

## DEVELOPMENT OF CASTING TECHNIQUES FOR POLYETHERSULFONE ULTRA FILTRATION MEMBRANES AND THEIR EFFECTS ON FLUX AND REJECTION

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### ABSTRACT

Polyethersulfone (PES) membranes were prepared by phase inversion process. Membrane dope formation consisting of commercial –grade PES resin and N, N dimethylformamide and the polyethylene glycols (PEG). Tap water was used as the coagulant bath at room temperature. The polymer solution was formulated by varying polymer concentrations, which is for PES in the range of 19-23 wt%. Polyethylene glycols (PEG) with varying molecular weights were used to characterize the flux and rejection of membrane. Results showed that the flux of the membrane decreases with increase in polymer concentrations. This means that outer skin layer of the membranes became apparently thicker and denser with increasing polymer concentration. On other hand, an UF membrane from a dilute polymer solution produced a thin and porous skin layer, leading to a high value of flux but a relatively low percentage of rejection for PEG.

**Keywords:** polyethersulfone, Ultra filtration, flux, rejection, ultrafiltration.

### 1. INTRODUCTION

Ultra filtration, a novel and powerful pressure driven separation technology, has been widely used in wastewater treatment and food industry [1-3] to concentrates or fractionates protein and aqueous solutions. During ultra filtration, smaller suspended particles and dissolved macromolecules (surface pore size in the range of 50 to 1 nm) pass through the membranes, [4] while the bigger molecules are mostly rejected. Some of the rejected molecules absorb or deposit on membrane surface causing considerable membrane fouling. [10]

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 [13]. Solvent/nonsolvent 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 [14]. The physical factor in the ternary polymer system responsible for change in morphology are heat of mixing of solvent and nonsolvent, and polymer-solvent interaction which depends on the differences 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.[2] The physical factors include solvents evaporation time, temperature and humidity[7]

Currently there is 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), Polycarbonate (PC), Polyamide (PI), polyamide (PA) and cellulose acetate [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 in to the membrane, leading to good membrane performance in terms of a high productivity and high selectivity[9]. polysulfone is an excellent UF membrane material because of its film and membrane forming properties and high mechanical and chemical stability[8]. In addition to being commercially available and relatively inexpensive, it is one of the most widely used polymers for making UF membranes[6]. In order to obtain membranes with special properties, additives can be dissolved in the casting solution[5]. The role of these additives is to create a spongy membrane structure but prevents the formation of macro void, enhances pore formation, improves pore interconnectivity and/or introduces hydrophilicity. Generally frequently used additives are: glycerol, alcohols, dialcohols, water, polyethylene glycols (PEG), polyethylene oxide (PEO), LiCl and ZnCl<sub>2</sub> [12]. Development of integrally skinned asymmetric membranes by Loeb and Sourirajan in the 1960s was a major breakthrough in membrane technology. Integrally skinned asymmetric membranes can be prepared through the phase inversion method where a multi-component casting solution is immersed in a coagulation bath. An asymmetric membrane having a very thin dense skin layer can be prepared by dry /wet phase inversion process. The skin layer of this asymmetric membrane becomes defect free by introduction of evaporation. PSF was selected as the membrane material because of its commercial availability, ease of processing and favorable selectivity –permeability characteristics. It possesses good mechanical,

