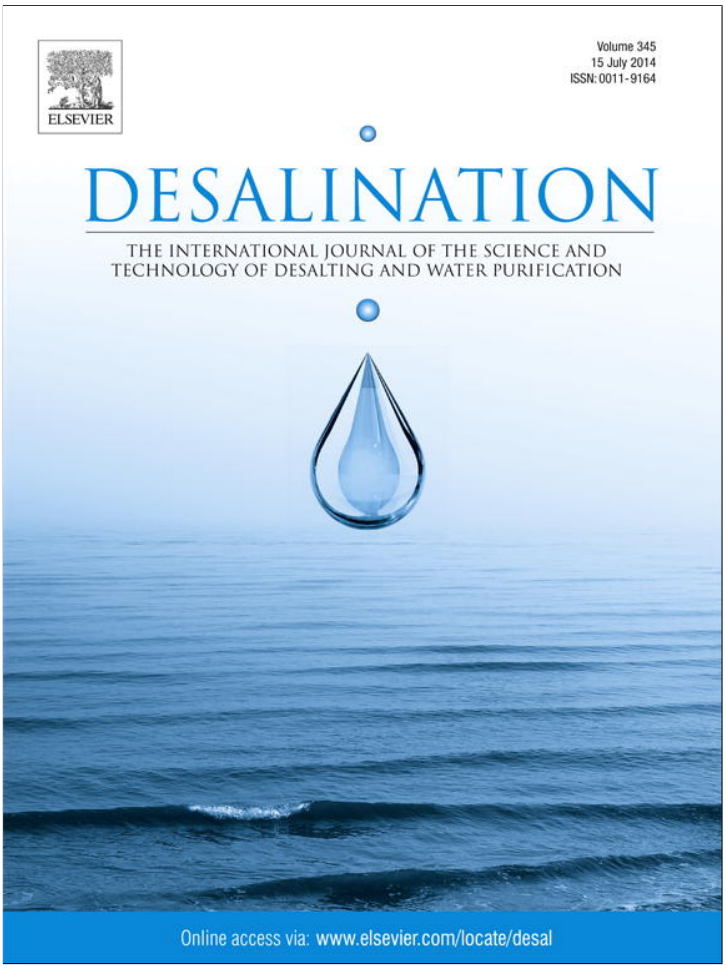

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Poly(ether sulfone) (PES) hollow-fiber membranes prepared from various spinning parameters

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HIGHLIGHTS

- Fabricate PES hollow-fiber by a steam/dry/wet phase inversion method
- Analysis effects of various spinning conditions on PES properties
- The PWP increases about 300%, keeping BSA rejection above 99% with PEG concentration
- The mechanical properties were depending on the PEG, bore fluid type and flow rates.

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ABSTRACT

A steam/dry/wet phase inversion method was used to fabricate hollow-fiber membranes for ultrafiltration (UF) applications from polyethersulfone (PES) as a polymer material, gamma butyrolactone (GBL) as a solvent and polyethylene glycols (PEGs) as a pore-former additive. Pure water, 30 wt.% ethanol and 30 wt.% isopropanol were used as bore fluids. The effect of PEG concentration, type of bore fluid, and bore fluid flow rate (BFR) on the structure, permeability, separation performance and mechanical properties of PES hollow fiber was studied. The PES hollow-fiber membranes were characterized by scanning electron microscopy (SEM), capillary flow porometer and porosity measurement. From the results it was found that all PES hollow fibers have a sponge-like structure in the cross-sectional area. Using 30% ethanol as a bore fluid produced fiber with pore density higher than that produced using water or 30% isopropanol. With an increase of the bore fluid rate from 7.67 to 23.06 g/min, the pore density and the PWP increased from 14,698.6 to 29,440.2 (pores/mm^2 × 10^2) and from 45.2 to 107.4 l/m^2·h·bar respectively, with a minor change in protein rejection. The mechanical properties in terms of Young's modulus, tensile strength and elongation at break were dependent on PEG concentration, and bore fluid type and concentration.

1. Introduction

It is well known that the morphology, separation performance and mechanical properties of the polymeric membranes fabricated by phase inversion technique depend upon various factors such as polymer type and composition, type and concentration of the additives, design of the spinneret, type, composition and temperature of the internal and external coagulants, bore liquid flow rate, gas gap type and length, dope flow rate (dope extrusion pressure), fiber take-up velocity, humidity and so on. The most important factor among them is the type of the additives. Many researchers have focused their studies on the effect of water-soluble polymers as additives, using different polymer solvents and composition, on the properties and performance of the membranes [1–10].

Kim and Lee [1] investigated the effect of PEG additive as a pore-former on the structure formation of polysulfone (PSF) membranes and their permeation properties. The membranes were prepared by using *N*-methyl-2-pyrrolidone (NMP) as a solvent. Poly(ethersulfone) (PES) hollow-fiber membranes were prepared by using NMP as a solvent and water, poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG) as a non-solvent additives [2]. Wang et al. [3] prepared poly(vinylidene fluoride) (PVDF) hollow-fiber membranes by wet and dry/wet phase inversion methods. Dimethylacetamide (DMAc) and poly(vinyl pyrrolidone) (PVP) were used as a solvent

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and an additive respectively. The effects on the permeation properties and membrane structures of polymer composition, air-gap distance, PVP molecular weight, PVP composition in the dope solution, and the internal coagulant were examined. It was concluded that highly permeable PVDF hollow fiber could be prepared from a polymer dope containing PVP with low molecular weight.

Liu et al. [4] prepared (PES) hollow-fiber membranes using NMP as a solvent, and PEG 400 and water as non-solvents, respectively. It was observed that membranes prepared from a solution with an NMP/PEG ratio of 1:1 resulted in higher fluxes than when a ratio of 1:4 was used. Using a different bore liquid composition with the components NMP, PEG 400 and water was shown to be a powerful method of controlling the pore size of the inner surface. Xu and Alsalhy investigated the effects of PEG molecular weights and PEG Mw600 concentrations, as well as the combination of PVP and PEG Mw600 in the dope solution, on the separation properties, morphology, and mechanical properties of PES hollow-fiber membranes [5].

Yoo et al. [6] obtained a macrovoid-free, porous membrane with a sponge-like structure of a polyimide (PI)/(GBL)/water system, whereas a membrane with a finger-like structure was obtained from a PI/NMP/water system. The effect of the molecular weight of PVP additive in two systems on membrane morphology was investigated through the differences in phase separation rates and compatibility. Chakrabarty et al. [7] prepared flat-sheet asymmetric polymeric membranes from a solution of PSF by the phase inversion method. PEG of three different molecular weights such as 400, 6000 and 20,000 Da respectively, was used as the polymeric additive in the casting solution. It was found that the pore number as well as pore area increase with an increase in PEG molecular weight. Membranes with PEG of higher molecular weights have higher pure water permeation flux (PWP) and higher hydraulic permeability.

Saljoughi et al. [8] investigated the effects of cellulose acetate (CA) and PEG composition in the casting solution and coagulation bath temperature (CBT) on the morphology of the prepared membranes. It was found that increasing the PEG composition in the casting solution and CBT accelerates the exchange rate of solvent (NMP) and non-solvent (water) and then expedite formation of macrovoids in the membrane structure. Pure water flux through the prepared membranes is strongly dependent on the size and density of macrovoids in the membrane structure.

Simone et al. [9] prepared microporous hydrophobic poly(vinylidene fluoride) (PVDF) hollow fibers by the dry/wet spinning method. Water and (PVP) were used as pore-forming additives. Mixtures of DMF or ethanol in water were used as bore fluids. The study focused on the PVP concentration and the composition of the bore fluid. The prepared fibers exhibited good structure, good mechanical properties, high porosity and an average pore size ranging from 0.12 to 0.27 μm. Culfaz et al. [10] fabricated hollow-fiber membranes with microstructured inner surfaces from a PES/PVP blend using a spinneret with a microstructured needle. The effect of spinning parameters such as polymer dope flow rate, bore liquid flow rate, air gap and take-up speed on the microstructure and shape of the pore and its deformation was investigated.

The literature surveyed above includes rare work using gamma-butyrolactone (GBL) as a polymer solvent in preparation of the membrane. In this work, polyethersulfone (PES) hollow-fiber membranes were prepared by steam/dry/wet spinning process using gamma-butyrolactone (GBL) as a solvent for the first time with PES. GBL has several advantages for using in membrane preparation such as water soluble, non-volatile solvent, good dissolving properties of polymer and lower toxicity than other solvents such as NMP, DMAC, DMF, and DMSO [11]. Khayet et al. [12] prepared PES hollow fibers using different gas gaps, namely, air, oxygen, nitrogen, carbon dioxide and argon. In this effort, a steam gap was used as a gas gap during the spinning process in order to achieve the goal of preparing a hollow fiber with a sponge-like structure regardless of the effect of any other variables such as bore fluid type, flow rate and additive concentration. Moreover, the effects of poly(ethylene glycol) (PEG) concentration, type of bore fluid, and bore fluid flow rate (BFR) on membrane morphology, permeability, separation performance, pore size, pore size distribution, porosity and mechanical properties were investigated. The prepared hollow fibers were characterized using scanning electron microscopy (SEM), whereas the pore size and pore size distribution of the PES hollow fibers were measured using a PMI capillary flow porometer. Ultrafiltration experiments were conducted using bovine serum albumin (BSA) as a solute. Moreover, *in this work it is desirable to confirm our goal, to establish that the bore fluid type, composition and flow rate do not affect the structural morphology of the membrane, and that the polymer concentration and type of additives in the dope solution are the only factors controlling the structural morphology of the membranes when the viscosity of the polymer solution is higher than 1250 cp in the presence of steam gap distance.* Therefore, this study focused on the effects of the chemistry of polymer solution, coagulation bath, and bore fluid flow rate on membrane properties.

2. Experimental work

2.1. Materials

Poly(ethersulfone) (PES) in powder form of Mw = 30,000 Da and density of 1.37 g/cm^3 (Sigma Aldrich Company, Germany) was selected as a membrane material because of its commercial availability, processing ease, favorable selectivity permeability characteristics and good mechanical and thermal properties. Gamma butyrolactone (GBL) (Sigma Aldrich Co., Germany) was used as a solvent in the preparation of the dope solution. Distilled water, ethanol with purity of 99.8% (Georgia Gulf Co., USA) and isopropanol with purity of 99.99% (Georgia Gulf Co., USA) were used as internal coagulants (bore fluid). Polyethylene glycols (PEGs) of Mw = 12,000 Da, supplied by Sigma Aldrich Co., Germany, were used as an additive. Bovine serum albumin (BSA, Mw = 68,000 Da), supplied by AFCO, India, was used as a solute.

