Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.768423

51 (2013) 5191–5195
July

Taylor & Francis
Taylor & Francis Group

Preparation of newly synthesized forward osmosis membrane

In-Chul Kim[a,*], Su-Hyun Ahn[a,d], Yong-Sook Jin[a,e], Beom-Sik Kim[a], You-In Park[a], Jonggeon Jegal[a], Seok-Heon Lee[b], Young-Nam Kwon[c], Hee-Woo Rhee[d]

[a]*Research Center for Biobased Chemistry, Korea Research Institute of Chemical Technology, P.O. Box 107, Sinseongno 19, Yuseong, Daejeon 305-600, Republic of Korea*
Tel. +82 42 860 7638; Fax: +82 42 861 4151; email: ickim@krict.re.kr
[b]*Water Environment Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea*
[c]*School of Urban & Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-798, Republic of Korea*
[d]*Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 121-742, Republic of Korea*
[e]*Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Republic of Korea*

Received 15 June 2012; Accepted 28 September 2012

ABSTRACT

Forward osmosis (FO) membrane was fabricated with a newly synthesized acetylated methyl cellulose (AMC) membrane. The FO membrane performance was compared with a commercially available reverse osmosis (RO) membrane for seawater desalination. Interfacial polymerization was done on the AMC support membrane for FO membrane preparation. Polyamide layer was successfully formed. The membranes were characterized by scanning electron microscopy and atomic force microscopy analysis. The surface of two membranes shows similar ridge-and-valley structure. However, the support layer of two membranes was completely different. The polyamide membrane based on the AMC support layer shows much better FO and RO performance than the RO membrane due to difference at the membrane cross-section between two membranes. The big macrovoids of the AMC support layer make flux much higher. In contrast, the RO membrane shows sponge-like structure at the membrane cross-section.

Keywords: Forward osmosis; Acetylated methyl cellulose; Interfacial polymerization

1. Introduction

The supply of safe drinking water in water-stressed countries is limited due to industrialization, population growth, contamination of freshwater, and climate change. Seawater desalination seems to be a strong option to solve the water shortage problems. Seawater desalination plants have been installed in the past decades to increase the water supply. In recent years, reverse osmosis (RO) has been used instead of thermal desalination because of its decrease in energy consumption [1]. The energy-efficient RO process results in the development of high-performance membranes, energy recovery device, and pumps. Despite energy-efficient innovative RO technologies, there is a demand for lower energy consumption technologies than RO technology. Among challenging desalination technologies such as forward osmosis (FO), aquaporin [2], and carbon nanotube [3], FO seems to be a potential process.

*Corresponding author.

7th Aseanian Membrane Society Conference (AMS7), 4–7 July 2012, Busan, Korea

FO is an emerging process for seawater desalination with low-energy consumption. FO consists of a selective membrane and draw solution. FO utilizes an osmotic pressure between the membrane and the draw solution. Due to these advantages of the FO process, many researchers have made tremendous efforts to develop FO membranes [4–9] and draw solutes [10–12]. The FO membrane should lower resistance to water flow and enhance salt rejection. To lower resistance to water flow, the FO membrane needs to involve highly porous and finger-like structure. Elimelech and Phillip suggested that the high water flux of the fabricated thin-film composite FO membranes was directly related to the thickness, porosity, tortuosity, and pore structure of the polysulfone support layer [4].

In this study, we synthesized the thin-film composite FO membrane consisting of polyamide selective layer and cellulosic support layer. The performance of the membrane was compared with commercialized FO membrane and RO membrane.

2. Experimental

2.1. Chemicals and materials

Dimethylacetamide (DMAc), 1,3-phenylenediamine (MPD), triethylamide (TEA), and 1,3,5-benzenetricarbonyl chloride (TMC) were used as received from Sigma-Aldrich (St. Louis, MO). TMC was dissolved in ISOL-C (SK Chemical, Korea). Acetylated methyl cellulose (AMC, Mw of 300 kDa) was kindly supplied from Samsung fine chemicals (Korea). A polyester non-woven fabric (PET, Sanko, Japan) was used as a support. Sodium chloride (Junsei, Japan) was dissolved in DI water obtained from a Milli-Q water system (Millipore). A seawater RO membrane was supplied from Woonggin Chemical (Korea).

