

## Effect of Ethanol Concentrations in Internal Coagulant on the Morphology and Separation Performance of Polyethersulfone (PES) Hollow Fiber UF Membranes Prepared by PES/Ethanol/NMP Solution

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### Abstract

Polyethersulfone (PES) hollow fiber UF membranes were fabricated using ethanol (non-solvent) as additive and N-methyl-2-pyrrolidone (NMP) as a solvent. Asymmetric hollow fiber UF membranes were spun by wet phase inversion method from 18 wt.% solids of 18:10:72 (weight ratio) PES/Non-solvent/NMP solutions. Effect of ethanol concentrations in internal coagulant 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 (PEG10,000 and 20,000  $M_w$ ), PVP 40,000 $M_w$ , and PVA 78,000 $M_w$  as a solute. It was found that with an increase of ethanol concentration from 30 to 50 wt.% in the internal coagulant, membrane internal surfaces were dense and smooth, While the cracks phenomenon was appear on the internal surfaces of PES hollow fiber membrane with increase of ethanol concentration up to 100 wt.% (pure ethanol). The external surfaces for all of the PES membranes are smooth and dense because water is used as external coagulant; moreover, there is no change observed in the cross-section of PES hollow fiber with increase of ethanol concentration in the internal coagulant. Pure water permeation fluxes were decreased from 39 to 23.3 (L/m<sup>2</sup>hbar) and solutes rejection increased within less than 50 wt.% ethanol concentration in internal coagulant and then pure water permeation fluxes increased up to 65.4 (L/m<sup>2</sup>hbar) and solutes rejection decreased with an increase of ethanol concentration.

**Keywords:** Ultrafiltration membrane; hollow fiber; phase inversion; polyethersulfone; internal coagulant;

تأثير تركيز الأيثانول في المخثر الداخلي على أداء عمل الأغشية المصنعة من البولي إيثر سلفون

الخلاصة

أغشية البولي إيثر سلفون المجوفة تم تصنيعها مخبرياً باستخدام الأيثانول كمادة مضافة و ن - مثيل ٢-بارلايدون كمذيب. الأغشية تم تصنيعها بطريقة تعاكس الطور من ١٨% مادة البولييمر الصلبة في ٧٢:١٠:١٨ نسبة وزنية من محاليل PES/Non-solvent/NMP. تم التحقق من تأثير تركيز الأيثانول في المخثر الداخلي على بنية وإداء الفصل للأغشية. خواص الأغشية تم اختبارها باستخدام جهاز (أس أي أم) بينما أداء الأغشية تم اختبارها

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بأستخدام بولي أثيلين كلايكول , بولي فينل بارلايدون و بولي فينل الكحول كمذيبات. النتائج أظهرت بأن زيادة تركيز الأيثانول في المخثر الداخلي من ٣٠% الى ٥٠% فإن الأغشية كانت كثيفة وناعمة بينما ظاهرة التشققات ظهرت على السطوح الداخلية عند زيادة تركيز الأيثانول الى ١٠٠%.

السطوح الخارجية كانت كثيفة وناعمة لأنه تم أستخدام الماء كمخثر خارجي , علاوة على ذلك لا يوجد هناك تغيير في المساحة المقطعية للأغشية بتغير تركيز الأيثانول في المخثر الداخلي.

معدل تدفق الماء النقي النافذ خلال الأغشية قل من ٣٩ الى ٢٣,٣ لتر/(ساعة بارمتر مربع) ورفض المذاب أزداد في حدود اقل من ٥٠% تركيز الأيثانول في المخثر الداخلي وبعد ذلك معدل الماء النقي أزداد الى ٦٥,٤ لتر/(ساعة بارمتر مربع) ورفض المذيب قل مع زيادة تركيز الأيثانول.

كلمات مرشدة: متعدد الترشيح, اغشية مجوفة, بولي ايثر سلفون, مخثر داخلي, تغيير الطور.

