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Sulfonated poly(arylene ether sulfone) RO membranes for high water flux and chlorine resistance

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ABSTRACT

Sulfonated poly(arylene ether sulfone) copolymers containing carboxylic groups (cPES) were successfully prepared by an aromatic substitution polymerization reaction from phenolphthalin (PP), 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS), phenolphthalein containing amino group (PPH-NH_2) as novel thin film composite (TFC) reverse osmosis (RO) membrane material for high water flux. TFC membranes were fabricated by an interfacial polymerization (IP) reaction with trimesoyl chloride (TMC) and amine solution, containing *m*-phenylenediamine (MPDA) and cPES, on a polysulfone (PS) ultrafiltration (UF) support membrane. The synthesized copolymers and fabricated membranes were characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), salt rejection and water permeability measurements. The chlorine resistance is evaluated using sodium hypochlorite solution. The cPES RO membrane has much higher chlorine resistance than that of PA RO membrane and shows good RO performances such as water flux (31 L/m^{2}h) and salt rejection (95.1%).

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

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1. Introduction

In recent years, reverse osmosis (RO) by polymeric membranes has been considered the most advanced technique for seawater purification. The membrane plays an important role in the seawater purification process [1–3]. The first seawater desalination membrane consisted of an asymmetric cellulose acetate membrane. The second biggest breakthrough was the development of the thin-film composite (TFC) membrane through interfacial polymerization (IP) [4]. Thin-film composite membranes are made of an active layer, which consists of various polymers, and a porous support layer. The support layer is usually an ultrafiltration (UF) membrane made of polysulfone (PS) [5]. The UF support layer provides the membrane necessary mechanical strength, while the active layer is mainly responsible for performing the separation function. A large number of membranes have been developed from various polymers such as polyurea, polyamide, polyether. Recently, aromatic polyamides (PA) have been shown to exhibit better transport properties and be more stable over a wider range of pH values than others membranes. Thus, polyamide TFC membranes are the most widely used commercial seawater desalination membranes [6,7].

The polyamide TFC membrane has high salt rejection, good mechanical stability and water permeability, and the salt rejection of the TFC membrane has improved

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over the last 30 years. However, aromatic polyamides are very sensitive to chlorine disinfectants, which lead to a performance loss of the TFC membrane over time. In addition, low water permeability is one of the main problems associated with polyamide TFC membranes [2–9].

To overcome the disadvantages of polyamide TFC membranes, much effort has been centered on developing membranes with higher water permeability and chlorine resistance through design and synthesis of new polymers or modifications of the membrane. Chemical modifications of the active layer materials by introducing sulfonic groups or carboxylic groups or incorporation of various polymers such as poly(vinyl alcohol) to the aromatic polyamides have been used to increase water permeability and chlorine resistance [10–12].

Sulfonated poly(arylene ether sulfone)s (PESs), based on polysulfone, have excellent mechanical properties and good biological, chemical, and thermal stability [13–15]. Polysulfone is hydrophobic, thus, if used in a TFC membrane, water permeation will be very low. Therefore, to achieve high water permeability while maintaining good salt rejection, the chemical structure of polysulfone must be changed to increase and control its overall hydrophilicity. PESs do not possess the vulnerable amide bond that is susceptible to chlorine attack.

Kim et al. prepared a sulfonated poly(arylene ether sulfone) copolymer that contained carboxylic groups using phenolphthalein [13]. Carboxylic groups in phenolphthalein provided the polymer matrix with a degree of hydrophilicity. The carboxylic groups in the sulfonated poly(arylene ether sulfone) copolymer could react with a crosslinking agent containing a hydroxyl or amide group to form a crosslinked membrane material. Sulfonation has been reported as a materials design technique for increasing the hydrophilicity of a polysulfone membrane [16].

The objectives of this paper were to synthesize sulfonated poly(arylene ether sulfone) copolymers containing carboxylic and amino groups (cPES), and to investigate the chemical resistance of the cPES TFC membrane through comparison study with typical PA TFC membrane. We fabricated an asymmetric TFC membrane on a UF supporting membrane through interfacial polymerization (crosslinking) with an amine solution containing cPES-NH_2 and a chloride solution containing trimesoyl chloride (TMC). The membranes were immersed in aqueous sodium hypochlorite (NaOCl) solution (500 ppm) for various exposure times to evaluate the variation of the chlorine resistance of the membrane on exposure time. The performance of membranes was evaluated in a cross-flow cell apparatus.

