

Novel Method of Synthesizing Poly(ether sulfone) Membranes Containing Two Solvents and a Lithium Chloride Additive and Their Performance

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ABSTRACT: The influence of a lithium chloride (LiCl) additive on poly(ether sulfone) (PES) membranes was investigated. A microwave technique was used to prepare membrane dope solutions, and two different types of solvent systems were used: single-solvent (SS) and double-solvent (DS) systems. In the SS system, PES was dissolved in *N,N*-dimethylformamide (DMF), and in the DS system, PES was dissolved in DMF and acetone. In the DS system, the control ratio of DMF to acetone was kept at 3.47, and the concentration of LiCl in both solvent systems was varied from 1 to 4 wt %. We observed that the microwave technique was able to dissolve the polymer rapidly, in less than

1 h. The performance of the PES membrane was evaluated in terms of poly(ethylene glycol) separation and molecular weight cutoff (MWCO). The results reveal that the presence of LiCl improved both the flux and rejection rates, and its concentration was best kept at 3 wt % for the tested conditions. In addition, we found that the mean pore size of the membranes produced from the DS system was smaller and the MWCO was lower as compared to the SS system. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1428–1437, 2010

Key words: inorganic materials; irradiation; membranes; morphology; poly(ether sulfones)

INTRODUCTION

The possibility of enhancing amorphous polymer membrane performance beyond the generally recognized intrinsic values has always attracted the attention of most membranologists. Hydrophobic materials such as poly(ether sulfone) (PES) display excellent mechanical and chemical stabilities in aqueous environments and possess favorable thermooxidative stabilities.^{1–3} These attributes make it very attractive for membrane materials. Membrane materials should also exhibit enough affinity toward water so that they can be preferentially adsorbed into the membrane.

The compatibility of polymers with additives can often play a significant role in the physical modification of the membrane-forming polymer. The role of organic and inorganic additives, such as methyl cellulose, glyc-

erin, poly(vinyl pyrrolidone), poly(ethylene glycol) (PEG), water, lithium chloride (LiCl), and zinc chloride (ZnCl₂), in casting solutions has been reported as a pore-forming agent that enhances the permeation properties.^{4,5} Among these additives, inorganic salts are promising candidates for the fabrication of membranes with an appropriate structure and high performance.^{6–11} Inorganic salt additives in casting solutions are known to change the solvent properties or the interaction between the macromolecular chains.⁷

Additionally, the use of double solvents (DSs) for membrane dope solutions was reported. Baker¹² prepared the first high-flow polysulfone anisotropic membranes from a mixture of two solvents. It was reported that a mixture of polar aprotic and volatile solvents, such as dioxane and acetone, caused rapid evaporation on the surface, which led to the formation of a dense layer on the surface.¹² Other physical factors that influence membrane formation are the solvent evaporation time, temperature, and humidity.¹³ Bellantoni and Loya¹⁴ produced composite ultrafiltration membranes made from a combination of two solvents containing both organic and inorganic salt additives.

The influence of LiCl on the solution properties and membrane morphology of poly(amic acid)

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(PAA) was studied.¹⁵ The addition of LiCl to a mixture of PAA and *N,N*-dimethylformamide (DMF) solution resulted in the formation of complexes between LiCl and DMF. This reduced the solvent power, which, in turn, increased the solution viscosity and eventually resulted in the formation of transient crosslinks, as observed in dynamic light scattering analysis.¹⁵ Inorganic salts are known to form complexes with the carbonyl group in polar aprotic solvents via ion-dipole interaction.¹⁶ In most of the studies done with LiCl, the polymers used have been cellulose acetate,⁴ polyamide,⁸ PAA,¹⁵ and poly(vinylidene fluoride) (PVDF).¹⁰

The preparation of membrane polymer solution is currently rather expensive, tedious, and time-consuming because the dissolution process takes a long time (6–24 h) depending on the solubility of the polymer in the solvent. Also, the number of appropriate initial processes for the preparation of polymeric membrane solutions that can be used are limited. This limitation slows down the development and dissemination of polymeric membrane separation technology in the industry. Generally, the current approach for polymer dissolution is to have the mixture heated for a long period of time with electrothermal heating, oil, or water baths. The exposure of a casting solution to extremely high temperatures may produce membranes with undesirable characteristics, whereas exposure to temperatures that are too low result in undissolved polymer and additives and, thus, a lengthy preparation time. To this end, microwaves have been used in organic chemistry to reduce the reaction times from hours to minutes and increase the yield and selectivity.¹⁷ The use of microwave techniques as a replacement for conventional heating has already been applied in inorganic membranes for biochemical and gas separation processes but not for polymeric membranes.¹⁸ However, that finding seems to have been treated as a novelty of little practical value for inorganic membranes. In the case of organic polymeric membranes, no study has been conducted on the use of microwave techniques for their preparation of polymeric membranes except as report in our recent article.¹⁹ The results reveal that the viscosities of polymeric solutions prepared with the microwave technique were generally lower than those of polymeric solutions prepared with the conventional method.

Thus, in this study, the microwave technique was used to prepare a PES dope solution. In addition, the influence of incorporating different concentrations of LiCl (1–4 wt %) on membrane performance was investigated. Two different solvent systems were used; the single-solvent (SS) system consisted of only DMF, whereas the DS system consisted of both DMF and acetone. The performance of these membranes was also compared with those prepared without vol-

atile acetone and LiCl. The performance of the membranes was evaluated with PEGs of various molecular weights. The molecular weight cutoff (MWCO) and flux rates of the membranes were also determined.