## Introduction

It is well known that the preparation of hollow fiber membranes involves various factors during membrane formations such as the large numbers of spinning parameters like the structure and dimension of the spinneret, bore fluid composition, polymer dope viscosity, flow rate of the bore fluid, the dope extrusion rate, the length of the air-gap and take-up speed, *etc.*

Several authors studied the effect of bore fluid composition on the performance of the hollow fiber membranes. For example, the effects of water-flow rate (WFR) (5 or 7.5 ml/min) and length of air gap (LAG) (in the range of 50 to 120 cm) on the characteristics of PES/NMP/PVP hollow-fiber membranes produced by the solution-spinning technique using two polymer solution components C1 and C2 were studied experimentally by Miao et al <sup>[1]</sup>. They found that, for both C1 and C2 fibers, an increase in WFR at a given LAG tended to increase OD and ID and to decrease wall thickness, whereas an increase in

LAG at a given constant WFR tended to decrease OD, ID, and wall thickness for the resulting fibers. Chung et al <sup>[2]</sup>, reported that the ultrathin skin-layer hollow-fiber membranes with a skin layer of 474 Å can be prepared using mainly a one-polymer and one-solvent system. In order to yield a high-permeance polyether-polysulfone (PES) membrane with a skin layer of approximately 500 Å, the addition of non-solvents into spinning dopes may not be the pre-condition to form ultrathin skin-layer hollow-fiber membranes for gas separation. The keys to fabricate ultrathin skin-layer hollow-fiber membranes are (1) to control the chemical of the internal coagulant and the bore-fluid flow rate and (2) to have a dope exhibiting significant chain entanglement. The newly developed polyethersulfone (PES) hollow fibers have an O<sub>2</sub>/N<sub>2</sub> selectivity of 5.80.

It is generally accepted that the structure of the membrane skin layer is responsible for membrane selectivity while membrane flux

depends on the total transmembrane resistance to material flow. Polysulfone (Udel 3500) ultrafiltration hollow fiber membranes were made using the "dry-wet" fiber spinning process through a tube-in-orifice spinnerette. By using a mixture of water and 1-methyl-2-pyrrolidone in various proportions as the internal coagulant, demixing rates of the polymer in the spinning solution could be adjusted to yield a more open surface structure in the fiber inner surface layer and a more porous sublayer in the fiber wall to reduce the total transmembrane resistance. The rate of polymer demixing can be related to the difference between the solubility parameter of the internal coagulant and that of the polymer. This difference can serve as a scale to indicate the coagulation power of the internal coagulant. At low coagulation power, fibers with a more open structure in the fiber wall and its inner surface could be made which yielded higher membrane flux due to the lower transmembrane resistance in these fibers [3]. Preparation of polyvinylidene fluoride (PVDF) asymmetric hollow fiber membranes was studied by introducing small mol. additives, which include non-solvents (water, ethanol and 1-propanol) and inorganic salt (LiCl) [4]. Water was used as an external coagulant, while water, ethanol or a mixture of water and ethanol was used as an internal coagulant. The effect of polymer concentration, non-solvents, the mixture of non-solvent and LiCl, internal coagulant and post-treatment was studied in details. Polyethersulfone (PES) asymmetric hollow fiber membranes with

excellent gas separation properties were fabricated from spinning solutions containing PES, N-methyl-2-pyrrolidone (NMP) and water by Wang et al [5]. The internal coagulants used include water, EtOH, i-PrOH, EtOH/water and i-PrOH/water. Effects of various spinning conditions including polymer concentration, length of air gap, non-solvent strength of the internal coagulant and post-treatment, on the permeation properties and structures of the resulting hollow fibers were investigated. They found that the use of an internal coagulant with a moderate non-solvent strength improves hollow fiber integrity and suppresses macrovoid formation. Polyvinylidene fluoride (PVDF) hollow fiber membranes were prepared by dry/wet and wet phase inversion methods [6]. In spinning these PVDF hollow fibers, dimethylacetamide (DMAc) and polyvinyl pyrrolidone (PVP) were used as a solvent and an additive, respectively. Water or ethanol was used as the internal coagulants. The effects of polymer concentration, air-gap, PVP mol. wt., PVP content in the polymer dope, and the internal coagulant on the permeation properties and membrane structures were examined. Highly permeable PVDF hollow fiber membranes could be prepared from a polymer dope containing low PVP molecular weight and using ethanol as the internal coagulant. Polysulfone hollow fiber membranes with high gas separation performance were prepared from N-methyl-2-pyrrolidone (NMP)/H<sub>2</sub>O and NMP/ethanol solvent systems by Wang et al.[7]. The internal

