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High Performance Ultrafiltration Membranes Prepared by the Application of Modified Microwave Irradiation Technique

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ABSTRACT: In the present work, the influence of the lithium bromide (LiBr) additive on the performance of polyethersulfone (PES) membranes was studied using various formulations of dope solutions to which the microwave assistance (MWA) method was applied. The amount of PES was kept at 20 wt %, and the weight ratios of LiBr to dimethylformamide (DMF) were varied in the range 1−5 wt %. Results revealed that MWA irradiation increases the kinetics of dissolution of PES even in the presence of higher ratios of LiBr. It was found from viscosity, FTIR, water uptake, contact angle, and SEM-EDX analyses that the interaction between PES and LiBr is strongest when their mole ratio is unity. Performance data and the pore size distributions on the membrane surface have also been investigated. The structure of the MW casting solution under a strong interaction force attributed to the irradiation causes a decrease in the pore sizes and results in an increased rejection rate through the ultrafiltration membrane.

1. INTRODUCTION

The selection of membrane materials for use in liquid and gas separations has often been made based on either an Edisonian or a common-sense approach. For example, membrane research efforts focus on the determination of the permeability and selectivity of candidate polymers.[1] Recent literature surveys reveal an increasing number of polymers, copolymers, and blends that are being considered as potential materials that can be used to modify membrane morphology.[1,2] Much research into polyethersulfone (PES) membranes has been conducted with the goal of finding a correlation between membrane morphology and membrane performance under various preparation conditions. These conditions include varying dope compositions, additives, coagulation media, quenching bath temperatures, and evaporation times.[2,3] Membranes with good permeabilities and high mechanical strengths are highly sought after. These properties are related to the membrane morphology.[4] Polyethersulfone possesses outstanding oxidative, thermal, and hydrolytic stability along with excellent strength and flexibility, high resistance to extreme pH, and good mechanical and film-forming properties.[4] However, despite these benefits, its relatively hydrophobic nature is a considerable limitation in some aqueous membrane applications. Hydrophilicity enhancement has been achieved by various physical and chemical surface treatment procedures on preformed polysulfone membranes or by doping the casting solution of the membranes with additives.[5−9]

Additives used in the fabrication of PES membranes can be broadly categorized into the polymeric additive groups of polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG), and weak solvents such as glycerol. The addition of PVP and PEG has become a standard method to obtain "hydrophilized" membranes.[3,7,10] Other less common additives include inorganic salts with low molecular weights such as lithium chloride (LiCl),[10,11] zinc chloride (ZnCl$_2$),[12] magnesium chloride (MgCl$_2$), calcium chloride (CaCl$_2$), magnesium perchlorate (Mg(ClO$_4$)$_2$, and calcium perchlorate Ca(ClO$_4$)$_2$.[2,13] Recently, Ahmed et al.[10] used LiCl in the preparation of PES membranes. Their results were very encouraging, as they produced membranes with both high flux and good rejection rates using a microwave technique. Because lithium ions are typically small, they are generally solvated in solutions. Lithium salts have high solubility in dimethylformamide (DMF), and accurate conductance data are available for its solutions.[14] In one study, Botvay[15] modified derivatives of aromatic PES by bromination under various conditions including in solution, in suspension, with and without solvent, with and without catalyst, and at low and high temperatures.

Membrane production is a very complicated process, which involves polymer dissolution in a chosen solvent or solvent mixture. First, a dope polymer solution is prepared by electrothermal heating in an oil or water bath. The process may take from 4 to 8 h depending on the ease of polymer dissolution. Exposure of the casting solution to extremely high temperatures often produces membranes with undesirable characteristics, whereas temperatures that are too low might cause undissolved polymer aggregation, which might result in lengthy preparation times.[16] To overcome this problem, microwave techniques have been employed to reduce the reaction time from hours to minutes while increasing the yield and selectivity.[17] The use of a microwave oven for rapid sample dissolution in a closed system

Table 1. Formulation of Different Dope Solutions for Ultrafiltration Membrane

membrane no.	membrane dope composition			microwave parameters low−high pulse level	
	PES (wt %)	DMF (wt %)	LiBr (wt %)	total heat (min)	temperature (°C)
1	20	80	0	12	95 ± 5
2	20	79	1	12	95 ± 5
3	20	78	2	12	95 ± 5
4	20	77	3	12	95 ± 5
5	20	76	4	12	95 ± 5
6	20	75	5	12	95 ± 5

is an attractive procedure to be employed in the production of dope polymer solutions. It is a well-known fact that, on average, microwave heating saves about two-thirds of the energy used by conventional heating[18] and the cost of the microwave oven is not much more than that of conventional heaters. Previous reports using microwaves in this way have found an enhanced permeability of cellulose acetate membranes after microwave application.[19] Previously, Idris and Iqbal[20] reported the first microwave synthesis of a cellulose acetate−polyethersulfone blend membrane for palm oil mill effluent treatment. Cellulose acetate (CA)/PES ultrafiltration blend membranes produced from dope solutions prepared using the microwave technique are superior in terms of their rejection rates compared to membranes prepared using conventional methods.[20]

Until now, the use of microwave irradiation for the preparation of polymeric membrane solutions has never been investigated. Herein, we present the use of the microwave assistance (MWA) technique for polymer dissolution using the additive of lithium bromide anhydride (LBA). An attempt was also made to investigate the influence of LiBr and the effects of heating the system during its preparation on the performance of PES flat-sheet membranes.

2. EXPERIMENTAL SECTION

2.1. Materials. PES (Ultrason E6020P; molecular weight = 58 000 g/mol) was provided by BASF Co. (Germany). Analytical grade DMF ($HCON(CH_3)_2$; molar mass = 73.10 g/mol) was purchased from Merck (Germany). Analytical grade anhydrous LiBr (molecular weight = 86.85) was obtained from Acros Organic. Tap water was used in the coagulation bath. For the ultrafiltration experiments, PEG with various molecular weights (from PEG 200 to PEG 35 000) was obtained from Fluka (Germany).

2.2. Preparation of Dope Solution Using the MWA Closed Heating Technique. The dope solutions prepared consisting of 20 wt % PES and various compositions of DMF and LiBr are tabulated in Table 1. The solutions were prepared using the MWA closed heating technique described as follows.

A schematic diagram of the modified microwave experimental setup for membrane dope solution preparation used in these studies is shown in Figure 1. 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 with sa fluid sealed stirring device. The details of the vessel and
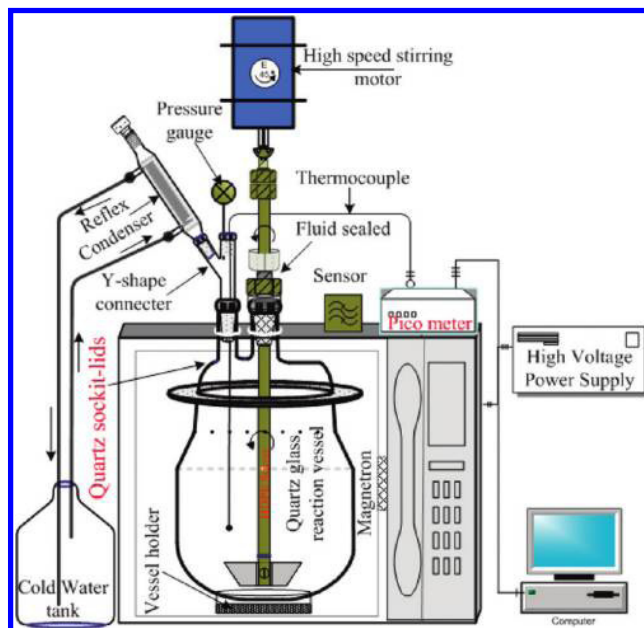

Figure 1. Schematic diagram of modified microwave experimental setup for membrane dope solution preparation.[21]

microwave modification are described elsewhere.[21,22] PES and LiBr were initially dried in the microwave oven for about 10 min at medium-high pulse (450 W) to remove any moisture present.

