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Research Article

Cellulose Acetate Membrane with Improved Perm-selectivity through Modification Dope Composition and Solvent Evaporation for Water Softening

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Abstract: Membrane technology has been developed because applicated on several fields. Hence, in this study carried the production of cellulose acetate nano-filtration membranes for water softening. The main objective of this study was determined the effect of solvent evaporation time and the effect of adding PEG to the morphology and perm-selectivity of asymmetry membrane for water treatment. Membranes prepared by dry/wet phase inversion method with variation of solvent evaporation time of 10-15 sec and addition of 2.5-5 wt% PEG in the dope solution. 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 results of FTIR analysis showed the larger absorption peaks indicates that the increasing concentrations of PEG addition make the PEG molecular weight and the unit re-CH_2-CH_2O-greater. The results of SEM analysis exhibited that all the membranes are formed has an asymmetric structure consisting of a thin fine porous structure selective barrier and sub-structure of the porous layer is thicker. Moreover, the addition of PEG, the larger pore of membrane will be formed. Performance optimum membrane was obtained on the composition of 23 wt% cellulose acetate, polyethylene-glycol 5 wt%, 72 wt% acetone and 1 wt% of distilled water in the solvent evaporation time of 25 sec and temperature coagulant at room temperature. Characterization of the optimum membrane were flux 22.33 L/m^2/h/bar, 92% rejection for turbidity, rejection for dissolved solids 85 and 81% rejection for ions Ca^{2+}, with modulus young around 12433 N/cm^2, respectively.

Keywords: Additives, asymmetric membrane, cellulose acetate, PEG

INTRODUCTION

Membrane is a thin layer, a barrier between the two phases that are semi-permeable and serves as a selective separation media based on the coefficient of diffusivity, electrical charge and the difference in solubility (Mulder, 1996). Membrane technology is the latest technology in water treatment because of its strategic, related to the process, separation, purification and concentration. This technology also uses more efficient in energy because it doesn't use high operating temperature. Membrane technology uses modular equipment so easy to scale-up. Its classified in a clean technology because its relatively no waste and the process can be merged with other separation process (Khayet and Matsuura, 2011). Asymmetric membrane is one type of membrane that the most widely applied in water treatment process. Flux resulted from performance of asymmetric membrane is higher than symmetric membrane because its dense layer is thinner than symmetric membrane. Asymmetric membrane with a pore size of porous membranes having the outer skin layer with a thickness of 0.1 to 0.5 μm and below the top layer there is another layer with a thickness of approximately 50-100 μm. The upper layer of the asymmetric porous membrane serves as a filter, while the bottom layer serves as a buffer medium of the upper layer. Therefore, the asymmetric membranes are widely used in water treatment applications (Ren and Rong, 2011). 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*. (2002) 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 (Saljoughi, 2010;

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Saljoughi *et al*., 2009). Increasing amount of PEG can increases the porosity of the chitosan-cellulose composite membrane, which is shown through an increase in flux of the membrane (Yang *et al*., 2001). PEG is a biocompatible compound, highly hydrophilic and anti-fouling.

The other important factor affected the membrane performance has solvent evaporation time in fabrication membrane process with phase inversion technique. A different of solvent evaporation time can result in different membrane performance. In the previous study conducted by Bhongsuwan and Bhongsuwan (2008) in the preparation of nano-filtration membranes with different solvent evaporation time can be conclude that the difference solvent evaporation time in 40 sec can increase the selectivity of tanin up to 21.68% and can decrease the flux up to 69.78%. Permeate flux decline of NF membrane in such a short range 40 sec, showing the evaporation time of solvent become one of important variable in the membrane fabrication. Therefore, further research needs to be done to get the time evaporation of which produce an optimal membrane performance.