coagulants used include water, ethanol, 2-propanol, the mixture of water/ethanol and water/2-propanol. The effect of air gaps, the polymer concentration and the coagulation bath temperature on the membrane structure and gas permeation properties was investigated.

Rare work has been done to find the effect of internal coagulant concentration on the properties and separation performance of hollow

## 2. Experimental

### 2.1. Materials

PES in powder form as membrane material was obtained from Jida High Performance Materials Co. Ltd. (P.R. China). Reagent grade N-methyl-2-pyrrolidone (NMP-98%) was used as a solvent and ethanol used as a non-solvent additive (NSA) as well as PEG 10,000MW, PEG 20,000MW, PVP 40,000MW, and PVA 78,000MW used as a solutes for UF experiments were obtained from Shanghai Chemical Agent Company (P.R. China).

2.2. Preparation of polymer solution, hollow fiber membranes and modules  
Ethanol as non-solvent additive was mixed separately with NMP in glass bottle. Dried PES added into the mixture in the bottle and mixed until the solution became homogeneous. Hollow fiber PES membranes were spun at room temperature employing the wet-spinning method, described elsewhere [8,9,10,11]. Tables 1 and 2 summarize process parameters, spinning conditions and outer diameter/inner diameter dimensions of the fabricated hollow fiber membranes. The ratio of dope flow rate to bore fluid flow rate was constant in all spinning processes. All

fiber UF membranes. In this study, an attempt is made to study the effect of ethanol concentration in internal coagulant on characterization and performance of PES hollow fiber UF membranes fabricated using wet spinning process. PES UF experiments are conducted using pure water, polyethylene glycol (PEG 10,000 and 20,000MW), PVP 40,000MW and PVA 78,000.

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 coagulation bath. The coagulation bath and bore fluid were maintained at room temperature. The fabricated hollow fibers were stored in the water bath for 24 h to remove the residual NMP. After this period, the fibers were kept for a post-treated in a 50 wt.% glycerol aqueous solution for 24 h 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 24 cm. The shell sides of the two ends of the bundles were glued into two stainless steel tees using a normal-setting epoxy resin. 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.

### 2.3. Measurements of permeation flux and rejection

Hollow fiber PES UF experiments were done employing the solute–water membrane separation unit described elsewhere [12]. 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), were obtained as follows:

$$J = \frac{Q}{A} \quad (1)$$

where J= water permeation flux of membrane (L/m<sup>2</sup> h bar), Q= volumetric flow rate (L/h),  $\Delta P$  = transmembrane pressure drop (bar), A = membrane surface area (m<sup>2</sup>).

PEG, PVP and PVA of 0.05 were used for the measurement of solute rejection of each hollow fiber module and to realize the separation efficiency for different molecular weights. The membrane rejection R (%) is defined as

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

where C<sub>f</sub> and C<sub>p</sub> represent the solute concentration in feed and separated solution, respectively. The concentration of polymer is measured by a TOC-VCPH Analyzer (Shimadzu, Japan), respectively.

### 2.4. 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 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 ethanol concentration in internal coagulant on the PES hollow fiber membrane morphology

Polyethersulfone (PES) hollow fiber membranes were prepared from PES/Ethanol/NMP (18:10:72) dope solution with different ethanol concentrations in internal coagulant (30-60 and 100wt %) and water alone was used as the external coagulant.

