

Effect of Alcohol as Additives on the Morphology and Separation Performance of Polyethersulfone (PES) Hollow Fiber Ultrafiltration Membranes

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Abstract

Hollow fiber ultrafiltration (UF) membranes were prepared using Polyethersulfone (PES), alcohol (n-Propanol) as additive and N, N-dimethylacetamide (DMAc) as a solvent. Asymmetric hollow fiber UF membranes were spun by wet phase inversion method from 17 wt% solids of PES/additive/NMP solutions. The alcohol additive was n-Propanol while the external coagulant was water. Effects of n-Propanol concentrations in the dope solution on morphology and separation performance of PES hollow fiber UF membranes were investigated. UF membranes were characterized in terms of scanning electron microscope (SEM) while UF experiments were conducted using polyethylene glycol (PEG20,000M_w) and poly (vinyl pyrrolidone) (PVP 40,000M_w), as a solute. It was found that the PES UF membrane morphology changed from long two finger-like structure through a short two finger-like structure to the two void-like structure as n-propanol concentration in the dope solution increased from 5 to 20 wt % using water as a bore fluid; pure water permeation fluxes (PWP) increased from 47 to 201 L/m².h.bar while rejections of PEG MW20,000 and PVP MW40,000 for wet-spun PES hollow fiber membranes were decreased with increased of n-propanol concentration up to 20%. Using above method, PES hollow fiber UF membrane with high pure water permeation flux could be prepared while the molecular weight cut-off of PES hollow fiber membranes is approximately 20,000.

Keywords : Ultrafiltration membrane; hollow fiber; phase inversion method; polyethersulfone; alcohol additive;

الخلاصة

اعشية بولمرية مجوفة حضرت من مادة بولي ايثر سيلفون (PES) وكحول البروبانول كمضاف ومادة (DMAc) كمذيب للبولمر. تحضر الاغشية تم باستخدام طريقة تغير الطور (wet phase inversion method) من (17%) من مادة (PES) الصلبة من محاليل (PES/additive/NMP). المادة المضافة كانت البروبانول بينما الماء استخدم كمخثر خارجي للاغشية. تأثير تركيز البروبانول في محلول (PES) على البنية الداخلية والخارجية للاغشية واداءها تم التحقق منها في هذه الدراسة.

(ultra filtration) للاغشية وصفت بدلالة (SEM) بينما التجارب التي تمت باستخدام بولي اثيلين كلايكول (PEG) (20000 MW) وبولي فينيل بروليدون (PVP) (40000MW) كمذيبات. من النتائج تم ايجاد تغيير في تركيب الاغشية من طبقتين طويلتين نوع الاصبع الى طبقتين قصيرتين نوع الاصبع ومن ثم الى طبقتين نوع (Void) كلما زاد تركيز البروبانول في محلول البوليمر من (5-20%) باستخدام الماء كمخفف داخلي وان معدل جريان النافذ (PWP) زاد من (47-201) (L/m².hr.bar) باستخدام الطريقة اعلاه يمكن الحصول على معدل تدفق عالي للماء النقي ويمكن استخدام هذه الاغشية لفصل كافة المواد المذابة التي تمتلك وزن جزيئي اكثر من (20000).

1. Introduction

Conventional mass separation techniques such as distillation, crystallization, evaporation, solvent extraction and so on have been supplemented by a class of processes that utilize semi-permeable membranes as the essential element for the separation of molecular or particulate mixtures. The primary role of a membrane is to act as a separation barrier. It should permit passage of certain components and retain certain other components of a mixture. By implication, either the permeating stream or the retained phase should be enriched in one or more components. The major membrane separation processes are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), dialysis, electro dialysis (ED), and pervaporation (PV)-cover a wide range of particle/molecular sizes and applications^[1]. Ultrafiltration is a filter technology that removes suspended or dissolved solids, which have different molecular weights and sizes, respectively, from water or other liquids. This process is easy to realize and, more importantly, without extensive chemical additives and with very low energy usage. It has been reported that the properties of polymer membranes could be improved by introducing non-solvent additives in the polymer solution. Various studies illustrated that the addition of organic non-solvents in polymer solution could greatly improve the performance and structure of the asymmetric membranes. For example, several authors^[2-6] have reported that adding a second polymer (polyvinylpyrrolidone, PVP) in the solutions polyethersulfone (PES), polyetherimide (PEI) and Poly (vinyl chloride) (PVC) produced high porous

