Preparation, characterization and performance of poly(arylene ether sulfone)/modified silica nanocomposite reverse osmosis membrane for seawater desalination

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HIGHLIGHTS

• We synthesized sulfonated poly(arylene ether sulfone) material containing amine groups.
• We synthesized aminated hyper branched silica nanoparticle.
• The aPES/HBP nanocomposite membrane was prepared using the interfacial polymerization procedure with synthesized materials.
• The aPES and HBP materials increased chlorine resistance and water flux of membrane.

In this paper, composite reverse osmosis (RO) membranes made from sulfonated poly(arylene ether sulfone) containing amino groups (aPES) and hyper-branched aromatic polyamide-grafted silica (HBP-g-silica) were prepared, with the aim of enhancing chlorination resistance and improving membrane performance. The performance of the RO membranes containing aPES and HBP-g-silica was evaluated; the salt rejection and water flux were 96% and 34 L/m²/h, respectively. After the chlorination test, the salt rejection decreased by only 14% and the water flux increased by 4 L/m²/h. The aPES/HBP-g-silica significantly modified the three-dimensional polyamide (PA) network structures and contributed to the high performance because of the chain stiffness of the copolymer with a high degree of cross-linking in the RO membranes. Therefore, the aPES and HBP-g-silica, which helped improve water permeability, also protected the active layer structure from degradation and enhanced the chlorine resistance of the RO membrane.

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1. Introduction

Globally, the scarcity of water resources and the lack of access to fresh water are two of the most serious problems encountered. Reverse osmosis (RO) is an important available membrane technique, which is widely used for water purification processes such as desalination [1]. However, the currently available polymeric membranes are often limited by the trade-off between the water flux and selectivity [2–5]. RO membranes with higher water flux, improved salt rejection, and better fouling resistance are needed in order to reduce both the capital and the energy costs entailed in producing a highly purified product.

After the development of polymeric RO membranes, the design of thin-film composite (TFC) membranes was a significant advancement in membrane technology. TFC membranes are composed of an upper polyamide active layer fabricated via interfacial polymerization (IP) of m-phenylenediamine (MPDA) in an aqueous solution and trimesoyl chloride (TMC) in an organic solution, a porous middle polysulfone (PS) ultr filtration (UF) support, and a non-woven fabric base [6–11]. These membranes have been used widely in commercial water desalination processes [12,13]. Continual efforts have been devoted to the development of porous supports, polymer reactants, and membrane structures [14–17] that improve either the membrane water flux or the salt rejection for specific applications, or the fouling resistant and chemical/thermal/mechanical stability of the membranes [18–22]. Polyamide membranes with enhanced water flux and reasonable salt rejection have been prepared through the addition of alcohols, sulfur-containing compounds, or monohydric aromatic compounds in aqueous solutions [23–25]. Although these methods have their advantages, the improvement of performance is needed for high water flux and chlorine resistance.
Sulfonated poly(arylene ether sulfone) (PES) materials are one of the proper substitution materials of membrane. The sulfonation of PES yields the corresponding materials with improved hydrophilicity and higher water flux [26]. The sulfonated poly(arylene ether sulfone) (sPES) exhibits good film-forming properties and excellent chemical stability. In addition, they showed excellent chlorine resistance, as demonstrated by the fact that their water permeability and salt rejection remained unaffected even after continuous exposure to chlorine solution [27].

Organic–inorganic nanocomposite membranes that can improve membrane performance have attracted considerable interest. Recently, advances in nanocomposite membrane technology have led to the development of various nano-materials, such as zeolite, silica, and metal oxide nanoparticles. Many studies have demonstrated that nanocomposite membranes may enhance the membrane performance such as permeability, selectivity and durability compared with that of a pure polyamide membrane [28–30]. Some studies described about nanocomposite RO membranes which have been developed by incorporating various nanoparticles into the active layer of membrane [31].