Scanning electron microscope (SEM) of the PES internal surfaces with different ethanol concentrations in internal coagulant were shown in Fig. 1. It can be seen that the internal surface of the PES membranes were dense and smooth with increase of ethanol concentration from 30 to 50wt% (Membrane nos.2-4). Pores on the internal surface were too small to be observed. It seems that the ethanol concentration in internal coagulant up to 50 wt% had a little effect on the internal surface because water was a strong solvent. While the cracks phenomenon was appear on the internal surfaces of PES hollow fiber membrane with increase of ethanol concentration up to 100wt % (pure ethanol) (Membrane nos.5 and 6). The crack formation on the internal membrane surfaces appeared during of membrane drying in air at room temperature; due to the effect of

surface tension force which is depends on the forces of attraction among the particles of water itself and with the particles of hollow fibers with which it comes in contact [13].

Figs. 2 and 3 show the structures of external surfaces and cross-sectional scanning electron microscope (SEM) pictures of hollow fiber PES membranes fabricated with different ethanol concentrations of the internal coagulant. In Fig. 2, the external surfaces for all of the PES membranes (Membrane nos.2-6) are smooth and dense because water is used as external coagulant and the dense skin layer is formed due to instantaneous liquid-liquid demixing process because water is a strong solvent. While in Fig. 3, it can be seen that, the cross-section of PES hollow fiber was double-layer finger like structure as well as inner and outer skins. Meanwhile, there is no change observed in the cross-section of PES hollow fiber with increase of ethanol concentration in the internal coagulant. 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.

### 3.2. Effect of ethanol concentration in internal coagulant on the separation performance of PES hollow fiber membranes

Permeation fluxes and solutes rejection for PES hollow fiber membranes fabricated according to the conditions listed in Table 1 are illustrated in Table 3, Fig.4 and Fig.5. It can be seen that, when increasing the ethanol concentration in internal coagulant from 30 wt% up to 50 wt%,

pure water permeation flux of the PES hollow fiber membranes decreased from 39 to 23.3 L/m<sup>2</sup>.h.bar, whereas rejections of PEG, PVP, and PVA increased. These results were supported by the respective morphologies mentioned in the previous section because the PES hollow fiber membrane spun with 30-50 wt% ethanol concentration in internal coagulant had smaller pore size and denser skin, which resulted in lesser permeation flux and higher solute rejection. It might be suppose that, when increasing the ethanol concentration in internal coagulant, the exchange rate of solvent and non-solvent through the diffusion process increased, and instantaneous liquid-liquid demixing process increased. The polymer concentration in the polymer rich phase increased, resulting in fast solidification process, which leads to reduce the pore size and dense skin formation. While an additional increase of ethanol concentration in internal coagulant cause increase the permeation flux of the hollow fiber membranes, whereas rejections of solutes decrease. This is due to reduce the exchange rate of solvent and non-solvent through the diffusion process, and then, reduction of the rate solidification process, in addition to the cracks phenomenon on the surface of the PES hollow fiber membranes (Membrane nos. 5 and 6) as reported by Xu and Qusay [13]. Besides, comparison was made between the effect of pure water (from previous work) and ethanol solution as internal coagulant on membrane separation performance. It can be said that, the effect of internal coagulant using pure water on the PES

membrane performance in the previous work is better than the ethanol solution as internal coagulant as shown in Table 3, Fig.4 and Fig.5 [12]. Fig.6 shows the effects of ethanol concentrations on the solute rejection of PES hollow fiber membranes as a function to the solute molecular weight. It can be seen that with increase of ethanol concentration in internal coagulant, the solute rejection decrease. This is due to increase of pore size of the internal surfaces of PES hollow fiber membrane in addition to the cracks phenomenon appear on the internal surfaces with increase of ethanol concentration in internal coagulant. While, using pure water as internal coagulant, the solute rejection was high because water is a strong solvent. Based on the preparation method in this case, 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 40,000 MWCO as shown in Fig.6.

