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# Desalination properties of a novel composite membrane prepared by electrospinning method

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## ABSTRACT

A novel composite membrane for potential desalination was prepared by coating of sulfonated poly(arylene ether) on the non-woven web. The non-woven web was made of end-group crosslinkable flurorinated poly(arylene ether) nanowires fabricated by electrospinning method. The crosslinked non-woven web was obtained by covalent crosslinking among ethynyl groups at the polymer chain end via thermal curing. The salt rejection and permeability of the crosslinked non-woven web were controlled by varying degrees of sulfonation (DS) of sulfonated poly(arylene ether). The compostie membranes show the increase of NaCl rejection as DS decreases from 20% to 60%, while water permeability decreases due to the increase of hydrophilicity. The order of salt rejection was as follows: $Na_2SO_4$ (88.4%), NaCl (79.3%), $MgSO_4$ (70.2%), $Mg_2Cl_2$ (62.3%).

*Keywords*: Electrospinning, Desalination, Composite membrane, Poly(arylene ether)

## 1. Introduction

Water on earth consists of 96.5% sea and ocean water of and of 1.7% ice [1]. Only 0.8% of water exists as drinking fresh water and the brackish water, slightly salty water found as surface and ground water in salty aquifers is another remaining portion. More than 1 billion people suffer from shortage of fresh drinking water and approximately 2.3 billion people (41% of world population) reside in water-stressed areas [2]. Such problem will be expected to be serious as the global population continues to increase and the demand for new sources of fresh water will grow with it.

Desalination of brackish or seawater, which are a sustainable resource, is the most realizable candidate to satisfy the demand of humans. To obtain fresh water desalination using membranes, such as reverse osmosis (RO), is an energy efficient way compared to other technologies such as multi-stage flash distillation (MSF), multiple-effect distillation (MED) and vapor compression (VC) [1,3]. For last three decades, many researchers have continued a lot of efforts to develop efficient RO membranes. Commercial RO membranes are classified as two kinds of polymer materials. One is a cellulose acetate (CA) membrane and another is a polyamide (PA) membrane. CA membranes are only stable at the pH range of 3.5–6.5, and are weak to bacterial attack and to temperature rises [4,5]. Compared with CA membranes, PA

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membranes as another commercial RO membranes have many advantages which are high salt rejection ability and stability within the pH range of 3–11, and therefore they have been wildly used as RO membranes recently [6,7]. However, PA membranes are high unstable in high chlorine concentrations used to prevent biofouling at the water purifying step [7–11]. Such vulnerability of PA membranes for chlorine environment would lead to the irreversible operation even for the continuous exposure of chlorine at a few parts per million (ppm) [7–9]. Thus, the additional dechlorination step of chlorine-treated water is required to prevent chemical degradation of the membranes before it is fed to PA membranes and that leads to the increase of process cost [12].

Sulfonated poly(arylene ether) (SPAE) membranes are regarded as one of chlorine-resistant RO membranes to replace PA membranes because thye do not contain amide bond which is weak for chlorine attack [13–18]. 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 chlorine-resistant RO membranes [20,21]. Park et al. reported that sulfonated poly(arylene ether sulfone) as 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].

Recently, an electrospinning method has received a great attention because of its special characteristics [22,23]. Electrospinning is a fiber spinning process of making fibers with a diameter of a few hundred nanometers to a few micrometers. The continuous fibers could be formed as a non-woven web with simultaneous rapid evaporation of the solvent. The non-woven webs as fibrous materials made by electrospinning provide advantages of high filtration and low air resistance [24]. Thus, a number of polymer fibers such as polyvinylidene fluoride (PVDF), poly(ethylene oxide) (PEO) and polytetrafluoro ethylene (PTFE) have been constructed by the electrospinning method for various applications [25,26].

