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Sulfonated poly(arylene ether sulfone) thin-film composite reverse osmosis membrane containing SiO_2 nano-particles

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ABSTRACT

Novel thin-film nano-composite membranes containing SiO_2 nano-particles are successfully fabricated via interfacial polymerization with trimesoyl chloride (TMC), sulfonated poly(arylene ether sulfone) copolymers and silica (SiO_2) nano-particles on a polysulfone (PS) support membrane. Sulfonated poly(arylene ether sulfone) copolymers containing carboxylic and amino groups (cPES) are successfully prepared via direct polymerization as novel thin-film composite (TFC) reverse osmosis (RO) membrane material. Mesoporous SiO_2 nano-particles are also successfully synthesized. The synthesized cPES copolymers, SiO_2 nano-particles and fabricated cPES membranes are characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM). The incorporation of SiO_2 nano-particles were confirmed by energy dispersive X-ray spectroscopy (EDX). Moreover, the effects of different fabrication conditions on performance are investigated. The cPES membrane with 1% (w/w) SiO_2, which is cured at 70°C, exhibited the high salt rejection value (96.8%) with respect to NaCl and good water flux value (32 L/m^{2}h).

Keywords: RO membrane; Sulfonated poly(arylene ether sulfone); Nanocomposite membrane; Desalination

1. Introduction

In recent years, there has been an increasing worldwide need for fresh drinking water. About 41% of the total population in the world lives in water-stressed areas. Desalination technology using membrane, such as reverse osmosis (RO) process, is an attractive and energy efficient way to develop new sources of pure water. Reverse osmosis (RO) technology is by far the most widespread type of membrane based desalination process. It is capable of rejecting almost all colloidal or dissolved matter from an aqueous solution, producing concentrate brine and permeated pure water. In these days RO membrane materials are required to have high water flux, high salt rejection and good chlorine resistance [1–5].

RO membrane separation process has developed rapidly over the last three decades into the dominant technology for desalination of seawater. Commercial RO membranes are derived from the asymmetric cellulose acetate (CA) membrane by Loeb and Sourirajan in the 1960s. However, CA membranes are susceptible to biological attack, undergo compaction at higher temperatures and pressures, and are limited to a relatively narrow pH range [6–8]. The second breakthrough in the RO membrane

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field was achieved by the development of a thin-film composite (TFC) membrane with high separation performance. The TFC membranes for RO are the membranes typically consisting of an ultra thin active layer formed in situ on the surface of a porous substrate via interfacial polymerization (IP). Aromatic polyamides (PA) were widely used in the ultra thin active layer materials of TFC RO membranes in the commercial use. PA membranes exhibit better transport properties and are more stable over a wider range of pH values than CA membranes [9–11]. Unfortunately, commercial PA membranes suffer from poor resistance to continual exposure to oxidizing agents such as chlorine, and this leads to irreversible performance loss over time. This problem necessitates the use of expensive dechlorination and rechlorination steps when using PA membranes [4,12].

To overcome the disadvantages of PA membranes, much effort in the area of TFC RO membranes has been centered on developing membranes through (i) design and synthesis of new polymers forming active layers of the TFC membranes or (ii) physical/chemical modification of the TFC membranes [13–15]. Recently, the synthesis of sulfonated poly(arylene ether sulfone) copolymers by direct copolymerization for RO membrane applications has been carried out [16,17]. These copolymers have good mechanical properties and excellent chemical and thermal stability, and do not possess the vulnerable amide bone that is susceptible to chlorine attack. Albany International Corporation reported sulfonated polysulfone follow fiber membranes with constant flux and salt rejection even after exposure to 100 ppm chlorine in feed water [18]. Kim et al. prepared a sulfonated poly(arylene ether sulfone) copolymer that contained carboxylic groups (cPES) using phenolphthalein (PPH) [4]. The carboxylic groups in the sulfonated poly(arylene ether sulfone) copolymers increase hydrophilicity of the copolymer.