Subsequently, the polymer and additive were dissolved in the solvents placed in the glass vessel setup equipped with glass connecters attached to the reflux condenser, a thermocouple to control the temperature, and a fluid sealed stirrer inside the vessel to ensure homogeneity. The temperature of the dope solution was kept at 90 °C (±5 °C). Heating time by microwave was 12 min (low to high pulses), while the dissolution time was kept to a maximum of 1 h.

2.3. Viscosity Measurement of Dope Solutions. The apparent viscosities of the polymer dope solutions were measured with a Brookfield digital rheometer (Mode1 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 as described elsewhere.[14]

2.4. 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 a previous article.[20] 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.

2.5. Posttreatment of 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. The glass container was then placed in a microwave oven for 10 min at medium-high pulse with the temperature controlled at 90 ± 5 °C using a pico data logger. The conductance of the deionized water was measured by a standardized digital conductivity meter (Hanna Instruments Model H18633, Selangor, Malaysia) to make sure that the excess additive inside the membrane pores was totally removed. The treated membranes were then rinsed again in deionized water until the conductance readings reached values equivalent to those of pure deionized water.[23] The membranes were then ready for testing.

2.6. Fourier Transform Infrared Spectroscopic Analysis. In this study, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was recorded on a Perkin-Elmer spectrometer. The infrared spectra were recorded with an FTIR Perkin-Elmer System 2000, using the SplitPea accessory (Harrick Scientific), provided with a silicon internal reflection element and configured for external reflectance mode. The membrane samples were cut at random positions from casting films dried under vacuum for more than 48 h at 60 °C and then clamped to the ATR crystal. The spectra were obtained from a 200 μm diameter sampling area; 16 scans were averaged for each spectrum at a 4 cm^{-1} spectral resolution. All spectra were corrected for the ATR characteristic progressive increase in the absorbance at lower wavenumbers, using the equipment software. Peak identification was obtained from the correspondent second-derivative spectra in the range between 4000 and 600 cm^{-1}.

2.7. Measurement of Water Uptake. After the sample coupon was cut into equal sizes, the membranes were dried in a vacuum oven at 60 °C for 48 h, and then weighed using a balance (Mettler Toledo, Model MS204S, Switzerland). The sample membranes were soaked in deionized water at room temperature for 48 h. The liquid water on the surface of wetted membrane was wiped using filter paper before weighing. Each membrane was run six times, and then average water uptake was calculated from eq 1:[24]

$$\text{water uptake} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\% \tag{1}$$

where M_{wet} is the weight of the wet membranes and M_{dry} is the weight of the dry membranes.

2.8. Contact Angle Measurement. The hydrophilicities of the prepared membranes were scrutinized to observe the differences in wetting characteristics of the membranes using contact angle measurements. The contact angle of posttreated membrane surface was measured at 25 °C using a goniometer 14° horizontal beam comparator (G-23, serial no. 91314, KRÜSS, GmbH, Hamburg, Germany). Sample coupons were prepared by cutting pieces at random locations within the membrane sheets. The sample was placed on a glass plate (top side up) and fixed with tape. Then, a drop of distilled water (5 μL) was placed on the surface using a microsyringe (Hamilton Company, Reno, NV).

The position of the moving bed was adjusted so that the water drop was fitted to the scale when projected on the screen. The contact angle was measured at three different spots on each membrane sample so as to ensure reproducibility of data.[23]

2.9. Membrane Evaluation. The ultrafiltration experiment was performed in a stainless steel cross-flow test cell at 3.5 bar, as described elsewhere.[10] A membrane sample with an area of 2.0 × 10^{-3} m^2 was placed in the test cell with the active skin layer facing the incoming feed. The ultrafiltration experimental details are described elsewhere.[10] The pure water permeation (PWP) and solute permeation rates (PRs) of the membranes were obtained as follows:

$$J = \frac{Q}{(\Delta t)A} \tag{2}$$

where J is the permeation flux (L·m^{-2}·h^{-1}) for the PEG solution or pure water, Q is the volumetric flow rate of permeate solution (L·m^{-2}·h^{-1}), Δt is the permeation time (h), and A is the membrane area (m^2). The solute rejections of the membranes were evaluated with various molecular-weight PEG solutions ranging from 0.6 to 35 kDa with a concentration of 1000 ppm. Experiments were performed three times for each membrane to ensure reproducibility.

The concentrations of the feed and permeate solutions were determined by the method described elsewhere.[10] The absorbance was measured with a spectrophotometer (Shimadzu UV-160, Japan) at a wavelength of 535 nm against a reagent blank.[10] The membrane solute rejection was defined as

$$\text{solute rejection} = \left(1 - \frac{C_{\text{p}}}{C_{\text{f}}}\right) \times 100\% \tag{3}$$

where C_{f} and C_{p} are the poly(ethylene glycol) concentration in the feed solution and permeate solution, respectively.

2.10. Pore Size and Pore Size Distribution. The pore sizes of PES membranes were determined using transport data as derived by Singh et al.[25] The solute diameter (d_{s}) is given by the equation

$$d_{\text{s}} = 2a \tag{4}$$

where a is the Stokes radius of PEG (cm), and a can be obtained as a function of the molecular weight (M) according to Singh et al.:[25]

$$a = (16.73 \times 10^{-10})M^{0.557} \tag{5}$$

The mean pore size and standard deviation of the membranes could be determined from the solute separation curve as plotted. The solute separation curve was plotted to find out the mean pore size, μ_{p} (nm), and standard deviation, σ_{p}, of the membranes. The data of solute separation versus solute diameter were plotted on lognormal graph paper. The mean pore size was calculated with solute diameter corresponding to $R = 50\%$ on the linear regression line. The standard deviations were calculated from the ratio of solute diameter at $R = 84.13\%$ and $R = 50\%$[25] for membranes 1, 2, and 6. However, for membranes 3−5 the standard deviations were calculated from the ratio of solute diameter at $R = 90\%$ and $R = 60-76\%$ due to the consistently high separation solute obtained.

2.11. Scanning Electron Microscopy (SEM) Energy-Dispersive X-ray (EDX) Analysis. The membranes were broken in liquid nitrogen to give a generally clean break. These samples were then placed onto carbon holders and sputter coated with
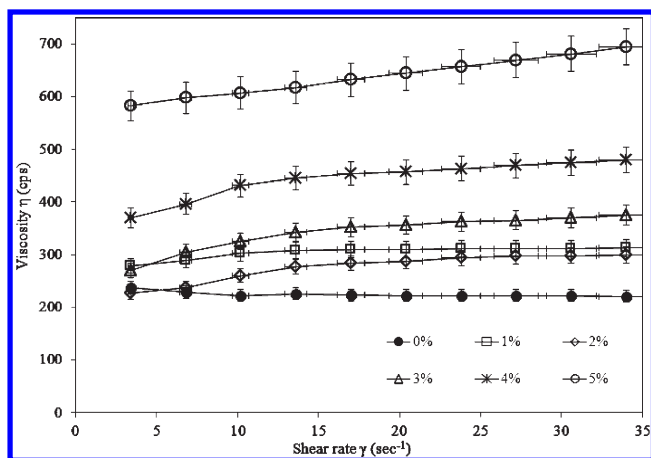
Figure 2. Apparent viscosities of PES/DMF dope solutions with various concentration of LiBr (0−5 wt %).

