Desalination and Water Treatment
www.deswater.com

43 (2012) 230–237
April

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.672177

Novel thin-film composite membrane for seawater desalination with sulfonated poly(arylene ether sulfone) containing amino groups

Sang Gon Kim, Si Young Park, Jeong Hwan Chun, Byung-Hee Chun, Sung Hyun Kim*

Department of Chemical & Biological Engineering, Korea University, 1 Anam-Dong, Seongbuk-Gu, Seoul 136-701, Korea
Tel. +82 2 3290 3297; Fax: +82 2 926 6102; email: kimsh@korea.ac.kr

Received 25 December 2011; Accepted 10 February 2012

ABSTRACT

Sulfonated poly(arylene ether sulfone) containing sulfonic acid and amino groups (SDADPS) were successfully synthesized using direct-step polymerization as a novel thin-film composite (TFC) reverse osmosis (RO) membrane material for high chlorine resistance. TFC membranes were prepared using an interfacial polymerization (IP) reaction with trimesoyl chloride (TMC) and amine solution, containing m-phenylenediamine (MPDA) and SDADPS, on a polysulfone (PS) ultrafiltration (UF) support membrane. The synthesized SDADPS and fabricated TFC RO membranes were characterized by nuclear magnetic resonance spectroscopy and scanning electron microscope. Moreover, RO performances, salt rejection and water flux, were measured using a cross-flow cell instrument. Chlorine resistance was evaluated using sodium hypochlorite solution. The membrane fabricated with SDADPS was compared with a typical polyamide (PA) TFC membrane which was prepared by IP reaction with TMC and MPDA on a PS support membrane. The SDADPS RO membrane had much higher chlorine resistance than PA RO membrane and showed good RO performances, such as water flux (32 $L/m^2 h$) and salt rejection (95%).

Keywords: Desalination; Reverse osmosis; RO membrane; Sulfonated poly(arylene ether sulfone); Chlorine resistance

---

1. Introduction

Recently, desalination technology using membranes, especially RO seawater desalination, is an attractive and efficient technique for new sources of water. The RO membrane plays an important role in the seawater desalination process. RO membrane technology is the widespread technique of membrane desalination process. RO membrane is required to have high salt rejection and high water flux [1–4].

The first RO desalination membrane was developed by Loeb and Sourirajan in the 1960s. The first desalination RO membrane started from the cellulose acetate (CA) membrane [5,6]. The development of PA thin-film composite (TFC) membrane is a major turning point in the membrane desalination field. PA TFC RO membranes consisted of a top active layer formed in situ on the surface of a support layer via interfacial polymerization (IP) technique. The support layer is usually an ultrafiltration (UF) substrate made of PS or polyethersulfone. The UF support substrate gives the membrane necessary mechanical strength, while the

---

*Corresponding author.

The 4th International Desalination Workshop (IDW4), 16–18 November 2011, Jeju Island, South Korea

top active layer is used for performing the separation function. The active top layer and the support substrate layer can be independently improved to enhance the membrane performance [7,8].

PA RO membranes exhibit good transport properties and are more stable over a wider range of pH than CA membranes. Thus PA TFC RO membranes are the most widely used commercial seawater desalination membranes. However, PA TFC RO membranes are sensitive to chlorine attacks, which led to a performance loss of the membrane. Moreover, low water flux is one of the problems of PA TFC RO membranes [9,10].

In order to overcome these disadvantages, much effort has been centered on developing membranes with higher water flux through design and synthesis of new active layer materials or modifications of the membranes. Among them, sulfonated poly(arylene ether sulfone) (PES) materials, based on polysulfone (PS) which has a PES structure, are of considerable interest, because these materials have good physical properties and good chemical and thermal stability. PS is a hydrophobic material, thus, if used in a TFC membrane, water permeation will be very low. Therefore, to improve water flux, chemical modification of the membrane materials by the introduction of hydrophilic functional groups, such as sulfonic acid groups, has been employed. Sulfonated aromatic materials are one of the promising materials for desalination RO membranes, which have high water flux and chlorine resistance [11–15].

The objective of this study was to synthesize sulfonated PES materials containing sulfonic acid groups and amino groups, desulfonated 4,4′-bis(3-aminophenoxy) phenylsulfone (SDADPS), and to prepare asymmetric TFC RO membranes using IP. To synthesize the SDADPS, we prepared 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) from dichlorodiphenyl sulfone (DCDPS).The synthesized SDCDPS and SDADPS were characterized by nuclear magnetic resonance (NMR). The fabricated membranes, PA and SDADPS, were characterized by field emission scanning electron microscope (SEM). The membranes were immersed in 2000 ppm aqueous sodium hypochlorite (NaOCl) solution to evaluate the chlorine resistance of the membranes. The performances of membrane were evaluated in a cross-flow cell apparatus.

