



Journal of Applied Sciences

ISSN 1812-5654

science
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Preparation of PES Ultrafiltration Membrane using Novel Modified Microwave Casting Solution Technique

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Abstract: In this study the influence of anhydrous lithium fluoride (LiF) and the novel modified microwave casting solution technique on membrane performance are investigated. The polyethersulfone (PES) asymmetric membrane was prepared by the dry/wet phase inversion process. In order to observe the effect of microwave dissolution technique on membrane performance, PES concentration in the dope solutions was kept to 20 wt.% through out the experiments. The concentration of lithium fluoride was varied from 1-5 wt.% and N, N-dimethylformamide (DMF) is used as the solvent. Viscosities of the dope solutions were measured and membrane performance was characterized in terms of pure water permeation (PWP), permeation rate (PR) and solute separation of PEG solutions of different molecular weights ranging from 600-35000 Da. The molecular weight cut off (MWCO), mean pore size and pore size distribution of the membranes were subsequently determined. Results disclosed that the addition of lithium fluoride to the PES/DMF solution and the microwave irradiation technique increases the membrane permeability while maintaining their separation properties. However, the LiF concentration was best kept to 2 wt.% concentration.

Key words: Ultrafiltration membrane, LiF, PES

INTRODUCTION

Membrane research worldwide is still concerned with the development of new techniques and the comprehension of the phenomena in membrane formation, due to the difficulties to obtain membranes with the desired properties, i.e., ultra-thin and defect-free dense skin. Different methods of polymer membrane preparation have been covered in several reviews. Dense homogeneous polymer membranes are usually prepared from solution by solvent evaporation only or by extrusion of the melted polymer. There may be a number of reasons for polymer to be chosen, e.g., thermal, chemical and solvent stability, price, etc. but the most important one is that membranes prepared from these polymers can separate solute from solvent. Ultrafiltration (UF) is a process of separating extremely small particles and dissolved macromolecules from fluids using asymmetric membranes of surface pore size in the range of 50 to 1 nm and often operated in a tangential flow mode where the feed stream sweeps tangentially across the upstream surface of membranes as filtration occurs, thereby maximizing flux rates and membrane life. It imposes

specific requirements on the membrane material and membrane structure and the efficiency of UF is determined by the porosity and the pore size of the membrane.

Polyethersulfone (PES) polymer is well used for membrane fabrication as it produces high performance asymmetric membrane. Aromatic polysulfone family of polymers is extensively used due to their wide temperature, pH and chlorine tolerance. PES consists of phenylene ring structures connected together with sulfone groups (SO₂) or ether linkages (-O-) in the backbone chain to form a polymer. The sulfone groups tend to make the polymer stiff with a high glass transition temperature and together with the ring structures, it makes the polymer chemically resistant and relatively hydrophobic (Kesting, 1985). For better membrane properties, a third component as additive can be dissolved in the casting solution (Barth *et al.*, 2002). These additives affect membrane in developing spongy structure and prevent the formation of macrovoid as it enhances pore formation and hydrophilicity of membrane (Katarzyna, 1989; Wienk *et al.*, 1996). There are many kinds of additives including polymers, nonsolvents and inorganic

salts. Inorganic salts were found effective for the fabrication of membrane having an appropriate structure and high performance (Kim *et al.*, 1999). Although, the membrane preparation techniques are well known, the precise membrane casting procedure outlining choice of solvent, additive, concentration and other relevant details are not available for several polymer candidates.

Less fouling behavior was found in modified polyethersulfone membranes and it has a wide range of retentate pH values, giving more protection (Wienk *et al.*, 1996). The water permeability, salt permeability and water regain studies of sulfonated PES membranes have been studied (Brousse *et al.*, 1976) and constant research are carried out by applying polymer, nonsolvent and inorganic salt as additives in casting dope to study the performance and structure improvement. Inorganic salt additive was found to be more effective for membrane performance and structure improvement (Kesting, 1985; Kraus *et al.*, 1976) as it affects the thermodynamic/kinetic properties of the membrane-forming system, thus resulting in changes in the membrane structure and performance.

Several commonly used additives include low-molecular-weight inorganic salts such as lithium chloride (LiCl), zinc chloride (ZnCl₂), magnesium chloride (MgCl₂), calcium chloride (CaCl₂), magnesium perchlorate, (MgClCO₄) and calcium perchlorate (CaClCO₄). However no work has been reported regarding the use of LiF additive in PES membranes. Thus the objective of this study is to investigate the influence of LiF on separation performance of PES membranes.