gold to prevent the charging 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. SEM-EDX analysis was performed on the samples to identify the chemical compositions and critical characteristics of the membranes.[10]

3. RESULTS AND DISCUSSION

3.1. Effects of Applying the MWA Technique on the Viscosity of the Dope Solution. The widely varying viscosities and broad molar mass distributions of the polymer during dope solution preparation cause the formation of high performance membranes.[10,14,22] Figure 2 shows the viscosities at 26 ± 0.5 °C of the PES/DMF dope solutions with various concentrations of the additive LiBr. Results show that the PES/DMF prepared dope solutions had small viscosity differences when compared to those solutions that were prepared with 2−4 wt % LiBr. Specifically, the PES/DMF solution had a lower viscosity (approximately 20% lower) than the ones prepared using 1−3 wt % LiBr (Figure 2). It should be noted that the microwave synthesis in a closed system utilized solvents with nonconventional boiling points that might contribute to the observed "rate enhancement," as has been observed in other studies.[10,14] Further, the low viscosity might be caused by the high dielectric constants of DMF and PES, which result in low dielectric losses. When these molecules are irradiated with microwaves, they will attempt to align themselves with the electric field by rotating. If the frequency of molecular rotation is equal to the frequency of microwave irradiation (2.45 GHz), then the molecules will continually align and realign themselves with the oscillating field, thus absorbing the electric energy. This process is known as dipolar rotation.[26] The ability of these compounds to absorb energy readily under microwave irradiation and convert the absorbed energy into heat results in very short dissolution times and produces solutions of low viscosity.

When part of the DMF is replaced by LiBr (1−3 wt %), the dope viscosity rises slightly to 10−20% (Figure 2). This can be explained by the fact that the anhydrous form of LiBr possesses low dielectric loss properties. Both the solvent and the additive interact efficiently with PES because of their polar and ionic properties. However, LiBr works well with microwave irradiation because of its higher polarity and anhydrous behavior.

Specifically, because the stone structure is shorter than DMF, its molecules align very swiftly, which causes its temperature to rise substantially. Mingos et al.[27] claimed that different rates of acceleration are caused by solvent superheating that is generally induced by microwave irradiation during the material dissolution process.

Previous studies[12−14,28] reported that the dissolution of engineered polymers with low viscosities in the presence of salt additives (<3 wt %) is usually impossible beyond a certain value because of solubility limitations. Other recent results have revealed that by use of the MWA technique PES dope solutions can be made with higher concentrations of salt additives if the salt compound contains highly electropositive ions such as Li^+ that are combined with highly electronegative halogen groups including fluorine, chlorine, and bromine.[29] The viscosity of the solution increased 2−3 times when the concentration of the salt was increased beyond 4 wt %. This viscosity increase at higher concentrations might be caused by salt−solvent interactions and/or the association between Li^+ cations and the polymer network.[10,15] Bottino et al.[11] and Kim et al.[12] revealed similar findings where higher viscosity polymer solutions of poly-(vinylidene fluoride) (PVDF) and polysulfone were formed with N-methyl-2-pyrrolidone (NMP) solvent when LiCl and $ZnCl_2$ were present compared to the salt-free solutions, and this is due to not only the salt−solvent interactions but also interactions between Li^+ and Zn^+ cations and the strong electron donating groups of engineered polymers.

Consequently, in our previous study, we reported that, in the presence of LiBr, the microwave technique produced somewhat lower viscosity solutions compared to conventional electroheating techniques (especially when LiBr concentrations were ≥3 wt %).[15] Beyond the aforementioned phenomena that occur during the application of the MWA technique, heating during MWA could also occur as a result of a different mechanism known as "ionic conduction".[30] When the Li^+ ions move through the solution under the applied field, frictional losses generate heat in a way that depends on the size, charge, and conductivity of the ions.[14,26]

3.2. Performance of the Membranes. *3.2.1. Pure Water and PEG Permeation Rates.* The pure water permeation rates (PWPs) of the membranes (membranes 1−6) produced from the various dope solutions are illustrated in Table 2. It is observed that, as the concentration of LiBr additive increases, the PWP rates increase. However, when the concentration of LiBr is increased beyond 3 wt %, the PWP rates start to decrease. In general, the MWA prepared membranes 2−4 show higher PWPs compared to membranes 1, 5, and 6. These results show that membranes 2−4 are more hydrophilic. These differences could be due to different solubility parameters or to different salt−solvent interactions. The added monovalent salts have the same cations but different anions on an equal molar basis. Therefore, it can be observed that LiBr added at concentrations between 1 and 3 wt % has a greater dissociation affinity with DMF. This dissociation affinity was more effective in increasing membrane flux, especially for membrane 4. This is likely due to the efficient polar interaction between LiBr, DMF, and PES under microwave irradiation conditions. Kraus et al.[28] as well as Ahmed et al.[10] have found similar effects on the performance of reverse osmosis and ultrafiltration (UF) membranes that were cast from salts containing additive solutions. A similar trend is also observed for the PEG permeation rates (PRs) (as shown in Table 2). The results reveal that membrane 4, which contains 3 wt % LiBr, exhibits the highest permeation rates

2275

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Table 2. Pure Water Permeation (PWP) and Permeation Rates of PES Membranes with Various Concentrations of LiBr

membrane no.	PWP (L·m^{-2}·h^{-1})	permeation rate of 1000 ppm solution (L·m^{-2}·h^{-1}) for PEG MW					
		600 Da	1000 Da	3000 Da	6000 Da	10 000 Da	35 000 Da
1	15.00	14.30	14.32	13.87	13.00	12.68	11.80
2	80.53	75.90	69.43	65.11	57.00	55.27	51.70
3	121.59	112.11	108.00	99.32	92.74	88.58	81.00
4	157.91	132.69	125.11	117.69	112.11	110.20	107.00
5	77.38	65.27	62.1	61.10	56.52	50.35	45.00
6	63.16	51.58	49.00	47.90	42.00	38.40	35.00

(approximately 132.69 L·m^{-2}·h^{-1} when separating PEG solutions) compared to membranes 1, 2, 3, 5, or 6.

These results clearly show that LiBr addition enhanced the hydrophilic properties of the membrane, as demonstrated through the improved PWPs and PRs. The permeation rates for membranes 2−5 with LiBr were nearly 75% higher than those without LiBr. Permeation rates that were 6−8-fold higher than those of the other membranes were achieved when 2 and 3 wt % LiBr were used to form membranes 3 and 4, respectively. This means that these membranes have increased productivities. Mechanistically, we suggest that because LiBr has high swelling properties, the PES becomes "hydrophilized". This hydrophilicity becomes very pronounced when the solutions contain 3 wt % LiBr (membrane 4). It is possible that at this concentration the balance between hydrophilic and hydrophobic has been shifted to the former. A restructuring of the membrane composition due to the application of the MWA technique on the dope solutions is a likely contributor to this increased hydrophilicity. Microwave posttreatment causes a clustering effect on the hydrophobic and hydrophilic groups. Specifically, membranes 3 and 4 are thought to become more hydrophilic. In addition, during MW irradiation, the heat transfer occurs through volumetric heating. Thus, the temperature can increase 25 °C higher than 65 °C, the conventional method temperature.[29] Such volumetric heating increases the energy levels, which can cause molecular transitions from strongly bound to completely ionic states that result in a nonionic repulsive state. Such volumetric heating under irradiation probably promotes the formation of LiBr and DMF complexes, which promote the hydration effect and, subsequently, cause swelling of the polymer gel. Similar findings have been reported and explained by Kesting[31] for cellulose acetate using inorganic salt additives. Similar results regarding the influence of inorganic additives such as LiCl and ZnCl$_2$ on the permeation properties of polysulfone (PSf) and polyamide[12,13,28] membranes have also been disclosed. Contact angles and water uptake measurements provide even more support to this hypothesis.

