

상전이 및 가압법에 의한 나노여과 중공사 복합막의 제조 및 이의 성능 연구

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Preparation of Hollow Fiber NF Membranes by Phase Separation and Pressurization (PSP) Method and Their Performance Studies

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초록: 염석효과를 이용한 “상전이 및 가압법”으로 복합막을 제조하였다. 수용성고분자인 폴리스티렌설포산(poly(styrene sulfonic acid; PSSA)과 폴리에틸렌이민(polyethylene imine; PEI)을 코팅소재로 사용하였다. 질산마그네슘의 첨가에 의해 생성된 고분자 입자들을 다공성 폴리비닐리덴플루오라이드 막의 표면에서 가압하여 기공 내부로 흘러 들어가게 하여 기공 막힘에 의한 복합막을 여러 실험 조건에서 제조하였다. 제조된 막은 가정용 정수기에 적용 가능성을 알아보려고 4기압 하에서 100 ppm 소금 염용액에 대해 배제율과 투과도의 향으로 특성파악을 수행하였다. PSSA를 4분 동안 그리고 PEI를 2분 동안 코팅한 2중층 코팅 복합막은 배제율 81.7% 그리고 투과도 148.3 LMH를 보여주었다.

Abstract: A new technique named “phase separation and pressurization” (PSP) was introduced for the preparation of composite membranes by utilizing the salting-out effect. The water-soluble polymers such as poly(styrene sulfonic acid) (PSSA) and polyethylene imine (PEI), were used as the coating materials. Polymer particles formed by the addition of $Mg(NO_3)_2 \cdot 6H_2O$ were pressurized and flown to the surface of microporous polyvinylidene fluoride (PVDF) membrane to prepare composite membranes by pore blockings under various conditions. The resulting membranes were characterized in terms of the flux and rejection for 100 ppm NaCl at 4 atm to examine their suitability for application in a household water purifier. The double layer composite membrane prepared by a first coating of PSSA for 4 min and then a second coating of PEI for 2 min showed the best performance with flux of 148.3 LMH and rejection rate of 81.7%.

Keywords: hollow fiber membrane, nanofiltration, layer-by-layer, salting-out, phase separation.

Introduction

It is well-known that the nanofiltration (NF) membrane process is a type of pressure-driven membrane process between the reverse osmosis and ultrafiltration membrane processes. Its use has been increasing gradually worldwide because of the high retention of multivalent anion salts and organic molecules with a molecular weight range from 100 to 1000 as well as other advantages such as low operating pressure, low investment, and low operation and maintenance costs.¹ Furthermore, NF is a promising technique for production of drinking water

from surface and ground water.^{2,3}

With all these advantages, the development of better NF membranes has received increasing interest globally. The typical configuration of an NF membrane is the composite type obtained by forming a 100-200 nm thick ultra-thin dense layer on a 50 μm thick porous substrate. Many commercial thin film composite NF or reverse osmosis (RO) membranes are prepared by interfacial polymerization of a polyamide layer on top of a porous polysulfone support,^{4,8} plasma-initiated polymerization,⁹⁻¹² photo-initiated polymerization,¹³ photo grafting,^{14,15} electron beam irradiation,¹⁶ dip-coating,¹⁷ phase inversion,¹⁸ chemical cross-linking,¹⁹ or layer-by-layer (LbL) deposition.²⁰ Among these methods, the LbL technique has been used to prepare high water flux NF composite membranes.²¹⁻²³ The properties of LbL membranes can be altered

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easily by changing polyelectrolyte type, charge density, ionic degree, etc., but bulk production is limited because LbL membrane preparation is time consuming. As a result, NF membrane preparation techniques are changing to relatively simple and low-cost chemical cross-linking methods. Gao *et al.*²⁴⁻²⁷ prepared a series of charged NF membranes of different chitosan derivatives cross-linked by various cross-linking agents. Xu and Yang²⁸ prepared a positively charged NF membrane from poly(2,6-dimethyl-1,4-phenylene oxide) by *in situ* amines cross-linking. Then researchers of these LbL multilayer film making methods turned to more convenient preparation techniques with polyelectrolyte complex (PEC) membranes where both LbL and PECs have the same ionic cross-linking structures.²⁹⁻³¹