In this work, we describe a novel composite membrane by brush coating of sulfonated poly(arylene ether) on top of the non-woven web which was made by electrospinning. The non-woven web of the end-group crosslinkable poly(arylene ether) was cured by thermal energy. NaCl rejection and permeability were controlled by degree of sulfonation (DS) of the top layer of sulfonated poly(arylene ether) in the main chain ranging from 20% to 60%. The desalination membrane is characterized by salt solution as sodium chloride, sodium sulfate, magnesium chloride and magnesium sulfate. The desalination properties such as salt rejection and water permeability of membranes were measured by dead-end filtration, ATR-IR, and scanning electronic microscopy (SEM).

## 2. Materials and methods

### *2.1. Materials*

Potassium-2,5-dihydroxybenzenesulfonate (SHQ), 4,4′-biphenol (BP), 4,4′-(hexafluoroisopropylidene) diphenol (6F-BPA), benzene, and *N,N*-dimethylacetamide (DMAc) 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 ($MgSO_4$) and magnesium chloride (MgCl2) were purchased from DC Chemical Co.

### *2.2. Synthesis of crosslinkable copolymers for electrospinning*

The crosslinkable copolymers (6F-DF) for electrospinning were prepared from two monomers, DFBP, 6F-BPA, as shown in Fig. 1. A 250 mL round-bottom flask was equipped with a Dean-Stark trap, condenser, and nitrogen gas inlet. 6F-BPA (3.36 g, 10.002 mmol), DMAc (60 mL), benzene (20 mL), and potassium carbonate (4.32 g, 31.25 mmol) were added to a round bottom flask. The contents of the flask were then heated at reflux for 6 h at 150°C. After 6 h, water was evaporated as an azeotrope with benzene and was removed in the Dean-Stark trap, and the remaining benzene was distilled from the flask. A solution of DFBP (3.38 g, 10.02 mmol) and 10 mL DMAc was added to the flask, the reaction mixture was heated to 140°C, and this temperature was maintained for 12 h to ensure complete dehydration. Benzene was refluxed into the Dean-Stark trap, following which the reaction mixture was stirred at this temperature for a further period of 2 h. Benzene got refluxed into the Dean-Stark trap. After removing benzene, the reaction mixture was stirred at this temperature for a further period of 2 h. In order to attach the ethynyl group at the end of polymer, 3-ethynylphenol (0.2 g), DMAc (10 mL) and benzene (10 mL) were added to the reaction mixture and then the reaction continued for 3 h. The reaction mixture was cooled and then precipitated into 1 L of ethanol/water (9.8:0.2) solution. The precipitated polymer was filtered and washed with ethanol. The brown solid was dried under vacuum (60°C) for 3 days. The yield of 6F-DF was above 90%.

### *2.3. Synthesis of sulfontaed copolymers*

ESFx-BP copolymers (ESFx-BP, x refers sulfonation degree (SD) of the copolymers) were synthesized via step growth polymerization (Fig. 2) [27]. The synthesis method and results are described in detail in our previous work [27].