Many studies have demonstrated that thin-film nanocomposite (TFN) membranes may significantly enhance the membrane properties such as permeability, selectivity and stability in various membrane separation processes [21,22]. For example, TFN reverse osmosis (RO) membranes have been developed by incorporating pure metal, metal oxide and zeolite nanoparticles into the polyamide (PA) rejection layer [23].

However, nanocomposite technology of RO membrane is still early days. The incorporated nanoparticles might have provided a direct path for water transport or modified the membrane network structure, thereby increasing water permeability a little. Herein, we describe the synthesis of a membrane material consisting of a sulfonated poly(arylene ether sulfone) material containing amino groups (aPES). Furthermore, modified nanoparticles were synthesized to improve the effect of nanoparticles in the RO membrane. A nanocomposite TFC RO membrane containing aPES and hyper-branched polyamide grafted onto silica (HBP-g-silica) was prepared using the IP method. The synthesized materials and fabricated RO membranes were characterized by Fourier transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). The chlorine resistance of the RO membrane was also evaluated. The separation performance of the RO membrane was measured with a 32,000 ppm sodium chloride (NaCl) solution.

2. Materials and methods

2.1. Materials

4,4′-Dichlorodiphenyl sulfone (DCDPS), m-aminophenol, silica nanoparticles with an average diameter of 7 nm, 1,3-aminopropyl triethoxysilane (APS), 3,5-diaminobenzoic acid (DABA), 4-(4,6-dimethoxy-1,3,5-triazine-2-yl)-4′-4-methyl-morpholinium chloride (DMTMM), and potassium carbonate (K2CO3) were purchased from TCI, Korea. Toluene, methanol, and ethanol were of analytical grade and purified. Toluene, methanol, and ethanol were of analytical grade and purified. TMC in cyclohexane (used as the organic phase) were obtained from Aldrich. The solvents, toluene, methanol, and ethanol were of analytical grade and purchased from TCI, Korea.

2.2. Synthesis of sulfonated poly(arylene ether sulfone) material containing amino groups

The 3,3′-disulfonated-4,4′-dichlorodiphenyl sulfone (SDCDPS) material was synthesized according to previously published methods [32]. The aPES material was synthesized based on the method reported earlier [33]. The mixture of m-aminophenol (6.65 g), K2CO3 (9.27 g), DMAc (90 mL), and toluene (37.5 mL) was stirred while heated at reflux (145 °C) for 6 h. SDCDPS (15 g) was added to the mixture along with more DMAc (15 mL), and the reaction mixture was stirred while heating at 170 °C for 20 h. The reaction solution was filtered to remove the salt, and then cooled down to room temperature. The synthesized aPES was isolated by precipitation in ethyl acetate solution, yielding a very light brown solid.

2.3. Synthesis of HBP-g-silica

The following experimental procedures were used for the synthesis of HBP-g-silica. A mixture of silica nanoparticles (5 g), toluene (150 mL), and APS (5 g) was stirred at reflux temperature for 8 h under a nitrogen atmosphere. The APS-silica particles were filtered and extracted with ethanol for 24 h to remove excess silane adsorbed on the silica. The light brown powder obtained was then dried overnight at 60 °C under vacuum conditions. A mixture of APS-silica (5 g), DABA (15.2 g), DMTMM (2.76 g), and methanol (500 mL) was stirred for 24 h at room temperature under a nitrogen atmosphere. The product, HBP-g-silica, was filtered and extracted with methanol for 12 h. Finally, the HBP-g-silica was washed with methanol and dried overnight at 60 °C under vacuum.