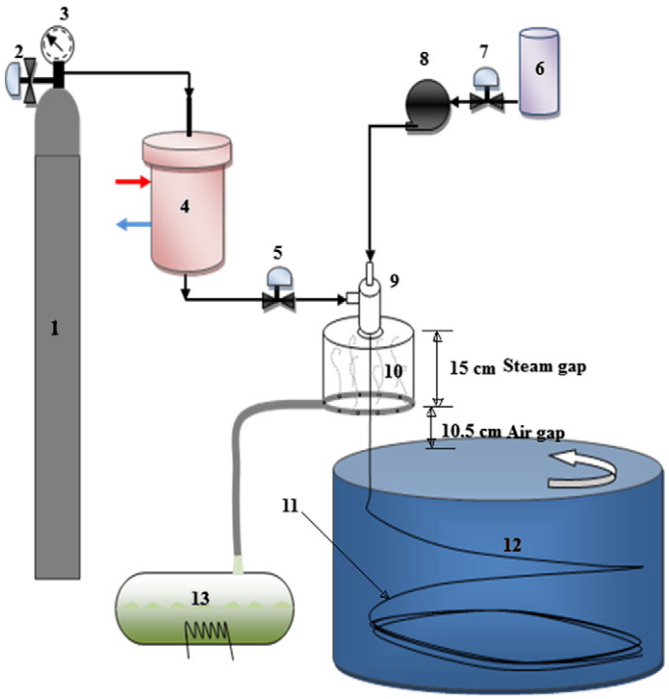

Fig. 1. Hollow fiber membrane spinning setup unit. 1 — nitrogen gas cylinder. 2 — a regulating pressure valve. 3 — pressure gauge (in the range of 10 bar). 4 — jacketed vessel of the dope solution (750 ml). 5 — dope solution valve. 6 — bore fluid container. 7 — bore fluid valve. 8 — bore fluid pump. 9 — spinneret. 10 — steam channel. 11 — hollow fiber membrane. 12 — external coagulation bath. 13 — electric evaporator.

2.2. Preparation of PES hollow-fiber membranes

Poly(ether sulfone) (PES) powder and poly(ethylene glycol) (PEG) were dried separately in an oven for about 5 h at 70 °C to remove their moisture content. PEG 12,000 Da was mixed with the gamma butyrolactone (GBL) in glass flask using a magnetic stirrer at 55 °C. Then, PES was added to the PEG/GBL solution and mixed until a homogeneous dope solution was obtained. Hollow-fiber PES membranes were spun by using the steam/dry/wet spinning method in the experimental rig shown in Fig. 1. The composition and spinning parameters of the PES hollow-fiber membranes are summarized in Table 1. The PES dope solution was loaded into a stainless-steel jacketed reservoir at a temperature of 55 °C. Then the dope solution was pressurized with pure nitrogen (N_2) at a flow rate of 11 g/min to the tube-in-orifice spinneret, which had an inner diameter (ID) of 600 μm and an outer diameter (OD) of 1600 μm. The bore fluid was simultaneously pumped to the inner tube of the spinneret at different flow rates using a peristaltic pump. The steam gap distance was 15 cm, whereas the air gap distance was 10.5 cm. All hollow fibers were spun at a temperature of 22 °C inside a steam channel, allowing circulation of the steam. All nascent fibers were not drawn (free falling velocity), which means that the take-up velocity of the hollow-fiber membrane was nearly the same as the falling velocity in the coagulation bath. All experiments were conducted at laboratory temperature (~22 °C), while the coagulation bath was maintained at ~20 °C and the bore fluid at 50 °C. The fabricated PES hollow-fiber membranes were rinsed in water for 24 h to remove the residual solvent GBL. Then, the hollow-fiber membranes were kept in an aqueous solution of 40% glycerol (by volume) for 8 h, to prevent the collapse of porous structures. Finally the fibers were dried in air at room temperature to perform the module test.

2.3. Scanning electron microscopy (SEM) observations

SEM is a powerful technique for analyzing the structure of the prepared membranes. The membranes morphology was observed using a scanning electron microscope (Quanta FENG 200, FEI Company) at the Institute of Membrane Technology, University of Calabria, Italy. To study the cross-sections of the fibers, samples were prepared by freeze fracturing in liquid nitrogen, to produce a clean, brittle fracture. To study the inner and outer surfaces, the fibers were carefully cut in half in the direction of length and fixed on a sample holder. After drying under vacuum, the samples were coated with a thin gold layer using a sputter apparatus.

2.4. Preparation of PES hollow-fiber membrane modules

To test quantitatively the hollow-fiber separation performance in terms of permeation flux and solute rejection, PES modules were prepared. Each module consisted of five fibers with an effective length of 22 cm, which were put inside a glass tube, which was epoxy glued at both ends, and then left overnight to cure.

Table 1
Composition and spinning parameters of the PES hollow fiber membranes.

Fiber no.	Polymer solution (20 wt.% PES)			Bore fluid (wt.%)		Bore rate (g/min)
	PEG	Solvent	H_2O	ETOH	ISOP	
I	5	75	100			12.84
II	10	70	100			12.84
III	15	65	100			12.84
IV	10	70		30		12.84
V	10	70			30	12.84
VI	15	65	100			7.67
VII	15	65	100			23.06

2.5. Measurements of membrane dimensions

The inner and outer diameters of the prepared PES hollow fibers were measured using a digital micrometer with a precision of ±0.0001 mm. Five fibers were used for each membrane.

2.6. Porosity measurements

Membrane porosity can be defined as the volume of the pores divided by the total volume of the membrane. In order to evaluate the porosity of the membrane, hollow fibers not previously treated with the glycerol solution were dried for 4–5 h at 50 °C and weighed with a precision balance, then impregnated with kerosene for about 24 h and weighed again after wiping away superficial kerosene with filter paper [13]. It is worth to mention here that the use of kerosene instead of water in porosity measurement is due to the lower surface tension which making it more pervasive within the pores of the membrane. The porosity of the fiber membrane (ε) was calculated using the following formula [14].

$$\varepsilon\% = \left\{ \frac{\frac{(w_1 - w_2)}{D_k}}{\frac{(w_1 - w_2)}{D_k} + \frac{(w_2)}{D_p}} \right\} \times 100 \quad (1)$$

where

w_1 is the weight of the wet membrane.
w_2 is the weight of the dry membrane.
D_k is the kerosene density (0.82 g/cm^3).
D_p is the polymer density (1.37 g/cm^3).

2.7. Pore size and pore size distribution

The mean pore size, density and distribution in hollow-fiber membranes were determined using a capillary flow porometer (Porous Materials Inc., CFP 1500, A6XL, USA). Fibers not treated with glycerol were immersed in a pore wick (surface tension 16 dyn/cm) overnight to ensure complete wetting before using. The fibers were analyzed with wet-up/dry-up method.

2.8. Mechanical properties

The tensile strength of the prepared fibers was measured by means of a Zwick/Roell Z 2.5 test unit. Each sample was stretched unidirectionally at a constant rate of 5 mm/min, the initial distance between the clamps being 50 mm. Five specimens were tested for each sample. Tensile strength, elongation at break and Young's modulus were determined.

2.9. Ultrafiltration (UF) experiments

Pure water flux experiments were performed using deionized water. Each module was immersed in deionized water for 24 h, and run in the test system for 1 1/2 h, to eliminate the effect of the residual glycerol on the hollow-fiber membranes before any sample collection.

A UF experimental unit designed to evaluate the PWP and protein rejection is shown in detail elsewhere [15]. At a transmembrane pressure of 1 bar and feed solution temperature of 20 °C, all

experiments were performed in hollow-fiber modules with cross-flow mode. Two modules were prepared for each hollow-fiber sample. Pure water permeation fluxes (PWP) were obtained as follows:

$$J_w = \frac{Q_w}{\Delta P\, A_s} \tag{2}$$

where

J_w is the permeation flux of membrane ($l/m^2 \cdot h \cdot bar$).
Q_w is the volumetric flow rate of the permeate (l/h).
ΔP is the transmembrane pressure drop (bar)
A_s is the membrane surface area (m^2).

$$A_s = n\,\pi\, D\, L \tag{3}$$

where

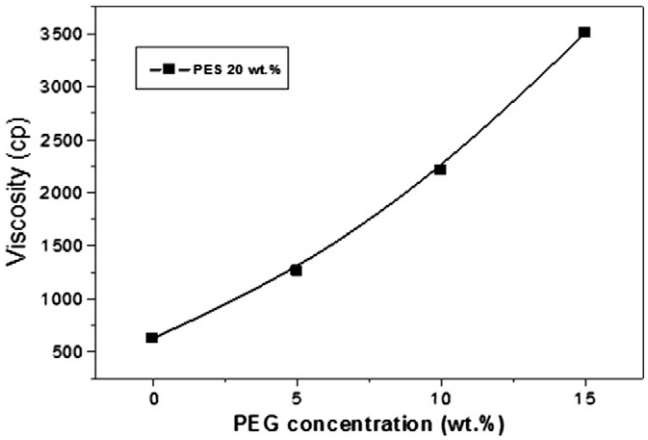

Fig. 3. Effect of PEG concentrations on the viscosity of the PES dope solution.

