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Effects of PEG on Morphology and Permeation Properties of Polyethersulfone Membranes

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Abstract: Flat sheet asymmetric polyethersulfone (PES) ultrafiltration (UF) membranes were prepared from a homogenous solution of PES via immersion precipitation in a water coagulation bath. The effect of the solvents (N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF)) in preparation of the casting solution was studied. The effects of the molecular weight of polyethylene glycol (PEG) (400, 1500, and 6000 Da) on the morphology and the permeation properties of PES membranes were also investigated. Surface and cross-sectional morphology of the prepared membranes were studied by Scanning electron microscopy (SEM). The permeation performance of the prepared membranes was evaluated in terms of pure water flux (J_w), water content, porosity, hydraulic permeability, protein solution flux, and protein rejection. A solution of human serum albumin (HSA, $Mw = 66{,}000$ Da) was used as feed to study the permeation properties of the prepared membranes. Increasing molecular weight of PEG additives from 400 to 6000 Da enhances pure water permeation flux and HSA solution permeation flux while it reduces the protein rejection.

Keywords: Membrane performance, morphology, phase inversion, polyethersulfone membrane, polyethylene glycole

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INTRODUCTION

The phase inversion process is the most widely used technique for fabrication of asymmetric membranes, in which a solvent in a casting solution film is exchanged with a non-solvent and phase separation occurs in the cast film (1–3). The asymmetric membranes prepared via the phase inversion are characterized by thin and dense skin layers on top of the porous substrates. These membranes are widely used today in various applications such as microfiltration (MF), UF, and reverse osmosis (RO) processes because of their ideal cross-sectional morphology, i.e., the thin top layer plays a role of selective barrier film for the solute while the porous sublayer, that includes macrovoids and micropores, offers excellent mechanical strength to the membrane. It is well known that the morphology of asymmetric membranes depends on various factors, such as kinetic parameters and thermodynamic parameters (1–5). Polyethersulfone (PES) membrane is a favorable material for making membranes that can be employed in many industries such as, hemodialysis (6,7), milk industries (8) and etc. Addition of organic or inorganic components as a third component to the casting solution has been one of the important techniques to control the membrane morphology used in membrane preparation. The role of organic and inorganic additives such as methyl cellulose, glycerine, polyvinylpyrrolidone (PVP), PEG, water, LiCl and $ZnC1_2$ etc. in the casting solution has been reported as pore-forming agents enhancing the permeation properties of the membranes. This behavior was explained in terms of their water-soluble characteristics (9–12,13). Polymer additives such as PVP and PEG have been widely used to control the membrane structure in preparation of UF and MF membranes. To reduce the fouling tendency of these membranes, their wettability should be improved and their biocompatibility enhanced by adding hydrophilic polymeric additives such as PVP and PEG (13,14). Wienk et al. (15) investigated the effects of addition of high and low molecular weight components to the casting solution and proposed a mechanism for the formation of nodular structures in the membrane top layer. The effect of PVP as a polymeric additive on morphology and permeation properties of PES membranes have been investigated by Jimenez et al. (16) and found that the addition of PVP increases its molecular weight cut off (MWCO) and pure water permeation of the membranes. Xu et al. (17) also studied the effect of molecular weight of PVP on the morphology of polyetherimide hollow fiber membranes. They found that the higher the molecular weight of PVP, the bigger the pores. The effects of the molecular weight of PEG on the formation of Polyetherimide (PEI) asymmetric membranes have been also investigated by Kim and Lee (18) and found that small molecular weights of PEG such as PEG 200 and PEG 400 act as pore reducing agents for the PEI membranes. Idris et al. (19) also found that the presence of PEG with different molecular weights exhibits a significant effect on the performance of the PES membranes. The main purpose of this work is to investigate the effects of molecular weight (400, 1500, and 6000 Da) of PEG as an additive on the morphology and the performance of the asymmetric PES membranes prepared via phase inversion induced by an immersion precipitation method.

EXPERIMENTAL

Materials

Polyethersulfone (PES Ultrason E6020P with $M_W = 58{,}000$ Da) supplied by BASF was used as polymer for the preparation of the membrane casting solutions. These polymer flakes absorb moisture very rapidly. Therefore, the flakes were dried for more than 12 hr at 100–120°C prior to the process. N-methyl-2-pyrrolidone (NMP) and *N,N*-dimethyl formamide (DMF) were used as solvent from Merck. Polyethylene glycol (PEG, reagent grade, $M_W = 400$, 1500, and 6000 Da) supplied by Merck were used as pore former polymeric additives in the casting solutions. De-ionized water was used as the main non-solvent in the coagulation bath. Human Serum Albumin 20% (HSA $M_W = 66$ KDa, Biotest AG, Germany) was used as protein in preparation of the model feed solution.

Preparation of Membranes

Asymmetric flat sheet PES membranes were prepared by the phase inversion method. PES was homogeneously dissolved in the two solvents DMF and NMP. Then the PEG additives (400, 1500, and 6000 Da) were added to the PES solution by 5 wt.% and mixed by stirring for 8 hr at room temperature. The stirring was carried out at 200 rpm. An ultrasonic bath (KUDOS SK3310HP, China) was employed to free up the air bubbles entrapped in the polymeric solution. The prepared homogeneous solutions were cast using a film applicator to 250 μm clearance gap on a glass plate substrate. It was moved to a distilled water coagulation bath at room temperature for immersion precipitation and kept for 24 hr. Finally the membranes were dried by placing between two sheets of filter papers for 24 hr at room temperature. The composition of the casting solutions is shown in Table 1.

