

Preparation and characterization of porous polyethersulfone nanofiltration membranes via combined phase separation method for water desalination

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ABSTRACT

Porous polyethersulfone (PES) membranes were prepared by combined phase separation method in which both non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) occurred in the membrane-formation procedure. The membrane-forming solution consisted of PES, phenylbenzoate as diluent and N-Methyl-2-pyrrolidone (NMP) as solvent. The morphology of the prepared membranes was investigated by scanning electron microscopy (SEM). Pure water permeation flux, salt (NaCl) rejection rate, pure water contact angle, and thermal gravimetric analysis (TGA) were also investigated. SEM images revealed that the membrane finger-like structure was converted to a continuous porous structure by increasing mass ratio of phenyl benzoate to NMP. All membranes immersed in coagulation bath at 45°C were more hydrophobic than other prepared samples. The highest pure water permeation flux of 766.2 Lm⁻²h⁻¹ (0.2 MPa) and the highest salt rejection of 73.3% were obtained via combined thermally and non-solvent phase separation methods described in this work at feed concentration of 5000 ppm.

Keywords: porous membrane, combined method, NIPS, TIPS

1 INTRODUCTION

Membrane technology requires no chemical additives, thermal inputs and regeneration of spent media. Because of these characteristics, this technology can be favored to answer the global water challenges consisted of population increase [1], overall water shortage [2] and poor water quality [3]. Pressure-driven processes are the most widely used membrane technologies in water treatment applications [4]. A desirable membrane used in water treatment should have high productivity, selectivity, fouling resistance, stability and lower cost. These favored features may be possible not only by using appropriate materials but also by using suitable formation method. Polymeric membranes have been made by phase separation [5, 6], interfacial polymerization [7] and evaporative casting [8]. Among these methods, the phase separation is the most commonly used method for the preparation of polymeric membranes and classified in two main methods known non-solvent induced phase separation (NIPS) and thermally

induced phase separation (TIPS). Asymmetrical structure and finger-like pores resulted from NIPS method are unfavorable because of poor mechanical properties, creation of additional resistance against mass transfer and low flux [9]. In contrast, TIPS method leads to membranes with higher porosity and good mechanical properties [10]. However, there is some limitation in using TIPS method commercially. In this study, the combined phase separation process was employed to prepare the desired membrane structure by mixing PES, phenyl benzoate as diluent and NMP as the solvent at relative lower temperature compared to conventional TIPS method. The performance of the prepared membranes was evaluated by measuring the pure water permeation and salt rejection.

2 METHODS AND MATERIALS

2.1 Materials

Polyethersulfone (PES) (Ultrarason E6020, $\eta=82$ mL.g⁻¹, Mw=51000, $\rho=1.37$ g.cm⁻³) was purchased from BASF Chemical Co. Ltd. (Germany). The polymer was dried for 8 h at 100°C and 0.7 bar. N-Methyl-2-pyrrolidone (NMP) and ethanol (bp=78.4°C, $\rho=0.709$ g.cm⁻³) were purchased from Merck Co. phenyl benzoate (bp=66 °C) and sodium chloride (NaCl) were purchased from Sigma Aldrich Co. NaCl solution was used to characterize desalination performance of the prepared membranes. Also, all of the water used was distilled water.

2.2 Preparation of membranes

Mixture of solvent (NMP) and diluent (phenyl benzoate) were mixed and then an amount of dried PES were dissolved in the mixture of solvent and diluent at 140 °C. After being mixed by mechanical mixer for 2 h, a homogenous hot solution was degassed at 140 °C for 1 h to remove air bubbles. The solution was casted onto glass preheated at 100 °C with 15×15 cm² surface using a mechanical casting machine with a gap of 250 μm and immersed in a water bath colder than solution for 1 h to form membrane. For extraction of phenyl benzoate, the prepared flat sheet membrane was immersed into ethanol bath for 48 h.

The extracting ethanol was evaporated in open air for 1 day at room temperature. Studied parameters and conditions are listed in Table 1.