2. Materials and methods

2.1. Materials

4,4′-dichlorodiphenyl sulfone (DCDPS), phenolphthalin (PP), phenolphthalein (PPH) and anhydrous potassium carbonate were obtained from Aldrich. DCDPS, PP and PPH 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) and PPH-NH_2 were synthesized according to previously published methods [6, 17] and dried under vacuum at 100°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) copolymer containing carboxylic group

A typical polymerization of a 3.2 kg mol^{-1} sulfonated poly(arylene ether sulfone) copolymers containing carboxylic groups were synthesized using direct polymerization. The copolymerization procedure used to synthesis the copolymer (PP/PPH-NH_2 = 10/90) was as follows. 4.9125 g (10 mmol) of SDCDPS, 3.2437 g (9 mmol) of PPH-NH_2, 0.3203 g (1 mmol) of PP, 3.041 g (22 mmol) of anhydrous potassium carbonate were added to a three neck flask equipped with a Dean-Stark trap, nitrogen inlet, magnetic stirrer and thermometer. 50 mL of NMP and 25 mL of toluene were added into the flask. Toluene was used as an azeotroping agent. The reaction mixture was heated at 145°C with stirring for dehydration. After toluene and water had been distilled off, the temperature was slowly raised to 170°C. The mixture was further reacted for 12 h to produce a viscous solution. Then, the solution was cooled to room temperature and diluted with DMAc. The solution was filtrated to remove inorganic salts. After filtration, the filtrate was slowly poured into ethanol for precipitation. The precipitated white copolymer was successively washed several times with ethanol and dried under vacuum at 100°C for 12 h.

2.3. Fabrication of thin-film composite membrane

Both polyamide and cPES reverse osmosis composite membranes were fabricated via conventional interfacial polymerization using polysulfone UF membranes (UE50, Trisep Corporation, USA). The procedure used for the formation of the polyamide composite membrane is as follows. The polysulfone UF membrane was placed in an aqueous solution of 2% (w/v) MPDA for 2 min, and then rolled with a roller to remove excess solution. Next, the membrane was immersed into a solution of 0.1% (w/v) TMC in cyclohexane for 1 min. After removing the excess solution, the membrane was heated in an oven at 65°C for 1 min.

A cPES membrane was prepared according to the method reported in the literature [6]. The polysulfone

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 copolymer and MPDA, triethylamine (1%) and dodecyl sulfonic acid sodium salt (0.05%) for 90 min. The molar ratio of MPDA to cPES is 4:1. The solution was then rolled with a roller to get rid of excess solution. The membrane was immersed into a solution of 0.5% (w/v) TMC in cyclohexane for 4 min. After removing the solution, the membrane was treated in an oven at 65°C for 1 min.

2.4. Characterization

The monomers (PPH-NH_2, SDCDPS) and copolymers were identified by elemental analysis, such as C, H, N. ^{1}H-NMR spectra of the products were obtained at 300 MHz on the Varian Mercury 300 spectrometer using dimethyl sulfoxide-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 membrane surface and cross-section were imaged by electron microscopy (SEM) with a S-4300, Hitachi, Japan. The hydrophilicity of the membrane was determined using an Automatic Contact Angle Analyzer (Surface Electro Optics, Phoenix 300), by measuring the contact angle of water droplets on the membranes.

2.5. RO performance

Separation performance of the TFC membranes was tested with 2,000 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 Fig. 1.

The membranes were immersed in various solvents, NMP, DMAc, DMSO, Tetrahydrofuran (THF), acetone, and water, for 24 h at room temperature to evaluate their chemical stability. Especially, for the measurement of chlorine resistance, the membranes were immersed in aqueous sodium hypochlorite (NaOCl) solution (500 ppm) for various exposure times. The pH value was maintained at 10.0.

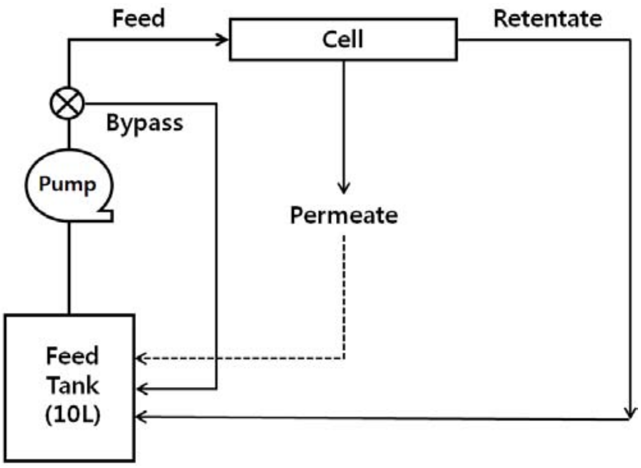

Fig. 1. The construction of cross-flow cell apparatus.

