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A PRODUCTION OF POLYETHERSULFONE ASYMMETRIC MEMBRANES USING MIXTURE OF TWO SOLVENTS AND LITHIUM CHLORIDE AS ADDITIVE

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Abstract. Polyethersulfone (PES) asymmetric membranes were prepared by the wet / dry phase inversion process. Membrane dope formulation consisting of commercial-grade PES resin and a mixture of two different solvents dimethyleformamide (DMF) and commercial grade acetone with control ratio 3.47 was prepared. Tap water was used as the coagulant bath at room temperature. With a focus on the PES solvent mixtures DMF/acetone economical system, the effect of lithium chloride anhydrous ($LiClH_2O$) as additive on the membrane's performance was investigated. The performances of the PES membranes were evaluated in terms of various molecular weight PEG separation and permeation flux. Its molecular weight cut off is then determined. The PES membranes prepared from the two solvent mixture systems with $LiClH_2O$ additive possess excellent hydrophilic properties exhibited by the high permeation rates. Its solute rejection rates obtained were also superior compared to the membrane prepared from single solvent without $LiClH_2O$ additive.

Keywords: Asymmetric membranes, dry/wet phase inversion, lithium chloride anhydrous

Abstrak. Membran asimetrik polieter sulfon (PES) disediakan dengan menggunakan kaedah fasa balikan kering/basah. Formulasi membran mengandungi resin PES gred komersial dan campuran dua pelarut berbeza; dimetilformamid (DMF) dan aseton bergred komersial dalam nisbah kawalan 3.47. Air paip digunakan sebagai takungan pengental pada suhu bilik. Dengan memberi tumpuan pada sistem campuran pelarut DMF/aceton yang berekonomi, kesan litium klorida anhidrat ($LiClH_2O$) sebagai bahan tambah terhadap prestasi membran dikaji. Prestasi membran dikaji dari segi pemisahan polietilin glikol(PEG) yang berlainan berat molekul dan fluks. Membran PES yang mengandungi bahan tambah $LiClH_2O$ mempunyai sifat hidrofilik yang sangat baik dan ini dapat dilihat dari kadar fluksnya yang tinggi. Kadar pemisahan larutan membran tersebut adalah lebih menyerlah berbanding dengan membran yang disedia dari sistem satu pelarut tanpa ahan tambah $LiClH_2O$.

Kata kunci: Membran asimetrik, fasa balikan kering/basah, litium klorida anhidrat

1.0 INTRODUCTION

Ultrafiltration, a novel and powerful pressure-driven separation technology, has been widely used in wastewater treatment and food industry [1, 2] to concentrate or fractionate protein and aqueous solutions. During ultrafiltration, the smaller suspended particles and dissolved macromolecules (surface pore size in the range of 50 to 1 nm) pass

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through the membranes [3], while the bigger molecules are mostly rejected. Some of the rejected molecules adsorb or deposit on membrane surface causing considerable membrane fouling [4].

The efficiency as well as the economics of the various industrial processes can be greatly improved if the membrane processes are suitably integrated in the exiting process, particularly, to control membrane structure and membrane performance. This objective is not easy to achieve because membrane structure and performance depend on different factors such as polymer choice, solvent and nonsolvent choice, composition and temperature of coagulant, and casting solution [5]. Solvent/non-solvent mixture changes the solubility parameter of the solvent system thus changing the polymer–solvent interaction in the ternary-phase polymer system, which changes the polymer morphology of surface layer and sub-layer [6, 7].

The physical factors in the ternary polymer system [6, 7] responsible for the change in morphology are heat of mixing of solvent and non-solvent, and polymer–solvent interaction which depends on the difference in solubility parameter. Moreover, a mixture of polar, aprotic solvent and volatile solvent such as dioxane and acetone causes rapid evaporation on the surface, leading to the formation of a dense layer on the surface [8]. The physical factors include solvent evaporation time, temperature and humidity [9].

