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Structural analysis of PES nanoporous membranes under different conditions of preparation

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ABSTRACT

In this study we have focused on the structure of the prepared membranes which have been fabricated under different conditions. First, the different concentrations of polyethersulfone (PES) (15, 20 and 25 wt%) for preparation of casting solution were used. Then by adding polyethyleneglycol (PEG) in different concentrations (2, 5 and 8 wt%) and different molecular weights (200, 600, 1500), the membranes were prepared via the immersion precipitation procedure in a non-solvent bath (water) with different temperatures (5 and 35˚C). The flat-sheet membranes were characterized using scanning electron microscope which shows remarkable changes in the morphology and structure of prepared membranes. Flux and rejection capability of membranes were estimated using pure water and salts, respectively. Structural analysis of membranes show that the membrane including 25 wt% PES has the narrow pores or voids (nearly 3 μm) comparing to the membrane composed of 15 wt% PES (about 7 μm). Results show that introducing PEG changes the hydrophilicity and viscosity of casting solution. The membrane with 20 wt% PES which in the amount of PEG 1500 is about 2 wt% shows the best performance. The rejection of this membrane is in the order of $Na_2SO_4 > MgSO_4 > NaCl$.

Keywords: PES membranes; Structural analysis; Thickness; Preparation conditions

1. Introduction

Polyethersulfone (PES) is widely used for the fabrication of membranes. This polymer possesses the favourable characteristics of extensive temperature limits, wide pH tolerances and good resistance against chlorine and chemicals including aliphatic hydrocarbons, alcohols and acids [1]. PES has a high mechanical, thermal and chemical resistance which is classified as a high-Tg polymer. This is widely used in manufacturing asymmetric membranes [2,3]. A well-known procedure to fabricate membranes is phase inversion process [4–6]. In this process an asymmetric structure is resulted which in a dense top layer and a porous sub-layer is created. During the formation of membrane in coagulation bath, two main factors are controlling i.e. thermodynamics and kinetics. Thermodynamic depends on phase equilibrium between components in the system, and kinetics related to the diffusivities of them. Instantaneous demixing occurred when the phase equilibrium is decreased and diffusivities increased. In these

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conditions, a membrane with high porosity in sublayer is formed. The membrane morphology can be influenced by adding a tiny amount of organic/inorganic additives [7–9]. Polyvinylpyrrolidone (PVP) and polyethyleneglycol (PEG) as polymeric additives were largely used in casting solution to affect on membrane morphology and its performance during the preparation of membranes [10–13]. PEG is one of the best polymeric additives due to the miscibility with membrane materials and solubility in water and solvents [14]. These additives were added to the casting solution to achieve the desired enhanced membrane performance such as low fouling, high flux and selectivity [15–20].

In this work, the effect of different fabrication conditions such as PES and PEG concentrations as well as coagulation bath temperature on membrane preparation was investigated. Scanning electron microscope (SEM) analysis was used for better determination and understanding how the variation in membrane condition can affect the morphology and structure of membranes by considering the thermodynamic and kinetic parameters.

2. Experimental

2.1. Materials and apparatus

PES (Ultrason E6020P with $M_W = 50{,}000\,\text{g/mol}$) was supplied by the BASF Company (Germany). PVP (40,000 g/mol), some different types of PEG (200, 600 and 1,500 g/mol) and acrylic acid from Merck were used. Dimethylacetamide (DMAc) was purchased from Scharlau (Germany). Na_2SO_4, $MgSO_4$ and NaCl salts (Merck) were used to investigate the ion rejection capability of membranes. Distilled water was used throughout the study.

2.2. Membrane ingredients and preparation procedure

The blend dope solution was prepared by dissolving different concentrations of PES (15, 20, and 25 wt %) in DMAc with 2 wt% acrylic acid, different amounts of PEG (2, 5, and 8 wt%) and 3 wt% PVP as pore former. The stirring was carried out at 200 rpm for 5 h at 40°C. After formation of a homogeneous solution, the dope solution was held at the ambient temperature for around 24 h to remove the air bubbles. Afterwards, the dope solution was cast on the glass support at 120 μm thickness by using a film applicator at the room temperature without evaporation. After coating, the support was immersed into a distilled water bath for at least 20 h for removing most of the solvent and water-soluble polymer.

2.3. Physical characterization methods

2.3.1. SEM test

The cross-section of membranes was examined using a SEM. The samples of the membranes were frozen in liquid nitrogen and fractured. After sputtering with gold, they were viewed with a Philips microscope at 25 kV.