Table 1. Membrane preparing conditions

Name	Bath temperature (°C)	Mass ratio of phenylbenzoate/NMP	Polymer concentration
S ₁	0	1.5	27.5
S ₂	0	2.25	27.5
S ₃	0	3	27.5
S ₄	22.5	1.5	27.5
S ₅	22.5	2.25	27.5
S ₆	22.5	3	27.5
S ₇	45	1.5	27.5
S ₈	45	2.25	27.5
S ₉	45	3	27.5

2.3 Characterization methods

The fractured membranes in liquid nitrogen were deposited on holders. After sputtering with gold in vacuum, the morphology of cross section and surface of membranes were observed by scanning electron microscopy (SEM, Tescan VEGA II XMU, USA). The permeation flux of the membranes was measured using a home-made cross-flow nanofiltration cell. All experiments were conducted at room temperature and under a feed pressure of 0.2 MPa for 1 min after achieving equilibrium condition. Salt (NaCl) rejection was measured at feed concentration of 5000 ppm.

The hydrophobicity of the membranes was studied by measuring the water contact angle.

Heat resistance of the prepared membranes was investigated by TGA test (Mettler Toledo DSC/TGA 1). A small piece of flat sheet membranes was placed into aluminum pans to seal. The scanning range was 25-600 °C with rate of heating of 10 °C/min in argon atmosphere.

3 RESULTS AND DISCUSSION

In the process used for preparing membranes, the PES was dissolved in a mixed solvent at relatively elevated temperature (140 °C); the homogeneous solution was casted and immersed in water bath at a temperature lower than casted solution. Phase separation due to gradient of temperature and gradient of concentration between coagulation bath and casted solution occurred to produce a membrane structure.

The cross-sectional structure of all samples is shown in Fig.1. As shown in Fig.1 (a), typical instantaneous demixing occurred and finger-like pores were formed in the bottom section of the membrane. Porous structure was observed as dominant structure. Lower bath temperature is associated with lower exchange rate between bath and casted solution and higher viscosity. Thus, this phenomenon led to slow precipitation rate, and the delayed demixing process accrued which resulted in a porous structure in the cross section of the prepared membranes.

Cellular structure happened during both L-L TIPS [11] and delayed demixing NIPS. Therefore, it was expected that by increase of the mass ratio of diluent to solvent, from 1.5 to 2.25 and 3, the contribution of the TIPS phenomenon against the NIPS increased. Thus, finger-like pores got smaller and porous structure got more dominant as shown in Fig.1 (b) & Fig.1(c).

The cross section of immersed samples into coagulation bath of 22.5 °C are shown in Fig.1 (d), Fig.1 (e), and Fig.1 (f). Typical finger-like pores were disappeared but continues grooves from top layer to below layer (throughout the cross section) were formed. Decreasing the viscosity of a casting solution due to increase of the bath temperature will increase the tendency of macrovoid formation [12]. The same phenomenon was observed when bath temperature reached to 45°C but the formed grooves were deeper (Fig.1 (g), Fig.1 (h), Fig.1 (i)). By increase of the bath temperature, release of the solvent increased and grooves got larger and deeper under the same casting condition. Comparing structural morphology of the S₁, S₄, and S₇ membrane samples indicates this fact.

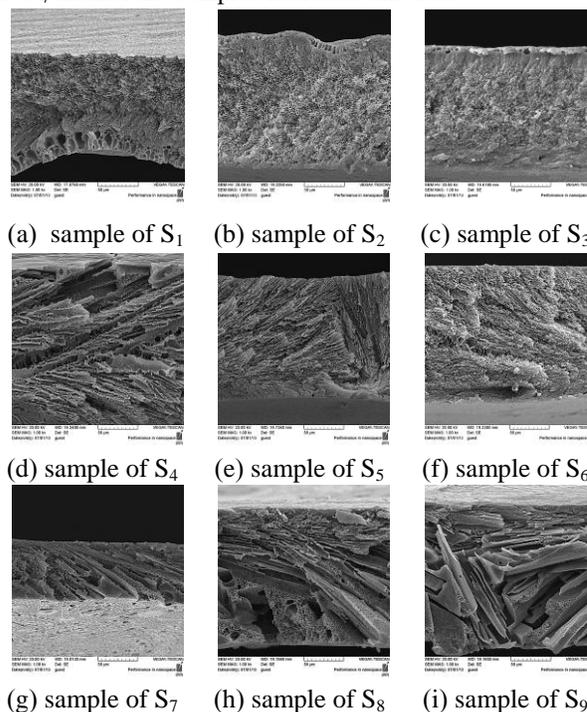


Fig. 1 SEM of cross section of prepared samples

In Table.2 the water permeation flux (J_w) of the porous membranes is presented.