MATERIALS AND METHODS

Commercial grade polyethersulfone (PES) in resin form was supplied by BASF. The solvent N, N-dimethylformamide (DMF: HCON (CH₃)₂/Mw; 80.14 g mol⁻¹, 99.8%) was purchased from Labscan Asia Co. Ltd and used without further purification. Inorganic salt additive lithium fluoride anhydrous (LiFH₂O) 99.7% (mol. wt. 12) was obtained from Fischer Scientific Chemicals. Tap water was used as the coagulation bath. For UF experiments, PEG with various molecular weights (PEG 600, PEG 1000, PEG 3000, PEG 6000 and PEG 10,000) were obtained from Fluka.

Dope solution preparation: PES and LiFH₂O were dried in microwave for 10 min at medium to high pulse before dissolving them in DMF. The 500 mL polymer solution consists of 20% PES in various concentrations of DMF and LiFH₂O as shown in Table 1. The dope solution was prepared in the modified microwave at low to high pulse.

Table 1: Dope solution compositions

Dope solution No.	Composition in wt. %		
	PES	LiF	DMF
0	20	0	80
1	20	1	79
2	20	2	78
3	20	3	77
4	20	4	76
5	20	5	75

Temperature was kept at 90-95°C. Temperature was monitored by a thermocouple.

Membrane casting: The membranes are prepared by phase inversion method. The dope solution thus obtained was spread over a smooth glass plate with the help of a casting knife. The thickness of the membranes was 200 μm. The casted polymer film was then immersed in a tap water at room temperature, where exchange between the solvent and water is induced. It was then transferred to another container containing distilled water. All membranes were inspected for defects and good areas were chosen for evaluation.

Viscosity measurements: The average apparent viscosity of the dope solutions were measured with Brookfield Digital Rheometer (model DV-III ultra, USA) equipped with a suitable-sample adaptor (SC4-31). The viscosity for dope solutions was measured at room temperature. The spindle was SC4-31 type.

Determination of permeation flux and solutes rejection: Pure water permeation fluxes (PWP) and solutes water permeation fluxes (PR) of membranes were obtained as follows:

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

where, J is the permeation flux of membrane for PEG solution (L/m/h) or pure water and Q is the volumetric flow rate of permeate solution. Δt is the permeation time (h) and A is the membrane surface area (m²). Solute rejection of membranes was evaluated with various molecular weight of PEG solutions ranging from 600 to 40,000 Da at 4.5 bar. The concentration of PEG solution used is 500 ppm. The concentration of the feed and permeate solution were determined by the method described elsewhere (Sabde *et al.*, 1997).

The membrane rejection (SR) is defined as:

$$SR = 1 - \frac{C_p}{C_f} \times 100 \quad (2)$$

where, C_f and C_p are the polyethylene glycol concentration in the feed solution and permeate solution, respectively. The concentration of PEG was determined based on absorbency in a UV-spectrophotometer at a wavelength of 535 nm.

Pore and pore size distribution: The pore size of PES membrane produced was determined using transport data (Sabde *et al.*, 1997). Solute diameter (d_s) is given by:

$$d_s = 2a \tag{3}$$

where a is the Stokes radius of polyethylene glycol, with a function of molecular weight, M . This is given by:

$$a = 1673 \times 10^{-10} M^{0.557} \tag{4}$$

Stokes radius of a macromolecule can be obtained from its diffusivity in a solution using Stokes-Einstein equation as reported by Singh *et al.* (1998). The Stokes radius was explained as radius of hypothetical sphere that would diffuse with the same (Ani *et al.*, 2007) speed as the particle under study (Park *et al.*, 2000). To determine the mean pore size (μ_p) and standard deviation (σ_p) of the membranes, the data of solute separation versus solute diameter that formed solute separation curve was plotted on log normal graph. The mean pore size was calculated with d_s corresponding to $R = 50\%$ on the linear regression line. The standard deviation was calculated from the ratio d_s at $R = 84.13\%$ and at 50% . Moreover, MWCO can be measured from the regression line at $R = 90\%$.

RESULTS AND DISCUSSION

Performance of the membranes: Table 2 observed that membranes produced from dope solution containing LiF exhibits high pure water permeation (PWP) compared to those prepared without additive. Membranes containing 4% LiF exhibits highest PWP. In general, the PWP for membranes having 3-5% LiF has approximately 50% higher than the 1% LiF.

