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Desalination properties of a novel composite membrane with a lamination method

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ABSTRACT

Side chain crosslinked (C-SFPEx-CMy) sulfonated poly(arylene ether) (SPAE) membranes containing fluorine moiety with varying degree of sulfonation (DS) were prepared and evaluated for use as a thin-film composite membrane for seawater desalination. C-SFPEx-CMy membranes were obtained by covalent crosslinking among ethynyl groups at the polymer side chain through thermal curing. The crosslinked network structure suppressed the water uptake and swelling ratio. A novel type of composite membranes (TC-SFPEx-CMy) were prepared side chain crosslinked SPAE layer containing fluorine moiety on top of PET non-woven with epoxy resin as bonding agent. TC-SFPEx-CMy show the increase in NaCl rejection as DS decreases from 30% to 70%. NaCl rejection of the membranes increased with increasing corsslinking moiety (CM) while water permeability decreases due to the crosslinked net work structure. Particularly, crosslinked membrane of 30 mol % of CM could enhance the salt (NaCl) rejection property up to 85.3 % as compared to of crosslinked membrane (69.5%) containing 10 mol % of CM under same DS. However crosslinked membrane showed the decrease in water permeability from 6.89 L/m^2·h (TC-SFPE30-CM10) to 2.06 L/m^2·h (TC-SFPE30-CM30). For TC-SFPE30-CM30 membrane, the order of salt rejection was observed Na_2SO_4 > NaCl > $MgSO_4$ > $MgCl_2$.

Keywords: Composite membrane; Seawater; Lamination method

1. Introduction

Recently more than 1 billion people have been suffering from the shortage of fresh drinking water [1]. Desalination of brackish and seawater, which are a sustainable resource, is a realizable candidate to obtain fresh water through membrane-based desalination methods. Reverse osmosis (RO) is an energy-efficient way compared to other technologies such as multi-stage flash distillation (MSF) and vapor compression desalination (VC) [2,3]. For the last three decades, a lot of efforts to develop efficient RO membranes have been done by many researchers. Commercial RO membranes are classified as two kinds of polymer materials: one is a cellulose acetate (CA) membrane and the other is a polyamide (PA) membrane. CA membranes are only stable under acid conditions with the pH range of 3.5–6.5, and are weak to bacterial attack and to temperature rises [4–6].

In contrast to CA membranes, PA membranes have many advantages such as high salt rejection ability and stability within a broad pH range of 3–11, however, they needs to be exposed to chlorine to prevent biofouling in the water purifying step [7–12]. Such vulnerability of PA membranes under highly chlorine environment would lead to the irreversible performance even for the continuous exposure to chlorine at low concentration [7–9]. Thus,

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an additional dechlorination step of chlorine-treated water is required to prevent the membrane from chemical degradation before it is fed to the PA membrane and that leads to the increase of the process cost [13].

Sulfonated poly(arylene ether) (SPAE) membranes are considered as one of chlorine-resistant RO membranes to replace PA membranes because they do contain amide bond which is unstable for chlorine attack [14–18]. In addition, SPAEs have wide applications as engineering plastics due to good mechanical, thermal and chemical stabilities [19]. Sulfonated poly(arylene ether sulfone) membranes have also been suggested as a chlorine-resistant RO membranes [20,21]. Park et al. showed that sulfonated poly(arylene ether sulfone) for a desalination membrane could retain the flux and salt rejection ability after exposure to 500 ppm NaOCl solution in the feed water at pH values ranging from 4 to 10 for 40 h [21]. However, poly(ether sulfone) membranes had shown also the degradation of chemical structure and diminution of mechanical properties for 28 days under highly-concentrated hypochlorite solution (NaOCl 4000 ppm) [22–25]. Maurin et al. reported that the degradation of a polysulfone membrane in the hypochlorite solution was observed by mechanical testing (tensile test), molar mass (size exclusion chromatography; SEC), and spectrochemical measurements such as Fourier transform infrared spetrophotometry (FT-IR). In the study, the chain scission of a polysulfone main chain occurred at the sulfone linkage ($-SO_2-$) part between the aromatic benzene rings [23].