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. The water flux 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^{2}h). The salt rejection was measured by the salt concentration in the feed solution and permeates solution using a conductivity meter (PC 650, EUTECH). The rejection rate was calculated using the following equation:

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

where C_f and C_p are the concentrations of the feed solution and permeate solution.

3. Results and discussion

3.1. Synthesis and characterization of monomer

SDCDPS was prepared via electrophilic aromatic substitution using DCDPS and fuming sulfuric acid. PPH-NH_2 was synthesized by condensation of PPH and ethylenediamine. For purity of monomers, recrystallization of the SDCDPS and PPH-NH_2 from alcohol–water mixture was performed. The synthesis sequence of the monomers is outlined in Fig. 2.

^{1}H-NMR was used to confirm the chemical structure of SDCDPS and PPH-NH_2. The spectrum of SDCDPS with DMSO-d_6 as the solvent and the ^{1}H-NMR spectrum of PPH-NH_2 with DMSO-d_6 as the solvent are shown in Fig. 3 and Fig. 4, respectively.

Assignment of each proton is given in these figures, and these agree with the proposed molecular structures of the SDCDPS and PPH-NH_2.

3.2. Characterization of copolymer and membrane

Sulfonated poly(arylene ether sulfone) containing carboxylic groups was synthesized through polycondensation using phenolphthalin (PP), 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS), phenolphthalein containing amino group (PPH-NH_2) in the presence of anhydrous potassium carbonate in NMP. Toluene was used as an azeotroping agent to remove water during the reaction. The reaction sequence of the sulfonated poly(arylene ether sulfone) containing carboxylic groups is shown in Fig. 5.

We synthesized cPES, where ‘c’ means the carboxylic groups in the sulfonated poly(arylene ether sulfone) copolymer. ^{1}H-NMR was used to confirm the chemical

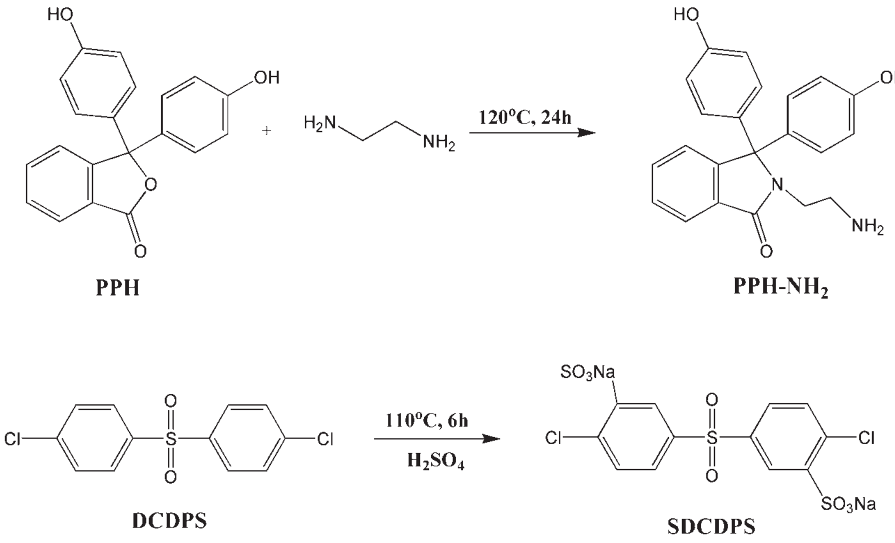

Fig. 2. The synthesis sequences of monomers.

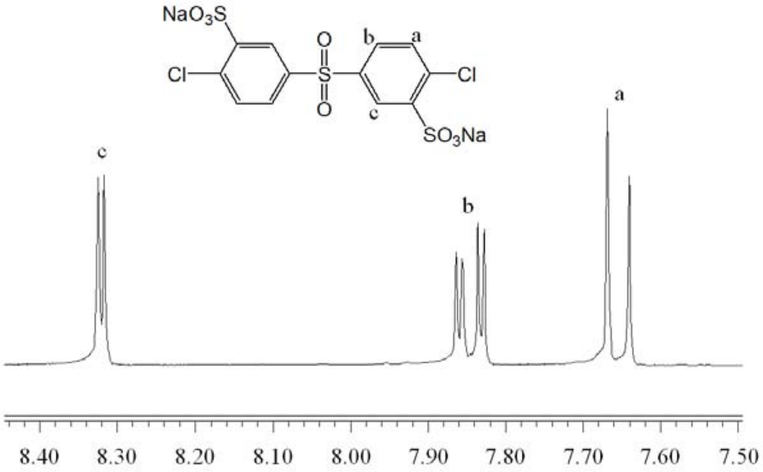

Fig. 3. ^{1}H NMR spectroscopy of SDCDPS in DMSO-d_6.