2.3.2. Viscosity measurement

A dynamic rheometer apparatus (Model MCR 501) from Anton Parr Company (Austrian) was utilized to measure the viscosity of prepared casting solutions at a constant temperature of 25°C.

2.4. Membrane performance evaluation

The performance of prepared membranes was analyzed using a cross-flow system. The details of the experimental set-up have been described elsewhere [21] and shown in Fig. 1. The membrane surface area in the filtration cell was $22\,\text{cm}^2$. The flux of each membrane was determined at 10 min intervals under the 1.0 MPa transmembrane pressure. The experiments were carried out at 25°C. The cross-flow velocity was approximately 0.6 m/s for all tests. The permeation rate and salt rejection were determined for all membranes using the Na_2SO_4, $MgSO_4$ and NaCl solutions in the 1,000 ppm concentration. The rejection was obtained by:

$$R\% = \left[1 - \frac{\lambda_p}{\lambda_f}\right] \times 100 \tag{1}$$

where λ_p and λ_f are the ion conductivity in the permeate and feed, respectively. The ion rejection was investigated by measuring the permeate conductivity using a conductivity meter (Hanna 8733 Model, Italy).

3. Results and discussion

3.1. Influence of PES concentration

Using SEM images, the cross-section of different membranes was investigated. The effect of PES concentration and PEG concentration as well as coagulation bath temperature is shown in the figures. As seen in Fig. 2, by increasing the PES concentration, the structure of membranes was changed. At higher percentage of PES, a structure with thick skin layer was formed (Fig. 2(c)). On the other hand, the area of pores in the sub-layer became smaller and the shape of macrovoids (Fig. 2(a)) was changed to the finger-and sponge-like

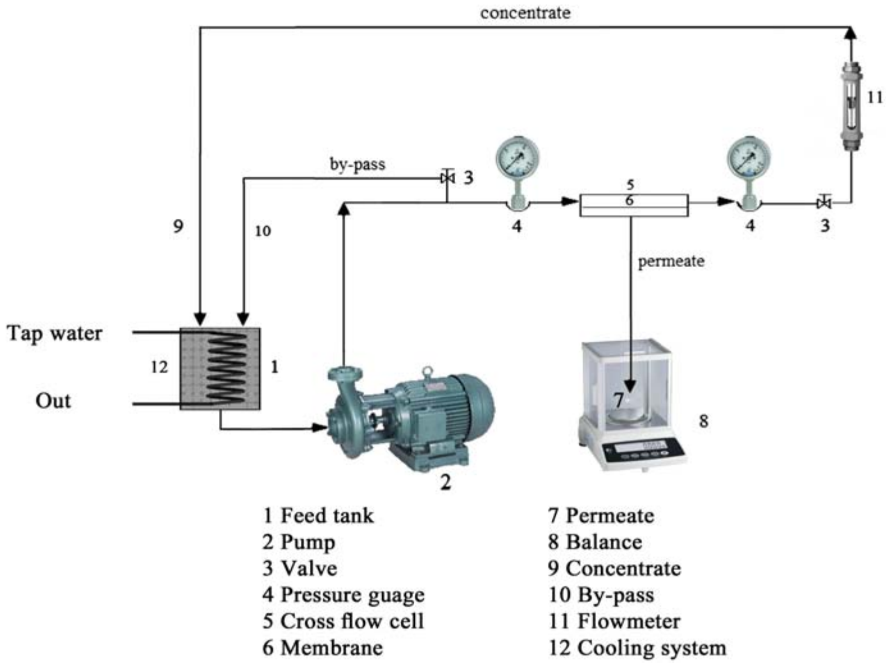


Fig. 1. Cross-flow filtration system.

pores. Fig. 2(a) clearly shows a few big pores in the sub-layer (macrovoids). One remarkable change in the membrane morphology was observed in skin layer which has become thicker. Fig. 3 clearly shows that the distance from the top surface of the membrane to the starting point of pores is about 2 μm (Fig. 3(a), 15 wt% PES) and 6 μm (Fig. 3(b), 25 wt% PES), respectively. By considering the pore shapes near the membrane surface (Fig. 3), the membrane including 25 wt% PES has the narrow pores (nearly 3 μm) comparing to the membrane composed of 15 wt% PES (about 7 μm). This proves that by increasing the PES concentration, the area of pores becomes smaller, resulting in the decrease of thickness of the membrane.