There are two obvious approaches to solve such problem. The introduction of crosslinking system among the polymer chains and the choice of fluorinated monomer for the final polymer system give rise to improve dimensional, mechanical, and chemical stability of the polymer membrane. Ionically crosslinked RO membranes improve the NaCl rejection, mechanical strength, thermal stability and resistance to chemicals [26,27]. The covalent crosslinking system of the polymer chain not only decreases the water absorption with enhancement of the dimensional stability but also prevents highly sulfonated polymer from dissolving in common organic solvents [20,28–31]. Our group has also studied the covalent crosslinkable poly(arylene ether) for fuel cell applications [32–34]. Riffle et al. reported that covalent crosslinking of epoxy material with disulfonated poly(arylene ether) sulfone improved the salt rejection without significantly impairing water flux as RO membranes [20]. Many studies have reported that the sulfonated aromatic polymers containing fluorine components improve the chemical resistance and thermo-oxidative stability of membranes with long-term durability due to strong C–F bond in the polymer structure [34].

In this work, we describe a novel type of a composite membrane of side chain crosslinked sulfonated poly(arylene ether) (SPAE) containing fluorine moiety as a top layer coated on top PET non-woven as a base layer with epoxy resin as bonding agent. By means of ethyl groups, the SPAE of side chain crosslinkable was cured by thermal energy among the main chains. NaCl rejection and permeability were controlled by degree of sulfonation (DS) in the main chain ranging from 20% to 70% and crosslinking ratio of the side chains. The desalination membrane will be characterized by salt solution as sodium chloride, sodium sulfate, magnesium chloride and magnesium sulfate. The desalination properties such as the salt rejection and water permeability of RO membranes were measured by dead-end filtration, and composite membranes cross-sectional and surface images were measured by scanning electronic microscopy (SEM).

2. Materials and methods

2.1. Materials

Potassium-2,5-dihydroxybenzenesulfonate (SHQ), 4,4′-(hexafluoroisopropylidene) diphenol (6F-BPA), benzene, N,N-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) were purchased from Aldrich Chemical Co. and used without further purification. Potassium carbonate was dried at 120°C before use. Decafluorobiphenyl (DFBP) was purchased from Fluorochem Ltd. and used without purification. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), magnesium sulfate (MgSO4) and magnesium chloride ($MgCl_2$) were purchased from DC Chemical Co. Epoxy resin was used poFlx Resin from Struers Co. And PET non-woven was purchased from LG Chem.

2.2. Preparation of membranes (Fig. 1)

Side chain crosslinkable sulfonated copolymers (SFPEx-CMy) were synthesized by polycondensation. Detail synthesis method and results were referred as our previous work [32].

Potassium form (K^+) membranes were prepared from casting solution of SFPEx-CMy dissolved in DMSO on the glass plate. The polymer solutions were filtered by using a syringe filter before casting. For the preparation of crosslinked membranes (SFPEx-CMy), after casting, the membranes were annealed on a hotplate increasing the temperature gradually from 50 to 200°C for 1 h and then the membranes were baked at 250°C until a crosslinking between polymer chains was formed enough via reacting among the ethynyl moieties [32–34]. The thickness of all membranes was controlled by different concentrations of the solution in the ranges of 7–15 μm.