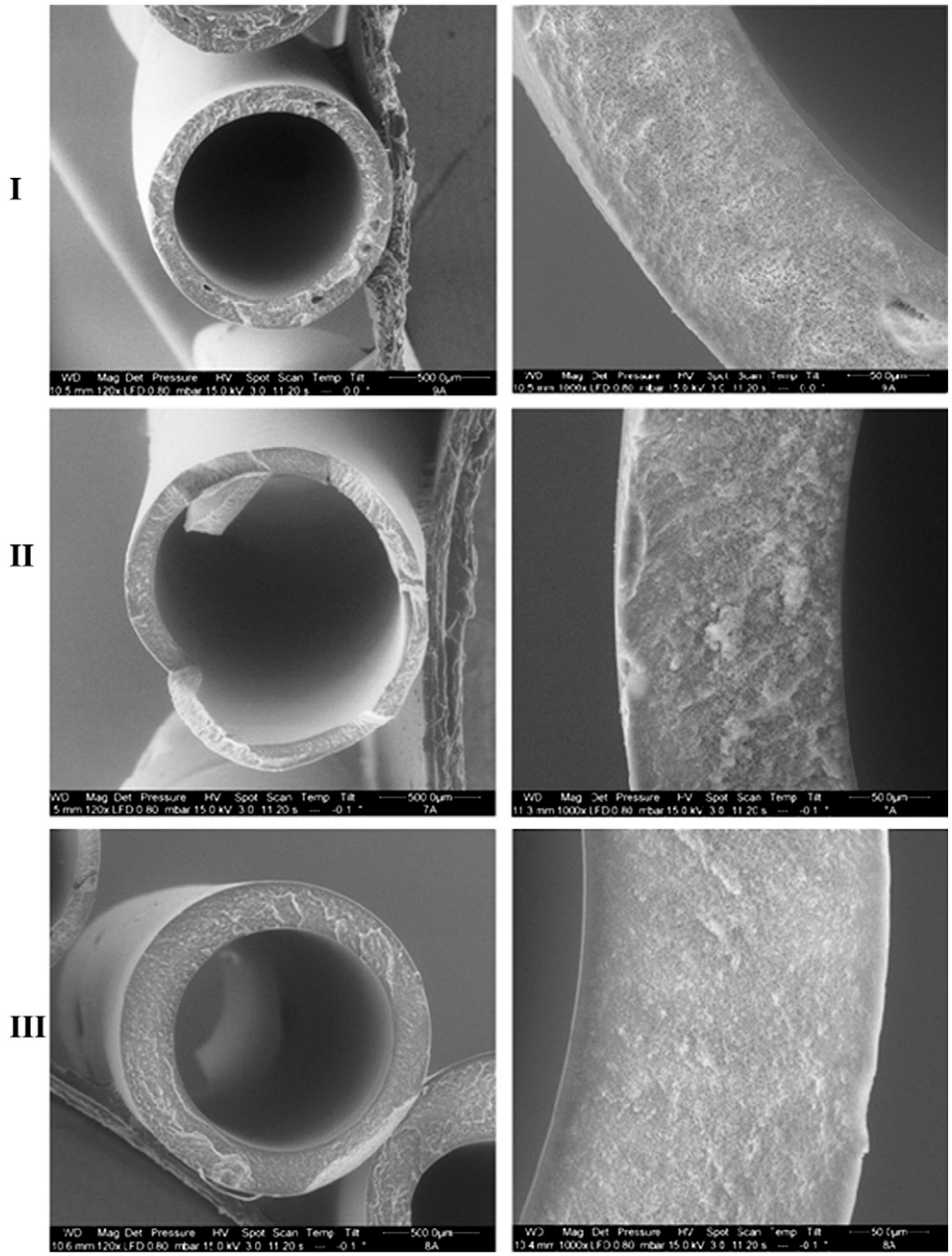

Fig. 2. SEM images of cross-section of the PES hollow fibers: (magnification 120 and 1000×); I) 5 wt.% PEG; II) 10 wt.% PEG; III) 15 wt.% PEG.

n is the number of fiber in the module.
D is the outside diameter of the fiber (m).
L is the effective fiber length (m).

To measure the solute rejection, a BSA solution with 500 ppm was prepared and used for each hollow-fiber module. The filtration experiments were carried out at the applied transmembrane pressure of 1 bar. The membrane rejection R (%) was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (4)$$

where C_f and C_p are the solute concentration in feed and permeate solution respectively. The concentration of BSA was determined based on absorbency in a UV-spectrophotometer (Shimadzu-UV160 A, Japan) at a wavelength of 280 nm.

3. Results and discussion

3.1. Effect of PEG concentration

3.1.1. Effect of PEG concentration on morphological structure

Three dope solutions containing 20 wt.% PES were prepared with different concentrations of PEG as additive (i.e. 5, 10 and 15 wt.%). The bore fluid was pure water with a flow rate of 12.84 g/min.

Fig. 2 shows how the SEM images of the cross-section of the PES hollow-fiber membrane were prepared by using different PEG concentrations (i.e. 5, 10 and 15 wt.%) as a pore-former additive. It will be noticed that the PES hollow-fiber membranes prepared from different PEG

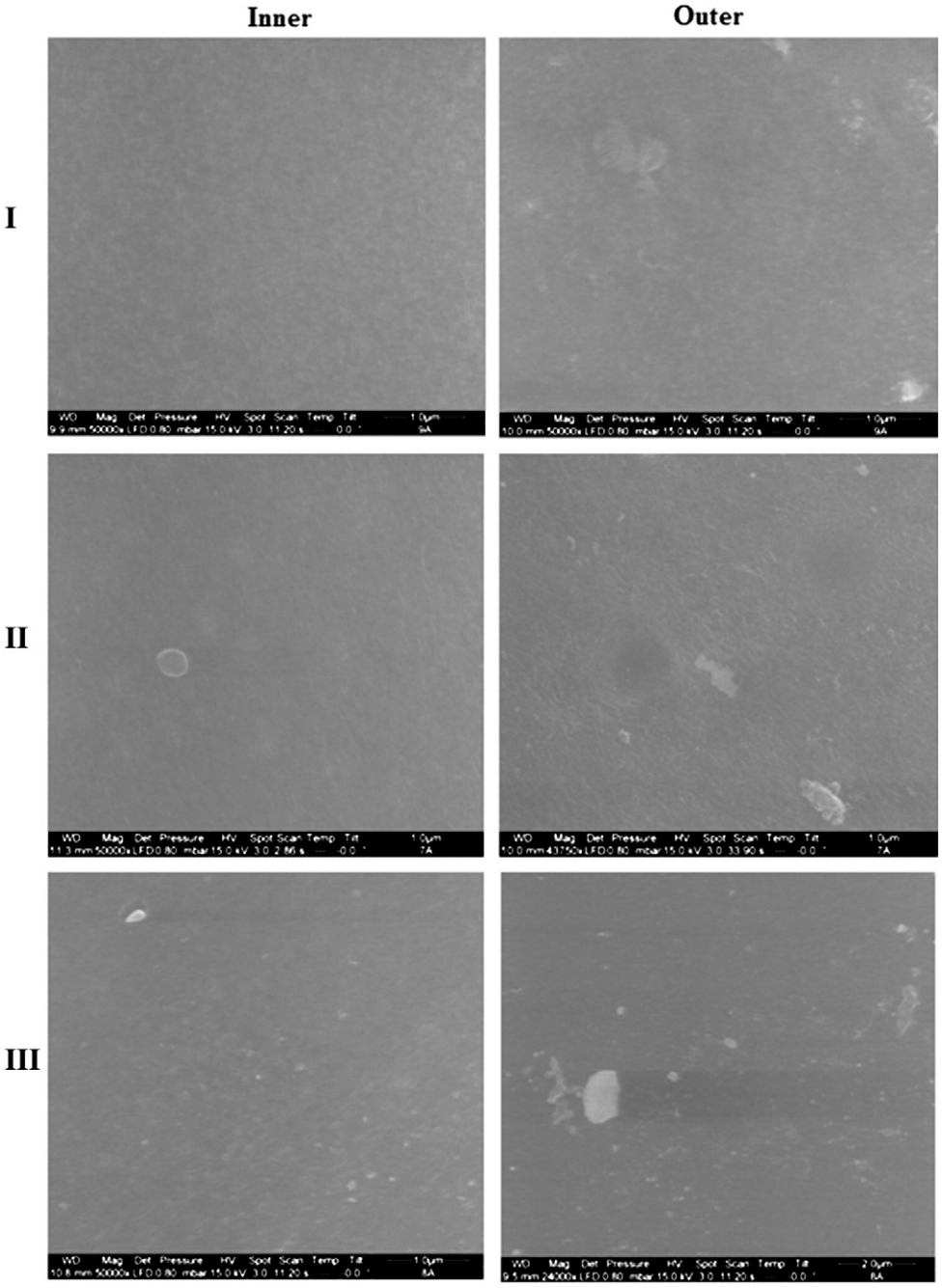

Fig. 4. Inner and outer surface of PES hollow fibers (magnification 50,000×), I) 5% PEG; II) 10% PEG; III) 15% PEG.

concentrations have a sponge-like structure with two dense skin layers, and that some macro-voids have appeared in the middle of the cross-section of the hollow-fiber membrane prepared from 5 wt.% PEG as additive (see Fig. 2: fiber no. I). An increase of PEG concentration in the dope solution has the result of repressing the macro-voids, as shown in Fig. 2: II and III. This is due to the increase in dope solution viscosity, as shown in Fig. 3. The presence of PEG in the PES dope solution results in an increase in the viscosity of the polymer solution, and this leads to a reduction in the exchange rate between the solvent and non-solvent in the polymer solution, possibly delaying the liquid–liquid demixing process and forming a sponge-like structure [16]. The addition of a low concentration of PEG in the polymer solution may result in a fast formation of nuclei (i.e. PEG-rich phase) and high solvent composition, thus enhancing the macrovoid structure. A high concentration of PEG in the polymer solution, on the other hand, slows the formation of nuclei (i.e. polymer-rich phase), and the low solvent composition results in the formation of a sponge-like structure [17,18].

The SEM images of the inner and outer surfaces of PES hollow-fiber membranes spun from different concentrations of PEG are shown in Fig. 4. It can be seen that the inner and outer surfaces have a dense skin layer, and that no pores are visible on the surfaces until a magnification of 50,000 is reached. This is attributed to the steam effect during the passage of the nascent hollow-fiber throughout the 15 cm steam gap length. When the PES dope solution leaves the nozzle of the spinneret, evaporation of the GBL will start from the external surface of the nascent hollow fiber in the water vapor channel. Therefore coagulation of the skin external surface of the nascent hollow-fiber membrane will be rapid on account of the higher heat transfer rate from the water vapor to the external polymer surface. Moreover, the internal surface of the nascent hollow fiber will be brought into contact with the bore fluid (water) as soon as the nascent fiber escapes from the nozzle of the spinneret, so that the solidification of the skin internal surface will be rapid.

3.1.2. Effect of PEG concentration on membrane thickness and porosity

Fig. 5 shows the thickness of the PES hollow fibers using different PEG concentrations in the dope solution. It can be observed that the thickness of the PES hollow fiber increased significantly with an increase of the PEG concentration in the dope solution. This behavior is attributed to the increase in the PES dope solution viscosity. It is expected that the increase of the viscosity of the polymer solutions will reduce the effect of gravity on the nascent fiber while it moves through steam and air gaps towards the external coagulation bath; it is well known that the presence of an air gap tends to reduce the dimensions of the nascent fiber and increase its porosity [14,19]. This increase in thickness can be observed in the SEM image in Fig. 2. Torrestiana-Sanchez et al. [2] reported that the viscosity of the polymer solution affects physical membrane features and found that the membrane thickness increases as the polymer solution viscosity increases.