In the study of making asymmetric membranes, aceton solution is commonly used as a solvent with a cellulose acetate as a polymer (Bhongsuwan and Bhongsuwan, 2008; Ismail *et al*., 2002). Cellulose acetate was chosen as the polymer component due to the cellulose acetate can form an asymmetric structure with a very thin active layer and the dissolved material can withstand the rough on the support layer, as well as chlorine tolerant and resistant to the occurrence of precipitation (Uemura and Henmi, 2008; Kumano and Fujiwara, 2008). Therefore, as mentioned above, membrane stability and high performance become one of the important factors for the application of membranes. Therefore, the main objective of this study is to investigate the effect of addition PEG into dope solution and evaporation time in order to increase the permselectivity of cellulose acetate nanofiltration membrane for softening brackish water from Jepara.

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 Jepara.

Fabrication of asymmetric cellulose acetates: In this study, the polymer solution consists of 23 wt% cellulose acetates, acetone, distilled water and PEG as additives with various concentration of 2, 5-5 wt%. The homogeneous cellulose acetates were prepared according to the following procedure; the cellulose acetate polymers were dispersed in to the solvent and stirred for 6 h followed by the addition of a desired amount of PEG. The solution was agitated with a stirrer at least 6 h to ensure complete dissolution of the polymer. A desired amount of distilled water was added

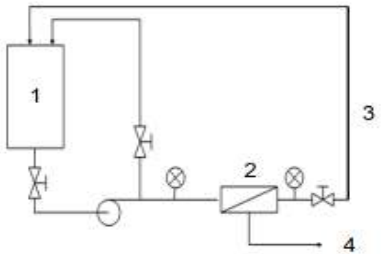


Fig. 1: Dead-end nano-filtration cell
1: Feed; 2: Membrane; 3: Retentate; 4: Permeate

to the homogenous solution. This dope solution was than agitated at high speed for at least 12 h. After all the ingredients mix completely fit variable, then the dope solution allowed to stand for 1 h 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 10-15 sec and then dipped into a coagulation bath containing distilled water in place for 1 day at room temperature. The modify membranes were tested using a dead-end nano-filtration testing system. Subsequently membrane filtration cell is cut to size for the characterization of the flux and rejection.

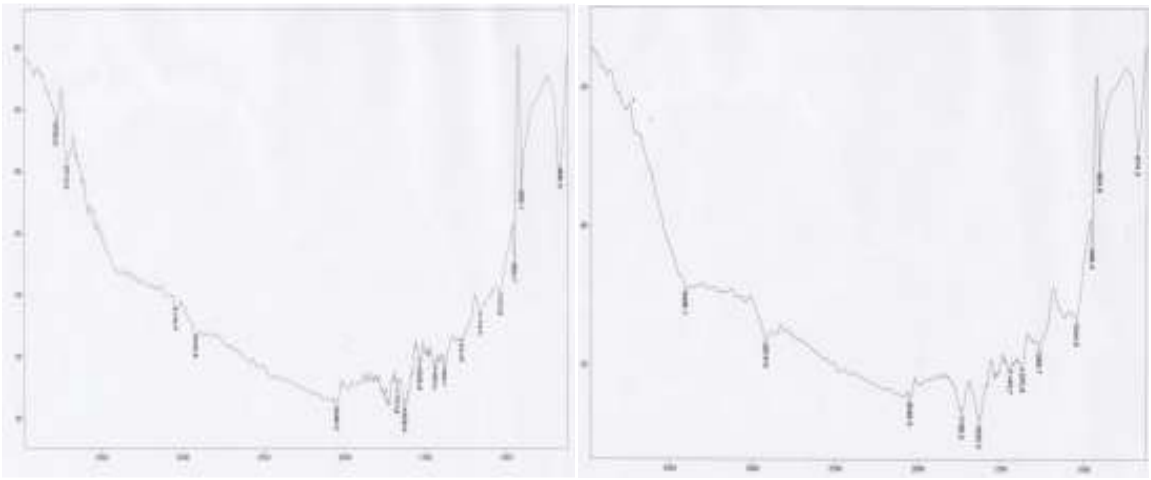
Characterization of cellulose acetates membranes: Measurement of flux and rejection values using dead-end filtration cell. Before the permeability test, membrane first doing compaction using distilled water for 30-45 min so that the polymer chains arrange themselves. After the compaction process, distilled water was replaced with brackish water. Brackish water flux measurement is done by measuring the volume of brackish water every 5 min. Determination of membrane rejection was performed by determining the concentration of TDS, Ca^{2+}, Mg^{2+} and brackish water turbidity before and after passing through the membrane. Determination of brackish water TDS performed using a TDS meter, the analysis of brackish water turbidity is determined by turbidimeter, while the determination of Ca^{2+} and Mg^{2+} ion is using substitution and hardness titration. Figure 1 illustrated the schematic diagram of a dead-end nano-filtration cell testing apparatus to measure the flux and rejection of cellulose acetate membranes.

