

Preparation of new composite membranes for water desalination using electro dialysis

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ABSTRACT

The use of polyethersulfone (PES), an excellent but highly hydrophobic thermoplastic, as a matrix material for ion-exchange membranes was investigated. To make PES ion-exchangeable, sulfonate groups were introduced to the polymer chains by sulfonation reaction with chlorosulfonic acid. The degree of sulfonation of sPES was estimated to be 21%. Preliminary experiments investigated the effect of polyethylene glycol (PEG) and Pluronic F127 as fillers to improve the hydrophilicity of the membranes. Moreover, a lab scale electro dialysis cell has been designed and set up to evaluate the performance of these novel membranes compared to the benchmark of commercial membranes. The results show promising properties of ion-exchange capacity, water uptake, conductivity and hydrophilicity from blended membranes, comparable to commercial membranes, though the performance of the prepared membranes did not exceed the commercial one. Further characterization of the transport properties of ion-exchange membranes need to be investigated to be able to understand the effects of the fillers on the performance of the membranes in ED application.

Keywords: ion-exchange membrane, electro dialysis, composite membranes

1. INTRODUCTION

Electro dialysis is a promising desalination technology that removes ionic species through ion-exchange membranes under the influence of an electric potential. Though this technique has been invented for more than 50 years, it has not been widely used in desalination application due to lack of proper ion-exchange membranes, which should possess high ion-selectivity and conductivity and good mechanical and chemical stability, and as well as resist organic fouling.

Polyethersulfone (PES) is one of the most widely used thermoplastic in membrane separation processes due to its excellent mechanical, thermal and chemical stabilities^[1]. Although PES possesses many good characteristics, the hydrophobicity of this material often limited its application especially in desalination process. To apply PES in desalination by electro dialysis, charged groups often from sulfonic acid were introduced into the polymer chains making them ion-exchangeable.

It is well known that surface properties of membranes are one of the most important factors affecting organic fouling as well as selectivity of membranes in separation process. Thus, the hydrophilic modification by incorporating hydrophilic modifiers becomes an effective strategy not only to improve fouling resistance but also change the ion selectivity of membranes. Among various modifiers, polyether compounds and poly(ethylene oxide) is widely used and studied^[2-4]. It had been reported that these modifiers can effectively improve hydrophilicity of membranes without significantly reducing conductivity of ion-exchange membranes^[5].

In this work, preliminary experiments have investigated the use of polyethersulfone (PES) as a matrix material and polyethylene glycol (PEG) and Pluronic F127 as fillers. Membranes were characterized in term of key properties for electro dialysis membranes such as ion-exchange capacity (IEC), water uptake, conductivity and hydrophilicity. Thermal

stabilities of these membranes were also investigated. Moreover, a lab scale electro dialysis cell (with active area 3.147 cm²) has been designed and set up to evaluate the performance of these novel membranes compared to the benchmark of commercial membranes.

2. EXPERIMENTAL

2.1 Materials

Polyethersulfone (RADEL A) provided by Solvay Advanced Polymers was dried at 100 °C for 24 hours before used. The other chemicals were obtained commercially and were used as received without further purification.

2.2 Membrane preparation

(1) Sulfonation of polyethersulfone

Polyethersulfone (PES) was sulfonated with chlorosulfuric acid as the sulfonating agent and dichloromethane as the solvent^[6]. 20 g of PES was dissolved in 400 g of dichloromethane under N₂ atmosphere with stirring condition at room temperature. Then, 25 cm³ of chlorosulfuric acid was gradually and slowly added in the solution with in 90 minutes. The solution continued the reaction further for 150 minutes. The reaction was terminated by precipitating the solution into cold water. The products were filtered and washed many times with deionized (DI) water until pH became approximately 5-6. Finally, sulfonated polyethersulfone (sPES) was obtained after dried at 120 °C for 2 days under vacuum. This sPES will be used as a polymer matrix for cation-exchange membranes.

(2) Membrane preparation

Membranes were formed using conventional phase inversion technique. sPES was dissolved in N-N dimethylformamide at 60 °C for 4 hours with stirring condition. The polymer solution then was cast on glass substrates and precipitated in DI water forming a membrane sheet. Membranes from various polymer compositions as shown in Table 1 were prepared and kept in DI water before use.