2. Methods

2.1. Materials

DCDPS, m-aminophenol and anhydrous potassium carbonate (K_2CO_3) were obtained from Aldrich. DCDPS, m-aminophenol were dried under vacuum at 80°C for 12 h prior to use. Anhydrous potassium carbonate was used as received. 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) was synthesized according to previously published methods [16,17] and dried under vacuum at 100°C for 24 h before use. N,N-dimethylacetamide (DMAc), m-phenylenediamine (MPDA), ethylenediamine, trimesoyl chloride (TMC) (Sigma-Aldrich), toluene, ethanol (J.T. Baker) and sulfuric acid (Daejung reagents and chemical) were used as received.

2.2. Synthesis of sulfonated PES material containing sulfonic acid and amino groups

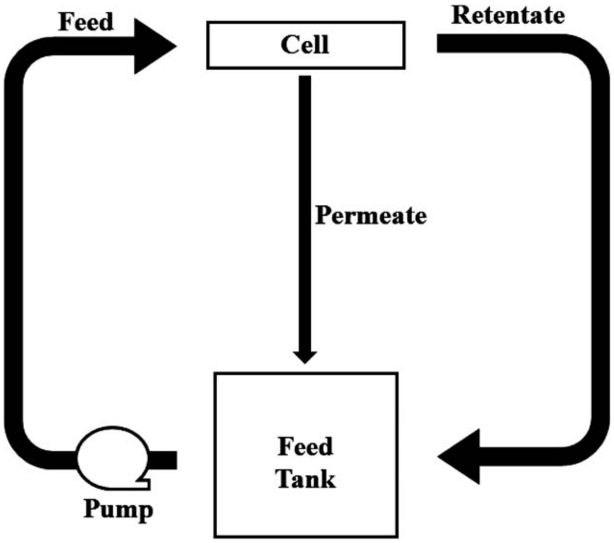
The sulfonated PES materials containing sulfonic acid and amino groups were synthesized using nucleophilic aromatic substitution.

First, into a three-necked round-bottomed flask (250 mL) equipped with a mechanical stirrer, a nitrogen inlet-outlet and a Dean-Stark trap fitted with a condenser, m-aminophenol (3.33 g) and K_2CO_3 (4.63 g) were charged along with DMAc (45 mL) as a solvent and toluene (18.0 mL) as an azeotropic agent. The mixture was stirred by refluxing at 145°C for 6 h. Finally, the azeotropic solvent was completely removed after 6 h, and then SDCDPS (7.5 g) was added into the reaction flask along with more DMAc (10 mL) and the reaction mixture was stirred by heating at 170°C for 24 h. The reaction solution was cooled to room temperature and diluted with DMAc. The solution was filtrated to remove inorganic salts. After filtration, the product was isolated by precipitating in ethyl acetate solution resulting in a light brown solid. The precipitated material was successively washed several times with ethanol and dried under vacuum at 100°C for 12 h.

2.3. Fabrication of thin-film composite reverse osmosis (RO) membrane

Both polyamide (PA) and SDADPS TFC RO membranes were fabricated via typical IP using PS UF membranes (UE50, Trisep Corporation, USA). The method used for the formation of the PA TFC RO membrane is as follows. The PS UF membrane was placed in an aqueous solution of 1% (w/v) MPDA for 2 min, and then rolled with a roller to remove excess solution off the membrane surface. Then, the membrane was immersed into a solution of 1% (w/v) TMC in cyclohexane for 1 min. After removing the excess solution, the membrane was heated in an oven at 70°C for 1 min for further polymerization.

An SDADPS membrane was prepared according to the method as follows. The PS UF membrane was placed in the aqueous solution, which was adjusted to pH 10 by camphor sulfonic acid, containing a 1% (w/v) mixture of SDADPS and MPDA, triethylamine (1%) and dodecyl sulfonic acid sodium salt (0.05%). The solution was then rolled with a roller to get rid of excess solution off the membrane surface. The membrane was immersed into a solution of 1% (w/v) TMC in cyclohexane for 5 min. After removing the solution, the membrane was treated in an oven at 70°C for 1 min.



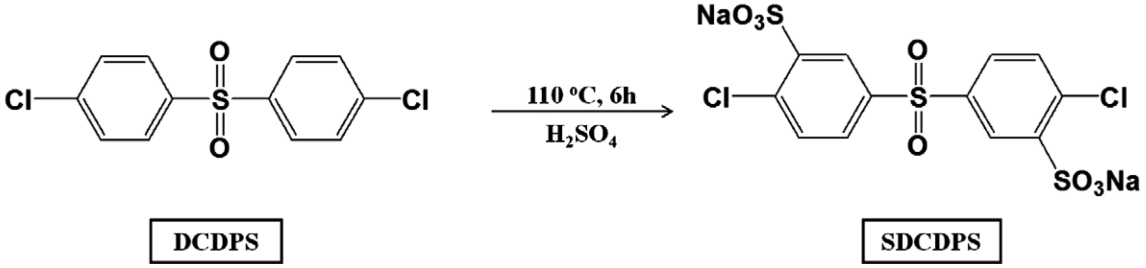
Scheme 1. The simplified structure of the cross-flow cell apparatus.