Table 2. Pure water permeation flux of prepared membranes

Bath. Tem (°C)	Phenylbenzoate/NMP	$Lm^{-2}h^{-1} J_w$ (l)

S ₁	0	1.5	156.7
S ₂	0	2.25	110.6
S ₃	0	3	35.8
S ₄	22.5	1.5	356.3
S ₅	22.5	2.25	296.6
S ₆	22.5	3	216.4
S ₇	45	1.5	774.1
S ₈	45	2.25	766.2
S ₉	45	3	565.4

All membranes prepared at bath temperature of 0 °C had the lowest flux compared with other membranes immersed at hotter coagulation baths. By increase of diluent to solvent ratio, pure water flux decreased in the following descending order: S₁, S₂ and S₃.

As shown in Table 2, when the ratio of phenyl benzoate to NMP was kept at 1.5, decrease of the bath temperature resulted in lower pure water flux. At the lower ratios of the diluent to solvent, NIPS process had comparable contribution to formation of the membrane. Therefore, decrease of the coagulation bath temperature resulted delayed dimixing, smaller pore sizes and lower water flux consequently. The maximum water permeation flux 766.197 Lm⁻²h⁻¹ was measured for the S₈ polymeric membrane sample.

Salt rejection percent of the prepared membranes at 0.2 Mpa pressure and salt concentration of 5000 ppm is presented in Table.3.

Table 3. Salt rejection percent of samples at feed concentration of 5000ppm at 0.2 MPa

	Bath. Tem (°C)	Phenylbenzoate/NMP	Salt rej. (%)
S ₁	0	1.5	60.4
S ₂	0	2.25	62.1
S ₃	0	3	73.3
S ₄	22.5	1.5	52
S ₅	22.5	2.25	54.2
S ₆	22.5	3	56.8
S ₇	45	1.5	46.4
S ₈	45	2.25	41
S ₉	45	3	47.6

Comparing of the results from Table.3 shows that as the mass ratio of the diluent to solvent increased, salt rejection increased too. Salt rejection is related to morphology of membranes directly. The effect of delayed dimixing and

contribution of the TIPS enhanced the performance, which led to cellular pores and continuous structure in the cross-section of the prepared membranes. Therefore, porosity and mean pore size of the membranes decreased and rejection percent increased.

The effect of casting conditions on contact angle which is related to the pure water flux is reported in Table 4.

Table 4. Pure water contact angle of samples

	Bath. Tem (°C)	Phenylbenzoate/NMP	Contact angle
S ₁	0	1.5	72.26
S ₂	0	2.25	80.7
S ₃	0	3	71.12
S ₄	22.5	1.5	80.55
S ₅	22.5	2.25	79.1
S ₆	22.5	3	75.7
S ₇	45	1.5	89.55
S ₈	45	2.25	79.45
S ₉	45	3	90.58

It was observed that the increase in the mass ratio of the diluent to solvent from 1.5 to 2.25 for S₁ and S₇ samples resulted to more hydrophobic surface. However, further increase in the ratio resulted in lower contact angles.

In addition, for membranes containing diluent to solvent ratios of 1.5 and 3 times, increase in bath temperature enhanced the hydrophobicity.

The weight loss curve of the S₄ sample is shown in Fig.2. Also TGA data of the prepared samples are presented in Table 5.

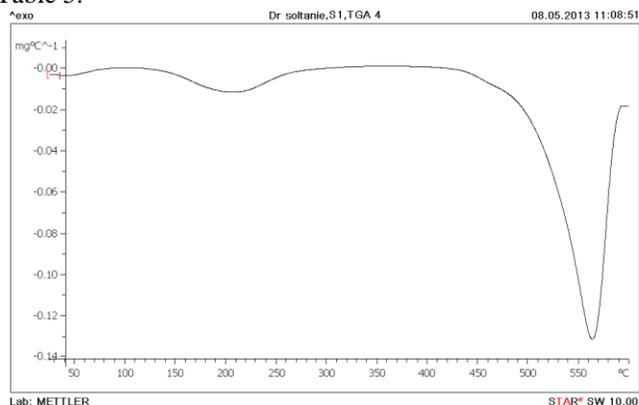


Fig. 2 Weight loss curve of S₄ sample against temperature

According to Fig.2, it can be concluded that there are two weight loss stages starting from around 200 °C and 560 °C. First stage is ascribed to the evaporation of residual phenylbenzoate or NMP and second stage is related to

decomposition of PES main chains. Reported data in the Table 5 indicates good thermal resistance of the prepared membranes.