Table 1 The composition of materials used for membrane preparation

Name	Composition			
	DMF (g)	sPES (g)	PEG (g)	F127 (g)
C1	7	3	0	0
C2	7	3	1.0	0
C3	7	3	1.5	0
C4	7	3	3.0	0
C5	7	3	1.5	0.2

2.3 Characterization

(1) Thermal analysis

Thermal stability of the membranes was investigated using thermogravimetric analysis (TGA) (Mettler Teledo) under nitrogen flow of 20 cm³ min⁻¹ using a heating rate of 10 °C min⁻¹ from 25-800 °C.

(2) IR analysis

The chemical structures of materials were investigated using Fourier transform infrared (FTIR) spectra in the wavenumber range 500-4000 cm⁻¹.

(3) Ion-exchange capacity and water uptake

Ion-exchange capacities were measured using a titration method [5]. The cation-exchange membrane was soaked in 1 mol dm⁻³ HCl. After that, the membrane was washed with DI water to get rid of excess HCl and then was immersed into 1 mol dm⁻³ NaCl solution. The isolated hydrogen ions from CEM were determined by titration with 0.01 mol dm⁻³ NaOH using phenolphthaleine as the indicator.

Then the same ion-exchange membrane was soaked in deionized water for 24 hours or more. After that, the membrane was taken out and water on the surface was wiped off with tissue paper. The wet weight of the membrane was measured. Then the membrane was placed in an oven at 50 °C for 10 hours or until weight of membrane did not change. The dry weight of the membrane was measured. The ion-exchange capacity and water uptake of membranes was calculated using the following equations:

$$\text{Ion-exchange capacity (IEC)} = \frac{ab}{W_{\text{dry}}} \quad (1)$$

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (2)$$

Where

a	=	Concentration of NaOH (mol dm ⁻³)
b	=	Amount of NaOH used (dm ³)
W _{dry}	=	Dry weight of membranes (g)
W _{wet}	=	Wet weight of membranes (g)

(4) Measurement of membrane resistance

An ion-exchange membrane was placed in a 2-compartment cell and the both sides of the ion-exchange membrane were filled with 0.5 mol dm⁻³ NaCl. Platinum was used as electrodes (effective membrane area is 1.0 cm²). The resistance between the electrodes at 25 °C was measured using a Soltatron 225B and an impedance technique [7].

(5) Contact angle measurement

The contact angle of water droplets on prepared membranes was determined with contact angrometer at room temperature.

2.4 Performance evaluations in electro dialysis cell

Electrodialysis experiments were performed in a custom-designed laboratory scale ED unit as shown in Figure 1. It contains a pair of anion and cation - exchange membranes with 3.147 cm² effective area. The cation-exchange membrane was facing a platinum cathode, while the anion-exchange membrane was facing a platinum anode. Both membranes were facing each other. A constant potential of 2 Vcm⁻¹ was applied between two electrodes using a DC power supply. A known concentration of electrolyte solution was fed through each of the separate compartments. The flow rate of each stream was kept constant at 3 cm³ min⁻¹. After 20 minutes the electrolyte solution was recirculated back into each cell compartment. The ion concentration from each compartment was measured every 20 minutes using a conductometer.

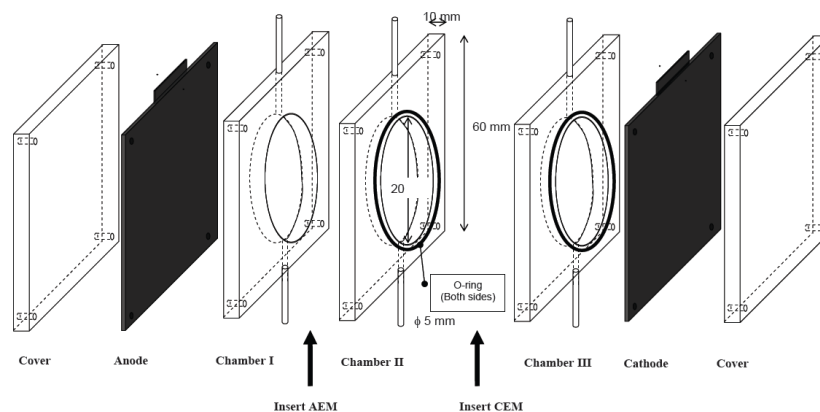


Figure1 The schematic illustration of a home-designed lab-scale electro dialysis cell