Table 1 represents the viscosity of different membranes at the presence of 2 wt% PEG. The viscosity is 436, 2,280, and 8,540 cp for the membranes including 15, 20 and 25 wt% PES, respectively. Preferably a spongy membrane structure without macrovoids is interesting, resulting in mechanically more stable membranes. By immersing the cast film into the distilled water bath (nonsolvent) and due to the low miscibility between polymer and water, precipitation starts. In this condition, exchange of solvent and non-solvent takes place and nuclei of the polymer-poor phase are formed. Growth of these nuclei continues until the polymer concentration at the pores/solution interface becomes high, resulting in solidification. In instantaneous demixing condition, the composition in front of the nuclei remains stable for a long period of time. Generally, macrovoids are formed where instantaneous demixing takes place [22,23].

From Table 1, it can also be concluded that the viscosity of dope solution increases with increasing the PES concentration, resulting in reduction of solvent and non-solvent exchange rate during solidification. Thus, delayed demixing occurred which results in thinner and denser membrane (see Fig. 2).

As clearly seen in Fig. 4, when the PES concentration raises up to 20 wt%, remarkable difference between membranes in terms of pure water flux is not observable. The membrane composed of 15 wt% PES shows higher pure water flux (about 160 L/m^2 h) comparing to that in other membranes. It is predictable because the formation of macrovoids in membrane morphology causes more flux. Probably, when the membrane with 15 wt% PES forms, the exchange rate of solvent and non-solvent is facilitated that comes from increasing thermodynamic instability. But the difference of exchange rate of solvent and non-solvent for membranes with 20 and 25 wt% PES is not very considerable, resulting in no significant difference between the morphology of membranes.

3.2. *Influence of PEG concentration*

Table 2 represents the viscosity quantities of dope solution (20 wt% PES) at the presence of different concentrations (2, 5, and 8 wt%) of PEG 1500. The results

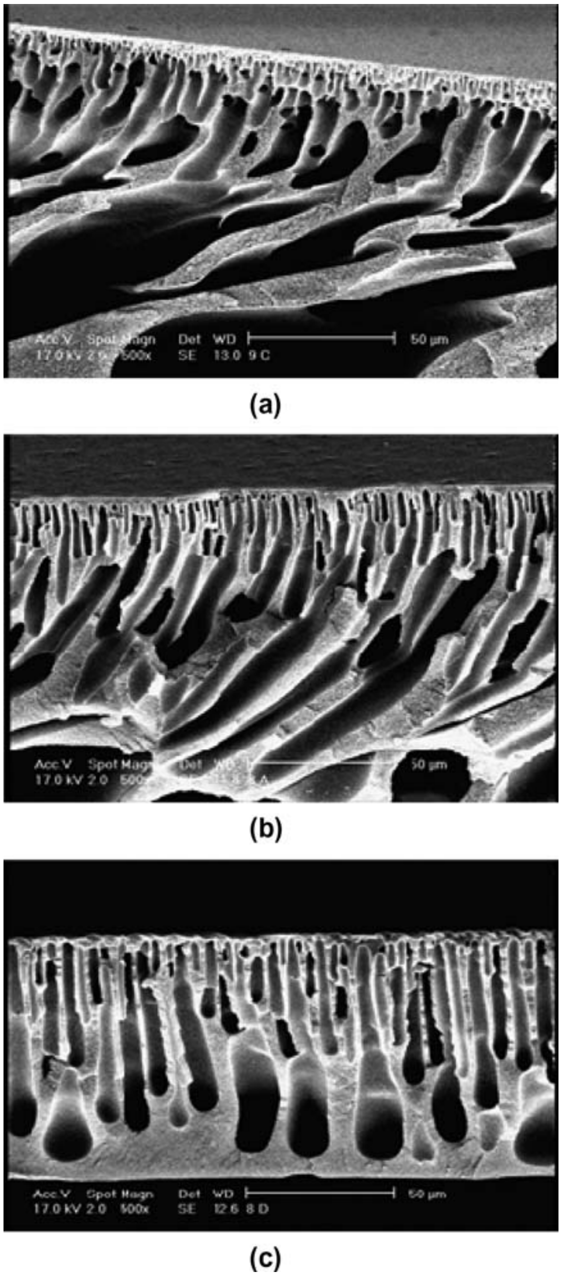


Fig. 2. SEM images of prepared membranes with different PES concentrations: (a) 15%, (b) 20% and (c) 25%.

show that the viscosity of dope solution increases from 2,280 cp for the membrane including in 2 wt% of PEG to 3,160 cp for that of including 8 wt% PEG. Consequently, the increase of casting solution viscosity can hinder the diffusional exchange rate of solvent and non-solvent, resulting delayed demixing. Delayed or instantaneous demixing is influenced by thermodynamic stability and kinetic processes, resulting in alterations in the membrane morphology as well as performance [10].

