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A novel sulfonated poly(arylene ether ketone) reverse osmosis membrane: Effect of casting condition on separation characteristics

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ABSTRACT

A novel sulfonated poly(arylene ether ketone) (sPAEK) reverse osmosis (RO) membrane was prepared. This sPAEK is composed of a mechanically strong hydrophobic group and an anionic hydrophilic group wherein water is soluble. Since this poly(arylene ether ketone) showed a high chlorine resistance, it could be one of the candidate materials for a practical desalination RO. After this polymer was coated on a porous polysulfone support, a post-treatment was carried out to densify the morphology of the separating layer. It was investigated how the coating condition can affect the separation phenomena in terms of a water flux and a rejection of salts. As the weight % of sPAEK increased, the water flux decreased and the salt rejection increased. A post-treatment of the RO membrane significantly improved the separation characteristics.

Keywords: Reverse osmosis membrane; Poly(arylene ether ketone); Salt rejection; Water flux

1. Introduction

In the past decades, the reverse osmosis (RO) membranes have been utilized for separation of water from the saline water [1–2]. The life time of the commercial RO membranes made of either cellulose acetate (CA) or polyamide (PA) is relatively short because the polymer material is not chemically stable against the attack of chlorine ions abundantly available in saline water [3–4]. Although commercial polyamide PA membranes show excellent RO performance, low chlorine stability can reduce the membrane life- time. On the other hand, the sulfonated copolymer membranes show a strong tradeoff relationship between a salt rejection and a flux, depending upon sulfonation degree and membrane structure. The sulfonated copolymer membranes exhibit a high water flux and a reasonable salt rejection. While commercial polyamide PA membranes have suffered from low chlorine tolerance over a broad pH range (4–10), these sulfonated copolymer membranes show excellent chlorine tolerance as well as good fouling resistance against protein and oily water[5]. Park et al. [6] (2008) also reported that the sulfonated poly(arylene ether sulfone) RO membrane showed the excellent resistance to chlorine[6]. As a result, a new polymer material is needed to be developed for a RO membrane which possibly shows a high chlorine tolerance.

Recently, sulfonated poly(arylene ether sulfone) has been synthesized as a candidate material for the chlorine resistant RO membrane [7]. Since the sulfonated ions on the polymer tends to take up water and swell, the sulfonated poly(arylene ether sulfone) was crosslinked for prevention of swelling. After crosslinking, the membrane showed 97% salt rejection compared to 73% rejection without crosslinking at the expense of slight loss for water permeability [8].

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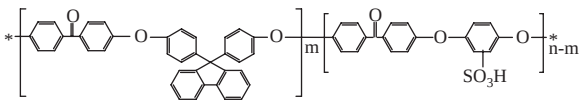

Fig. 1. Chemical structure of sPAEK.

Sulfonated poly(arylene ether ketone) (abbreviated to sPAEK) showed an excellent physical properties: thermal stability, chemical resistance, mechanical strength and good solubility in a solvent [9]. The water uptake of sPAEK is comparable to PA and CA. sPAEK is composed of two important polymer blocks: a hydrophilic part and a hydrophobic part. The hydrophobic part is known to be responsible for the chlorine tolerance.

In this study, sPAEK is coated as a thin film on the porous ultrafiltration membrane of polysulfone for a RO application. The effect of the weight % of sPAEK in a casting solution was investigated in terms of morphology of the RO membrane and the separation behavior. After casting, the thin film is post-treated with a strong alkaline aqueous solution to reduce a water swelling and to enhance the rejection of salt. The effects of both casting condition and post-treatment are investigated in terms of the flux of water and the rejection of salt through the prepared RO membrane.

2. Experimental

2.1. Materials

Synthesized sPAEK was obtained from LG Chemical Company and it was used as received. Fig. 1 represents the chemical structure of sPAEK. Formic acid was purchased from Samchun Chemical Co. as a solvent for sPAEK and used as received. NaOH was obtaind from Samchun Chemical Co. NaCl was obtained from Junsei Chemical Co. The ionized water was prepared in the laboratory. The ultrafiltration membrane of polysulfone was obtained from Woongjin Coway Co.

