Preliminary Study of Asymmetric Ultrafiltration (UF) Membrane: The Effect of Coagulation Bath Temperature (CBT) and Forced Convection Resident Time (FCRT) on the Permeability and Morphology of UF Polysulfone Membrane

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ABSTRACT

Previous studies have shown that the forced convection resident time (FCRT) and coagulation bath temperature (CBT) have significantly influenced the permeability characteristics of the membrane, thus affected the membrane performances. In this study, the UF Polysulfone membranes were prepared by varying of two rheological factors, which applied with different coagulation bath temperature at 10 °C, 30 °C, and 50 °C and different forced convection resident time which was at 10 s, 15 s, and 20 s. The objective of this study is to investigate the effect of those rheological factors to pure water permeability (flux) and morphology of UF Polysulfone membranes. The membranes were fabricated using a ternary dope formulation of 14.4% Polysulfone (PSF), 81.6% N–methyl–2 pyrrolidone (NMP), and 4% water by a dry/wet phase inversion process by using an electrically controlled flat sheet membrane casting machine. The membranes were characterized by the permeation test of pure water flux and its morphology via scanimg electron microscope (SEM). The permeability and morphology of the UF Polysulfone membranes which were prepared via phase inversion technique are strongly influenced by varying forced convection residence time and coagulation bath temperature.

Keywords: *Coagulation bath temperature, flux, forced convection resident time, morphology*

Introduction

Nowadays, membrane technology is the latest fast growing technology. This technology has been used in a wide range of application including the water treatment process and gas separation. Membrane has received a lot of attention from both, industry and academic field. A few definitions can be considered as membrane definition. Although it is difficult to outline clearly the meaning of membrane, the general definition of membrane could be it is a selective barrier between two phases, the term selective being inherent to a membrane or a membrane process (Mulder, 1996). Mulder (1996) also found that it is also can be defined as a thin layer of material that is proficient of separating the feed water due to its chemical and physical properties when application of driving force was made across the membrane.

Transport through the membrane takes place because of driving force acting on the components in the feed. The permeation rate through the membrane is proportional to the driving – force. The membrane can acts as a filter medium, which will let the water flow through its porous layers. This phenomenon is known as the permeability of the membrane. Consequently, for any given separation, there is usually a trade-off between permeability (skin thickness) and selectivity (skin integrity), where both parameters tend to exhibit a contradictory relation, representing a major problem in productions and applications of asymmetric membranes (Ismail

& Lai, 2003).

In the early 1990s, Pinnau and Koros (1992) had developed a theory for skin formation and developed a forced convection technique to produce thin defect-free active layer. They postulated that at low residence times, skin formation and coalescence of the polymer-rich phase is incomplete. As the residence time increased, the skin layer will be matured and properly formed. Thus, the selectivity increases while the pressure-normalized flux will decrease (Puri, 1996). Previous studies have shown that the forced convection resident time (FCRT) and coagulation bath temperature (CBT) have significantly influenced the permeability characteristics of the membrane, thus affected the membrane performances. From the experimental data obtained, the varying of forced convection resident time and coagulation bath temperature has an effect on the performance of asymmetric membrane produced.

The morphological characteristics of the filament, such as the presence of macro pores and non-circular cross-sectional shapes, are greatly influenced by coagulation conditions. The coagulation temperature is one of the elements to change the layer shape, due to the different temperature of coagulant in the coagulation process (Um et al., 2004). In addition, the coagulation bath temperature can also be considered as an important parameter in the coagulation process because it governs the porosity and density of the membrane (Broens et al., 1980).

In this study, forced convection resident time and coagulation bath temperature were study in UF membrane fabrication in order to investigate their influence in membrane permeability and morphology. The UF membrane were characterized in term of pure water permeability by using dead-end permeation cell and measured as pure water flux. The morphology of membranes were investigated via scanning electron microscope (SEM).

Experimental

Materials, Membrane Preparation and Characterization

A ternary dope formulation of 14.4% Polysulfone (PSF) (Udel – P1700), 81.6% N–methyl–2 pyrrolidone (NMP) (Merk), and 4% water was cast by a dry/wet phase inversion process using an electrically controlled flat sheet membrane casting machine set up by Atrish Technic Services Sdn. Bhd and UMT. The membrane cast has been applied with various forced convection resident time (FCRT) and different coagulation bath temperature (CBT). The nitrogen was flushed across the membrane surface for 10s, 15s and 20s. The membrane then immersed into coagulation bath with different temperatures which at 10°C, 30°C and 50°C for one day. Then, the membrane was soaked in ethanol solution for eight hours to remove the residual left.

After that, the membrane was left dried in the ambient air. The membrane fabricated was tested using pure water to measure the flux and permeability and has been tested with salt solution with the concentration of 0.01 M to evaluate it rejection performance and it selectivity respectively. The tests were done in a dead-end permeation cell (Sterlitech HP 4750) with 1 - 5 bars operating pressure. The test of each flat sheet membrane was repeated for at minimum three times to ensure that the results were reproducible. The membranes were characterized according to its morphology via Scanning Electron Microscopy (JSM P/N HP475) in the cross section images.

