Effect of Kenaf MCC composition on Thin Film Composite membrane for NaCl Rejection

Azman Ismail[1], *Ramlah Mohd* Tajuddin[1,*], *Hamizah* Mohktar[1] and *Ahmad Fauzi* Ismail[2]

[1]Faculty of Civil Engineering, Universiti Teknologi MARA (UiTM), Selangor.
[2]Advanced Membrane Technology Research Center (AMTEC), UTM Johor.

Abstract. A modified thin film PSf-MCC reverse osmosis membrane was prepared by interfacial polymerization between aqueous MPD and TMC as the organic monomer. Aim of this study is to determine the effect of MCC in membrane formulation and fabrication. The surface and cross section morphology of TFC PSF/MCC membrane shows MCC particle which able to improve hydrophilicity of the membrane. The SEM images showed dense and porous structure of the MCC incorporated membranes. In addition, the water contact angle measurement also confirmed the increased hydrophilicity of the modified membranes. The effect of MCC on membrane matric influence the membrane performance in terms of NaCl rejection and pure water flux. Results showed that TFC PSf/MCC membrane shows NaCl rejection up to 98.9% compared with TFC PSf membrane. TFC PSf/MCC membrane also showed the highest pure water flux which is 3.712 Lm^2/hr compare with TFC PSF membrane which is 3.606 Lm^2/hr. The overall result proved that MCC particle could improve membrane hydrophilicity hence, increased pure water flux and salt rejection.

1 Introduction

Membrane technologies have gained great attention due to continuing decline of available freshwater sources and the increasing demand of freshwater. Membrane process basically depends on physical properties such as the hydraulic permeability, thickness and also feed concentration. Reverse osmosis is widely being used as the filtration process to treat waste water and desalination [1]. Apart from that, reverse osmosis also has high permeability for monovalent ions and a low permeability for divalent ions. Reverse osmosis have a lower molecular weight cut off (MWCO) 100 Da. Therefore, reverse osmosis process widely used for the treatment of wastewater and desalination process [2].

Along with the different polymeric material that are used for the preparation of phase-inversion membrane, Microcrystalline Cellulose (MCC) is known to have good toughness and relatively low cost. Microcrystalline Cellulose were used in many industries such as food, medical and cosmetic. Many industries used hydrolysis process to treat wood into MCC [3]. MCC is usually isolated from various cellulosic resources by mechanical, biological and chemical treatments. Basically, MCC is more stable, safe, and also inactive chemically. MCC also have several other advantages includes renewability, biodegradability, low density, high surface area and its hydrophilic characteristic [4]. Therefore, MCC is considered as a great substitute for membrane material.

Interfacial polymerization is the most common method to produce polyamide NF/RO membrane on the surface. The reaction between two monomers, is based on polycondensation reaction. There are two most common chemical used to construct polyamide layer which is m-phenyl diamine and trimesoyl chloride. At first, the aqueous amine solution was saturated the support. Then, organic phase containing acid chloride monomer was poured to the respective membrane support, forming a thin polyamide layer [5]. There are many strategies used to enhance the membrane performance via interfacial polymerization method. For example, Yin et al. [6] incorporated Graphene Oxide into the trimesoyl chloride solution. The resulting membranes showed enhancement in filtration performance. The as-prepared membrane showed increased in permeate flux due to interlayer spacing between GO nanosheets that served as water channel. Emadzadeh et al. [7] prepared thin film nanocomposite membrane embedded with TiO2. It was found that TiO2 addition effect membrane improvement both hydrophilicity and porosity.

In this paper, Polysulfone membrane were prepared by embedded microcrystalline cellulose as the additives. The TFC PSf/MCC membrane are fabricated by interfacial polymerization method. The goal is to compare the TFC PSf membrane with TFC PSf MCC

* Corresponding author: ramlah160@salam.uitm.edu.my

membrane and study their characteristics and performance. For this purpose, the effect of NaCl rejection and water flux is investigated and the surface properties, hydrophilicity and morphology were investigated using contact angle and Scanning Electron Microscope (SEM). Based on author's knowledge, there is still no research of TFC polyamide layer on PSf membrane embedded with Kenaf microcrystalline cellulose.

