -CH<sub>3</sub>, -COOH, C-C, and -CH. Meanwhile, in Table 3 was shown the shift of the wavelength from the chemical compounds contained in the cellulose acetate membrane with annealing treatment at temperature of 60°C and 70°C and annealing time for 5 seconds and 15 seconds. Post treatment was given on cellulose acetate membrane after the membrane is formed. Based on the functional groups

contained in the cellulose acetate membrane, it can be observed that the functional group of -OH can be represented the water content in membrane. On cellulose acetate membrane with annealing treatment at temperature of 70°C, for wave numbers 3464.15 cm<sup>-1</sup> has smaller area than cellulose acetate membranes with annealing treatment at temperature of 60°C, in wave number 3464.15 cm<sup>-1</sup>, respectively.

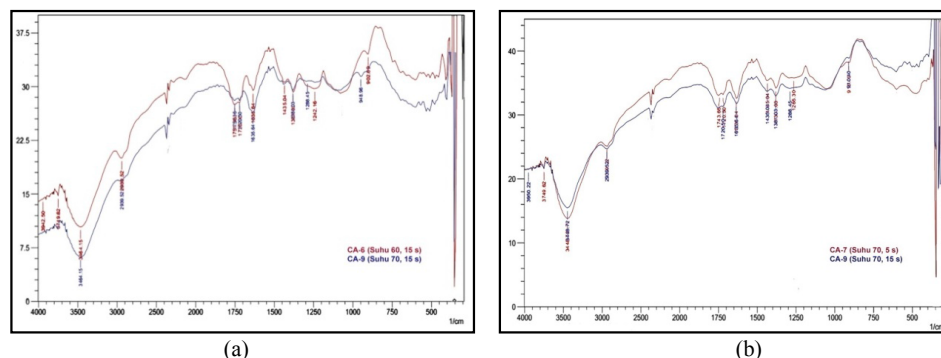


Figure 6: FTIR result for cellulose acetate membrane with: (a) annealing treatment at temperature 60 °C and 70 °C, and (b) annealing treatment for 5 seconds and 15 seconds.

No	Chemical Compound	Wavelength (cm <sup>-1</sup> )	
		PEG 1 wt%	PEG 5 wt%
1	-OH	3464.15	3448.72
2	-CH	2939.52	2900.94
3	C=O	1635.64; 1720.5; 1751.36	1635.64; 1743.65
4	-CH <sub>3</sub>	1381.03	1381.03; 1435.04
5	-COOH	1288.45	1242.16
6	C-C	948.98	902.69; 948.98

Table 2: Functional groups in cellulose acetate membranes with PEG concentration of 1% and 5% wt.

No.	Chemical compound	Wavelength (cm <sup>-1</sup> )			
		60°C	70°C	5 detik	15 detik
1.	- OH	3464.15; 3749.62	3448.72	3448.72	3448.72
2.	- CH	2939.52	2900.94	2939.52	2939.52
3.	C=O	1635.64; 1720.5	1635.64; 1720.5	1635.64; 1743.65	1635.64; 1720.5
4.	CH <sub>3</sub>	1381.03	1381.03; 1435.04	1381.03; 1435.04	1381.03; 1435.04
5.	- COOH	1288.45	1242.16	1265.3	1288.45
6.	C – C	948.98	902.69	910.4	910.4

Table 3: Functional groups in cellulose acetate membranes with effect of temperature and time of annealing treatment.

While on cellulose acetate membrane with annealing time for 15 seconds, to wave number 3448.72 cm<sup>-1</sup> also has smaller extents than cellulose acetate membrane with annealing time for 5 seconds, which is the wave number 3448.72 cm<sup>-1</sup>, respectively. The absorption area and extent showed indicate the water content in membrane and the intensity of the interaction between water molecules. Therefore, the smaller the absorption area showed that the interaction between water molecules in the membrane become smaller, which means the lower water content in the membrane [15].

### Effect of PEG additive concentration on the characterization of membrane by SEM analysis

The performance of asymmetric cellulose acetate membranes depends on many factors. The structure and geometrical characteristics of the produced asymmetric cellulose acetate membranes were studied by scanning electron microscopy (SEM). Figures 7 and 8 shown the cross section near outer surface of the membranes at different PEG. As shown in Figure 7, all the structures of membrane consisted of a dense skin layer supported by a spongy porous substructure with small macrovoids. Generally, production membrane by coagulation process typically generates microporous structure containing macrovoids structure [16].