2.2. Preparation of RO membrane

A sPAEK powder was dissolved at 80°C in 85 % formic acid and vigorously stirred for 30 minutes until a homogeneous solution was prepared. The weight % of sPAEK was varied from 0.5, 1.0 and 3.0 wt%. The solution was cast on the pretreated porous polysulfone ultrafiltration membrane using a doctor blade (Model JP/YBA-3, Yoshimitsu). The polysulfone was immersed in 85 wt% formic acid for 2 min and used as a support for casting. The cast film was dried at the room temperature for 24 hours and it was stored in deionized water until it was used for desalination

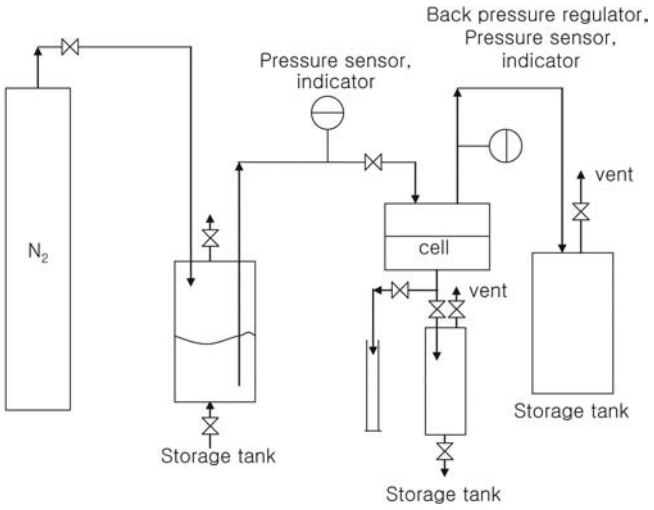

Fig. 2. Schematic flow diagram of membrane test apparatus.

experiment. The post- treatment of the sPAEK membrane was carried out by immersion in 0.5 N NaOH solution for 2–4 h. The surface morphology of the membrane was observed with a field emission scanning electron microscope (SEM, JSM-7000F, JEOL) and the roughness of the membrane surface was examined using an atomic force microscope (AFM, AUTO PROBE UP, Park Scientific Instrument).

2.3. Measurement of flux and salt rejection

Fig. 2 shows a schematic diagram of RO membrane test apparatus. The sPAEK membrane was cut in size of 49 mm in diameter and placed in a membrane cell for measurement of the flux and the salt rejection. The pressure was applied using a highly pressurized N_2 gas. The pressure was controlled using a back pressure regulator. After the upper part of the membrane cell is filled with the aqueous salt solution, the volumetric flow rate of the permeate and the rejection of salt were measured. The concentration of NaCl as a model of salt was 2,000 mg/L. The applied pressure was changed from the atmospheric pressure to 53.2 atm with a constant interval so that the flux and the salt rejection were measured at a different applied pressure. After the system was in the steady state, the permeate samples were collected during the regulated time. It usually took longer than 30 min to reach the steady state. The concentration of NaCl was measured with an electrical conductivity meter (Model CON-11, Futech Instrument).

3. Results and discussion

Fig. 3 shows the typical water flux through the sPAEK RO membrane at the applied pressure of 40 atm

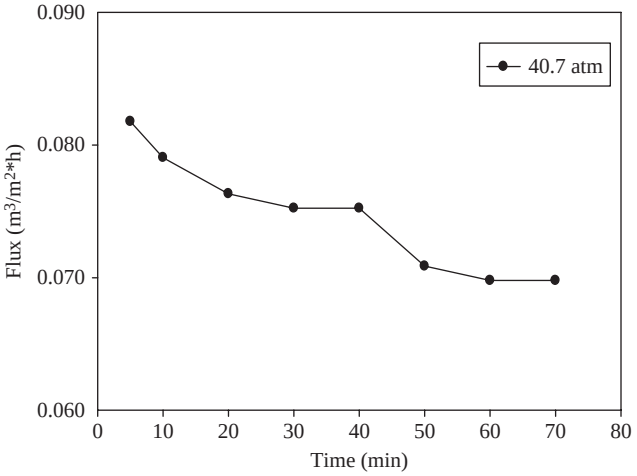

Fig. 3. Water flux versus time: concentration of NaCl = 2,000 mg/L.

