



## Research Paper

## Fabrication of Crosslinkable Hollow Fiber Membranes for Pervaporation Dehydration

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## Highlights

- A new type of crosslinkable integrally-skinned asymmetric hollow fibers were developed.
- The material for the hollow fibers is Polyetherimide/Polyvinyl alcohol blend.
- The external coagulant composition has influence on the hollow fiber performance.
- Chemical crosslinking using maleic acid dissolved in water enhances the separation factors of the hollow fibers.
- Chemical crosslinking was confirmed by FTIR and XPS analyses.

## Abstract

Integrally-skinned asymmetric Polyetherimide/Poly (vinyl alcohol) (PEI/PVA) hollow fiber membranes for pervaporation dehydration were fabricated by non-solvent induced phase inversion. PVA inside the PEI matrix could be crosslinked to provide membrane performance stability during long term operation. The effects of different PEI/PVA blend ratio, external coagulant type and flow rate, and crosslinking conditions on the membrane structure and the separation performance were investigated. Generally, hollow fibers using PEI/PVA blend are less selective than those of neat PEI, probably due to the defects evolved between PEI and PVA. The influence of coagulant type on membrane pervaporation performance was specific to dope formulation; when using n-butanol as external coagulant, the higher the coagulant flow rate, the better the membrane separation performance. PVA crosslinking by maleic acid (MA) enhanced the membrane performance, obviously. PEI/PVA Hollow fibers formed using n-butanol as external coagulant obtained a separation factor of 28 after crosslinking, much better than 4.4 with the original one. The crosslinked membrane exhibited higher stability than the neat PEI membrane. The separation factor of the latter degraded by more than half after around 200 h operation. Finally, this work has provided a new approach for fabricating crosslinkable asymmetric membrane suitable for pervaporation dehydration.

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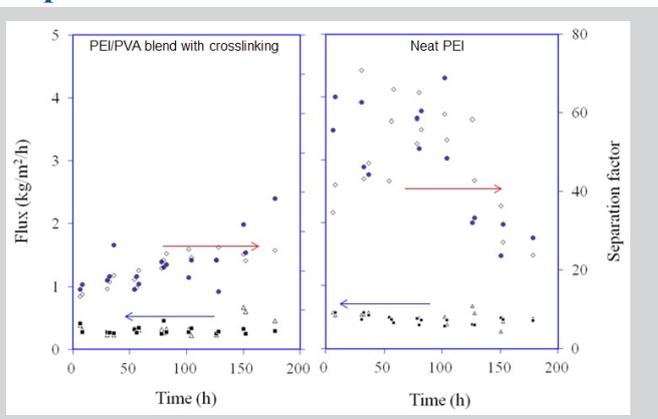
## 1. Introduction

Pervaporation, which was first proposed by Kober in 1917 [1], is a very promising separation technology for molecular level liquid/liquid separation. Compared with other separation methods for similar purpose, such as solvent extraction, distillation and adsorption, pervaporation has the advantages of energy efficiency, environmental friendliness, convenient operation, etc. [2-6]. Being a relatively new technology among the commercialized ones, pervaporation is considered to be a promising substitute for "rectification". At present, the applications of pervaporation mainly cover dehydration of

organic compounds, recovery of valuable organics, and organic/organic separations. Among them, the organic dehydration [7-9], especially alcohols dehydration [4, 10-14], is already widely used at industrial level. A very important aspect regarding alcohol dehydration using pervaporation is that it can break azeotropic point, which it can be translated to save energy [15].

Anisotropic membranes dominate the commercial membrane market, due to the ultra-thin function layer and hence lower resistance toward mass transfer. A comparison of different membrane structures indicates that

## Graphical abstract



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integrally skinned membranes by phase inversion excel the others in its simple formation and integrity of multinary structures. Nevertheless, a critical problem identified with this type of membranes when applied in pervaporation is feed-induced swelling, which will finally reduce the membrane to be non-selective [16]. Addressing the challenge, many methods such as thermal treatment, chemical crosslinking, etc., are employed to tune the physical and chemical characteristics of membranes for promoting the selectivity and/or resistance to chemical attack and plasticization. In dehydration of 85 wt.% isopropanol aqueous solutions, the integrally skinned P84 co-polyimide hollow fibers obtained a separation factor of more than 10,000 after thermal treatment at 300°C [17]. For Matrimid polyimide asymmetric hollow fibers [18], it is found that an increase in the degree of cross-linking by 1, 3-propane diamine (PDA) resulted in a rise in separation factor and a decrease in flux. However, most of the commercially available polymers suitable for asymmetric membrane formation are not ready for direct crosslinking as purchased. In addition, chemical crosslinking can lead to fragility for membranes made of some polymers (e.g. polyimide).