Table 1. Compositions of the PES casting solutions

	Polymer (wt.%)	Additives (wt.%)			Solvents (wt.%)	
Membrane	PES	PEG 400	PEG 1500	PEG 6000	DMF	NMP
PES 1	16	5	__	__	79	__
PES 2	16	__	5	__	79	__
PES 3	16	__	__	5	79	__
PES 4	16	5	__	__	__	79
PES 5	16	__	5	__	__	79
PES 6	16	__	__	5	__	79

Characterization of Membranes

Scanning Electron Microscopy (SEM)

The surface and cross-sectional structures of the prepared membranes were examined by SEM. The samples were frozen in liquid nitrogen and then fractured. They were then sputter coated with gold before being viewed with SEM (Cam Scan, Model MV2300).

Water Content

Water content is considered to be an important characterization parameter as it indirectly indicates the degree of hydrophilicity or hydrophobicity of the prepared membranes and also it is related to the porosity of the prepared membranes (20). The membranes were soaked in distilled water for 24 hr and weighed after mopping with blotting papers. The dry weights were determined after the wet samples were placed in an oven at 80°C for 24 hr. From these two values, the percent of water content was obtained using the following equation (21):

$$\text{Water content}(\%) = \frac{(Q_0 - Q_1)}{Q_0} \times 100 \qquad (1)$$

where Q_0 is the weight of wet membrane (g) and Q_1 is the weight of dry membrane (g).

Porosity Measurement

To evaluate the membrane porosity, they were soaked in distilled water and then weighed after mopping superficial water with filter papers.

The wet membrane was placed in an air-circulating oven at 80°C for 24 hr before measuring the weight of the dry membrane. From the two weights (wet and dry membranes), the membrane porosity was calculated using the following equation (22):

$$P(\%) = \frac{(Q_0 - Q_1)}{Ah} \times 1000 \tag{2}$$

where P is the membrane porosity; Q_0 is the weight of wet membrane (g); Q_1 is the weight of dry membrane (g); A is the membrane surface area (cm^2); h is the membrane thickness (mm). In order to minimize the experimental errors, the membrane porosity of each sample was measured three times and the results were presented in average.

Permeation Experiment

Cross Flow UF System

The performance of the prepared membranes was characterized using the cross flow UF system. This laboratory scale system consists of a reservoir, a pump, valves, pressure regulators and a membrane cell. Details of the experimental setup are illustrated in Fig. 1. As seen, the retentate was re-circulated to the reservoir and permeate was collected and then weighed. The cross-flow cell houses a flat sheet membrane with an effective area of 25 cm^2.

Membrane Compaction

The prepared membranes were compacted before using in the separation experiments. They were cut into the desired size needed for fixing it up in the UF setup and initially pressurized with distilled water at a transmembrane pressure of 220 kPa for 3 h. The pure water flux was measured at every 20 min.

Hydraulic Permeability and Pure Water Flux

Hydraulic permeability is very important particularly for the membranes used in pressure-driven separation processes such as the UF process. Hydraulic permeability of the prepared membranes was determined by allowing de-ionized water to pass through the compacted membranes.

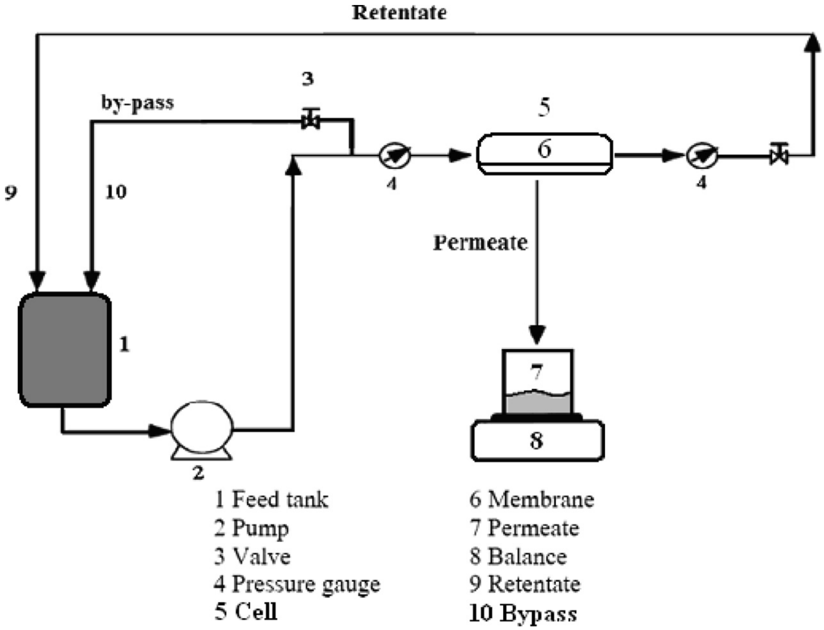

Figure 1. Cross-flow UF setup.

Pure water flux through the membranes was measured under steady state condition. The experiments were carried out using the cross flow UF system at different transmembrane pressures (0–220 kPa). Pure water flux was calculated as follows:

$$J_W = \frac{Q}{A \Delta T} \tag{4}$$

where J_W is the pure water flux (kg/m^2hr); Q is the quantity of permeate (kg); A is the membrane area (m^2); and ΔT is the sampling time (hr). Hydraulic permeability of the prepared membranes was obtained from the slope of the linear relationship between the pure water flux (J_w) and the transmembrane pressure as follows:

$$P_m = \frac{J_W}{\Delta P} \tag{5}$$

where, J_W is the pure water flux (kg/m^2hr); P_m is the hydraulic permeability (kg/m^2hrkPa); ΔP is the transmembrane pressure (kPa).