The flux was calculated using the equation as stated by Dasilva (2007):

$$J = V/(P.A.t)$$

J = Flux (L/m^2/bar/h)
V = Volume of Permeate (Liter)
P = Pressure, bar
t = Time (hour)
A = Membrane Surface Area (m^2)

Characterization is then performed by measuring the membrane thickness, selectivity and permeability



(a) (b)

Fig. 2: The absorbance of cellulose acetate membranes with time of evaporation, (a) 15 sec, (b) 25 sec

determination, Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) -spectrometer and a tensile test. 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 aluminum 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 cm^{-1} with a spectral resolution of 8 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 DISCUSSION

FTIR characterization of solvent evaporation time and PEG in the dope solution: FTIR (Fourier Transform Infrared) analysis on Membrane is used to determine the compounds present in the membrane. The effect of solvent evaporation time on the structure of membrane can be seen in Fig. 2 and Table 1. In Fig. 2a and b can be seen that membranes have a groups of-OH, C = O, CH_3, -COOH and C-O-C ether represented by the wavelength listed in Table 1. In the Table 1 can be seen that the wavelength shift of chemical compounds during the evaporation time 15 and 25 sec. Wavelength shift indicate that the evaporation time effect on the structure of the membrane morphology. On the absorbance of cellulose acetate membrane with

Table 1: Absorbance peaks of cellulose acetate membrane

Wavelength (cm^{-1})		
Evaporation time 15 sec	Evaporation time 25 sec	Chemical compounds
2920.8; 3196.9	2918.9; 3406.1	-OH
1629.6; 1703.8	1633.3; 1738.2	C = O
1398.7; 1480.6	1370.9; 1489.7	CH_3
1264.8	1269.7	-COOH
1022.8	1044.9	C-O-C ether

Table 2: Absorbance peaks of cellulose acetate membrane

Wavelength (cm^{-1})		
Membrane without additives	Membrane with additives	Chemical compounds
3413.6	3417.4	-OH
1629.6	1734.5 dan 1643.9	C = O
-	1438.4 dan 1375.2	CH_3
679.4 dan 679.9	669.3	R-COH

the evaporation time of 25 sec on the wavelength 1269.7 cm^{-1} has a greater area than the absorbance of cellulose acetate with the time evaporation of 15 sec on the wavelength 1264.8 cm^{-1}. In Table 1 can be seen that the membrane rejection with 25 sec time of evaporation showed a better results than a membrane with 15 sec time of evaporation. It can be suggested that the wavelength shift affect the membrane performance.

The effect of PEG on the formation of cellulose acetate membrane was shown in Fig. 3 and Table 2. As shown in the Fig. 3 and Table 2, the membrane structure was mostly influenced by the PEG into the dope solution. The larger absorption peaks indicated that the increasing concentrations of PEG addition make the PEG molecular weight and the unit re-CH_2-CH_2O-greater, which is a flexible group in poly ethylene glycol, which causes the chain stiffness, is reduced. Therefore, it can affect the properties of PEG as soft segments forming (Harris, 1992; Rohaeti, 2003).