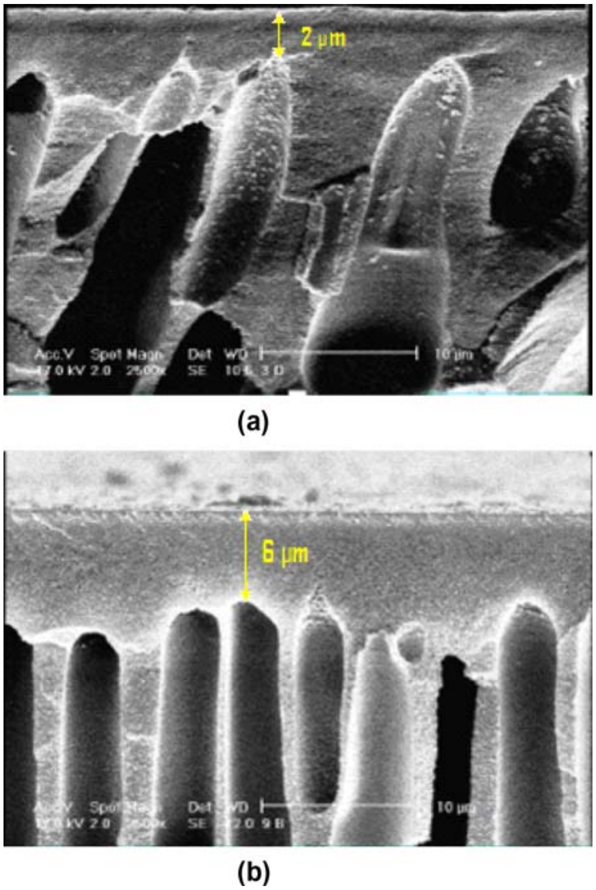


Fig. 3. Cross-section SEM images of membranes with (a) 15% and (b) 25% of PES (higher magnification).

Table 1
Viscosity of different dope solutions

Membrane (wt%)	PEG (wt%)	Viscosity (cp)
15	2	436
20	2	2,280
25	2	8,540

SEM images for showing the effect of PEG on the morphology and structure of membranes are presented in Fig. 5. This figure shows that with increase of PEG (8wt% PEG) the spongy-like membrane is formed (Fig. 5(c)). Fig. 4(a) clearly represents that a membrane composed of macrovoids is fabricated in the presence of 2 wt% PEG. Presence of PEG as an additive either increases thermodynamic instability or decreases the exchange rate of solvent and non-solvent due to enhanced viscosity (see Table 2). Thus, addition of PEG on the dope solution has inverse effects but hindering the exchange of solvent and non-solvent is much considerable [5].

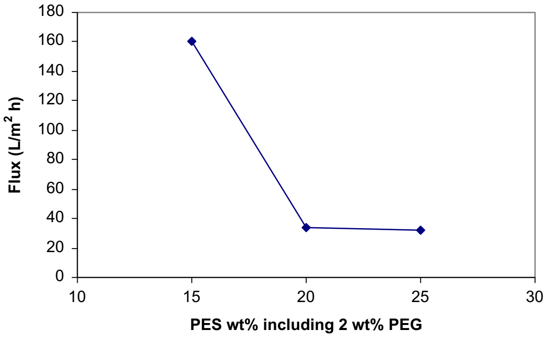


Fig. 4. Effect of different PES concentrations on pure water flux.

Table 2
Viscosity of dope solutions at different PEG concentrations

Membrane (wt%)	PEG (wt%)	Viscosity (cp)
20	2	2,280
20	5	2,400
20	8	3,160

The alteration in rejection capability of prepared membranes in the presence of different concentrations of PEG is clearly illustrated in Fig. 6. With increase of PEG concentration, the Na_2SO_4 rejection increases from 68 to 76%. This proves the statements above.

3.3. *Influence of coagulant bath temperature*

In this section, the membranes with the same concentrations of PES and PEG were investigated while the temperature of distilled water bath is different (5 and 35˚C). As clearly seen in Fig. 7, the structure of membranes has become completely different. Membrane which was formed under 5˚C, is thinner and denser (Fig. 7(a)). Considering this image, it is clearly observable that macrovoids disappeared. This is due to the reduction of diffusion, resulting in lower exchange of solvent and non-solvent. Probably, kinetic process overcomes thermodynamic instability which causes a thick top layer along with a lower porous sub-layer to be formed. Fig. 7(b) shows a thicker membrane including in some more/big pores which in the thickness of the top layer becomes thinner (under 35˚C).