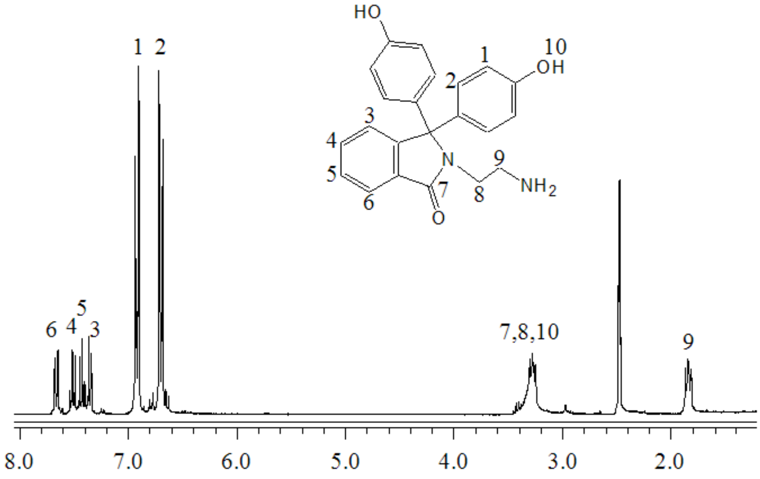

Fig. 4. ^{1}H NMR spectroscopy of PPH-NH_2 in DMSO-d_6.

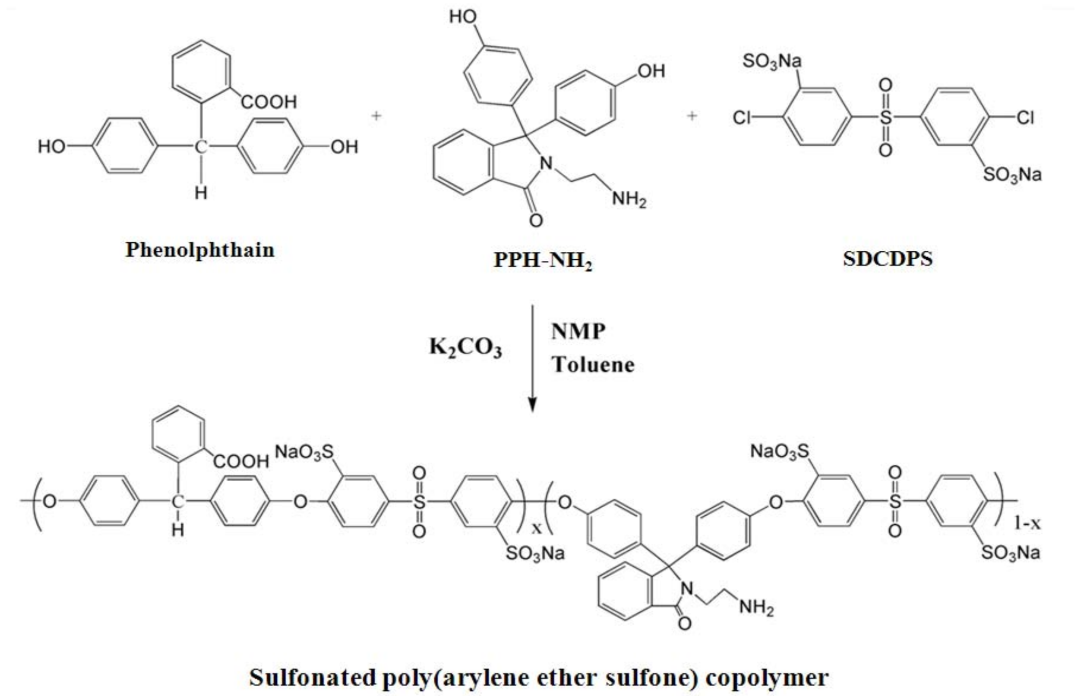

Fig. 5. The reaction sequence of the cPES copolymer.