2.4. Characterizations

The SDCDPS and SDADPS were identified by elemental analysis, such as C, H, H. ^{1}H NMR spectra of the products were obtained at 300 MHz on the Varian Mercury 300 spectrometer using dimethyl sulfoxied-d_6 (DMSO-d_6) as a solvent. The membrane surface was imaged by electron microscope (SEM) with S-4300, Hitachi, Japan.

Separation performance of the TFC membranes was tested with 32,000 ppm NaCl solution using the cross-flow cell apparatus and evaluated in terms of water flux and salt rejection. The simplified structure of the cross-flow cell apparatus is shown in Scheme 1.

The effective membrane area was around 12.56 cm^2. All tests were conducted at room temperature at an applied pressure of 55 bars. The water flux



Scheme 2. The synthesis sequence of the SDCDPS.

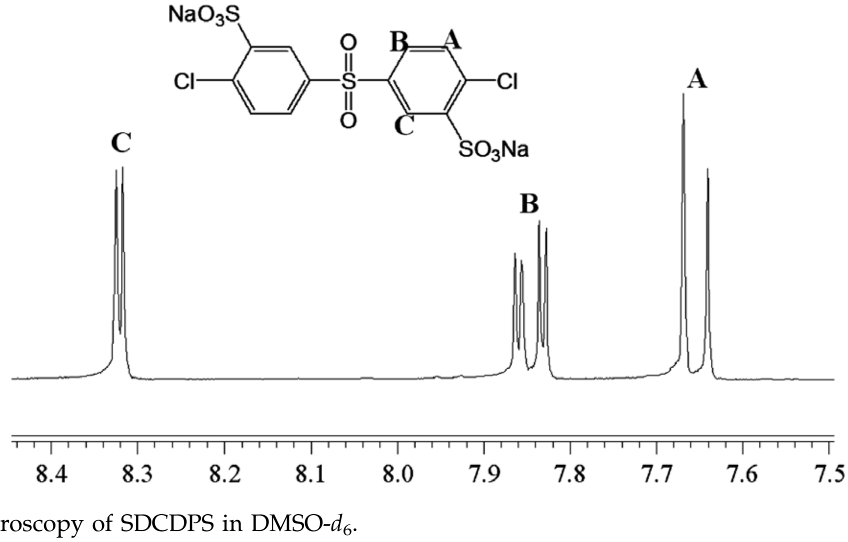


Fig. 1. ^{1}H NMR spectroscopy of SDCDPS in DMSO-d_6.

was determined by measuring the weight of the permeate solution through the membrane per unit time in terms of liter per square meter per hour (L/m^2h). Salt rejection was measured by the salt concentration in the feed and permeated solutions using a conductivity meter (PC 650, EUTECH). The rejection rate was calculated using the following equation:

$$\text{rejection } (\%) = \left(\frac{C_{\text{feed}} - C_{\text{permeated}}}{C_{\text{feed}}}\right) \times 100$$

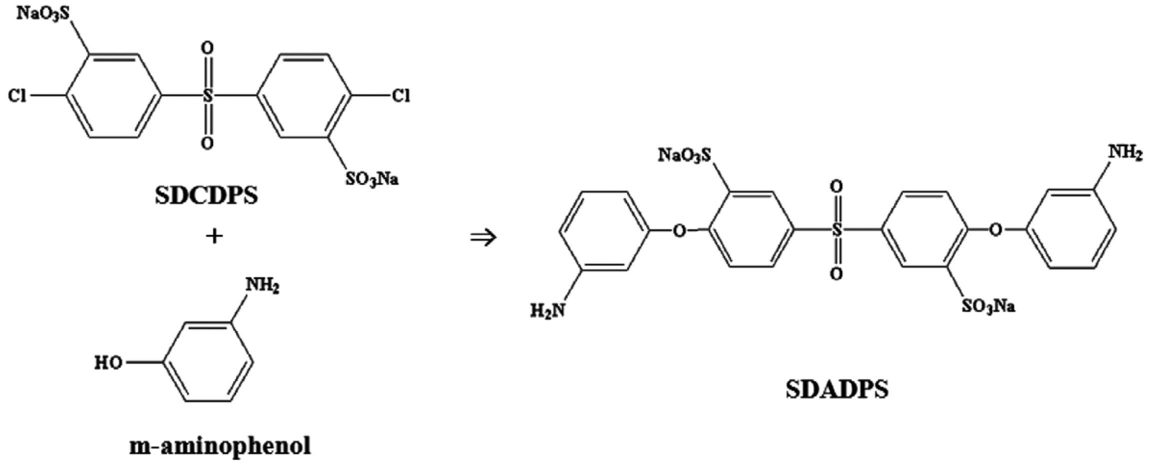
where C_{feed} and $C_{\text{permeated}}$ are the concentrations of the feed solution and permeate solution.