Nanotechnology has produced entirely new classes of functional materials whose application to desalination and water treatment need exploration. Mixed matrix or nano-composite membranes could exhibit enhanced mechanical, chemical and thermal stability as well as enhanced separation performance [19–21].

In this paper we reported the preparation of sulfonated poly(arylene ether sulfone) copolymer containing carboxylic and amino groups (cPES) for reverse osmosis TFC membrane. In addition, we have prepared nanocomposite membranes (cPES-N) containing mesoporous silica nano-particles and investigated the effects of the incorporation of nano-particles on RO performances. The cPES copolymer and TFC membranes were characterized by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR). Synthesized mesoporous silica nano-particles have been characterized by field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectroscopy (EDX). The performance of membranes was evaluated in a cross-flow cell apparatus.

2. Materials and methods

2.1. Materials

Tetraethyl orthosilicate (TEOS), *n*-cetyltrimethylammonium bromide (CTAB), 4,4′-dichlorodiphenyl sulfone (DCDPS), phenolphthalin (PP), phenolphthalein (PPH) and anhydrous potassium carbonate (K2CO3) were purchased from Aldrich. DCDPS, PP and PPH were dried under vacuum at 80°C for 12 h prior to use. All other chemicals were used as received. 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) and PPH-NH_2 were synthesized according to previously reported methods [16,22] and dried under vacuum condition at 110°C for 24 h before use. *N*-methyl-2-pyrrolidone (NMP), *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 poly(arylene ether sulfone)

The sulfonated poly(arylene ether sulfone) copolymers containing carboxylic and amino groups were synthesized through direct polymerization. The typical copolymerization procedure to prepare the cPES copolymer was as follows. 4.9125 g (10 mmol) of SDCDPS, 3.2437 g (9 mmol) of PPH-NH2 and 0.3203 g (1 mmol) of PP was added in a three neck flask equipped with a nitrogen inlet, Dean-Stark trap and magnetic stirrer. 60 mL of NMP was added into the flask and stirred until the monomers were dissolved. After 50 mL of toluene was added to the reaction flask, 3.041 g (22 mmol) of anhydrous potassium carbonate was added. The reaction mixture was refluxed at 145°C with stirring to dehydrate the system. After toluene and water had been distilled off, the temperature was slowly raised to 170°C. The mixture was further reacted for 12 h during which the solution became viscous. Then the solution was cooled to room temperature and diluted with DMAc. The solution was isolated by coagulation in excess ethanol after filtration to remove most of the inorganic salts. Finally, the precipitated white copolymer was washed several times with ethanol and dried under vacuum condition at 110°C for 12 h.

2.3. Synthesis of mesoporous SiO_2 nano-particles

Mesoporous silica nano-particles were synthesized similar to previously reported procedures [23]. 1.00 g (2.7×10–3 mol) of CTAB was first dissolved in 500 mL of distilled water. 4 mL (2.00 M) of aqueous NaOH solution was added to CTAB solution, and then the solution temperature was raised to 80°C. 5.00 mL (2.5×10–2 mol) of TEOS was then introduced dropwise to the surfactant solution. The mixture was stirred for another 4 h. The white precipitated produced were filtered, washed several times with ethanol, and dried in the oven at 60°C for 24 h.

2.4. Fabrication of a thin-film composite membrane

Conventional interfacial polymerization on polysulfone UF membrane (UE 50, Trisep Corporation, USA) was selected as the method of fabrication of the TFC membrane. The procedure used for the formation of the polyamide composite membrane is as follows [15]. The polysulfone UF membrane was placed in an aqueous solution of 2% (w/v) MPDA for 2 min, and then removed excess solution. The MPDA saturated UF membrane was then immersed in a solution of 0.1% (w/v) TMC in cyclohexane for 1 min. The membrane was heated in a convection oven at 70°C for 1 min after removing the excess solution.