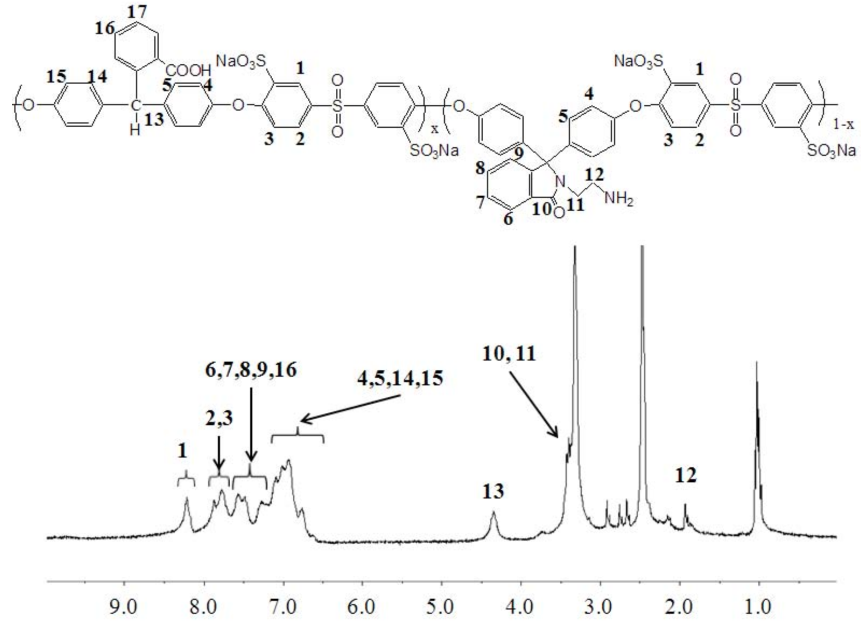

Fig. 6. ^{1}H NMR spectroscopy of cPES in DMSO-d_6.

structure of the copolymers and the spectrum of cPES with DMSO-d_6 as the solvent is shown in Fig. 6.

Assignment of each proton is given in this figure, and these agree with the proposed molecular structure of the sulfonated poly(arylene ether sulfone) containing carboxylic groups.

The TFC membranes for use in the reverse osmosis process were prepared by interfacial crosslinking of trimesoyl chloride with the cPES copolymer on a PS UF support membrane.

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

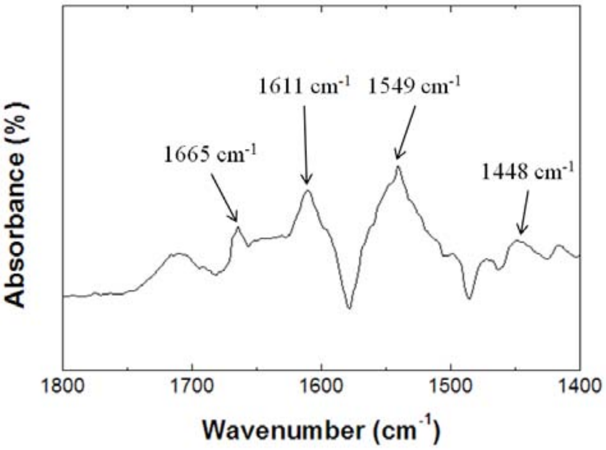

Fig. 7. FT-IR spectra of the TFC membranes.

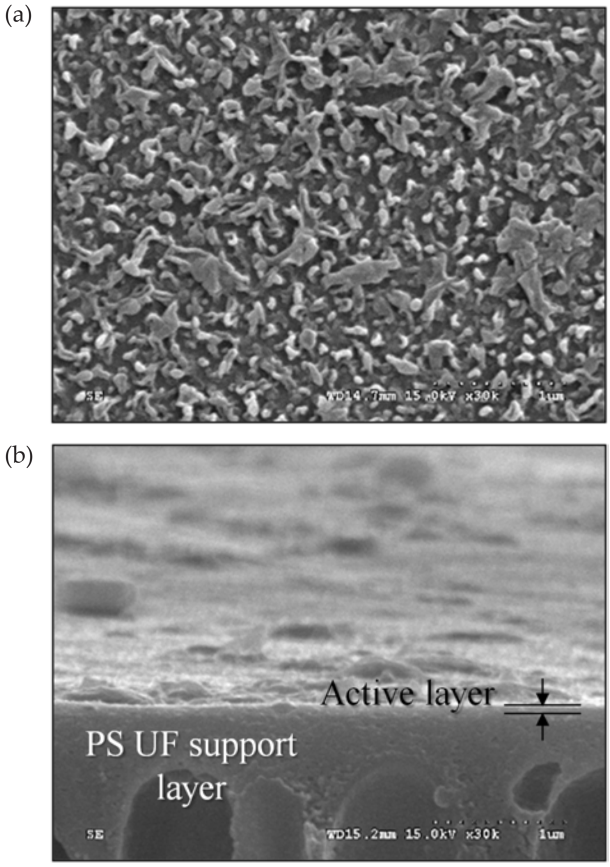

Fig. 8. SEM images of RO membranes; (a) surface and (b) cross-section.

membranes. The FT-IR spectrum of the TFC membrane is shown in Fig. 7.