Table 3 indicates that membranes with LiF showed both higher permeate rate and rejection compared to that without LiF. However, membrane with 5% additive has low rejection rates with MWCO greater than 40 kDa although it has the highest permeate rate. Improved permeation flux of the membranes has confirmed that the hydrophilic property of the membrane has improved by the presence of LiF. The presence of LiF has helped improved both the PR and rejection rates of the membranes but its concentration is best kept to 3%. Increasing LiF concentration to above 3% will not only

Table 2: Pure water permeation of LiF membranes

Concentration of LiF (%)	PWP (L/m ² /h)
0	41.05
1	31.60
2	71.00
3	126.30
4	237.00
5	221.00

Table 3: Permeation rate and rejection rate of LiF membranes

PEG 10 ³ ppm	600	1000	3000	6000	10000
0%					
PR (L/m ² /h)	39.4	36.3	22.10	25.3	23.7
R (%)	5.0	8.0	25.00	38.3	52.0
1%					
PR (L/m ² /h)	25.3	24.2	23.00	22.0	21.2
R (%)	39.0	54.0	76.00	84.0	94.0
2%					
PR (L/m ² /h)	52.1	50.0	36.30	16.0	11.1
R (%)	50.0	57.0	71.00	85.0	97.0
3%					
PR (L/m ² /h)	106.0	79.0	69.50	39.5	28.4
R (%)	29.2	47.5	62.34	85.6	91.3
4%					
PR (L/m ² /h)	158.0	126.3	111.00	79.0	69.5
R (%)	8.6	18.4	29.70	46.3	79.5
5%					
PR (L/m ² /h)	142.1	126.3	118.40	111.0	79.5
R (%)	6.3	8.2	14.50	23.4	42.8

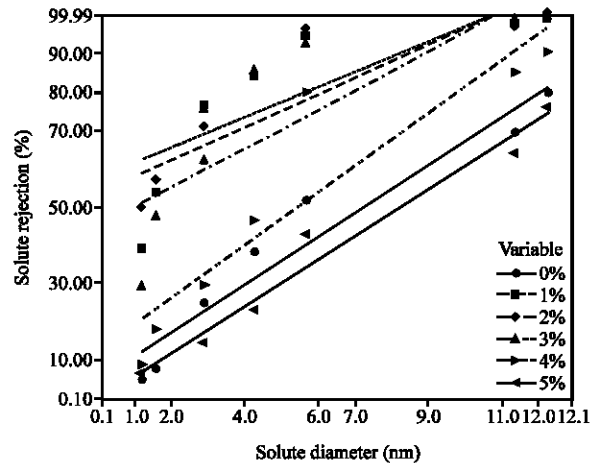


Fig. 1: Solute separation curve

increase the permeation rates but decrease its rejection rates.

Mean pore size and pore size distribution: From Fig. 1, the mean pore size (μ_p), standard deviation (σ_p) and MWCO were calculated. Mean pore size is define as pore diameter when solute separation is 50% (Ani *et al.*, 2007). Results tabulated in Table 4 showed that the membrane without additive has 35 kDa MWCO and 3.75 nm mean pore size. As for 1, 2 and 3% LiF additive membranes, results found membranes has 8.1, 7.1 and 8.45 kDa MWCO and the mean pore size were 0.884, 0.649 and

Table 4: Geometric mean pore size (μ_p) and genomic standard deviation (σ_p) for various membranes

LiF (%)	MWCO (kDa)	Mean pore size μ_p (nm)	SD (σ_p)
0	35.00	3.750	4.5814
1	8.10	0.884	1.4124
2	7.10	0.649	1.0840
3	8.45	1.043	2.0240
4	40.00	4.152	5.2110
5	51.12	4.800	4.9400

1.043 nm, respectively. These values displayed a linear relationship between the mean pore size and MWCO. Smaller pore size of 1 and 2% LiF membrane contributed to low flux although the rejection rate is high. While 4% LiF membrane has high flux but less rejection. The pore sizes obtained in Table 4 further explains the performance of the membranes. Increasing LiF concentration to more than 3% will not reduce the pore size of membranes. Thus the best concentration of LiF that should be used is 3% as the membranes produced has small pore sizes which displays high rejection rate and permeate rates.

CONCLUSION

Membranes produced from dope solutions containing LiF are superior in terms of permeation flux rates, rejection rates and quality of membranes compared to those prepared without additive. The addition of LiF has a significant effect on solution properties and resulted in high permeation rate which implies the membrane porosity has increased. It can be concluded that LiF additive with formulation 1-3% exhibited the best rejection rates and permeation rate with MWCO of 8.9 kDa.

ACKNOWLEDGMENTS

Financial support from the Ministry of Science, Technology and Environment through the IRPA funding vote No. is gratefully acknowledged.

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