thermal and chemical properties. Moreover, it is generally easy to prepare asymmetric membranes by the immersion phase inversion method using water as a coagulant. The usual method for preparing PSF membranes is a wet phase inversion process. A thin layer of PSF solution in an appropriate solvent is immersed into the nonsolvent coagulation bath. Many solvents can be used for this : N-N, methylpyrrolidone(NMP), N,N-dimethylacetamide (DMA), N,N-dimethylacetamide (DMA), N,N-dimethylformamide(DMF), dimethylsulfoxide(DMSO), morpholine (MP), etc. Also, different nonsolvents are used as coagulants: water, methanol, propanol, etc. The most important parameter for membrane properties which has been identified is polymer concentration. In addition, the solvent ratio also plays an important role along with polymer concentration. In addition, the solvent ratio also plays an important role along with polymer concentration during membrane formation. The simultaneous adjustment of these two key parameters allows for an increase in the viscosity of the dope solution without significant loss in productivity and selectivity. In order to induced chain entanglement and therefore reduce the formation of the macro void in the skin layer, a higher polymer concentration is required. Therefore, the separation capacity (rejection) of the membrane will be increased but the permeability (flux) will reduce. The addition of more polymers to the dope solution increases its viscosity and tends to promote selective but less productive membranes. pesek and koros investigated the effect of polymer concentration and solvent ratio on membrane morphology and separation performance. The results show that increases in polymer concentration at the constant solvent ratio produced higher solution viscosities and selectivity but generally lower pressure-normalized flux. These flux losses were the result of thicker selective skins and transition

layers believed to be caused by slower redissolution of initial phase outermost separated regions of nascent membranes from an underlying homogeneous solution during dry phase separation. On the other hand, simultaneous increases in polymer concentration and solvent ratio allow increases in viscosity with little change in membrane performance. The rejection and flux characteristics of the membrane strongly depend on the chemical structure of the active layer and features of the surface where primary separation of solutes occurs. Because of the important role of polymeric membranes in separation technology, many studies of membrane formation mechanisms by wet phase separation of different ternary systems (polymer/ solvent/additive) were carried out.

The objective of the current study was to find out the effect of polymer concentration on membrane performance, especially in flux and rejection. Polyethylene glycols (PEG) with varying molecular weights were used to characterize the flux and rejection of the membrane, systematic work was performed regarding concentration of PES in the cast solution.

## 2 EXPERIMENTAL

### 2.1 Materials

Polysulfone (PSF) supplied by BASf was used as polymer in preparation of membrane casting solution. N, N-dimethylformamide (DMF) was used as solvent. Polyethylene glycol 200 supplied by Merck was used as additive. Polyethylene glycols of different molecular weights ranging from 6 000, to 20000 Dalton were used as additive. Feed solutions were prepared using distilled water. Other chemicals used were sodium iodide (KI) purchased from sure Chem. product Ltd, barium chloride ( $BaCl_2$ ) and hydrochloric acid from Merck

### 2.2 preparation of Dope solution

Polysulfone was dried in an oven with air circulation at 80<sup>0</sup>c for 24 hours to remove any

moisture present. Dope solution was prepared by dissolving polyethersulfone in N, N-dimethylformamide with constant stirring for several hours. When polymer was completely dissolved, PEG200 was subsequently added, and the solution temperature was maintained at 80<sup>0</sup>c with continuous stirring for five hours until the additive was completely dissolved and homogeneous. The resultant polymer solution was filled in a glass bottle. The air bubbles in the resultant polymer solution were removed using ultrasonification process. Three new developed polymer solutions which have different levels of polymer concentration were used in this experiment. The compositions of dope solutions are shown in table1.

Table1, Dope solution with different polymer concentrations

Component	solution composition, wt%		
	PSF1	PSF2	PSF3
PSF	19	21	23
DMF	66	64	62
PEG	15	15	15

### 2.3 Measurement of flux and rejection

Membrane sample was placed in a cross flow test cell with the active skin layer facing incoming feed. The method to characterize an UF membrane is to measure its performance in terms of pure water permeability, flux and percentage rejection with different molecular weights. for this purpose, PEG with varying molecular weights was used as the solute rejection: PEG6000( average molecular weight 6000 Dalton), PEG 10000 ( average molecular weight 10000 ) and PEG 20000 ( average molecular weight 20000Dalton). A permeation test was carried out at different pressures: 100, 150 and 200 Kpa. Membrane was subjected to pretreatment for one h before the permeation experiments. The pure water flux was determined as

$$1. \quad J_w = Q/A \Delta T$$

Where Q is the quantity of permeate collected (L)

$J_w$  is the water flux ( $L\ m^{-2}h^{-1}$ ) A is the membrane area ( $m^2$ )  $\Delta T$  sampling time (h)