EXPERIMENTAL

Materials

PES (Ultrason E6020P; molecular weight = 58000 g/mol) was provided by BASF Co (Germany). Analytical-grade DMF [$\text{HCON}(\text{CH}_3)_2$; molar mass = 73.10 g/mol] was purchased from Merck (Germany). Analytical-grade anhydrous LiCl (molecular weight = 42.4) was procured from BDH (United Kingdom), and commercial-grade acetone was used without further purification. Tap water was used in the coagulation bath. For the ultrafiltration experiments, PEG with various molecular weights (from PEG 200 to PEG 35,000) were obtained from Fluka (Germany).

Preparation of a dope solution with the microwave technique

In this study, a domestic microwave oven (model NN-5626F, Panasonic, Singapore) was used. It had a rated power output of 900 W (240 V and 50 Hz) with an operation frequency of 2450 MHz. The microwave oven was modified such that the wavelength was less than 5 cm to ensure safety and also to accommodate the two-necked vessel. The details of the vessel were described elsewhere.²⁰ Subsequently, the polymer and additive were dissolved in the solvents placed in the glass vessel setup equipped with glass connectors attached to the reflux condenser, a thermocouple to control the temperature, and a stirrer inside the vessel to ensure homogeneity. The temperature of the dope solution was kept at 90°C (± 5) when only DMF was used as the solvent. However, when both DMF and acetone were used as solvents, the temperature was reduced to 80°C (± 5). The heating time by microwave was 15 min (low to high pulses), and the dissolution time was kept to a maximum of 1 h.

Different dope solutions were prepared. The polymer concentration was fixed at 20%, as shown in Table I. The SS system consisted of 20% PES and the solvent DMF. The DS system contained 20% PES and two solvents; DMF and acetone, and the ratio of DMF to acetone was kept at 3.47 just to avoid gelation of the solution. If the acetone concentration had exceeded 18 wt %, the solution would have been too close to the cloud point, and this would have caused gelation to occur. In both cases, the amount of LiCl was varied from 1 to 4 wt %. In addition, a membrane without LiCl containing 20% PES and 80% DMF for the SS system was also prepared. Similarly,

TABLE I
Dope Solution Compositions

SS system composition (wt %)			DS system composition (wt %)			
PES	LiCl	DMF	PES	LiCl	DMF	Acetone
20	0	80	20	0	62.11	17.89
20	1	79	20	1	61.33	17.67
20	2	78	20	2	60.55	17.45
20	3	77	20	3	59.77	17.23
20	4	76	20	4	59	17

for the DS system membrane without LiCl containing 20% PES, 62.11% DMF, and 17.89% acetone was also prepared.

Viscosity measurement of the dope solutions

The apparent viscosities of the polymer dope solutions were measured with a Brookfield digital rheometer (model DV-III, Middleboro, MA) equipped with a sample adaptor (SC4-31). The viscosity measurements as a function of shear rate were performed at ambient temperature (25°C). Each point on the flow curve was obtained as an average of at least three measurements.

Membrane casting

The dope solution was poured onto a clean glass plate at room temperature, and it was cast on a glass plate with a casting knife with a thickness of 200 μm , as discussed in previous article.²¹ The glass plate was immediately dipped into distilled water at room temperature. After a few minutes, a thin polymeric film was separated out from the glass plate because of the phase-inversion process. All flat sheet membranes were visually inspected for defects, and good areas were chosen for the membrane property evaluation.

Posttreatment of the membranes

To remove the additive of each membrane, the cast asymmetric membranes were posttreated; first, we washed them three times with deionized water and then immersed them in 500 mL of deionized water covered with aluminum foil for 30 min in a microwave oven. The applied temperature in the microwave oven during membrane posttreatment was 90°C (± 5). The conductance of the deionized water was measured by a standardized digital conductivity meter (Hanna Instruments model H18633, Belangor, Malaysia) to make sure that the excess additive inside the membrane pores was totally removed. The treated fibers were then rinsed again in deionized water until the conductance readings reached values equivalent to those of pure deionized water. The membranes were then ready for testing.

Membrane evaluation

The ultrafiltration experiment was performed in a stainless steel cross-flow test cell at 3.5 bars, as depicted in Figure 1. A membrane sample with an area of $2.0 \times 10^{-3} \text{ m}^2$ was placed in the test cell with the active skin layer facing the incoming feed. The ultrafiltration experimental details were described elsewhere.²¹ The pure water permeation (PWP) and solute permeation rates (PRs) of the membranes were obtained as follows:

$$J = \frac{Q}{\Delta t \times A} \quad (1)$$

where J is the permeation flux ($\text{L m}^{-2} \text{ h}^{-1}$) for the PEG solution or pure water, Q is the volumetric flow rate of permeate solution ($\text{L m}^{-2} \text{ h}^{-1}$), Δt is the permeation time (h), and A is the membrane area (m^2).

The solute rejection of the membranes were evaluated with various molecular-weight PEG solutions ranging from 0.2 to 36 kDa with concentration of 500 ppm. The concentrations of the feed and permeate solutions were determined by the method described by Ashutosh et al.²² The absorbance was measured with a spectrophotometer (Shimadzu UV-160, Japan) at a wavelength of 535 nm against a reagent blank.²² The membrane solute rejection was defined as

$$\text{Solute rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where C_f and C_p are the PEG concentrations in the feed and permeate solutions, respectively.