Currently there is a possibility of enhancing membrane performance beyond the generally recognized intrinsic value for the amorphous polymer. This has been accomplished in a number of different ways for various polymers: polysulfone (PSf), polyethersulfone (PES), polyestercarbonate (PC), polyimide (PI), polyamide (PA) and cellulose acetate (CA) [10, 11]. Hydrophobic materials show excellent mechanical stability in aqueous environment. This attribute is very attractive for them to be used as membrane materials and should exhibit enough affinity to water so that it can be preferentially adsorbed into the membrane, leading to good membrane performance in terms of a high productivity and high selectivity [12]. PES, an important engineering thermoplastic possesses favorable mechanical properties and thermo oxidative stability [13], is a closely related derivative of polysulfone which is totally devoid of aliphatic hydrocarbon groups and has a high glass transition temperature of 230°C [14]. It is an excellent ultrafiltration (UF) membrane material because of its film and membrane forming properties and high mechanical and chemical stability. In addition to being commercially available and relatively inexpensive, it is one of the most widely used polymers for making UF membranes [15].

In order to obtain membranes with special properties, additional additives can be dissolved in the casting solution [16]. The role of these additives is to create a spongy membrane structure but prevents the formation of macrovoid, enhances pore formation, improves pore interconnectivity and/or introduces hydrophilicity. Generally, hydrophilic structures are obtained by the addition polyvinylpyrrolidone (PVP). Other frequently used additives are: glycerol, alcohols, dialcohols, water, polyethylene glycols (PEG), polyethylene oxide (PEO), LiCl and $ZnCl_2$ [17-19].

Qualitatively addition of lithium chloride to the casting solution of poly(amic-acid) solution in DMF results in complexes between lithium chloride and DMF, resulting in reduced solvent power and increased viscosity and transient cross-links, as shown by dynamic light scattering [20]. Inorganic salts are known to form complexes with the carbonyl group in polar aprotic solvent via ion–dipole interaction [21]. The polymer aggregates which form due to reduced solvent power result in sponge-like structure and hinder macro-void formation during phase-inversion. In most cases, the concentration of $LiClH_2O$ is kept less than 3% and has never been used as additive for PES polymer membranes.

In this study the effect of $LiClH_2O$ additive greater than 3 wt% using a two solvent system is investigated. The polymer solution, which consists of polyethersulfone in a mixture of polar aprotic solvents DMF and volatile solvent acetone; additive lithium chloride anhydrous is prepared. The performances of these membranes were compared with those prepared without volatile acetone and $LiClH_2O$. The performances of the membranes were evaluated using various molecular weight polyethylene glycols, PEG. Its molecular weight cut off and flux rates are determined [21].

2.0 EXPERIMENTAL

2.1 Materials

Commercial grade Polyethersulfone (PES) in resin form was obtained from BASF. Analytical grade N, N-dimethyleformamide DMF [$HCON(CH_3)_2$, M = 73.10 g/mol] was purchased from Merck (Merck Germany). Inorganic salt additive Lithium Chloride (42.4) analytical grade, was procured from BDH and commercial grade acetone was used without further purification. Tap water was used as the coagulation bath. For UF experiments, PEG with various molecular weights (PEG200, PEG 400, PEG 600, PEG 1000, PEG 3000, PEG 6000 and PEG 10,000), were obtained from Fluka.

2.2 Dope Preparation

Different dope solutions were prepared. The polymer concentration was fixed at 20 wt% as shown in Table 1. In this study, Sharp domestic microwave oven model: R-4A53 with the following specifications: rated power output of 850 watts (240V~50 H_Z), operation frequency of 2450 MHz is used. A 500 ml Schott Duran is used as the sample reaction vessel at atmospheric pressure. Mercury thermometer was used manually to control the temperature at every 20 sec. The temperature of the dope solutions was kept at 85 – 95°C for dope solutions 1 and 3, 65 – 70°C for dope solution 2 as shown in Table 2. Heating time by microwave was 10 minutes. The absolute viscosities of dope solutions 1, 2 and 3 were measured using Brookfield Viscometer (DV-II) at 28°C.

Table 1 Dope solution compositions

Dope	**Composition in Wt. %**			
Solution	**PES**	**DMF**	**Acetone**	**LiClH$_2$O**
1	20	80	0	0
2	20	59	17	4
3	20	76	0	4

2.3 Determination of Permeation Flux and Solutes Rejection

The performances of the various membranes were evaluated in terms of pure water permeation fluxes (PWP), solvent permeation fluxes (PR) and solute rejection rate (SR) in a test cell described elsewhere [22, 23]. A minimum of three flat sheet samples were prepared for each technique and the average data are tabulated. Pure water permeation fluxes (PWP) and solutes water permeation fluxes (PR) of membranes are obtained as follows:

$$J = \frac{Q}{\Delta t \times A} \tag{1}$$

where J (L m^{-2} h^{-1}) is the permeation flux of membrane for PEG solution or pure water, Q is the volume of permeate solution (L), Δt is permeation time (hour) and. A is membrane area in m^2.