3.2.2. Rejection Rates and Molecular Weight Cutoff. Figure 3 shows the rejection rates of membranes 1−6 for the various PEG solutions. The presence of LiBr improves not only the permeation rates but also the rejection rates. Increases in LiBr concentration to 2−3 wt % (membranes 3 and 4) also leads to increases in the membrane rejection rates. Increasing LiBr beyond 3 wt % does not result in increased rejection and permeation rates. The molecular weight cutoff (MWCO) of the membranes at 90% rejection rates for 2 and 3 wt % LiBr is 3.460 and 2.842 kDa, respectively, with permeation rates of 112.11 and 132.69 L·m^{-2}·h^{-1} for PEG 600 solutions, respectively.

The PES/DMF membrane (membrane 1) without LiBr additive had a MWCO of about 35.00 kDa, whereas membranes
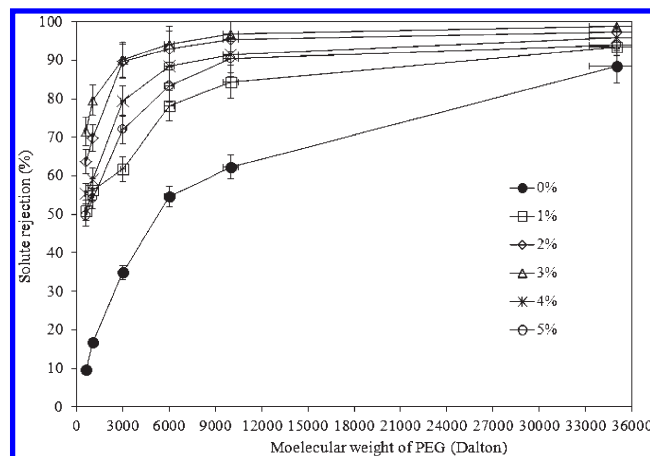
Figure 3. Molecular weight cutoff profiles of PES membranes with various concentrations of LiBr (membranes 1−6).

2, 5, and 6 had MWCOs of 24.820, 7.630, and 9.740 kDa, respectively. In general, the MWA-prepared membranes 3 and 4 had smaller pore sizes. This explains their higher rejection rates. It appears that the presence of LiBr improves the hydrophilic properties of the membrane, which improves not only the permeation rate but also the rejection rates of the membranes. LiBr acts as a pore reducer, as demonstrated by the reduction in the MWCOs of the membranes that corresponded to their smaller pore sizes. The swelling propensities of both DMF and LiBr are balanced by the introduction of the microwave technique for dope solutions and the posttreatment microwave irradiation, respectively. This balance produces membranes with excellent rejection and flux rates. In addition, the production cost of the membranes is lowered because the polymeric membrane can be produced within a 1−2 h period that uses far less energy consumption (only 12 min of energy usage is necessary).

3.2.3. Influence of LiBr on Membrane Pore Sizes and Pore Size Distributions. Log/lognormal plots of solute separations versus solute diameters for MWA PES ultrafiltration membranes that have been prepared with additives of different molecular weights are presented in Figure 4. The Stokes diameter d_s was determined using eq 4. The values of the mean pore size, standard deviation, and MWCO of each of the PES ultrafiltration membranes were calculated from solute separation curves. The results are presented in Table 3.

The mean pore sizes were calculated with d_s values that correspond to the solute separation $R = 50\%$. PES ultrafiltration membranes without additives exhibited a MWCO of 35.00 kDa with a mean pore size of 4.872 nm. Singh et al.[25] and Idris et al.[22]

2276

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also tested the filtration of PEG of various molecular weights using PES membranes with varying pore sizes and pore size distributions.
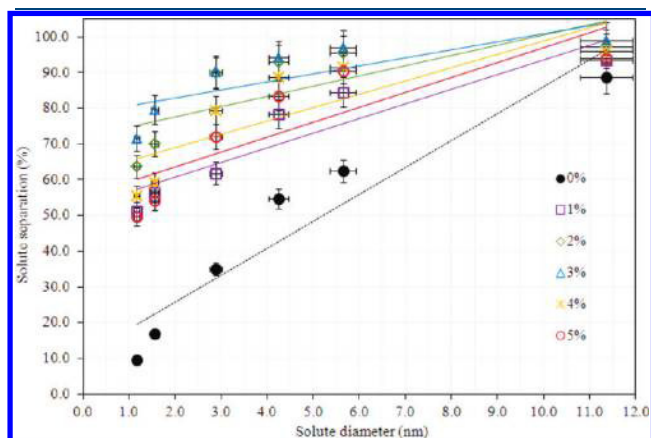

Figure 4. Pore size distribution of PES membranes with various concentrations of LiBr (membranes 1−6).

Our results showed that an increase in LiBr concentration from 3 to 6 wt % (membranes 4−6) caused pore sizes to increase from 0.250 to 1.602 nm. However, the deviations decreased from 1.385 to 1.177 for membranes 5 and 6. This showed that the pore size of the membranes increases linearly with the concentration of LiBr additives. Nevertheless, for PES ultrafiltration using membranes 2 and 3, which both contain LiBr, the molecular weight cutoffs were observed to be approximately 24.820 and 3.460 kDa, respectively.

These results revealed that membranes 5 and 6 had large pore radii but low PWPs and PRs. Kesting[13] reported that the MWCO acts as a rough guide to the pore size of the membranes; i.e., large MWCOs imply the presence of larger membrane pore sizes. Further, our results revealed that the use of MWA-treated dope solutions with posttreatment in membranes 3 and 4 with 2−3 wt % LiBr not only created membranes with high rejection rates but also created membranes with high fluxes and smaller pore sizes and low MWCOs (between 3.460 and 2.842 kDa) compared to PES ultrafiltration membranes 1 and 2 and membranes 5 and 6.

3.3. Effect of Our Preparation Techniques on the Structure of Membranes. *3.3.1. Infrared Spectroscopic Analysis.* The

Table 3. Mean Pore Size, Standard Deviation, and Molecular Weight Cutoff of UF Membranes with and without LiBr