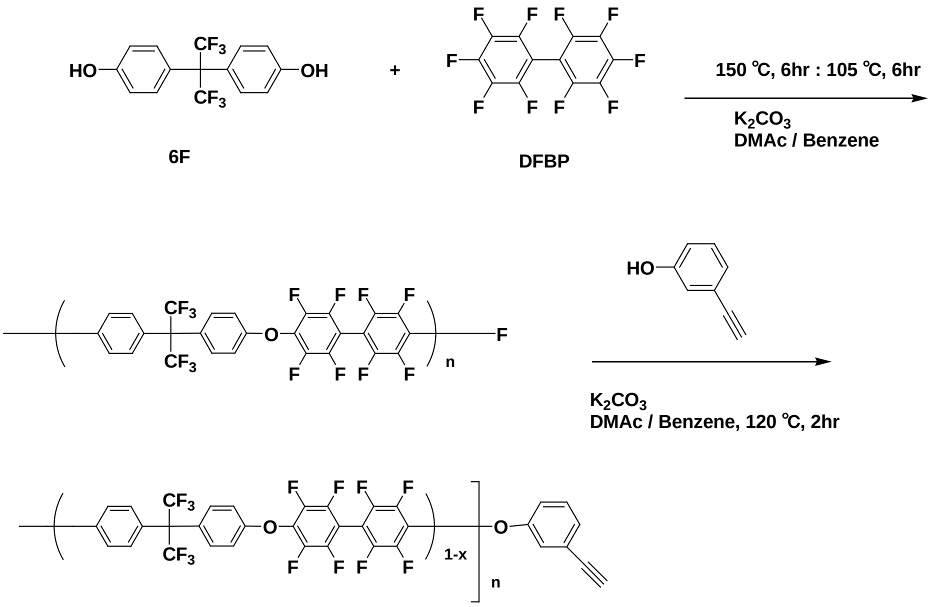

Fig. 1. Chemical structures of end-group crosslinkable copolymer for electrospinning.

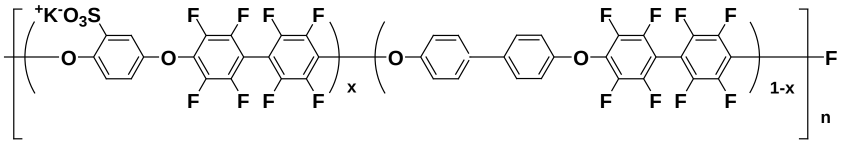

Fig. 2. Chemical structures of sulfonated poly(arylene ether) copolymer.

### 2.4. Electrospinning and fiber preparation

The experimental setup used for the electrospinning process of this study is schematically shown in Fig. 3. It consists of an adjustable DC power supply (CPS-40K03VIT, Chungpa EMT Co., Ltd., Korea) capable of generating DC voltage in a range of 0–50 kV, a syringe pump (KDS-100, KD scientific Inc., Holliston, MA) with a 5 ml syringe having an inner diameter of 1.0 mm. When the needle was charged to a high DC voltage of positive polarity from the power supply, the polymer solution was ejected from the tip of the needle to generate fine fibers, and the resulting non-woven fiber mat was collected on the collector. The syringe pump was used to push the syringe so that a constant and stabilized mass flow of the polymer solution could be delivered during the electrospinning. In this study, a constant mass flow rate of 1.2 ml/h was applied at 10 kV potential, and the tip to collector distance was 8 cm. The 6F-DF polymer dissolved in THF at concentration of 9 wt%. After electrospinning, the fiber mats were placed on the glass plate and covered with a glass plate to flatten. Then, the fiber mat was placed on a hotplate with gradually increasing temperature from 50 to 200°C over 1 h and at 300°C for 100 min for thermal crosslinking reaction of the copolymer membranes.

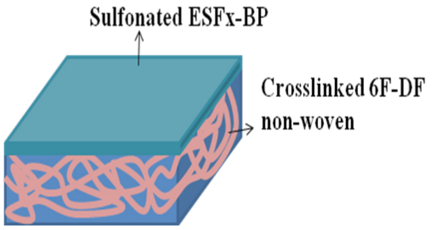

Fig. 3. Structure of the composite membrane.

### 2.5. Coating procedure of ESFx-BP onto crosslinked 6F-DF non-woven

DMAc was used as solvent for ESFx-BP. The concentration is 5 wt/vol % and the solutions were filtered with a 45 μm macro-filter and coated on the end-group 6F-DF fiber no-nwoven web with a brush as seen Fig. 3. After coating, the composite membrane was dried at room temperature for 1 h and the membrane was placed on a hotplate with gradually increasing temperature from 50°C over 6 h and vacuum dryed at 60°C for 6 h.