Polymer blend is another choice that has been investigated intensively and extensively to produce new and versatile materials [19-27]. PVA is a highly hydrophilic polymer and has hydroxyl groups for chemical crosslinking [28-33], which are highly useful for achieving sound and stable performance in pervaporation. Free-standing PVA membrane lacks sufficient mechanical strength. Construction of composite structure using mechanically strong support is an established approach that gives full play to its potential in dehydration of alcohols and other solvents. Another direction attracting attention is polymer blend [34-37]. Notwithstanding, polymers that are miscible with PVA and at the same time possess good membrane formation property and reasonable mechanical strength are few. Therefore, researches adopting PVA in blend for pervaporation membrane are almost unanimously about flat dense films or composite structure [38]. In effect, investigations focusing on integrally-skinned asymmetric membranes of polymer blends for pervaporation are very few. Probably, the only work in recent years was reported by Teoh et al. [39]. In their work, Torlon and Torlon/P84 blend single-layer hollow fibers have been prepared by phase inversion for isopropanol dehydration. It was found that both neat Torlon and blended membrane have poor membrane separation performances, due to the extensive swelling. Chemical cross-linking by diamine was then used to stabilize the pervaporation performance.

Undoubtedly, new way to conduct crosslinking of asymmetric membranes is needed. In current research Polyetherimide/Poly (vinyl alcohol) (PEI/PVA) blend is employed to fabricate integrally-skinned asymmetric pervaporation hollow fibers for alcohol dehydration. PEI is a kind of glassy polymer which has good engineering feasibility, flexibility in film formation and excellent mechanical strength [40-41]. Membrane of PEI has already been used for molecular-level gas separation [41]. The blend of PEI and PVA, combined with crosslinking as membrane post-treatment is expected to synergize the advantages of respective materials to produce single-layer asymmetric membrane with sufficient structural strength and stable pervaporation performance. The two polymers are partially miscible and stable solutions can be maintained. Phase separation blend has been investigated by Kanjilal et al. for pervaporation [42]. Based on PEI/PVA blend, this research will investigate the effect of following factors on hollow fiber separation properties: the PEI/PVA blend ratio, the external coagulant type, the flow rate of first external coagulant in dual-bath mode, and finally the cross-linking conditions.

## 2. Experimental

### 2.1. Materials

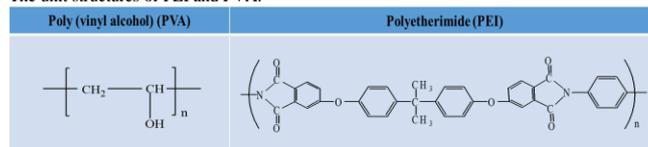
Commercial PEI was from Saudi Basic Industry Corp (SABIC). PVA (T-350, Mw 800,000) was purchased from Nippon Synthetic Chemical Industry Co. Ltd. Both polymers were dried at 100 °C for 12 h in vacuum oven prior to be used. The formulae of the unit structures for PEI and PVA are shown in Table 1. *N*-methyl-pyrrolidinone (NMP) (Hushi, MW 99.13g/mol), *n*-butanol (Hushi, MW 74.12g/mol), methanol (Hushi, MW 32.04g/mol), and hexane (Hushi, MW 86.18g/mol) were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water is laboratory produced and tap water employed in membrane fabrication.

### 2.2. Preparation of hollow fiber membranes

The dope preparation and hollow fibers fabrication were mainly following the procedures in Jiang and Song's work and Zhu et al.'s work [43-44]. The compositions for dopes and coagulants are shown in Table 2(a). Firstly, a specific amount of solvent NMP is measured and fed into a three-

neck bottle. Thereafter the polymer powders with a specific mass determined according to the dope formulation designed are added into the solvent at temperature of 95 °C. PEI was first dissolved, followed with PVA followed with mechanically stirring the solutions for 24 h. The homogeneous dope solutions generated are then transferred to the feed tank of spinning line and degassed for 12 h. The fabrication conditions of PEI/PVA hollow fiber membranes are displayed in Table 2(b). In hollow fiber spinning, the polymer dopes and the 1<sup>st</sup> external coagulant are driven by metering gear pump and syringe pump, respectively to the tube-in-orifice spinneret. The polymer solution gets in contact with the 1<sup>st</sup> coagulant upon its coming out from the spinneret, and goes through an air gap before immersing into the 2<sup>nd</sup> external coagulant. Phase separation is triggered by both internal and external coagulants. The freshly spun fibers are put into water bath and washed for at least three days to remove the residual solvent; replacement of fresh water is carried out every day. Subsequently, solvent exchange is performed using methanol soaking three times, followed by hexane soaking three times, each time 30 minutes. Finally, the membranes are dried naturally in air.