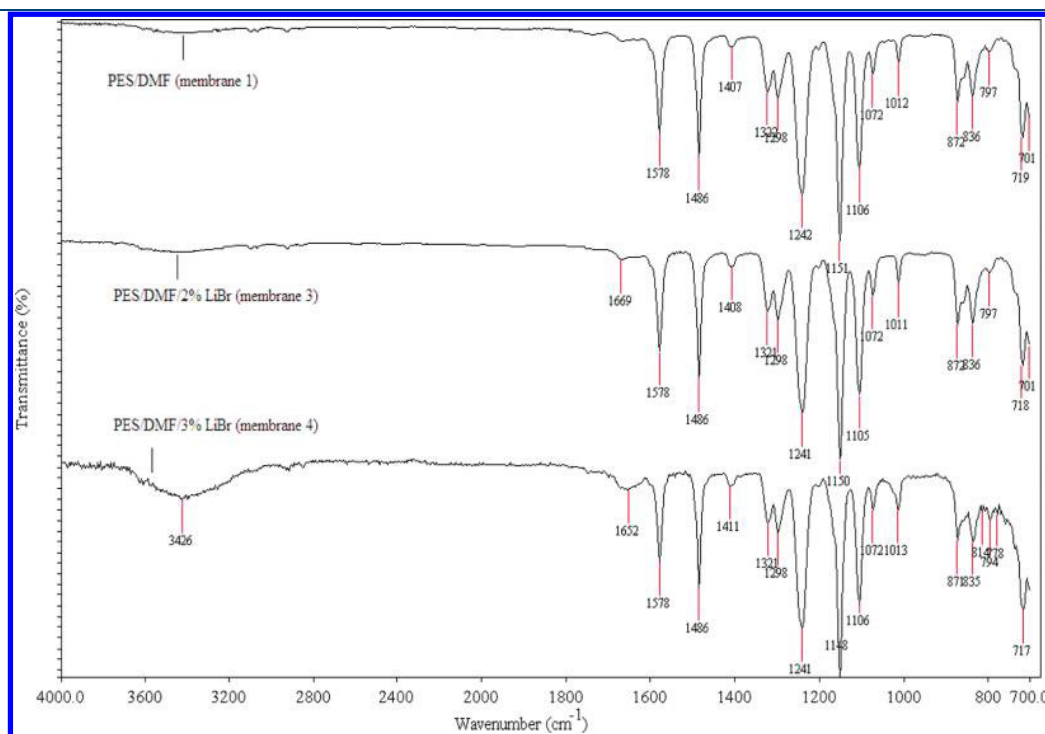| membrane no.	molecular weight cutoff (kDa)	mean pore size, μ_p (nm)	standard deviation, σ_p	R^2
1	35.00	4.872	4.864	0.905
2	24.820	1.831	1.158	0.837
3	3.460	0.977	0.924	0.558
4	2.842	0.250	0.776	0.621
5	7.630	1.496	1.385	0.665
6	9.740	1.602	1.177	0.707

Figure 5. Infrared spectra from 700 to 4000 cm^{-1} of PES membranes with 0 wt % LiBr (membrane 1), 2 wt % LiBr (membrane 3), and 3 wt % LiBr (membrane 4).
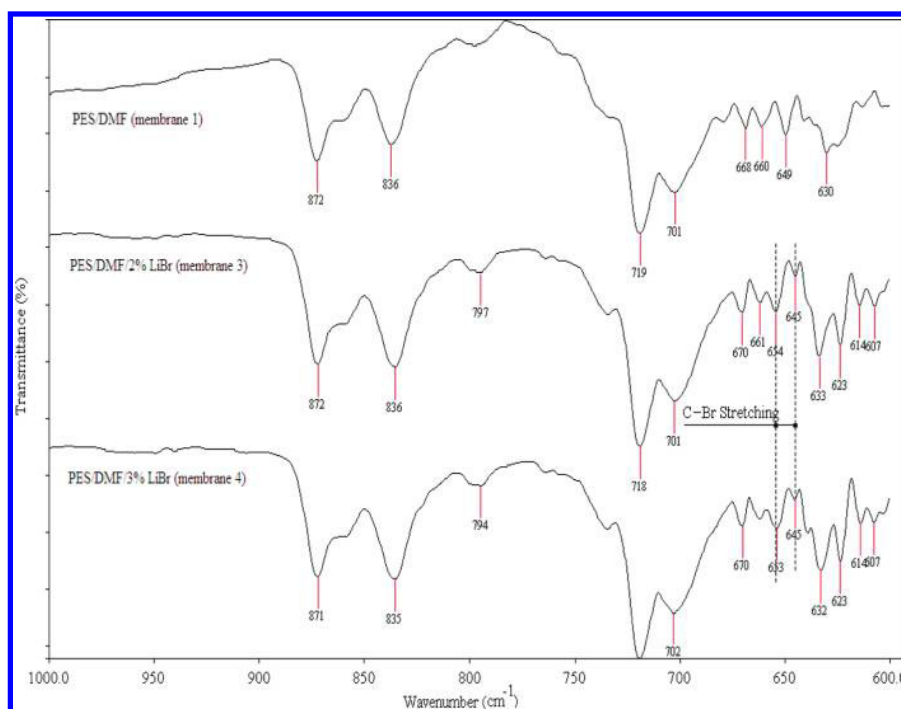
Figure 6. Infrared spectrum from 600 to 1000 cm^{-1} of PES membranes with 0 wt % LiBr (membrane 1), 2 wt % LiBr (membrane 3), and 3 wt % LiBr (membrane 4).

spectra of PES membranes with and without additives are presented in Figures 5 and 6, respectively. FTIR spectra of the membranes over a broad range of wavenumbers from 4000 to 700 cm^{-1} are illustrated in Figure 5. Figure 5 shows the ATR-FTIR spectra of membrane 1 without additives and membranes 3 and 4 with additives. In the spectra of the membrane 1, 3, and 4 films, the bands present at 1578 and 1486 cm^{-1} are attributed to the aromatic skeletal and asymmetric stretching vibrations, which are characteristic bands for PES. Fairly weak bands are observed in the region 1407−1412 cm^{-1} due to the stretching vibration of the SO$_2$ groups. As was expected, the electronegative substituent (Br$^-$) tended to increase the frequency of the SO$_2$ stretching vibration mode.[32] The peaks between 1242 and 1315 cm^{-1} are very high and are attributed to the asymmetric and symmetric vibrations of the C−O−C groups of the alkyl aryl ethers.[32] The peaks found at 1322 and 1298 cm^{-1} result from the antisymmetric O=S=O stretching of the sulfone group. The peak at 1151 cm^{-1} is due to the symmetric O=S=O stretching of the sulfone group. Simultaneously ring vibrations of para-substituted phenyl ethers at 1012 cm^{-1}, out-of-plane C−H deformations that are characteristic of para-substituted phenyls at 836 cm^{-1}, and C−S stretching vibrations at 719 cm^{-1} were also detected.[32,33]

Figure 5 shows the FTIR spectra of PES membranes 3 and 4 in the presence of LiBr. There are new absorbance bands that appear in the range of wavenumbers from 1300 to 1800 cm^{-1}, which are attributed to the end groups or radical recombination segments caused by chain scission events.[34] The spectra also display the emergence of a new band belonging to membrane 4 that corresponds to the O−H stretching mode at 3426 cm^{-1}. However, the band due to water in PES is normally found at 3650 and 3550 cm^{-1}.[35] The new bands in membranes 3 and 4 (Figure 5) are associated with the C−O−C (1011 and 1013 cm^{-1}) vibration mode. They have reduced intensities in these

membranes, which indicates that the C−O−C bond might break down to create an O−H bond and a C=O with modes between 1669 and 1652 cm^{-1}.[33,35] This new band would be caused by H-bonding or by the attachment of a halogen group with a repeating unit at the ortho position. Rivaton[36] and Norrman[37] made the same observation and attributed it to electromagnetic stress on the PES structure. The SO$_2$ symmetric stretching bands of C−O were observed at 1148 and 1150 cm^{-1} for membranes 4 and 3 (Figure 5), respectively, because of their insensitive response to microwave irradiation in the presence of LiBr. This means that the Li$^+$ ions and Br$^-$ ions primarily interact with the sulfonyl moiety under irradiation conditions. These effects are in agreement with the mechanism suggested by Brown and O'Donnell[38] that radiation-caused chemical reactions mainly occur at the diphenyl sulfone groups. The development of peaks associated with aliphatic C−H stretching provides evidence that the phenyl ring structure is modified and causes straight chain carbon structures to form.[33,35,36] The absorption peaks associated with the ring vibration of para-substituted phenyl ethers at 1012 cm^{-1}, the out-of-plane C−H deformation characteristic of para-substituted phenyl at 835 cm^{-1}, and the C−S stretching vibration at 719 cm^{-1} were also observed (see Figure 6). The changes in the chemical structure of PES as a result of microwave irradiation stress are similar to the changes observed after exposure to UV radiation.[39] This suggests that IR absorption occurs when the interface of the molecule is irradiated and produces a change in the dipole moment during a irradiation vibration. Spectral peaks result when molecular motions produce a change in the polarizability of the molecule.[33] It can be concluded that during the membrane dope solution preparation halogen groups are introduced into the polymer chains.