A cPES-N membrane was prepared according to the method reported in the literature [16,21]. The procedure for the fabrication of cPES-N nano-composite membrane is illustrated in Fig. 1.

A polysulfone UF membrane was soaked for 90 min in the aqueous amine solution containing 1% (w/v) of a mixture of cPES copolymer and MPDA, triethylamine (TEA) and dodecyl sulfonic acid sodium salt (DDS) was prepared with pH 10 adjusted by camphor sulfonic acid. The UF membrane was then immersed into 0.5% (w/v) TMC solution containing SiO_2 nano-particles in cyclohexane after the excess amine solution was removed. The dispersion of SiO_2/cyclohexane was obtained by ultra-sonication for 1 h. After reaction for 4 min, organic solution was poured off. To evaluate the appropriate fabrication condition, the resulting membrane was subsequently cured in an air-circulation oven at a different curing temperatures and time.

2.5. Characterizations

The prepared monomers (PPH-NH_2, SDCDPS) and copolymers were identified by elemental analysis. ^1H nuclear magnetic resonance (NMR) (300 MHz) spectra were recorded on a Varian instrument with dimethylsulfoxide-d_6 (DMSO-d_6) as a solvent.

Fourier transform-infrared (FT-IR) characterization of the TFC membrane surface was accomplished using a Bomen DA-8 spectrometer.

The synthesized silica nano-particles were imaged by electron microscopy (SEM) with S-4300, Hitachi, Japan.

The presence of SiO_2 in the cPES-N membranes was confirmed by energy dispersive X-ray spectroscope (EDX) with EX-200, Horiba, Japan.

2.6. RO performance

The TFC membranes were tested with 2,000 ppm NaCl solution at room temperature with the cross-flow cell apparatus. The RO performances were evaluated in terms of water flux and salt rejection. The water flux was calculated 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^{2}h). The salt rejection (*R*) was calculated as

$$R(\%) = \left(\frac{C_f - C_p}{C_f}\right) \times 100 \tag{1}$$

where C_p is the salt concentration in the permeant and C_f is the salt concentration of the feed water. Both concentrations were measured with a digital conductivity meter (PC 650, EUTECH).

The effective membrane area was around 12.56 cm^2. All tests were conducted at room temperature at an applied pressure of 15.5 bar.

3. Results and discussion

3.1. Characterizations of copolymer and SiO_2 nano-particles

SDCDPS was prepared using DCDPS and fuming sulfuric acid. PPH-NH_2 was synthesized by condensation of PPH and ethylenediamine. A sulfonated poly(arylene ether sulfone) copolymer containing carboxylic and amino groups was synthesized by direct polymerization reaction using phenolphthalin (PP), 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) and phenolphthalein containing amino group (PPH-NH_2) in the presence of anhydrous K_2CO_3 in NMP. The reaction sequence of the sulfonated poly(arylene ether sulfone) copolymer containing carboxylic and amino groups is shown in Fig. 2.

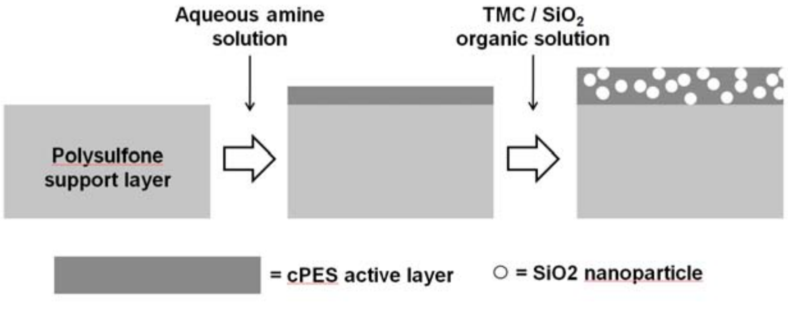

Fig. 1. The procedure for the fabrication of cPES-N nanocompostie membrane.