In addition, the dipping method and dipping accompanied by the salting-out method, which is defined as the separation of an organic phase from an aqueous phase by the addition of a salt, could be alternatives for the preparation of NF composite membranes. Because the solubility of water-soluble polymers in water is reduced by the addition of the inorganic salts, the polymers are precipitated owing to the change of solubility.³² In this way, precipitated organic molecules (polymer particles by phase separation) in the aqueous solution produced by the salting-out effect can be easily adsorbed on any membrane surfaces³²⁻³⁵ and also be deposited on (or block) the porous structure, thereby leading to a new technology for the preparation of NF/RO membranes. McDonald and Ries have invented a preparation method for composite membranes by depositing a dispersion of discrete polymer particles in a liquid on a porous substrate to obtain composite membranes and then annealing the deposited membranes to stabilize them.³⁶

In this study, a new technique is introduced for the preparation of composite membranes based on the salting-out effect. The precipitated polymers by the salting-out effect can be coated onto porous membrane surfaces by the following two methods: (i) dipping and (ii) blocking the pore structures and then deposition by pressurizing the precipitated polymer particles. In general, the typical fouling phenomena can be regarded as the blocking of membrane pores and/or forming of a gel layer by pollutants so that both reduce the intrinsic flux. The proposed method in this study is similar to the fouling formation process. The coating material (usually water-soluble polymers or mostly polyelectrolytes) dissolved in water becomes particulates through addition of the appropriate salts so that the polymer particles are precipitated, and the process is controlled by the polymer concentration and the quantity of

salts, that is, the ionic strength. Then the porous membranes to be coated are soaked in this polymer precipitated coating solution with vigorous stirring for the desired time or the polymer precipitated coating solution is pressurized and flown to the porous membrane surface so as to form a top skin layer by both blocking the pores and being deposited on the surface. The resulting membranes are water-soluble; therefore, they may be subject to post-treatments such as cross-linking or deposition of a counter-ion, i.e., LbL multilayer, etc. From now on, we call the former “phase separation and solution (PSS)” coating method and the latter “phase separation and pressurization” (PSP) method. In this study, the PSP method will be investigated in more detail for the preparation of NF hollow fiber composite membranes. An opposite ionic polymer is deposited on the first layer by the PSP method to enable the formation of a water-resistant LbL skin layer.

The polyelectrolytes poly(styrene sulfonic acid) (PSSA) and polyethylene imine (PEI) were used as coating materials. To prepare the composite membranes, the PSP method was used. The polymer particles formed by the addition of $Mg(NO_3)_2 \cdot 6H_2O$ were pressurized and flown to the surface of a porous PVDF membrane under varying conditions of polyelectrolyte concentration, annealing temperature, coating time, cross-linking agent concentration, etc. The resulting membranes were characterized in terms of flux and rejection for 100 ppm NaCl at 4 atm to determine their suitability for application in a household water purifier.³⁷

Experimental

Materials. Poly(styrene sulfonic acid) (PSSA, M_w 10000) and polyethylene imine (PEI, M_w 750000) were purchased from Sigma-Aldrich (Milwaukee, USA). The magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 99%) along with isophthaloyl acid (IPC) as the cross-linking agent were also provided by Sigma-Aldrich (Milwaukee, USA). Ultra-pure water was provided by Younglin Instrument, Aqua MAX™. All reagents and solvents were used without further purification.