2.2. Membrane fabrication

2.2.1. AMC support membrane

AMC was dissolved in DMAc by stirring at 60°C for 5 h. The AMC solution was poured and cast with a casting knife on the PET fabric. The cast solution was immersed into DI water at room temperature for 24 h.

2.2.2. Thin film composite (TFC) membrane

Interfacial polymerization was used for the polyamide composite layer formation onto the AMC support membrane. The AMC support membrane was immersed in a 2 wt% MPD solution for 1 min and then, the excess MPD solution was removed by squeezing with silicon roller. The membrane was immersed in a 0.1 wt% TMC solution for 1 min. The membrane was dried at room temperature for 10 min and then stored in DI water.

2.3. Membrane test

The performance of membrane was evaluated in a cross-flow RO test unit. Water flux and salt rejection were measured. The effective membrane area was 18.52 cm^2, the flow rate was 3.0 L/min, the operating pressure was 225 psi, and the temperature was fixed at 20 ± 1°C. The concentration of NaCl solution was 0.2 wt%. The salt rejection rate was measured using a conductivity meter.

The same membrane tested in the RO unit was used for FO performance. 2 M NaCl solution, and DI water was used as a draw solution and a feed solution, respectively. The active layer was contacted with the feed solution. The flow rate of gear pumps was 90 mL/min. The temperature of the two solutions was constant at 20 ± 1°C.

2.4. Membrane characterization

A Field Emission Scanning Electron Microscope (FE-SEM) was used for evaluating surface and cross-section of the membrane. The samples were fractured in liquid nitrogen and coated with gold by sputtering machine. Atomic force microscope was used for the analysis of the surface roughness.

3. Results and discussion

3.1. Membrane morphology

The properties of the FO and RO membranes fabricated by the newly synthesized AMC polymer were compared with the commercialized RO membrane for seawater desalination. Tiraferri et al. have reported that the structure of support layer of the membrane could affect the performance of the FO membrane. In other words, if highly porous macrovoids exist at the support layer, water flux of the FO membrane can be enhanced. Fig. 1 shows the difference SEM images of cross-section between polyamide AMC and polyamide polysulfone membrane. The AMC support membrane has a very thin skin layer and highly porous macrovoids. Moreover, the macrovoids occupy much more than the AMC matrix, which means that the support layer structure is dominated by the macrovoids. In contrast, the support layer of the polyamide RO membrane

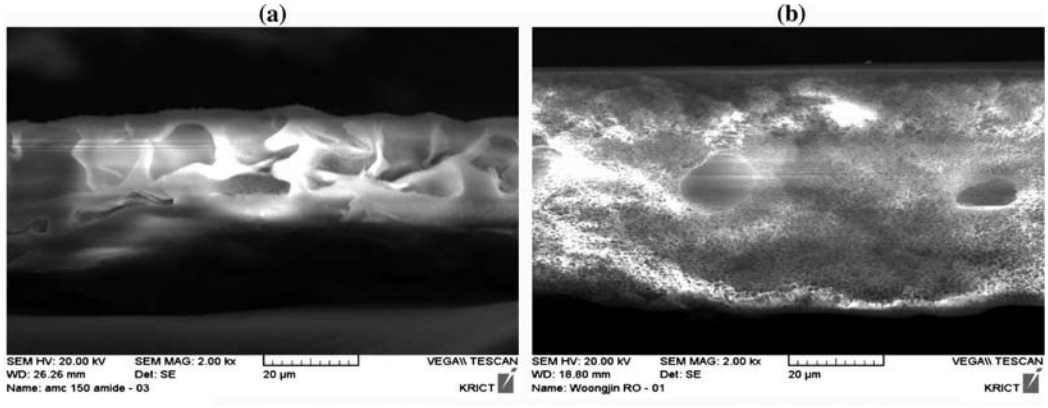

Fig. 1. Cross-sectional SEM images of (a) polyamide AMC and (b) polyamide polysulfone membrane.

for seawater membrane has completely the sponge-like structure, which means that the membrane has no macrovoids. It can be expected that the resistance of water transport of the polyamide AMC membrane will be even less than that of the polyamide RO membrane. The surface of two membranes in Fig. 2 shows very rough ridge-and-valley structure. Those surfaces can be formed during interfacial polymerization with MPD and TMC. Atomic force microscopy (AFM) images of Fig. 3 support the rough surface of two polyamide membranes. According to Fig. 3, the polyamide polysulfone RO membrane reveals better roughness than the polyamide AMC FO membrane. In general, rough membrane shows higher flux. However, flux of the polyamide AMC FO membrane is higher than that of the polyamide polysulfone RO membrane, which means that the support layer of the composite membrane can affect the water flux. In other words, the polyamide AMC FO membrane having more porous support layer can transport water better.