Table 2 and Fig. 6 show the porosity of PES hollow-fiber membranes prepared from various PEG concentrations. It is noticed that the porosity of PES hollow-fiber membranes increases from 66.11% to 76.49% with an increase of the PEG concentration in the PES dope solution from 5 to 15 wt.%. This result is expected because PEG is a hydrophilic (pore-former) additive that is combined with the polymer to promote the formation of porous structure [20,21].

3.1.3. Effect of PEG concentration on pore size, pore size distribution and pore density

Table 2 and Fig. 7 show the influence of PEG concentration on the pore size, pore size distribution and pore density of the PES hollow-fiber membrane. For the hollow fiber prepared with 5 wt.% PEG, the effective pores showed a distribution between 0.13 and 0.39 μm [see Fig. 7 I]. The frequency of the pores having an average size of 0.15 μm was ≈20% and that of 0.37 μm was ≈80%, while pore density was 4034.4 (pores/mm^2 × 10^2). For hollow fiber prepared with 10 wt.% PEG concentration, the effective pores showed a narrow distribution, mainly between 0.37 and 0.41 μm, with a frequency of ≈94%, as shown in Fig. 7 II. The pore density of this fiber was 17,063.3 (pores/mm^2 × 10^2), as shown in Table 2. The effective pores for the fibers prepared with 15 wt.% PEG showed a narrow distribution, between 0.41 and 0.45 μm, with a frequency of more than 97% and a density of 16,822.6 (pores/mm^2 × 10^2) as depicted in Fig. 7 III. From the above results, it can be concluded that with increasing PEG concentration in the dope solution, the pore size increased and the pore size distribution became narrower, and the same behavior was obtained by Sinha and Purkait [22]. However, pore density increased with an increase of the PEG concentration up to 10 wt.%. Further increase in the PEG concentration to 15 wt.% resulted in a decrease in pore density, however, the increase in pore size and

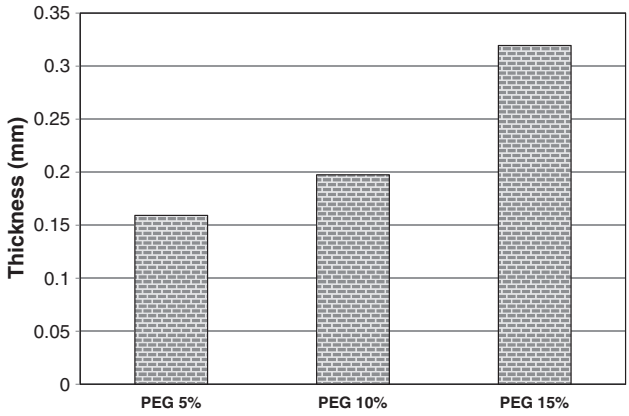

Fig. 5. Thickness of PES hollow fiber membranes with different PEG concentrations.

Table 2
Dimensions, porosity, pore size and pore density of the PES hollow fiber membranes.

Fiber no.	O.D. (mm)	I.D. (mm)	Thickness (mm)	Porosity (%)	Average pore size (μm)	Pore density (pore/mm^2) × 10^2	PWP (l/m^2·h·bar)	R (%)
I	1.359	1.04	0.159	66.11 ± 0.36	0.326	4034.4	19.2	100.0
II	1.495	1.10	0.198	74.24 ± 0.67	0.383	17,063.3	76.7	99.2
III	1.629	0.99	0.320	76.49 ± 0.18	0.432	16,822.6	54.4	100.0
IV	1.507	1.18	0.163	74.17 ± 0.90	0.382	41,041.4	236.4	84.6
V	1.638	1.40	0.119	75.68 ± 0.67	0.390	21,902.5	143.0	93.2
VI	1.555	0.87	0.343	75.64 ± 0.03	0.328	14,698.6	45.2	98.1
VII	1.707	1.24	0.233	77.54 ± 0.30	0.387	29,440.2	107.4	92.3

density can be related to the nature of PEG, a hydrophilic additive that controls the exchange rate between the solvent in polymer solution and nonsolvent (water) in the coagulation bath during the phase inversion process. Moreover, the decrease in pore density with an increase of PEG concentration up to 15 wt.% is due to the increase in polymer solution viscosity.

Liu et al. [4] showed that, in the proper concentration, PEG can be used as a polymeric additive to improve PES dope solution viscosity while at the same time enhancing the pore size and pore interconnectivity of the membrane.

On the other hand, Zheng et al. [23] found that when PEG concentration is less than 12 wt.%, the pore density of the membranes increases with increasing PEG concentration. They attributed this phenomenon to the increase in the exchange rate between solvent in the dope solution and non-solvent in the coagulation bath, whereas the pore density of membranes decreases when PEG concentration is increased to more than 12 wt.% on account of the increased dope viscosity.

3.1.4. Effect of PEG concentration on pure water permeability and solute rejection

The pure water permeability (PWP) and bovine serum albumin (BSA) rejection of the PES hollow fibers prepared from various PEG concentrations is illustrated in Table 2. It will be noticed that the pure water permeability of the PES hollow-fiber membranes increased from 19.18 to 76.68 (l/m^2·h·bar) with an increase in the PEG concentration from 5 to 10 wt.%. Further increase of the PEG concentration up to 15 wt.% results in a decrease in the pure water permeability to 54.4 (l/m^2·h·bar). It will also be noticed from Table 2 that the PWP is highly improved, with no significant decrease in solute (BSA) rejection with an increase of PEG concentration in the PES dope solution. It is well known that membrane performance is affected by different factors such as membrane morphology, pore size, pore density, membrane thickness and porosity. In this case, the PWP and solute rejection trends obtained with an increase in PEG concentration are mainly generated by the pore density of the hollow fibers. Kim et al. [24] reported that the pure water permeability should be related to pore intensity on the membrane surface. The literature reports that a certain value of the additives in the dope solution results in a positive effect on the performance of the membranes [4,5].

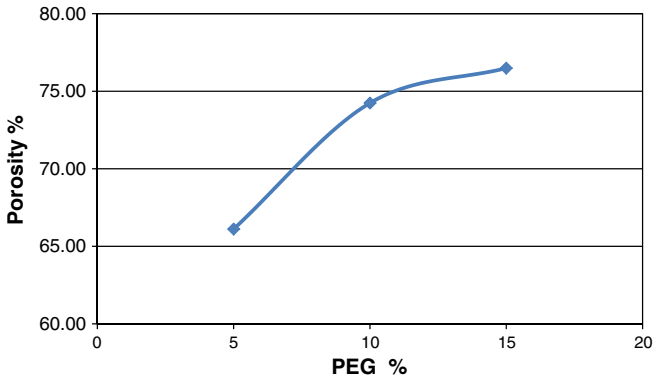

Fig. 6. Porosity (%) of PES hollow fiber membranes with different PEG concentrations.

3.1.5. Effect of PEG concentration on the mechanical properties

Young's modulus, tensile strength and the elongation at break of the PES hollow-fiber membranes prepared from various PEG concentrations are summarized in Table 3. As can be seen from Table 3, the elongation at break decreases from 45.33% to 37.51%, whereas the tensile strength and Young's modulus decrease from 8.78 to 2.91 N/mm^2 and 223.95 to 62.92 N/mm^2 respectively with an increase in the PEG concentration in the dope solution from 5 to 15 wt.% (fiber nos. I, II and III). This reduction in mechanical properties with the increase in PEG concentration can be related to the increase in porosity of the PES hollow fibers. Xu and Xu [21] found that the hollow-fiber membranes present higher mechanical properties with lower porosity.

3.2. Type of bore fluid

Three dope solutions containing 20 wt.% PES and 10 wt.% PEG as additives were spun with different types of bore fluid such as pure water, 30 wt.% ethanol solution and 30 wt.% isopropanol solution. The bore fluid flow rate is constant at 12.84 (g/min) during the preparation process of the PES hollow-fiber membranes.

3.2.1. Effect of bore fluid type on morphological structure

Fig. 8 illustrates the SEM pictures of the cross-sections of the PES hollow fibers prepared from different types of bore fluid. It can be noticed that the cross-sections of the hollow-fiber membrane show a sponge-like structure for all hollow fibers, and that there is no significant effect of the type of the bore fluid on the morphological structure of the PES cross-section. *This behavior confirms our goal of establishing that bore fluid type does not affect the structural morphology of the PES hollow-fiber membranes when the viscosity of the polymer solution is higher than 1250 cp with the effect of the presence of steam gap distance during the spinning of PES hollow-fiber membranes.* From the SEM pictures of the PES hollow-fiber surfaces in Fig. 9, it can be observed that the outer surfaces of the hollow fibers prepared from different PEG concentrations have dense skin texture. Moreover, no pores can be observed on the inner surfaces of the hollow fibers prepared from water or 30 wt.% isopropanol solution as a bore fluid, even at a magnification of 24,000×. Whereas there are both huge and very small pores on the inner surface of the hollow fiber prepared from 30 wt.% ethanol solution as a bore fluid. This difference between the effects of the bore fluid types is related to their ability to coagulate the dope solution; water and isopropanol, for example, are strong coagulants compared to ethanol. As reported by Bonyadi and Chung [13], when a strong coagulant such as water is used, it induces formation of a dense skin layer. Deshamukh and Li [25] reported that ethanol, on the other hand, is not a strong nonsolvent like water, which means that the addition of ethanol will