An epoxy resin was mixed to the ratio of 4 : 1 and was coated on PET non-woven with doctor blade coater. The side chain crosslinked sulfonated poly(arylene ether) membranes were covered on epoxy resin-coated non woven. With pressure, the composite membranes were cured at room temperature for 5 h. After curing, the composite membranes were immersed into DI water for

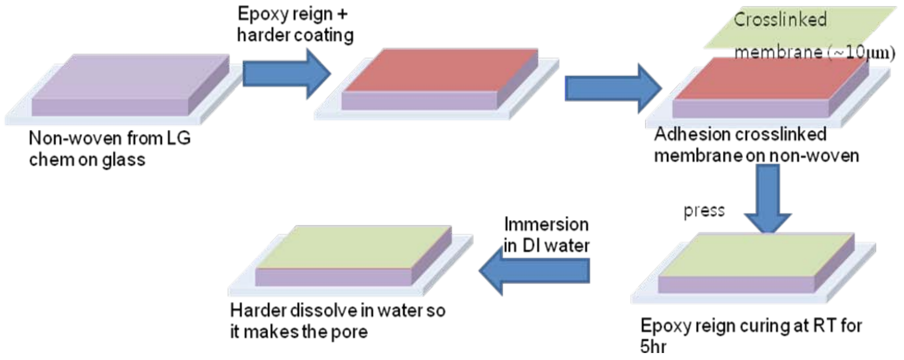

Fig. 1. The method of composite membrane preparation.

4 h, and then the composite membrane was dried at room temperature for the desalination test.

2.3. Water uptake and swelling ratio

The water uptake of the crosslinked membranes with the sulfonate potassium form was determined by measuring their weight change after they were immersed in deionized (DI) water for 24 h at room temperature. The weight of the dried membranes (W_{dry}) was investigated after they were dried enough in a vacuum oven at 60°C for 24 h. The membranes were then immersed in deionized water for 24 h at room temperature and were weighed immediately after removing the surface-attached water to determine the weight of the wetted membrane (W_{wet}). The water uptake was calculated using the following equation [32–34]:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\,(\%) \tag{1}$$

In addition, the area swelling ratio was evaluated by measuring the area of the immersed membrane and as-prepared membrane.

2.4. Gel fraction

Gel fractions of the crosslinking were measured by the weight change via solvent extraction [20,32]. The amount of ca. 0.5 g was extracted in Soxhlet extractor using an extraction solvent of DMSO at room temperature. Side chain crosslinked sulfonated poly(arylene ether) membranes were placed in an excess of DMSO, and the solvent was replaced for 24 h until no further extractable polymer could be detected. The extracted samples were dried until constant weight. The gel fractions could be explained with the following equation:

$$\text{Gel fraction} = \frac{W_2}{W_1} \times 100\,(\%) \tag{2}$$

where W_1 is the weight of the sample before extraction and W_2 is the weight of the dried sample after extraction.

2.5. Characterization of membranes

The composite membrane was observed under scanning electronic microscopy (SEM, Hitachi S-4700) using a machine with the acceleration voltage of 15 kV. Before SEM observation, all of the samples were sputter coated with platinum under a coater for 40 s. In addition, the ion exchange capacity (IEC) of the polymer membranes was investigated via the titration method. All membranes were thoroughly rinsed with deionized water several times and were soaked in a large excess of 0.01 M NaCl solution for a sufficient time. The protons released due to the exchange reaction with Na^+ ions were titrated against a 0.01 N NaOH solution using pH meter (pH/ion analyzer 350, Corning) [32–34].

2.6. Desalination test

Water permeability was measured using deionized water (Milli-Q, Millipore Korea Co., Ltd.) in the dead-end filtration system (Sterlitech TM HP4750, Sterlitech Corp). In all experiments, the membrane with the diameter of 49 mm, the active area of 14.6 cm^2 was used. Water permeability (P_w) was calculated using Eq. (3) from the volumetric flux (V) per unit time (t) through a membrane with active area A:

$$P_W = \frac{V}{A \cdot t} \tag{3}$$

Salt rejection was also measured from he concentration change of the feed solution of NaCl aqueous solution of 2000 ppm in the dead-end filtration system. The salt rejection (R (%)) could be shown in the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \tag{4}$$

where C_p and C_f are the salt concentration in the permeance and the salt concentration in the feed water, respectively. Both Cp and Cf were measured by a digital TDS meter (Oakton® TDS 6, Cole Parmer). The salt rejection data was measured under the feeding pressure of 1000 psi.