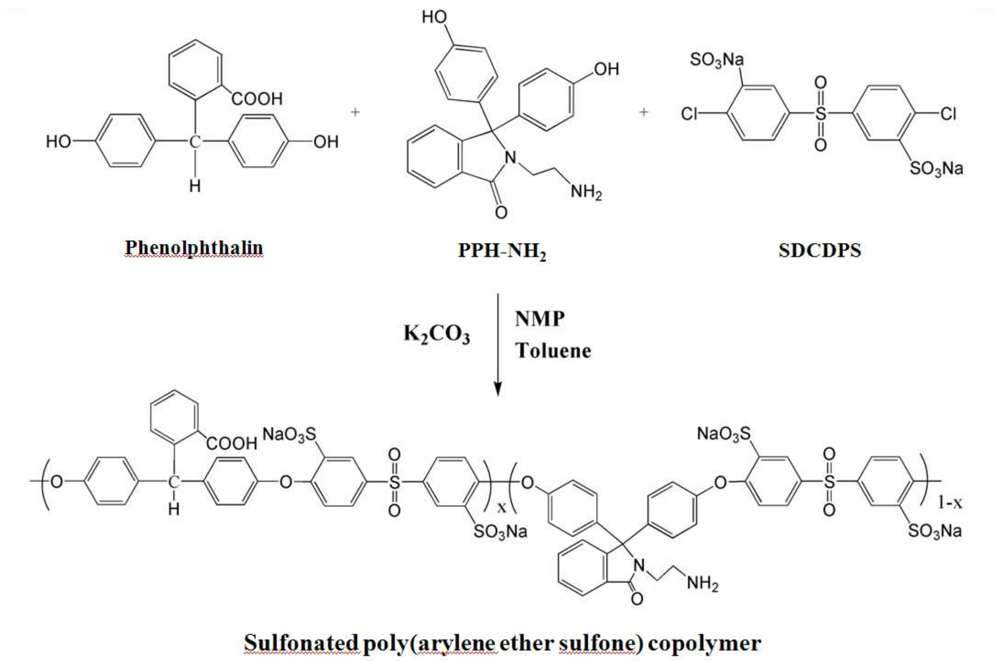

Fig. 2. The reaction sequence of the copolymer.

^{1}H-NMR was used to identify the chemical structure of the copolymers. The spectrum of cPES with DMSO-d_6 as the solvent is shown in Fig. 3.

Assignment of each proton is given in this figure, and these agree with the proposed chemical structure of the cPES copolymer.

SiO_2 nano-particles were successfully synthesized by sol-gel technique. The SEM image of synthesized SiO_2 nano-particles is illustrated in Fig. 4. The average diameter of nano-particles was about 100 nm.

3.2. Characterizations of membranes

The FT-IR spectroscopy was used to confirm the presence of functional groups in the active layer of TFC