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), 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 carboxylic 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 active layer surface and structure of the TFC membrane were observed by SEM. Fig. 8 shows a SEM image of the fabricated TFC RO membrane surface and a SEM cross-section.

As shown in Fig. 8, the surface of the TFC RO membrane exhibited the familiar "hill and valley" structure of polyamide RO membranes [18] and the cross-section of TFC RO membrane indicated the presence of a thin selective active layer, that was a few hundred nanometers thick and was supported on a polysulfone UF support layer. The SEM images of the membrane confirmed that the thin-film composite membrane was successfully fabricated.

3.3. *Performance of TFC RO membranes*

Separation of the salt and water through the membranes occurs via the solution–diffusion transport mechanism. The solution–diffusion transport mechanism postulates that the salt and water are separated because of the different diffusivity and solubility through the membrane. The RO performance of TFC RO membranes was characterized with the cross-flow cell apparatus at 15.5 bar using a 2,000 ppm NaCl solution at room temperature. The performance of TFC membranes fabricated in this study was compared with that of the polyamide membrane produced in a laboratory.

Fig. 9 shows the effect of the carboxylic group on the salt rejection and the water flux of the TFC membrane (cPES) compared with a typical polyamide membrane and poly(arylene ether sulfone) membrane without the addition of carboxylic groups (PES).

In these comparative studies, the water flux was found to be enhanced for membranes containing the poly(arylene ether sulfone) copolymers (PES and cPES), while the decrease in salt rejection was negligible. The good performance of the PES membrane comes from the incorporation of the rigid and hydrophilic copolymer [5]. When comparing the PES with cPES (Fig. 9), the cPES membrane showed better water flux than that of PES membrane, but the salt rejection value was almost the same for both membranes. The improved water flux of the membranes containing poly(aylene ether sulfone) copolymers is due to the hydrophilicity of the functional groups, such as sulfonic acid groups (–SO_3H), in the copolymers. Moreover, the cPES membrane had not only the sulfonic acid groups (–SO_3H) but also the carboxylic acid groups (–COOH). The carboxylic acid groups in the cPES copolymer provided additional hydrophilic domains to

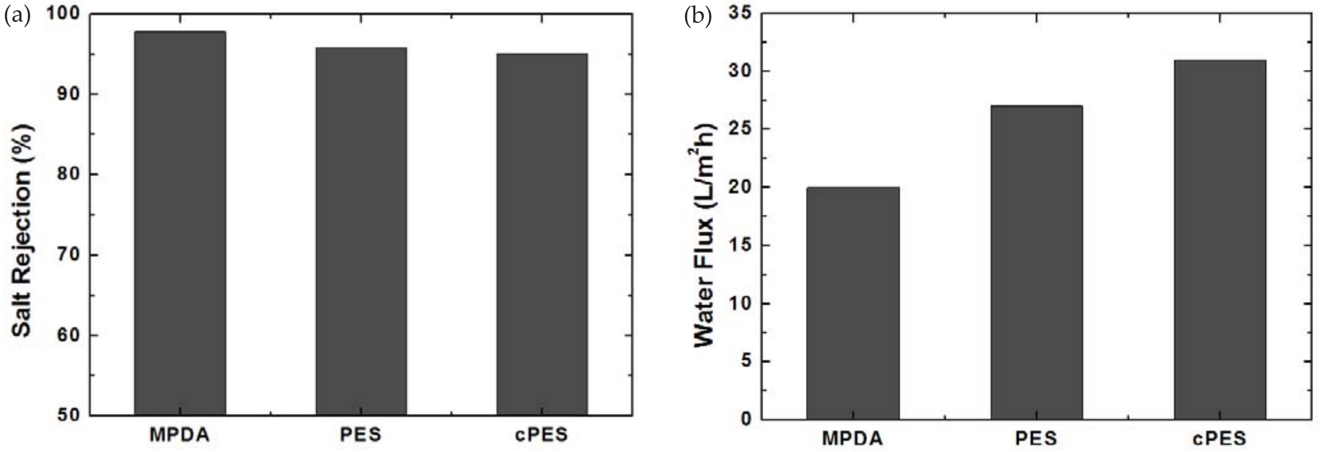

Fig. 9. RO performance of TFC membranes formed using different active layer materials; (a) salt rejection and (b) water flux.