3. Results and discussion

3.1. Membrane properties

The side chain crosslinked SPAE membranes are denoted as a C-SFPEx-CMy, where x is the degree of sulfonation (DS) of the side chain crosslinkable copolymer and CM is the crosslinking moiety and y is CM mol % of polymer main chain as shown in Fig. 2. Theoretically, the ion exchange capacity (IEC) increases as a function of DS. IEC value of C-SFPEx-CMy membranes shows in the range from 1.46 to 2.07 meq/g with increasing the DS of the membranes as summarized in Table 1. The water uptake and swelling ratio of the salt form (K^+ form) of C-SFPEx-CMy membranes were measured at room temperature as varying the DS (and/or IEC). The change of CM mol % does not affect the IEC value considerably. From 30 to 10 mol % of CM in the polymer main chain, IEC values were similar to each other.

The water uptake and swelling ratio of the membranes increase as DS increases due to the presence of the sulfonation group in the polymer chain. As shown in Table 1, the water uptake for C-SFPEx-CM30 observed at room temperature varied from 3.6 to 16.2 wt% for IEC from 1.29 to 0.50 meq/g. The swelling ratio for C-SFPEx-CM30 varied from 1.3 to 9.6 % for IEC from 0.50 to 1.29 meq/g. However the water uptake and swelling ratio decrease with increasing molar ratio of CM monomer within the membranes with the same DS (Table 1). C-SFPE30-CM30 membrane has better dimensional stability such as water uptake and swelling ratio than C-SFPE30-CM10 membrane because crosslinking networks result in smaller hydrophilic channels for water absorption [34,35].

It can be concluded that crosslinking of polymer chains could contribute to constraining the water uptake and swelling of the polymer membrane in practical conditions.

3.2. Gel fraction

The crosslinkable copolymers were heated to form a crosslinked network structure. The thermal crosslinking was carried out until the ethynyl moieties of copolymer fully reacted. The gel fraction of crosslinking membranes evaluates the degree of crosslinking in polymer membrane through assessing the extent of crosslinking [20,32]. Thus, the gel fractions of our crosslinked membranes

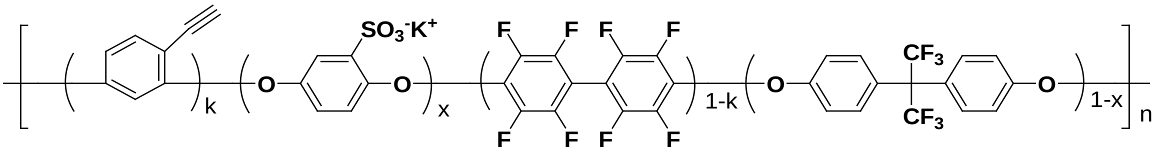

Fig. 2. Chemical structures of side chain crosslinkable copolymer.

Table 1
Membrane properties of the C-SFPEx-CMy series

Polylmer membrane[a]	Cal. DS (%)	IEC (meqv/g)		Water uptake (%)[d]	Swelling ratio (%)[e]	Dry density (g/cm³)[f]	Gel fraction (%)[g]
		Cal.[b]	Obs.[c]	Room temp	Room temp		
C-SFPE70-CM30	70	1.32	1.29	16.2	9.6	1.66	99.5
C-SFPE50-CM30	50	0.91	0.89	11.3	5.2	1.56	98.6
C-SFPE30-CM30	30	0.53	0.50	3.6	1.3	1.47	98.5
C-SFPE30-CM20	30	0.53	0.51	5.4	2.1	1.67	62.3
C-SFPE30-CM10	30	0.53	0.52	8.2	2.9	1.54	37.2

[a] C-SFPEx-CMy are side chain crosslinked membranes of K^+ form, respectively.