**Table 1**  
The unit structures of PEI and PVA.



**Table 2(a)**  
The dope and coagulant compositions.

ID	Dope Composition	External coagulant		Bore fluid
	Inner-layer	First	Second	
HF1	PEI/NMP (22/78wt. %)			
HF2	PEI/PVA/NMP (21.78/0.22/78 wt. %)	W: water B: n-butanol	Water	NMP/water (85%/15%)
HF3	PEI/PVA/NMP (21.12/0.88/78 wt. %)			

**Table 2(b)**  
Hollow fiber fabrication conditions.

Parameters	Values
Dope flow rate ( ml/min )	2 ml/min
Bore flow rate ( ml/min )	1
Take up rate ( cm/min )	6±0.5
Room temperature ( °C )	20

### 2.3. Hollow fiber crosslinking

For post-treatment, Maleic acid (MA) is used as the crosslinking agent [45-46]. About 2 wt. % MA solution is prepared using water or ethanol as solvent. Table 3(a) summarizes the crosslinking conditions of the hollow fiber membranes. The PEI/PVA hollow fiber membrane are soaked in the MA solutions for 4 h, at 60 or 90 °C. Thereafter, they taken out and air dried at room temperature. The schematic for the reaction between PVA and MA is illustrated in Figure 1.

**Table 3(a)**  
The crosslinked conditions of hollow fiber membrane.

Crosslinking solution A	Crosslinking solution B	Crosslinking duration ( hr )	Crosslinking temperature ( °C )
2% MA in ethanol	2% MA in water	4	60, 95



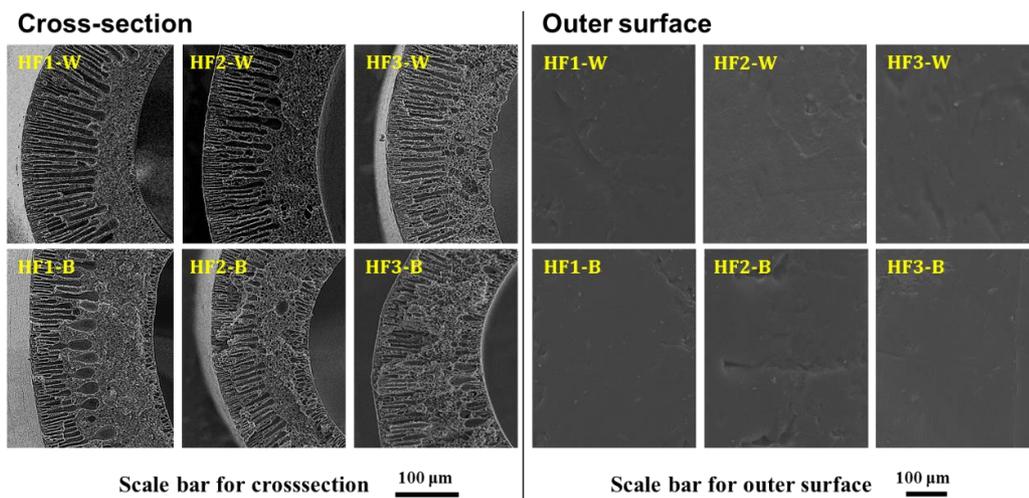


Fig. 3. SEM images showing the cross-section and external surface morphologies of the hollow fiber membranes.

The XRD patterns of pure PVA, PEI and their blend are shown in Figure 4. The pure PVA shows a strong and sharp peak at  $2\theta$  of  $20^\circ$ , and two weak peaks at  $2\theta$  of  $11.0^\circ$  and  $40^\circ$ , respectively. They correspond to d-space of 2.52 Å, 7.81 Å and 5.11 Å, respectively. The pure PEI has a characteristic peak centering at  $2\theta$  of  $22^\circ$  and a relatively broad shoulder peak around  $2\theta$  of  $18^\circ$ , indicating d-space of 3.93 Å and 4.80 Å.