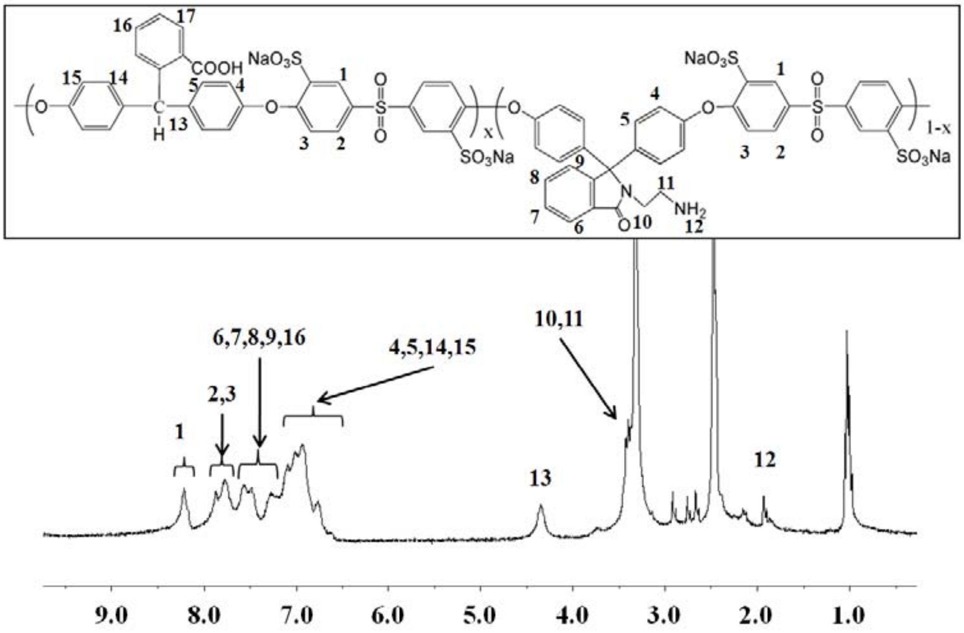

Fig. 3. ^{1}H NMR spectroscopy of cPES in DMSO-d_6.

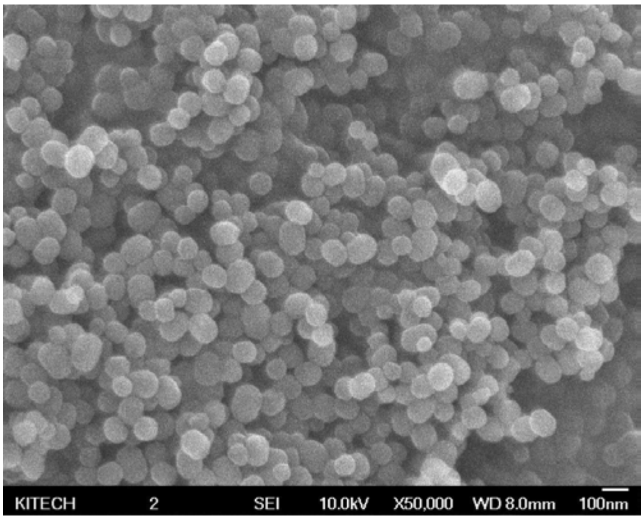

Fig. 4. SEM image of synthesized SiO_2 nano-particles.

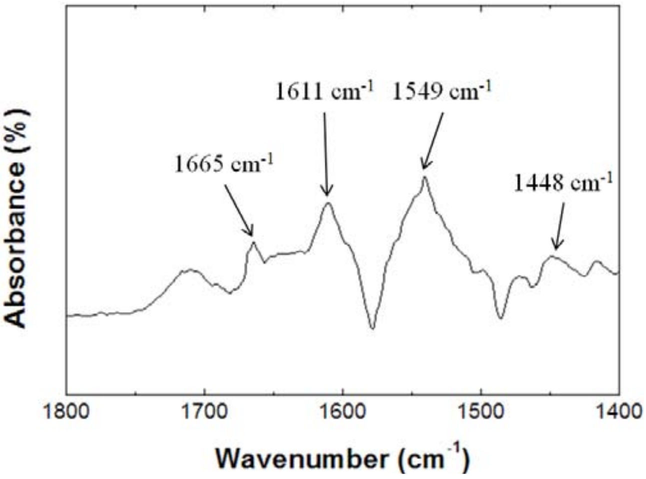

Fig. 5. FT-IR spectra of the cPES membrane.

membranes. The FT-IR spectrum of the cPES membrane is shown in Fig. 5.

In the FT-IR spectrum, the membrane displayed the characteristic absorption bands of the amide bond, which appeared near 1665 cm^{-1} (amide I, C=O stretch) and 1549 cm^{-1} (amide II, C–N stretch). The 1611 cm^{-1} band was assigned to polyamide aromatic ring and the 1448 cm^{-1} band was due to the presence of the carboxylate carbonyl group. The FT-IR spectrum of the TFC membrane confirmed that the sulfonated poly(arylene ether sulfone) containing carboxylic groups was successfully conjugated to the aromatic polyamide.