Fig. 8 shows the effect of non-solvent bath temperature on the Na_2SO_4 rejection. It is seen that the rejection increases (under 5˚C) due to the dense structure of the membrane. Under 35˚C, the rejection increases from 38 to 65%. On the other hand and for membranes prepared under 5˚C, the rejection enhances from 50 to near 85%. By comparing the data, it is clearly observed that the mean difference of rejection is between 12 and 20%, approximately. This is due to the fact that the thickness and pores of the membranes become thinner and smaller, respectively.

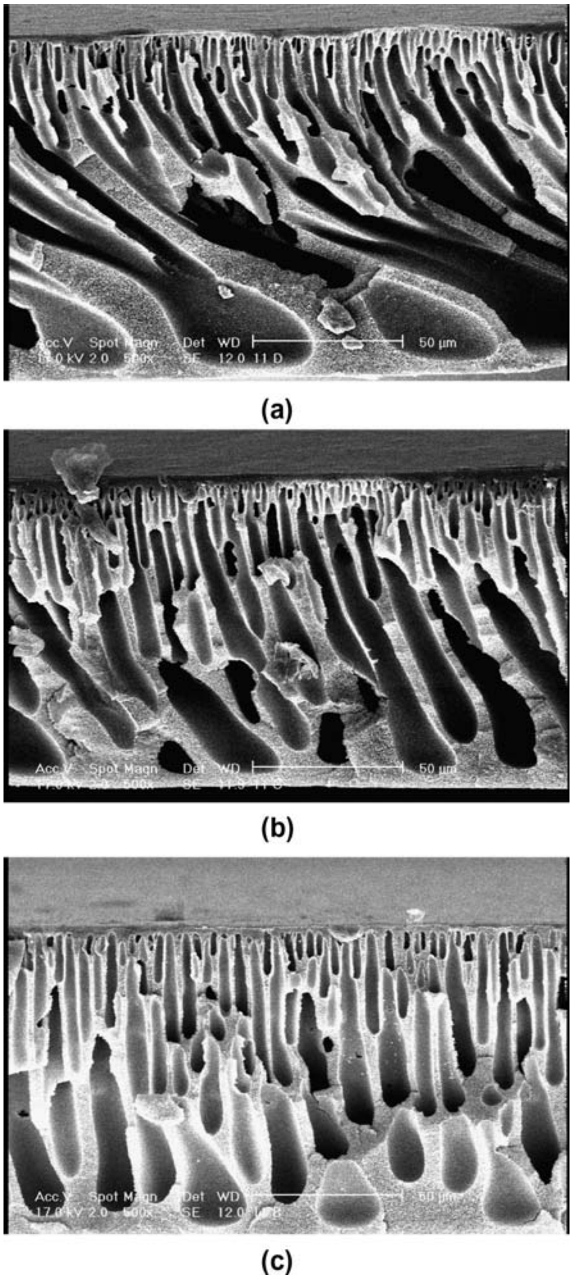


Fig. 5. SEM images of different membranes at the presence of different PEG concentrations: (a) 2%, (b) 5% and (c) 8 wt%.

3.4. *Influence of membrane thickness*

Effect of two membrane thickness (90 and 120 μm) on the flux and rejection of membranes was investigated. Fig. 9 clearly shows that in 90 μm thickness, the flux and Na_2SO_4 rejection are 29 (L/

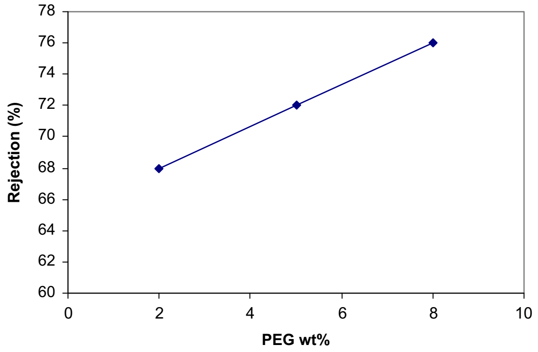
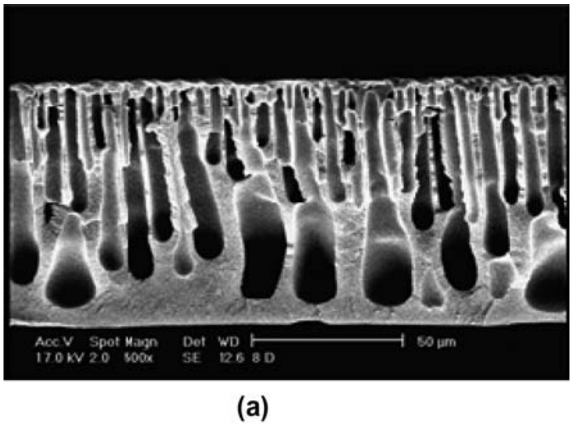