For the blend, the peaks of PVA are no longer obvious anymore, due to its low concentration inside the membrane. Comparison of the four spectra confirms that the relative intensity of the PEI characteristic peaks for the blend has been depressed slightly as compared with that of pure PEI. In addition, the shape of the shoulder with blend containing 4% of PVA is different from that with pure PEI, with the acme shifting to a higher  $2\theta$  value of  $20^\circ$ . These observations indicate that the two polymers have mutually affected each other in their polymer chain packing.

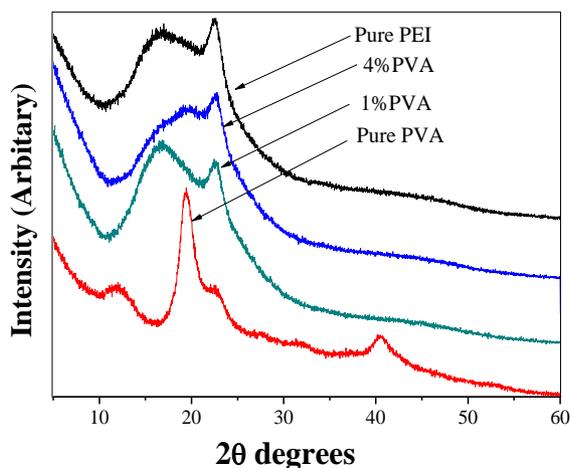


Fig. 4. The XRD patterns of PVA, PEI and their blend.

Figure 5(a) shows the FT-IR spectra of neat PVA, PEI and PEI/PVA blend hollow fiber before and after crosslinking. The spectrum of PVA is characterized of a series of absorption peak; the one at around  $2945\text{ cm}^{-1}$ , is attributed to  $\nu_a(\text{CH}_2)$  [53]. For hydroxyl group (-OH), there exists a characteristic peak at around  $3385\text{ cm}^{-1}$ . As for the spectrum of PEI, it exhibits characteristic absorptions for imide group at 1778 and  $1743\text{ cm}^{-1}$ , indicating carbonyl asymmetrical and symmetrical stretch, respectively. The peaks at  $1357$  and  $744\text{ cm}^{-1}$  indicate the stretching and bending properties of imide C-N group. The absorption for aromatic ether group (C-O-C) is

positioned at  $1238\text{ cm}^{-1}$  [54]. With enhancing the concentration of PVA in the blend, the peaks between  $3300\text{--}3400\text{ cm}^{-1}$  and at around  $2940\text{ cm}^{-1}$  become more apparent.

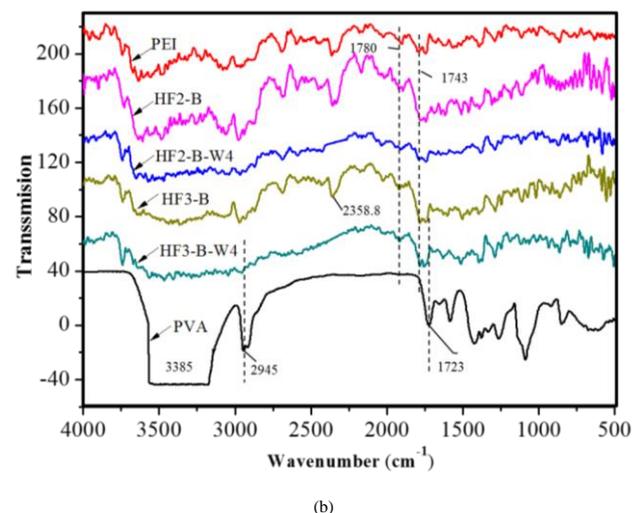
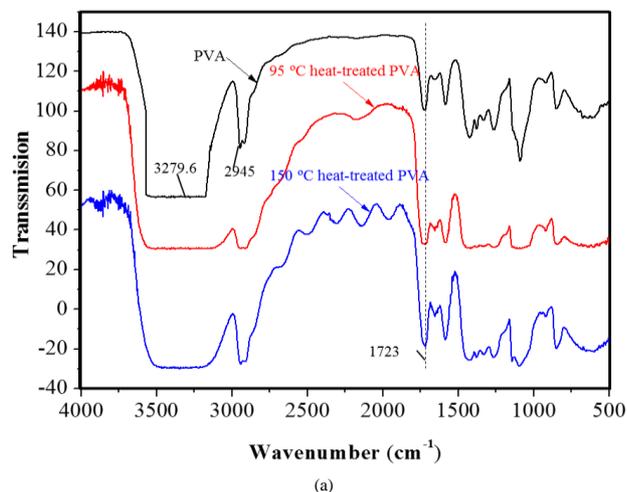


Fig. 5. (a) The FT-IR spectra of PVA, 95 °C heat-treated PVA and 150 °C heat-treated PVA, (b) The FT-IR spectra of PEI, PVA and their blend crosslinking membrane.