Pore size and pore size distribution

The pore sizes of PES in the SS and DS systems were determined with transport data as derived by Singh et al.²³ The solute diameter (d_s) was given by the equation

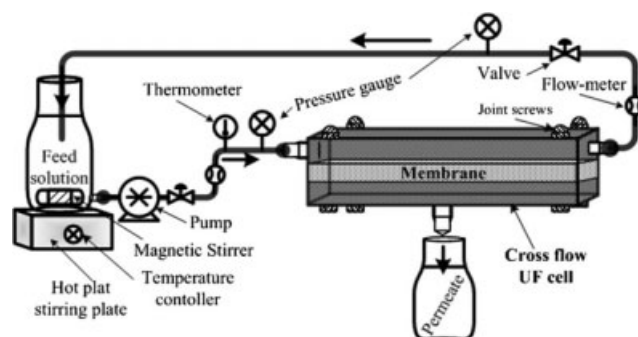


Figure 1 Schematic diagram of the crossflow ultrafiltration (UF) cell for membrane testing.

$$d_s = 2a \quad (3)$$

where a is the Stokes radius of PEG (cm). a can be obtained as a function of the molecular weight (M) according to Singh et al.:²³

$$a = 16.73 \times 10^{-10} M^{0.557} \quad (4)$$

The mean pore size and standard deviation of the membranes could be determined from the solute separation curve as plotted. The solute separation versus solute diameter was plotted on log normal graph. The mean pore size was determined at a solute diameter corresponding to the rejection rate $R = 50\%$ on a linear regression line. The standard deviation was calculated from the ratio of the solute diameter at $R = 90\%$ to the solute diameter at $R = 50\%$. Finally, MWCO was determined from the regression line at $R = 90\%$.

Scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) analysis

The membranes were broken in liquid nitrogen so as to give a generally clean break. These samples were then placed onto carbon holders and sputtered coated with gold to prevent the charging up of the surface by the electron beam. Cross sections of the flat sheet membrane images were obtained with a SUPRA 35VP (Germany) field emission scanning electron microscope. In addition to SEM, EDX analysis was performed on the samples to identify the chemical compositions and critical characteristics of the membranes.

RESULTS AND DISCUSSION

Effect of LiCl and acetone on the viscosity of the dope solution

Viscosity is considered one of the important parameters influencing the exchange rate between the solvent and nonsolvent during the phase-inversion process.²⁴ The viscosities of the various dope solutions are represented clearly in Figure 2. The presence of LiCl additive increased the viscosity of the dope solution in both the SS and DS systems. The viscosity of the solution increased with increasing LiCl concentration. However, a much higher and steep viscosity increment was observed in the SS system compared to the DS systems. This indicated that the influence of the LiCl additive on the viscosity was greater for the SS system compared to the DS system.

The formation of complexes between LiCl and DMF molecules occurred when LiCl was added to the SS casting solution. LiCl interacted more strongly

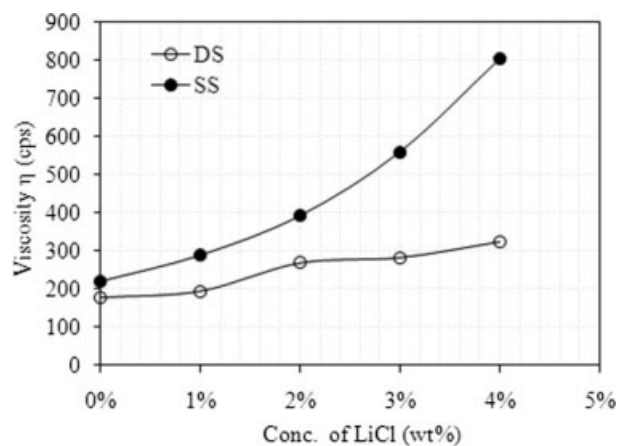


Figure 2 Relationship between the viscosity and concentration of LiCl for the SS and DS dope solutions.

with DMF because of the favorable interactions between them. Such interactions reduced the solvent power for PES; thus, the viscosity of the solution was found to increase. Also, both DMF and LiCl had high swelling properties; this resulted in high-viscosity solutions. When the concentration of LiCl was 4 wt %, the SS system experienced an almost fourfold increment in viscosity compared to only a one-and-a-half-fold increment in the DS systems. The increase in the solution viscosity could have been due to the presence of LiCl and not to the reduced amount of solvent used. This was because the decrease in the solvent concentration was only 4 wt %. On the basis of previous experiments,²⁰ such small concentration differences in the solvent did not usually result in a drastic change in viscosity. In fact, the results were similar to the findings of Bottino et al.,¹⁰ who suggested that the higher viscosity of their LiCl-containing PVDF-*N*-methylpyrrolidone (NMP) system, relative to that of the salt-free system, resulted not only from LiCl-solvent interactions but probably also from interactions between Li^+ cations and the strong electron-donating groups in PVDF.

In the DS system, when part of the DMF was replaced by acetone, the dope solution viscosity increment was lower and more gradual. This was observed because both acetone and DMF are aprotic solvents that possess low dielectric loss properties and are very suitable for microwave applications. Under the influence of microwaves, the boiling point of acetone is increased by 30–33°C at atmospheric pressure. This phenomena is known as the *superheating effect*, which has been reported in various studies.^{25–28} Unlike in the SS system, where the ionic salt LiCl interacted with DMF, in the DS system, Li^+ -DMF interactions still existed but to a lesser degree. This was because the concentration of DMF was reduced and replaced by acetone. The interactions

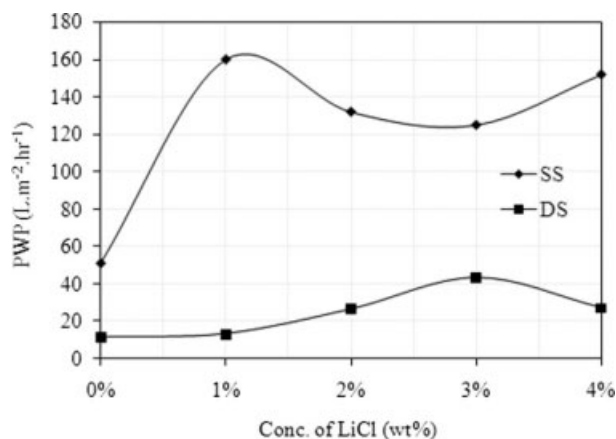


Figure 3 PWP rates versus the concentration of LiCl for the SS and DS membranes.

between Li^+ and acetone were probably relatively weak compared to those between Li^+ and DMF; this resulted in acetone behaving like a cosolvent in the DS system. In this study, the concentration of LiCl was kept to 4 wt % because of its solubility in aprotic solvents and organic solvents.²⁹

Performance of the membranes

The PWP rates of the membranes produced from the various solutions are depicted in Figure 3. The results reveal that the presence of LiCl improved the PWP rates of the PES membranes produced from both the SS and DS solutions. As the concentration of LiCl additive increased, the PWP rate increased but only up to a certain point. Beyond this concentration, the PWP rate decreased. The SS and DS membranes exhibited their highest PWP rates with 1 and 3 wt % LiCl, respectively.