Fig. 6. Effect of PEG concentration on the rejection of Na_2SO_4 at different temperatures.



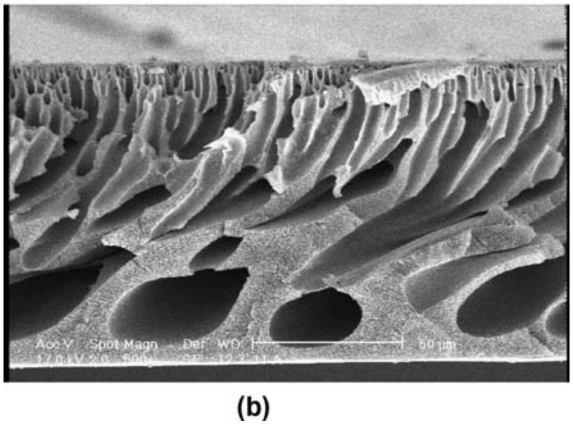


Fig. 7. Cross-sectional SEM images of membranes at different bath temperatures: a) 5˚C and b) 35˚C.

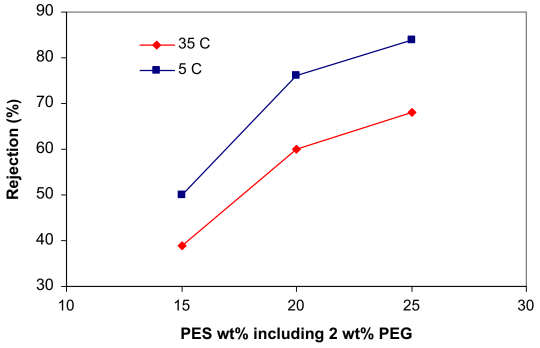


Fig. 8. Variations of Na_2SO_4 rejection vs. PEG concentration.

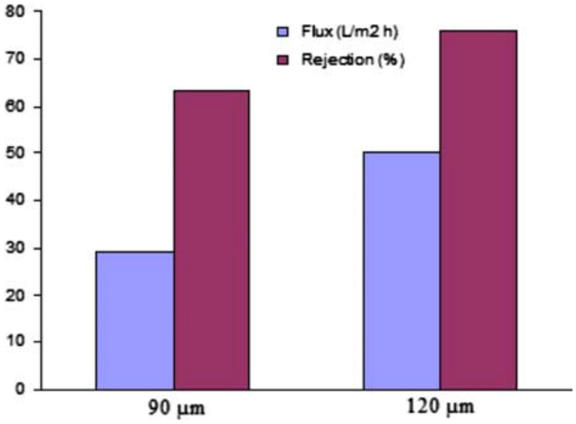


Fig. 9. Effect of membrane thickness on membrane flux and rejection.

m^2 h) and 63%, respectively. In the other membrane (with 120 µm thickness), these parameters are 50 (L/m^2 h) and 76%, respectively. Probably, due to the increase of film thickness, the diffusional exchange rate of solvent and nonsolvent reduces which leads to delayed demixing. In this situation, the growth of the polymer-poor phase was hindered while the number of nuclei increases. This phenomenon leads to the formation of a membrane without big macrovoids. Consequently, more flux (due to more pores in the membrane surface) and high rejection (due to delayed demixing) were observed (for more information see Section 3.1). In addition, further thickness of membrane increases the rejection due to the development of the membrane resistance for transferring of materials.