3. RESULTS AND DISCUSSION

3.1 Sulfonation reaction

In this work, PES was sulfonated using chlorosulfonic acid. FTIR spectra were used to confirm the presence of the SO_3H group on the polymer chains. Figure 2 shows the spectra of PES and sPES. The peak at 1580 cm^{-1} and 1490 cm^{-1} are attributed to vibration of the aromatic ring skeleton. The characteristic absorption band for the aromatic sulfone group appears at 1150 cm^{-1} and the peak for aryl oxide appears at 1240 cm^{-1} [9]. In sPES the adsorption peak at $\sim 1020\text{ cm}^{-1}$ was characteristic of the aromatic SO_3H symmetric stretching vibration and the peak at $\sim 1180\text{ cm}^{-1}$ is the characteristic peak of the asymmetric one which could not be observed here due to the overlapping effect [10, 11]. However, we can still conclude that the charged groups from sulfonic acid have been successfully introduced into the polymer. The degree of sulfonation (DS) can be calculated via titration of sPES with a standard NaOH. The following equation[10] was used to calculate the DS;

$$DS = \frac{0.232[M(\text{NaOH}) \times V(\text{NaOH})]}{W - 0.08[M(\text{NaOH}) \times V(\text{NaOH})]} \times 100 \quad (4).$$

Where $M(\text{NaOH})$ was the concentration of standard NaOH solution (mol dm^{-3}), $V(\text{NaOH})$ the NaOH solution volume used to neutralized (dm^3), W the sample weight (g), 232 the molecular weight of PES repeat unit and 81 the molecular weight of the SO_3H . The DS of sPES used as matrix polymer in this work is calculated to be $\sim 21\%$.

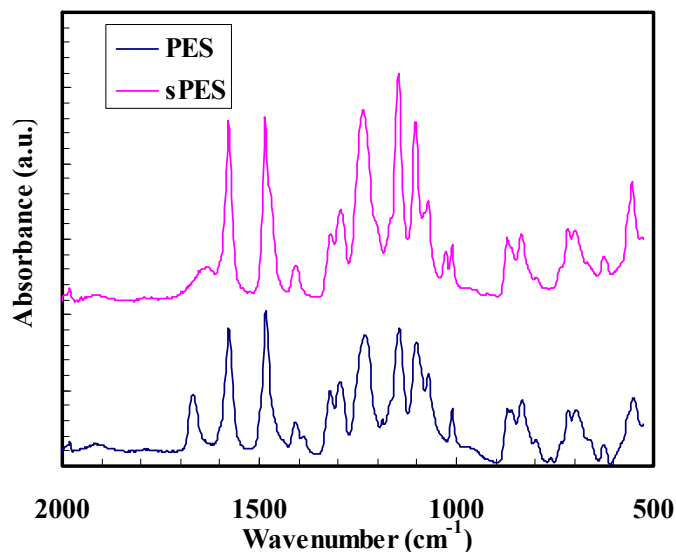


Figure 2 FTIR spectra of polymer PES and sPES

3.2 Thermal stability

Thermal stabilities of PES, sPES and blended polymeric membranes were investigated using TGA as shown in Figure 3. The parent PES is an excellent thermostable polymer which decomposes at high temperature around 500 °C with weight loss at the end of the experiment around 60%. There are three steps of weight loss in the case of sPES including the loss of absorbed water at around 100 °C, the thermal decomposition of $-\text{SO}_3\text{H}$ groups^[11] at 300 °C and the degradation of polymer chains near 500 °C. It can be clearly seen that sPES loses weight at a lower temperature compared to PES. The introduction of sulfonic groups in polymer chains made the polymer less regular and less stable^[10].