2 Materials and methods

2.1 Material

Polysulfone (PSf) with average molecular weight of 35 000 g/mol was provided by Sigma-Aldrich. DMAc (Synthesis Grade, Acros Organic, >99%) was used as solvent without further purification. Microcrystalline Cellulose were taken from Kenaf Cellulose Extraction. Polyvinyl Pyrrolidone K30 with molecular weight of 50,000 g/mol was provided by Acros Organic. M-Phenylenediamine, (MPD, >99%) were purchase from Merck and 1,3,3-benzenetricarbonyl trichloride (TMC, 98%) were purchase from Acros Organic. All the materials were used as received

2.2 Extraction of Cellulose

The extraction process for Kenaf cellulose were done by using Elementary Chlorine Free (ECF) method. The process was done at the Forest Research Institute Malaysia (FRIM). The Kenaf extraction method was followed based on research elsewhere [8]. Kenaf bast weighted 500g were cut into a length of about 3mm. After that, Kenaf bast were treated with soda pulping and bleaching processes. In this processes, Sodium Hydroxide (NaOH) and Antraquinone (0.1%) were used. Temperature was set at 170ºC with 150 psi for 1h treatment. The processes were repeated for five times until the color of the sample become white. Sample were spin using spin dryer to remove liquor from the sample in each steps.

2.3 MCC Extraction

The sample was then treated with Hydrochloric Acid (HCl) with a ratio of 1:20 to bleached pulp for 1 hour at 70ºc. The mixed sample were refluxed for another 1 hour to make sure that the required texture and colour of the sample achieved. The samples were then washed using distilled water and dry milling / sieving to get appropriate sizes, 10-0.1 microns as shown in Figure 1.

Fig. 1. MCC extracted from Kenaf core

2.4 Membrane fabrication

The porous PSf-MCC membrane were prepared by the phase inversion technique. Formula and method used in this research is based on research by [9]. First 0.9 % (w/w) MCC were dissolve into the DMAc solvent then stirred vigorously at 60ºc for 30 min. Afterwards, the solution was sonicated for 1 h. PSf and PVP was then added into the solution and stirred at 60ºC for at least 6 hours. The solution was degassed for 30 min to remove microbubble from the solution. After that the solution was then poured into glass bottle and stored in the chemical cabinet until further used.

The solution was cast on the glass plate using glass rod with 2 mm diameter. The glass plate was then immersed in distilled water at room temperature. After 2 min, the formed PSf-MCC porous support layer was washed with distilled water for several times and stored in the distilled water until further used.

2.5 Polyamide active layer fabrication

Dense and thin polyamide layer was casted on the PSf-MCC membrane surface using the interfacial polymerization. The PSf/MCC support membrane was clamped between two Teflon frames. An aqueous solution of 2% (w/w) MPD was poured on the top of the support membrane and allowed to soak for 2 min in the ambient temperature. The excess monomer on the membrane surface was then poured back to the beaker. The excess solution was then removed from the top surface by using rubber roller. Then, a solution of 0.1% (w/w) TMC in n-hexane was poured to the membrane surface and soaked for 1 min. After the predetermined time, the excess organic solution poured back to the beaker. Afterwards, the resulting membrane are cured by heating in an oven at 60ºc for 8 min. After that the membrane were immersed in a distilled water at room temperature until further used [10].

2.6 Membrane characterization

Scanning Electron Microscope (SEM) were used to get the images of thin film surface and cross-section respectively. Small piece of membrane sample was cut by 1cm x 1cm size and mounted on sample stubs. The membrane then coated with titanium layer using a sputter coater. The section was examined at an accelerating voltage of 80kV.