The relationship between flux and osmotic pressure was expressed by Loeb et al. [13].

$$J_W = K \ln \frac{\pi_{Hi}}{\pi_{Low}}$$

J_w is the water flux, π_{Hi} and π_{Low} are the osmotic pressures of the draw and feed solutions, and K is expressed as the resistance to solute diffusion within the membrane porous support layer. Therefore, K is a measure of the severity of internal concentration polarization (ICP).

$$K = \frac{t\tau}{\varepsilon D_s}$$

t is the membrane thickness of porous support layer, τ is the tortuosity of the membrane porous support layer, ε is porosity of the porous support layer, and D_s is the diffusion coefficient of the draw solute. The value of ε/τ is an indicator of the inherent resistance to diffusion provided by the structure. The value can

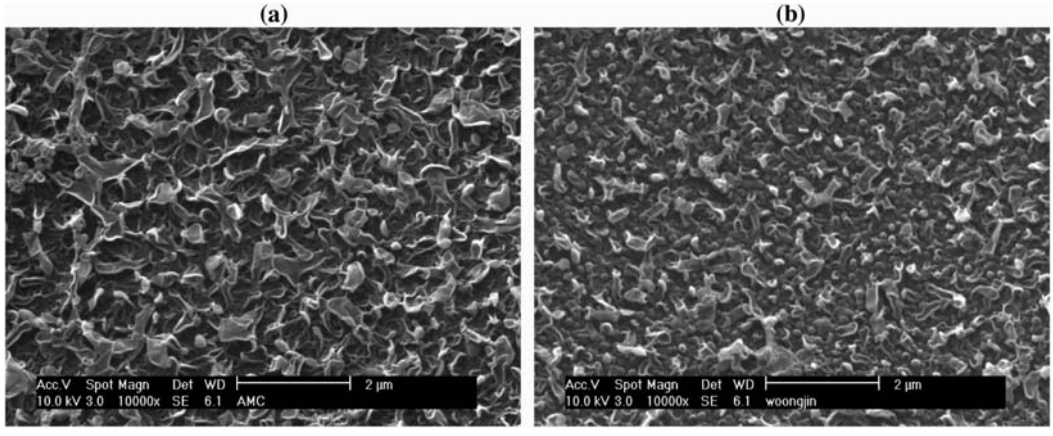

Fig. 2. SEM micrographs of the membrane surface of (a) polyamide AMC and (b) polyamide polysulfone membrane.

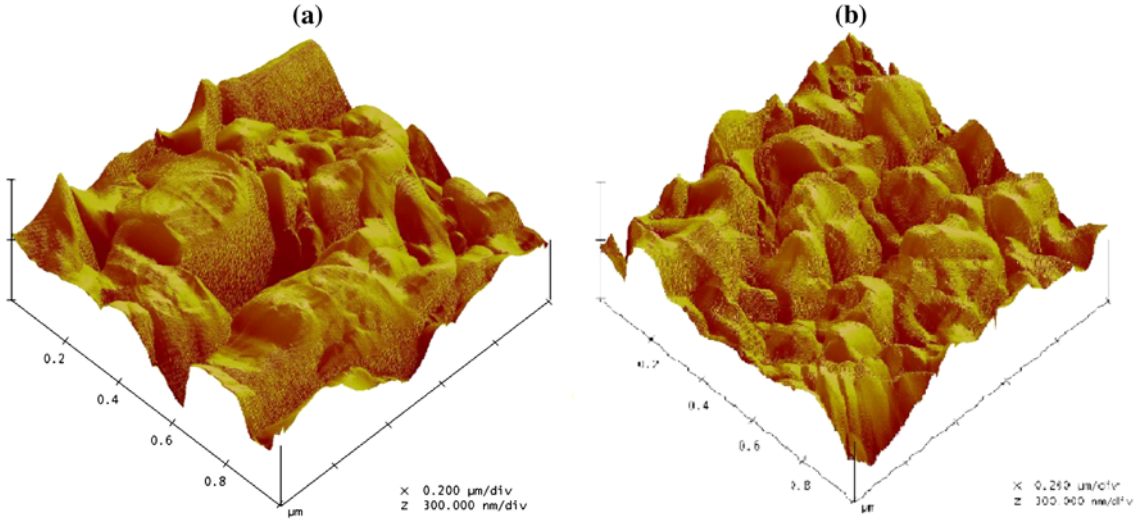

Fig. 3. AFM micrographs of the membrane surface of (a) polyamide AMC and (b) polyamide polysulfone membrane.