#### 4. Conclusions

Polyethersulfone (PES) hollow fiber UF membranes were spun by wet phase inversion process. The polymer

solutions were prepared from 18 wt% of PES in 72wt.% NMP as a solvent using ethanol as additive. SEM images illustrated that PES membrane morphology were dense and smooth with an increase of ethanol concentration from 30 to 50 wt.% in the internal coagulant. While the cracks phenomenon was appear on the internal surfaces of PES hollow fiber membrane with increase of ethanol concentration up to 100 wt.% (pure ethanol). The external surfaces for all of the PES membranes are smooth and dense because water is used as external coagulant; moreover, there is no change observed in the cross-section of PES hollow fiber with increase of ethanol concentration in the internal coagulant. Based on the preparation method in this work, 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 40,000MWCO.

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Table 1 Process parameters and spinning conditions of hollow fiber membranes  
prepared from PES/Ethanol/NMP (18:10:72) dope solution

Fiber No.	Bore fluid composition	External coagulant	Air gap distance	Bore fluid flow rate (ml/min)	Dope pressure (MPa)	External coagulant temperature
1	0:100 EtOH/H <sub>2</sub> O	Water	0 (wet spun)	1.3	0.1	25 °C
2	30:70 EtOH/H <sub>2</sub> O	Water	0 (wet spun)	1.3	0.1	25 °C
3	40:60 EtOH/H <sub>2</sub> O	Water	0 (wet spun)	1.3	0.1	25 °C
4	50:50 EtOH/H <sub>2</sub> O	Water	0 (wet spun)	1.3	0.1	25 °C
5	60:40 EtOH/H <sub>2</sub> O	Water	0 (wet spun)	1.3	0.1	25 °C
6	100:0 EtOH/H <sub>2</sub> O	Water	0 (wet spun)	1.3	0.1	25 °C

Table 2 Resulting dimensions of PES hollow fiber membranes

Fiber No.	Internal Diameter (μm)	External Diameter (μm)	Wall Thickness (μm)
1	683	1056	186.5
2	571	956	192.5
3	608	989	190.5
4	559	1031	236
5	571	962	195.5
6	584	994	205

Table 3 Permeation flux and solute rejection of PES hollow fiber membranes

Fiber No.	Permeation Flux (PWP) (L/m <sup>2</sup> hbar)	Rejection (%)			
		PEG 10,000 M <sub>w</sub>	PEG 20,000 M <sub>w</sub>	PVP 40,000M <sub>w</sub>	PVA 78,000M <sub>w</sub>
1	92.4	87.4	89.8	94	99
2	39	65.5	69	91	99
3	33.5	67	70	90.6	99
4	23.3	70	73	91.6	99
5	37.2	65	72.6	86	99
6	65.4	60	73.5	78.5	99