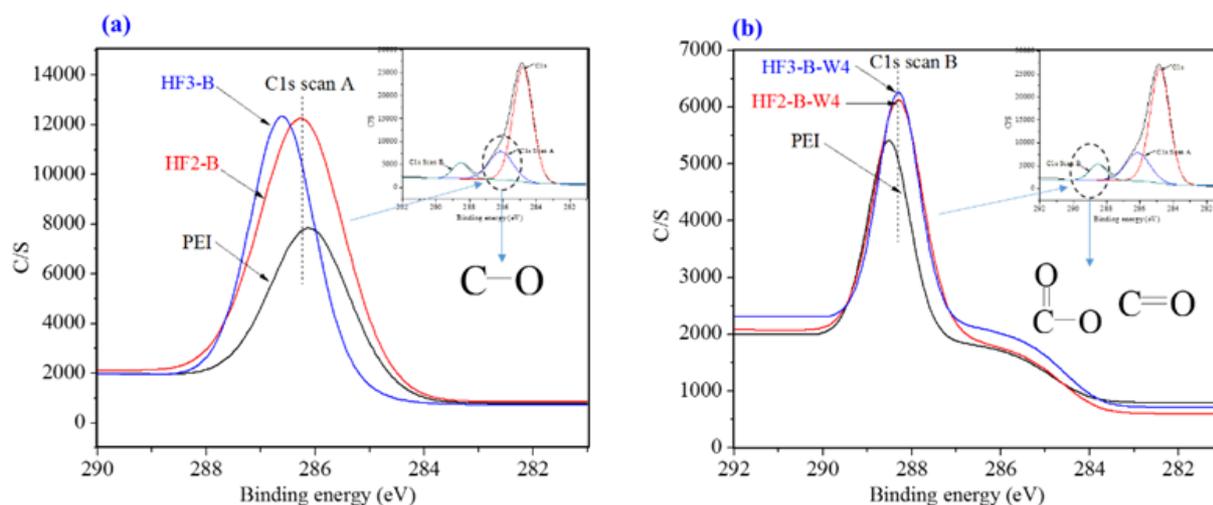


Fig. 6. XPS analysis for (a) PEI membrane and hollow fibers HF2-B and HF3-B; (b) PEI membrane and crosslinked hollow fibers HF2-B-W4 and HF3-B-W4.

With crosslinking, only very trivial change occurs with HF3-B. The broad peak around  $3385\text{ cm}^{-1}$  was flattened, which may indicate that OH groups reacted with MA to form new structures. In order to further prove the feasibility of the crosslinking approach used in this study, two indirect characterizations are used: FTIR characterization of pure flat membrane with embedded MA to confirm that  $95^\circ\text{C}$  w/o catalysis can trigger crosslinking; XPS analysis of C-O, carbonyl group (C=O) and ester (CO-O). The flat membranes were prepared according to research by Guan et al. [33]. As shown in Figure 5(b), the intensity of the absorption at  $1725\text{ cm}^{-1}$ , typical to the CO-O band became stronger with thermal treatment at both temperatures. This implies that the two temperatures have the ability to cause crosslinking. The XPS curves in Figure 6 also reveal some information. For hollow fibers HF2-B and HF3-B, the oxygen (O) characterized of C-O group obtains higher peak intensity; after crosslinking, the peaks representing the O element of CO-O and C=O become higher. These findings suggest that PVA has been retained inside hollow fiber during fabrication and the crosslinking was actualized.