Solute rejection of membranes were evaluated with various molecular weight PEG solutions ranging from 600 to 10000 kDa 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 as follows:

Reagent A: 5% (w/v) $BaCl_2$ in 1 N HCl (100 ml)
Reagent B: 2% (w/v) KI diluted 10 times + 1.27g I_2.

Four (ml) of sample solution was added to 1 ml reagent A. To this mixture 1 ml of reagent B was added. Color was allowed to develop for 15 min at room temperature, and adsorption was read using a spectrophotometer at 535 nm against a reagent blank [21, 23]. The membrane rejection (R) is defined as

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

where C_f and C_p are the polyethylene glycol concentrations 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.

2.4 Scanning Electron Microscope

For morphology study, the membranes were immersed in liquid nitrogen and fractured to obtain neat cross- sections. These samples were then attached to a carbon holder and sputtered with gold to prevent charging up of the surface by the electron beam. A narrow beam of electrons with kinetics energies in order of 1 – 25 kV hits the membrane sample, and low- energy electrons were liberated from the atoms in the surface to create the image on the micrograph. Cross sections of the hollow fiber membranes images were obtained using the SUPRA 35VP FE- SEM.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Lithium Chloride (LiClH$_2$O) and Acetone on Viscosity Of Dope Solution

Viscosity is considered as one of the important parameters influencing the exchange rate between solvent and non-solvent during the phase inversion process [22]. Therefore, the absolute viscosities of dope solutions 1, 2 and 3 are listed in Table 2. Absolute viscosities of PES solutions in a single solvent without additive (1) is the lowest compared to those prepared in a mixture of solvents (2) and that containing additives. The presence of 4% additive lithium chloride has increased the viscosity by almost 6 times. However when part of the DMF is replaced by acetone the viscosity of the dope solution decreases. The salt concentration used was kept to 4 wt% because of the solubility of salts in aprotic solvents and organic solvents [24].

Table 2 Dope solution preparation time and viscosities.

Dope solution	Preparation time (hrs)	Viscosity at 28°C (cps)
1	0.5 at 85 – 95°C	175
2	0.5 at 65 – 75°C	800
3	0.5 at 85 – 95°C	1100

3.2 Performance of the Membranes

The performances of the membranes produced from the various solutions were depicted in Figures 1 and 2. It is observed that the membranes produced from dope solution 3 containing LiClH$_2$O exhibits highest pure water permeation (Jpw) and permeate flux (Js) rates compared to those produced by from dope solutions 1 and 2. The use of acetone has also a positive influence on the membrane performance shown by the improved permeation rates compared to dope solution 1. However its permeation rates are slightly lower compared to those prepared from dope solution 3. The pure water permeation and permeation flux for membranes 2 and 3 were approximately 50