3.5. *Influence of different PEGs*

As seems in Fig. 10, the addition of PEG with different molecular weight results in significant changes in flux and rejection of the membranes. By increasing the molecular weight of PEG the pore number of the membranes increases, resulting in more porous membranes [24,25]. Flux increases from 25 to near 50 L/m^2 h. In contrary, rejection ability of the membrane decreases from 80% to about 75%. According to Chakrabarty et al. [26] PEG not only acts as a pore former

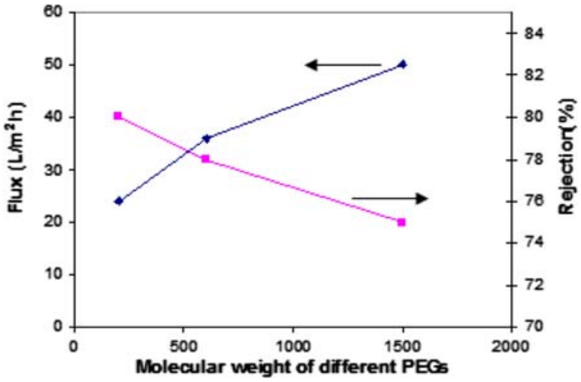


Fig. 10. Effect of molecular weight of different PEGs on flux and rejection.

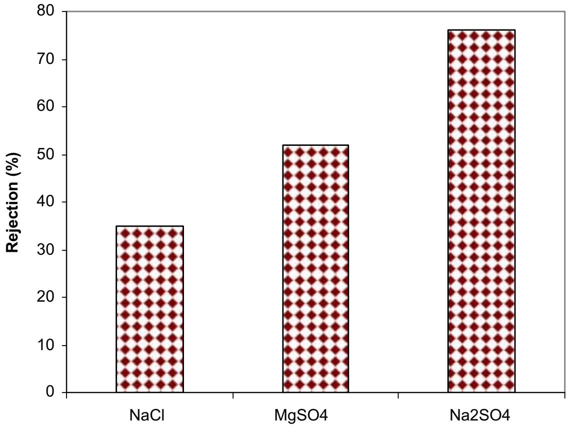


Fig. 11. Capability of optimized membrane for rejection of different salts.

but also reduces the pore size of the membranes and when the molecular weight increases, the capacity of PEG to form pores increases.

The capability of the optimized membrane for salt rejections is presented in Fig. 11. The best membrane is well known as a membrane with an outstanding rejection and a moderate flux. So, the membrane with 20 wt% PES which in the amount of PEG 1500 is about 2 wt% shows the best performance. The order of membrane rejection is 78, 50 and 35% for $Na_2SO_4 > MgSO_4 > NaCl$ salts, respectively.

4. Conclusion

Using SEM, the cross-section of different membranes was studied. The effect of PES concentration and PEG concentration as well as coagulation bath temperature was investigated. Results show that with increasing of PES concentration, the structure of membranes was changed. The difference of exchange rate of solvent and non-solvent for membranes with 20 and 25 wt% PES is not very considerable, resulting in no significant difference between the morphology of membranes. In addition, the effect of PEG on the morphology and structure of membranes are studied using SEM images. Images show that with the increase of PEG, the spongy-like membrane is formed. As a result, addition of PEG on the dope solution has inverse effects but hindering the exchange of solvent and non-solvent is much considerable. Membrane, which was formed under lower temperature has a thinner and denser shape. This is due to the reduction of diffusion, resulting in lower exchange of solvent and non-solvent.