2.4. Fabrication of thin-film composite membrane

Porous PS UF membranes (UE50, Trisep Corporation, U.S.A.) were used as support membranes. Different types of RO membranes were fabricated by interfacial polymerization. Table 1 describes the fabrication and inorganic particle contents of the RO membranes. First, the inorganic particles, aPES, MPDA, and TEA were mixed mechanically. The inorganic particle content in the mixture was 2% (w/w). The aqueous solution was then prepared by diluting the mixture containing the inorganic particles with distilled water. The content of the mixture in aqueous solution was fixed at 1% (w/v). The aqueous solution was poured over the support membrane and allowed to soak for 5 min. The excess solution was drained from the surface using a rubber roller until no liquid remained. Subsequently, the membrane was placed into an organic-phase solution of 1% (w/v) TMC in cyclohexane for 1 min. After removal of the excess organic-phase solution, the membrane was heated in an oven at 60 °C for 1 min.

2.5. Characterization

The molecular structure of aPES was identified by elemental analysis of C, H, and N. 1H nuclear magnetic resonance (NMR) spectra of the products were obtained at 300 MHz on a Varian Mercury 300 spectrometer using dimethyl sulfoxide-δ6 (DMSO-δ6) as a solvent. The synthesized HBP-g-silica on the RO membrane was characterized by Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectra were recorded using a Bomen DA-8 spectrometer. TGA (TGA Build 36, TA instruments, Korea) was performed at a heating rate of 20 °C/min in N2 (40 mL/min). The membrane surface was imaged by SEM (S-4300, Hitachi, Japan). The hydrophilicity of the membranes was evaluated from contact-angle measurements (Phoenix–300, SEO, Korea).

Table 1

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Polyfunctional amine</th>
<th>Inorganic particles</th>
</tr>
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<tbody>
<tr>
<td>PA</td>
<td>MPDA</td>
<td>–</td>
</tr>
<tr>
<td>aPES</td>
<td>aPES-MPDA (1:1)</td>
<td>Neat silica</td>
</tr>
<tr>
<td>aPES/Si</td>
<td>aPES-MPDA (1:1)</td>
<td>HBP-g-silica</td>
</tr>
<tr>
<td>aPES/HBP</td>
<td>aPES-MPDA (1:1)</td>
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</table>

Types of RO membranes and mixture component of aqueous-phase solution.
The membrane was placed in the cross-flow test-cell apparatus with the active layer facing the incoming feed. The salt rejection was calculated by using the following equation:

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

The salt concentrations in the feed solution \(C_{\text{feed}}\) and permeated solution \(C_{\text{permeated}}\) were determined by a conductivity meter (PC 650, EUTECH). Each test was conducted using 32,000-ppm NaCl solution at room temperature at a pressure of 55 bar. The water permeation was measured by the amount of water permeation flux in terms of liters per square meter per hour (L/m²/h). The chlorine resistance of the RO membrane was evaluated by comparing the measurements (e.g., salt rejection and water permeation) before and after exposure to hypochlorite (500 ppm NaOCl solution) for 1 h at room temperature. A structure of the cross-flow cell apparatus is shown in Scheme 1.

The percentage of the grafting efficiency of amide groups onto HBP-g-silica was evaluated by TGA. As shown in Fig. 3, two consecutive weight-loss steps were observed in the thermogram of HBP-g-silica. The weight loss from approximately 270 to 550 °C corresponds to the decomposition of amino groups that were grafted onto the silica surface. The weight losses from 270 to 350 °C and from 450 to 550 °C are due to the decomposition of the main chain and cross-linked backbone chain, respectively. From these results, it was determined that 59.5 wt.% of amino groups were grafted on the HBP-g-silica.

### Results and discussion

#### 3.1. Synthesis and characterization of materials

The aPES was synthesized via aromatic nucleophilic reaction chemistry using an SDCDPS intermediate and m-aminophenol as a nucleophile in the presence of K₂CO₃ in DMAc. Toluene was used as an azeotroping agent to remove water. The reaction sequence for aPES is presented in Scheme 2.

The \(^1\)H-NMR spectrum of aPES is shown in Fig. 1. The aromatic amine proton shows a peak at 5.23 ppm, which is due to the amine functional group in aPES. The assignments of all the protons are given in Fig. 1, and these agree with the proposed molecular structure of aPES.