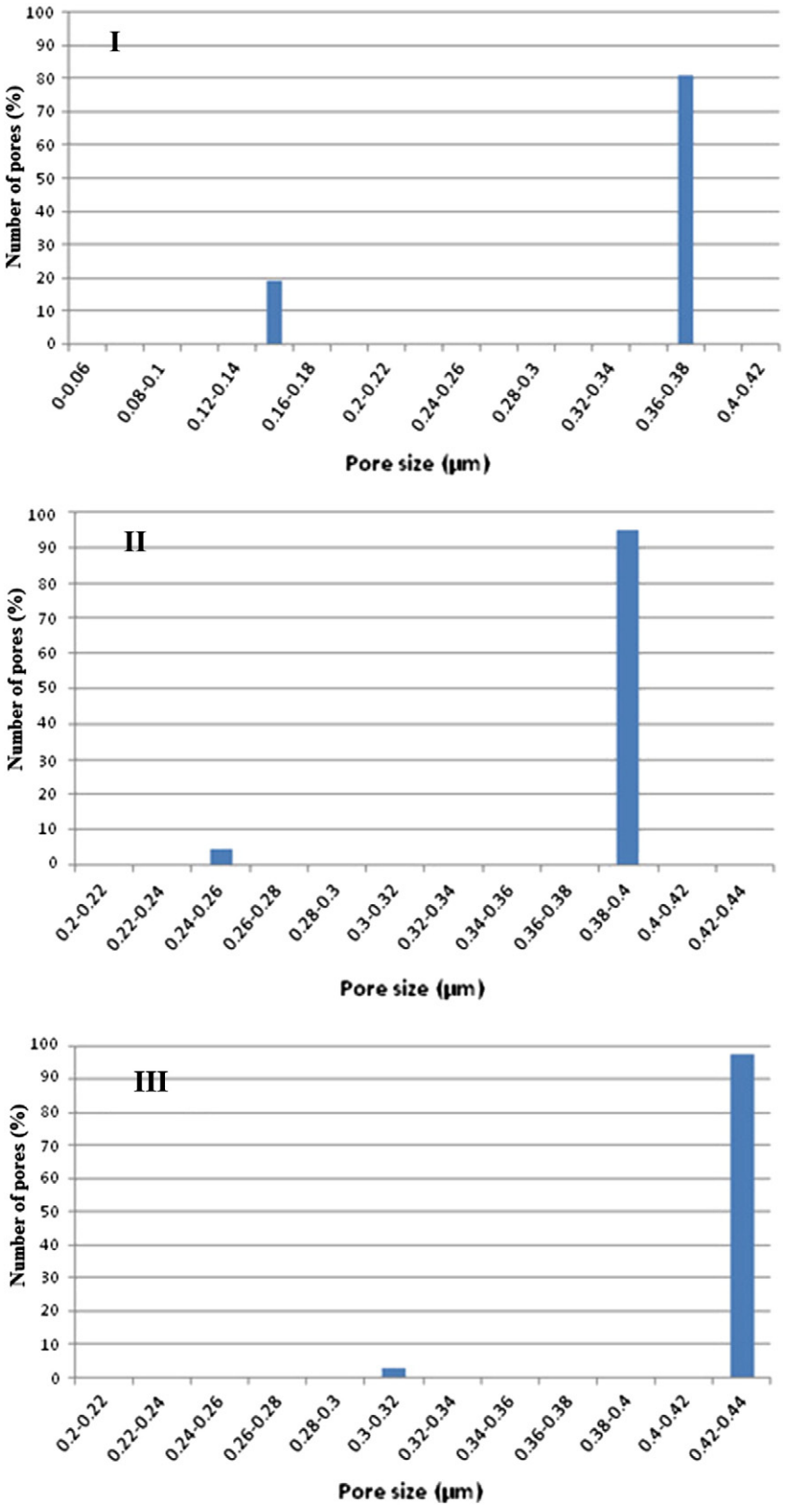

Fig. 7. Pore size distribution of fiber no. I; no. II; and no. III.

delay the coagulation process and eliminate the skin layer. Moreover, Alsalhy [26] observed that using ethanol solution as bore fluid results in a cracking phenomenon on the inner surface of PES hollow-fiber membranes.

3.2.2. Effect of bore fluid type on pore size and pore density

Fig. 10 shows the pore size distribution of PES membrane produced with different types of bore fluid. It can be seen that the membrane prepared from 30 wt.% ethanol, 30 wt.% isopropanol and pure water as a

Table 3
Mechanical properties of PES hollow fiber membranes.

Fiber no.	Young's mod. (N/mm^2)	Tensile strength (N/mm^2)	Elongation at break (E %)
I	223.95 ± 17.80	8.78 ± 0.40	45.33 ± 12.74
II	89.47 ± 1.30	3.55 ± 0.08	43.54 ± 5.34
III	62.92 ± 2.43	2.91 ± 0.04	37.51 ± 2.37
IV	92.18 ± 4.87	3.28 ± 0.15	23.83 ± 7.86
V	80.03 ± 3.24	3.09 ± 0.34	30.32 ± 13.69
VI	91.46 ± 2.86	4.2 ± 0.14	38.55 ± 5.04
VII	73.87 ± 2.87	3.41 ± 0.08	36.94 ± 3.10

bore fluid had narrow pore size distribution between 0.37 and 0.41 μm, while the pore frequency was in the following sequence

88%(30 wt.%ethanol)<94%(pure water)<100%(30 wt.%isopropanol).

The pore size distribution of the membrane prepared from pure water as a bore fluid is shown in Fig. 7 and mentioned in details in Section 3.1.3. Thus, it is worth noting that using an isopropanol solution as a bore fluid has a strong effect on the distribution of the pores on the surface of the hollow-fiber membranes.

The obtained pore density of the prepared PES fibers with different bore fluid types is presented in Table 2. It will be noticed that the fibers prepared using 30 wt.% ethanol as a bore fluid had the highest pore density (41,041.4 pores/cm^2), while the pore density of the hollow fiber prepared by using 30 wt.% isopropanol as a bore fluid was 21,902.5 (pores/$mm^2 \times 10^2$). Moreover, the pore density of PES fiber using pure water as a bore fluid was 17,063.3 (pores/$mm^2 \times 10^2$). This phenomenon is attributed to the diffusion rate between solvent in dope solution and non-solvent in bore fluid. A bore fluid of 30% ethanol solution has a weaker effect on the coagulation process of the dope solution,

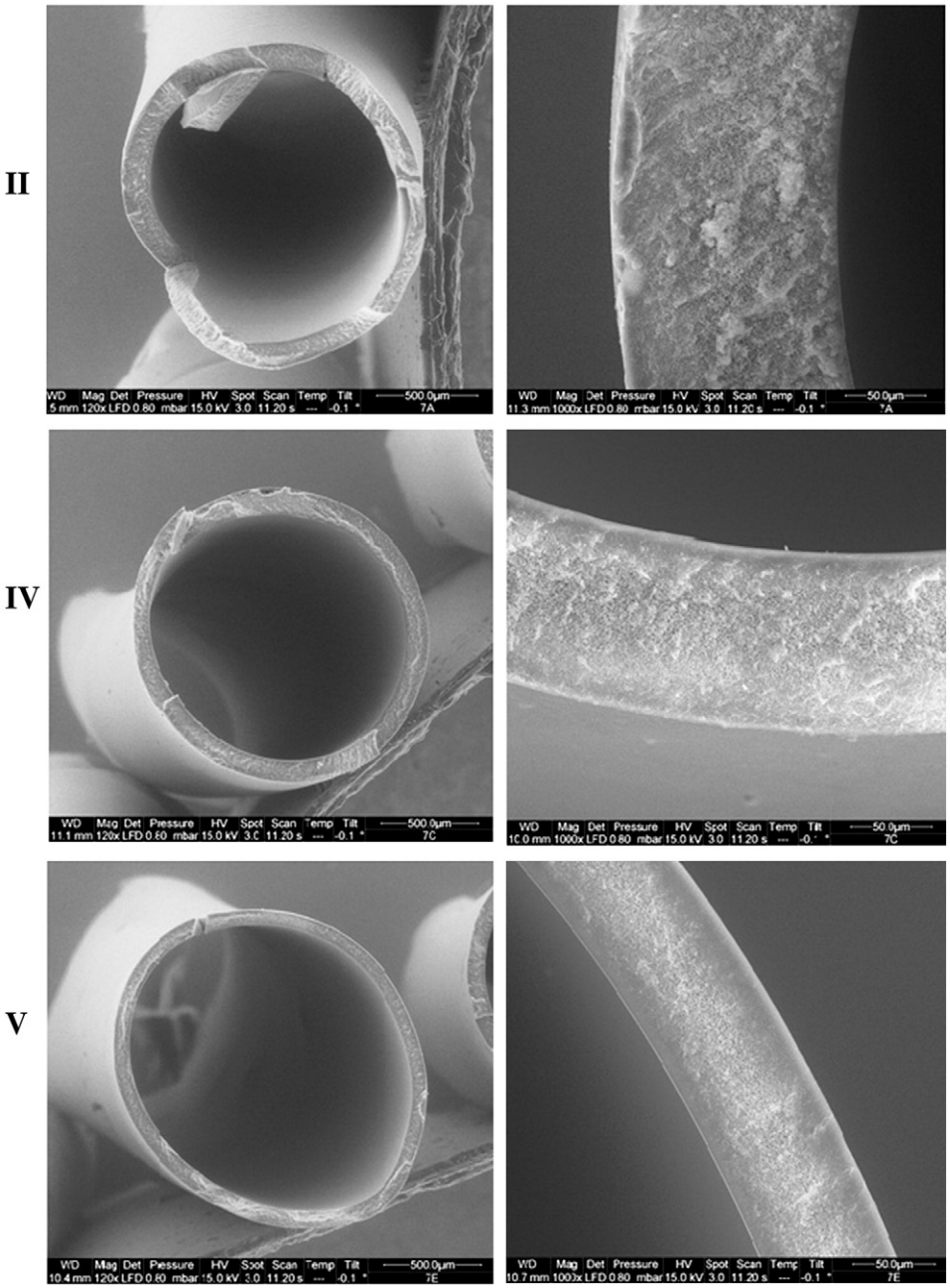

Fig. 8. Cross-section of PES hollow fibers (magnification 120 and 1000×), II) pure water; IV) 30 wt.% ethanol; V) 30 wt.% isopropanol.