Table 1
Contact angle measurement of membranes

Samples	Contact angle (°)
MPDA	63.6
PES	55.8
cPES	51.2

the RO membranes, which led to a better water flux. The contact angle measurements of the membranes are summarized in Table 1.

A lower contact angle of membrane means a higher hydrophilicity. The contact angle gradually decreased as membrane contains more functional groups. The effect of carboxylic group on RO performance is presented in Fig. 9. The water flux of membranes increased from 20 L/m^{2}h (MPDA) to 31 L/m^{2}h (cPES). In addition, the contact angle of membranes decreased from 63.6° (MPDA) to 51.2° (cPES), which explains the increase in water flux. A carboxylic group in the copolymer makes the membrane surface more hydrophilic. The carboxylic group is a hydrophilic functional group, like the sulfonic group, so the presence of these hydrophilic functional groups at the surface allowed for a much higher water flux. However, as the number of carboxylic groups increases, the number of amino groups in the copolymer decreases. This leads to a decrease in the number of amide bonds in the active layer of membrane, which was the reason that the salt rejection decreased from 97.8% (MPDA) to 95.1% (cPES).

3.4. *Variation of salt rejection and water flux with chlorine exposure*

We compared the RO performance of cPES membrane which immersed in various typical solvents for 24 h with the original membrane for chemical stability test. Fig. 10 shows the slat rejection and water flux of the cPES membrane after immersion in various solvents for 24 h.

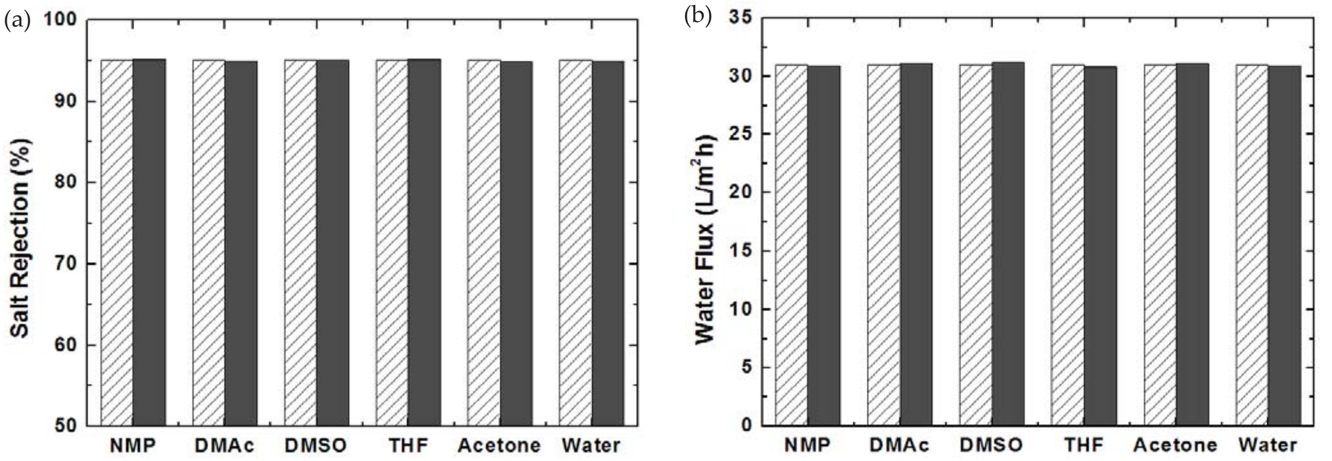

Fig. 10. Chemical stability of cPES membranes in various solvent; (a) salt rejection and (b) water flux (▨ : before immersion, ■ : after immersion).