### 2.6. Characterization of the membrane

C-ESFx-BP and N-ESFx-BP membranes were analyzed by attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectroscopy (Jasco 460 Plus, Japan), which were recorded at a 4 $cm^{-1}$ resolution in the wave number range of 4000–700 $cm^{-1}$. The fiber morphology 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. $^1$H-NMR and $^{19}$F-NMR spectra were measured on a JEOL JNM-LA 400 WB FT-NMR in $CDCl_3$ and DMSO-$_{d6}$. Chemical shifts of $^1$H-NMR and $^{19}$F-NMR were referenced to tetramethysilane (TMS) at 0 ppm, deuterated chloroform at 7.25 ppm and deuterated DMSO at 2.5 ppm, respectively. The end-group crosslinkable copolymer was characterized by size exclusion chromatography (SEC, Waters M 77251, M510). The molecular weight (MW) of the copolymer was estimated using SEC with 4 columns (HR 0.5, HR1, HR3 and HR4, Waters Styragel columns run in series). The pore size of the columns is 50, 100, 103 and 104 Å, respectively with a refractive index detector at a flow rate of 1.0 mL/min, at 40°C and calibrated relative to polystyrene standards (American Polymer Standards Corp.) using THF as elution solvent. Glass transition temperatures ($T_g$) of the membranes were measured in the range of 40–350°C at a heating rate of 5°C/min using the differential scanning calorimeter (DSC) measurement. In addition, the ion exchange capacity (IEC) of the polymer membranes was investigated via the titration method. All membranes were thoroughly rinsed with deionized (DI) 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).

### 2.7. 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 from the volumetric flux ($V$) per unit time (t) through a membrane with active area of $A$:

$$P_w = \frac{V}{A \cdot t} \quad (1)$$

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

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \quad (2)$$

where $C_p$ and $C_f$ are the salt concentrations 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. Synthesis and characterization of 6F-DF copolymer

The synthesis of crosslinkable fluorinated poly(arylene ether) copolymers for electrospinning was prepared from an aromatic nucleophilic substitution (SNAr) polycondensation, and the copolymers were prepared with the appropriate molar ratio of 4,4′-(hexafluoroisopropylidene) diphenol (6F-BPA) with decafluorobiphenyl (DFBP). Crosslinkable copolymers are denoted as 6F-DF. Fig. 1 outlines a typical procedure for the synthesis of the end-group crosslinkable copolymer.

The synthesized copolymers were identified by $^1$H-NMR and $^{19}$F-NMR spectra (Fig. 4). The $^1$H NMR spectra of all copolymers include peaks corresponding to the protons of the crosslinkable moiety in the range of 4.51–4.43 ppm. Proton peaks due to the 6F-BPA moiety appeared in the range of 7.19–7.38 and 7.47–7.56 ppm. The integration of these proton signals is consistent with the theoretical values. In the $^{19}$F NMR spectra, the ortho and meta positions of fluorine peaks for DFBP are centered at –136.25 and –151.70 ppm, respectively. The disappearance of the para-positioned fluorine atom confirmed the formation of the polymers. And fluorine peak for 6F-BPA appeared in the range of –60.2 ppm.

FT-IR spectrum was used to analyze the functional groups of the polymer structure as shown in Fig. 5. The chemical structures of the crosslinked membranes were confirmed by FTIR-ATR spectra. In Fig. 5, the characteristic stretching vibration band of the aromatic C=C group can be observed at 1650 and 1607 $cm^{-1}$. The absorption bands at 932 $cm^{-1}$ were assigned to the $–CF_3$ group. In addition, the IR absorption bands at 795 $cm^{-1}$ were characteristic of aromatic –CH out of plane (OOP) peaks of phenyl moieties.

Molecular weight ($M^n$) and $M^w$ of the end-group crosslinkable copolymer were measured with 20,000 and 35,000 by SEC-GPC, respectively. Molecular weight distribution (MWD) of copolymer was 1.6.