Higher PWP rates were observed for the SS membranes compared to the DS membranes. The PWP rate for the SS membranes fluctuated significantly between 1 and 2 wt % LiCl, and this trend was not observed for the DS membranes. We believe that the higher viscosity of the SS solution compared to that of the DS solution contributed to the different rates of exchange between the solvent and nonsolvent during the precipitation process. In general, the high-viscosity solution had the tendency to promote delayed demixing, and this feature decreased the membrane resistance and increased the PWP with some minor fluctuations at 2 and 3% LiCl.

The solute PRs of the DS and SS membranes are shown in Figures 4 and 5, respectively. For the DS system, 3 wt % LiCl concentrations exhibited the highest PR, which was approximately $25 \text{ L m}^{-2} \text{ h}^{-1}$, whereas in the SS system, the highest PR was obtained when the LiCl concentration was 1 wt %. In both cases, the presence of LiCl increased the PR

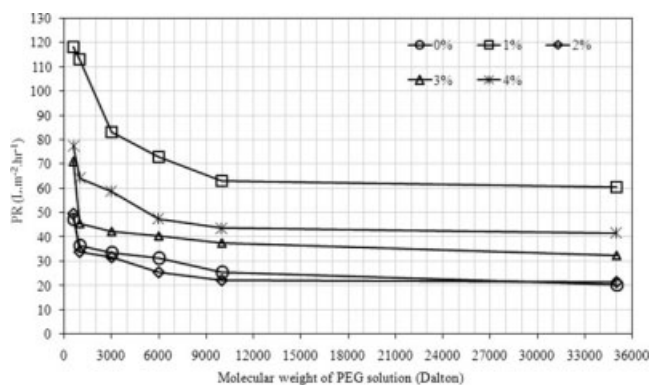


Figure 4 PR versus the molecular weight of PEG for SS membranes with 0–4 wt % LiCl concentrations.

by many folds. The results clearly indicate that LiCl, when used as an additive, enhanced the hydrophilic properties of the membrane, and this was demonstrated by the higher PWP and PR. However, the solute PR for the SS membranes was much higher than for the DS membranes. The formation of the LiCl and DMF complexes created a hydration effect and caused swelling in the polymer gel. Similar findings were reported by Kesting³⁰ for the effect of inorganic salt additives on the formation and properties of cellulose acetate membranes, where it was revealed that the PR of cellulose acetate membranes significantly increased when salts were added to the casting solutions. According to Kesting,³⁰ the increase in water PR was attributed to the following factors; first, a complex between the salt cations and the nonsolvent water molecules in the casting solution was formed (i.e., a hydration effect); then, the polymer gel structure was swollen by this complex. Other membranes whose permeation properties have also been strongly influenced by the addition of inorganic salts include aromatic polyamide,⁸ PVDF,¹⁰ and polysulfone.⁷

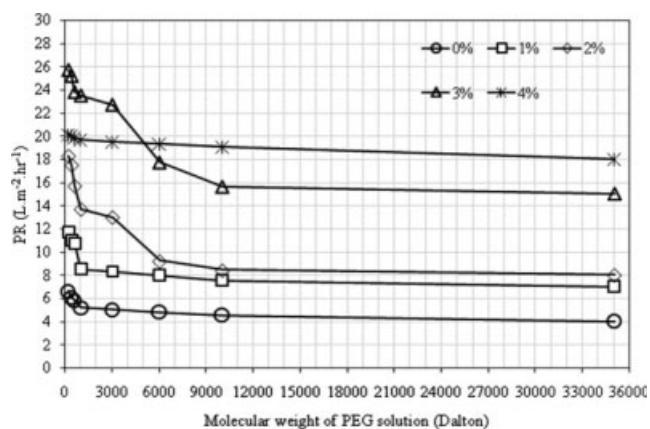


Figure 5 PR versus the molecular weight of PEG for DS membranes with 0–4 wt % LiCl concentrations.

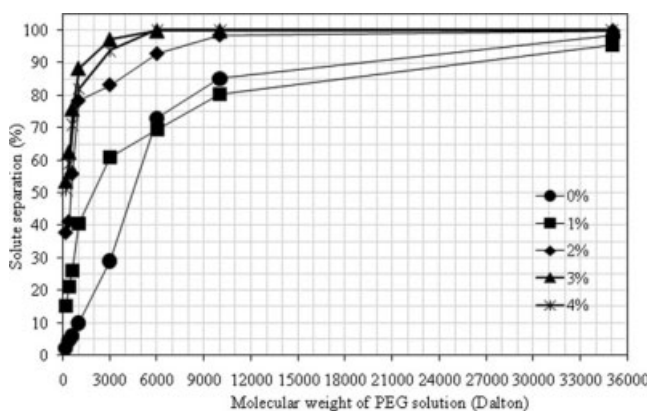


Figure 6 MWCO profiles of PES DS membranes with 0–4 wt % concentrations of LiCl.