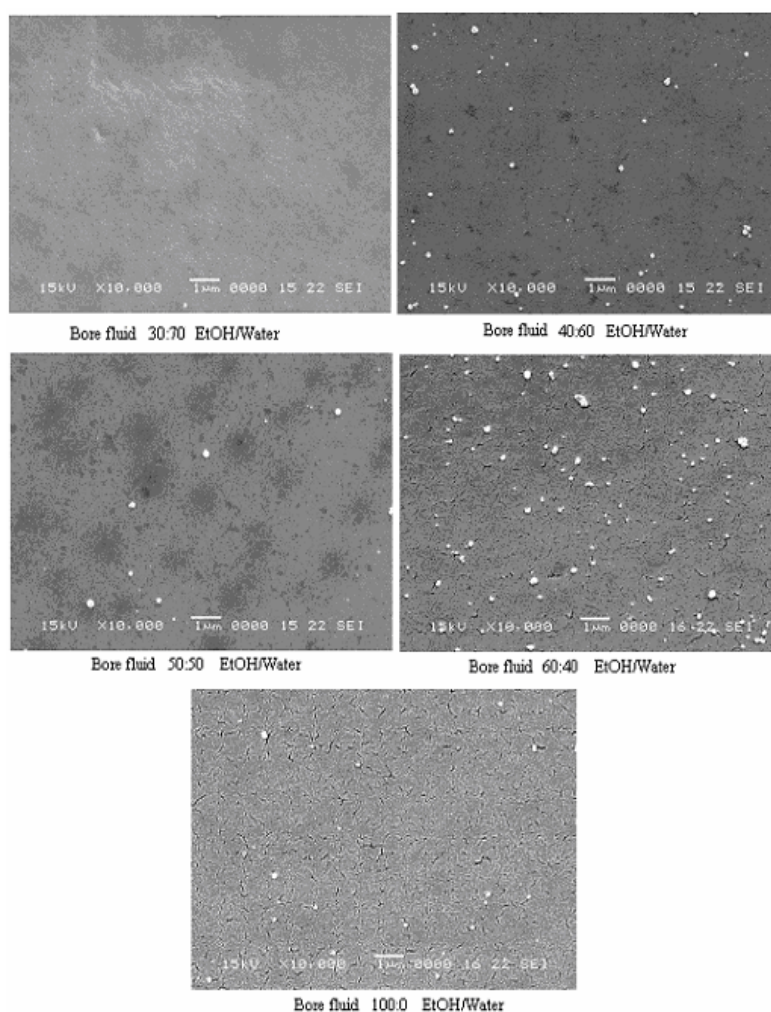


Fig. 1 Scanning electron micrographs of the internal surface of wet spun PES hollow fiber membrane with different EtOH/water composition as internal coagulant ; (original magnification: 10,000×)

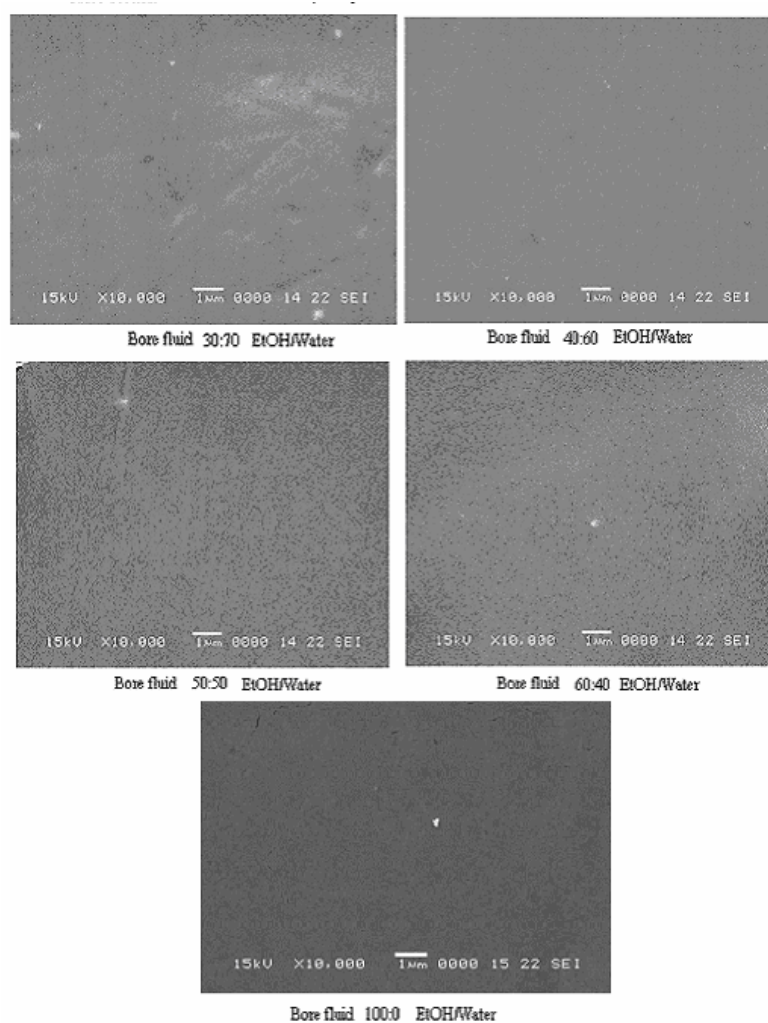


Fig. 2 Scanning electron micrographs of the external surface of wet spun PES hollow fiber membrane with different EtOH/water composition as internal coagulant ; (original magnification: 10,000×)