Preparation of Composite Membrane. The preparation method is based on the forced fouling induction of polymer particles precipitated by the salting-out effect. The salt used for the salting-out effect was $Mg(NO_3)_2 \cdot 6H_2O$ ³³⁻³⁶ and its ionic strength (IS) as calculated by eq. (1) ranged from 0.1 to 0.3.

$$IS = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (1)$$

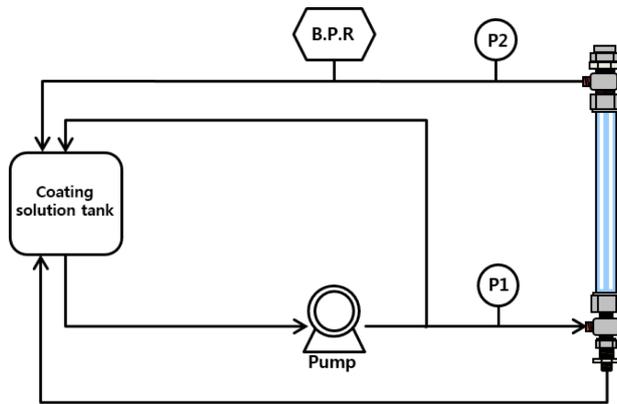


Figure 1. Schematic diagram of the experimental apparatus for the preparation of hollow fiber composite membranes by the PSP method.

where c_i is the concentration of ion i , z_i is the charge of ion i , and Σ is the sum taken over all ions in the solution.

The concentrations of polymer solutions used for the PSP methods were in the range of 1% to 4% by weight. First, the appropriate polymer was dissolved in water and then the desired IS quantity of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added. Next, a simple potting module was prepared with 20 cm-long hollow fibers of polyvinylidene fluoride (PVDF) microfiltration (MF) membranes supplied from Waters Co. Ltd. (Daejeon, Korea, average pore size 0.03 μm), and this was installed in the PSP coating apparatus (Figure 1). The polymer precipitated solution was circulated for the desired time and pressure. Then the prepared membrane was dried in the air and annealed for the desired time at the desired temperature. In case an LbL membrane was prepared, another ionic polymer was then deposited on the first formed layer.^{33,34} Afterwards, if necessary, the resulting coated membranes were soaked in a cross-linking bath for the desired time.

Surface Characterization. The surface morphologies of the pristine and coated surfaces of the NF PVDF membranes were analyzed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Tokyo, Japan).

Membrane Performance. Nanofiltration performance was determined in terms of water flux and salt rejection by a permeation apparatus (Figure 2) using a hollow membrane cell with an effective area of 32.1 cm^2 . The membrane performance determination was carried out at an operating pressure of 4 atm using a 100 ppm NaCl solution at 25 °C under a constant flow rate of 1.2 L/min. Water flux was determined by direct measurement of the permeate flow.

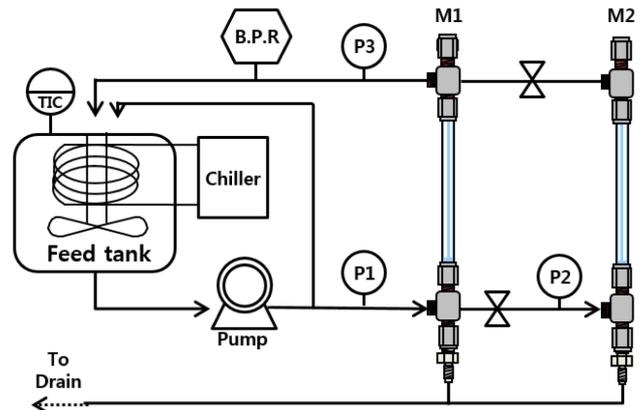


Figure 2. Performance test apparatus for NF hollow fiber composite membranes.

$$\text{Flux [LMH]} = \frac{\text{Permeate (L)}}{\text{Membrane area (m}^2\text{)} \times \text{Time (h)}} \quad (2)$$

Salt rejection was determined in accordance with the salt concentration in the permeate solution, which was obtained through measurement of the electrical conductance of the permeate and feed solutions using a conductivity meter (Orion, Model 162).

$$\text{Rejection (\%)} = \frac{1 - \text{Permeate concentration}}{\text{Feed concentration}} \times 100 \quad (3)$$

Results and Discussion

Surface Analysis. With the PSP coating method, the resulting membranes appeared to be well-coated because observation of the pores showed that the pores were not open. In a similar manner to the fouling phenomena, with the PSP coating method the precipitated polymer particles, which are precipitated after the addition of salt leads to a change in the solubility of the polymer in the water, block pores of all sizes. Hence, this PSP coating method does not make a distinction between ultrafiltration (UF) or MF membranes used as the support layers, and it is not affected by any wide distribution of pore size in the porous UF or MF membranes. For membranes with only a single coating of PSSA (Figure 3(b)), the surface roughness appears a little high, while the surface with an added PEI coating (Figure 3(c)) appears relatively smooth. Therefore, a double coating appears to be better than a single coating in terms of surface morphology.