Especially for the measurement of chlorine resistance, the membrane was immersed in aqueous sodium hypochlorite (NaOCl) solution (2,000 ppm).

3. Results and discussion

3.1. Characterization

SDCDPS was prepared via electrophilic aromatic substitution using DCDPS and fuming sulfuric acid. For purity of monomers, recrystallization of the SDCDPS from alcohol–water mixture was performed. The synthesis sequence of the SDCDPS is outlined in Scheme 2.



Scheme 3. The synthesis sequence of the SDADPS.

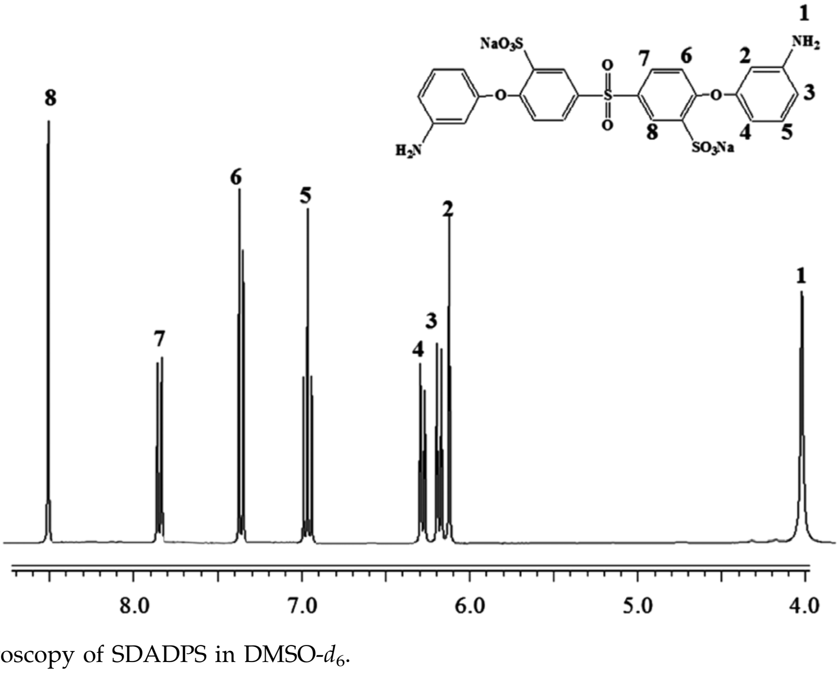


Fig. 2. ^{1}H NMR spectroscopy of SDADPS in DMSO-d_6.

The chemical composition and structure of the SDCDPS were confirmed by elemental analysis, ^{1}H NMR spectroscope using DMSO-d_6 as the solvent. The spectra of SDCDPS are shown in Fig. 1. Assignment of each proton is given in this figure, and these agree with the proposed molecular structures of the SDCDPS.

Sulfonated PES containing sulfonic acid and amino groups was synthesized through polycondensation 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) and m-aminophenol in the presence of anhydrous potassium carbonate in DMAc. Toluene was used as an azeotroping agent to remove water during the reaction. The reaction sequence of the sulfonated PES sulfonic acid and amino groups is shown in Scheme 3.

The ^{1}H NMR spectra of SDADPS are shown in Fig. 2. Assignment of each proton is given in this figure, and these agree with the proposed molecular structure of the sulfonated PES containing sulfonic acid and amino groups.

The active layer surface and structure of the TFC membrane were observed by SEM. Fig. 3 shows a SEM image of the PS UF membrane surface, fabricated TFC RO membrane surface and fabricated TFC RO membrane cross section.

As shown in Fig. 3, the surface of the TFC RO membrane exhibited the familiar "hill and valley" structure of PA RO membranes [18] and the cross-section of TFC RO membrane indicated the presence of a thin, selective active layer, which was a few hundred nanometers thick and was supported on a PS UF support layer. The SEM images of the membrane confirmed that the TFC membrane was successfully fabricated.