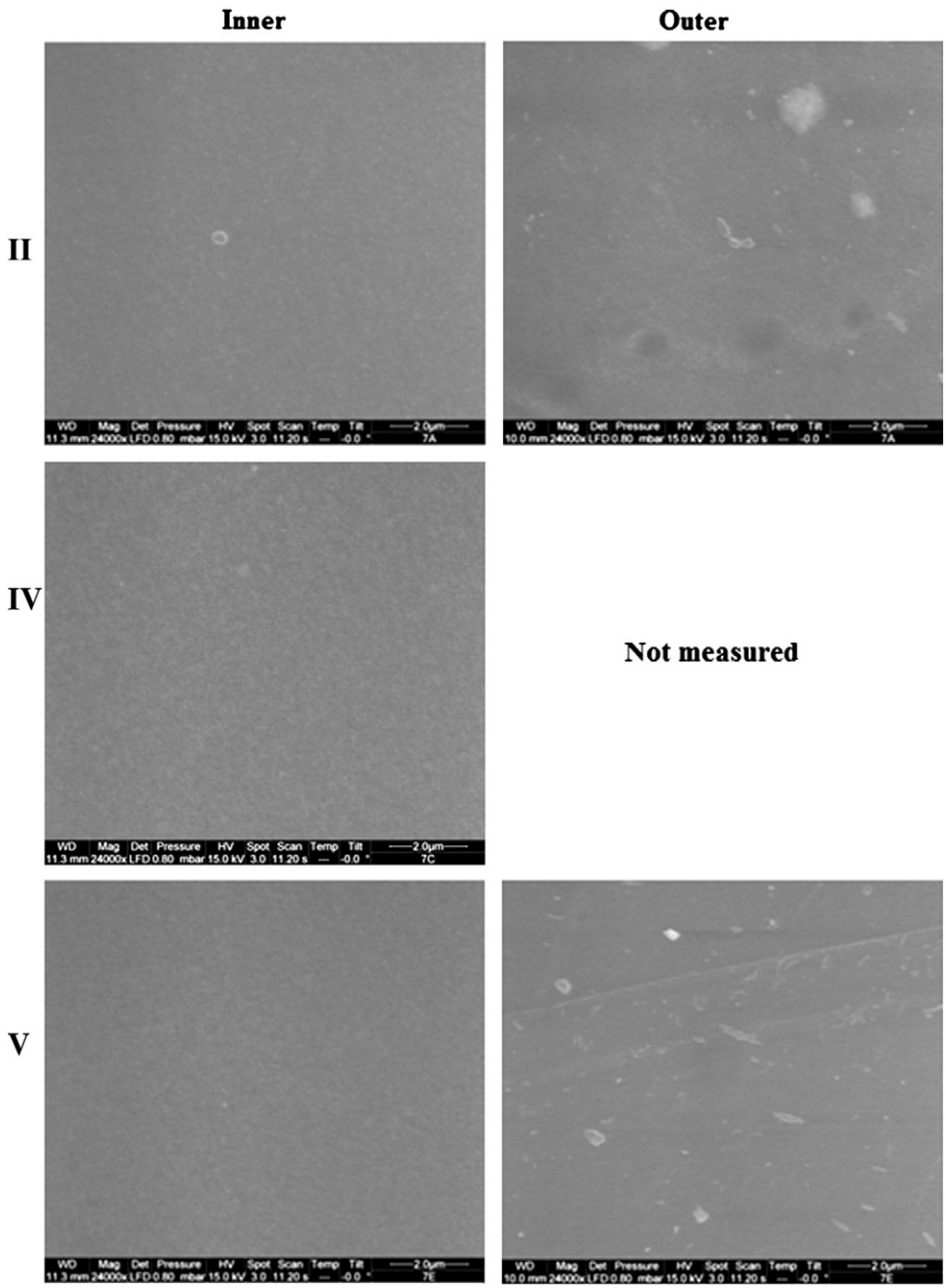

Fig. 9. Inner and outer surfaces of the PES hollow fibers (magnification 2400×), II) pure water; V) 30% isopropanol.

which results in the formation of a membrane with high pore density and more open pores in the skin layer, as shown in Fig. 9.

3.2.3. Effect of bore fluid type on dimensions and porosity

Table 2 shows the dimensions and porosity of the spun fibers with different bore fluid types (nos. II, IV and V). It is worth noting that the hollow fiber prepared with pure water as a bore fluid has a larger thickness compared to those prepared from 30 wt.% ethanol and 30 wt.% isopropanol solutions. This is due to the difference in the diffusion process between the polymer solution and the various internal coagulants. With pure water as internal coagulant the diffusion process is faster than with the other two internal coagulants, 30 wt.% ethanol and 30 wt.% isopropanol solutions, because water is a strong solvent, and therefore as soon as the nascent fiber emerges from the spinneret nozzle, the inner surface coagulates directly, so the dimensions of the membrane maintain values closer to those of the spinneret, as shown clearly in Table 2. The diffusion velocity of the internal coagulant through the polymer solution was in the sequence listed as follows:

Pure water>30 wt.%ethanol>30 wt.%isopropanol.

3.2.4. Effect of bore fluid type on pure water permeability and protein rejection

Table 2 shows the effect of the bore fluid type on the PES hollow-fiber membrane permeability and BSA rejection. The highest permeability of PES membranes was 236.4 ($l/m^2 \cdot h \cdot bar$), achieved with 30 wt.% ethanol solution as a bore fluid, while the lowest was 76.7 ($l/m^2 \cdot h \cdot bar$), using pure water as a bore fluid. Moreover, the pure water permeability of PES hollow-fiber membrane was 143 ($l/m^2 \cdot h \cdot bar$), using 30 wt.%

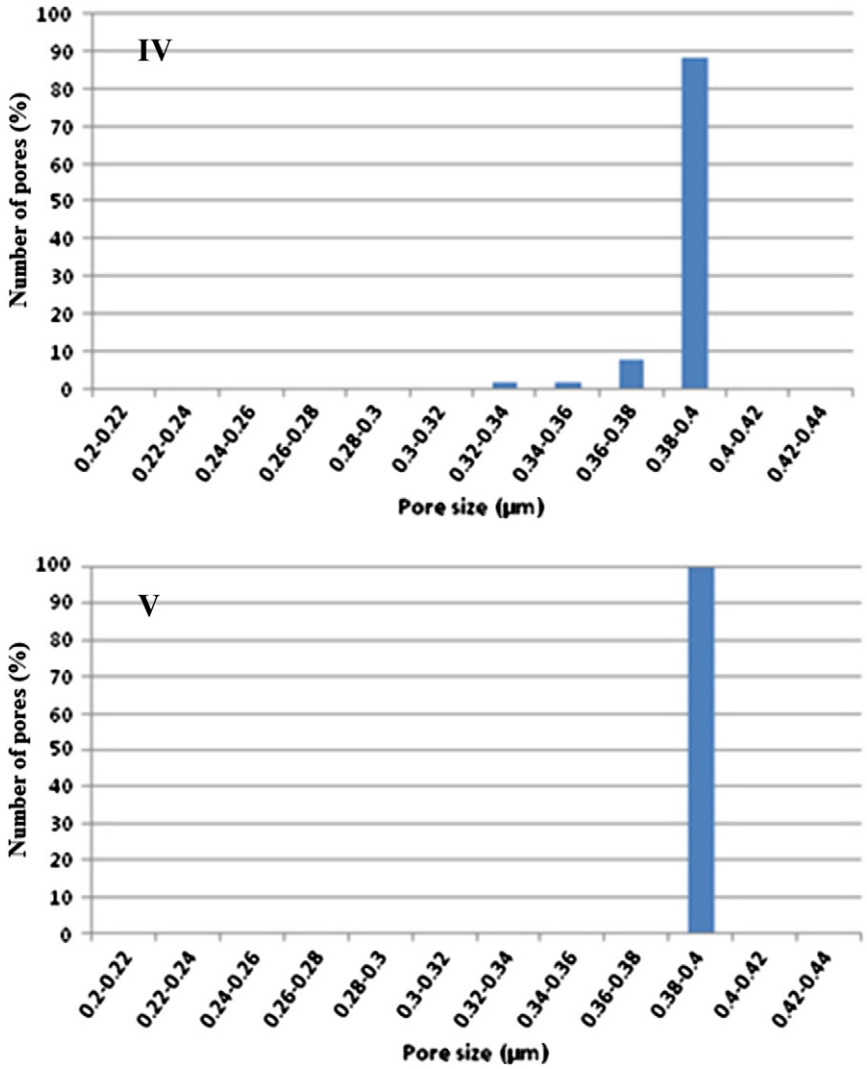

Fig. 10. Pore size distribution of fiber no. IV; and no. V.

isopropanol as a bore fluid. This behavior can be attributed to the effects of pore density for each type of bore fluid, where the pore density of the PES membrane was 41,041.4 (pores/mm^2 × 10^2) using 30 wt.% ethanol, compared with 21,902.5 and 17,063.3 (pores/mm^2 × 10^2) using 30 wt.% isopropanol and water respectively as a bore fluid. In Table 2 (fibers II, IV and V), it can also be seen that the solute rejection of the bovine serum albumin (BSA) of the PES hollow-fiber membrane was 99.23, 93.21 and 84.62% using water bore fluid, 30 wt.% isopropanol and 30 wt.% ethanol respectively. It is obvious that there are several parameters that control the separation performance of the membranes, for example, porosity, membrane thickness, pore size, and pore density. From Table 2, it can be seen that membrane thickness, pore size and porosity of PES hollow fiber membranes do not pursue the same trend as that obtained for separation performance. While, the pore density of the PES membranes is the only parameter which controls the separation performance of the membranes, therefore, the increase in the pore density of the membrane results to the increase in the water permeability and decrease in solute rejection as shown in Table 2. In general, the increase in the pure water permeability is accompanied by a decrease in the solute rejection. In addition, it was found from the literature that the pure water permeation flux and solute transport are related to the pore size, pore size distribution, pore density, thickness and porosity of the membranes [15,27].

3.2.5. Effect of bore fluid type on the mechanical properties

Table 3 shows the effect of bore fluid type on the mechanical properties of the PES hollow-fiber membranes. It can be seen that the Young's modulus of PES hollow fiber prepared from different bore fluid types was in the order: 30% ethanol > pure water > 30% isopropanol. Whereas the tensile strength of the PES hollow fiber was in the order: pure water > 30% ethanol > 30% isopropanol. Moreover, the elongation at break (%) of the PES hollow-fiber membranes was in the order: pure water > 30% isopropanol > 30% ethanol. It can be concluded that the mechanical properties of the PES hollow-fiber membrane prepared from pure water as bore fluid were better than those with ethanol and isopropanol solutions. This is mainly attributed to the thickness of the hollow-fiber membrane, where the values of the thickness of the membranes were: pure water; 0.198 mm > ethanol; 0.163 mm > isopropanol; 0.119 mm. The values of all other parameters of the PES hollow-fiber membranes, such porosity and pore size, were similar.

3.3. Bore fluid flow rate

Three dope solutions containing 20 wt.% PES and 10 wt.% PEG as additives were spun with different bore fluid flow rates of 7.67, 12.84 and 23.06 g/min. Deionized water was used as a bore fluid in this effort.