Figure 6 shows the IR spectra of PES membranes 1, 3, and 4 over the range of wavenumbers from 600 to 1000 cm^{-1}. When we compare the spectra of membranes 3 and 4, it is very clear that
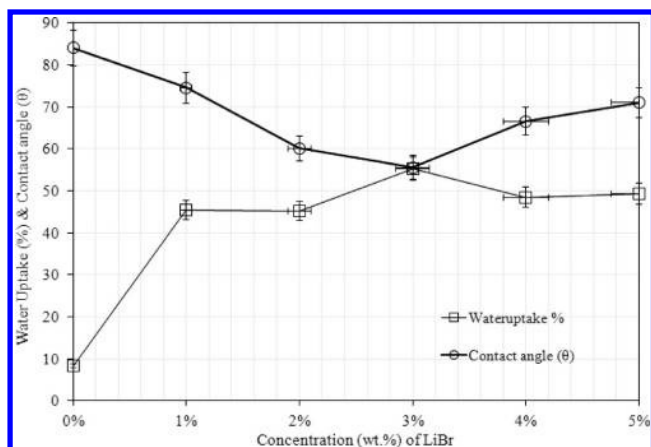
Figure 7. Water uptake measurement and contact angle measurements of PES membrane with various concentrations of LiBr (membranes 1−6).

the membranes with LiBr exhibit six new absorption bands at 654, 645, 632−633, 623, 614, and 607 cm^{-1}. Among the bands, the peaks at 654 and 645 cm^{-1} correspond to the C−Br stretching vibration caused by the putative ortho-substituted ring.[35,38,40] This suggests that the attachment of Br$^-$ with PES occurs in the membrane sample. Thus, the absorption ratios of both peaks were correlated to the weight ratios of LiBr to PES.

3.3.2. Influence of LiBr on the Hydrophilicity of PES Membranes. The hydrophilicities of the membranes were evaluated using water uptake and contact angle measurements. The water uptake and contact angle value analyses are illustrated in Figure 7. It was observed that the values of water uptake and contact angles for each membrane are different.

As illustrated in Figure 7, the water uptake of the membrane increases with increases in LiBr concentration up to 3 wt %. However, when the amount of LiBr is increased beyond 3 wt %, the water uptake starts to decrease. Because LiBr has a greater dissociation tendency, it has increased membrane flux. It acts as a pore former and enhances the hydrophilic properties of the membranes especially when the LiBr concentration is 3 wt %. The water uptake values of membranes 2, 3, 5, and 6 are very similar to each other. The reduced water uptake values show that membranes 2, 3, 5, and 6 are less hydrophilic compared to membrane 4. However, the lowest water uptake value was observed for membrane 1 that had no LiBr added to it.

The contact angle measurements (Figure 7) also demonstrated changes in the hydrophilicity of the membrane when LiBr was integrated into the membrane. Increasing the LiBr content from 2 to 4 wt % (membranes 3−5) reduced the contact angle measurements (Figure 7). However, when the amount of LiBr is increased beyond 3 wt %, the contact angle starts to increase. The reduced contact angle values show that the membranes with LiBr are more hydrophilic. In fact, this explains the improved permeation rates observed when LiBr is added. Membrane 4 had the lowest contact angle value and was also the membrane with the highest permeation rate. In addition, membranes 3 and 4 have smaller contact angles (60.15° and 55.50°, respectively) compared to the 84° contact angle for membrane 1. The performance results also revealed that membranes 3 and 4 exhibited 8−9 times higher permeation rates compared to membrane 1. Moreover, membranes 2, 5, and 6 also showed smaller contact angles than membrane 1, but these values were

still higher than those for membranes 3 and 4. The interaction of LiBr with the membrane matrix resulted in the enhancement of the hydrophilicity of the membrane prepared with LiBr dope solutions. This last observation is likely attributable to Br$^-$ that was left in the fabricated membrane. These studies relate the contact angle and hydrophilic properties with the wettability of PES membranes containing LiBr.

The results of the water absorption and contact angle measurements revealed that the membranes with LiBr become more hydrophilic. There is the possibility that, during the MWA dope preparation, the halogen group introduced itself into the polymer chains and, because of the continual irradiation, surface modification might have occurred. In addition, irradiation causes heating that increases the energy levels. This can cause molecular transitions from an efficiently bound state to an ionic state and then to a nonionic repulsive state.[10,23] Such volumetric heating by irradiation possibly promotes surface modification including those that result from the interaction between Li$^+$ and Br$^-$ within the membrane matrix that results in increased hydrophilicity of the membrane.[23] In FTIR spectra, the bands observed at 1150 and 1148 cm^{-1} were insensitive to incorporation of LiBr and the membrane hydrophilicity. Further, our current discussion explains why the absorption ratios of the water uptake and contact angles were correlated to the weight ratios of LiBr to PES.

3.3.3. Membrane Morphologies. The cross-sectional structures at 500× magnification of the PES/DMF membranes produced from the MWA dope solutions and posttreatment without LiBr are shown in Figure 8 (membrane 1). Prior research had shown that the casting solution characteristics and formulations have direct influences on asymmetric membrane formation and structure.[2,3,9] An examination of the cross-sectional structures revealed that membrane 1 (Figure 8) has a thick and dense skin layer built upon a spongy support containing many macrovoids. The fine fingerlike structure gradually develops into larger macrovoids toward the bottom. These structures are characterized by the lowest rejection rates, and the thick skin layers create a high resistance to flow, which explains this sample's low flux rates. These results suggest that on immersion of the cast polymer solution (PES/DMF) in the nonsolvent water bath there is a fast solvent−nonsolvent exchange across the interface that is combined with the large repulsive forces between PES and water. Water is a very powerful nonsolvent for PES that causes immediate precipitation of the polymer at the interface. This phase-inversion process is too fast for any segregation of the polymer solution into either a polymer-rich phase or a polymer-lean phase. Because the PES concentration is moderately low (20 wt %), a thick and dense skin layer with many macrovoids forms.