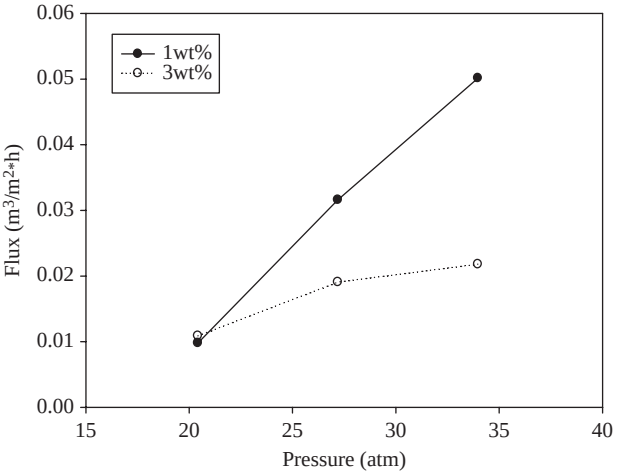

Fig. 4. Water flux at 2,000 mg NaCl/L through membrane prepared with different weight % of sPAEK: 1 wt% and 3 wt%.

as a function of time. The sPAEK membrane was prepared with a solution of 1 wt% sPAEK dissolved in formic acid. The height between the doctor blade and the porous support was fixed at 150 μm. As seen in Fig. 3, the water flux decreases and becomes constant as the time increases. This phenomenon might be due to two reasons: the first reason is that the membrane becomes more dense compared to the initially prepared when the pressure is applied; the second reason is that the concentration polarization of NaCl is occurred on the surface of the membrane, leading to the increase of the osmotic pressure difference. The water flux through the RO membrane is expressed in terms of a pressure and an osmotic pressure as follows:

$$J_v = P_w(\Delta P - \Delta\pi), \quad (1)$$

where J_v is the volumetric flux of water, P_w represents the water permeability, ΔP denotes the pressure difference across the membrane and $\Delta\pi$ means the osmotic pressure difference. If the membrane becomes more compact, the water permeability is expected to be lower. Also as the osmotic pressure difference increases, the water flux decreases. As a result, the water flux seems to be decreased.

Fig. 4 shows the effect of the weight % of sPAEK in a casting solution on the water flux as a function of the applied pressure. As the weight % of sPAEK increases, the water flux decreases. The other casting condition is the same as in Fig. 3. Since the open height between the doctor blade and the surface of the polysulfone is fixed, the weight of sPAEK per unit surface area of the cast RO membrane increases with increasing the weight % of sPAEK in a casting solution, leading to the formation of the thicker film of sPAEK on the support. As a result, the water flux may be decreased at the same applied pressure. It is quite important to obtain the high pure water permeability and the high rejection of salts by the prepared RO. In order to achieve those goals, the surface should be homogeneous without any defect and its preparation also has to be reproducible. If the weight % of sPAEK is high enough for production of RO membranes, the latter may be guaranteed at the expense of the water flux.

On the other hand, the salt rejection by the RO membrane was improved by increasing the weight % sPAEK in a casting solution as shown in Fig. 5. Increased weight % of sPAEK is associated with more dense morphology of the thin film. To confirm the

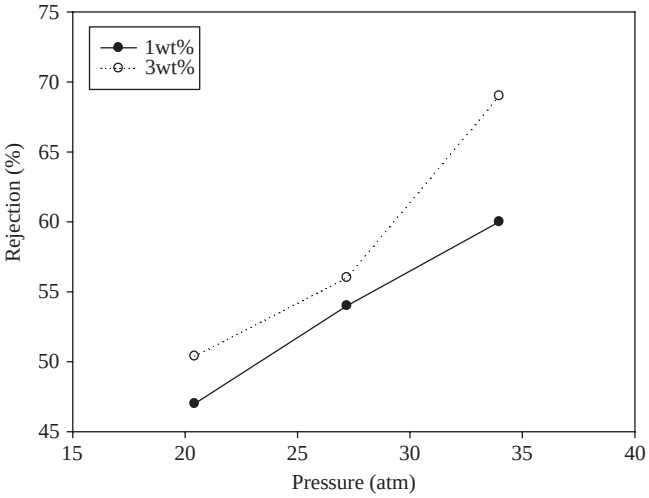

Fig. 5. Salt rejection at 2,000 mg NaCl/L by membrane prepared with different weight % of sPAEK: 1 wt% and 3 wt%.