HSA Rejection

HSA is a starting material for the preparation of a number of important therapeutic proteins, which are collectively referred to plasma proteins (23). It was used as protein for the preparation of model solutions by other scientists (23,24). The protein, HSA, was dissolved in de-ionized water and its concentration was kept constant at 1 g/L for all the experiments. In all experiments, the pH of the feed solution was adjusted at a value of 7.2 using buffer solutions, since changing the pH may increase the fouling resistance of the membranes (25,26). Furthermore, if the pH of the solution changes, intermolecular forces between the protein molecules and the membrane predominate and this may reduce the performance of membranes (26,27). The flux was calculated using Eq. (4). Rejection of HSA was calculated using the following equation:

$$R(\%) = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \tag{6}$$

where, C_p is the protein concentration in the permeate stream and C_f is the protein concentration in the feed stream. All the experiments were performed under a transmembrane pressure of 120 kPa. The permeate was collected in a measuring cylinder over a certain time for calculating the flux. The main objective of the UF experiments was to investigate the rejection behavior of the HSA protein by the different membrane samples prepared in the present work under identical conditions. Samples from the permeate and the retentate were taken in order to determine their protein concentrations using UV spectrophotometry (Shimadzu® UVmini-1240) at 280 nm.

RESULTS AND DISCUSSIONS

SEM Images of the Prepared Membranes

SEM images from the cross-section and the surface of the prepared membranes are illustrated in Figs. 2 to 3, which show the effects of different molecular weight of PEG as polymeric additives as well as two different solvents (DMF and NMP). As observed from the SEM cross-sectional images (Fig. 2), all the prepared membranes have asymmetric structure consisting of a dense top layer and a porous sub layer with finger like cavities as well as macrovoids structure. The SEM surface images of the prepared membranes are illustrated in Fig. 3. Formation of

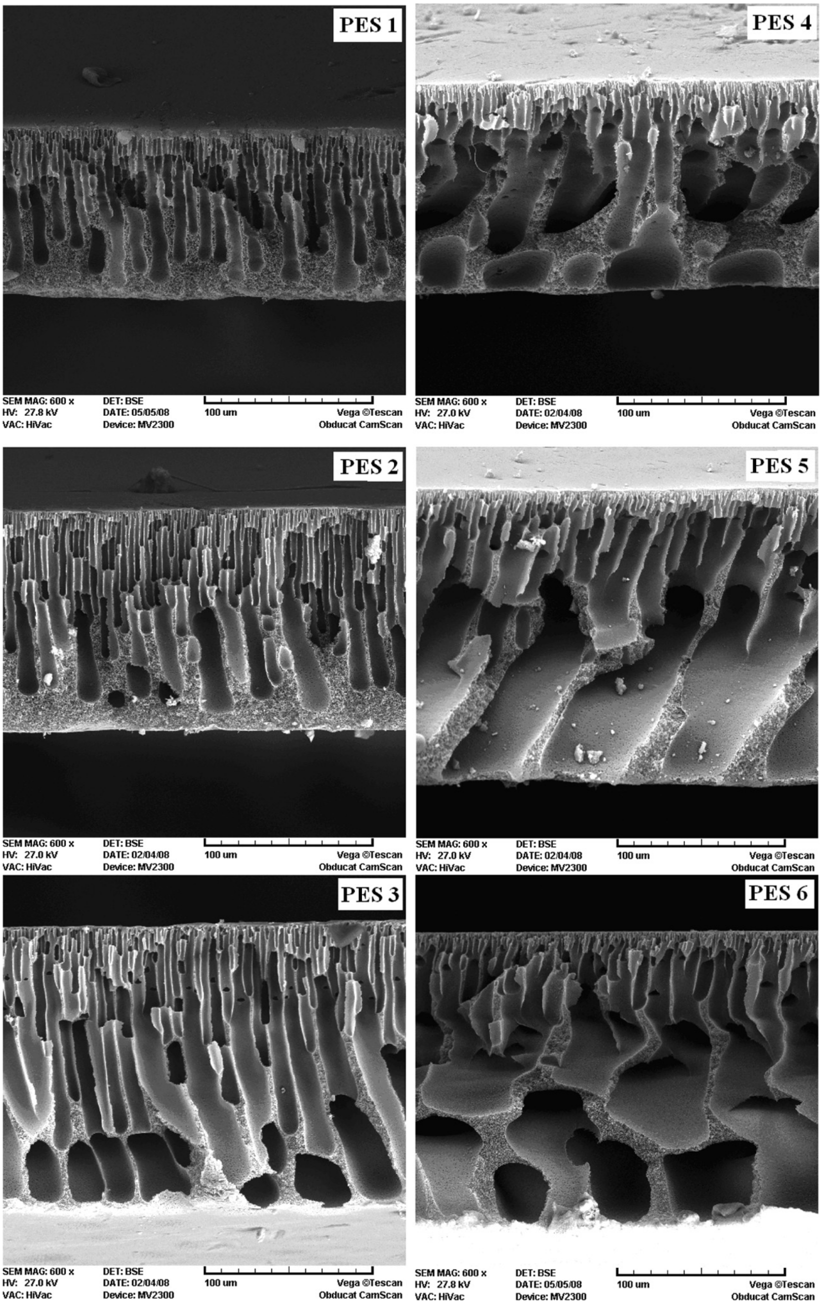

Figure 2. SEM cross-sectional images of the PES membranes.