membranes, well-interconnected pores and surface properties. Besides, Kim and Lee^[7] investigated the effect of PEG additive as a pore-former on the structure formation of membranes and their permeation of thermodynamic and kinetic properties in phase inversion process. Torrestiana-Sanchez *et al.*^[8] studied the relationship among the presence of non-solvent additive, the rheological behavior of spinning solutions and properties of hollow fiber membranes. The additives tested were water, PVP and polyethylene glycol (PEG), and the base mixture was PES/NMP. The effect of combining water and PVP or PEG was also studied. Pesek and Koros^[9] successfully elevated the porosity of asymmetric polysulfone membranes by adding two different nonsolvents in the polymer solution. Lai *et al.*^[10] proved that the addition of nonsolvent in casting solution was an efficient method to elevate the porosity of TPX membranes. They concluded that the coagulation value and the solubility parameter difference are good criteria for selecting suitable nonsolvent additives. The combined effect of the addition of nonsolvent and the evaporation of casting solution can have drastic influence on the membrane morphology. Khayet *et al.*^[11] reported that with increase of non-solvent additive to the PVDF ultrafiltration hollow-fiber membranes which prepared by the dry/wet spinning technique from polyvinylidene fluoride (PVDF) dope solutions containing the solvent N, N-dimethylacetamide and the non-solvent additive 1,2-ethanediol, the liquid entry pressure of water decrease, while the porosity and mean nodule size of the membrane increase. In addition, the pure water flux

increases with increasing of non-solvent in the dope solution with decreasing of solute separation. The effects of n-propanol concentration on morphology, separation performance and mechanical properties of PES hollow fiber UF membranes were studied. PES UF membranes are characterized by the scanning electron microscope (SEM), while UF experiments are conducted using pure water, polyethylene glycol (PEG 20,000M_w) and poly (vinyl pyrrolidone) (PVP 40,000M_w).

2. Experiments

2.1 Materials

Polyethersulfone (PES) in powder form as membrane material was obtained from Jida High Performance Materials CO. LTD (P. R. China). Reagent grade N, N-dimethylacetamide (DMAc) was used as solvent and aliphatic alcohol (n-propanol) used as additive as well as PEG 20000M_w and poly (vinyl pyrrolidone) (PVP 40,000M_w) used as a solutes were obtained from Aldrich Chemical Company.

2.2 Preparation of polymer solution, hollow fiber membranes and modules

Propanol was mixed separately with DMAc in glass bottle for 15 min. Dried polyethersulfone (PES) added into the mixture in the bottle and mixed until the solution became homogeneous. Hollow fiber PES membranes were spun at 25 °C employing the wet-spinning method, Figure (1). Table 1 and Table 2 summarize composition, the spinning conditions and outer diameter/inner diameter dimensions of the prepared hollow fiber membranes. All nascent fibers were not drawn (no extension), which means that the take-up velocity of the hollow fiber membrane was nearly the same as the falling velocity in the external coagulation bath. The coagulation bath and bore fluid were

maintained at 25 °C. The prepared hollow fibers were stored in the water bath for 24 h to remove the residual DMAc. After this period, the fibers were kept for a post-treated in a 30wt% glycerol aqueous solution for 48h to prevent the collapse of porous structures and dried in air at room temperature for making test modules.

To test quantitatively the hollow fiber separation performance in terms of permeation flux and rejection, permeation modules were prepared. Each module consisted of five fibers with a length of 20 cm. The shell sides of the two ends of the bundles were glued into two stainless steel stees

These modules were left overnight for curing before tested. To eliminate the effect of the residual glycerol on module performance, each module was immersed in water for 1 day, and run in the test system for one and half hour before any sample collection.