3.2. Performances of RO membranes

The TFC RO membranes were fabricated by IP of the tri-functional biphenyl acid chloride with a mixture of SDADPS and MPDA on the PS UF membrane. The RO performance of TFC membranes was evaluated with the cross-flow cell apparatus at 55 bar using a 32,000 ppm NaCl solution at room temperature. The RO performance of TFC membranes fab-

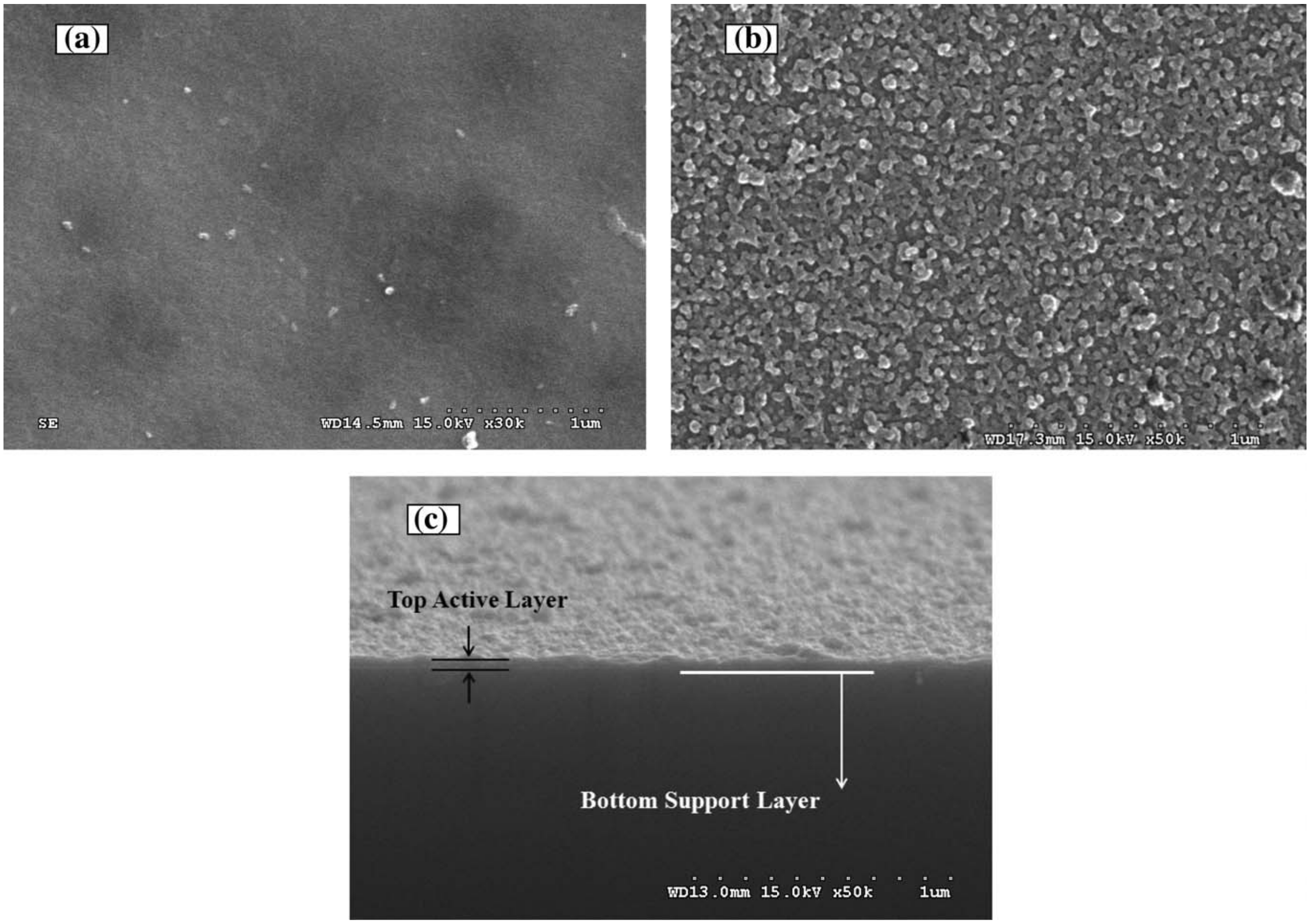


Fig. 3. SEM images of membranes; (a) PS UF membrane surface, (b) SDADPS TFC RO membrane surface and (c) SDADPS TFC RO membrane cross section.

ricated in this study was compared with that of the PA membrane produced in our laboratory.

Fig. 4 shows the salt rejection and the water flux of the membranes.