Contact angle of the membrane were studied using sessile technic as shown in figure 2. It was done on air dried sample of synthesized membrane in an environmental chamber mounted to the contact angle goniometer (DSA 10, KRuSS). The average value between the left and right side was taken as the equilibrium value. For the measurement of the contact angle, 4uL of de-ionized water was poured onto the membrane surface with micro syringe. After 3s, the value of the water contact angle was recorded. At least five measurements at different locations of the membrane surface sample were carried out and averaged to yield the contact angles.

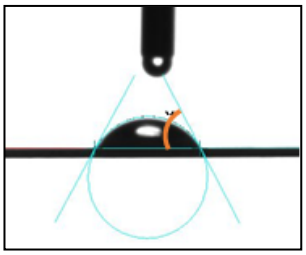

Fig. 2. Sessile drop technique to check membrane contact angles.

Pure water flux and NaCl rejection were used to study the separation performance. Reverse Osmosis dead end cell systems was used with affective membrane area of 14.6 cm^2. Membrane were first compressed with 16 bar pressure for 30 min at room temperature (20ºc). The NaCl rejection test was then carried out using 2000 ppm of NaCl solution with operating pressure of 15 bar. The desalination experiments were conducted triplicate for each sample, and the average value were reported. The salt rejection (R) and pure water permeability were determined using the following two equations,

$$R = \left(1 - \frac{Cp}{Cf}\right) \times 100\ \% \qquad \text{Equation 2.1}$$

$$J = \frac{V}{A \times t} \qquad \text{Equation 2.2}$$

where Cf and Cp are the salt concentrations (ppm) in the feed and permeate, respectively. V is the volume of permeate collected over a time interval t for a membrane area of A.

3 Result and discussion

Figure 3 shows pure water flux of TFC PSF membrane and TFC PSF/MCC membrane for 4 different pressure which is 12 bar, 13 bar, 14 bar and 15 bar. From the figure, it is show that the pure water flux increase when the pressure increase. Highest pure water flux is from TFC PSF/MCC membrane which is 3.712 Lm^2/hr compare with TFC PSF membrane which is 3.606 Lm^2/hr.

The highest flux in TFC PSF/MCC membrane was due to the presence of MCC in membrane sublayer as shown in figure 4. The MCC are spherical in shape at the size range of 200 to 400 nm. MCC is commonly known as hydrophilic behaviour. Due to the hydrophilic characters of MCCs, the simplest polymer solution that incorporated with MCCs are water based. Hence, the presence of MCC could enhance the hydrophilicity of membrane which gives highest pure water flux [11]. Previous studies also revealed the similar trend of flux where the MCC able to increase the hydrophilicity hence increased pure water flux [2, 7].

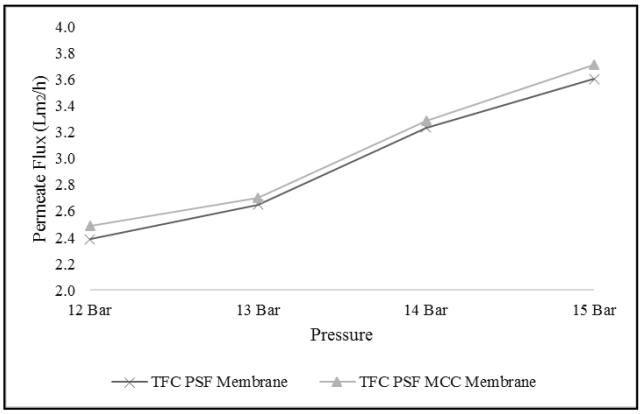

Fig. 3. Pure water flux for TFC PSF membrane and TFC PSF MCC membrane.