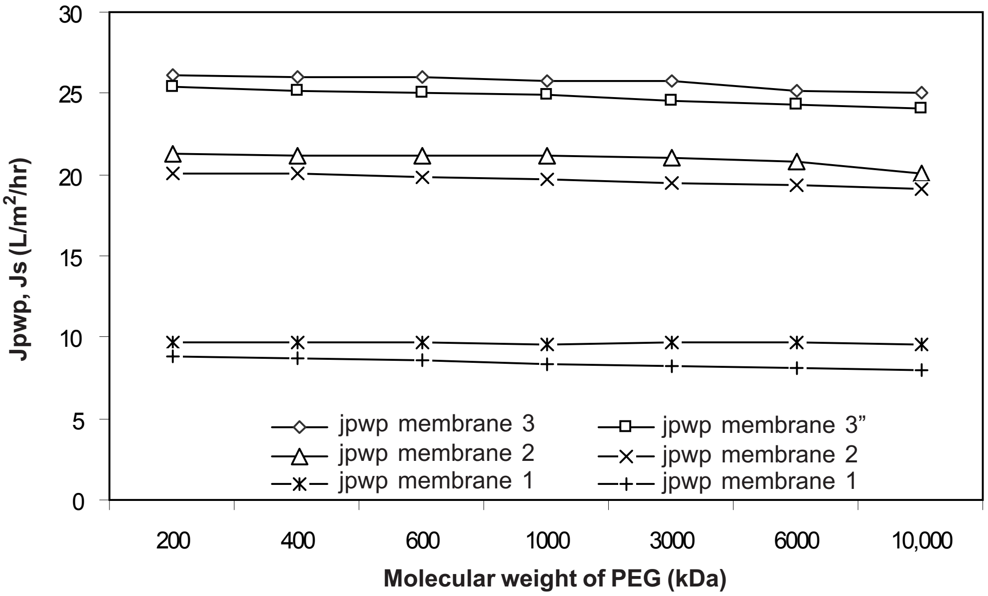


Figure 1 Pure water permeation flux (Jpwp), permeate rates (Js) versus molecular weights of PEG of the various membranes

% higher than membrane 1 which means increase in productivity. Apparently membranes produced from the dope solution 2 containing both the acetone and additive exhibits highest rejection rate with molecular cut off (MWCO) at 90% of approximately 2000 kDa. Membrane 3 has rejection rate higher than membrane 1 with MWCO close

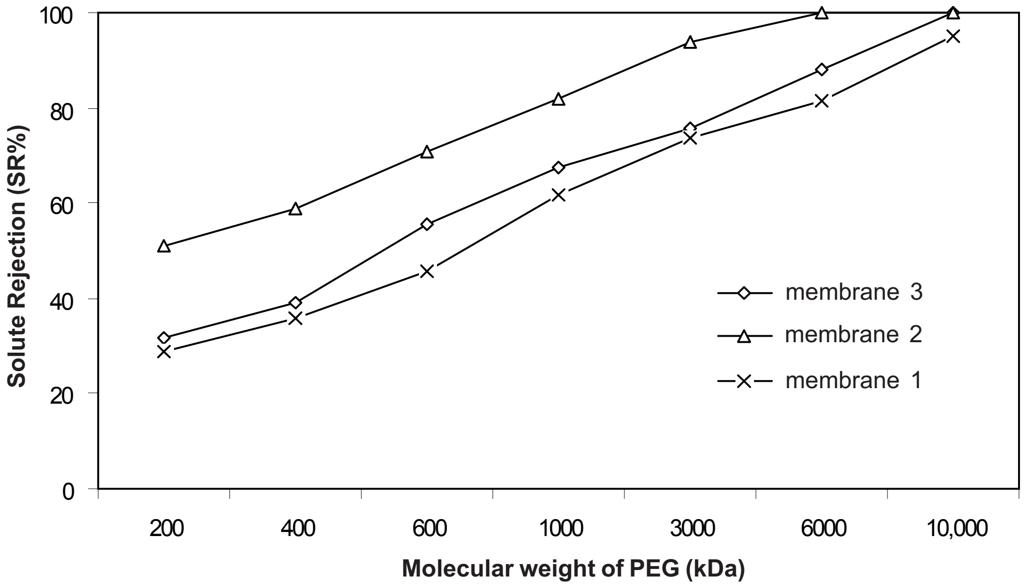


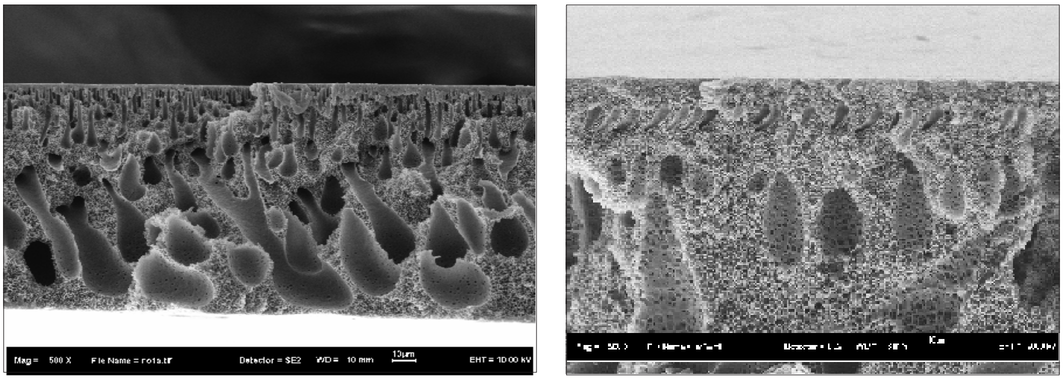
Figure 2 PEG rejection rate versus molecular weights of PEG of the various membranes

to 6000 kDa. Membrane 1 that does not contain any acetone and additive shows MWCO of about 8000 kDa and very low flux rates.