[b] Calculated from the feed monomer ratio {IEC = (1000/MW repeat unit) × degree of sulfonation × number of $–SO_3H$,or IEC = 1000/EW}.

[c] Measured after soaking in 0.01 N NaCl solution for 24 h, then titrated with 0.01 N NaOH solution using pH meter as an indicator at room temp.

[d] Calculated from weights of the membranes {Water uptake (%) = $(W_{wet} – W_{dry}) \times 100 / W_{dry}$, where W_{wet} and W_{dry} are the weights of swollen and dried membranes, respectively}.

[e] Calculated from lengths of the membranes {Swelling ratio (%) = $(l_{wet} – l_{dry}) \times 100 / l_{dry}$, where l_{wet} and l_{dry} are the lengths of swollen and dried membranes, respectively}.

[f] Based on dry state.

[g] Soxhlet extraction in DMAc for 48 h.

are given in Table 1. The gel fractions of the membranes increased with increasing the molar ratio of CM monomer. Side chains of the SPAE polymer were crosslinked sufficiently as reported in our previous work [32].

3.3. Composite membrane

The composite membranes were prepared by side chain crosslinked sulfonated poly(arylene ether) coated on the non-woven made of PET (Fig. 3). Then, the epoxy resin was used as a bonding agent for adhesion between two different polymers. Fig. 3a shows SEM surface image of pure PET, which displays holes with the size of the several micrometers. The small amount of epoxy resin mixed with harder was coated on top of the porous non-woven with doctor blade coater. After coating of epoxy resin, the surface obtained smooth with defect-free coating (Figs. 3b,c). Figs. 3d,e shows that epoxy resin coated on the non-woven membrane was immersed into DI water for 6 h to remove excess epoxy resin and harder. When dipped into DI water, the residual harder would be dissolved in DI water, remaining the disorderly pores. These pores make the water flow path through the composite membrane.

Fig. 4 shows the cross-sectional SEM image of the composite membrane. The top layer of crosslinked sulfonated poly(arylene ether) is an active layer to act with the injection salt. Thus, the top layer thickness shows the thickness of ca. 7–12 μm and moderate uniformity. Though the epoxy resin was used as binding agent, it forms the porous structure of SPAE by immersing in the water, which facilitates the water molecules to flow through the composite membranes.

3.4. Salt rejection and permeability

Table 2 shows the water permeability and sodium chloride (NaCl) rejection of TC-SFPEx-CMy membranes under the DS variation of 30–70%. For desalination, the membrane should have the high water permeability and the low salt permeability. In general, water permeability increases with increasing DS of the membrane even though salt rejection decreases [21]. As summarized in Table 2, TC-SFPEx-CMy shows the increase in NaCl rejection as DS decreases, while water permeability decreases because of the decrease of the hydrophilicity [19]. For the TC-SFPEx-CM30 membranes, NaCl rejection changes from 62.5% for IEC value of 1.29 to 85.3% for IEC value of 0.50, while the water permeability varies from 2.06 L/m^2·h for IEC value of 0.5 to 15.85 L/m^{2}h for IEC value of 1.29 as shown Fig. 5.

Fig. 6 shows the NaCl rejection and permeability through the side chain crosslinked membranes as a function of the CM molar ratio. The more crosslinkable moiety is employed, the higher is NaCl rejection while the lower is permeability in the side chain crosslinked membranes with same DS. The results indicate that NaCl rejection of the crosslinked membranes decreases with increasing