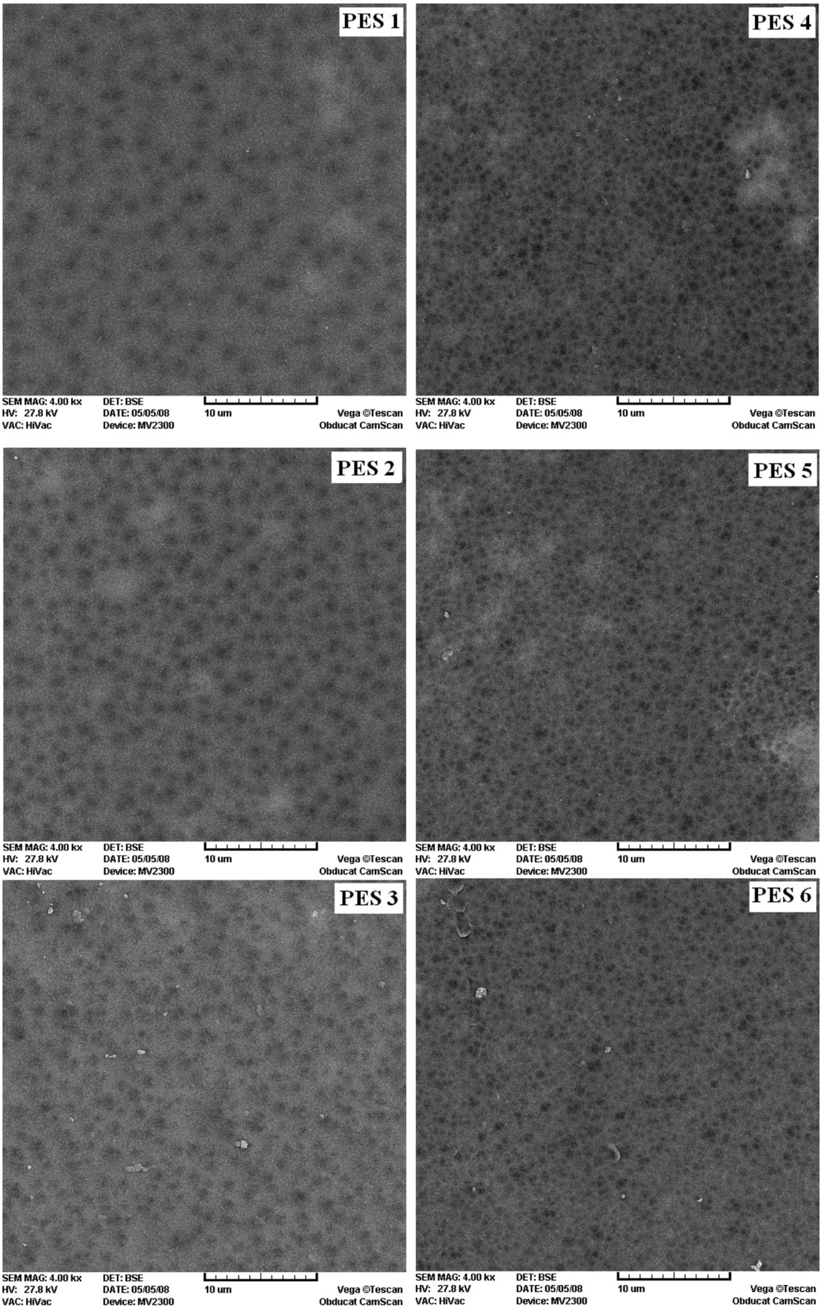

Figure 3. SEM surface images of the PES membranes.

the top surface is possibly due to demixing of the casting solution by means of nucleation and growth of the polymer rich phase, i.e., the solid phase (28,29).

Effects of the Molecular Weight of PEG on the Morphology of the PES Membranes

As observed in the SEM cross-sectional images (Fig. 2), the distance from the top layer of the membranes to starting point of macrovoids formation decreases by increasing the molecular weight of PEG additive for both types of the solvents (30). In the membranes prepared with DMF as solvent in the casting solution, increasing the molecular weight of the PEG additive from 400 to 1500 and 6000 Da, changes the size of the macrovoids gradually in structure from a tear drop shape to elongated macrovoids (19). The membranes prepared with PEG 400 as additive have finger-like tear drop macrovoids that end halfway, and there are some macrovoids in the bottom layer of the membranes, while the membranes prepared with PEG 1500 and PEG 6000 as additive have a finger-like structure that almost penetrates throughout the membranes and this improves the pore interconnectivity. In the membranes prepared with NMP as solvent in the casting solution, when the molecular weight of PEG increases from 400 to 1500 and 6000 Da, the macrovoids increase in number and size, promoting the formation of many large finger like pores. By increasing the molecular weight of the PEG from 1500 to 6000 Da, the membranes find big macrovoids. However, the size and shape of these macrovoids are different.