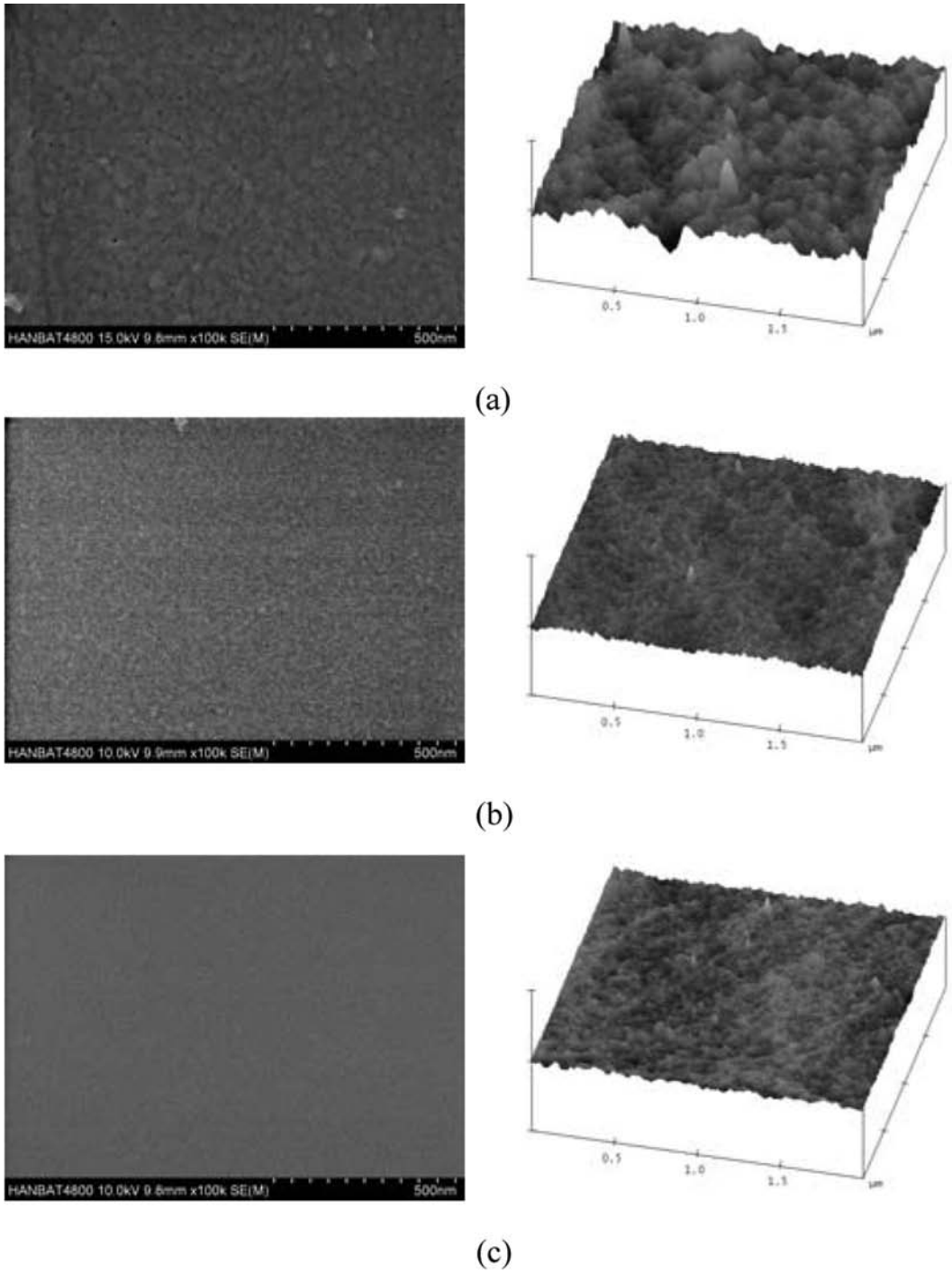

Fig. 6. Surface morphology of RO membrane prepared with different polymer concentration by SEM and AFM: (a) porous support, (b) 1 wt%, (c) 3 wt%.

morphology of the membrane, the surface of the membrane was examined by both SEM and AFM as shown in Fig. 6. It was observed by SEM that the high homogeneity of the membrane could be obtained with the high content of sPAEK in a casting solution. In addition to the homogeneity, a smoother membrane surface was observed via AFM image when coated with higher weight % sPAEK.