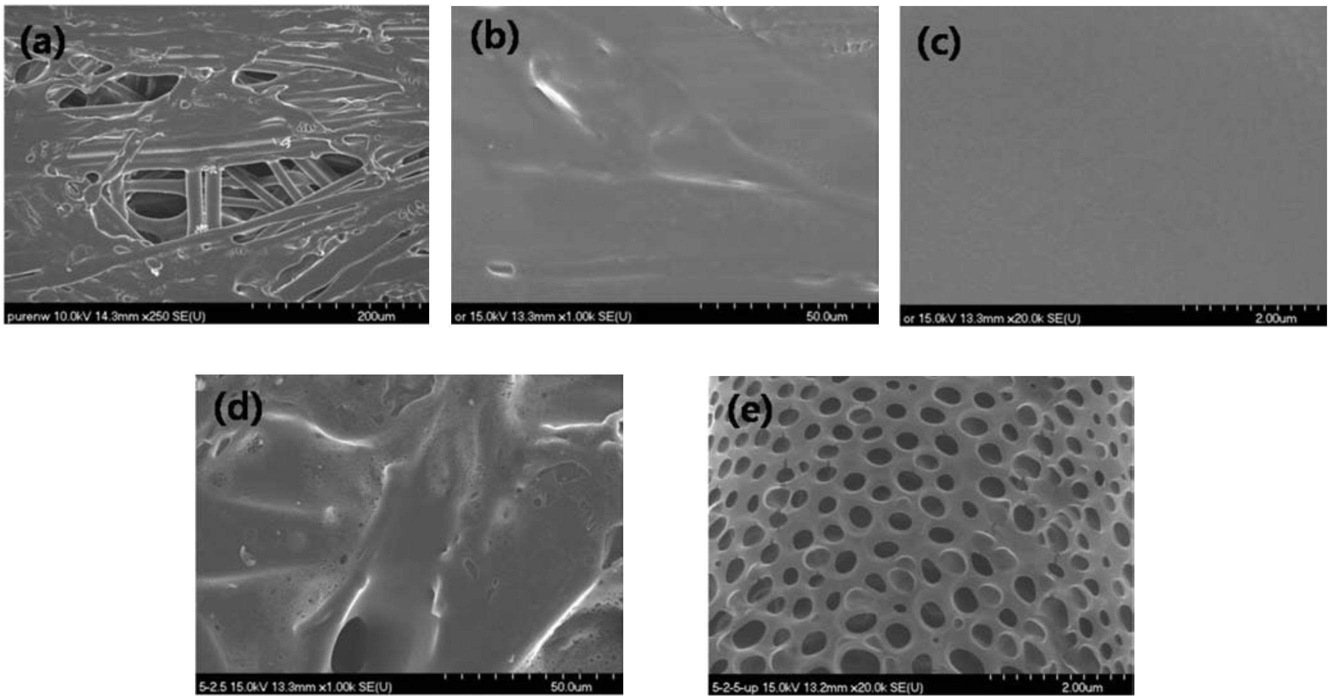

Fig. 3. (a) Original PET non-woven (b) after epoxy reign coating on the top of non-woven (c) magnification of (b) (d) after immersion of (b) into the DI water (e) magnification of (d).