range from zero to one, because range of porosity is from zero to one and tortuosity is greater than equal to one. If the value of ε/τ is one, effects of ICP are minimized. To increase ε/τ, decreasing the effective thickness of the boundary layer should improve FO performance. Generally, Finger-like morphology membranes have a higher ε/τ than the corresponding membranes with a sponge-like morphology. A finger-like morphology membrane having large macrovoids reduces ICP in FO operations. To maximize performance in FO, AMC/PA membrane having finger-like structure with a high porosity is suitable for FO performance.

3.2. Membrane performance

Table 1 shows the RO membrane performance of polyamide AMC and polysulfone membranes. The polyamide AMC membrane shows much higher water flux and similar salt rejection rate compared with the polyamide polysulfone membrane in RO test conditions. These results mean that the polyamide AMC membrane has similar polyamide active layer with the polyamide polysulfone membrane and less water transport resistance than the polyamide polysulfone membrane.

Table 1
RO performance of the polyamide AMC and polysulfone membranes

Membranes	Flux (gfd)	Rejection (%)
Polyamide AMC	35.6	99.1
Polyamide polysulfone	18.5	99.4

Test condition: NaCl 2,000 ppm; 225 psi; 3.0 L/min

Two membranes consist of a dense separation later and a porous support layer. In FO performance, water flux through the membrane is affected by the hydraulic resistance created by the membrane structure. And porous support layer affects mass transfer of solution across the membrane. FO process, the osmotic-driven membrane process, has concentration polarization caused by buildup solute at the active layer. Especially, ICP is important factor that causes reduction in the osmotic pressure and water flux. ICP consists of two phenomena depending on the membrane orientation. When the active layer of the membrane faces the feed solution and the porous support layer faces the draw solution, water permeates the active layer and the draw solution within the porous substructure becomes diluted. This phenomenon refers as dilutive ICP. When the porous support layer faces the feed solution, a polarized layer is established inside of the dense active layer. As time goes by, water and solute propagate within the porous layer. Generated concentrative ICP cannot be minimized by cross-flow. In case of active layer facing feed solution, dilutive ICP, the water flux through the FO membrane drastically dilutes the draw solution which results in a loss of the effective osmotic driving force and low water flux. Therefore, FO performance was progressed by porous support layer facing feed solution.

Table 2 represents the FO performance of polyamide AMC and polysulfone membranes. For water fluxes measurement, DI water and 2 M NaCl was used as a feed and a draw solution, respectively. The polyamide AMC membrane exhibited much higher flux than that of the commercialized polyamide polysulfone membrane. Fig. 4 exhibits trends the water flux dropped with decreasing osmotic pressure difference

Table 2
FO performance of the polyamide AMC and polysulfone membranes

Membranes	Flux (LMH)	Conductivity (μS/cm)
Polyamide AMC	13.2	11.0
Polyamide polysulfone	1.3	7.2

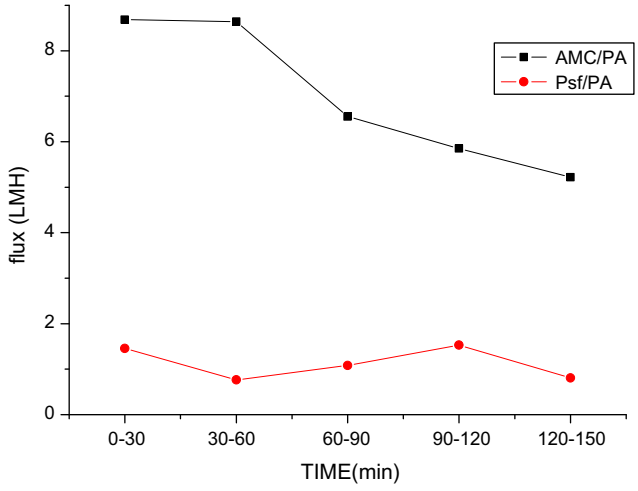

Fig. 4. Graph of FO performance of AMC and polysulfone for 150 min.