As mentioned earlier, the higher flux may be obtained with the thinner membrane. However, if the

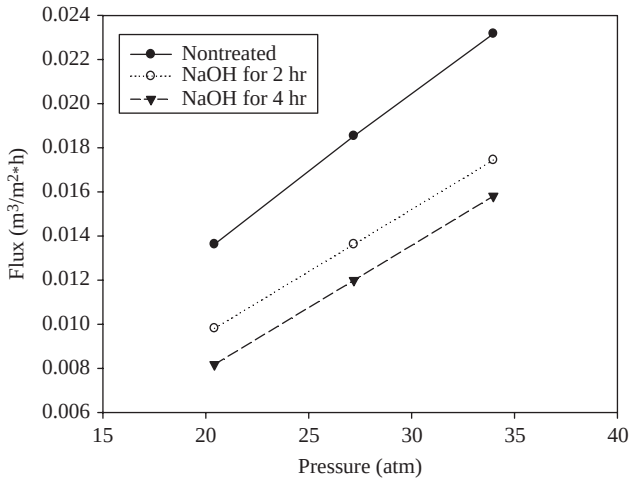

Fig. 7. Effect of post-treatment of RO membrane prepared with 1 wt% of sPEAK/PSF membrane on water flux; RO membranes were immersed in an aqueous NaOH solution for either 2 or 4 h (concentration of NaCl in feed = 2,000 mg/L).

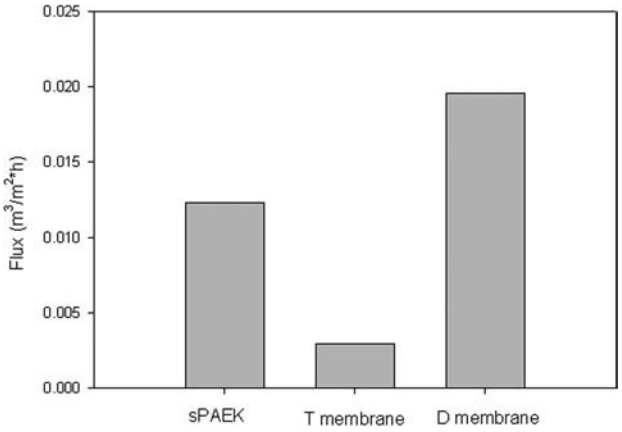

Fig. 9. Comparison between sPAEK membrane and commercial membranes on flux. (pressure = 54.4 atm, concentration of NaCl = 2,000 mg/L).

membrane is prepared with the low weight % of sPAEK, the thin membrane may be prepared while the salt rejection is relatively low as confirmed in Fig. 5. It would be desirable to prepare the sPAEK membrane which shows both a high flux and a high salt rejection. This could be established by the noble post-treatment of the sPAEK RO membrane as displayed in Fig. 7 and Fig. 8. When the cast sPAEK membranes are immersed in the 0.5 N NaOH aqueous solution, the flux of water decreases about half times compared to that through the nontreated membrane. However, the salt rejection significantly increases as shown in Fig. 8. It is also found that the salt rejection increases with increasing the post-treatment time. Improving the salt rejection may lead to decreasing the water flux. However, the RO membrane should show a high salt rejection to separate the salts from the saline water, eventually to produce pure water. In that sense, the high salt rejection is more important factor for preparation of the RO membrane while a reasonable water flux is obtained. The sulfonation of the sPAEK is responsible for water permeability by improving hydrophilicity, leading to high water uptake.