In these comparative studies, the water flux was found to be enhanced for SDADPS membranes, while a little decrease in salt rejection. The good performance of the SDAPDS membrane comes from the incorporation of the rigid and hydrophilic materials. The improved water flux of the membranes containing SDADPS material is due to the hydrophilicity of the functional groups, such as sulfonic acid groups (–SO_3H), in the materials. The sulfonic acid groups in the SDADPS provided additional hydrophilic sites to the TFC RO membranes, which could provide the increase in water flux. The water flux of membranes increased from 23 L/m^2 h (PA) to 32 L/m^2 h (SDADPS). However, as the amount of sulfonic group increases, the amount of amino groups in the materials is decreased. This leads to a decrease in the amount of amide bonds in the active layer of membrane, which was the reason why the salt rejection decreased from 98% (PA) to 95% (SDADPS).

We compared the RO performance of SDADPS membrane which is immersed in various typical solvents for 24 h with the original membrane for chemical stability test. Fig. 5 shows the salt rejection and water flux of the SDADPS membrane after immersion in various solvents for 24 h.

Actually, the SDADPS materials are soluble in polar solvents. However, it can be seen that the RO performance of SDADPS membrane was not decreased. These results represented that the SDADPS membrane was very stable in these solvents after the formation of an active top layer by IP reaction. The high chemical stability of the SDADPS membrane comes from the cross-linked structure in the top active layer.

The TFC RO membranes have been exposed to 2,000 ppm aqueous NaOCl solution for certain times.

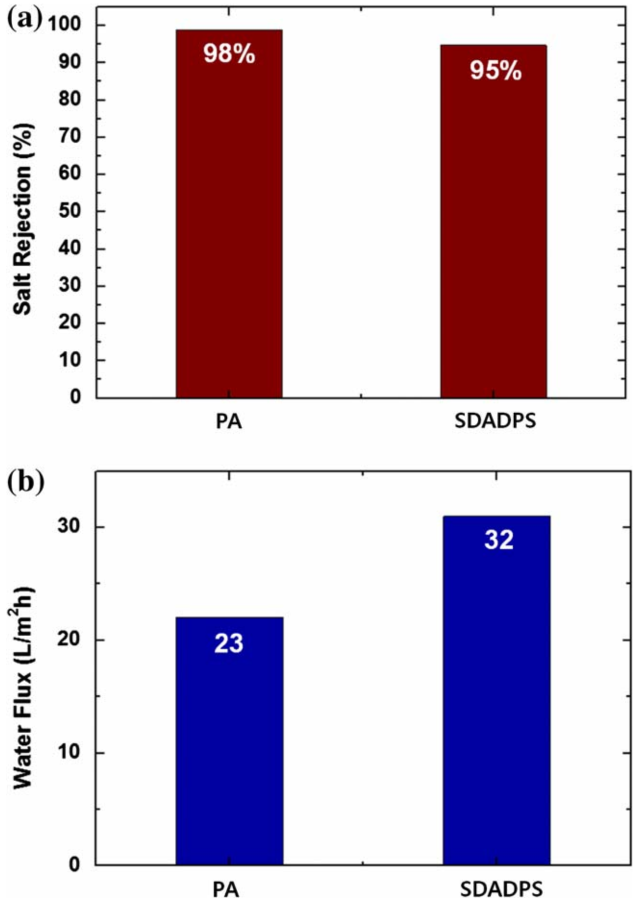


Fig. 4. Comparison of the RO performances of the SDADPS membrane with PA membrane; (a) salt rejection and (b) water flux.

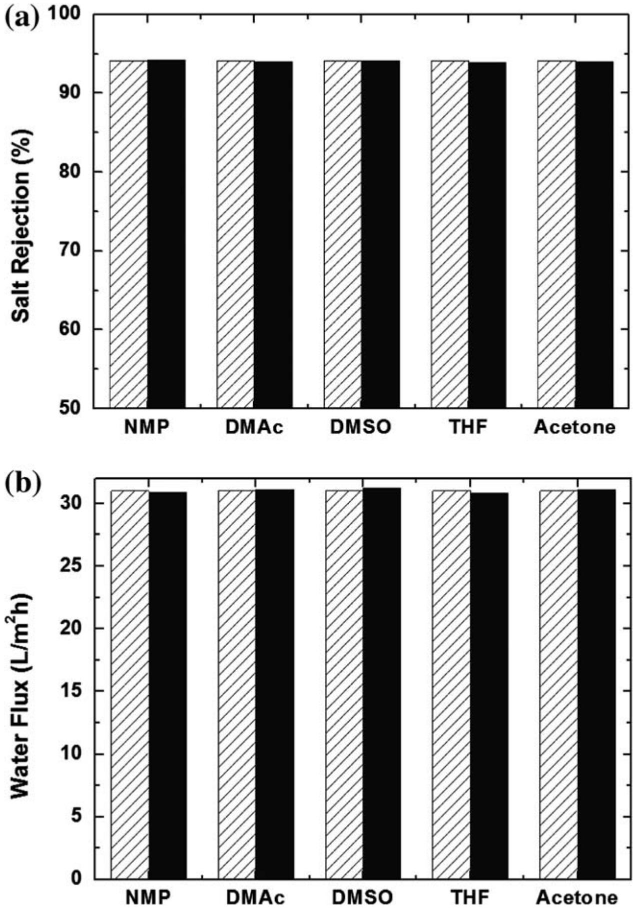


Fig. 5. Chemical stability of SDADPS membranes in various solvents; (a) salt rejection and (b) water flux (▨: before immersion, ■: after immersion).