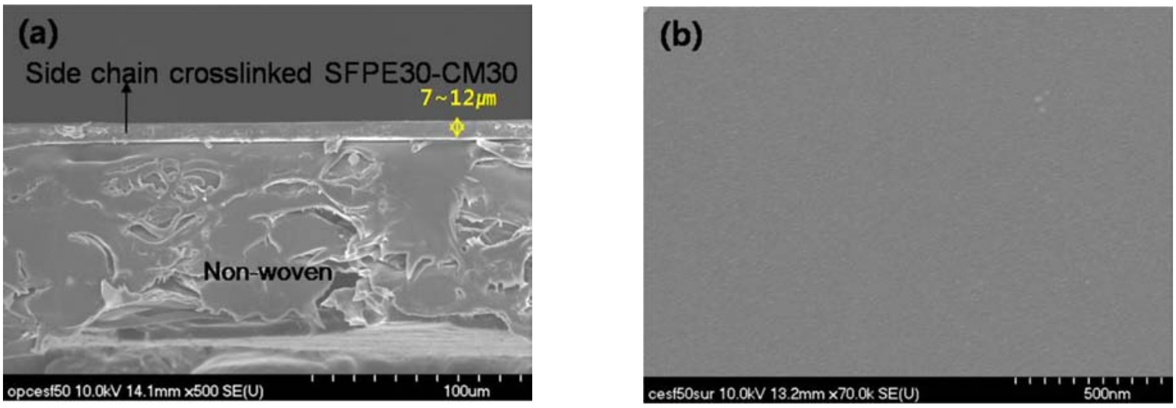

Fig. 4. (a) Cross-section of composite membrane (TC-SFPE30-CM30) (b) surface of composite membrane (TC-SFPE30-CM30).

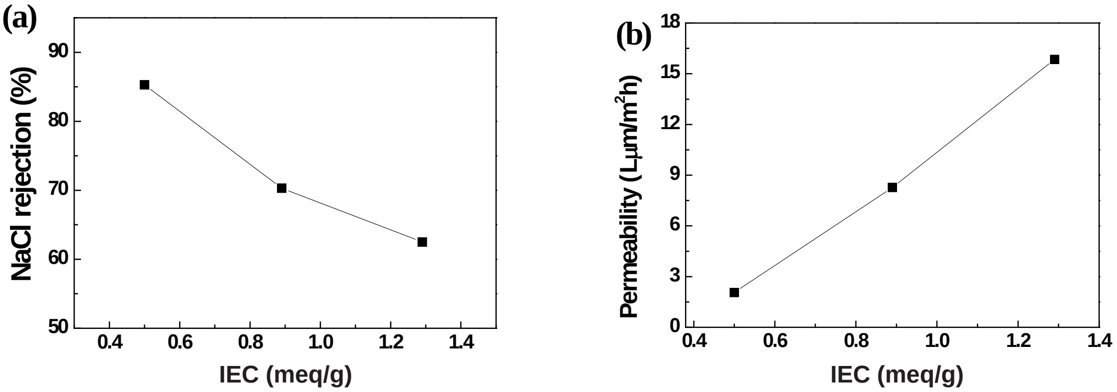

Fig. 5. (a) NaCl rejection (b) water permeability for side chain crosslinked membranes (K^+ form) as a function of IEC value.

Table 2
NaCl rejection and water permeability of the C-SPFEx-CMy series

Polylmer membrane[a]	Cal. DS (%)	IEC (meq/g)		NaCl rejection (%)[d]	Water permeability ($L/m^2 \cdot h$)[d]
		Cal.[b]	Obs.[c]		
C-SFPE70-CM30	70	1.32	1.29	62.5	15.85
C-SFPE50-CM30	50	0.91	0.89	70.3	8.27
C-SFPE30-CM30	30	0.53	0.50	85.3	2.06
C-SFPE30-CM20	30	0.53	0.51	78.2	4.20
C-SFPE30-CM10	30	0.53	0.52	69.5	6.89

[a] C-SFPEx-CMy are crosslinked membranes of K^+ form, respectively.

[b] Calculated from the feed monomer ratio {IEC = (1000 / MW repeat unit) × degree of sulfonation × number of $-SO_3H$, or IEC = 1000/EW}.

[c] Measured after soaking in 0.01 N NaCl solution for 24 h, then titrated with 0.01 N NaOH solution using pH meter as an indicator at room temperature.

[d] Feed = 2000 ppm NaCl ; Applied pressure = 1000 psi ; Temperature = 25 °C.

crosslinking density because the net work structure of membrane suppressed the transport of Na+ and Cl- ions through the permeability of the crossllinked membranes decreases.