Figure 6 shows the rejection rates of the DS membranes for various PEG solutions. The presence of LiCl improved both the PR and rejection rates. An increase in the LiCl concentration up to a maximum of 3 wt % increased the rejection rates of the membranes. Beyond this LiCl concentration, the rejection rate of the membrane decreased. The MWCO of the DS membranes at 90% rejection rates for 3 wt % LiCl was 1.2 kDa with PRs of $25 \text{ L m}^{-2} \text{ h}^{-1}$. Figure 7 demonstrates similar observations for the SS membranes. Maximum rejection rates were observed at 3 wt % LiCl concentration. A further increase in LiCl did not improve the membrane rejection rate, although its PR increased. The optimum concentration of LiCl for the SS membranes was 3 wt % with PRs of $40 \text{ L m}^{-2} \text{ h}^{-1}$, and its MWCO was 2.1 kDa.

Furthermore, Figure 6 indicates better rejection rates for all of the DS membranes. The DS and SS membranes without LiCl additive exhibited MWCOs of approximately 35 and 36 kDa, respectively. It appeared that the LiCl interacted strongly with PES, enhanced the membrane properties, and thus improved not only the PRs but also the rejection rates of the membranes. LiCl probably interacted

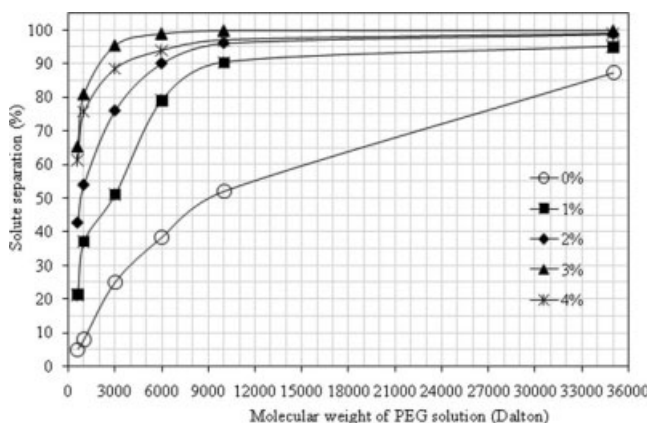


Figure 7 MWCO profiles of PES SS membranes with 0–4 wt % concentrations of LiCl.

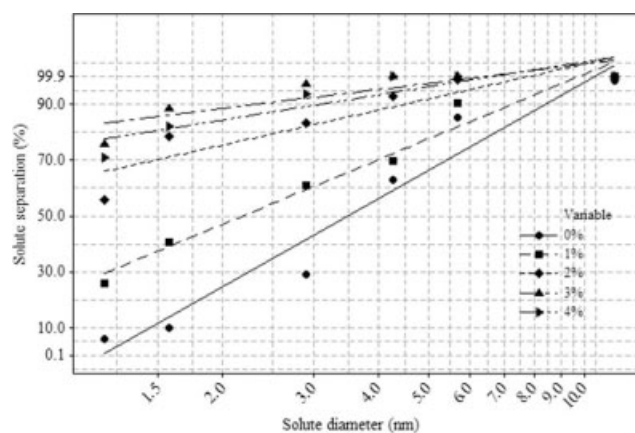


Figure 8 Solute separation curves for PES DS membranes without LiCl or with 1–4 wt % LiCl.

with PES and behaved as a charged pendant group for the polymer. This was similar to the findings reported by Kim et al.⁷ in his work with ZnCl_2 . The swelling properties of both the DMF and LiCl were stabilized by the introduction of acetone; this produced membranes with excellent rejection rates and reasonably high fluxes. We believe that the high-viscosity solutions led to a decrease in the membrane resistance and an increase in the water flux through the membrane. This observation was also shared by Munari et al.²⁵ In addition, the viscosity of the solution also influenced the rate of exchange between the solvent and nonsolvent during the precipitation process. As a result, this affected the skin-layer thickness of the membranes.

Membrane characterization with solute transport data

Log normal plots of solute separation versus solute diameter for the DS and SS membranes with various concentrations of LiCl additive are displayed in Figures 8 and 9. The Stokes diameter was determined

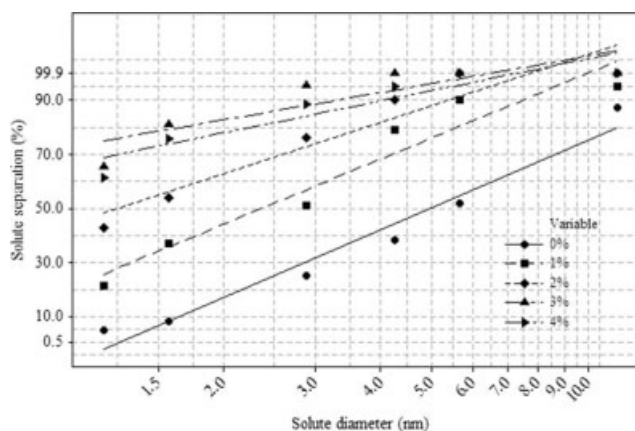


Figure 9 Solute separation curves for PES SS membranes without the LiCl additive or with 1–4 wt % LiCl.

TABLE II
Mean Pore Sizes, Standard Deviations, and MWCOs of the Various LiCl–PES Membranes in the SS and DS Systems

LiCl (wt %)	SS system			DS system		
	MWCO (kDa)	Mean pore size (nm)	Standard deviation	MWCO (kDa)	Mean pore size (nm)	Standard deviation
0	36	3.46	3.83	35	3.49	4.40
1	10	2.34	2.34	10.0	2.12	1.36
2	6	1.92	1.80	5.1	1.46	1.42
3	2.1	1.81	1.50	1.2	1.06	1.08
4	3.2	2.48	2.62	2.2	1.38	1.28

with Eq. (3), whereas the mean pore size, standard deviation, and MWCO of the DS and SS membranes were determined from the solute separation curves. The results are shown in Table II. The mean pore size implies a pore diameter at 50% of solute separation.²⁶ In the SS system, the membranes without LiCl exhibited an MWCO equivalent to 36 kDa, whereas in DS system, the MWCO was 35 kDa, with mean pore sizes of 3.49 and 3.46 nm, respectively. As the concentration of LiCl increased, the MWCO and the pore diameter decreased until the LiCl concentration reached 3 wt %. The smallest pore size

was observed in both SS and DS membranes containing 3 wt % LiCl, as shown in Table II; this explained its excellent separation efficiency. A further increase in the LiCl concentration did not result in a reduction of the MWCO or mean pore diameter. A similar trend was observed for both the DS and SS membranes. MWCO acts as guide for the pore sizes of membranes, where a small MWCO implies a small pore size of membranes.⁴ The separation efficiency in DS membranes was better than in SS membranes because of its finer mean pore size. This also explained the lower flux rates.