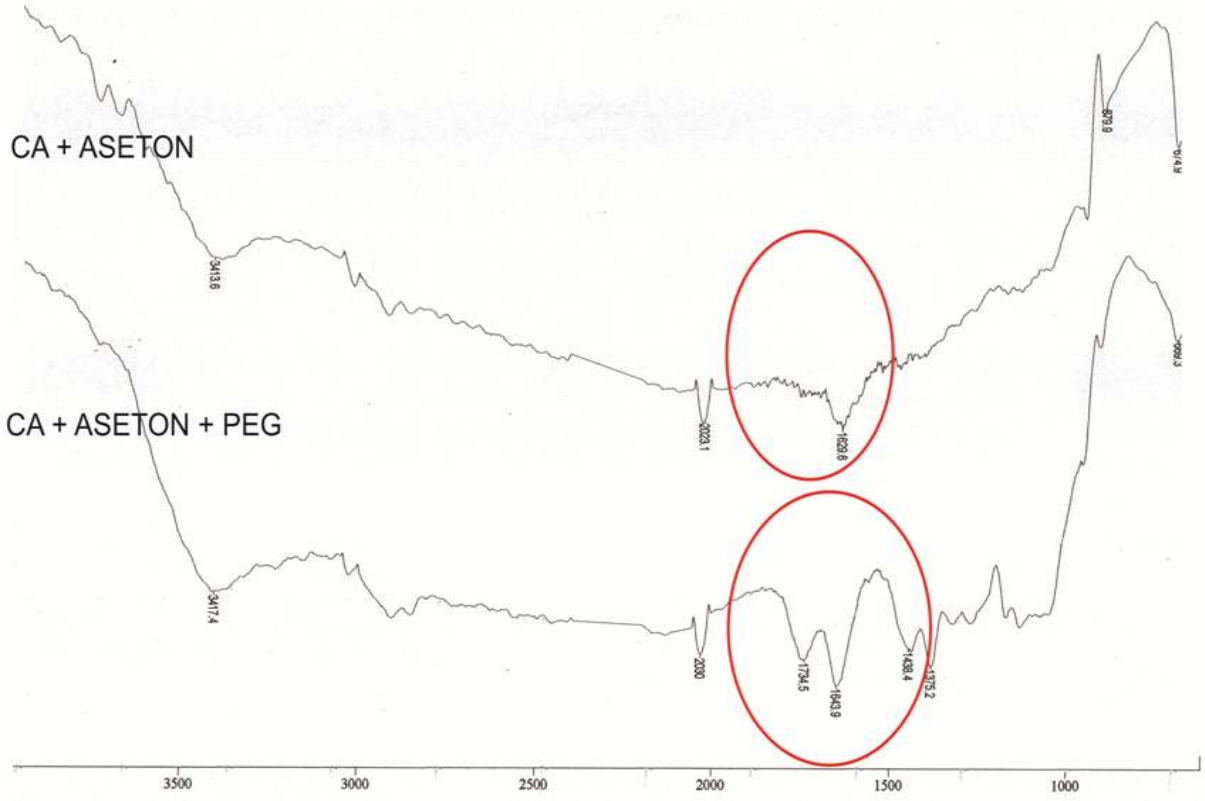
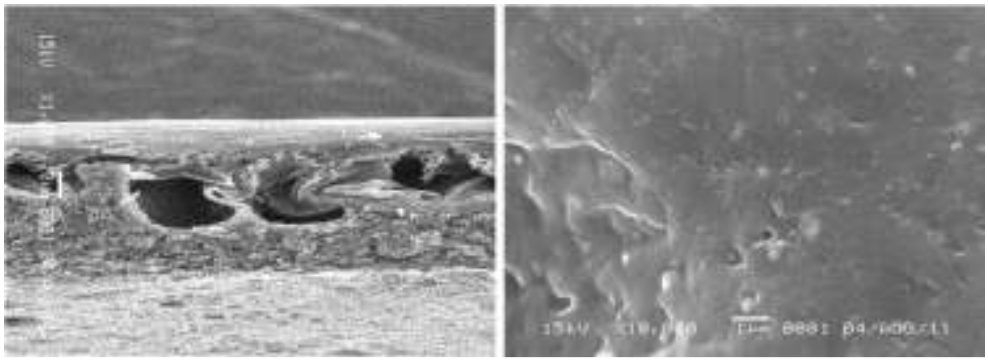


Fig. 3: Effect of PEG in the dope solutions on the absorbance of cellulose acetate membranes



(a) (b)

Fig. 4: SEM of cross and surface section at PEG composition 2.5 wt%

Effect of PEG and evaporation time on the morphology of cellulose acetate: 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). Figure 4 to 6 shows the cross section near outer surface of the membranes at different PEG. As shown in Fig. 4 and 5, all the structures of membrane consisted of a dense skin layer supported by a spongy porous substructure with small macro-voids. Generally, production membrane by coagulation process typically generates micro-porous structure containing macro-voids structure (Chung *et al*., 1998).