from an initial highest value. As DI water diffused from the feed to the draw solution, the osmotic pressure in the feed increases and draw solution decreases, respectively. Therefore, it causes reduction in the osmotic pressure difference across the membrane. This result shows that the water flux achieved by the AMC membrane was higher than Psf membranes. Back diffusion rate of the draw solution presents similar values. The similar back diffusion rate of two polyamide membrane results from the compact polyamide active layer, which can be expected from the RO performance data of Table 1. Table 1 showed that two membranes had similar salt rejection rate. Big FO performance difference between two membranes is attributed from the support layer morphology. The polyamide AMC FO membrane presents highly porous macrovoids at the membrane cross-section. In contrast, the polyamide polysulfone RO membrane shows compact sponge-like structure. There is no water transport resistance in case of the polyamide AMC FO membrane due to the existence of the macrovoids at the membrane cross-section. In case of the polyamide polysulfone RO membrane, there is no macrovoids at the membrane cross-section, which means that water transport can be inhibited.

4. Conclusions

A new FO membrane was successfully fabricated. The membrane could be prepared by an interfacial polymerization on the AMC support layer. The AMC support layer had fully developed porous macrovoids. In contrast, the thin film composite RO membrane consisted of a polyamide selective layer and a compact sponge-like support layer. The FO performance of the polyamide AMC FO membrane showed much better than that of the polyamide RO membrane. Two membranes had similar salt rejection rate. SEM and AFM analysis revealed that the polyamide AMC FO membrane had a similar surface structure with the polyamide RO membrane, which means that surface of two membranes showed the ridge-and-valley structure. There is less water transport resistance in case of the polyamide AMC FO membrane due to the existence of big macrovoids. No macrovoids of the polysulfone support layer interrupted the water transport.

References

[1] M. Elimelech, W.A. Phillip, The future of seawater desalination: Energy, Technol. Env. Sci. 333 (2011) 712–717.
[2] M. Kumar, M. Grzelakowski, J. Zilles, M. Clark, W. Meier, Highly permeable polymeric membranes based on the incorporation of the functional water channel protein aquaporin Z, Proc. Natl. Acad. Sci. USA 104 (2007) 20719–20724.
[3] M. Majumder, N. Chopra, R. Andrews, B.J. Hinds, Nanoscale hydrodynamics: Enhanced flow in carbon nanotubes, Nature 438 (2005) 930.
[4] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, Environ. Sci. Technol. 44 (2010) 3812–3818.
[5] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication of novel poly(amide–imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer, J. Memb. Sci. 369 (2011) 196–205.
[6] Q. Saren, C.Q. Qiu, C.Y. Tang, Synthesis and characterization of novel forward osmosis membranes based on layer-by-layer assembly, Environ. Sci. Technol. 45 (2011) 5201–5208.
[7] Q. Yang, K.Y. Wang, T.S. Chung, Dual-layer hollow fibers with enhanced flux as novel forward osmosis membranes for water production, Environ. Sci. Technol. 43 (2009) 2800–2805.
[8] K.Y. Wang, T.S. Chung, J.J. Qin, Polybenzimidazole (PBI) nanofiltration hollow fiber membranes applied in forward osmosis process, J. Memb. Sci. 300 (2007) 6–12.
[9] J. Su, Q. Yang, J.F. Teo, T.S. Chung, Cellulose acetate nanofiltration hollow fiber membranes for forward osmosis processes, J. Memb. Sci. 355 (2010) 36–44.
[10] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia–carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance, J. Memb. Sci. 278 (2006) 114–123.
[11] S. Phuntsho, H.K. Shon, S.K. Hong, S.Y. Lee, S. Vigneswaran, A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions, J. Memb. Sci. 375 (2011) 172–181.
[12] M.M. Ling, K.Y. Wang, T.S. Chung, Highly water soluble magnetic nanoparticles asnovel draw solutes in forward osmosis for water reuse, Ind. Eng. Chem. Res. 49 (2010) 5869–5876.
[13] S. Loeb, L. Titelman, E. Korngold, J. Freiman, Effect of porous support fabric on osmosis through a Loeb-Sourirajan type asymmetric membrane, J. Memb. Sci. 129 (1997) 243–249.