Table 5. TGA test results of S₂, S₄, S₅, S₆, and S₈ samples

	Bath. Tem (°C)	Phenylbenzoate/NMP	TGA test results	
			Temp (°C)	Percent of weight loss (%)
S ₄	22.5	1.5	209.04	7.34
			564.34	49.25
S ₅	22.5	2.25	208.54	6.17
			567.16	52.09
S ₆	22.5	3	190.85	7.27
			566.89	50.68
S ₂	0	2.25	202.40	6.81
			567.02	50.22
S ₈	45	2.25	209.61	8.46
			566.64	49.83

4 CONCLUSIONS

In this work, we used combined thermally (TIPS) and non-solvent induced phase separation (NIPS) methods for preparing polymeric nanofiltration membranes for water desalination. The coagulation bath temperature and mass ratio of the diluent to solvent were two important parameters to achieve the desired structure and a balanced contribution of each phase separation method.

As water bath temperature increased, the cross-sectional morphology of the produced membranes changed from cellular structure with some macrovoids to exhibited groove-like pores with continuous cellular pores among them. The separation performance of the prepared membranes was related to the phase separation process and the resulted morphology. Because of the application of both phase separations methods in forming membrane, the resulted structure strongly differed from one casting condition to another. As the mass ratio of the diluent to solvent increased and bath temperature decreased, porosity, mean pore size of the membranes and pure water permeation flux decreased and salt rejection increased. The highest pure water permeation flux of 766.2 Lm⁻²h⁻¹ (at 0.2 MPa) and the highest salt rejection of 73.3% were obtained

It is concluded that the combined method has the advantage of producing a symmetrical porous structure while at relatively lower temperatures compared to those

used in the conventional TIPS process. Also, the continuous structure obtained from the combined method is more similar to structure resulted from TIPS alone.

REFERENCES

- [1] Human Development Report 2006, United Nations Development Programme (UNDP), Chapter 4, 2006.
- [2] Coping with water scarcity. Challenge of the twenty first century, United Nations (UN) Water, Food and Agricultural Association (FAO), 2007.
- [3] Progress on Sanitation and Drinking-Water, World Health Organization (WHO)/United Nations International Children's Fund (UNICEF) Joint Monitoring Programme for Water Supply and Sanitation, 2010.
- [4] M. Ulbricht, Advanced functional polymer membranes, *Polymer*, 47, 2217-2262, 2006.
- [5] I.M. Wienk, R.M. Boom, M.A.M. Beerlage, A.M.W. Bulte, C.A. Smolders, and H. Strathmann, Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers, *Journal of Membrane Science*, 113, 361-371, 1996.
- [6] I. Kim, K. Lee, and T. Tak, Preparation and characterization of integrally skinned uncharged polyetherimide asymmetric nanofiltration membrane, *Journal of Membrane Science*, 183, 235-247, 2001.
- [7] P.W. Morgan, Interfacial Polymerization, in: J.I. Kroschwitz (Ed.), *Encyclopedia of Polymer Science and Engineering*, 8, 221-237, 1987.
- [8] B. Kunst and S. Sourirajan, Effect of casting conditions on the performance of porous cellulose acetate membranes in reverse osmosis, *Journal of Applied Polymer Science*, 14, 723-733, 1970.
- [9] Z. L. Xu, F. Alsalhy Qusay, Polyethersulfone (PES) hollow fiber ultrafiltration membranes prepared by PES/non-solvent/NMP solution, *Journal of Membrane Science*, 233, 101-111, 2004.
- [10] M. Liu, Y-M. Wei, Z-L. Xu, R-Q. Guo, L-B. Zhao, Preparation and characterization of polyethersulfone microporous membrane via thermally induced phase separation with low critical solution temperature system, *Journal of Membrane Science*, 437, 169-178, 2013.
- [11] C.B Funk, Microporous Mixed Matrix (ZeoTIPS) Membranes, PhD thesis, The University of Texas at Austin, 2008.
- [12] C. S. Feng, B. L. Shi, G. M. Li, Y. L. Wu, Preparation and properties of micro-porous membrane from poly (vinylidene fluoride-co-tetra fluoro ethylene F2.4) for membrane distillation, *Journal of Membrane Science*, 237, 15-24, 2004.