References

[1] M. Cheryan, Ultrafiltration and Microfiltration Handbook, Technomic, Lancaster, PA, 1998.
[2] B.K. Chaturvedi, A.K. Ghosh, V. Ramachandhran, M.K. Trivedi, M.S. HanTa, B.M. Misra, Preparation, characterization and performance of polyethersulfone ultrafiltration membranes, Desalination 133 (2001) 31–40.
[3] C. Barth, M.C. Goncalves, A.T.N. Pires, J. Roeder, B.A. Wolf, Asymmetric polysulfone and polyethersulfone membranes: Effects of thermodynamic conditions during formation on their performance, J. Membr. Sci. 169 (2000) 287–299.
[4] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, M. Adeli, M.Y. Hashemi, M.R. Moradian, Fabrication new PES-based mixed matrix nanocomposite membranes using polycaprolactone modified carbon nanotubes as the additive: Property changes and morphological studies, Desalination 277 (2011) 171–177.
[5] Y. Liu, G.H. Koops, H. Sthratmann, Characterization of morphology controlled polyethersulphone hollow fiber membranes by addition of polyethylene glycol to the dope and bore liquid solution, J. Membr. Sci. 223 (2003) 187–199.
[6] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, Z. Kheirollahi, M. Adeli, Changing the performance and morphology of polyethersulfone/polyimide blend nanofiltration membranes using trimethylamine, Desalination 256 (2010) 101–107.
[7] I.M. Wienk, R.M. Boom, M.A.M. Beerlage, A.M.W. Bulte, C.A. Smolders, Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers, J. Membr. Sci. 113 (1996) 361–371.
[8] D.B. Mosqueda-Jimenez, R.M. Narbaitz, T. Matsuura, G. Chowdhury, G. Pleizier, J.P. Santerre, Influence of processing conditions on the properties of ultrafiltration membranes, J. Membr. Sci. 231 (2004) 209–224.
[9] H.T. Yeo, S.T. Lee, M.J. Han, Role of polymer additive in casting solution in preparation of phase inversion polysulfone membranes, J. Chem. Eng. Japan 33 (2000) 180–185.
[10] M.J. Han, S.T. Nam, Thermodynamic and rheological variation in polysulfone solution by PVP and its effect in the preparation of phase inversion membrane, J. Membr. Sci. 202 (2002) 55–61.
[11] B.K. Chaturvedi, A.K. Ghosh, V. Ramachandran, M.K. Trivedi, M.S. Hanra, B.M. Misra, Preparation, characterization and performance of polyethersulfone ultrafiltration membranes, Desalination 133 (2001) 31–40.
[12] N.A. Ochoa, P. Pradanos, L. Palacio, C. Pagliero, J. Marchese, A. Hernandez, Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes: Characterisation of polyethersulfone UF membranes with dopes containing different PVP, J. Membr. Sci. 187 (2001) 227–237.
[13] J.J. Shieh, T.S. Chung, R. Wang, M.P. Srinivasan, D.R. Paul, Gas separation performance of poly(4-vinylpyridine)/polyetherimide composite hollow fibers, J. Membr. Sci. 182 (2001) 111–123.

[14] B. Jung, J.K. Yoon, B. Kim, H.W. Rhee, Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes, J. Membr. Sci. 243 (2004) 45–57.

[15] Q.Z. Zheng, P. Wang, Y.N. Yang, Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation via phase-inversion process, J. Membr. Sci. 279 (2006) 230–237.

[16] S. Deniz, Characteristics of polycarbonate membranes with polyethylene glycol prepared via dry/wet-phase inversion methods, Desalination 200 (2006) 42–43.

[17] B.T. Sanchez, R.I. Ortiz-Basurto, E.B. Fuente, Effect of nonsolvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes, J. Membr. Sci. 152 (1999) 19–28.

[18] J.J. Qin, M.H. Oo, Y. Li, Development of high flux polyethersulfone hollow fiber ultrafiltration membranes from a low critical solution temperature dope via hypochlorite treatment, J. Membr. Sci. 247 (2004) 137–142.

[19] I.C. Kim, K.H. Lee, Effect of poly(ethylene glycol) 200 on the formation of a polyetherimide asymmetric membrane and its performance in aqueous solvent mixture permeation, J. Membr. Sci. 230 (2004) 183–188.

[20] A. Idris, N.M. Zain, M.Y. Noordin, Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives, Desalination 207 (2007) 324–339.

[21] Y. Mansourpanah, S.S. Madaeni, A. Rahimpour, A. Farhadian, A.H. Taheri, Formation of appropriate sites on nanofiltration membrane surface for binding TiO_2 photo-catalyst: Performance, characterization and fouling-resistant capability, J. Membr. Sci. 330 (2009) 297–306.

[22] C.A. Smolders, A.J. Reuverse, R.M. Boom, I.M. Wienk, Microstructures in phase-inversion membranes, Part 1. Formation of macrovoids, J. Membr. Sci. 73 (1992) 259–275.

[23] J.Y. Lai, F.C. Lin, C.C. Wang, D.M. Wang, Effect of nonsolvent additives on the porosity and morphology of asymmetric TPX membranes, J. Membr. Sci. 118 (1996) 49–61.

[24] A. Idris, L.K. Yet, The effect of different molecular weight PEG additives on cellulose acetate asymmetric dialysis membrane performance, J. Membr. Sci. 280 (2006) 920–927.

[25] W.Y. Chuang, T.H. Young, W.Y. Chiu, C.Y. Lin, The effect of polymeric additives on the structure and permeability of poly (vinyl alcohol) asymmetric membrane, Polymer 41 (2002) 5633–5641.

[26] B. Chakrabarty, A.K. Ghoshal, M.K. Purkait, Effect of molecular weight of PEG on membrane morphology and transport properties, J. Membr. Sci. 309 (2008) 209–221.