Organic/inorganic conjugation was examined in HBP-g-silica. The FT-IR spectra shown in Fig. 2 were used to identify the presence of related bonds with inorganic materials. The band at 1610 cm\(^{-1}\) is due to the amide I band (C=O stretch). A relatively strong bending band is shown at around 1550 cm\(^{-1}\), and is assigned to the secondary amide structure because of its combination of a C-N stretching band and N-H bending band. Also, the bands at 3460 cm\(^{-1}\) are caused by the grafting of the functional amine groups onto the HBP-g-silica. These results verify that HBP-g-silica functional nanoparticles were prepared successfully.

The percentage of the grafting efficiency of amide groups onto HBP-g-silica was evaluated by TGA. As shown in Fig. 3, two consecutive weight-loss steps were observed in the thermogram of HBP-g-silica. The weight loss from approximately 270 to 550 °C corresponds to the decomposition of amino groups that were grafted onto the silica surface. The weight losses from 270 to 350 °C and from 450 to 550 °C are due to the decomposition of the main chain and cross-linked backbone chain, respectively. From these results, it was determined that 59.5 wt.% of amino groups were grafted on the HBP-g-silica.

#### 3.2. Characterization of membrane

FT-IR spectroscopy was used to identify the presence of functional groups in the active layers of the TFC membranes. Fig. 4 shows that
various peaks are observed on the aPES and aPES/HBP spectra compared with the PA spectrum, which shows only a few amide bond peaks. The peaks from aromatic benzene rings of the aPES spectrum appeared in the aPES spectrum. The peaks in the aPES and aPES/HBP FT-IR spectra are assigned as follows: the peak at $1610 \text{ cm}^{-1}$ corresponds to chemical bonding in the amide I band to amide (N–H) deformation and C–C ring stretching vibrations. The peak at $1550 \text{ cm}^{-1}$ corresponds to the amide II band and the semi-aromatic polyamide. The changes in the IR peaks of the amide bond means that aPES material was successfully introduced into membrane active layer, chemically. The presence of HBP-g-silica is well reflected in the strong bands at 675, 740 and 790 cm$^{-1}$. When the HBP-g-silica was added, the peaks of amide I ($1610 \text{ cm}^{-1}$) and amide II ($1550 \text{ cm}^{-1}$) bonds were expanded. Thus, the FT-IR spectra confirm that HBP-g-silica was chemically combined with membrane active layer. The presence of HBP-g-silica may change the matrix of the active layer into a firm and complex structure on the RO membrane.

XPS analysis is well appropriated for investigating the top active layer of membrane, as it probes only a short distance (10–90 Å) into the surface of the membrane. The elemental quantitative

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**Fig. 1.** $^1$H NMR spectrum of aPES in DMSO-d$_6$.

**Fig. 2.** FT-IR spectra of neat silica and HBP-g-silica.

**Fig. 3.** TGA spectra of neat silica and HBP-g-silica.

**Fig. 4.** FT-IR spectra of PA, aPES, and aPES/HBP.
composition of the top active layer can be calculated from the experiment results. The TFC RO membranes consisted of a thin active top layer of polyamide deposited on a polysulfone porous support. Thus, the chemical composition obtained through XPS analysis was derived only from the near surface, and the polysulfone layer was not obtained. The relative atomic concentration ratios of polyamide elements (C, O, and N) are shown in Table 2.

N existed in the –NH₂ groups of HBP-g-silica nanoparticles from the aPES/HBP membrane, was supported by the O/N (0.91) and N/C (0.26). These results clearly illustrate the existence of aminated nanoparticles in the near surface of membrane. The results also show the presence of a functional –NHCONH– bond in the near-surface top layer. The near surface top layer of the aPES/HBP membrane contained amide (–NHCONH–) groups and aromatic groups according to the XPS and FT-IR results.