### 3.2. End-group crosslinking of 6F-DF copolymer for electrospinning

DSC analysis was performed to study the effect of crosslinking time on the glass transition temperature ($T_g$) of the membrane and to observe the exact time to crosslink the membrane. DSC curves showed that the glass transition temperature increased with increasing crosslinking time of the membrane (Fig. 7). Additionally, an intense exothermic peak was seen as the reaction peak of ethynyl moiety [28–31] around 300°C. This indicates

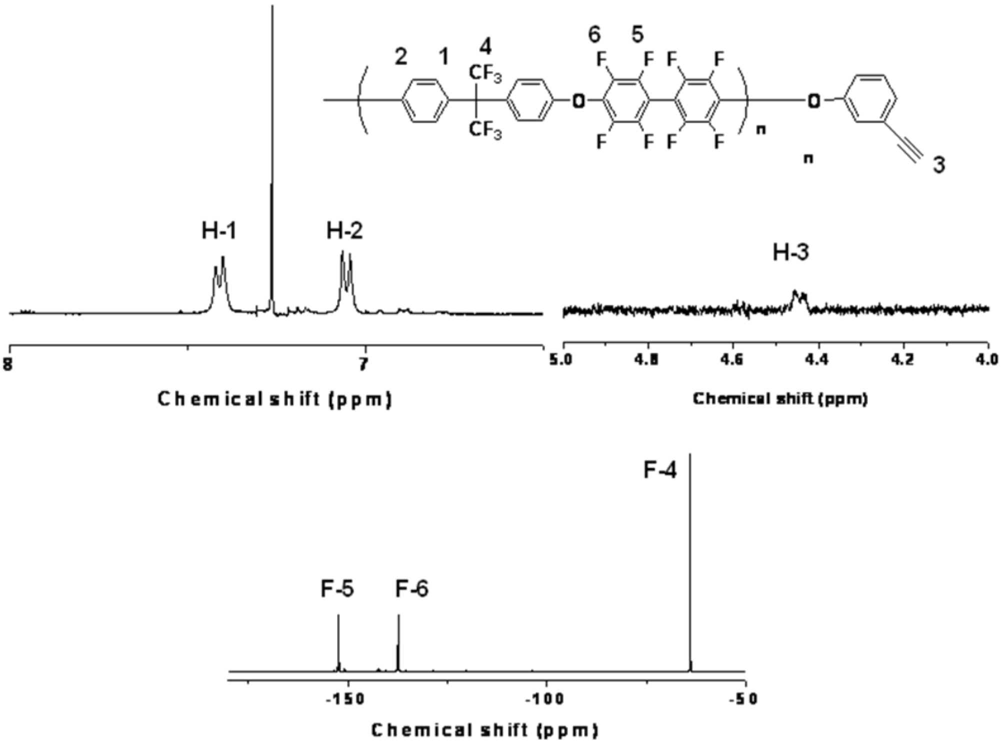

Fig. 4. $^1$H NMR and $^{19}$F NMR spectra of 6F-DF.

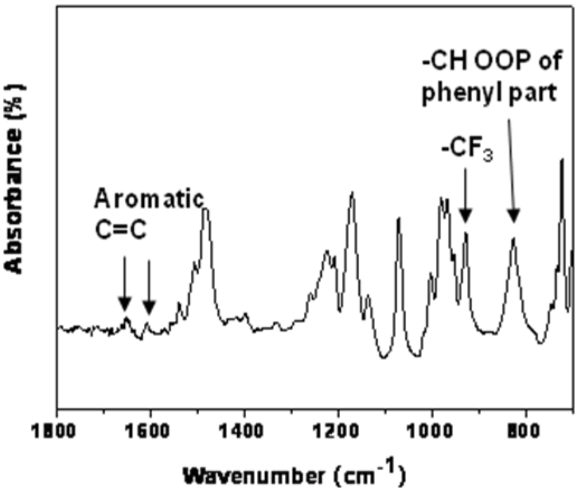

Fig. 5. ATR-FTIR spectrum of 6F-DF copolymer.