Results and Discussion

Pure Water Permeability

The measurements of water flux as a function of applied pressures were used to investigate the stability and hydraulic properties of UF membranes. The slope of the fitted scatter displayed the values of pure water permeability of six tested membranes with different rheological factors which are 10s, 15s, and 20s forced convection resident time and 10 °C, 30 °C, and 50 °C coagulation bath temperature. Noticeably, the permeability of membranes in Figure 1 was in the following sequence: FCRT 15s > FCRT 10 s > FCRT 20 s.

Based on the pure water permeability results for Figure 1, we can postulate that 20 second forced convection resident time applied to the membranes has the lowest flux and is less permeable compared to 10s and 15s. This indicates that with the increasing of FCRT, a denser and thicker skin layer would form, leading to a lesser permeability. The flux rate for 10s and 15s were in a similar way. However, at 5-bar pressure applied, the flux rate for the 15s FCRT was higher, which leads to produce a high productivity membrane.

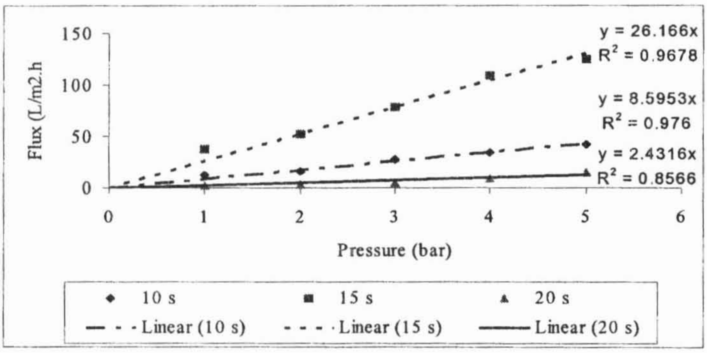
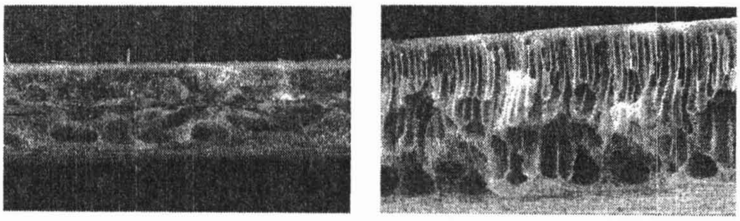
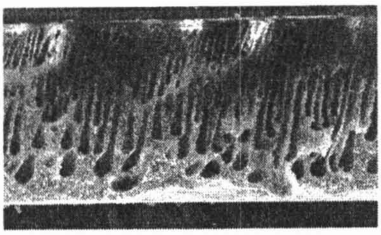


Figure 1: Pure Water Flux versus Pressure for Different Forced Convection Resident Time

The cross-section of PSF membranes applied with 10s, 15s and 20s forced convection resident time were examine via SEM and presented in Figure 2(a), (b), and (c). With the increasing of forced convection resident time, the support layer would form completely. From the observation, the image of 10s forced convection resident time applied influence the membrane support layer structure. It can clearly be seen that there was finger-like structures lead from top to bottom of the membrane. The sponge-like structures formed was tighter and closer to each other as illustrated in the Figure 2(a). Compared to the membrane applied with 20s forced convection resident time, the structures also have finger-like type but larger and shorter with some sponge type structure and macro voids as can be seen in Figure 2(b) below.

The morphology structure was also much alike with the membrane applied with 15s forced convection resident time which also consists of finger like voids and sponge type voids with some macro voids as shown in Fig. 2 (c). This structure significantly influences the productivity of the membrane and as a result the flux for 15 s FCRT is the highest compare to 10s and 20 s FCRT. This structure was identical to the 10s FCRT membrane which was the reason the fluxes of these two FCRT is higher than at the 20 s FCRT.


(a)
(b)



(c)

Figure 2: (a) 10s Forced Convection Resident Time, (b) 15s Forced Convection Resident Time, and (c) 20s Forced Convection Resident Time

Figure 3 showed that the flux rate of the pure water flux of membrane applied with different CBT. It can be seen that the trend was proportional with the temperature. The sequence was in following manner: CBT 50 °C > CBT 30 °C > CBT 10 °C. Refer to the permeability result obtained in the Fig. 3, it showed that with the increasing of coagulation bath temperature, the rate of water fluxes was also increased.