The surfaces of the RO membranes before and after chlorine exposure were characterized using SEM. SEM images of the fresh and chlorinated membrane surfaces of PA, aPES, and aPES/HBP are provided in Fig. 5. As shown in Fig. 5(a), (b), and (c), the surfaces of the fresh membranes appear to have regular patterns. The micro-scale surface morphology of aPES/HBP shows three-dimensional structures due to steric conformation with HBP-g-silica particles. After chlorine exposure, the membrane surfaces are flat and smooth because of the degradation of the membrane polymer matrix. Large, round deadly defects appear on PA, while some of linear and thin defects appear

<table>
<thead>
<tr>
<th></th>
<th>C%</th>
<th>O%</th>
<th>N%</th>
<th>O/C</th>
<th>N/C</th>
<th>O/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>aPES/Si</td>
<td>74.13</td>
<td>18.21</td>
<td>7.66</td>
<td>0.25</td>
<td>0.10</td>
<td>2.38</td>
</tr>
<tr>
<td>aPES/HBP</td>
<td>66.72</td>
<td>15.84</td>
<td>17.44</td>
<td>0.24</td>
<td>0.26</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Fig. 5. SEM surface images of (a) PA, (b) aPES, and (c) aPES/HBP before chlorine exposure, and (d) PA, (e) aPES, and (f) aPES/HBP after chlorine exposure.
on aPES. The surface features of aPES/HBP become denser and more compact than those of the other materials, and the degradable active layer is sparsely dotted with HBP-g-silica particles.

3.3. RO performances and chlorine resistance of membranes

Fig. 6 shows the results of the salt-rejection and water-flux performances of the RO membranes. The performances of the RO membrane, PA, aPES, aPES/Si, and aPES/HBP were evaluated with 32,000-ppm NaCl solution using the cross-flow cell apparatus with an applied pressure of 55 bar at room temperature. The performance of the RO membrane fluctuated at the beginning of the measurement, but reached steady state after 2 h. After chlorine exposure, the lower performance of the membrane resulted from the damaged membrane surface by chlorine. All of performance values in Fig. 6 were measured five times for one sample and the average value was used.

In Fig. 6, the PA membrane shows a salt rejection of 98% and water flux of 22 L/m²/h. The salt rejection of PA was higher than those of aPES, aPES/Si, or aPES/HBP. However, the membrane water permeations of the aPES membranes (aPES, aPES/Si, and aPES/HBP) were higher than that of the PA membrane, whereas salt rejection was about the same level. In the field of desalination membrane, there is a tendency that water flux increase when salt rejection decrease. By comparing aPES membrane with PA membrane, water flux increased (22 to 31 L/m²/h) with salt rejection decreasing (98 to 94%) as mentioned above. However, aPES/Si and aPES/HBP membrane performance changes did not follow general tendency. Especially, water flux of aPES/HBP was remarkably improved although salt rejection was almost the same with PA membrane. HBP-g-silica nanoparticles make membrane active layer dense and hydrophilic. Because of additional amide bond from HBP-g-silica, salt rejection increased, as confirmed by the FT-IR result.

The aPES and HBP-g-silica are effective in improving the hydrophilicity of the active layer of the TFC membrane. Sulfonic groups in the aPES material provided additional hydrophilic domains to the RO membranes, which may have increased water flux. Improved water flux of the aPES/HBP membranes was due to the hydrophilicity of the functional groups, such as the sulfonic acid groups (–SO₃H) in the material. The hydrophilicity of the membrane was evaluated through contact-angle measurements. Table 3 shows the contact angles of the composite TFC membranes. On hydrophilic surfaces, water droplets exhibit contact angles from 0° to 90°. As shown in Table 3, the water is strongly attracted to the aPES/HBP membrane surface with a contact angle of 50.1°, while the contact angle of the
PA membrane is 61.2°. From these results, the hydrophilicity of the TFC membrane was found to increase clearly upon the addition of aPES and HBP-g-silica, which means that materials have an impact on the membrane hydrophilicity.