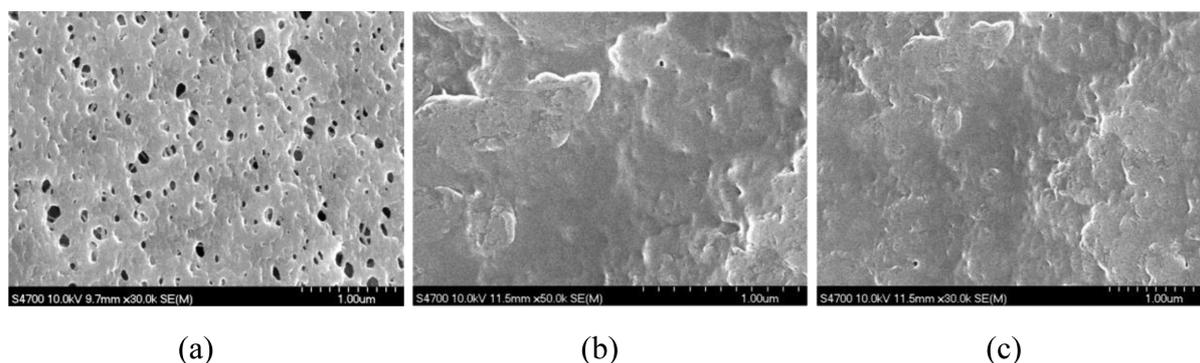


Figure 3. SEM images of PVDF membrane surfaces coated in accordance with the conditions (a) pristine PVDF membrane; (b) PSSA 2% for 2 min at 4 atm; (c) PEI 3% coating onto PSSA 2% coating layer for 1 min at 4 atm.

Membrane Performance. First, we examined the membrane performance with variations in coating concentration of PSSA (Figure 4). PSSA of various concentrations was coated onto the PVDF porous membrane surface under the coating conditions of IS=0.3, coating time 2 min, and pressure 4 atm. Then PEI 3 wt% was coated onto this layer for 1 min at IS=0.1 and the same pressure. PEI can be coated easily to form a polyelectrolyte complex through ionic cross-linking between the sulfonic acid group in PSSA and the amine groups in PEI. The pressure at the second coating provides the membrane with robustness.

As the PSSA concentration increased, the flux decreased noticeably from 183 LMH (L/m^2h) at 1 min coating to 102 LMH at 4 min. Meanwhile, rejection increased from 68% at 1 min coating to 79% at 3 min and then fell to 75% at 4 min, but there was no remarkable change in rejection for coating with

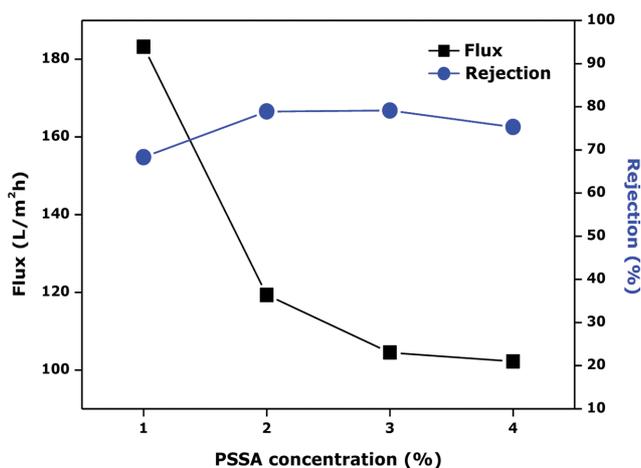


Figure 4. Effect of PSSA concentration on flux and rejection for 100 ppm NaCl (1st coating: IS = 0.3, coating time/pressure = 2 min/4 atm, 10 min drying at 60 °C; 2nd coating: IS = 0.1, coating time/pressure = 1 min/4 atm, 30 min drying at 60 °C).