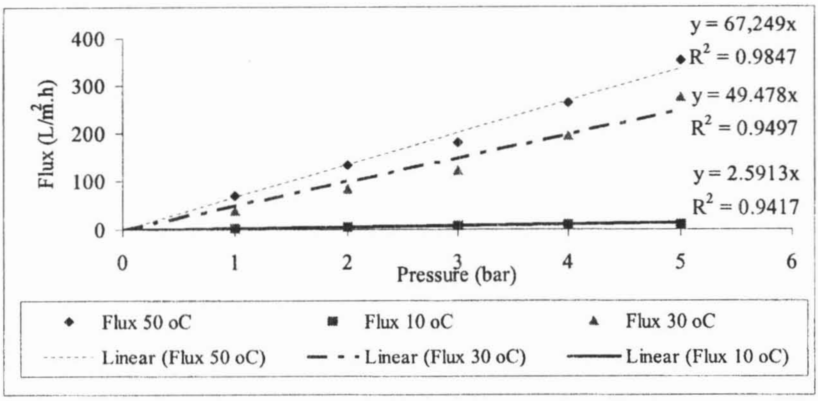


Figure 3: Pure Water Flux versus Pressure for Different Coagulation Bath Temperature

The flat sheet membrane immersed in 50°C coagulation bath temperature has higher fluxes and more permeable compared to the membrane soaked in 10°C and 30°C coagulation bath temperatures. It indicates that with the increasing of coagulation bath temperature, there are more open channel produced, thus leading to more productivity but less selectivity (Chaturvedi, 2001). For 30°C coagulation bath temperature, the flux rate was slightly lower compared to 50°C coagulation bath temperature, but much higher than 10°C coagulation bath temperature. In all cases of applied pressure in this study, the value of permeability rates of 50°C coagulation bath temperature were higher than the 30°C and 10°C. Thus, the membrane immersed in 10°C coagulation bath would produce a denser skin layer with tighter pores. This would produced a highly selectivity membrane but with lower productivity.

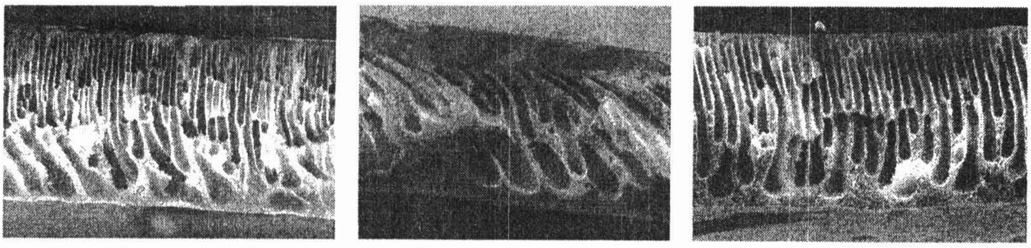
As shown in both figure above, it is noticeable that the flux increased directly proportional with the increasing of pressure. It indicates that the pure water flux was a liner function of the applied pressure, which shows a very good approximation. This result had agreed with the Hagen-Poiseuille equations shown in the Equation (1) below (Bowen & Muhammad, 1998).

$$J = \frac{\varepsilon r^2}{8\eta\tau} \times \frac{\Delta P}{\Delta x} \qquad (1)$$

This finding was supported by the results of the Scanning Electron Microscopy (SEM) micrographs. The cross-sectional images of SEM shows that occurrence, location, size, and uniformity of the pore strongly depend on the factor applied to the flat sheet membrane. The fabricated membranes show the expected typical asymmetric structure, which comprises a skin layer that is very well developed and supported by a porous support layer with macro-voids.

From the observation, an increasing of the coagulation bath temperature would also influence the morphology structure. Membranes, which have been soaked in lower coagulation bath temperature, in this case 10°C, have more sponge-type substructure with large macro-voids as illustrated in Figure 4(a). The present of sponge-type substructure would affect the membrane productivity; as a result, the water flux for this type of membrane was the lowest.

Compared to the membrane immersed in the 50°C coagulation bath temperature, the cross-section image in Figure 4(c) showed that there were more finger-like structures, which lead from the top to the bottom of the membrane. The formation of the finger-like structure was due to the rapid precipitation of fabricated membranes. These structures have significantly affected in the pure water flux evaluation. The water flux rate was higher compared to the membrane applied with lower coagulation bath temperature. Membrane bathed in 30 °C coagulation bath temperature has finger like voids with some macro voids structure as shows in Fig. 4 (b). This structure influences the flux rate and its separation performance.



(a) (b) (c)

Figure 4: (a) 10°C Coagulation Bath Temperature, (b) 30°C Coagulation Bath Temperature and (c) 50°C Coagulation Bath Temperature

Conclusion

The permeability and morphology of the UF Polysulfone membranes which were prepared via phase inversion technique are strongly influenced by varying forced convection residence time and coagulation bath temperature. The permeability of FCRT membranes is in the following sequence: FCRT 15s > FCRT 10 s > FCRT 20 s and the permeability of CBT membranes is in following manner: CBT 50 °C > CBT 30 °C > CBT 10 °C. Membranes which have more finger like structures and large macro-voids tend to produce higher flux which means it will increase permeability of the UF Polysulfone membranes.

Acknowledgement

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Notation

The following symbols are used in this paper:

J_v = Averaged solute volume over membrane surface, m/s
P = Applied pressure, bar
r = Pore size, m
Δx = Effective membrane thickness, m
E = Membrane porosity (dimensionless
η = Ratio of solute radius to membrane pore radius
τ = Tortuosity (dimensionless)

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