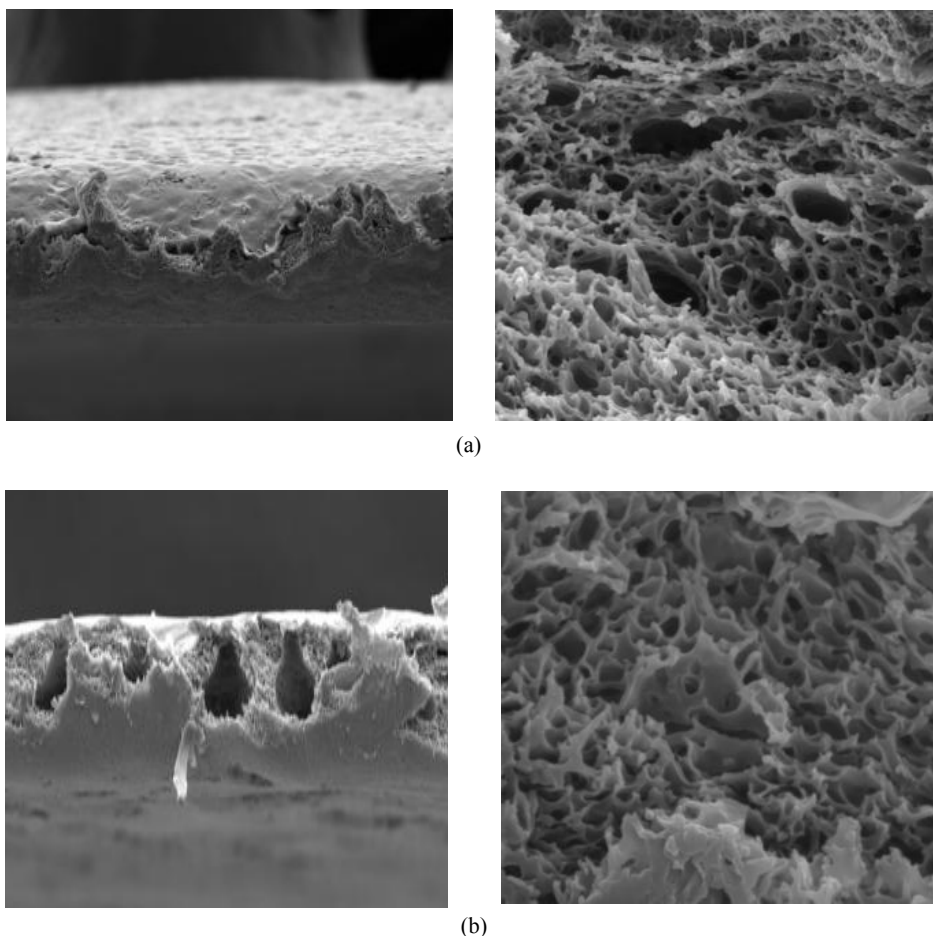
Figures 7 and 8 was also showed that the cellulose acetate membrane

is formed asymmetric structure membrane, where increasing PEG concentration also increasing the number and uniformity of pore membrane. In this case, PEG as an additive initially filling the matrix of prepared cellulose acetate membranes. Furthermore, in the process of dissolution with non solvent, additives together with solvent will dissolve into non-solvent, leaving a cavity or pore in the membrane. Consequently, the pore become larger and uniformly [8,9]. Based on cross-sectional morphology of membrane it appears that the pores of membrane with PEG concentration of 5 wt% are more evenly than in membrane with PEG concentration of 1% wt. This shows the function of PEG as a pore-forming and increase the porosity of the cellulose acetate membrane.