a PSSA concentration over 2%. This absence of any differential change may be due to the ionic cross-linking between PSSA and PEI. In case of a 1% PSSA concentration, there may be the least number of sulfonic acid sites that can react with the amine sites in 3% PEI. As the PSSA concentration increases, the number of reaction sites increases, which resulted in a salt rejection of 79% at 3% PSSA. Also the flux decreased to 104 LMH for 3% PSSA and then no step change was observed to 4% PSSA, although rejection was reduced from 79.1% to 75.3%. From the viewpoint of flux and rejection, the best coating condition was with a 3% PSSA concentration.

Next the effect of drying time after the second coating step was investigated (Table 1). As drying time increased, there was no distinction in rejection while flux was reduced. From this point, a drying time of 30 min was applied to the membrane preparation rather than 60 min because flux at a drying time of 30 min was larger. Normally, annealing at a higher temperature causes the membrane to become more compact, which could be expected to reduce flux and elevate rejection (or selectivity). Although our experimental results showed a reduction in flux of more than 10%, rejection was almost unchanged.

In case of double coating, the coating time at each coating step may have an important effect on the resulting membrane

Table 1. Effect of Drying Time at 2nd Step (PEI Coating) on Membrane Performance

Drying time (min)	Flux (LMH)	Rejection (%)
30	119.3	78.9
60	105.3	78.6

*1st coating conditions: PSSA 2%, IS=0.3, coating time/pressure=2 min/4 atm, 10 min drying at 60 °C; 2nd coating conditions: PEI 3%, IS=0.1, coating time/pressure=1 min/4 atm, drying at 60 °C.

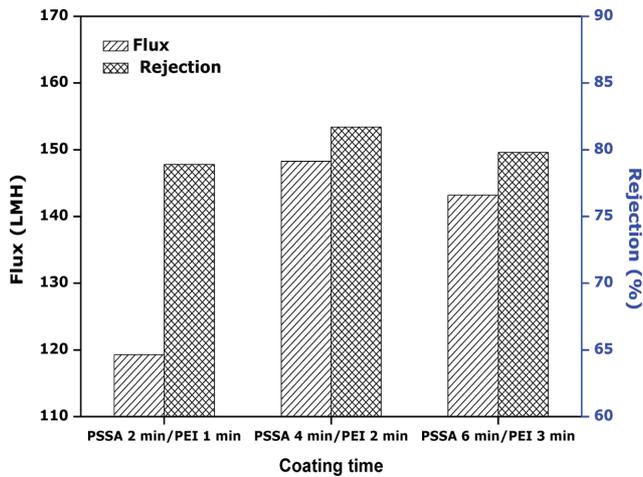


Figure 5. Effect of coating times for 1st and 2nd coating materials on flux and rejection for 100 ppm NaCl (coating conditions: PSSA 2%/PEI 3%, IS = 0.3/0.1, drying temp. = 60 °C, drying time = 10 min/30 min).

performance; therefore, the effect of the coating time at each step was investigated (Figure 5). In general, if the coating time increases, it is expected that flux will decrease while rejection will increase; however, unexpectedly as shown in Figure 5, initially as the coating time increased both flux and rejection increased. Then, as the coating time progressed, both flux and rejection decreased as shown by the result for the PSSA 6 min/PEI 3 min coating. From this experimental study, the optimum coating time condition is PSSA 4 min/PEI 2 min.

We do not have any explanation for some results obtained up to this point as follows: first, a decrease of rejection along with a decrease of flux (Figure 4); second, a stable rejection ratio despite a decrease in flux (Table 1); and, third, an increase of coating time leading to an increase of both flux and rejection followed by a further increase of coating time leading to a decrease of flux and rejection (Figure 5). These phenomena could not be understood in terms of changes in thickness, coating time, drying time, etc. We assume that the above mentioned phenomena are caused by other effects, for example, the ionic balance between the coated layers and the feed solution (the most probable cause). We will investigate in more detail and prepare another paper soon.