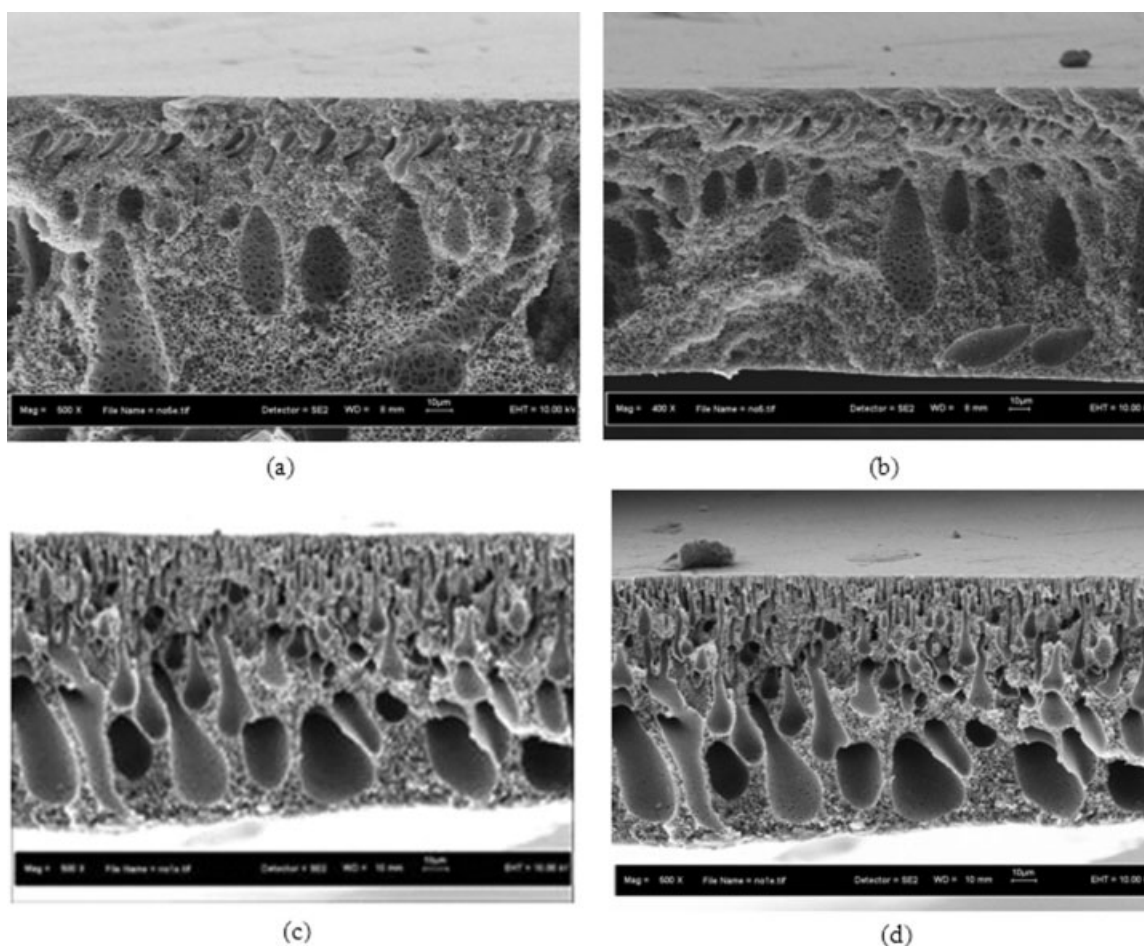


Figure 10 SEM cross-section images of SS PES membranes: (a) 2% LiCl, (b) 3% LiCl, (c) 4% LiCl, and (d) without LiCl.

Membrane morphologies and EDX analysis

The cross-section structures of the SS membranes produced from the various dope solutions are shown in Figure 10(a–d) at a magnification of 500 \times . Previous investigations have shown that casting solution characteristics and formulations have a direct influence on asymmetric membrane formation and structure.^{12,13} An examination of the cross-sectional structures revealed that the SS membrane without additive [Fig. 10(d)] had a thick and dense skin layer with many macrovoids. The fine fingerlike structure gradually developed into larger macrovoids, and the thick skin layer created a high resistance to flow, which explained the low flux rates.

By comparing Figures 10(a–c) and 10(d), we observed that the presence of LiCl altered and affected the morphology of the membrane. The overall porosity of the membrane increased because of the large number of fine and consistent pores. The skin layer, which was hardly visible, was relatively thinner, and the number of macrovoids was found to be substantially reduced. This explained the high rejection and improved permeation flux rates.

Figure 11(a–d) shows the cross-sectional morphology of the PES DS membranes. Large macrovoids were also observed in the membranes without LiCl, as shown in Figure 11(d), and these macrovoids decreased with the addition of LiCl, as shown in Figure 11(a–c), which explained the improved and high PR. Apparently, the presence of LiCl increased the dope solution viscosity. Such high-viscosity solutions tend to promote delayed demixing and suppress the formation of macrovoids.