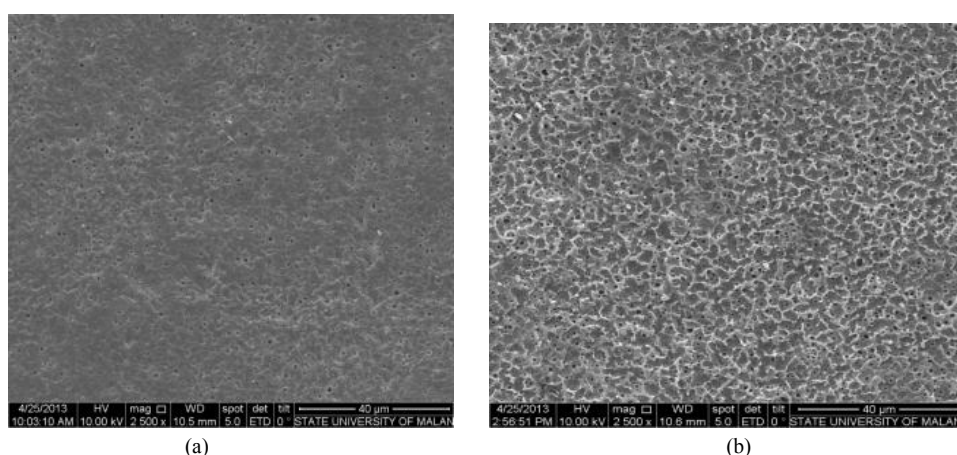
### Effect of annealing treatment on the characterization of membrane by SEM analysis

The effect of annealing on the membrane morphology is depicted in Figures 9-12. The membranes subjected to annealing post-treatment at 60°C and 70°C, with annealing time for 5 seconds and 15 seconds. As can be seen from the SEM pictures of all treatment temperature of membranes contained the porous structure in the cross-section of asymmetric membrane. The porous structures became increasingly denser with increasing the heat-treatment temperatures. Moreover, the





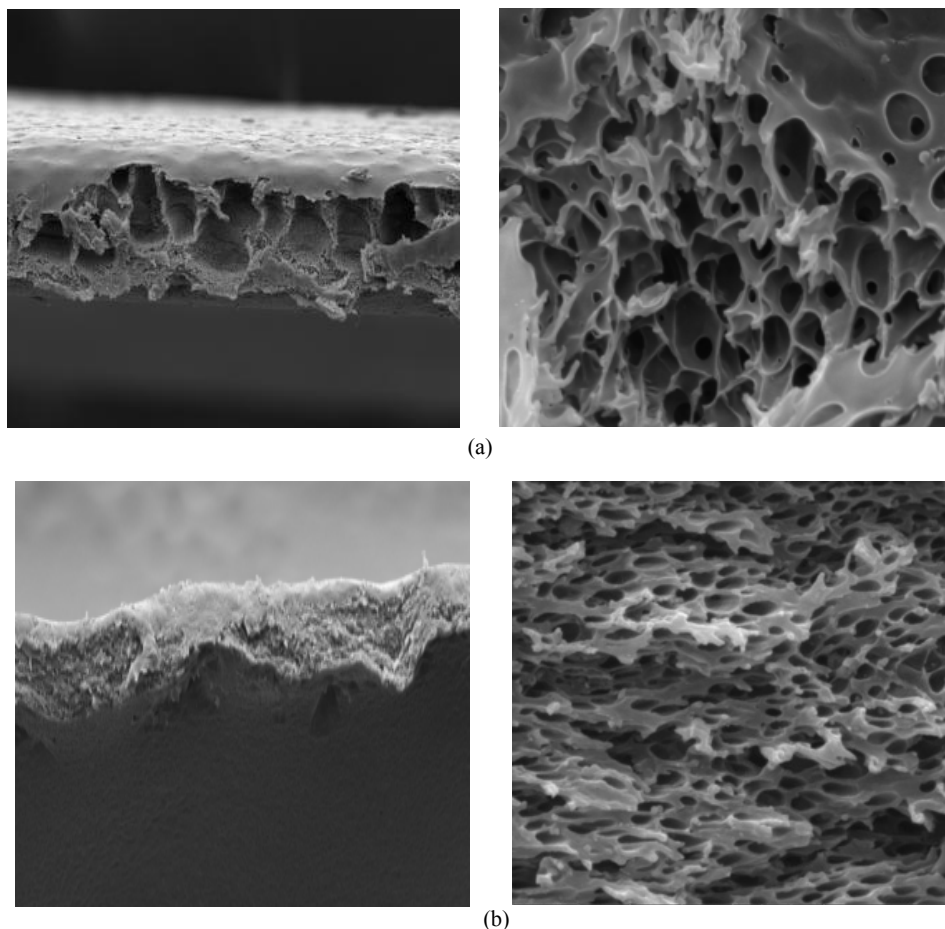
**Figure 7:** The cross-section morphology of cellulose acetate membrane with PEG concentration: (a) 1% wt and (b) 5%wt.