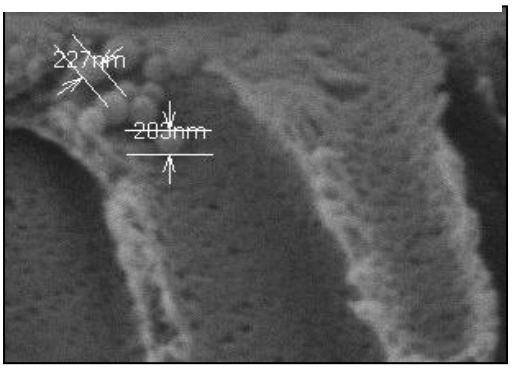

Fig. 4. Kenaf MCC particle were observed in membrane strcuture

NaCl rejection were evaluated to determine the effect of addition of MCC as an additive in membrane. From figure 5, it was observed that TFC PSF/MCC membrane has higher NaCl rejection compared with TFC PSF membrane. NaCl rejection was increase from 97.7% to 98.9%. Cellulosic molecules such as MCC have many

hydroxide radicals, hence strong hydrogen bonds can be formed within the molecule and other molecules. MCC also widely known as having small dimensions, thus it has a huge surface area and exposed hydroxide radicals. Addition of MCC into membrane matric eventually would improve membrane performance in term of NaCl rejection and pure water flux. The highest salt rejection also due to the smallest pore distribution on the membrane surface with TFC. Therefore, the TFC PSF/MCC membrane successfully enhance the membrane performance in terms salt rejection. This observation is in agreement with that of reported by Zhang et al. [12].

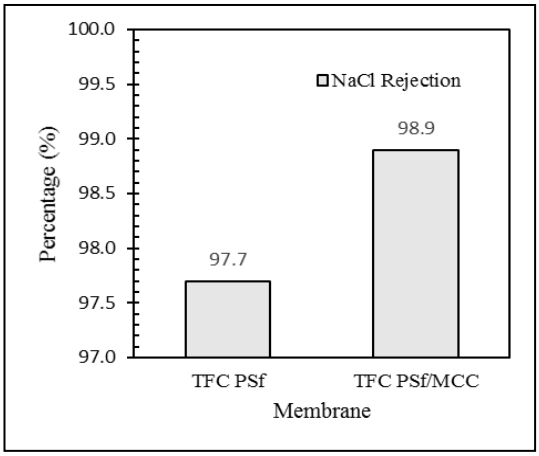

Fig. 5. NaCl rejection for TFC PSf membrane and TFC PSf MCC membrane.

Figure 6(a) and 6(b) shows the surface morphology of TFC PSf/MCC and TFC PSF membrane respectively. Both membranes exhibited the dense layer of membrane pores on thin layer surface morphology. This is due to the addition of TFC on membrane surface enhanced the pore formation and distribution.

The cross section area of TFC PSf/MCC membrane shows longer finger like structure than TFC PSF membrane as shown in Figure 7(a) and 7(b). This results indicated that the MCC able to improve the morphological structure of membrane cross section hence, lead to highest pure water flux. Therefore, the newly fabricate membrane of TFC PSf/MCC and TFC/PSF membrane are porous and asymmetric which has a dense top layer and a porous sub-layer.

MCC also known as pore forming agent hence larger pore size observed in TFC PSF/MCC membrane. This is due to the fact that MCC accelerated the velocity of water diffusion during casting process. It is also shown that MCC can increased membrane porosity with good connectivity [11].