2.5 Measurements of permeation flux and rejection

Figure (2) shows a schematic diagram of water separation membrane unit. At a transmembrane pressure 1 bar and room temperature, all experiments were performed in hollow fiber modules. Three modules were prepared for each hollow fiber sample. Table 3 shows the experimental data of hollow fiber membrane modules. Pure water permeation fluxes (PWP, J_w) of membranes was obtained as follows:

$$J_i = \frac{Q_i}{\Delta P \times A} \quad \dots \quad (1)$$

where J_i = permeation flux of membrane (L/m² h bar),

Q_i = volumetric flow rate (L/h),

ΔP = transmembrane pressure drop (bar), A = membrane surface area (m²).

0.05% of PEG and PVP were used for the measurement of solute rejection of each hollow fiber module, respectively. To realize the separation

efficiency for different molecular weights, two kinds polymers PEG ($M_w=20000$), and PVP ($M_w=40000$) were applied. The membrane rejection $R(\%)$ is defined as:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

Where C_f and C_p represent the solute concentration in feed and separated solution, respectively. The concentration of PEG and PVP is measured by a UV-spectrophotometer (Shimadzu-UV 360, Japan) at wavelength of 280 nm.

2.6 Membrane morphology of PES hollow fiber membranes

Inner and outer diameters of hollow fibers were estimated by means of an optical microscope. Membrane morphology was examined by using a scanning electron microscope (SEM) (JEOL Model JSM-6360 LV, Japan). The surface and cross-section of hollow fibers for the SEM were prepared after breaking the membranes in liquid nitrogen to avoid destroying the structure of the cross sections of hollow fibers.

3. Results and discussion

3.1 Effect of n-propanol concentrations on PES hollow fiber membrane morphology

The addition of organic additives in the polymer solution has been shown to play an important method in the development of membrane structure with improved separation performance. Here, hollow fiber UF membranes are wet-spun from a dope solution, which contains PES and n-propanol as additive.

Figure (3) shows the structures of cross-sectional scanning electron microscope (SEM) pictures of hollow fiber PES membranes fabricated from different n-propanol concentrations of the PES dope solution (0, 5, 10, 15 and 20wt%), using H_2O as bore fluid. In Figure (3), Fiber no.1 without

additives has a long and wide finger-like structure extend from inner surface to outer surface while Fiber no.2 with 5wt% n-propanol concentration shows that the finger-like structure became double layers. Membrane structure of Fiber no.4 with 15wt% n-propanol concentration seems to change from long double finger-like structure to two short finger-like structures with two skin layers as shown in Fig.3. The cross-sectional structure of PES hollow fiber membranes (Fiber no.5) with 20wt% n-propanol concentration had a void-like structure with double layers as shown in Figure (3). Therefore, membrane morphology change from long two layers finger-like structure

through short two layers finger-like structure to the double layers void-like structure as n-propanol concentration in the dope solution increases. Several authors ^[12-13] reported that appropriate amount of non-solvent additives enhanced the formation of macrovoids while too much non-solvent suppressed their formation because the delayed demixing in the growth stage is inhibited. This means that the membrane morphology is strongly affected by the amount of non-solvent additives. As reported by Kesting ^[14], large finger-like macrovoids is generally formed when the coagulation process is fast, whereas the slow coagulation rate results in a porous sponge-like structure. This indicates that increasing the concentration of n-propanol in PES dope solution reduces gradually the coagulation process.

As shown in Figure (4) and Figure (5), the internal and external surfaces for all the membranes were dense and smooth with very small pores in internal surfaces. This is due to water used as bore fluid and external coagulant, and the dense skin layer is formed due to instantaneous liquid-

liquid demixing process.

3.2 Effect of propanol concentrations on separation performance of PES hollow fiber membranes

UF experimental data are summarized in Table 3. Using pure H₂O as bore fluid, the pure water permeation fluxes (PWP) of wet-spun PES hollow fibers (no.1- no. 5) increases from 47 to 201 L/m².h.bar with an increase of n-propanol concentration in the dope solution as shown in Table 3 and Figure (6). Rejections of PEG (20,000 M_w), and PVP(40,000 M_w) for wet-spun PES hollow fibers (no.2- no.5) decrease with an increase of n-propanol concentration as shown in Table 3 and Figure (7). This was supported by the respective morphologies because the hollow fiber membranes wet-spun from the dope solution containing 0-20wt% n-propanol concentration have a dense external and internal surfaces. Figure (4) and Figure (5) confirm these results.