### 3.2. Hollow fiber pervaporation performance

#### 3.2.1. Effect of PVA content

The pervaporation performance of hollow fiber membranes with different PVA loading inside the polymer matrix is shown in Figure 7, for solely using water as external coagulant. The feed temperature is set at  $60^\circ\text{C}$  and volume flow rate is  $100\text{ L/h}$ . It is observed that neat PEI hollow fiber presents a flux of  $0.3\text{ kg/m}^2\text{h}$ , while that for fiber with 1% of PVA is  $2.8\text{ kg/m}^2\text{h}$ . As for separation factor, the highest value is achieved with fiber containing 4% PVA, which is 9.6, and the lowest with 1% PVA, around 1.3; the neat PEI fiber exhibits an intermediate separation factor of 4.0 among the three.

For conventional polymer/organic solvent dope system, water is a strong coagulant with small molecular size. It can penetrate easily into dope solution and can induce instantaneous demixing. The skin in direct contact with coagulant will experience gelation and its shrinking is more severe as compared with the sublayer following different phase inversion mechanism. When polymer concentration is not high enough, the accumulated stress may trigger the evolution of cracks on the membrane surface. Therefore, the three types of hollow fibers present relatively low selective property.

Concerning fibers loaded with 1% of PVA, its much higher flux and lower separation factor might be attributed to the micro-phase separation leading to interfacial defects. When the content of PVA is raised to 4%, the number of hydrogen bonding present inside the polymer solution is possibly big enough to facilitate the enhancement of viscosity. Comparison of the three dope solutions shows that the viscosity of the polymer dopes with PVA is higher. The higher viscosity may kinetically deter the disentanglement of PEI and PVA polymer chains that cause micro-phase inversion.

In addition, more densely populated hydrogen bonding delivers higher cohesive energy for polymer matrix, probably resulting in higher resistance towards stress accumulated aforementioned during phase inversion [55]. It should also be noted that the hydrophilicity of PVA itself favors water transport. With all these factors, therefore, this batch of fibers HF3 is characterized of relatively higher separation factor.

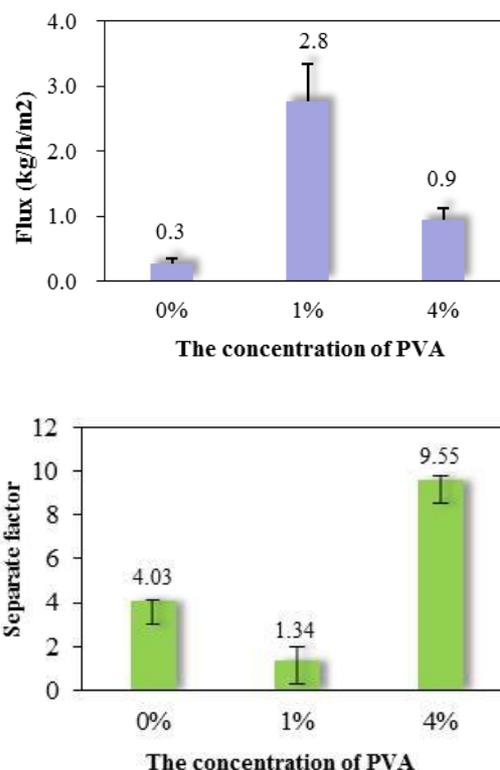


Fig. 7. The pervaporation performance of the hollow fiber membranes with different PVA content (The external coagulant is water and flow rate is  $1.0\text{ ml/min}$ ; the feed solution: ethanol/water (85/15 wt. %) mixture; the operating temperature:  $60^\circ\text{C}$ ).

#### 3.2.2. Effect of different external coagulant

Figure 8 displays the pervaporation performance of hollow fibers formed using *n*-butanol as the 1<sup>st</sup> external coagulant. Obviously the pattern for the relationship between performance and PVA loading is completely different from that observed in Figure 8. The neat PEI hollow fibers exhibit an average flux around  $0.55\text{ kg/m}^2\text{h}$ , and the flux for hollow fiber loaded with 1 and 4wt.% of PVA are  $0.46$  and  $1.19\text{ kg/m}^2\text{h}$ , respectively. As far as separation factor is concerned, the neat PEI hollow fibers have the best performance, much higher than those of the membranes blended with PVA.