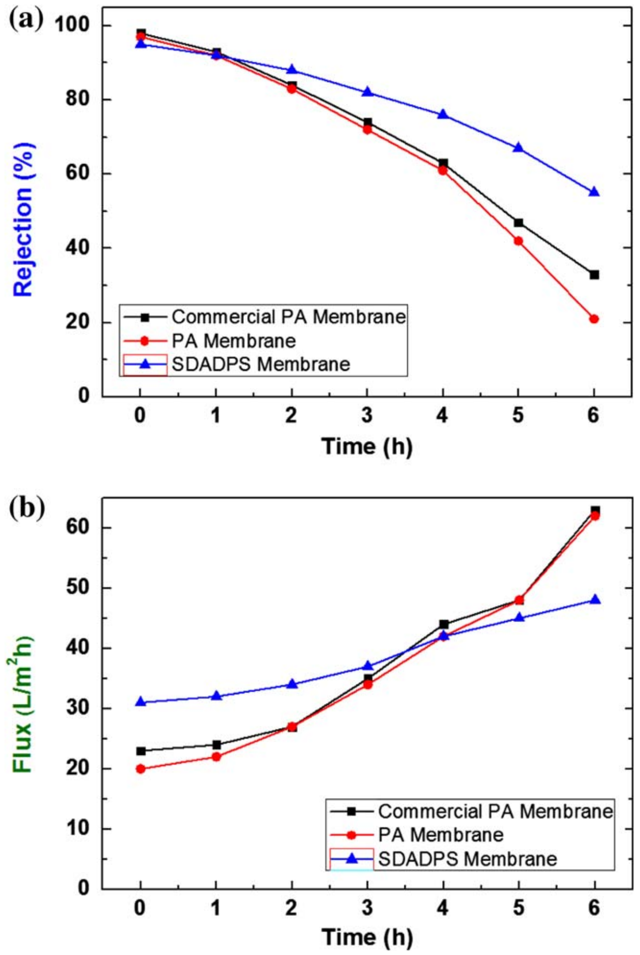


Fig. 6. Variation of RO performances of the membranes on chlorine exposure; (a) salt rejection and (b) water flux.

Fig. 6 shows the variation of RO performances of the membranes with chlorine treatment.

Fig. 6 clearly shows a decrease in salt rejection within 6 hours of exposure to 2,000 ppm chlorine solution. The salt rejection performance of SDADPS membrane was compared with PA membranes prepared by the MPDA and commercial PA membrane (RE4040-SHN, CSM). In the case of PA membrane, the salt rejection decreased rapidly with chlorine exposure time (98–21%) and (99–33% for commercial membrane), while salt rejection of SDADPS membrane a little decreased (95–55%). Water flux of PA membrane increased drastically with chlorine solution immersion time (20–62 L/m^2 h and 23–63 L/m^2 h for commercial membrane), while water flux of SDADPS membrane increased (31–48 L/m^2 h). For PA membrane, the decrease in salt rejection accompanying the abrupt increase in the flux of the PA membrane is due to the chemical deposition of amide bonds by free chlorine. However, the SDADPS membrane showed better chlorine resistance compared with the PA membrane, because the SDADPS has good chemical stability.

It is supposed that the high chlorine resistance and RO performance of the SDADPS membrane comes from the sulfonated PES materials containing sulfonic acid and amino groups.

4. Conclusions

A sulfonated PES containing sulfonic acid and amino groups was successfully synthesized via an aromatic substitution reaction from 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) and m-aminophenol in the presence of anhydrous potassium carbonate in DMAc, which was confirmed by 1H NMR spectrum.

Two kinds of TFC RO membranes were successfully fabricated through IP of the TMC with a MPDA (PA membrane) and mixture of SDADPS and MPDA (SDADPS membrane) on PS UF support membrane. The surface and cross-section structures were verified by SEM images.

The SDADPS membrane shows good chlorine resistance and comparable RO performance with typical PA membrane. The water flux of the SDADPS membrane was 32 L/m^2 h, which was significantly higher than the PA membrane (23 L/m^2 h), while a little decrease in salt rejection. This is because of the presence of the bulky, hydrophilic sulfonated PES material containing sulfonic acid groups. In addition, the SDADPS membrane showed much higher chlorine resistance than PA membrane.