The effect of operating time on the flux and rejection of the composite membranes formed by the ionic bonds between PSSA and PEI was determined (Figure 6). Flux increased at the initial stage and then stabilized at about 80 LMH, while rejection increased from 71% to reach 81% for an operating time of 4 h. These results indicate an ionic balance effect

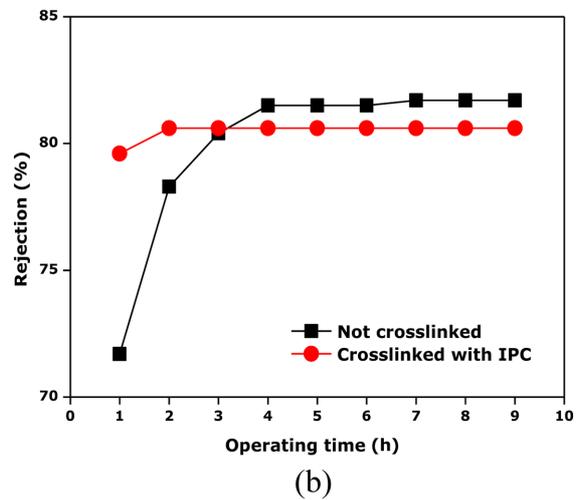
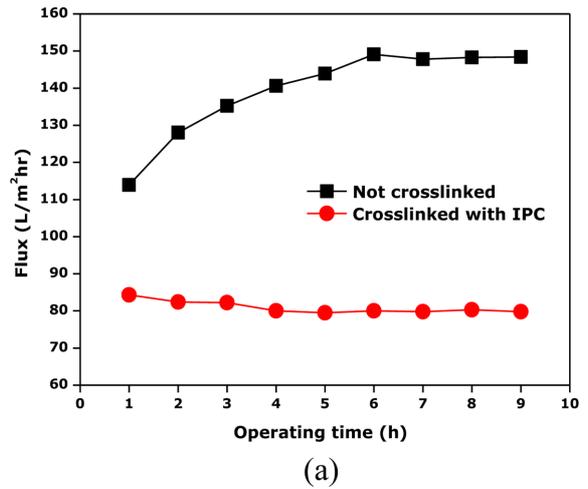


Figure 6. Membrane performance by operating time for not cross-linked and cross-linked with 0.1% IPC (coating conditions: PSSA 2%/PEI 3%, coating time and pressure = 4 min/2 min and 4 atm/4 atm, IS = 0.3/0.1, drying temp. = 60 °C, drying time = 10 min/30 min): (a) flux; (b) rejection.

because the increases in both flux and rejection appear at similar times. To shorten the stabilization time in both flux and rejection, the membrane surface was cross-linked with IPC 0.1% in hexane. The stabilization time decreased as expected, but there was a greater than expected reduction in flux. IPC reacts with the amines in PEI; therefore, amide groups may be formed that are not related with the ionic balance effect. Surface cross-linked composite membranes may be more durable than pristine composite membranes.

Then the cross-linking time was investigated to determine its effect on membrane performance (Figure 7). After the cross-linking reaction was carried out, there was a definite reduction in flux by about half, but contrary to expectations rejection was maintained with only slight differences. With the cross-linking

time extended to 10 min, further reaction led to a greater reduction in flux, but as before there was no big change in rejection. In this case, the time effect of the cross-linking concerns mainly flux changes rather than rejection changes.

Next the effect of using a cross-linking agent concentration of 0.3% IPC instead of the previous 0.1% was investigated (Figure 8). Rejection was elevated slightly because the increase of the cross-linking concentration leads to more reactions; however, the influence of reaction time on rejection was