The scanning electron micrographs (SEMs) of the membrane cross sections with the LiBr additive (membranes 3−5) are also presented in Figure 8. We note that the SEM images of membranes 3−5 change with the concentration of LiBr. The morphology of the membranes consists of two different top and bottom structures: the asymmetric layer with linear channels and the spongy porous layer. It is observed that the top layer of the membrane was thicker and denser. Further, there was a change in the formerly fingerlike structures that developed into a spongy layer. These changes occurred likely because the casting solution was more viscous at higher concentrations of LiBr. Specifically, the addition of LiBr contributes to the intermolecular aggregation between the polymer chains. This results in the diminished mobility of the polymer solution, which leads to a solidification in the top layer of the membrane.[41] Consequently, this increase in
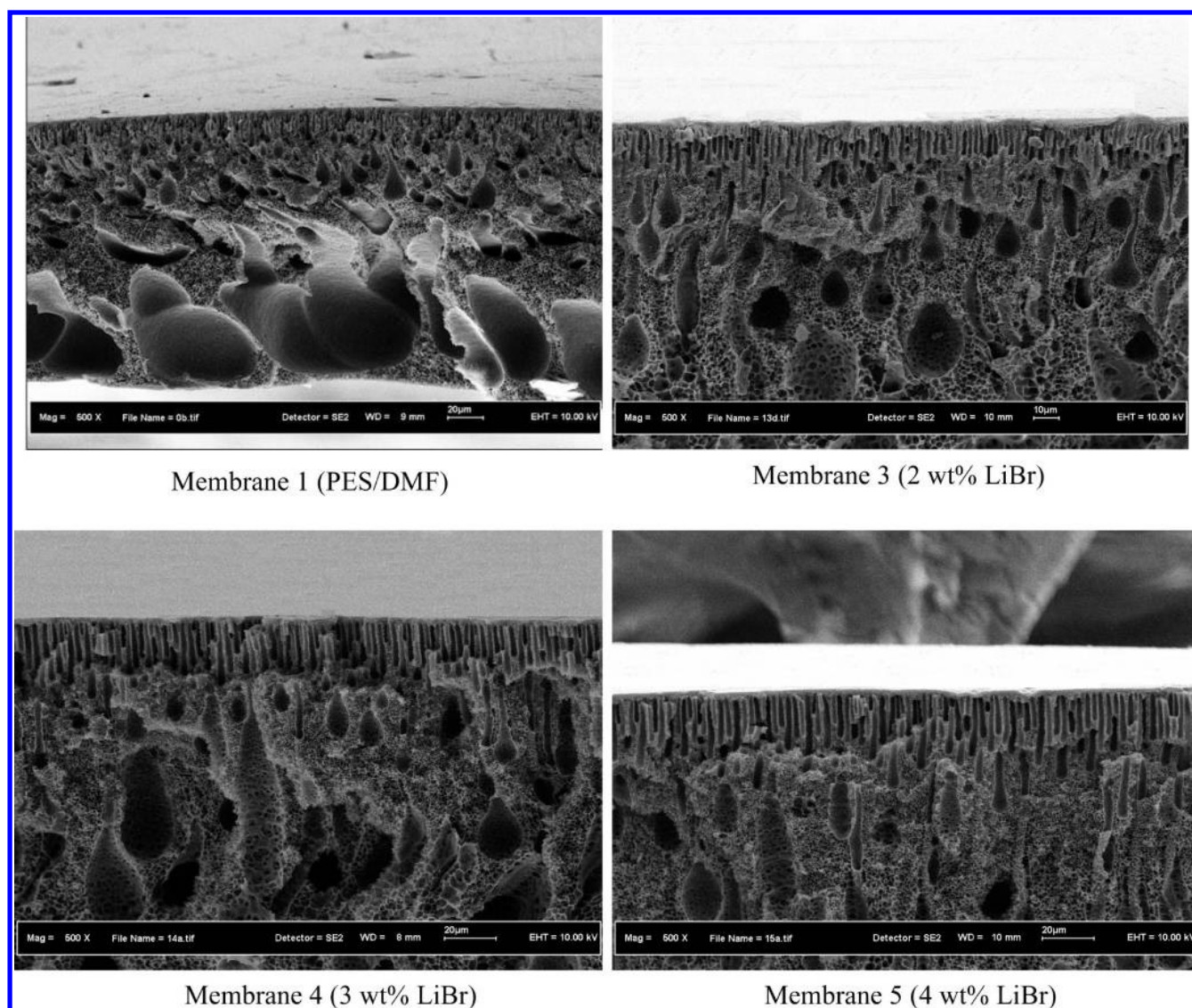
2279

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Figure 8. SEM micrographs of PES membranes with various concentrations of LiBr additive.
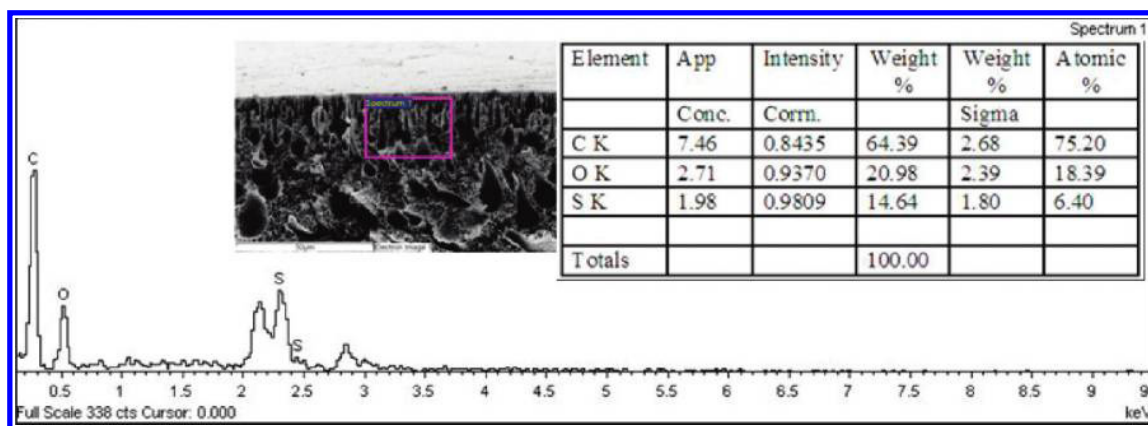

Figure 9. SEM-EDX of PES membrane without additive (membrane 1).

the viscosity of the casting solution makes the top layer relatively thick and dense and hinders the exchangeable diffusion between the solvent and the nonsolvent. This, in turn, reduced the precipitation rate of the sublayer while the demixing type of activity is maintained. Pure water permeation is dependent on the top layer and the sublayer of the membrane. The thin
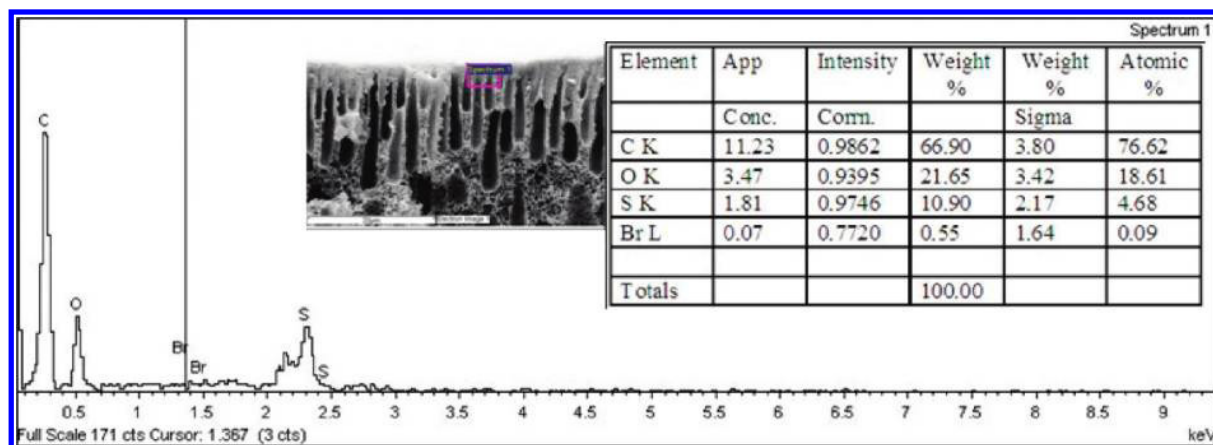
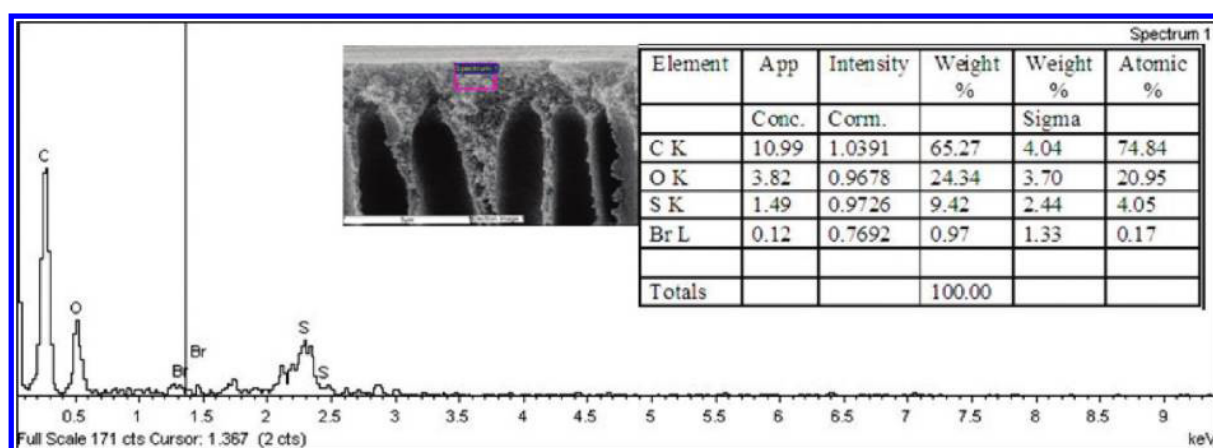**Figure 10.** SEM-EDX of PES membrane with 2 wt % LiBr (membrane 3).