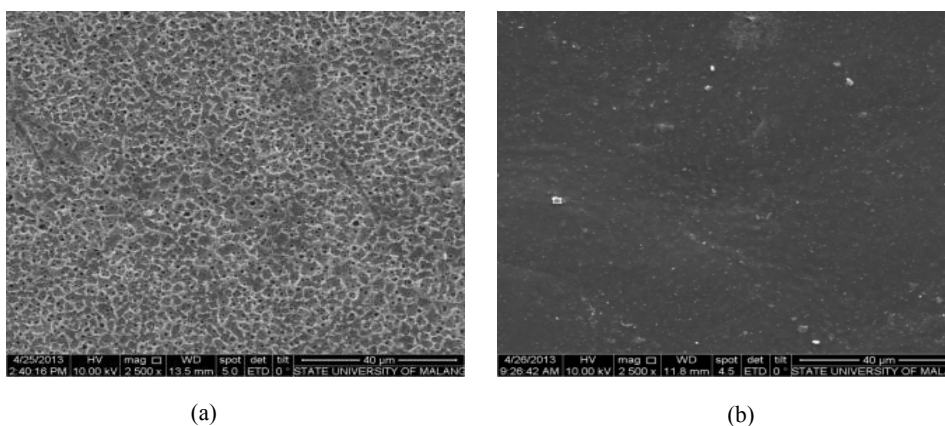
**Figure 8:** The surface morphology of cellulose acetate membrane with PEG concentration: (a) 1% wt and (b) 5%wt.

SEM pictures also reveal that the dense skin layer formed when the heat-treatment temperature was higher than 70°C. Furthermore because of the thermal effect the packed chains in the polymer membrane denser and the packed structure in the skin layer provide a high degree of size and shape discrimination between the particles. Therefore, after

heat treatment asymmetric membranes became more compact in the outer skin and substructure as compared to the untreated membranes. As result the flux for treated membrane was lower than untreated membrane. This is consistent with the reduction of flux and increasing the rejection as shown in Table 1 and Figure 4.



**Figure 9:** The cross-section morphology of cellulose acetate membrane with annealing treatment at temperature: (a) 60°C and (b) 70°C



**Figure 10:** The surface morphology of cellulose acetate membrane with annealing treatment at temperature: (a) 60°C and (b) 70°C.

Furthermore the effect of annealing time at 5-15 seconds on the morphology of cellulose acetate membranes is shown in Figures 11-12. Figure 11 and 12 show that the surface morphology of the membrane with annealing temperature of 70 °C and annealing time for 15 seconds has a smoother surface than the membrane by annealing at 60°C and the annealing time for 5 seconds. Moreover, the pores

or cavities formed in membrane are smaller and denser. Annealing treatment on membrane causes an adjustment of the movement of the polymer chains. When cellulose acetate membrane were annealed, the movement of the molecules from polymer chains become easier and affect the morphology structure of membrane. In addition, annealing treatment also decreases the free volume formed in membrane, due to