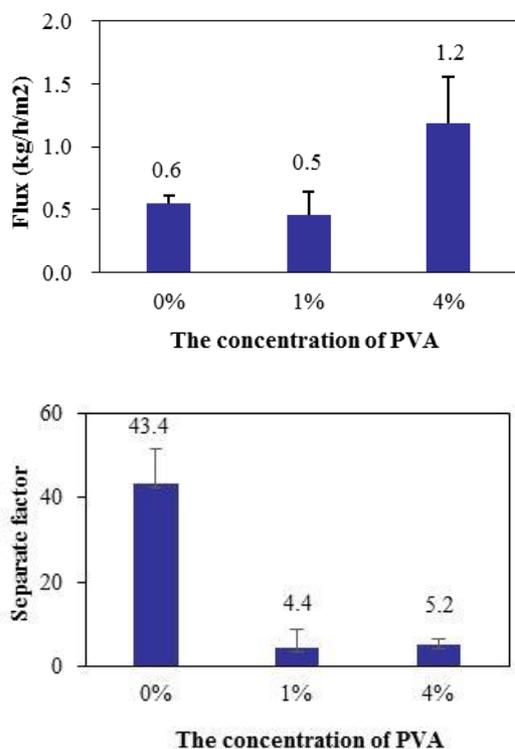


Fig. 8. The pervaporation performance of the hollow fiber membranes with *n*-butanol as external coagulant (the external coagulant flow rate is 1.0 ml/min. The feed solution: ethanol/water (85/15 wt. %) mixture; the operating temperature: 60 °C.)

As is known, *n*-butanol is a relatively weak coagulant for common polymer solutions. The solubility parameters for NMP, water, *n*-butanol, PEI and PVA are 47.8, 23.2, 28.0, and 39.1 MPa<sup>1/2</sup>, respectively. The closeness of *n*-butanol to PEI and NMP in terms of solubility parameter indicates that *n*-butanol will have smaller coagulation value than water for PEI/NMP dope. In addition, the kinetic diameter is 1.03 of *n*-butanol is larger than that of water; therefore, its penetration into and diffusion through the neat PEI dope of NMP is expected to be slower or intense. In other words, it will not induce instantaneous demixing and fast precipitation or glassification of polymer rich phase. Meanwhile, the outflow of NMP molecules from the dope into the thin external coagulant may happen in a faster manner than the inflow of *n*-butanol. This causes the enhancement of polymer concentration at dope/coagulant interface, hence favoring the formation of less defective skin. The different mechanisms between using water and *n*-butanol in the 1<sup>st</sup> coagulant is confirmed by the change of size, shape and number of finger-like macrovoids shown in Figure 3.

As far as PEI/PVA blend membranes are concerned, the physiochemical properties, principally the overall solubility parameters of the dope solutions, are expected to be dominated by PEI and NMP, the bulky components. Utilization of *n*-butanol as the 1<sup>st</sup> coagulant will not give rise to immediate phase separation for the bulk solution upon the contact of the two streams. In addition, further intensive micro-phase separation between PEI and PVA as compared with the original phase separation state in dope preparation probably doesn't happen, considering the weak interaction between PVA and *n*-butanol. In this regard, PVA/PEI hollow fibers formed using *n*-butanol should have better selectivity than with water. This expected phenomenon is registered with fiber loaded with 1wt.% of PVA. For 4wt.% loading, its original micro-phase separation is more severe; in addition, more defects may be evolved at the interface. The slower vitrification or precipitation of overall polymer matrix when using *n*-butanol as the 1<sup>st</sup> coagulant possibly allows the occurrence of differentiated shrinking of individual phase.

The curves for solutions analysis by DTS zetasizer are displayed in Figure 9. For neat PEI solution, the particle size is in the range of 5~50 nm with only one distribution peak. This peak is also observed with solutions loaded with PVA; nevertheless, some new peak appears. The change is attributed to the formation of new phase due to immiscible property of the two polymers. In addition, higher PVA loading is related with bigger size of particle (i.e. around 200~500nm). In Figure 10, the DSC curves of HF1-B and HF2-B are displayed. It can be found obviously that the  $T_g$  is higher than 210 °C, for the neat PEI hollow fiber HF1-B, For HF2-B, the  $T_g$  is slightly lower than 210 °C. This shift down in  $T_g$  after addition of PVA in the PEI matrix

may be the proof of partial miscibility of the two polymers.

AFM characterization is summarized in Figure 11. The angled views of the AFM reveal obvious difference in surface morphological. This further confirms the influence of formation condition and PVA content on the hollow fiber morphologies.