The results also reveal that when the concentration of LiCl was increased up to 3 wt % in both the SS and DS casting solutions, the performance of the membranes improved in terms of both permeation and rejection rates. This was consistent with the effect of other inorganic salt additives on membranes prepared from other polymer–solvent systems.^{7,8,10,14} The changes that were observed in both the morphology and performance of the membranes due to the increased salt concentration were explained in terms of the casting solution properties. Some studies^{8,27,28} have shown that casting solution characteristics have a direct influence on the asymmetric membrane and structure, which then affect

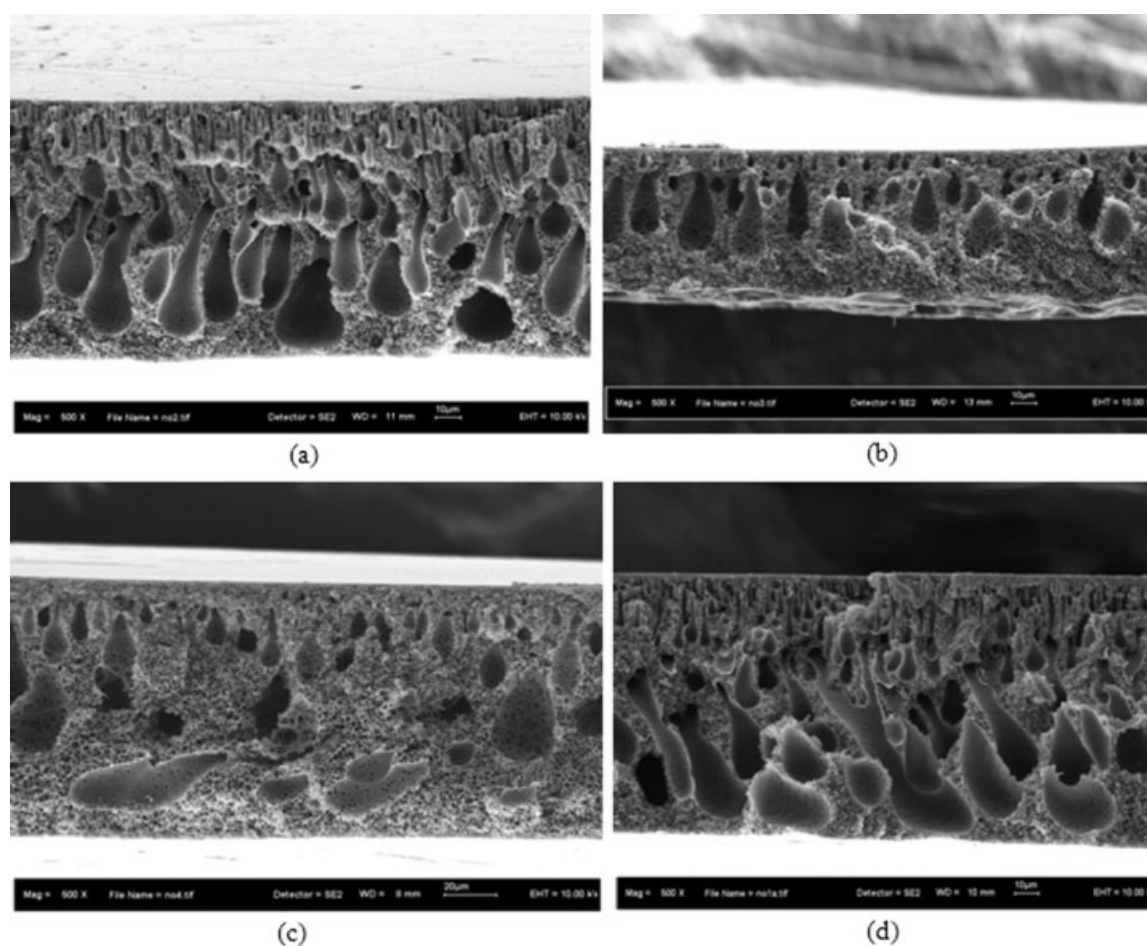


Figure 11 SEM cross-section images of DS PES membranes: (a) 2% LiCl, (b) 3% LiCl, (c) 4% LiCl, and (d) without LiCl.

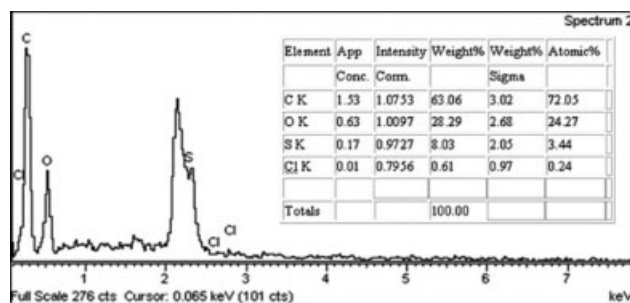


Figure 12 EDX of a PES DS membrane with 3% LiCl.

their performances. In the SS and DS systems, when the concentration of LiCl was increased, the polymer solution viscosity increased, and this resulted in a slower diffusivity rate of additives compared to the solvent. Therefore, the additives in the solvent took more time to reach the surface and provided ample time for the polymer aggregates to form a fine porous structure and thus suppressed macrovoid formation.

It is possible that under microwave irradiation, the state of PES chains in the LiCl free solution was different from that in the LiCl-containing DMF solutions. In the absence of LiCl, the PES chains existed in a highly swollen configuration, which is common for polymers in good solvents. However, for the LiCl-containing DMF solution, the interactions between LiCl and the DMF solvent seemed to be stronger than that with the PES polymer chains. This suggested that the effective solvating power of DMF for PES was progressively reduced with increasing concentration of LiCl. Subsequently, this promoted the presence of polymer aggregates and transient crosslinks, which affected membrane formation during the phase-inversion process. The polymer aggregates and transient crosslinks created a gel-like structure, which froze upon immersion precipitation, and this tended to hamper the development of macrovoids and assisted in the formation of a fine porous spongy structure with a very thin asymmetric skin. Similar findings have been reported by several researchers^{7,15} on various membranes containing salt.