As observed in the SEM surface images of the prepared membranes with DMF as solvent in the casting solution (Fig. 2), the pore size and the porosity of the membranes increase by increasing the molecular weight of the PEG from 400 to 1500 and 6000 Da. SEM observations illustrate that addition of the high molecular weight PEG increases the pore size of the top surface and the porosity of the top layer in the membranes. Generally, it can be said that the pore size of the membrane depends on the size of such aggregated particles as macromolecules, nodules, or nodule aggregates (13,31,32). The increase in the pore size can be roughly estimated from the increase in the roughness and the size of aggregated particles observed at the top surface (30).

The effects of different molecular weight of the PEG on the thickness of the prepared membranes are presented in Fig. 4. As observed, the thickness of the membranes increases with increasing in the molecular weight of the PEG. For example, the membrane thickness increases from 107 to 171 μm for the PES/DMF/PEG membrane and from 130 to

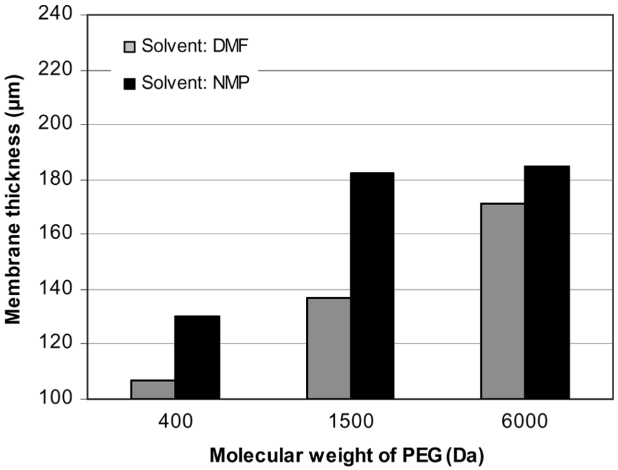

Figure 4. Effects of the molecular weight of PEG on thickness of the PES membranes.

185 µm for the PES/NMP/PEG membrane, when the molecular weight of the PEG increases from 400 to 6000 Da. In addition, as observed from the SEM cross-sectional images there is no significant difference between the thickness of the membranes prepared with NMP as solvent and PEG 1500 and PEG 6000 as polymeric additives in the casting solution. As observed, the thickness of the membranes increased slightly from 182 to 185 µm by increasing the molecular weight of PEG from 1500 to 6000 Da. When the cast film is immersed into the coagulation bath (water), precipitation starts and the cast film thickness gradually decreases. This results in increasing the polymer concentration in the cast film. Simultaneously, miscibility between the solvent (DMF or NMP) and the non-solvent (water) causes that in several points of the film top layer and the bottom layer, and diffusional flow of the solvent and the non-solvent (exchange of solvent and non-solvent) takes place (1) and consequently nuclei of the polymer-poor phase are formed. Ultimately, the growth of these nuclei continues until the polymer concentration at the pores or the macrovoids/solution interface becomes so high that solidification occurs. If the system exhibits instantaneous demixing, solidification occurs quickly after immersion of the cast film into the coagulation bath (1,30,33) and this inhibits the precipitation process. This results in increasing the membrane thickness and porosity because when the polymer content is constant and simultaneously the membrane thickness increases, the total volume of a certain content of the polymer increases and this has a direct relationship with the membrane porosity.

Acceleration of demixing has a direct relationship with the thermodynamic instability and the mutual diffusivities between the components in the system during the solidification of the casting solution (10,30). All of these accelerate demixing and facilitate solidification at the primary instants after immersion of the cast film into the coagulation bath and also rather inhibit the precipitation process results in increasing thickness and porosity of the prepared membranes.

Effect of Molecular Weight of PEG on Water Content of the Membranes

Water content is an important parameter in membrane characterization as it is closely related to pure water flux of membranes. Water content of the prepared membranes calculated using Eq. (1) is presented in Table 2. It is found that the addition of PEG with higher molecular weight to the casting solution enhances the water content of all the membranes. By comparison of water content for both types of the PES membranes prepared with NMP and DMF as solvents, it is illustrated that the water content of the PES/NMP membranes are higher than that of the PES/DMF membranes. From Table 2, it is observed that for the PES/DMF/PEG membrane, the water content increases from 65.1% to 78.8% when the molecular weight of PEG increases from 400 to 6000 Da. A similar trend is observed for the PES/NMP/PEG membrane, where the water content increases from 73.4% to 84% when the molecular weight of PEG increases from 400 to 6000 Da. This increasing trend confirms that the higher molecular weight of PEG the more pores in the membranes (as discussed in Section titled "Effects of the Molecular Weight of PEG on the Morphology of the PES Membranes"). The pores on the surface as well as the cavities in the sub layer are responsible for accommodating water molecules in the membranes (32,34).

Table 2. Water content, porosity and hydraulic permeability of the prepared membranes

Membrane	Water content (%)	Porosity (%)	Hydraulic permeability (kg/m^2.hr.kPa)
PES 1	65.1	49.6	0.26
PES 2	69.5	48.6	0.44
PES 3	78.8	55.6	0.89
PES 4	73.4	54.6	0.31
PES 5	79.2	62.5	0.55
PES 6	84.0	70.5	1.04