Fig. 7 shows the salt rejection of the TC-SFPE30-CM30 composite membrane. The order of salt rejection was as follows: Na_2SO_4 (92.4%), NaCl (85.3%), $MgSO_4$ (76.2%), Mg_2Cl_2 (67.3%). The order of salt rejection corresponds

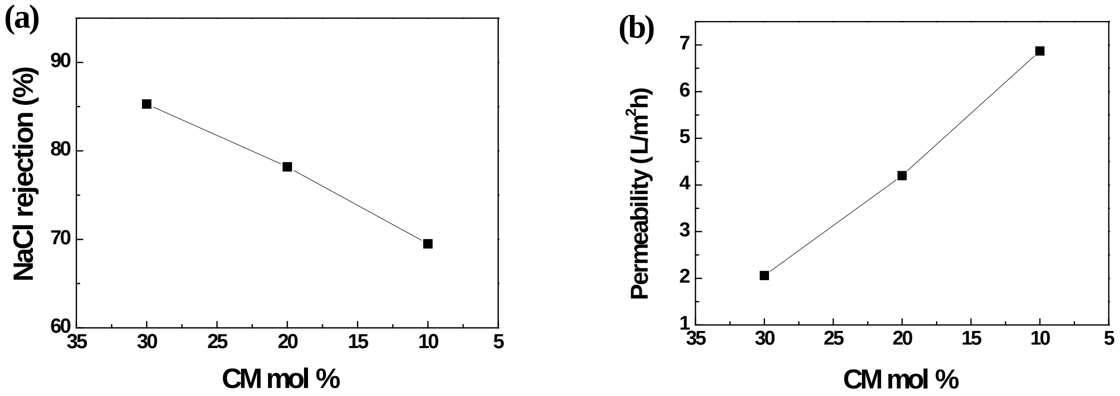

Fig. 6. (a) NaCl rejection (b) water permeability for crosslinked membranes (K^+ form) as a function of crosslinking moiety (CM) mol fraction.

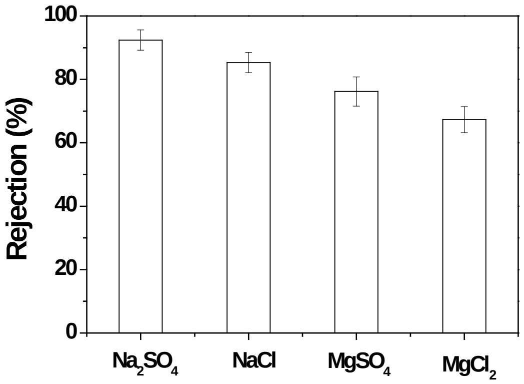

Fig. 7. Salt rejection of the TC-ESF40-BP composite membrane.

to the negatively charged membranes [36]. Salt rejection increases with increasing anion valance. Comparing Na_2SO_4 and NaCl, the salt with SO_4^- shows higher rejection rate than salt with Cl^- because the repulsion between sulfonic groups and SO_4^- is larger as well as the size of SO_4^- is bigger. In addition, $MgCl_2$ including positive ion exhibits lower rejection due to the positively charged Mg^{2+}. Sulfonic groups allow positively charged ions to transport [36]. Accordingly, the introduction of crosslinking moiety was indispensable in obtaining desirable properties of the membranes for desalination.

4. Conclusion

A novel type of desalination composite membrane was prepared with side chain crosslinked sulfonated poly(arylene ether) layer containing fluorine moiety on top of PET non-woven with epoxy resin as bonding agent. Depending on the sulfonation group ratio and crosslinking moiety (CM) ratio of poly(arylene ether), the NaCl rejection and permeability were controlled. The composite membrane was characterized by salt solutions as sodium chloride, sodium sulfate, magnesium sulfate and magnesium chloride. The rejection of salts was in the order of Na_2SO_4 > NaCl > $MgSO_4$ > $MgCl_2$. In this study we have proved that crosslinking is as effective as DS in changing the salt rejection properties. These results indicated that the TC-SFPEx-CMy series of crosslinked membranes are a promising candidate for desalination application.

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