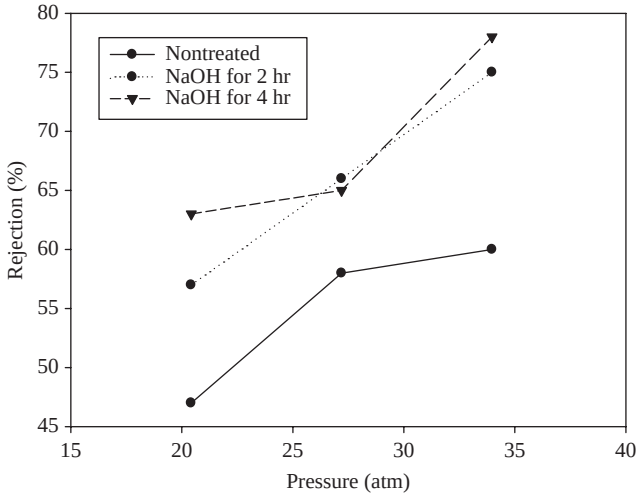

Fig. 8. Effect of post-treatment of RO membrane prepared with 1 wt% of sPEAK/PSF membrane on salt rejection; RO membranes were immersed in an aqueous NaOH solution for either 2 or 4 h (concentration of NaCl in feed = 2,000 mg/L).

At the same time, the salt rejection could be partly improved due to the repulsion effect of the negative charge on the surface. When the sPAEK membrane is treated with the NaOH solution, the sodium ions diffuse into the matrix of the sPAEK membrane, leading that sodium ions are strongly bound to the sulfonate groups via Coulombic force. As a result, the sPAEK matrix becomes a slightly basic or a neutral state so that the salt molecules may have a difficulty to diffuse through the polymer matrix. It is thought that this change of a state may affect the morphology of the sPAEK matrix due to the removal of the repulsion forces between the functional groups. When this treated sPAEK membrane is applied for the desalination experiment, the functional group on the surface is activated so that the rejection of chlorine ions are still improved due to the electrostatic repulsion while the matrix of sPAEK is maintained as post-treated. As expected, the water flux decreases and the salt rejection increases as the post-treatment time increases from 2 to

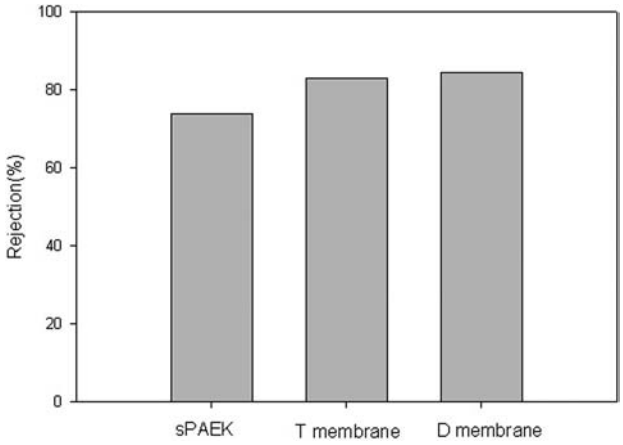

Fig. 10. Comparison between sPAEK membrane and commercial membranes on salt rejection. (pressure = 54.4 atm, concentration of NaCl = 2,000 mg/L) immersed in an aqueous NaOH solution for either 2–4 h (concentration of NaCl in feed = 2,000 mg/L).

4 h, indicating that the morphology of the post-treated sPAEK is more properly changed.

Finally, the post-treated sPAEK membrane was compared with commercial membranes in terms of the water flux and the salt rejection as seen in Figs. 9 and 10. The commercial membranes are denoted as D and T which are RO membranes. The D membrane has been applied for the treatment of brackish water and the T membrane has been used for the seawater treatment.

The typical sPAEK membrane shows a comparable water flux to that through the commercial membrane while the salt rejection is slightly smaller than that by the commercial membrane. Further improvement of the sPAEK membrane is required to be used as a RO membrane

4. Conclusions

A new chlorine resistant sPAEK RO membrane was prepared on the porous polysulfone support for RO application. It was found that the concentration of polymer in a casting solution significantly affected both the water flux and the salt rejection. Post-treatment of the RO membrane was found to be substantially effective for improvement of the salt rejection. However, the salt rejection through the developed RO membrane seems to be comparatively lower than the commercial RO membrane. More rigorous casting conditions are to be developed for improvement of the separation characteristics of the sPAEK RO membrane. Since this sPEAK polymer shows a very good chlorine tolerance, it would be one of the good candidates for RO application.

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Symbols

J_v	volumetric flux of water, $m^3/(m^2\ h)$
P_w	water permeability, $m^3/(m^2\ h\ atm)$
$\triangle P$	pressure difference across membrane, atm
$\triangle \pi$	osmotic pressure difference, atm

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