Figure 4 to 6 show 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 (Li, 2009). 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 2, 5 wt% and

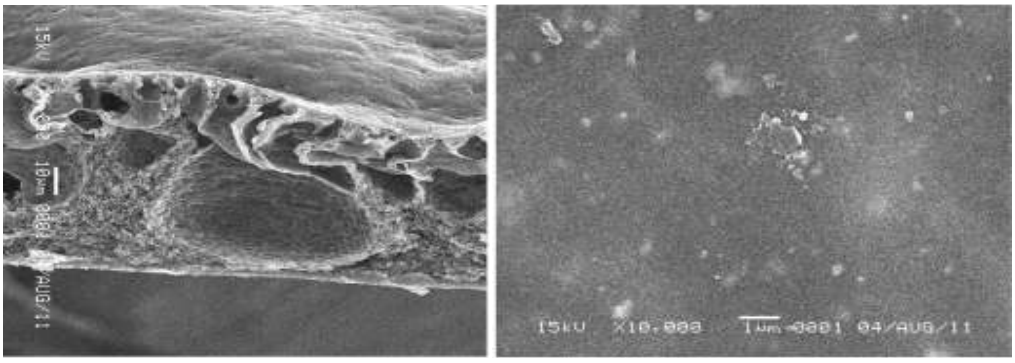


Fig. 5: SEM of cross and surface section at PEG composition 3.5 wt%

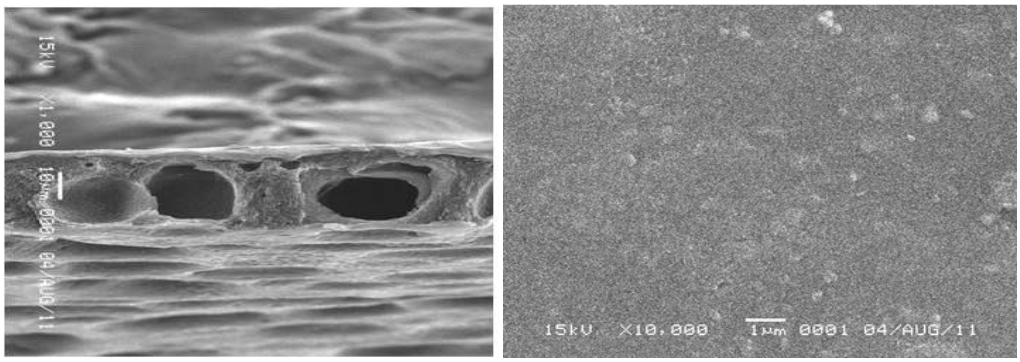


Fig. 6: SEM of cross and surface section at PEG composition 5 wt%

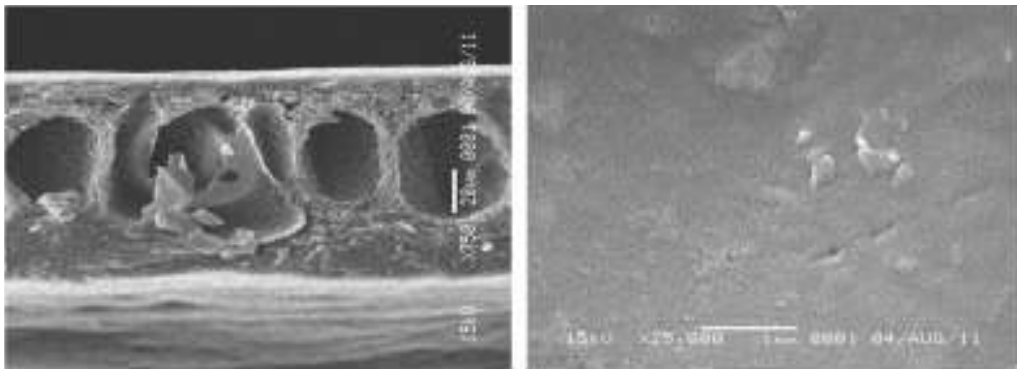


Fig. 7: SEM of cross and surface section at evaporation time 15 sec

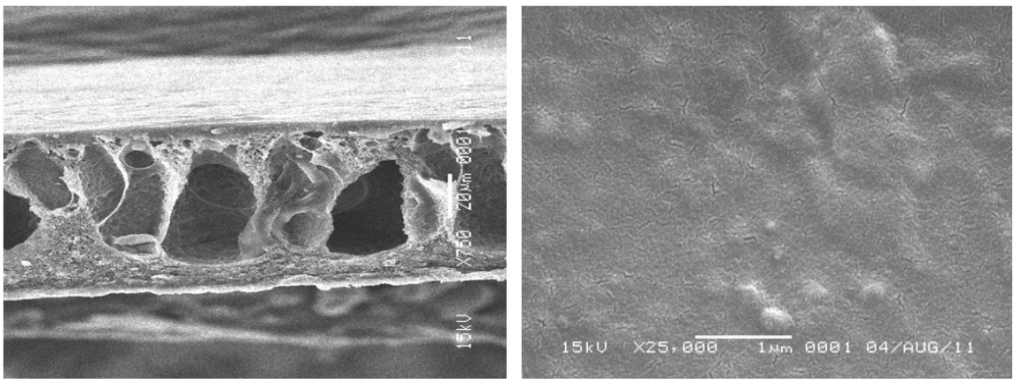


Fig. 8: SEM of cross and surface section at evaporation time 25 sec

3, 5 wt%. This shows the function of PEG as a pore-forming and increase the porosity of the cellulose acetate membrane. Moreover, in the presence of increasing concentrations of polyethylene glycol, membrane pore formed more dense (neat).

In this study, SEM analysis was tested to membranes 15 and 25 sec time of evaporation with optimum performance. SEM showing the shape changes or surface morphology from membrane sample. In principle, if there is a change of a material such as change in surface structure, the material is likely to have a change of energy. This energy can be emitted, reflected and absorbed and transformed into electron wave function that can be captured and read the results (Ismail *et al*., 2002). The effect of evaporation time on the membrane morphology is presented in Fig. 7 and 8. As presented in Fig. 7 and 8, the pictures are clearly show that the three layers was observed such as dense layer on the surface of membrane that serves as a selective layer, intermediate layer is a layer between dense and porous substructure layer and porous substructure layer which serves as mechanical support membrane.