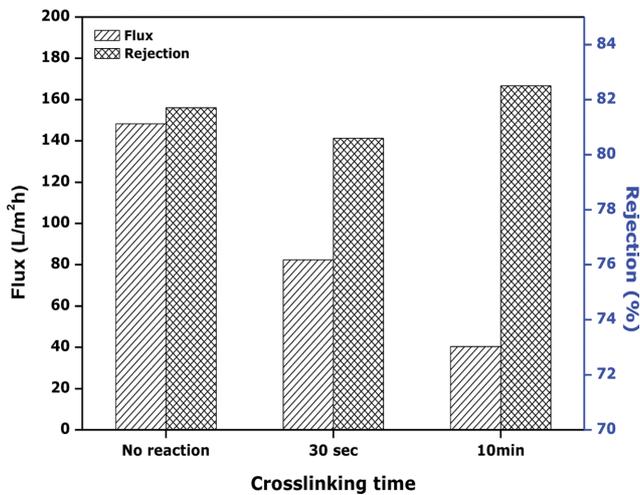


Figure 7. Effect of cross-linking time on membrane performance (coating conditions: PSSA 2%/PEI 3%, coating time and pressure = 4 min/2 min and 4 atm/4 atm, IS = 0.3/0.1, drying temp. and time = 60 °C/60 °C and 10 min/30 min).

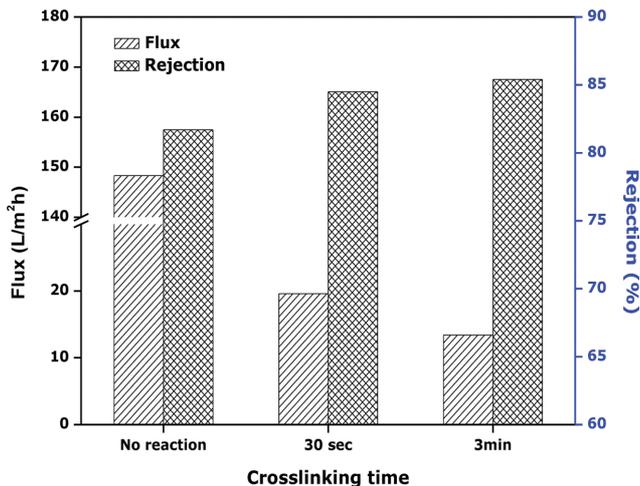
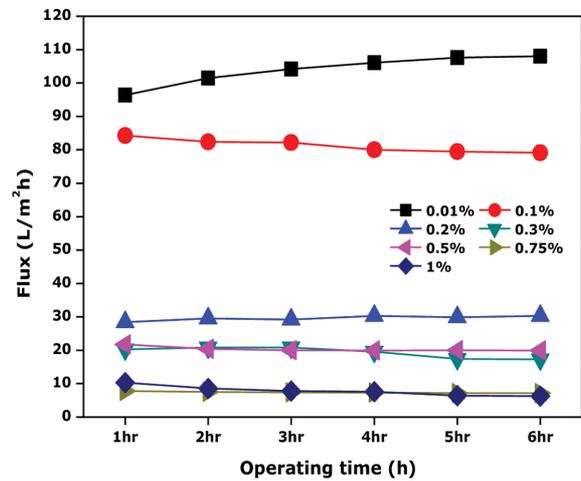


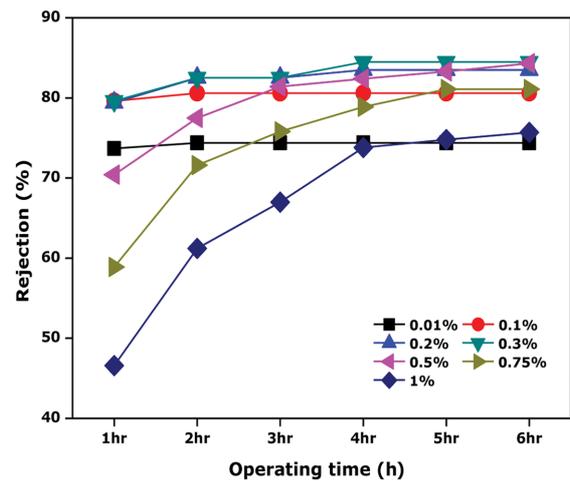
Figure 8. Membrane performance for different reaction times using 0.3% IPC as the cross-linking agent (coating conditions: PSSA 2%/PEI 3%, coating time and pressure = 4 min/2 min and 4 atm/4 atm, IS = 0.3/0.1, drying temp. and time = 60 °C/60 °C and 10 min/30 min).

relatively small. On the other hand, flux was reduced to one-seventh after a cross-linking time of 30 sec and then by one-third again after 3 min. From these results (Figures 7 and 8), it is concluded that membrane performance is more affected by the concentration of the cross-linking solution than by the cross-linking time; therefore, we decided to examine the effect of the concentration of the cross-linking solution in more detail.