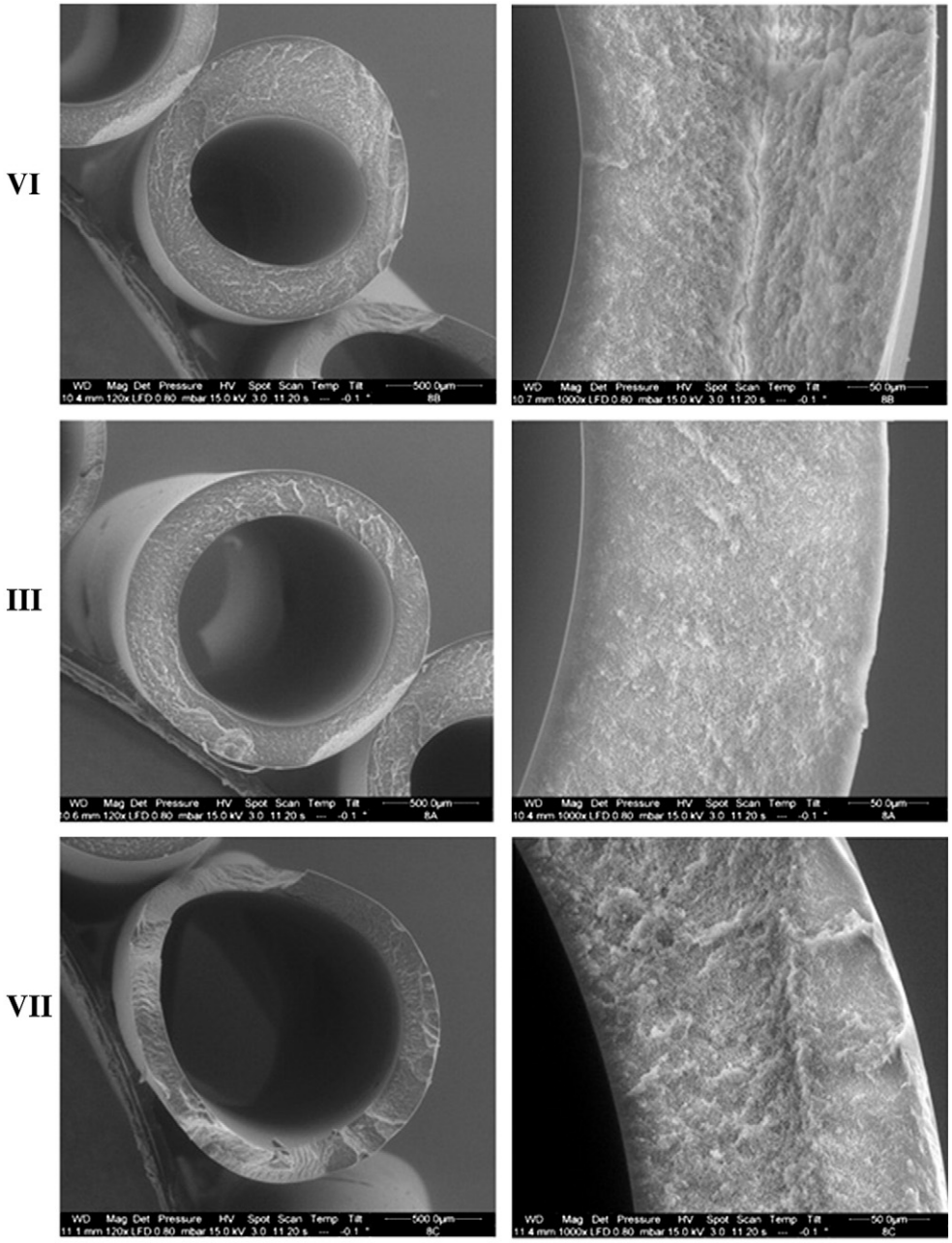

Fig. 11. Cross-section of hollow fibers (magnification 120 and 1000×) VI) 7.67; III) 12.84; VII) 23.06 g/min.

3.3.1. Effect of bore fluid flow rate on morphological structure

Fig. 11 shows the SEM pictures of the cross-section of PES hollow-fiber membranes with different bore fluid flow rates. It can be seen that the sponge-like structure was the dominant characteristic in the cross-section of the PES hollow-fiber membranes at different bore fluid flow rates. Therefore, it is worth saying here that the bore fluid flow rate had no manifest effect on the structural morphology of the PES membrane despite increasing the flow rate by a factor of three. This phenomenon is due to the high viscosity of the polymer solution, which prevented the occurrence of any change to the membrane structure. Therefore, the viscosity of the PES solution was the dominant factor affecting the properties of the hollow-fiber membrane. *It is also worth mentioning here that this behavior demonstrates the objective of this study, which is to show that the bore fluid flow rate, even when increased by a factor of three, does not affect the morphological structure of the PES hollow-fiber membranes when the viscosity of the polymer solution is higher than 1250 cp in conjunction with the effect of steam gap distance during the spinning process.*

Fig. 12 illustrates the SEM pictures of the inner and outer surfaces of PES hollow-fiber membrane. From Fig. 12 it can be noticed that as the bore fluid flow rate increased from 7.67 to 23.06 g/min, no pores appeared on the inner or outer surface even at a magnification of 24,000×.

3.3.2. Effect of bore fluid flow rate on dimensions and porosity

In Table 2, the increase of bore fluid flow rate results in an increase in the inner and outer diameters of the PES hollow fiber (VI, III and VII). The wall thickness of the hollow fiber decreased with an increase in bore fluid flow rate. An increase in bore fluid flow rate and all other spinning condition constants leads to the increase in the inner and outer diameters of the hollow fiber membrane and in turn results to the decrease in the wall thickness. Miao et al. [28] reported that an increase in bore fluid flow rate results to the reduction in the skin layer

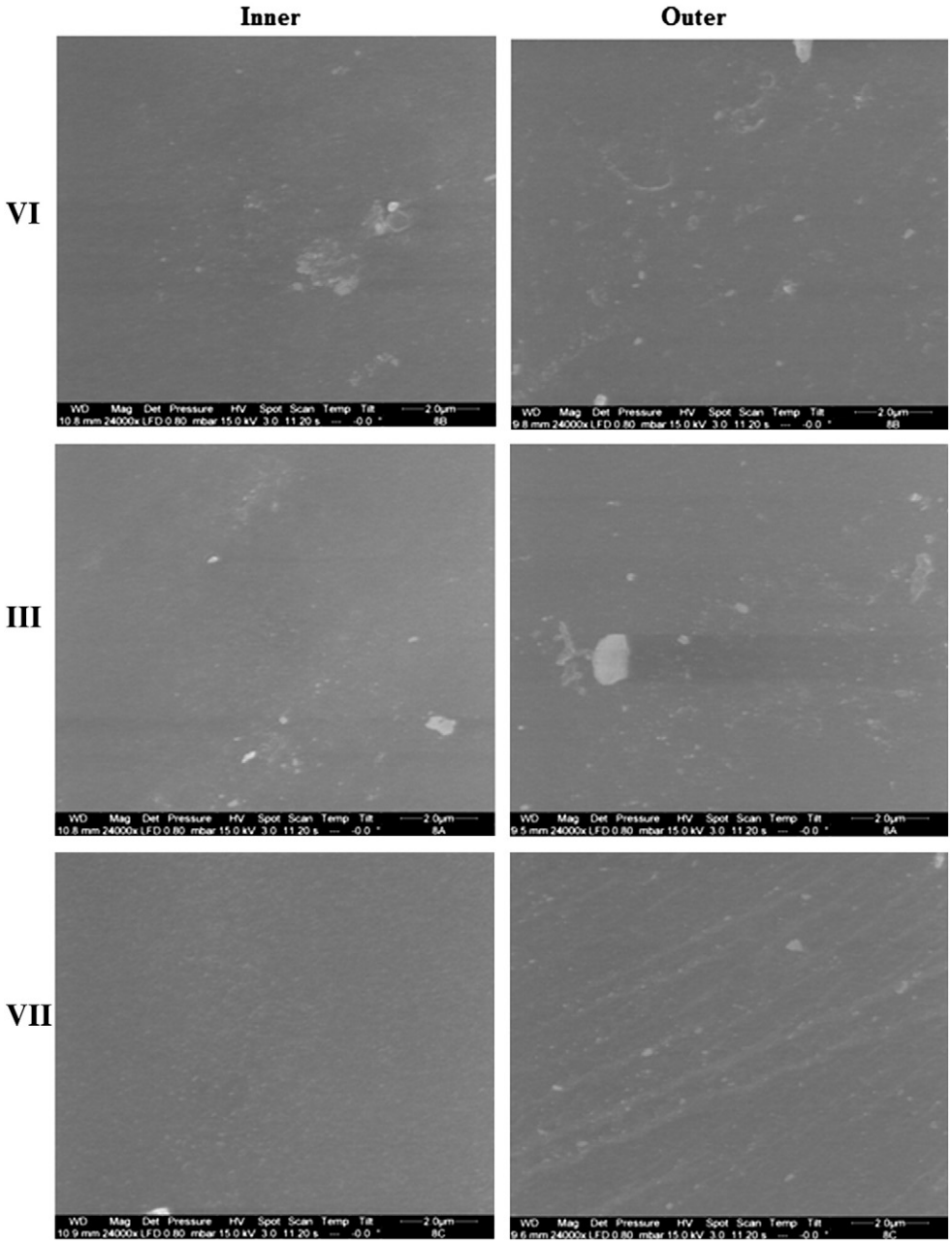

Fig. 12. Inside & outside surfaces of hollow fibers (magnification 2400×) VI) 7.67, III) 12.84 VII) 23.06 g/min.

thickness and the size of the skin layer pores. Also, they found that an increase of bore flow rate tended to reduce the inner, outer and thickness of the membrane. This is probably due to the effect of the high liquid pressure exerted towards the inner surface of the nascent hollow fiber during its formation and while the nascent fiber passed through the water vapor and air gap regions. This result conforms to the respective morphologies shown in Fig. 11. Also from Table 2, it can be seen that there is no huge difference in the porosity with an increase in bore fluid flow rate, and their porosities have values between 75.6 and 77.5%.

3.3.3. Effect of bore fluid flow rate on pore size, pore density and pore size distribution

The effects of different bore fluid flow rates on the pore density of PES hollow-fiber membranes are also presented in Table 2. With increases in bore fluid flow rate from 7.67 g/min (membrane VI) to 12.84 g/min (membrane III), the average pore size increased from 0.328 to 0.432 μm, while a further increase of bore fluid flow rate up to 23.06 g/min (membrane VII) results in a reduction of the average pore size to 0.387 μm. This phenomenon is attributed to the gradual increase in skin solidification of the inner surface of the hollow fiber membrane, which eventually restricts the water diffusion through the membrane wall and results in the reduction of the pore size of the membrane.

Regarding the pore density of the PES hollow-fiber membranes at different bore fluid flow rates, it can be seen from Table 2 that an increase in bore fluid flow rate from 7.67 to 12.84 mg/min results in an increase in the pore density of the PES hollow fibers from 14,698.6 to 16,822.6 (pores/mm^2 × 10^2). A further increase of bore fluid flow rate, i.e. to 23.06 g/min, led to a significant increase in pore density i.e., to 29,440.2 (pores/mm^2 × 10^2). This increase in pore density can be attributed to a decrease in the number of closed-end pores with decreasing wall fiber thickness because of the pressure exerted on the inner surface of the hollow fiber [28].