From Fig. 7 and 8, both membranes have a shape like a finger (finger-like). Finger-like phenomenon commonly occurs in asymmetric membranes preparation due to the high viscosity fluid in the membrane has been replaced by a low viscosity fluid in the immersion process in coagulation bath (Ehsan and Mohammadi, 2009; Ren and Rong, 2011). The formation of cavity can decrease the mechanical strength of membrane. The results were also in agreement with previous results from Ren and Rong (2011). Furthermore, with a smaller cavity formed, the mechanical strength of membrane will increase as measures by the larger value of Modulus Young.

Moreover, from cross section and surface of membrane with a magnification of 25.000 times can be seen the difference in the membrane with 25 sec time of evaporation look smoother and denser compare to membrane with 15 sec time of evaporation. This phenomenon was cause with longer evaporation time provide longer chance the top of membrane layer to bind so that membrane with a smoother and denser layer will be formed and may result in higher rejection and decrease the flux.

Effect of polyethylene glycol concentration on the membrane performance: The effect of PEG concentration on the flux of cellulose acetate membrane was depicted in the Fig. 9. Based on Fig. 9, it can be seen that the PEG concentration increased the flux will be decreased. This phenomenon may be due to the increasing of PEG concentration which can affect on formation of smaller pores and increasing the regularity of form pores in the membrane. Therefore, increasing the PEG concentration into dope solution will be obtained more lower flux values (Saljoughi, 2010;