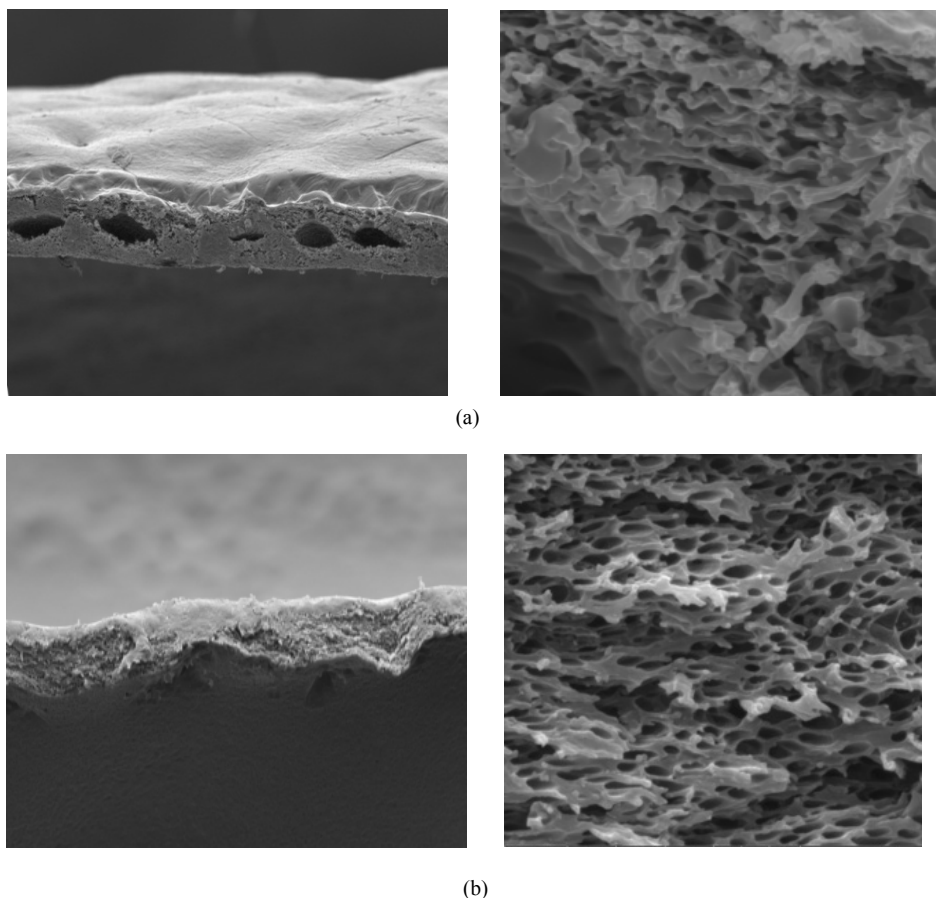


Figure 11: The cross-section morphology of cellulose acetate membrane with annealing time for: (a) 5 seconds and (b) 15 seconds.

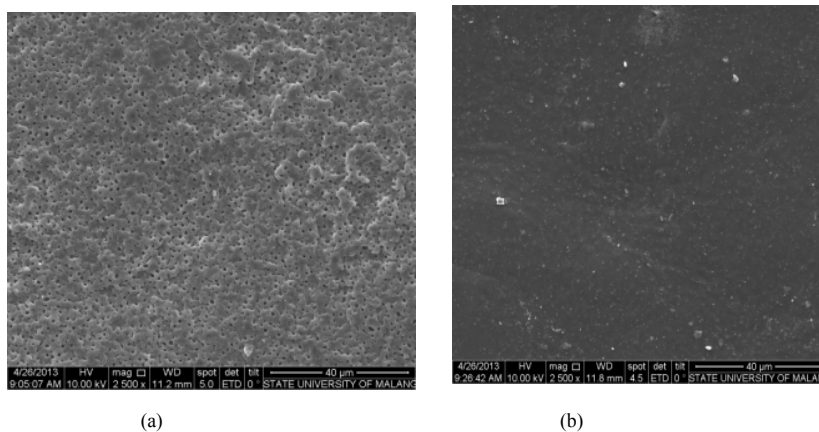


Figure 12: The surface morphology of cellulose acetate membrane with annealing time for: (a) 5 seconds and (b) 15 seconds.

the increasing of molecular movement in membrane [13-14,17]. The fewer free volume in membrane results in the smaller pores or voids are formed, so that the membrane becomes denser.

## Conclusions

Asymmetric cellulose acetate membranes were fabricated at different PEG concentration in the dope solution. The effects of

PEG concentration on the membrane morphology and filtration performance were analyzed. An attempt to improve the performance of the membranes also has been done by thermal annealing. Based on the experimental results and analysis, the following conclusions can be made.

- i. Asymmetric cellulose acetate membranes can be produced using



dry-wet phase inversion and the PEG can be used as additive to repair the membrane pore formation

ii. Both SEM and filtration test suggested that the annealing treatment can be used as a method to modify surface of membrane. The membrane surface layers become denser and smoother with increasing the time and temperature annealing.

iii. It is found that the combinations of PEG in dope solution and heat treatment can effectively improve the performance of cellulose acetate membrane with the flux  $6.52 \text{ L.m}^{-2}.\text{h}^{-1}.\text{bar}^{-1}$ , TDS rejection 71%, turbidity rejection 63.75%,  $\text{Ca}^{2+}$  ion rejection at 52.9%, and  $\text{Mg}^{2+}$  ion rejection was 41.9%, respectively.

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