3.3.4. Effect of bore fluid flow rate on the pure water permeability and protein rejection

Table 2 shows the effect of bore fluid flow rate on pure water permeability PWP of the polyethersulfone fiber membrane. It can be seen that PWP flux increased with increasing the flow rate of the bore fluid. This enhancement of the pure water permeability is a result of the increase of the pore density and the reduction in the fiber wall thickness, where the increase in the pore density led to the increase in the area of permeation, and the decrease in the fiber wall thickness reduction of the wall resistance.

From Table 2 it can be seen that the rejection ratio of PES hollow fiber (VI, III and VII) decreased with an increase in the bore fluid flow rate. The rejection was 100% at a bore fluid flow rate of 7.67 g/min, then it decreased to 98.1% with a flow rate of 12.84 g/min, while a further increase in the bore fluid flow rate to 23.06 g/min reduced rejection to 92.3%. This is can be attributed mainly to the reduction of wall resistance due to the decrease in the wall thickness of the hollow fiber with the increase in the bore fluid rate.

It is worth noting that the PWP and BSA separation performance behavior, obtained with the increase in bore fluid flow rates, is produced by the interaction of two factors, the pore density and wall thickness of the hollow-fiber membranes.

3.3.5. Effect of bore fluid flow rate on the mechanical properties

The mechanical properties of the PES hollow-fiber membranes as a function of bore fluid flow rate are depicted in Table 3. It can be seen that the tensile strength and Young's modulus of PES hollow-fiber membranes decreases from 91.46 and 4.2 to 62.92 and 2.91 with increase in bore fluid flow from 7.67 to 12.84 g/min respectively. Further increase in bore fluid flow rate results in an increase in tensile strength and Young's modulus of the PES hollow-fiber membranes. This phenomenon is attributed to the pore size and pore size distribution of the PES hollow-fiber membranes; for example, the pore size of the hollow fiber prepared from 12.84 g/min bore fluid flow rate is higher, at about 0.432 μm, with pore size distribution between 0.42 and 0.44 μm of the membrane. It is well known that tensile strength is the ultimate stress that a hollow-fiber membrane can endure while being pulled before breaking. Regarding the elongation at break of the PES hollow-fiber membranes, it can be seen from Table 3 that the elongation at break decreases with an increase in bore fluid flow rate. In fact, it is obvious that the elongation at break is the ratio between changed length and original length after fracture of the hollow-fiber membrane. Therefore, this behavior can be attributed to the diminution of the PES hollow-fiber membrane thickness.

Finally, it can be stated that the morphological results of PES hollow-fiber membranes prepared by this method accentuate our objective, which is to illustrate that the bore fluid type, composition and flow rate do not affect the structural morphology of the membrane, and that the polymer concentration and the type of the additives in dope solution are the only factors controlling the structural morphology of the membranes when the viscosity of the polymer solution is higher than 1250 cp in conjunction with the presence of steam gap distance during the spinning process, and that all the spinning conditions can affect the dimensions, porosity, pore size and pore size distribution, but not the main structure of the membranes.

4. Conclusions

Polyethersulfone (PES) hollow-fiber membranes for ultrafiltration applications were fabricated by the steam/dry/wet phase inversion method. Polyethersulfone (PES) was used as a polymer material. Gamma butyrolactone (GBL) and polyethylene glycols (PEG) were used as a solvent and an additive respectively. The effect of varying PEG concentration, type of bore fluid, bore fluid flow rate (BFR) and PES concentration on the membrane structure, pure water permeability, protein separation performance and mechanical properties of the produced PES fiber was studied. The following conclusions can be drawn:

1. The sponge-like structure of the cross-section of all PES hollow-fiber membranes prepared by steam/dry/wet spinning process was observed to be due to the effect of PEG concentration in conjunction with the presence of steam gap distance. This phenomenon is due to the high polymer solution viscosity and high thermal conductivity of the water vapor.
2. The porosity of the PES hollow-fiber membrane increased sharply from 66.11% to 76.49% with an increase in the PEG concentration in the dope solution from 5 to 15 wt.%. Using different bore fluid types and flow rates resulted in only a minor increase in the porosity of the PES hollow fibers.
3. Comparison between the effects of different types of bore fluid on the properties of PES hollow-fiber membranes showed that high pore density was produced using a 30 wt.% ethanol concentration, with no significant difference in the average pore size of the hollow fibers.
4. The pure water permeation flux of PES fibers increases about 300%, keeping protein rejection above 99% with increasing PEG concentration in the dope solution from 5 to 10 wt.%. High permeation flux was obtained using a 30 wt.% ethanol concentration as a bore fluid.
5. The mechanical properties of PES hollow-fiber membranes in terms of Young's modulus, tensile strength and elongation at break were shown to depend strongly on the PEG concentration, bore fluid type and flow rates.

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References

[1] J.-H. Kim, K.-H. Lee, Effect of PEG additive on membrane formation by phase inversion, J. Membr. Sci. 138 (1998) 153–163.
[2] B. Torrestiana-Sanchez, R.I. Ortiz-Basurto, E.B. La Fuente, Effect of non-solvents on properties of spinning solutions and polyethersulfone hollow fiber ultrafiltration membranes, J. Membr. Sci. 152 (1999) 19–28.
[3] D. Wang, K. Li, W.K. Teo, Preparation and characterization of polyvinylidene fluoride (PVDF) hollow fiber membranes, J. Membr. Sci. 163 (1999) 211–220.
[4] Y. Liu, G.H. Koops, H. Strathmann, Characterization of morphology controlled polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to the dope and bore liquid solution, J. Membr. Sci. 223 (2003) 187–199.
[5] Z.-L. Xu, Qusay F. Alsalhy, Effect of polyethylene glycol molecular weights and concentrations on polyethersulfone hollow fiber ultrafiltration membranes, J. Appl. Polym. Sci. 91 (2004) 3398–3407.
[6] S.H. Yoo, J.H. Kim, J.Y. Jho, J. Won, Y.S. Kang, Influence of the addition of PVP on the morphology of asymmetric polyimide phase inversion membranes: effect of PVP molecular weight, J. Membr. Sci. 236 (2004) 203–207.
[7] 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.
[8] E. Saljoughi, M. Sadrzadeh, T. Mohammadi, Effect of preparation variables on morphology and pure water permeation flux through asymmetric cellulose acetate membrane, J. Membr. Sci. 326 (2009) 627–634.
[9] S. Simone, A. Figoli, A. Criscuoli, M.C. Carnevale, A. Rosselli, E. Drioli, Preparation of hollow fiber membranes from PVDF/PVP blends and their application in VM, J. Membr. Sci. 364 (2010) 219–232.
[10] P.Z. Culfaz, M. Wessling, R.G.H. Lammertink, Hollow fiber ultrafiltration membranes with microstructured inner skin, J. Membr. Sci. 369 (2011) 221–227.
[11] Zhansheng Li, Jizhong Ren, Anthony G. Fane, Dong Fei Li, Fook-Sin Wong, Influence of solvent on the structure and performance of cellulose acetate membranes, J. Membr. Sci. 279 (2006) 601–607.
[12] M. Khayet, M.C. Garc´ıa-Payo, Q. Alsalhy, K.C. Khulbe, C.Y. Feng, T. Matsuura, Effects of gas gap type on structural morphology and performance of hollow fibers, J. Membr. Sci. 311 (2008) 259–269.
[13] S. Bonyadi, T. Chung, Highly porous and macrovoid-free PVDF hollow fibre membranes for membrane distillation by a solvent-dope solution co-extrusion approach, J. Membr. Sci. 331 (2009) 66–74.

[14] C.S. Feng, B. Shi, G. Li, Y. Wu, Preparation and properties of microporous membrane from poly(vinylidene fluoride cotetrafluoroethylene) (F2.4) for membrane distillation, J. Membr. Sci. 237 (2004) 15–24.
[15] Qusay F. Alsalhy, Sufyan F. Algebory, Ghanim M. Alwan, S. Simone, A. Figoli, E. Drioli, Hollow fiber ultrafiltration membranes from poly(vinyl chloride): preparation, morphologies, and properties, Sep. Sci. Technol. 46 (2011) 2199–2210.
[16] 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.
[17] I.M. Wienk, R.M. Boom, M.A.M. Beerlage, A.M.W. Bulte, C.A. Smolders, H. Strathman, Recent advances in the formation of phase inversion membranes from amorphous or semi crystalline polymers, J. Membr. Sci. 113 (1996) 361–371.
[18] J.J. Shieh, T.S. Chung, R. Wong, M.P. Srinivasan, D.R. Raul, Gas separation performance of poly(4-vinylpyridine)/polyetherimide composite hollow fibers, J. Membr. Sci. 182 (2001) 111–123.
[19] M. Khayet, M.C. García-Payo, Qusay F. Alsalhy, M.A. Zubaidy, Structural and performance studies of poly(vinyl chloride) hollow fiber membranes prepared at different air gap lengths, J. Membr. Sci. 330 (2009) 30–39.
[20] J.Y. Kim, H.K. Lee, S.C. Kim, Surface structure and phase separation mechanism of polysulfone membranes by atomic force microscopy, J. Membr. Sci. 163 (1999) 159–166.
[21] J. Xu, Z.L. Xu, Poly(vinyl chloride) (PVC) hollow fiber ultrafiltration membranes prepared from PVC/additives/solvent, J. Membr. Sci. 208 (2002) 203–212.
[22] M.K. Sinha, M.K. Purkait, Increase in hydrophilicity of polysulfone membrane using polyethylene glycol methyl ether, J. Membr. Sci. 437 (2013) 7–16.
[23] 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.
[24] N. Kim, C.S. Kim, Y.T. Leeb, Preparation and characterization of polyethersulfone membranes with polytoluenesulfonic acid and polyvinylpyrrolidone additives, Desalination 233 (2008) 218–226.
[25] S.P. Deshmukh, K. Li, Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fiber membranes, J. Membr. Sci. 150 (1998) 75–85.
[26] Qusay F. Alsalhy, Effect of ethanol concentrations in internal coagulant on morphology and separation performance of polyethersulfone (PES) hollow fiber UF membranes prepared by PES/ethanol/NMP solution, Eng. Technol. 25 (2007) 253–265.
[27] J. Yan, W.W.Y. Lau, Effect of internal coagulant on morphology of polysulfone hollow fiber membranes, Sep. Sci. Technol. 33 (1998) 33–55.
[28] X.Q. Miao, S. Sourirajan, H. Zhang, W.W.Y. Lau, Production of polyethersulfone hollow fiber ultrafiltration membranes: I. Effects of water (internal coagulant) flow rate (WFR) and length of air gap (LAG), Sep. Sci. Technol. 31 (1996) 141–172.