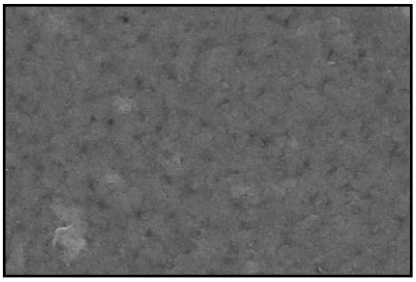

Fig. 6(a) Surface morphology of TFC PSF membrane

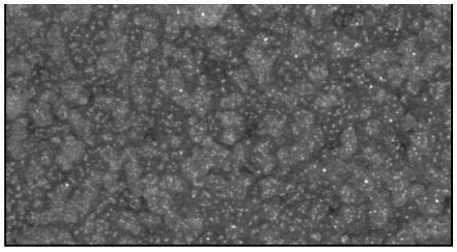

Fig. 6(b) Surface morphology of TFC PSF/MCC membrane

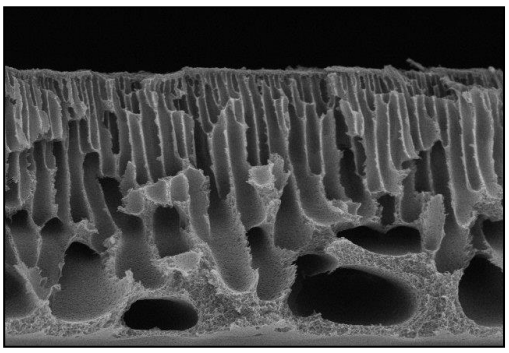

Fig. 7(a) Cross Section of TFC PSF membrane

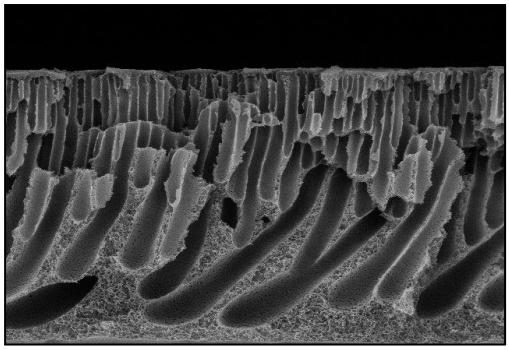

Fig. 7(b) Cross Section of TFC PSF/MCC membrane

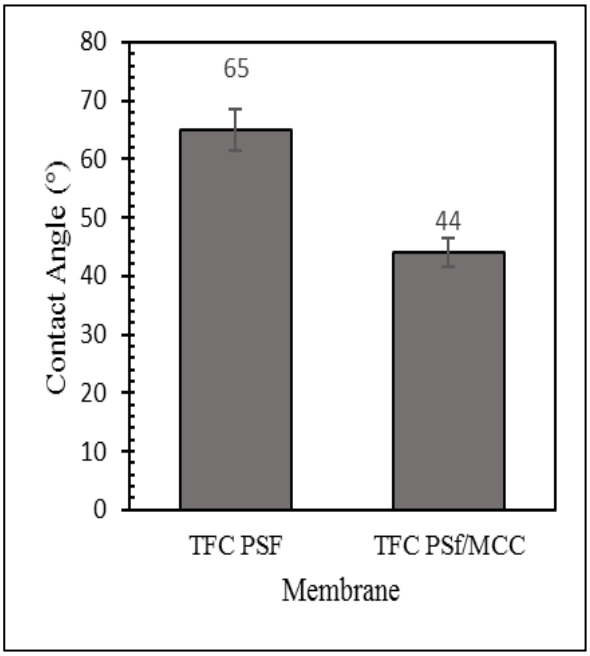

Fig. 8. Contact Angle of TFC PSf membrane and TFC PSf/MCC membrane

The hydrophilicity of the membrane can be evaluated through contact angle measurements. Water droplets that exhibit contact angle from 0º to 90º is referred as hydrophilic surface whereas 90º to 180º is considered as hydrophobic [13]. As shown in Figure 8, the water is strongly attracted to the thin film MCC membrane surface with 44º, while the contact angle for neat TFC PSF membrane is 65º. The different of contact angle between TFC PSf membrane and TFC PSF/ MCC membrane is approximately 32%. From this result, the hydrophilicity of the MCC membrane was found to increase clearly upon addition of MCC. Apart from that, both TFC PSF membrane and TFC PSf/MCC membrane are still considered under hydrophilic membrane. Table 1 which shows the contact angle based on previous study indicate that the contact angle of PSF membrane without any additive was highest in the range of 66 t0 60% [12,13]. Upon, addition of additives such as CNT cellulose acetate, cellulose ester and TFC, the contact angle decreased hence more hydrophilicity [14,15]. Lower contact angle of TFC PSf/MCC membrane indicated that this membrane is more hydrophilicity compared to previous study as shown in Table 1. Thus, the hydrophilicity of TFC PSf/ MCC membrane could enhance pure water flux due to attraction towards water [2].