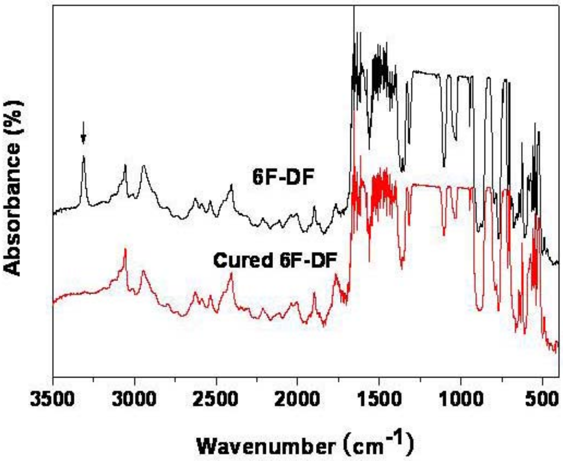

Fig. 6. FT-IR spectra of 6F-DF and cured 6F-DF.

that crosslinkable ethynyl groups of polymer chain ends react with each other around 300°C, increasing the crosslinking time of the membrane. After crosslinking the membrane for 6 h, this intense exothermic peak disappeared completely. The observed results were supported by the previously reported papers. [27,31] The changes for crosslinking of ethynyl moieties were comfirmed using the exothermic peaks and the glass transition temperature ($T_g$) observed by DSC analysis and using the ethynyl (acetylenic) C–H peak assignment around 3310 cm$^{-1}$ from FT-IR measurement during the curing process as shown Fig. 6. The acetylenic C–H peak at 3308 cm$^{-1}$ appeared after 3-ethynylphenol was attached to 6F-DF at the end and completely disappeared after curing at 300°C for 6 h.

Fig. 8 shows the view of scanning electron microscopy (SEM) for the surface of non-woven webs with electospinning. Figs. 8a and 8b exhibit the non-crosslinking non-woven web surface, which was partially aligned smooth. The

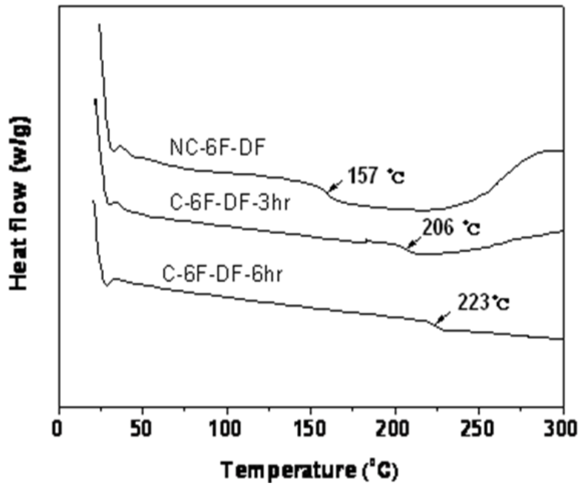

Fig. 7. DSC curves of cross-linked and non-crosslinked 6F-DF non-woven webs.

diameter was in the average range of 1–2.5 μm and the diameter distribution was narrower than the crosslinked non-woven web. The crosslinked non-woven web surface is shown in Figs. 8c and 8d, which was also aligned and had a smooth surface. The thickness of the crosslinked non-woven web was in the range of 0.5–2 μm, which was thinner than that of the non-crosslinked non-woven web. In addition, the diameter distribution was broader after crosslinking than before crosslinking. This indicates that rearrangement of copolymer chains resulted the thinner fiber web because the crosslinking temperature (300°C) was higher than $T_g$ temperature (223°C).

### 3.3. Composite membranes

The composite membranes were prepared by brush coating polymer solutions in DMAc onto end-group crosslinked 6F-DF non-woven as shown in Fig. 3. Fig. 9 presents a surface (SEM) image of C-ESF40-BP composite membrane. The surface image exhibits that the porous structure of end-group crosslinked 6F-DF non-woven web disappeared after polymer solution coating and the surface was smooth without small-sized pores, indicating defect-free coating. The change of IEC value of ESFx-BP copolymer influences the salt separation performance and permeability of the composite membrane. Theoretically, ion exchange capacity (IEC) increases as a function of DS [32,33]. IEC value of C-ESFx-BP membranes shows in the range of 0.59–1.16 meq/g with increasing the DS of the membranes as summarized in Table 1.