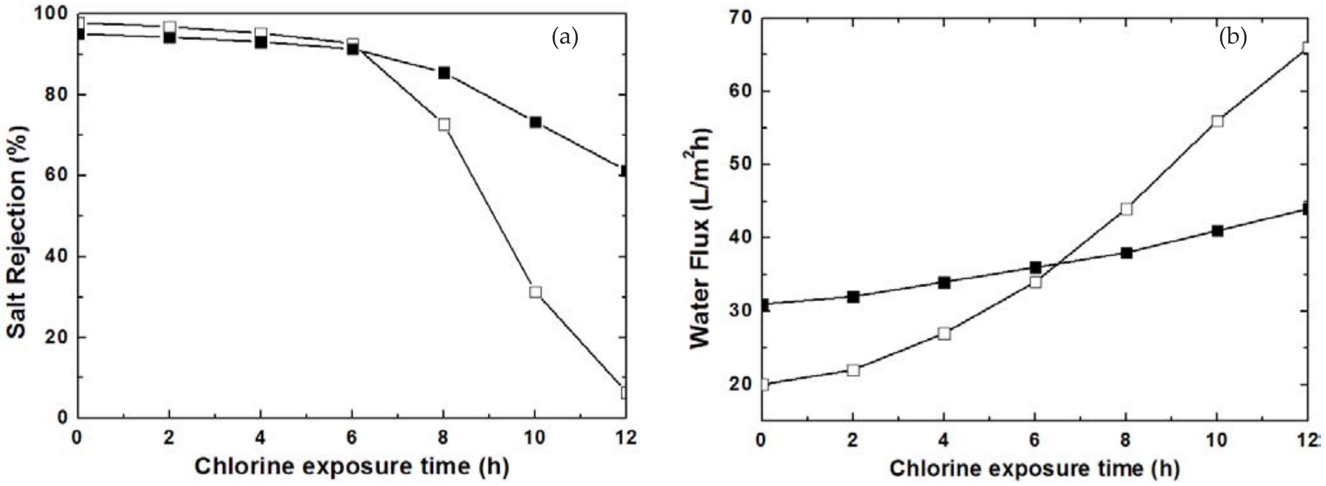

Fig. 11. Variation of RO performances of the membranes on chlorine exposure; (a) salt rejection and (b) water flux (☐ : PA membrane, ■ : cPES membrane).

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

The TFC RO membranes have been exposed to 500 pm aqueous NaOCl solution for different exposure times. Fig. 11 shows the variation of RO performances of the membranes with chlorine treatment.

Fig. 11 clearly shows a decrease in salt rejection within 12 h of exposure to 500 ppm chlorine solution. The pH value was maintained at 10.0. The salt rejection performance of cPES membrane was compared with PA membranes prepared by the MPDA. In the case of PA membrane, the salt rejection decreased rapidly with chlorine exposure time (from 97.8% to 6.8%), while salt rejection of cPES membrane a little decreased (from 95.1% to 61.2%). Water flux of PA membrane increased drastically with chlorine solution immersion time (from 20 L/m^{2}h to 66 L/m^{2}h), while water flux of cPES membrane increased (from 31 L/m^{2}h to 44 L/m^{2}h). For the PA membrane, the decrease of salt rejection accompanying the abrupt increase in the flux is due to the chemical deposition of amide bonds by free chlorine. However, the cPES membrane showed better chlorine resistance compared with the PA membrane, because the cPES copolymer has good chemical stability.

It is supposed that the high chlorine resistance and performance of the cPES membrane come from the incorporation of the rigid polymer backbone and the sulfonated poly(arylene ether sulfone) copolymer containing carboxylic groups and sulfonic groups.

4. Conclusions

Sulfonated poly(arylene ether sulfone) containing carboxylic groups was successfully synthesized via an aromatic substitution polymerization reaction from phenolphthalin (PP), 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS), phenolphthalein containing amino group (PPH-NH$_2$) in the presence of anhydrous potassium carbonate in NMP, which was verified by ^{1}H NMR spectrum.

TFC membranes were successfully fabricated through interfacial crosslinking of the TMC with a mixture of cPES and MPDA on polysulfone UF substrate and the chemical and physical structure were verified by FT-IR spectrum and SEM images. The hydrophilicity of the membrane was verified by contact angle analysis. In these experiments, the cPES membrane has lowest contact angle.

The cPES membrane shows good chlorine resistance and comparable performance with typical PA membrane. The water flux of the cPES membrane reached 31 L/m^{2}h, which was significantly higher than that of the polyamide membrane (20 L/m^{2}h) and PES membrane (27 L/m^{2}h). The higher water flux came from the presence of the bulky, hydrophilic sulfonated poly(arylene ether sulfone) copolymer, which contained carboxylic groups. The reason for the high salt rejection was the high degree of crosslinking and stiffness of the copolymer chain. The chemically stable structure of cPES copolymer and crosslinked structure of the active layer would contribute the high chlorine resistance and good performances, respectively. Consequently, the cPES membrane which has high chlorine resistance and good performance is favorable for the seawater desalination process without significant decrease of performance.

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