After the chlorine resistance test of the aPES/HBP membrane, the salt rejection decreased to only 14% and the water flux increased to 4 L/m²·h, while in the PA membrane, the salt rejection decreased to 31% and the water flux increased to 26 L/m²·h. The smaller damage area of aPES/HBP compared with the other membranes contributed to the low performance degradation in salt rejection and water flux. Fig. 6 clearly shows that the chlorine resistance of aPES/HBP is better than those of PA, aPES, or aPES/Si. The intermolecular hydrogen bonding is enhanced by the chemical combination between the HBP-g-silica and membrane active layer structure. This will impede the replacement of hydrogen with chlorine on the amide groups of the aromatic polyamide membranes. Furthermore, the amino groups on the HBP-g-silica and TMC are combined through the formation of additional amide bond in the RO membrane active layer. These amide bonds and unreacted amino groups of the HBP-g-silica protect the active layer from chlorine. Therefore, the HBP-g-silica protects the PA structure from degradation through chlorine exposure. Free amine groups in HBP-g-silica surface are much more sensitive to chlorine than the amide bonds in the membrane active layer. Those situations explain the high chlorine resistance of the aPES/HBP membrane, as shown in Fig. 3 and Scheme 3.

The chlorine resistance of aPES/HBP was superior to that of PA, aPES, and aPES/Si membranes, possibly due to the large number of NH₂ groups near surface of active layer, as confirmed by the XPS analysis (Table 2). Therefore, the aminated function HBP-g-silica nanoparticles protect the membrane active layer from degradation through chlorine.

In order to investigate the durability of membranes, long-term test carried out with 30-ppm NaOCl solution. As shown in Fig. 7, performance degradation of both membranes was observed. However, the performances of aPES/HBP membrane exhibited more stable than PA membrane. Salt rejection of aPES/HBP membrane was maintained more than 90% after 650 h, but salt rejection of PA membrane was decreased less than 70%. Similar tendency was also observed in water permeation performance. Water flux of aPES/HBP membrane was more stable than PA membrane. In comparison with PA membrane, the improved durability of aPES/HBP membrane was verified (Table 3).

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle (°C)</th>
</tr>
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<tbody>
<tr>
<td>PA</td>
<td>61.2</td>
</tr>
<tr>
<td>aPES</td>
<td>55.6</td>
</tr>
<tr>
<td>aPES/Si</td>
<td>50.7</td>
</tr>
<tr>
<td>aPES/HBP</td>
<td>50.1</td>
</tr>
</tbody>
</table>

4. Conclusions

The chlorine tolerance of an aPES/HBP-g-silica nanocomposite TFC membrane was presented in this study. The FT-IR spectra and TGA results of HBP-g-silica showed that amine groups were grafted onto the silica surface, and amide bonds were successfully conjugated between aPES and HBP-g-silica. The aPES/HBP composite membrane was prepared using the procedure of interfacial polymerization. The salt rejection and water permeation of aPES/HBP were shown to be 97.7% and 34.5 L/m²·h, respectively. After chlorine exposure, aPES/HBP showed a good performance, with a lower reduction in salt rejection and increase in water permeation than for PA. The different properties of the membranes were characterized by FT-IR spectroscopy and SEM. After chlorine exposure, aPES/HBP showed a decrease in salt rejection of 15% and an increase in water permeation of 4 L/m²·h. Therefore, the incorporating HBP-g-silica nanoparticles in active layer significantly modified the structure of active layer and contributed to the improved membrane performances. Functional amino groups of HBP-g-silica nanoparticle and additional amide bond of active layer from HBP-TMC effectively protect the membrane surface from chlorine attack in water and improve the hydrophilicity of membrane.

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