### 3.4. Salt rejection and permeability

Table 1 shows the water permeability and sodium chloride (NaCl) rejection of C-ESFx-BP membranes under the DS variation of 20–60%. For a desalination membrane, the membrane should have high water permeability and low salt permeability. Generally, water permeability even increases salt rejection as increasing DS of the membrane [21,33]. As summarized in Table 1, C-ESFx-BP shows the increase of NaCl rejection as DS decreases, while permeability decreases due to the decrease of their hydrophilic-

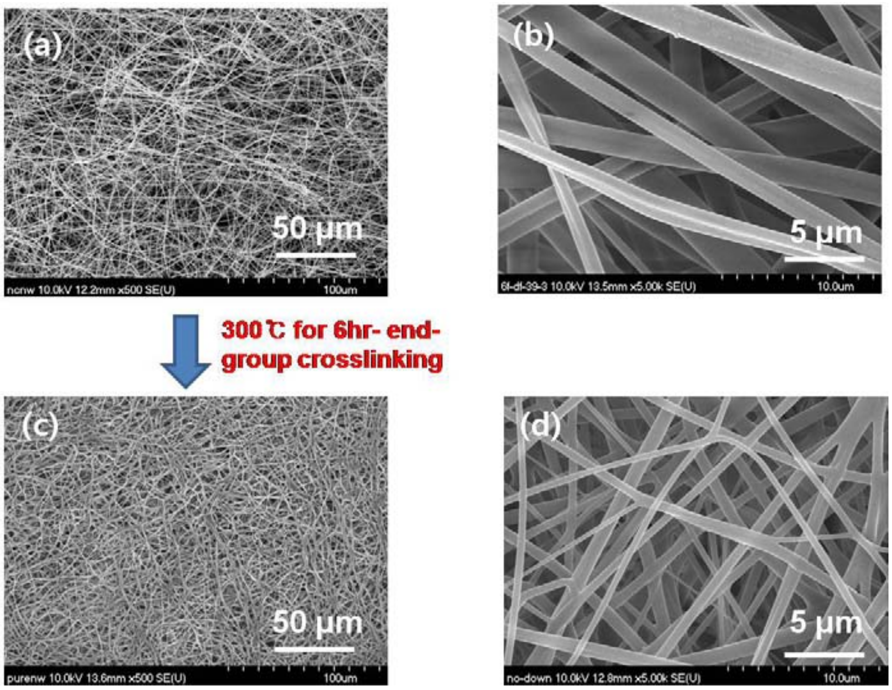

Fig. 8. (a) Before crosslinking of electrospinning mat (b) magnification of before crosslinking of electrospinning mat (c) after crosslinking of electrospinning mat (d) magnification of after crosslinking of electrospinning mat.

Table 1
NaCl rejection and water permeability of the C-ESFx-BP series

| Polylmer membrane[a] | Cal. DS (%) | IEC (meq/g) | | NaCl rejection (%)[d] | Water permeability (L/m$^2$·h)d |
|---|---|---|---|---|---|
| | | Cal.[b] | Obs.[c] | | |
| C-ESF60-BP | 60 | 1.16 | 1.16 | 46.5 | 41.36 |
| C-ESF40-BP | 40 | 0.79 | 0.80 | 79.3 | 27.57 |
| C-ESF20-BP | 20 | 0.60 | 0.59 | 81.3 | 6.89 |

[a] C-ESFx-BP are crosslinked membrane of K$^+$ form, respectively.