Effect of Molecular Weight of PEG on Porosity of the Membranes

Table 2 presents the variation in porosity of the PES membranes with the molecular weight of PEG in the casting solution calculated using Eq. (2). Table 2 shows that the membrane porosity increases from 49.6 to 55.6% for the PES/DMF/PEG and from 54.6 to 70.5% for the PES/NMP/PEG membranes when molecular weight of PEG used in the casting solution increases from 400 to 6000 Da. The effect of molecular weight of PEG on the porosity of the membranes can be considered on the basis of thermodynamics and kinetics. The addition of polymeric additives such as PEG, into the casting solution has two effects on the membrane formation process. First, it causes thermodynamics enhancement of the phase separation by reducing the miscibility of the casting solution with the non-solvent and this results in instantaneous demixing. Second, it causes kinetics hindrance against the phase separation by increasing the viscosity of the casting solution and this results in delayed demixing (1,28,32,35). This increase in viscosity of the casting solution hinders the overall diffusion. As a result, this can affect the exchange rate between the solvent and the non-solvent during the phase inversion process which according to the theory suggested by Young et al. (36) results in more porous membranes. Thus, the addition of PEG 6000 to the casting solution decreases the miscibility of the casting solution with water and increases the porosity of the prepared membranes.

Permeation Experiments

Flux Profile during Compaction

The compaction was aimed to make membranes with rigid pore structure and size, which could further yield reproducible results in characterization and performance evaluation. The prepared membranes were hydrostatically compressed at a constant transmembrane pressure of 220 kPa. The compaction was carried out for 200 min until a steady state flux was attained. The water flux was calculated using Eq. (4) from the experimental permeate flow rates measured at every 20 min interval. During compaction, initially pure water flux was found to be high. It declined gradually and reached a steady state value after 80 min for all the membranes, as shown in Figs. 5 and 6. This initial reduction in flux may be due to the fact that the membrane pores are compacted leading to uniform pore size and steady state water flux. The compaction of a polymeric membrane under hydraulic pressure reorganizes polymeric chains and this changes the membrane structure leading to a lowered

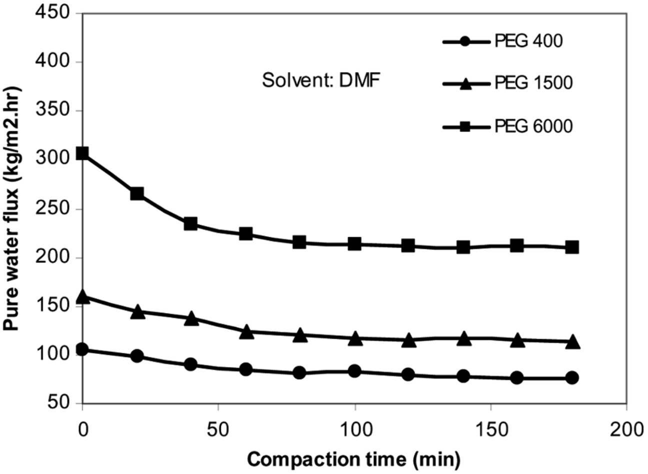

Figure 5. Effects of the molecular weight of PEG on pure water flux of the PES membranes prepared with DMF as solvent.

volume of porosity. Similar results were reported by Sivakumar et al. (34) for cellulose acetate membranes. The relatively higher flux in the presence of an additive may be due to increase in the network pore size of membrane with increasing PVP content (37). Similar results were also reported for the incorporation of PVP as an additive in the case of pure PSf

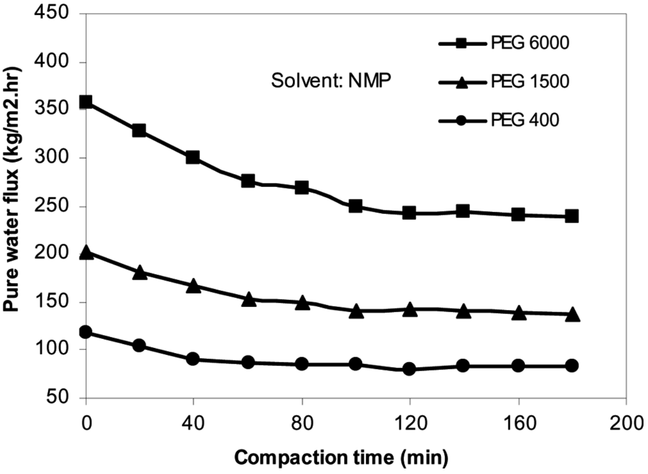

Figure 6. Effects of the molecular weight of PEG on pure water flux of the PES membranes prepared with NMP as solvent.

membranes (37). The steady state value of pure water flux for each membrane corresponding to the applied pressure (220 kPa) was found to increase with molecular weight of PEG for both the solvents (32). The steady state flux increases from 75.8 to 209.1 kg/m^2.hr for the PES/DMF/PEG membrane and from 83.1 to 238.7 kg/m^2.hr for the PES/NMP/PEG membrane, when the molecular weight of PEG increases from 400 to 6000 Da. Increasing the flux with molecular weight of PEG is due to increasing water content and porosity as already discussed.