The presence of SiO_2 nanoparticles in the cPES-N membrane was confirmed by EDX analysis. The EDX spectra are presented for cPES membrane in Fig. 6a and for cPES-N membrane in Fig. 6b.

The spectrum for the cPES-N membrane indicated the Si peak at ~1.8 keV, confirming the presence of the silica nano-particles, which are absent for the cPES membrane. Furthermore, the oxygen peak at ~0.5 keV is greater for the cPES-N membrane than for the cPES membrane due to oxygen atoms contained in the silica framework. The sulfur peak is from the polysulfone support layer. The EDX spectra of the membranes confirmed that the thin-film nano-composite membrane was successfully fabricated.

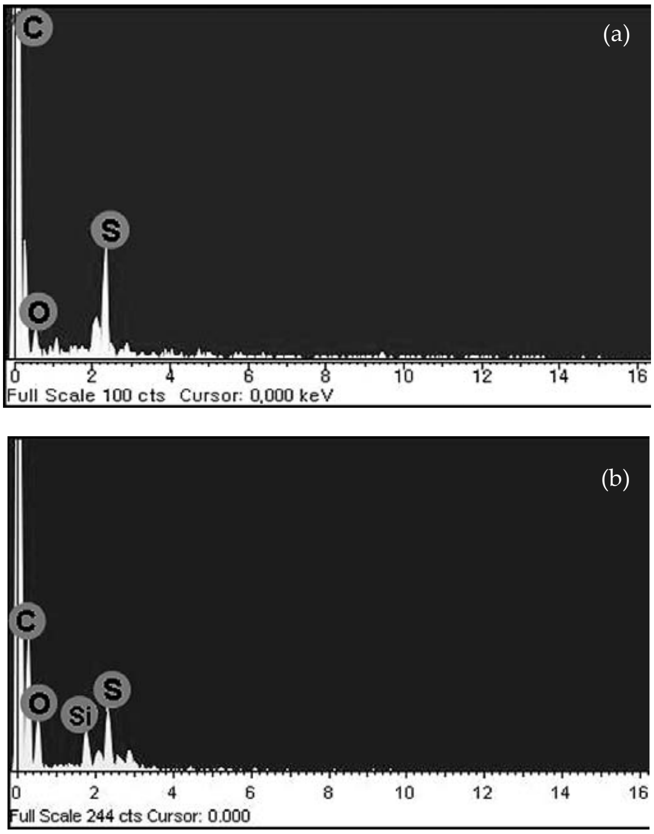

Fig. 6. EDX spectrum of TFC membranes; (a) cPES membrane and (b) cPES-N membrane.

3.3. RO performance of membranes

The TFC membranes were fabricated by IP reaction on the PS UF membrane. The RO performance of TFC membranes was evaluated with the cross-flow cell apparatus at 15.5 bar using a 2,000 ppm NaCl solution at room temperature. The RO performances of TFC membranes fabricated in this study were compared with that of the polyamide membrane produced in laboratory.

The effect of SiO_2 concentration on the performance of cPES-N membrane was evaluated in terms of salt rejection and water flux as shown in Fig. 7.

As the SiO_2 concentration increased up to 1.0% (w/w), the water flux slightly decreased and the salt rejection increased. However, above 1.0% (w/w), the water flux abruptly increased and the salt rejection decreased sharp-