Otherwise, using 20wt% n-propanol as additive, PES hollow fiber membrane (no.5) has higher pure water permeation flux (201 L/m².h.bar) and lower rejection than the other membranes in Table 3. Besides, using water as a bore fluid Fiber no.2-no.5 had a good separation performance as compared with membrane Fiber no.1, which is prepared without additives and NMP/H₂O 90:10 as a bore fluid. This means that the alcohol additives have a great effect on the separation performance compare with hollow fiber membrane prepared without additives.

3.3 Effect propanol concentrations on the mechanical properties of PES hollow fiber membranes

The mechanical properties are very important for the membrane performance in the industrial applications of membranes. Therefore, data of tensile strength and elongation of hollow fiber membranes were

determined. Table 4 shows the mechanical properties of PES hollow fiber membranes with different n-propanol concentration in dope solution. Within experimental error, the tensile strength at break, elongation at break and Young's modulus of PES/PEG hollow fiber membrane seem to be dependent on n-propanol concentration (membranes no.2-no.5). It can be seen that with increase of n-propanol concentration in the dope solution the mechanical properties decrease as shown in Table 4. This phenomenon is attributed to the fact that a smaller n-propanol concentration tends to form the denser external and internal skin in Figures 3, 4 and 5. In addition to using pure water as the bore fluid and external coagulation agent, higher mechanical properties were obtained, which is attributed to the fact that pure water is a powerful coagulation agent, which tends to form dense internal and external layers.

4. Conclusions

Polyethersulfone (PES) hollow fiber UF membranes were spun by wet phase inversion process. The polymer solutions were prepared from 17 wt% of PES in DMAc (solvent) using different concentrations of n-propanol (0, 5, 10, 15, and 20) as additive. Pure water was used as the bore fluid as well as external coagulant. The investigation was conducted to evaluate effects of addition aliphatic alcohols (n-propanol) as additive to the dope solution, different n-propanol concentrations on membrane morphology, separation performance and mechanical properties of PES hollow fiber membranes. SEM pictures illustrated that PES membrane morphology changed from long two finger-like structures through a short two finger-like structures to the two void-like structures with as n-propanol concentration in the dope solution increased from 0 to 20wt% with H₂O as a bore fluid. Depend on the preparation method in this

method, PES hollow fiber UF membrane with high pure water permeation flux might be prepared while the molecular weight cut-off of PES hollow fiber membranes was approximately 20,000.

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Table 1: Process Parameters Of Spinning Hollow Fiber UF Membranes

| Dope no. | Dope solution composition | Bore fluid composition | Air-Gap Distance (cm) | External Coagulant |
|----------|----------------------------|----------------------------|-----------------------|--------------------|
| 1 | PES/NMP 18:82 | NMP/H ₂ O 90:10 | 0 | Water |
| 2 | PES/DMAc/Propanol 17:78:5 | H ₂ O | 0 | water |
| 3 | PES/DMAc/Propanol 17:73:10 | H ₂ O | 0 | water |
| 4 | PES/DMAc/Propanol 17:68:15 | H ₂ O | 0 | Water |
| 5 | PES/DMAc/Propanol 17:63:20 | H ₂ O | 0 | Water |

Table 2: Bore Fluids And Dimensions Of PES Hollow Fiber Membranes

| Dope No. | Bore fluid | Fiber No. | OD (μm) | ID (μm) | Thickness (μm) |
|----------|------------------|-----------|---------|---------|----------------|
| 1 | H ₂ O | 1 W | 1000 | 670 | 165 |
| 2 | H ₂ O | 2 W | 1010 | 740 | 135 |
| 3 | H ₂ O | 3 W | 1014 | 770 | 122 |
| 4 | H ₂ O | 4 W | 935 | 720 | 107.5 |
| 5 | H ₂ O | 5 W | 920 | 730 | 95 |

Table 3: Permeation Fluxes And Solutes Rejection For PES Hollow Fiber Membranes

| Fiber No. | J_w^a (L/m ² h bar) | Rejection (%) | |
|-----------|----------------------------------|---------------|-----------|
| | | PEG20,000 | PVP40,000 |
| 1 | 47.0 | 92.1 | 94.0 |
| 2 | 69 | 91 | 95 |
| 3 | 93 | 82 | 92 |
| 4 | 167 | 71 | 79 |
| 5 | 201 | 64 | 71 |