Effect of Molecular Weight of PEG on Pure Water Flux and Hydraulic Permeability of the Membranes

The effects of different molecular weight of PEG on pure water flux at various transmembrane pressures are presented in Figs. 7 and 8. As observed, pure water flux through all the membranes within the range of transmembrane pressure of 0–220 kPa increases almost linearly with the pressure. This is because increasing the operating pressure increases the required driving force for permeation of water in UF process (38). Also, pure water flux through all the membranes increases with increasing molecular weight of PEG at a particular pressure. This agrees with the findings of the compaction study. For example, at 160 kPa, pure water flux increases from 38.5 to 140.2 kg/m^{2}h for the PES/DMF/PEG

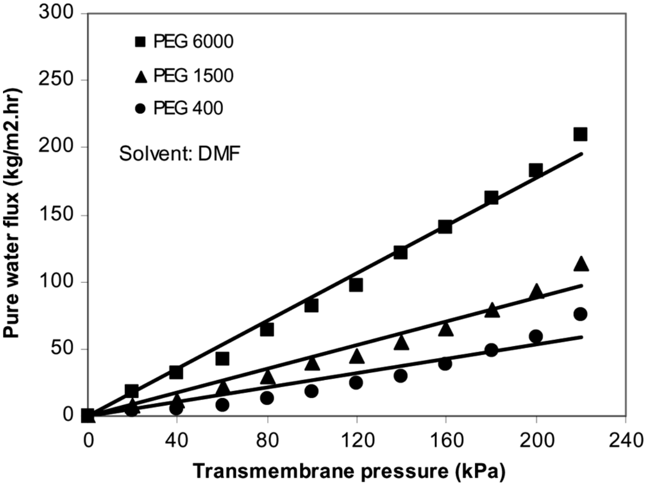

Figure 7. Effect of transmembrane pressure on pure water flux of the PES membranes prepared with DMF as solvent.

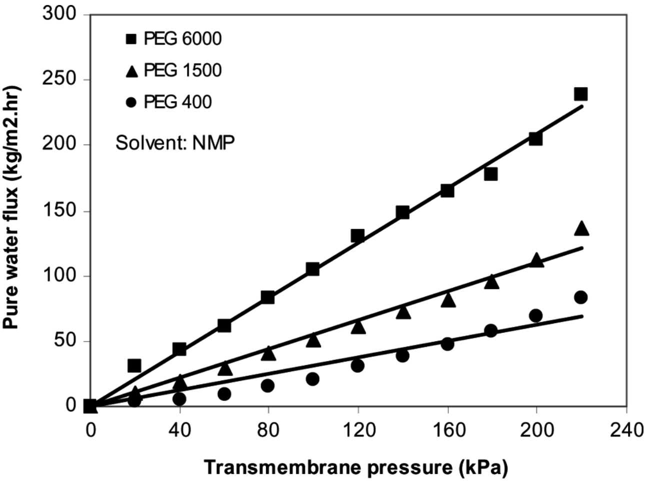

Figure 8. Effect of transmembrane pressure on pure water flux of the PES membranes prepared with NMP as solvent.

membrane and from 47.0 to 165.1 kg/m^{2}h for the PES/NMP/PEG membrane, the molecular weight of PEG increases from 400 to 6000 Da.

Hydraulic permeability as a key specification factor for all the prepared membranes was calculated using Eq. (5) and presented in Table 2. The results clearly indicate that addition of PEG with different molecular weights influences the formation of pores in the membranes affecting their permeabilities which are conceptually related to the pores for UF membranes (16,39). As observed in the SEM surface images of the prepared membranes (as discussed in section titled "Effects of the Molecular Weight of PEG on the Morphology of the PES Membranes"), addition of high molecular weight PEG increases the number and size of pores and the porosity of the prepared membranes. For example, as observed in SEM cross-sectional images, the membranes prepared with PEG 6000 as a polymeric additive in the casting solution (PES3 and PES6), have big macrovoids in their structure ($\leq$30 μm for PES3 and $\leq$70 μm for PES6) compared with the other membranes. This causes these membranes to have more pure water fluxes at a certain transmembrane pressure compared with the others. In addition, the porosity of these membranes is also higher.

Effect of Solvent Type on Permeation Properties of the Membranes

As observed in pure water flux measurements of the prepared membranes, the solvent type (DMF or NMP) influences on the membranes permeation performance. Permeation flux through the membranes is inversely proportional with the surface porosity of the top layer of the membranes. In other words, thicker denser top layers result in more resistance and less water flux. As seen, for example at 160 kPa transmembrane pressure, pure water flux was 64.9 kg/m^{2}hr for the PES/DMF/PEG 1500 membrane and 81.6 kg/m^{2}hr for the PES/NMP/PEG 1500 membrane. As observed in the cross-sectional SEM images of the prepared membranes (Fig. 2), the membranes prepared with NMP as solvent have bigger macrovoids compared to the membranes prepared with DMF as solvent. In addition, the membranes prepared with DMF as solvent have a denser top layer compared to the membrane prepared with NMP as solvent (Fig. 3). Miscibility or solubility parameters of solvent and non-solvent are important parameters in the membrane formation process. When the difference between solubility parameters of the solvent and the non-solvent is low (i.e., the miscibility of the solvent and the non-solvent is high), the non-solvent is able to diffuse more easily in the polymer film. This results in an increment in the exchange rate between solvent in the polymer film and non-solvent in the coagulation bath and leads to instantaneous demixing which is normally accompanied with a porous top layer and consequently formation of finger-like pores in the support layer (40). On the contrary, delay demixing which results from high differences between the solubility parameters of the solvent and the non-solvent (i.e., the solvent and the non-solvent are more and less immiscible) is often associated with the formation of a dense top layer (41). DMF has a higher enthalpy of solution in water than NMP as can be seen from DMF's solubility parameter (12.1 versus 11.3 (cal/cm^3)$^{0.5}$ for NMP). The transport of DMF into water is hence faster than the transport of NMP into water, while the uptake of water into both polymer solutions is almost similar. This results in a faster concentration of the polymer in the film for the DMF/PES system, giving a thicker denser top layer. The thicker denser top layer of the DMF membranes is also due to the fact that DMF is a better solvent for PES than NMP. This implicates that the polymer in the DMF/PES system is kept in the solution state at a higher water concentration, generating a thicker denser film (42).