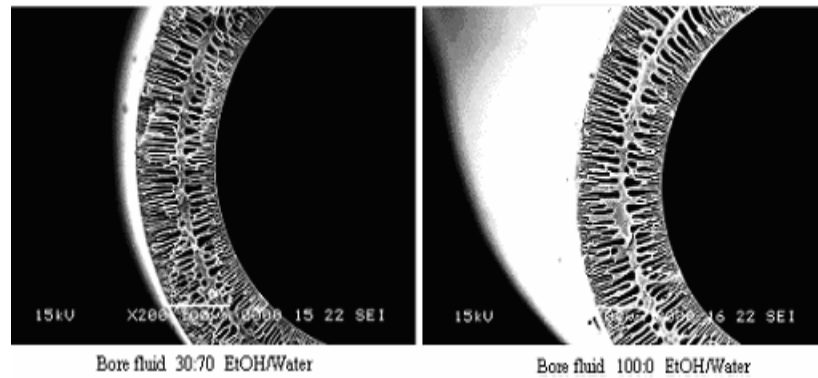


Fig. 3 SEM cross-sectional structures of PES hollow fibers wet using internal coagulant composition as 30:70 and 100:0 EtOH/water ;( original magnification: 200×).

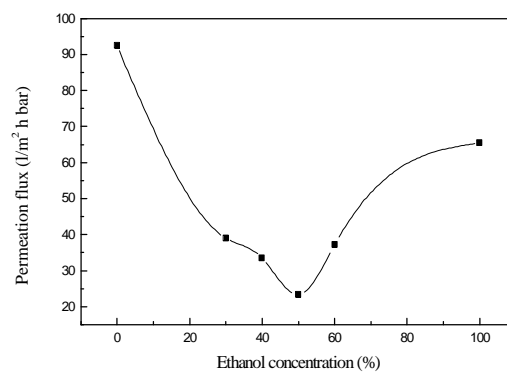


Fig. 4 Effects of ethanol concentrations in internal coagulant on the pure water permeation flux (PWP) of PES hollow fiber membranes

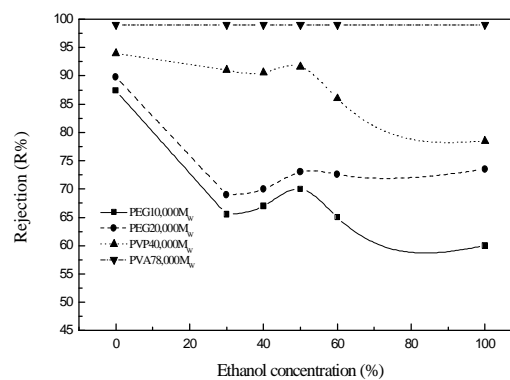


Fig.5 Effects of ethanol concentrations in internal coagulant on solute rejection of PES hollow fiber membranes

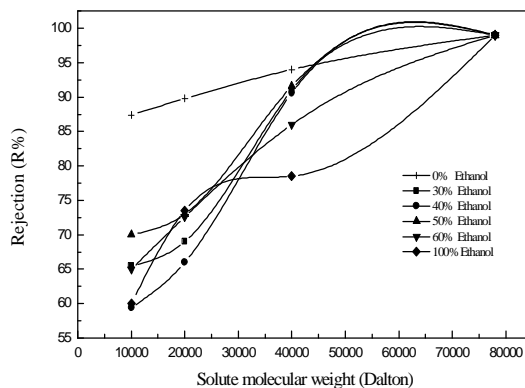


Fig.6 Effects of ethanol concentrations on the solute rejection of PES hollow fiber membranes

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