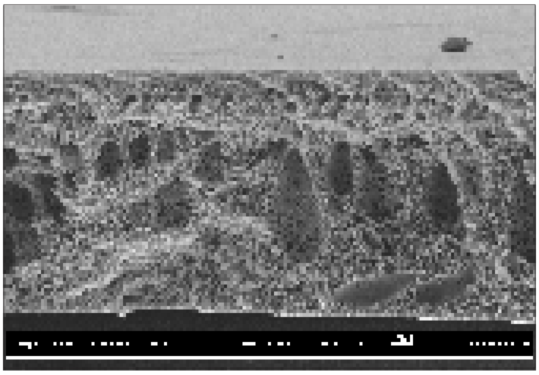
It appears that the presence of $LiClH_2O$ has improved the hydrophilic properties of the membrane thus improving the permeation flux of the membranes. It seems that $LiClH_2O$ acts as a pore reducer observed by the reduction in the MWCO of the membranes. In addition the presence of acetone has not only improved the membrane performance in terms of both flux and rejection rates but also reduce the production cost of the membranes because it is a cheaper solvent compared to DMF.

3.3 Membrane Morphologies

The cross section structure of the membranes produced from the various dope solutions are shown in Figure 3 at a magnification of 500X. Previous investigations have shown that casting solution characteristics and formulations have a direct influence on asymmetric membrane formation and structure [8, 9]. An examination of the cross-



Membrane 1 Membrane 2



Membrane 3

Figure 3 Scanning electronic micrographs at 500 × magnification of cross section structure of the PES flat sheet membranes prepared from the three dope solutions sectional structures revealed that asymmetric membrane 1 has a thick dense skin layer with many macrovoids. The very fine finger like structure developed into large macrovoids towards the bottom. The thick skin layer creates high resistance in flow thus explaining for the low flux rates.

Upon comparing this morphology with membrane 2, the presence of $LiClH_2O$ has obviously altered and affected the membranes. Membrane 2 has a very fine and consistent spongy structure with a very thin skin layer which is hardly visible thus explaining for the high rejection rates and improved permeation flux rates. No finger like structure is observed except for some isolated macrovoids. A slightly coarse spongy structure which appears to be very well interconnected is also observed in Figure 3 and this explains for the high permeation rates. However the skin layer is not as thin as membrane 2 thus explaining for the lower rejection rates.

Hydrophilic structures are obtained by the addition of additives $LiClH_2O$. The presence of the acetone in the polyethersulfone membranes also affects the separation properties of membranes. It is believed that during the dope preparation process in the microwave oven; the irradiation process could have caused some breakages in the bonds and realign the molecular structure of polymer. The presence of the free chlorine molecules could have improved the hydrophilic structure of the membranes thus influenced the permeation properties of membrane performance. With the addition of both acetone and lithium chloride the permeation rates are only slightly reduced but the rejection rates improved tremendously.

4.0 CONCLUSION

In summary membranes produced from dope solutions containing lithium chloride salts and acetone are superior in terms of permeation flux rates, rejection rates and quality of membranes compared to those membranes prepared without these additives. The addition of $LiClH_2O$ and acetone to PES–DMF casting solutions has a significant effect on both solution properties as observed from its viscosities. The disappearance of the macrovoids in the membrane structure has improved the membranes performance and it mechanical strength. The results indicate that $LiClH_2O$ interacts very strongly with DMF and acetone under microwave radiation leading to the formation of $LiClH_2O$ –DMF-acetone complexes and, hence, retain the solvation power of DMF for PES. With addition of $LiClH_2O$ additive alone in the casting solution, membrane porosity increases producing high permeation rate membranes. However with the addition both $LiClH_2O$ and acetone, membranes porosity decreases, asymmetric skin layer becomes very thin, producing membranes with slightly lower permeation rates but excellent the rejection rate.

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