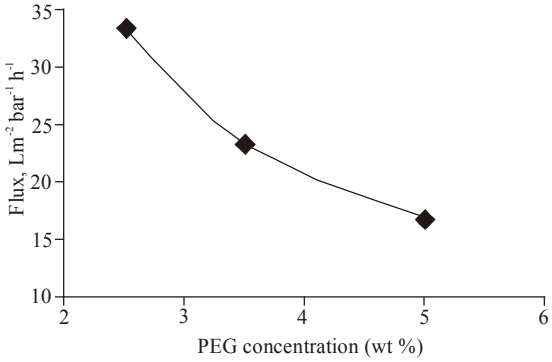


Fig. 9: The effect of PEG concentration on the flux

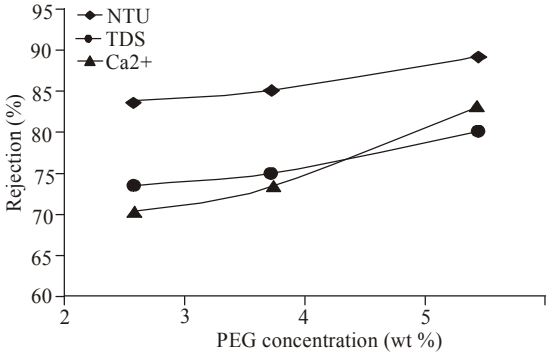


Fig. 10: The effect of PEG concentration on the rejection

Saljoughi *et al*., 2009). The results has been consisten with morphology membranes as shown in Fig. 4 to 6. Moreover, the smooth surface of cellulose acetate membranes was also obtained with increasing the PEG concentration, as shown in Fig. 4 to 6. The Fig. 4 to 6 also indicates that the denser of membrane was also caused the decreasing of flux values. This phenomenon was also indicated that the increasing of PEG concentrations may be also cause increased the viscosity of dope solution and will be produced the thicker membrane which can reduce the value of flux.

Figure 10 was presented the effect of PEG concentration on the % rejection. Based on Fig. 10, it can be observed that the increasing of PEG concentrations will be increased the rejection values for turbidity, dissolved solids and multivalent ions Ca^{2+} higher. This phenomenon indicated that the increasing of PEG concentrations was affected the formation of pore size in the membrane surface. The denser membrane with smaller pore size will be produced the higher selectivity (Mulder, 1996).

Effect of solvent evaporation on the membrane performance: Figure 11 was presented the effect of solvent evaporation time on the flux of nanofiltration cellulose acetate membrane with brackish water as a feed. As shown in Fig. 11, the flux values was decreased with increasing solven evaporation time. This phenomenon may be due to the membrane pore

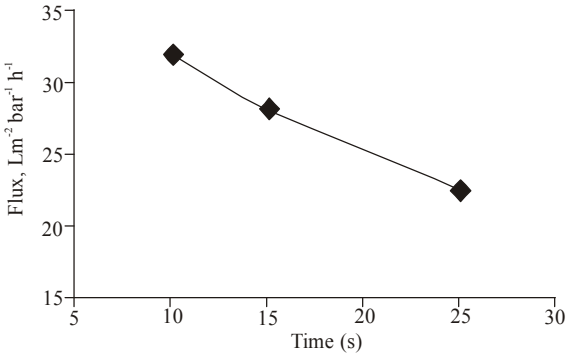


Fig. 11: The effect of evaporation time on the flux

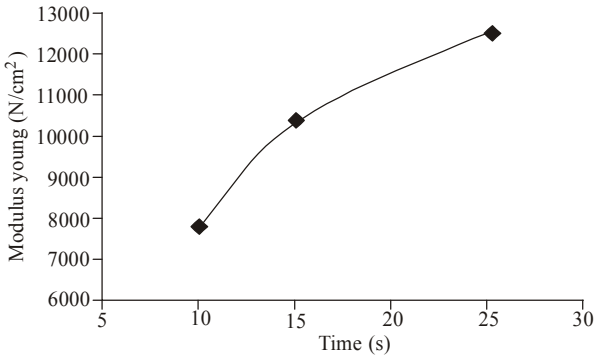


Fig. 12: The effect of solvent evaporation time on the mechanical properties of membrane