Table 4: Mechanical Properties Of PES Hollow Fiber Membranes

| Membrane no. | Break Strength (Mpa) | Elongation at Break (%) | Young's Modulus (Mpa) |
|--------------|----------------------|-------------------------|-----------------------|
| 1 | 10.3 | 73.0 | 184.3 |
| 2 | 7.3 | 70.0 | 157.6 |
| 3 | 5.4 | 59.6 | 151.0 |
| 4 | 3.0 | 51.0 | 140.7 |
| 5 | 2.7 | 46.4 | 138.6 |

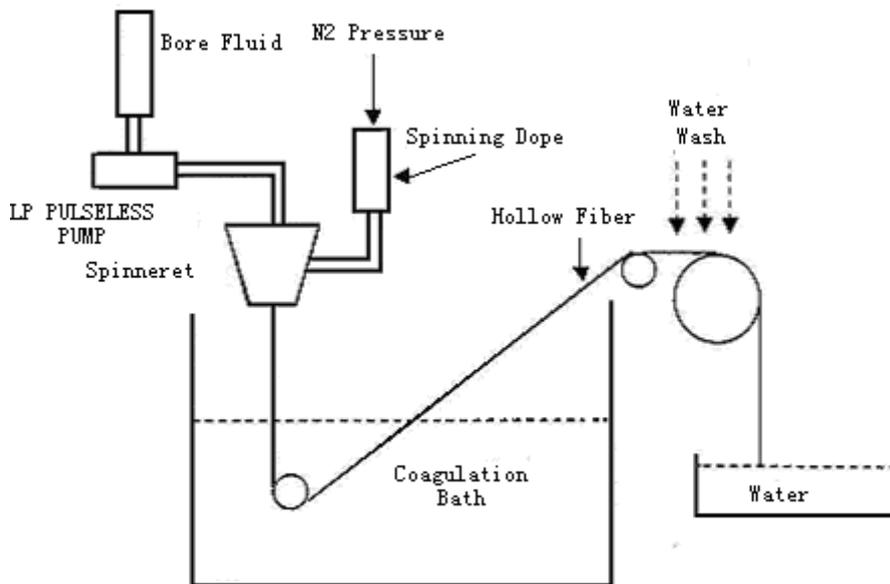


Figure 1: Schematic Diagram Of The Hollow Fiber Spinning Apparatus

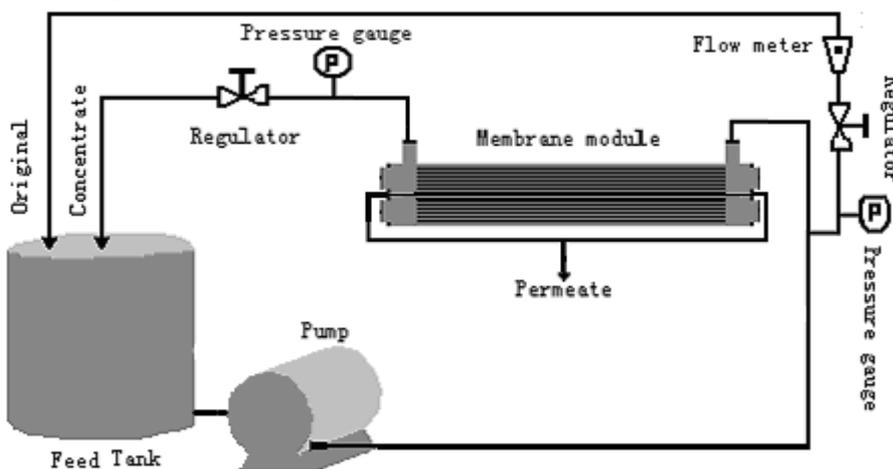


Figure 2: Schematic Diagram Of The Experimental System Used For UF Experiments

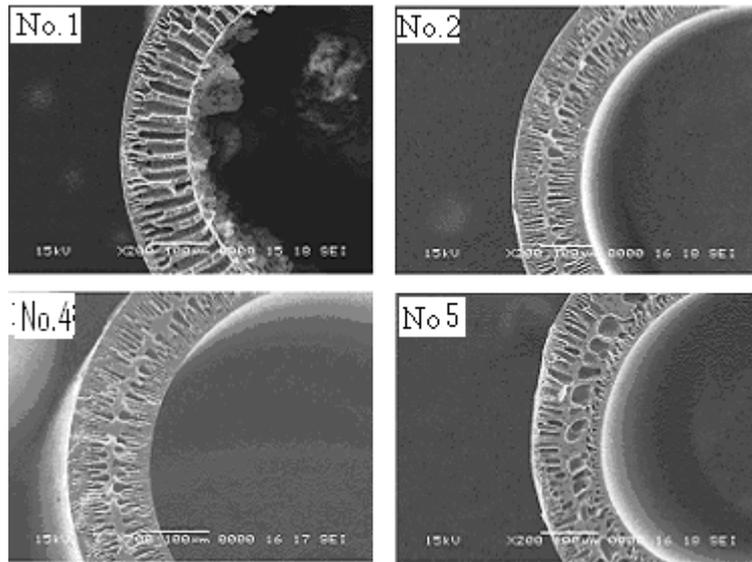