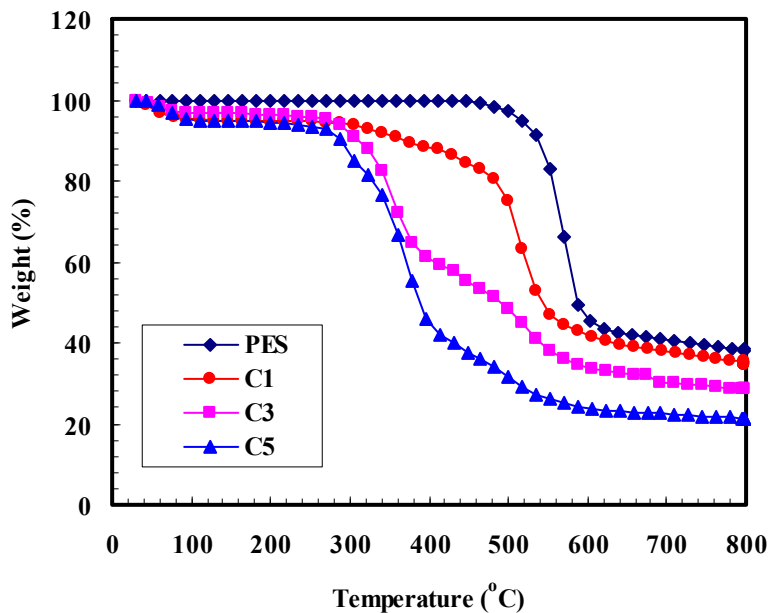


Figure 3 TGA analysis of the prepared membranes

3.3 Water uptake ion-exchange capacity and electrical conductance of membranes

Table 2 Ion-exchange capacity and electrical conductivity of the obtained membranes

Name	Water Uptake	IEC (meqv/g)	Conductivity (s/cm)	Contact angle
C1	1.36	0.865	0.00230	6.93
C2	0.99	0.682	0.00146	6.8
C3	1.94	0.623	0.00115	5.79
C4	2.55	0.733	0.00095	4.17
C5	2.148	0.843	0.00126	~0
FKE*	0.17	1.150	0.00117	-

* Commercial membrane for FuMA-Tech GmbH

** Data supplied from the manufacturer

The ion-exchange capacity (IEC) provides information on the charge density in the membranes, which is an important factor related to the conductivity of the membranes. The water uptake, ion-exchange capacity and conductivity of the membranes are summarized in Table 2.

The ion-exchange capacity of the membrane decreased with the increase of PEG due to the reduced fraction of the composite membrane comprised of ion-exchangeable polymer. On the other hand the water uptake of composite membranes increased with the amount of PEG (see Figure 4). This may be attributed to the hydrophilic properties of PEG enhancing water absorption on the membrane. As shown in Table 2, the contact angle of the membranes decreased with the increase of PEG, which indicated that the increase of PEG improved the hydrophilicity of the blended membranes.

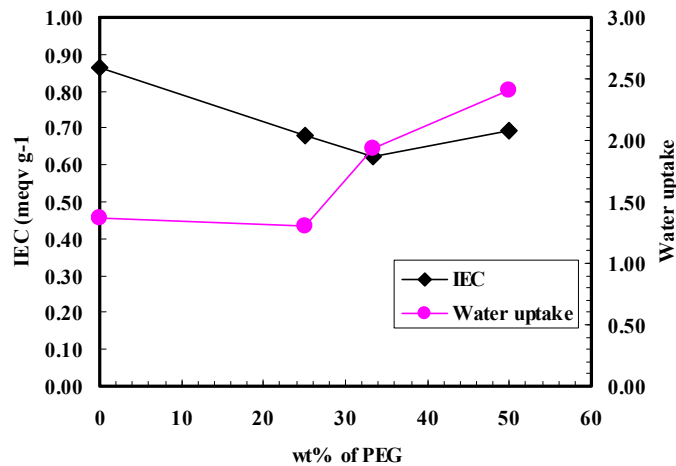


Figure 4 effects of PEG on the ion-exchange capacity and water uptake of the membranes

The influence of incorporating the amphiphilic polymer F127 was also investigated. As shown in Table 2, the membrane with the composition C5 displayed enhanced ion-exchange capacity as a result of the introduction of F127 (compared with C3). This resulted in an increase in the conductivity of the membrane, due to the higher concentration of ion-exchange sites. This may be attributed to the partially negatively charged PEO segment in F127 facilitating the transport of positive charges through the composite membrane.

3.4 Performance evaluation in electro dialysis (ED) cell

The composite membrane C5 was tested in the ED cell. As shown in Table 2 the key properties such as IEC water uptake and conductivity of the blended membrane C5 are comparable to the commercial membranes. However, from Figure 5 the commercial membranes exhibited better performance in ED cell. Further characterization such as transport number, membrane structure, membrane potential and limiting current density should be investigated to be able to explain the transport properties of the membranes.