Table 3: The effect of solvent evaporation time on the rejection

Solvent evaporation time (sec)	NTU rejection (%)	TDS rejection (%)	Ca_2+ rejection (%)
10	78.5		
15	75	75	75.5
25	92	79	71

produced with the longer solven evaporation became smaller or denser compare to the shorter evaporation. Longer evaporation time make the polymer concentration on the top layer will increase and will inhibit the exchange rate between solvent and non-solvent through the membrane surface during the immersion process in the coagulation bath. This phenomenon causes the formation of the membranes with smaller pore size and finally will be produced decreasing of flux (Li, 2009; Soroko *et al*., 2011). The results was consistent with the morphology of membrane as shown in Fig. 7 and 8.

The effect of solvent evaporation time on the membrane rejection was depicted on the Table 3. For the measurement of rejection, brackish water before and after passed through the membrane were tested using a Turbidimeter, TDS meter and Ca^{2+} concentration by titration substitution. Measurement of Ca^{2+} concentration are based on the ability nanofiltration membranes that can only reject the smallest particle like bivalent ions such as Ca^{2+} and Mg^{2+} with the molecular weight range of 200-5000 (Ren and Rong, 2011). Membrane selectivity is expressed in the rejection coefficient, the membrane ability to pass of certain species and other species withstand. To calculate the value of rejection using the equation as stated by Dasilva (2007):

$$R = (1 - Cp/Cf) \times 100\%$$

R = Coefficient rejection (%)
Cp = Concentration of solute in permeate
Cf = Concentration of in the feed

From Table 3, it can be seen that % rejection was increased with increasing the evaporation time. This phenemenon indicated that the smaller the pore size was produced using longer evaporation in the membrane fabrication. The result was also indicated that the smaller of pore size will be obtained the high selectivity. The results were also in agreement with previous results from Mulder (1996). Moreover, the results were also consistent with membrane morphology as shown in Fig. 7 and 8.

Effect of solvent evaporation on mechanical properties of cellulose acetate membrane: In this study, measurement of mechanical properties of the membrane with a tensile test carried out by using a Texture Analyzer. Tensile test carried out by pulling the membrane with a speed of 5 mm/sec until the membrane broke. From the tensile test can be known Young's modulus values. Tests conducted on the composition of 23% cellulose acetate, PEG concentration of 5 wt% with variation of solvent evaporation time. Figure 12 was showed that the evaporation of the solvent greatly affects the characteristics of the membrane, along the length of time the membrane will be obtained by evaporation of greater mechanical strength. The longer the time of solvent evaporation can produce membranes with a pore that meeting because when solvent was evaporated, the polymer solution is still a moving liquid filling the pores resulting in a more dense pore, the higher the concentration at the surface to make the membrane thicker. The thicker the membrane the increased modulus youngnya. Because of the thicker membrane will be more difficult to damage, the bond strength between the polymer stronger so it is not easy to decide.

In addition to the SEM analysis results can be diketehui that the finger-like membrane macrovoid formed by the evaporation time of 25 sec was smaller than the membrane with the evaporation time of 10 sec. Finger-like macrovoid with a larger size will decrease the mechanical strength of the membrane so that it will obtain the value of young modulus smaller.

CONCLUSION

Celullose acetate nanofiltration membranes were fabricated at different PEG concentration at dope solution and at different solvent evaporation time. The

effect of PEG concentration into dope solution on the membrane performance for water softening were analyzed. An attempt to improve the performance of the membranes also has been done by solvent evaporation time on the membrane fabrication. Based on the experimental results and analysis, the following conclusions can be made:

- The results of FTIR analysis showed the larger absorption peaks indicates that the increasing concentrations of PEG addition make the PEG molecular weight and the unit re-CH_2-CH_2O- greater. At variation 25 sec time of evaporation has the largest area of the -COOH group. This indicated that the solvent evaporation time was affected the membrane structure.
- Evaporation solvent effect on the skin membrane pore formation that the smaller the resulting value with the smaller flux values greater rejection.
- Increasing concentrations of poly ethylene glycol effect on the surface of the membrane pore formation that smaller and the resulting flux values are getting smaller and higher rejection value.

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