Figure 3: SEM Cross-Sectional Structures Of PES Hollow Fibers Wet Spun From Nos. 1, 2, 4, And 5 Dope Solutions Using Bore Fluid As H₂O;(Original Magnification: 200×)

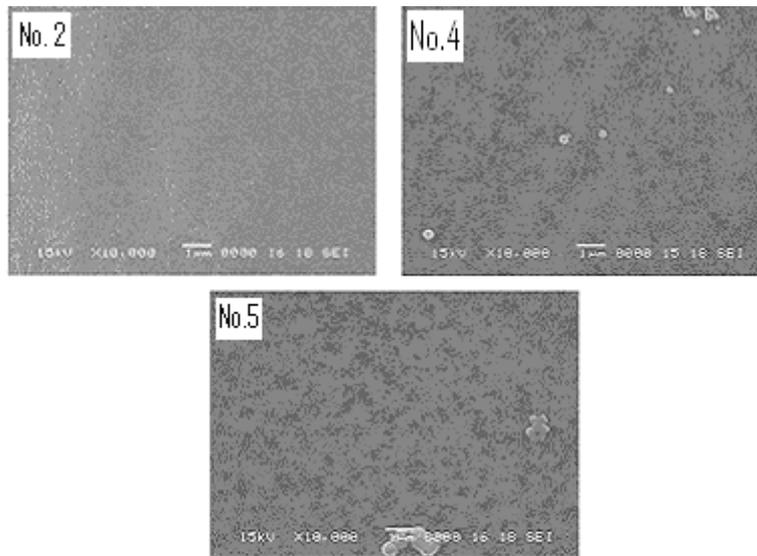


Figure 4: Scanning Electron Micrographs Of The Internal Surface Of PES Hollow Fiber Membranes Spun From Nos. 2, 4, And 5 Dope Solutions Using Bore Fluid As H₂O; (Original Magnification: 500×)

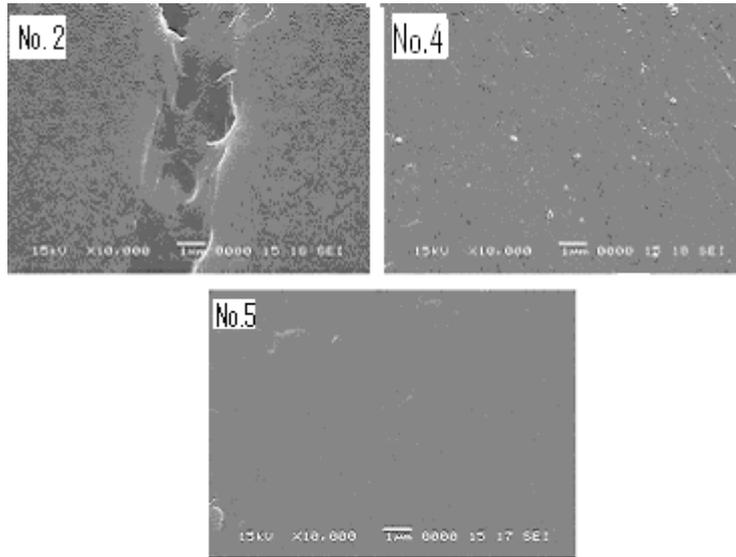


Figure 5: Scanning Electron Micrographs Of The External Surface Of PES Hollow Fiber Membranes Spun From Nos. 2, 4, And 5 Dope Solutions Using Bore Fluid As H₂O; (Original Magnification: 10000×)