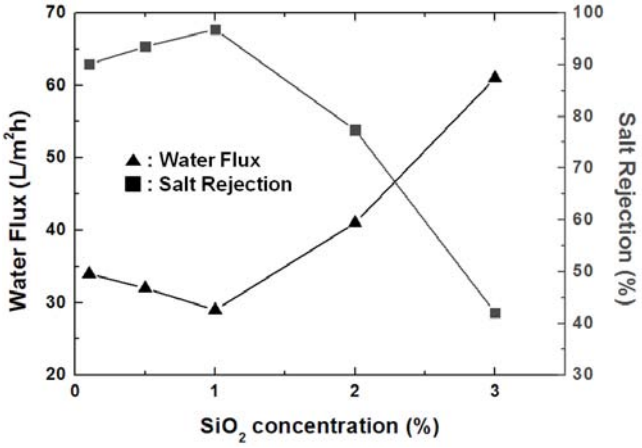

Fig. 7. Effect of SiO_2 concentration on the performance of the cPES-N membrane.

ly. These results may be due to the fact that the interference of interfacial polymerization by SiO_2 nano-particles starts to become significant at high SiO_2 concentration, leading to lower degree of crosslinking of active layer.

The effect of curing temperature on the cPES-N membrane performance has been investigated in order to find appropriate condition for the fabrication of cPES-N membrane as illustrated in Fig. 8.

As the curing temperature increased, the salt rejection increased but the water flux decreased. This is because the crosslink reaction occurred effectively at higher temperature, producing denser and more rigid membrane structure. This also contributes to the higher mechanical strength of the cPES-N membrane. It should be noted that the increase of salt rejection became less steep but the decrease of flux was not noticeable at a curing temperature of 70°C. The cPES-N membrane with 1% (w/w) SiO_2 cured at 70°C exhibited 32 L/m2h of water flux and 96.8% of salt rejection.

The condition of curing time also changed to examine the change of the cPES-N membrane performance. At a constant curing temperature of 70°C, the treatment time was changed from 1 min to 5 min. As shown in Fig. 9, the curing time does not greatly affect the cPES-N membrane performance.

Fig. 10 shows the RO performances of cPES and cPES-N membranes compared with a typical PA membrane. The cPES-N membrane exhibits the highest water flux and intermediate salt rejection. The high performance of the cPES membrane comes from the incorporation of the rigid and hydrophilic copolymer. The improved water flux of the membranes containing cPES copolymers is due to the hydrophilicity of the functional groups, such as sulfonic acid groups ($–SO_3H$), in the copolymers. Moreover, the cPES-N membrane contains not only the cPES copolymer but also the SiO_2 nano-particles within active layer. The SiO_2 nano-particles in the membrane could provide the additional hygroscopicity to the cPES-N membrane, which led to a higher water flux.

Hand-cast membranes evaluated herein have not been optimized for use in commercial RO applications, but nanocomposite RO membrane technology offers new degrees of freedom to design TFC membranes.

4. Conclusions

A sulfonated poly(arylene ether sulfone) containing carboxylic and amino groups was successfully synthesized via direct polymerization reaction, which was confirmed by 1H NMR spectrum. We demonstrated the fabrication of cPES and cPES-N membrane by interfacial polymerization, which resulted in RO membrane with enhanced RO performances when compared to polyamide TFC membrane. The cPES-N membrane was prepared from in-situ IP reaction between aqueous amine solution containing cPES and organic solution containing SiO_2 nano-particles. The cPES membrane shows high RO performance comparable with typical PA membrane.

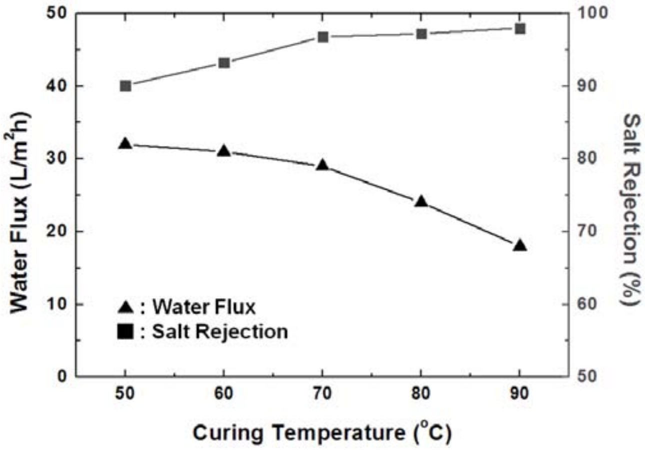

Fig. 8. Effect of curing temperature on the performance of the cPES-N membrane.