The solute rejection was calculated using the following expression

$$\%R = (1 - C_p/C_f) \times 100$$

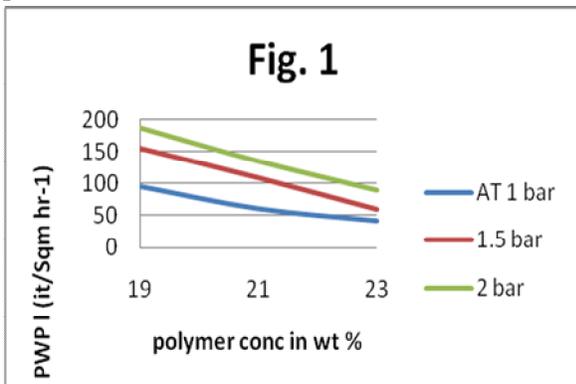
Where  $C_f$  and  $C_p$  are concentrations of solute in the feed and permeate, respectively

The feed and permeate solute concentration were determined using a spectrophotometer

The concentration of feed and permeate solutions were determined using the analytical method given by Sabde. This analytical method involved addition of 1 ml of 5%  $BaCl_2$  in 1 N HCL and 1ml of solution prepared from mixture 2% KI (w/v). The color developed was then analyzed using a UV –spectrophotometer at 535 nm against a reagent blank to measure the concentration of permeates.

**3. RESULT AND DISCUSSION**

Three dope solutions of different polymer concentrations-PSF1, PSF2, and PSF3 were made to cast the membranes. The pure water permeability (PWP) of membranes was first measured in order to confirm the stability of the membranes used, and it found that all membrane satisfied the requirements of UF membranes. Fig 1 shows that the effect of different polymer concentration on PWP at three different pressures.



The figure shows that the average pure water permeability decreased with increasing polymer

concentration from 19 to 23 wt%. based on experimental results, The average PWP of three membrane was decreased from 94.97 L /m<sup>2</sup>h at 19% polymer concentration to 1.3 L/m<sup>2</sup>h at 23% polymer concentration at 1 bar, but 154.92 L/m<sup>2</sup>h at 19% polymer concentration to 60.78 L/m<sup>2</sup>h at 23 % polymer concentration at 1.5 bar and 187.34 L/m<sup>2</sup>h at 19 % polymer concentration to 89.23L/m<sup>2</sup>h at 23% polymer concentration under condition of 27<sup>o</sup>c temperature and at 2 bar applied pressure

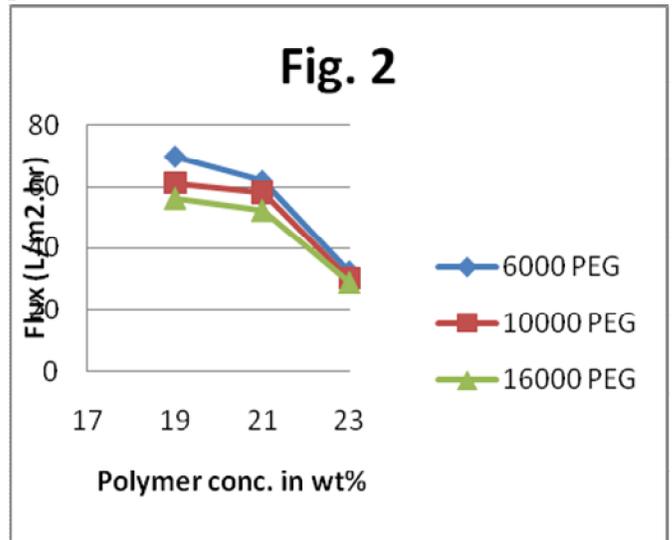


Fig 2 shows that the average fluxes of different molecular weights of PEG were similar to the PWP profile discussed in the preceding section where the average flux was also decreased with an increase in polymer concentration. Fig 2 shows that the value of flux was reduced from 69.94 L/m<sup>2</sup>h at 19 % polymer concentration to 32.48 L /m<sup>2</sup>h at 23% polymer concentration for PEG 6000 and 61.21 L /m<sup>2</sup>h at 19%polymer concentration to 30.2 L/m<sup>2</sup>h at 23% polymer concentration for PEG 10,000. For PEG16,000 the value of flux was reduced from 56.31L/m<sup>2</sup>h at 19% polymer concentration to 28.9 L/m<sup>2</sup>h at 23% polymer concentration. This indicate that increasing polymer concentration forms a denser and thicker skin layer, resulting in a more

selective but less productive UF membrane for liquid separation.