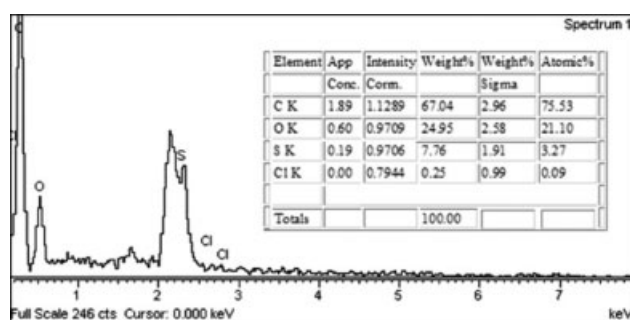


Figure 13 EDX of a PES SS membrane with 3% LiCl.

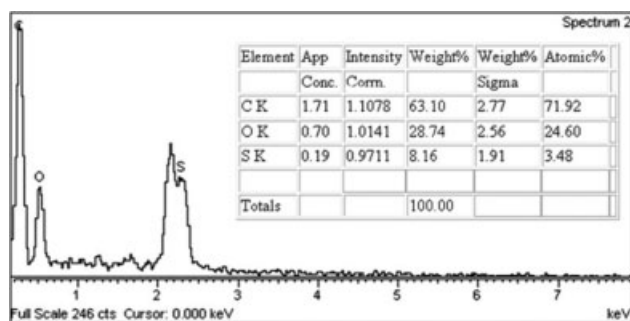


Figure 14 EDX of a PES SS membrane without LiCl.

The introduction of LiCl as an additive also improved the membrane's hydrophilic properties. It is reasonable to propose that during the dope preparation process in the microwave oven, the irradiation process could have caused LiCl bonds to vibrate and rotate.^{26,27} Thus, the highly electronegative chloride ions could easily have been attached to the polymer structure, and this was shown by EDX analysis. Both the SS and DS membranes containing 3 wt % LiCl showed the presence of chlorine, as shown in Figures 12 and 13. The presence of 0.61 and 0.25 wt % chlorine was detected in the SS and the DS membranes, respectively. However, no chlorine was detected for the salt-free membranes (see Figs. 14 and 15). The presence of chlorine could have been another contributing factor that led to the improved hydrophilic or hydrated structure of the membranes, and this was clearly proven by the high flux rates of both the SS and DS membranes containing LiCl. However, a higher amount of chlorine was observed to be present in the SS membrane containing 3 wt % LiCl, and this explained the higher flux rates of the SS membranes compared to the those of the DS membranes.

In the microwave technique, solvents were irradiated and heated above their boiling points, and this form of superheating contributed to the rapid dissolution of the PES polymers. The possibility that ionic polymerization occurred under microwave irradiation could not be discounted because ionic bonds

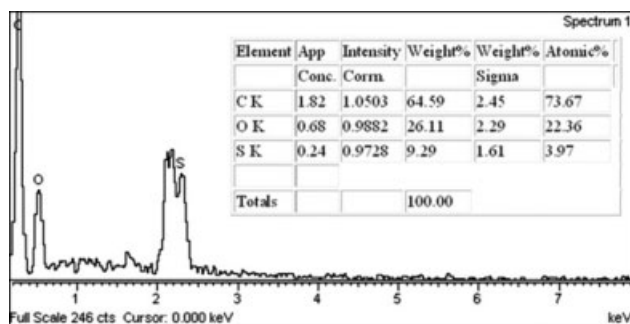


Figure 15 EDX of a PES DS membrane without LiCl.

were created, and this was proven by the EDX analysis.

Ultimately, for the SS membranes, LiCl interacted more strongly with DMF than with PES under the influence of microwave radiation; this led to the formation of LiCl-DMF complexes or aggregates. Such complexes have also been observed for ZnCl₂-poly-sulfone/NMP systems⁷ and LiCl-PAA-NMP systems.¹⁵ This subsequently reduced the solvation power of DMF for PES and thus produced very viscous solutions, which then promoted delayed demixing during phase inversion. Therefore, it was reasonable to hypothesize that the introduction of the second solvent acetone reduced the interaction between LiCl and DMF, which resulted in weak salt-solvent complexes and produced less viscous casting solutions. In the microwave heating, the presence of acetone improved the solvation power of DMF for PES. Subsequently, less viscous solutions were produced, and this eased the casting or spinning process. Also, the membranes produced with the DS system exhibited high rejection rates and reasonably high fluxes.

CONCLUSIONS

Membranes produced from dope solutions containing LiCl salts and acetone were superior in terms of permeation flux rates, rejection rates, and quality of membranes compared to membranes prepared without the additives. The addition of LiCl and acetone to PES-DMF casting solutions had a significant effect on both solution properties, as observed from their viscosities. The disappearance of macrovoids in the membrane structure improved the performance of the membrane. The results also indicate that LiCl interacted very strongly with DMF and acetone under microwave radiation; this led to the formation of LiCl-DMF-acetone complexes and, hence, maintenance of the solvation power of DMF for PES. The introduction of the LiCl additive alone in the casting solution increased the membrane porosity and thus produced high-PR membranes. However, when both LiCl and acetone were added to the polymer solution, the membranes porosity decreased. The asymmetric skin layer became very thin; this produced membranes that exhibited excellent rejection rates but slightly lower PRs. In the microwave technique, the solvents were irradiated; this contributed to the rapid dissolution of the polymers without a deterioration in the membrane performance. In addition,

the microwaves resulted in rapid heat transfer, which accelerated the polymer particle vibration and thus hastened the dissolution of the polymer in the solvent. The microwave method proved to be a rapid and an economical process and has the potential to bring membrane technology to new heights.

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