The chemically stable structure of SDADPS material and cross-linked structure of the active layer would contribute to the high chlorine resistance and good RO performances, respectively.

Consequently, the SDADPS TFC RO membrane which has high chlorine resistance and good RO performance is favourable for the seawater desalination process without significant decrease in performance.

Acknowledgements

This research was supported by a grant (#11 seaHERO B02-06) from Plant Technology Advancement Program funded by the Ministry of Land, Transport and Maritime Affairs of the Korean government.

This work was also supported by the Human Resources Development the Korea Institute of Energy Technology Evaluation and Planning (20114010203050) grant funded by the Korea government Ministry of Knowledge Economy.

References

[1] M.E. Williams, D. Bhattacharya, R.J. Ray, S.B. McCray, Selected applications reverse osmosis, In: W.S. Winstion Ho, K.K. Sirkar (Eds.), Membrane Handbook, Van Nonstrand Reinhold, New York, NY, pp. 3–15, 1992.

[2] M. Elimelech, The global challenge for adequate and safe water, J. Water Supply Res. Technol. Aqua 55 (2006) 3–10.

[3] M. Wilf, L. Awerbuch, C. Bartels, M. Mickley, G. Pearce, N. Voutchkov, The Guidebook to Membrane Desalination Technology, Balaban Desalination, Italy, 2007.

[4] S.G. Kim, K.T. Park, B.H. Chun, J. Bang, S.H. Kim, Sulfonated poly(arylene ther sulfone) RO membranes for high water flux and chlorine resistance, Desalin. Water Treat. 15 (2010) 205–213.

[5] R.J. Petersen, Composite reverse osmosis and nanofiltration membranes, J. Membr. Sci. 83 (1993) 81–150.

[6] J.E. Cadotte, C.V. Kopp Jr., K.E. Cobian, L.T. Rozelle, In situ formed condensation polymers for reverse osmosis: second phase, NTIS Report No. PB-234194, loc. Cit, June 1974.

[7] H. Zou, Y. Jin, J. Yang, H. Dai, X. Yu, J. Xu, Synthesis and characterization of thin film composite reverse osmosis membranes via novel interfacial polymerization approach, Sep. Purif. Technol. 72 (2010) 256–262.

[8] A.K. Ghosh, E.M.V. Hoek, Impacts of support membrane structure and chemistry on polyamide–polysulfone interfacial composite membranes, J. Membr. Sci. 336 (2009) 140–148.

[9] M. Kurihara, Y. Fusaoka, T. Sasaki, R. Bairinji, T. Uemura, Development of crosslinked fully aromatic polyamide ultra-thin composite membranes for seawater desalination, Desalination 96 (1994) 133–143.

[10] M. Liu, Z. Chen, S. Yu, D. Wu, C. Gao, Thin-film composite polyamide reverse osmosis membranes with improved acid stability and chlorine resistance by coating N-isopropylacrylamide–co-acrylamide copolymers, Desalination 270 (2011) 248–257.

[11] S. Yu, M. Liu, X. Liu, C. Gao, Performance enhancement in interfacially synthesized thin-film composite polyamide-urethane reverse osmosis membrane for seawater desalination, J. Membr. Sci. 342 (2009) 313–320.

[12] G. Chen, S. Li, X. Zhang, S. Zhang, Novel thin-film composite membranes with improved water flux from sulfonated cardo poly(arylene ether sulfone) bearing pendant amino groups, J. Membr. Sci. 310 (2008) 102–109.

[13] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—development to date and future potential, J. Membr. Sci. 370 (2011) 1–22.

[14] E.J. Moon, Y.S. Seo, C.K. Kim, Novel composite membranes prepared from 2,2 bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane, triethylene glycol dimethacrylate, and their mixtures for the reverse osmosis process, J. Membr. Sci. 243 (2004) 311–316.

[15] K. Lang, S. Sourirajan, T. Matsuura, G. Chowdhury, A study on the preparation of polyvinyl alcohol thin-film composite membranes and reverse osmosis testing, Desalination 104 (1996) 185–196.

[16] Y. Li, R.A. VanHouten, A.E. Brink, J.E. Mcgrath, Purity characterization of 3,30-disulfonated-4,40-dichlorodiphenyl sulfone (SDCDPS) monomer by UV–vis spectroscopy, Polymer 49 (2008) 3014–3019.

[17] S.J. Im, R. Patel, S.J. Shin, J.H. Kim, B.R. Min, Sulfonated poly (arylene ether sulfone) membranes based on biphenol for direct methanol fuel cells, Korean J. Chem. Eng. 25 (2008) 732–737.

[18] E.M.V. Hoek, S. Bhattacharjee, M. Elimelech, Effect of membrane surface roughness on colloid-membrane DLVO interactions, Langmuir 19 (2003) 4836–4847.