Effect of Molecular Weight of PEG on the Protein Solution Flux and Protein Rejection

To study the permeation performance of the prepared membranes, they were characterized using a UF experimental setup with the HSA solution as feed. Figures 9 and 10 present the effect of the PEG molecular weight on the protein solution flux and the protein rejection of the membranes

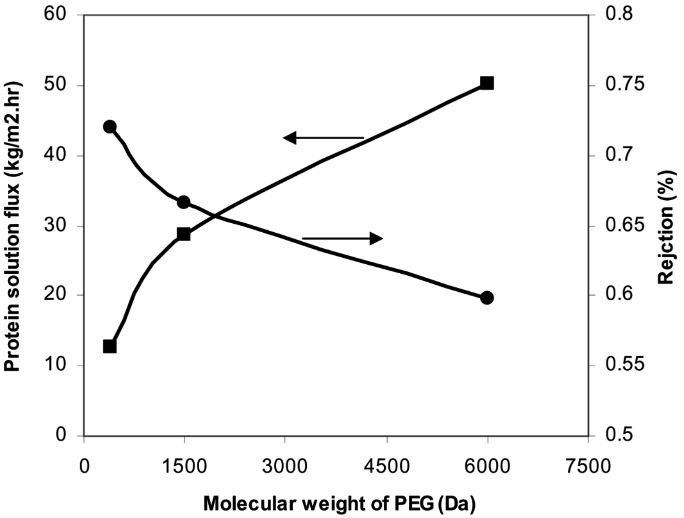

Figure 9. Effects of the molecular weight of PEG on the protein solution flux and the protein rejection of the PES membranes prepared with DMF as solvent.

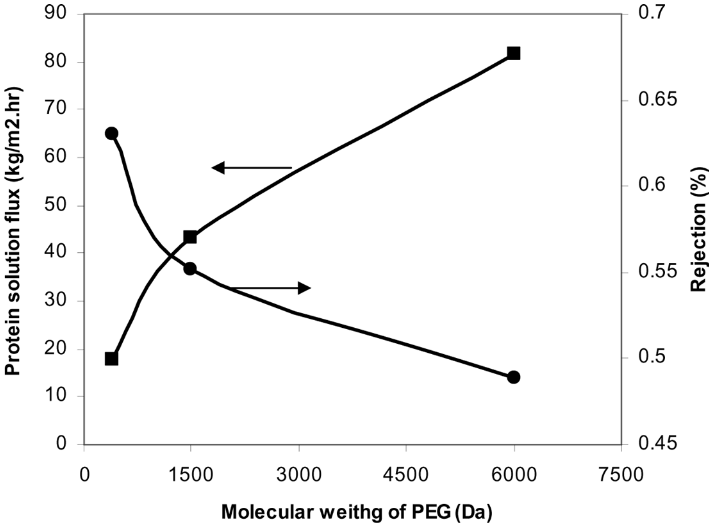

Figure 10. Effects of the molecular weight of PEG on the protein solution flux and the protein rejection of the PES membranes prepared with NMP as solvent.

prepared from PES/PEG/DMF and the PES/PEG/NMP solutions, respectively at a transmembrane pressure of 120 kPa. Protein solution flux and protein rejection in UF membranes can be explained under the concept of protein adsorption and consequent pore narrowing, as a result of both hydrophobic and electrostatic interactions between the membrane surface and the protein molecules (43). As observed in Figs. 9 and 10, the protein solution flux through the membranes increases by increasing the molecular weight of PEG in the casting solution, while the protein rejection decreases. For example, the protein solution flux increased from 12.7 to 50.1 kg/m^2.hr for the PES/DMF/ PEG membrane and from 17.6 to 81.7 kg/m^2.hr for the PES/NMP/ PEG membrane and the protein rejection decreased from 72 to 59% for the PES/DMF/ PEG membrane and from 63 to 48% for the PES/ NMP/PEG membrane when the molecular weight of PEG increased from 400 to 6000 Da. More porosity (as confirmed using water content and porosity measurements) as well as the presence of finger-like cavities in the sub layer (Fig. 2) and higher hydrophilicity when using the higher molecular weight of PEG in the casting solution lead to higher flux and less rejection.

CONCLUSION

Asymmetric PES membranes were prepared by the phase inversion process via the immersion precipitation method in a water coagulation bath. The effects of PEG molecular weight as a hydrophilic pore former additive in PES/DMF and PES/NMP casting solutions on the fundamental characteristics of the membranes such as morphology, pure water flux, water content and porosity, protein solution flux, and protein rejection were investigated. All the membranes have an asymmetric structure as observed in the SEM cross-sectional images. When PEG is used in the casting solution, the prepared membranes have an asymmetric finger like structure by spongy-structure in the bottom layer. By increasing the molecular weight of PEG, the size of the macrovoids increases and the prepared membranes have a porous top surface. In addition, increasing the molecular weight of PEG cause thickness of the prepared membranes to increase. The water content of the prepared membranes increases by increasing the molecular weight of PEG, while this slightly increases the porosity of the membranes. Pure water flux, hydraulic permeability, and protein solution flux are observed to enhance significantly, while protein rejection reduces by increasing the molecular weight of PEG in the casting solution.

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