Table. 1. Contact Angle of TFC PSf membrane and TFC PSf/MCC membrane

Authors/Year	Material	Contact Angle
Mollahosseini et al. (2012) [14]	PSf	60.9°
Misdan et al.(2013) [15]	PSf	66.3.0º
Choi et al. (2015) [16]	CNT CA	58°
Ong et al. (2014) [17]	TFC Cellulose Ester	58.3°
Present study	TFC PSF/MCC	44º

4 Conclusions

Kenaf Microcrystalline Cellulose (MCC) was successfully embedded into membrane matric. Membrane performance test was conducted using pure water flux and NaCl rejection. Result from Scanning Electron Microscope shows longer finger like structure in TFC PSf/MCC membrane compared with TFC PSf membrane. MCC particle were observed inside the membrane structure hence improving membrane hydrophilic characteristics. SEM result were then supported by contact angle measurement. Membrane with MCC shows improvement in contact angle thus could explain the increasing of pure water flux value. Membrane contact angle and membrane morphology study revealed that the TFC PSF/MCC membrane is hydrophilicity with 44º. Therefore, the newly developed TFC PSf/ MCC membrane shows increased in pure water flux which is 3.712 Lm^2/hr and NaCl rejection which is 98.9%.

The authors would like to acknowledge the financial support provided by the Malaysia Ministry of Higher Education for the AMTEC fellowship program under UTM-HiCOE Research Grants (A.J090301.5300.07092). The first author would like express the gratitude to the sponsorship offered by the Ministry of Higher Education under MyBrain15 (MyPhD) scheme during his Ph.D. studies.

References

1. P. S. Goh, A. F. Ismail, and B. C. Ng, *Desalination*, **308**, 2–14, (2013)
2. X. Wei, X. Kong, S. Wang, H. Xiang, J. Wang, and J. Chen, (2013)
3. S. Abdullah, N. M. Abdullah, and R. M. Tajuddin, (2015)
4. W. Liu, M. Fei, Y. Ban, A. Jia, and R. Qiu, *Polymers (Basel),* **9**, 10, (2017)
5. H. Zarrabi, M. E. Yekavalangi, V. Vatanpour, A. Shockravi, and M. Safarpour, *Desalination*, **394**, 83–90, (2016)
6. J. Yin, G. Zhu, and B. Deng, ,**379**, 93–101, (2016)
7. D. Emadzadeh, W. J. Lau, T. Matsuura, M. Rahbari-Sisakht, and A. F. Ismail, *Chem. Eng. J.*, **237**, 70–80, (2014)
8. Nor Munirah, M. T. Ramlah, and Sharifah, *Appl. Mech. Mater.*, **754–755**, 1023–1027, (2015)
9. D. Hu, Z. Xu, and C. Chen, Desalination, **301**, 75–81, (2012)
10. Y. Yu, S. Lee, and S. Hong, *J. Memb. Sci.*, **351**, 205–213, (2010)
11. Y. Habibi, L. A. Lucia, and O. J. Rojas, *Chem. Rev.*, **110**, 3479–3500, (2010)
12. L. Zhang, C. Guowei, and J. Lv, *Polym. Compos.*, **21**, 449–456, (2013)
13. A. Akbari, E. Aliyarizadeh, S. M. Mojallali Rostami, and M. Homayoonfal, *Desalination*, **377**, 11–22, (2016)
14. A. Mollahosseini, A. Rahimpour, M. Jahamshahi, M. Peyravi, and M. Khavarpour, *Desalination*, **306,** 41–50, (2012)
15. N. Misdan, W. J. Lau, a. F. Ismail, and T. Matsuura, *Desalination*, 329, 9–18, (2013)
16. H. G. Choi, M. Son, S. H. Yoon, E. Celik, S. Kang, H. Park, C. H. Park, and H. Choi, *Chemosphere*, **136**, 204–210, (2015)
17. R. C. Ong, T. S. Chung, J. S. de Wit, and B. J. Helmer, *J. Memb. Sci.*, **473**, 63–71, (2014)