[b] Calculated from the feed monomer ratio {IEC = (1000 / MW repeat unit) × degree of sulfonation × number of –SO$_3$H, 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 psig ; Temperature = 25°C.

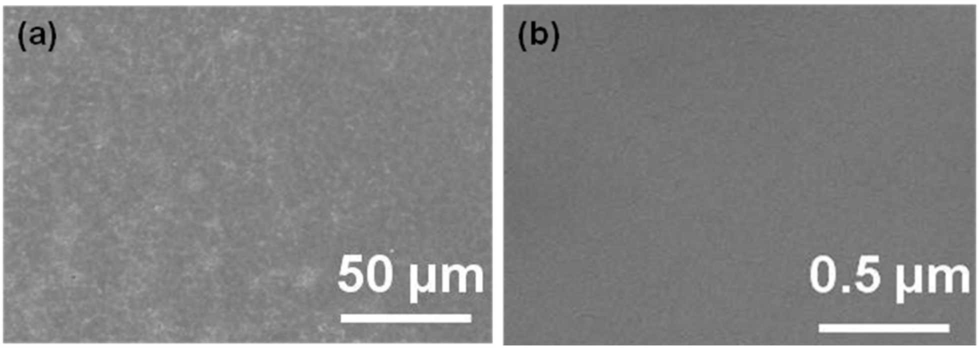

Fig. 9. (a) Surface of composite membrane (b) magnification of (a).

ity [21,33]. For the C-ESFx-BP membranes, NaCl rejection changes from 46.5% for IEC value of 1.16 to 81.3% for that of 0.59 meq/g, while the water permeability varies from 41.36 L/m$^2$·h for IEC value of 1.16–6.89 L/m$^2$·h for IEC value of 0.59 meq/g.

Fig. 10 shows the salt rejection of the C-ESF40-BP composite membrane. The order of salt rejection was as follows: Na$_2$SO$_4$ (88.4%), NaCl (79.3%), MgSO$_4$ (70.2%), Mg$_2$Cl$_2$ (62.3%).The order of salt rejection corresponds well for the negatively charged membranes [33]. Salt rejection generally increases with increasing the anion valance. Considering Na$_2$SO$_4$ and NaCl molecules, the negatively charged ions are SO$_4^-$ and Cl$^-$. The salt with SO$_4^{2-}$ shows a higher rejection rate than that with Cl$^-$ because the repulsion between the sulfonic groups is larger than that between the chlorine groups as well as the size of SO$_4^-$ is bigger than that of Cl$^-$.

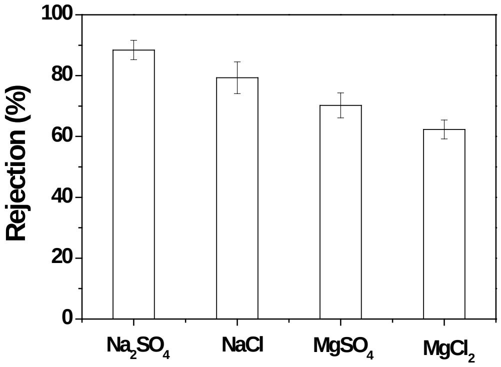

Fig. 10. Salt rejection of the C-ESF40-BP composite membrane.

For MgCl$_2$, the rejection was lower because of the positively charged Mg$^{2+}$. Sulfonic groups allow positively charged ions to transport [33].

## 4. Conclusions

A new type of desalination composite membrane was prepared by brush coating a sulfonated poly(arylene ether) layer on top of the non-woven web made by electrospinning. With electrospinning, 6F-DF non-woven web was prepared by thermal crosslinking at 300°C. NaCl rejection and permeability were controlled as the different sulfonation group ratio of poly(arylene ether). The composite membrane was characterized by salt solutions as sodium chloride, sodium sulfate, magnesium sulfate and magnesium chloride. The rejection for salts was in the order of Na$_2$SO$_4$ > NaCl > MgSO$_4$ > MgCl$_2$.

## Acknowledgment

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