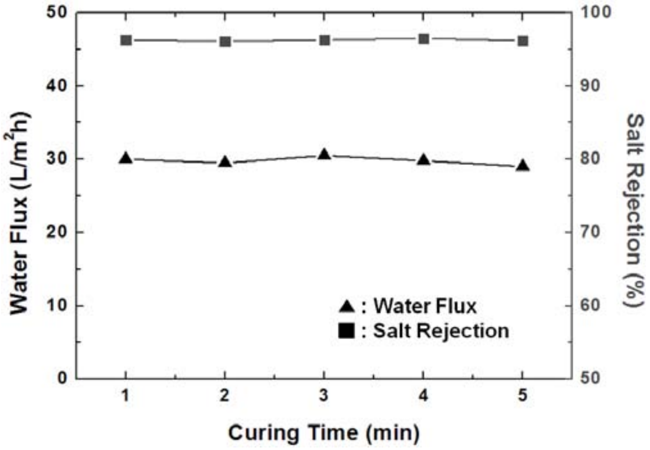

Fig. 9. Effect of curing time on the performance of the cPES-N membrane.

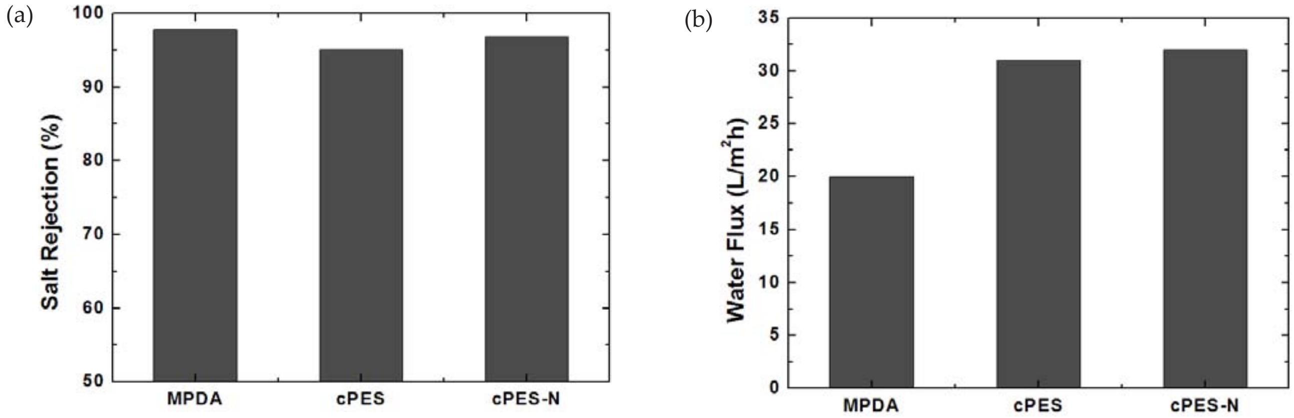

Fig. 10. Comparison of the RO performances of the nano-composite membrane with polyamide membrane; (a) salt rejection and (b) water flux.

The water flux of the cPES and cPES-N membrane was significantly higher than that of polyamide membrane, while a little decreased in salt rejection. This is because of the presence of the hydrophilic copolymer. In addition, the cPES-N membrane showed much higher RO performance than PA membrane, especially for water flux. The incorporation of SiO_2 nano-particles in active layer, which was confirmed by EDX spectra analysis, produced the increase of water flux due to the enhanced hydrophilicty in the membranes.

Consequently, the cPES-N nano-composite RO membrane which has higher water flux is favorable for the seawater desalination process without significant decrease of salt rejection.

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