To examine the effect of concentration of the cross-linking solution, membrane performance was examined at concentrations varying from 0.01% to 1% while the reaction time was fixed at 30 sec (Figure 9). At each concentration, flux showed



(a)



(b)

Figure 9. Membrane performance for different concentrations of IPC used as the cross-linking agent (coating conditions: PSSA 2%/PEI 3%, coating time and pressure = 4 min/2 min and 4 atm/4 atm, IS = 0.3/0.1, drying temp. and time = 60 °C/60 °C and 10 min/30 min): (a) flux; (b) rejection.

consistent values for all operating times, except with a concentration of 0.01%. Also flux decreased as the concentration increased with flux reduced by almost 10 times with the 1% concentration compared with the 0.01% concentration. On the other hand, rejection showed a steady state with consistent values from the earliest time at low concentration ranges up to 0.3%, but at concentrations from 0.5% the time to reach the steady state became longer and the rejection values were lower as the concentration increased. The lowest values for both flux and rejection at about 10 LMH and mid-70% respectively were found with the 1% concentration.

The coating layer of the membrane used in this study is formed by the first PSSA and the second PEI coatings and these two polymers bond ionically with each other, i.e. as an alternate expression, cross-linking by mutual ionic charges. The introduction of IPC after the ionic cross-linking induces further cross-linking between IPC and the amine groups in PEI that remain unreacted after amine groups in PEI had reacted with the carboxylic acid groups in PSSA. This additional cross-linking produces a very sturdy membrane surface that enables the feed to permeate the coated layer freely and, as a result, the flux is very low. This phenomena appears to start when the concentration of the cross-linking solution is 0.5% or higher. Generally, it can be said that rejection increases if a more compact structure is formed by cross-linking, i.e. the sieving mechanism has a substantial effect. As a result, rejection increased at concentrations up to 0.3%, but as the concentration increased further there were ever greater decreases in rejection so that rejection at 1% was the same as rejection at 0.01%. Another unusual thing is that with an increase in concentration from 0.5% to 1% it took longer for a steady state flux to be reached. Probably this is due to excessive cross-linking that leads to glassification of the membrane surface. Surface glassification results in less flux and the excessive modification of the surface changes the chemical properties so that the rejection is also decreased.

Conclusions

The composite membranes by utilizing “phase separation and pressurization” method were characterized in terms of flux and rejection for 100 ppm NaCl at 4 atm. From this study, several conclusions can be drawn as follows:

- Porous PVDF membranes were coated effectively as SEM images showed the disappearance of pores from the surfaces.
- After application of the second coating, the drying time had

no effect on rejection, but flux was reduced by about 10% to 105.3 LMH with a shorter drying time of 30 min.

- The optimum individual coating times for PSSA and PEI were 4 min and 2 min respectively with flux of 148.3 LMH and rejection of 81.7%.

- A PSSA/PEI coated membrane cross-linked with IPC showed no difference in rejection from a pristine PSSA/PEI coated membrane; however, flux decreased from 148 LMH to 80 LMH.

- Cross-linking time had no effect on rejection, which recorded 80.6% and 82.5% at 30 sec and 10 min respectively compared with 81.7% rejection for the pristine membrane; however, flux decreased to 82.4 and 40.4 LMH respectively from 148.3 LMH with the pristine membrane.

- A high concentration of the cross-linking agent IPC (above 0.5%) offered no advantages because no improvement was shown in either rejection or flux. It is recommended that the concentration used is below 0.3%.

- Finally, as mentioned above, some results cannot be understood and there may be some other effect that influences the relationship between the feed and the membrane such as ionic balance; therefore, this will be examined in more detail in the next paper.

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