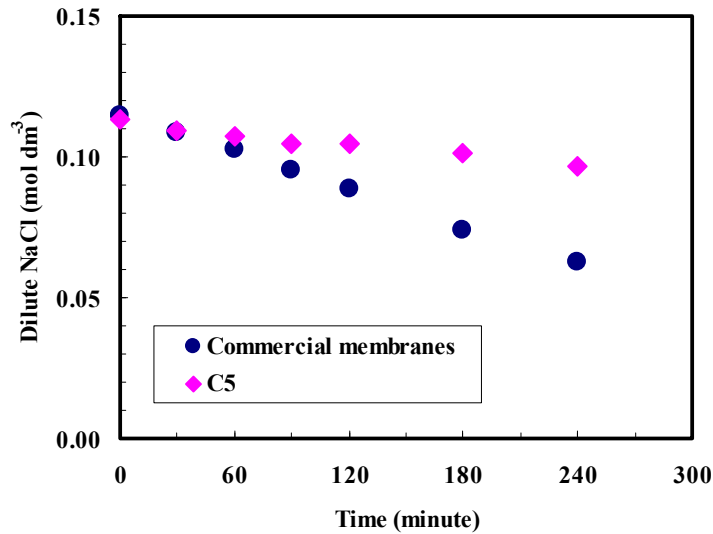


Figure 5 Electro dialysis test of the blended membrane (C5) compared with the commercial membrane

4. CONCLUSION

PES was sulfonated using chlorosulfuric acid and used as polymer matrix for cation-exchange membrane. A series of sPES membranes with different compositions of PEG and F127 were prepared and characterized. sPES and blend membrane exhibited less thermal stability compared with the parent PES, however this lower thermal stability is still acceptable when used at relatively low temperature in electro dialysis application in desalination. Preliminary results show that the hydrophilicity and water uptake increased with PEG, on the other hand the IEC decreased due to less charged polymer compartment. When F127 was added, the IEC, water uptake, conductivity and hydrophilicity of the membranes increased. It is hypothesized that this effect arises from the partial negative charge of the filler molecule. The key properties such as IEC and conductivity of the blended membrane C5 are comparable to the commercial ones. However the electro dialysis performance of prepared membranes did not exceed the commercial one. Further material modification, characterization and performance evaluation in ED cell will be investigated.

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REFERENCES

- [1] Lu, D., et al., *Sulfonation of polyethersulfone by chlorosulfonic acid*. Polymer Bulletin, 2005. **54**: p. 21-28.
- [2] Sata, T., K. Mine, and K. Matsusaki, *Change in transport properties of anion-exchange membranes in the presence of ethylene glycols in electro dialysis*. Journal of Colloid and Interface Science, 1998. **202**: p. 348-358.
- [3] Sata, T., et al., *Transport properties of cation exchange membranes in the presence of ether compounds in electro dialysis*. Journal of Colloid and Interface Science, 1999. **219**: p. 310-319.
- [4] Wang, Y.-Q., et al., *Pluronic polymers and polyethersulfone blend membranes with improved fouling-resistant ability and ultrafiltration performance*. Journal of Membrane Science, 2006. **283**: p. 440-447.
- [5] Aritomi, T. and M. Kawashima, *Ion-exchange membrane*, U.S. Patent, Editor. 2004, Tokuyama Corporation: Japan. p. 1-14.
- [6] Li, Y., W.B. Krantz, and T.-S. Chung, *A novel polymer to prevent nanoparticle agglomeration in mixed matrix membranes*. AIChE Journal, 2007. **53**(9): p. 2470-2475.
- [7] Nagarale, R.K., G.S. Gohil, and V.K. Shahi, *Recent developments on ion-exchange membranes and electro-membrane processes*. Advances in Colloid and Interface Science, 2006. **119**(2-3): p. 97-130.
- [8] Choi, S.-H., et al., *Desalination by electro dialysis with the ion-exchange membrane prepared by radiation-induced graft polymerization*. Radiation Physics and Chemistry 2001. **60**: p. 503-511.
- [9] Krishnan, N.N., et al., *Synthesis and characterization of sulfonated poly(ether sulfone) copolymer membranes for fuel cell applications*. Journal of Power Sources, 2006. **158**: p. 1246-1250.
- [10] Guan, R., et al., *Polyethersulfone sulfonated by chlorosulfonic acid and its membrane characteristics*. European Polymer Journal, 2005. **41**: p. 1554-1560.
- [11] Lu, D., et al., *Sulfonation of polyethersulfone by chlorosulfonic acid*. Polymer Bulletin, 2005. **54**: p. 21-28.