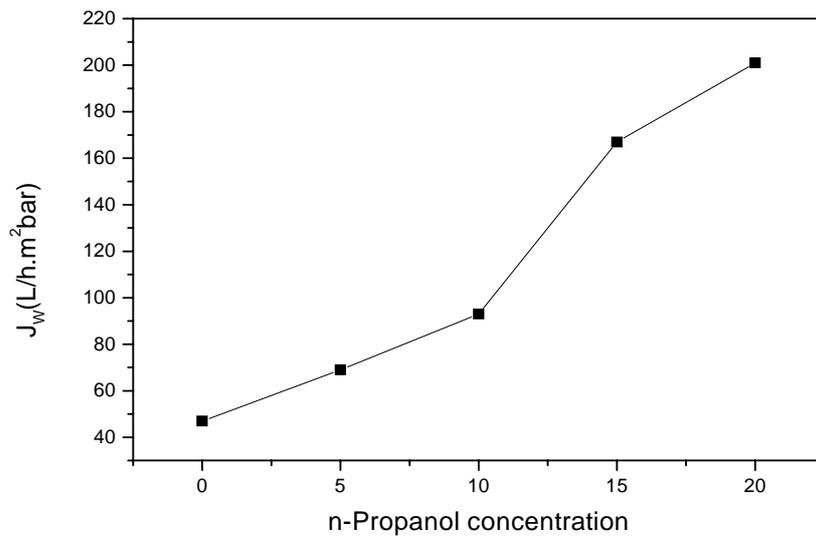


Figure 6: Effects Of N-Propanol Concentration On Pure Water Permeation Flux Of PES Hollow Fiber Membranes (No.1-No.5)

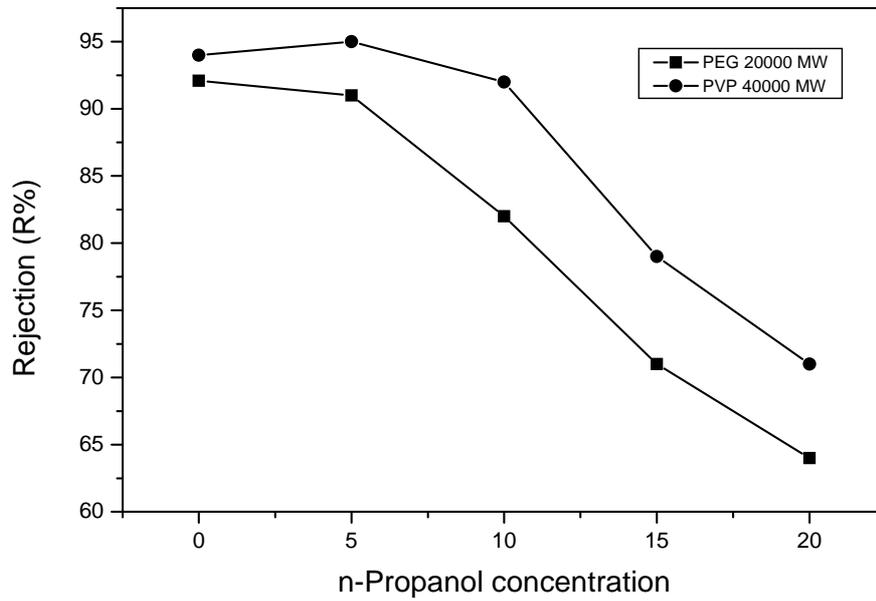


Figure 7: Effects Of N-Propanol Concentration On Rejection Of PEG 20,000, And PVP 40,000 (Membranes No.1-No.5)