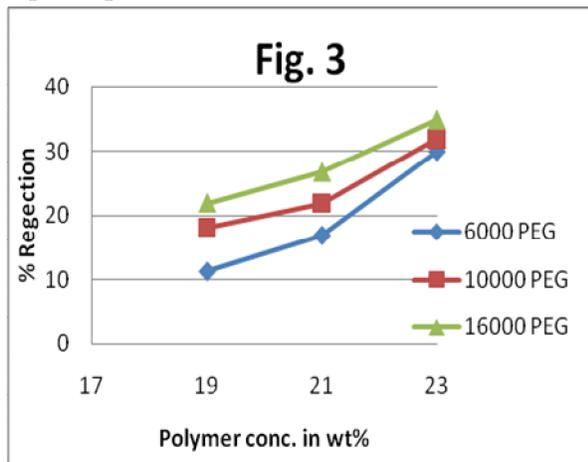


Fig 3 shows the effect of different polymer concentration on percentage rejection. There, as the polymer concentration increased from 19 to 23 wt%, the percentage rejection increased with different molecular weight of PEG. The rejection of the membrane for the PEG 6000 solution increased from 11.31% at 19% polymer concentration to 29.9% at 23% polymer concentration, and 18.13% at 19% polymer concentration to 31.92% at 23% polymer concentration for PEG 10,000. And for PEG 16,000 the value of percentage rejection was increased from 21.9% at 19wt% polymer concentration to 34.89% at 23wt% polymer concentration. This indicates that the membrane having a denser and thicker skin structure was prepared with PSF<sub>3</sub>. On other side, membranes from dilute polymer solution produced a thin and porous skin layer, leading to a high value of flux but relatively low percentage of rejection for liquid separation.

Increasing polymer concentration of the casting solution increases the solution viscosity. The coagulation value was reduced due to a stronger interaction of solvent and polymer and a greater interaction of non solvent and polymer that decreased the dissolving power of solvent for the polymer. Increasing an viscosity of polymer

solution that hinder the diffusional exchange rate of solvent and non-solvent in a sub layer. As a result of a fast phase separation at outer skin layer and a slow phase separation at the sub layer occur. The asymmetric membrane with a dense and skin layer supported by a closed cell sub layer was produced .on other side, an asymmetric membranes with a thin and porous skin layer and open cell sub layer was prepared by a polymer solution with a lower concentration.

### CONCLUSIONS

Polymeric membranes were prepared by phase inversion process. The three newly developed polymer solution were formulated with varying polymer concentration in the range of 19-23%. The experimental result shows that increasing in polymer concentration the PWP and Flux of the UF membrane decreases, while the rejection for solute increases. The outer skin layer of the membranes becomes thicker and denser with increasing polymer concentration in polymer solution. The higher rejection for PEG 16,000 separation was obtained from PES3 membrane solution, which is ---. However the flux resulting from this membrane is too slow compared to other membranes. Thus, we can conclude that, as polymer concentration increased, the percentage rejection increases and the PWP and Flux of the membrane decreases. This suggests that increasing in polymer concentration will form a denser and thicker skin layer, resulting in more selective but less productive UF membranes for liquid separation. While membrane from a dilute polymer solution produced a thin and porous skin layer, leading to a high value of flux and low percentage of rejection

**ACKNOWLEDGEMENTS**

We greatly acknowledge the support from Sant Gadge baba Amravati, university, and Dr V.SSapkal whose guides us about the topics

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