Element	App Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %
C K	11.23	0.9862	66.90	3.80	76.62
O K	3.47	0.9395	21.65	3.42	18.61
S K	1.81	0.9746	10.90	2.17	4.68
Br L	0.07	0.7720	0.55	1.64	0.09
Totals			100.00		

Figure 11. SEM-EDX of PES membrane with 3 wt % LiBr (membrane 4).

Element	App Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %
C K	10.99	1.0391	65.27	4.04	74.84
O K	3.82	0.9678	24.34	3.70	20.95
S K	1.49	0.9726	9.42	2.44	4.05
Br L	0.12	0.7692	0.97	1.33	0.17
Totals			100.00		
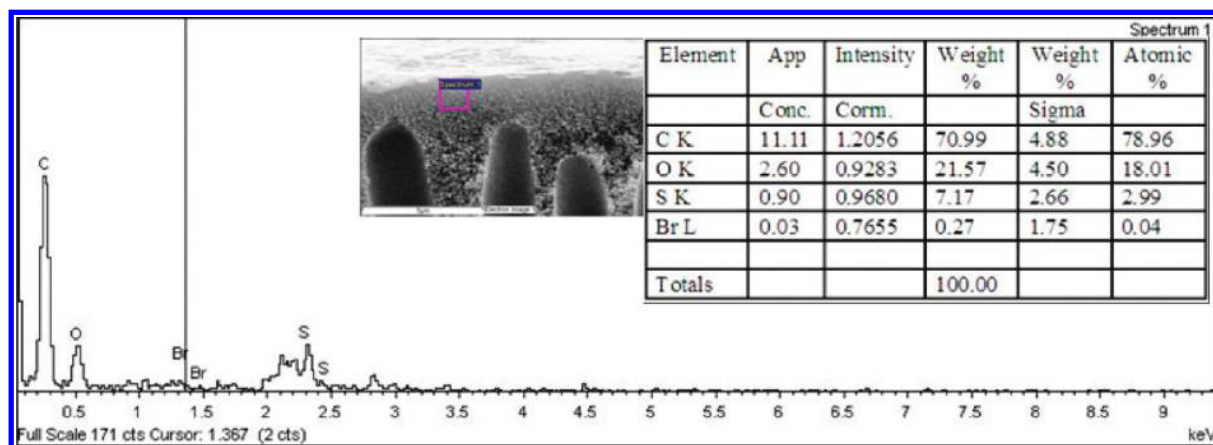
Figure 12. SEM-EDX of PES membrane with 4 wt % LiBr (membrane 5).

Element	App Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %
C K	11.11	1.2056	70.99	4.88	78.96
O K	2.60	0.9283	21.57	4.50	18.01
S K	0.90	0.9680	7.17	2.66	2.99
Br L	0.03	0.7655	0.27	1.75	0.04
Totals			100.00		

asymmetric layer is a probable cause for the increased rejection rate; however, the thick spongy structure causes an increase in resistance and, thus, low flux rates.[4] As can be seen in membranes 3−5, the sizes and shapes of the macrovoids are different. The voids gradually changed in structure from elongated microvoids to "teardrop" shapes. Membrane 4 with 3 wt % LiBr had a relatively thin asymmetric layer with very fine fingerlike structures near the

top layer and the presence of elongated macrovoids. It was thus concluded that LiBr promoted the formation of macrovoids.

3.3.4. SEM-EDX Analysis. The FTIR study was found to be in good agreement with the ring breathing mode because the C−Br stretching modes at 645 and 654 cm^{-1} were observed.[34] Moreover, swelling measurements and contact angle measurements confirmed that LiBr changed the hydrophilicity of PES

membrane surfaces, leading to different water permeabilities. Pore size distribution analysis and SEM micrographs confirmed the assumption that a restructuring of the membrane material occurred, which led to differences in pore size and porosity. Accordingly, scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis also provided supporting information concerning the membrane characterization.

The spectra of SEM-EDX of the PES/DMF membrane (membrane 1) and the LiBr dope solution based membranes of membranes 3, 4, and 5 are shown in Figures 9, 10, 11 and 12, respectively. The results of SEM-EDX revealed that introduction of LiBr as an additive also improved the membranes' hydrophilic properties. The dope preparation process in a microwave oven is a practical way to potentially allow the LiBr bonds to vibrate and rotate rapidly.[11] Thus, the highly electronegative bromine ions could easily attach to the polymer structure as is shown in the EDX analysis and Figures 10–12. The presence of 0.55, 0.97, and 0.27 wt % bromine was detected in the membranes in Figures 10, 11, and 12, respectively. However, no bromine was detected for the salt-free membranes (Figure 9). The presence of the bromine might be another contributing factor that led to the improved hydrophilic and hydrated structures of the membranes. This is proven by the high flux rates of the PES/DMF membranes containing LiBr. However, a higher ratio of Br was observed in membrane 4 containing 3 wt % LiBr. This explains the higher flux rates of membrane 4 when compared to membranes 1–3 or membranes 5 and 6.

In our previous work,[10,14] it was shown that, in the MWA closed heating system, solvents were irradiated and heated to above their boiling points. This form of superheating contributed to the rapid dissolution of PES polymers even in the presence of additives. We attribute this to ionic polymerization that occurred under the microwave irradiation. However, also ionic bond formation cannot be discounted because we saw the formation of such bonds by FTIR and EDX analyses.

4. CONCLUSION

Results revealed that the microwave technique is capable of producing a membrane-manufacturing process in very short times. The membranes prepared from the microwave technique offer good rejection and permeation rates. In addition, the performances of membranes prepared with LiBr additives are superior compared to membranes prepared without LiBr. Adding LiBr in the range of 2–3 wt % enhanced both its rejection and permeation rates. However, increasing the LiBr beyond 4 wt % is not recommended since both its rejection and permeation rates tend to decrease. The IR spectra analyses suggested that some amount of chain scission might have occurred, as we saw the emergence of peaks that belonged to OH, C=O, C–O, and C–Br groups in the PES membrane. However, these peaks showed no signs of affecting the membranes' performance characteristics. In addition, the SEM-EDX analyses also supported the emergence of Br$^+$ into PES structure. Water uptake and contact angle measurements revealed that the membranes made using this technique have higher hydrophilicity than membranes made using conventional methods.

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2282

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