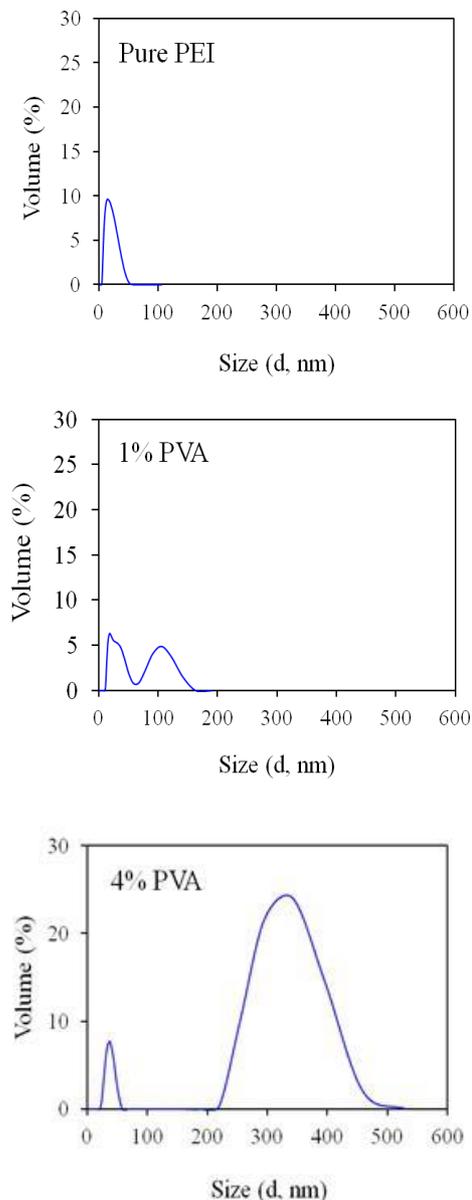


Fig. 9. Dope solutions characterization by Laser Light Scattering.

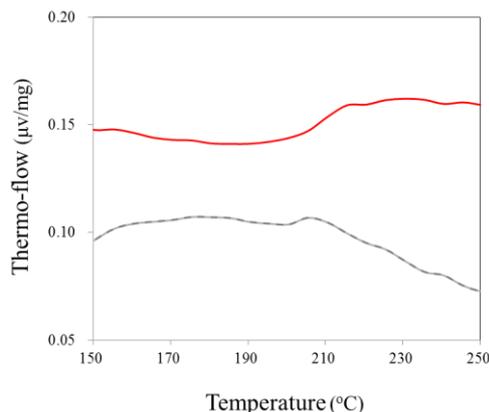


Fig. 10. DSC thermograms of HF1-B and HF2-B hollow fibers.

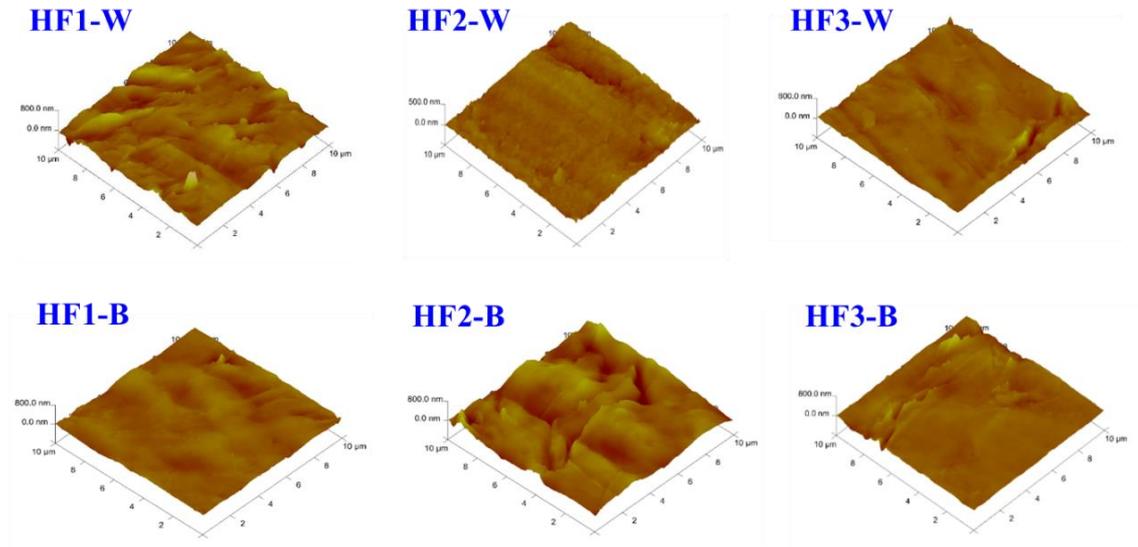
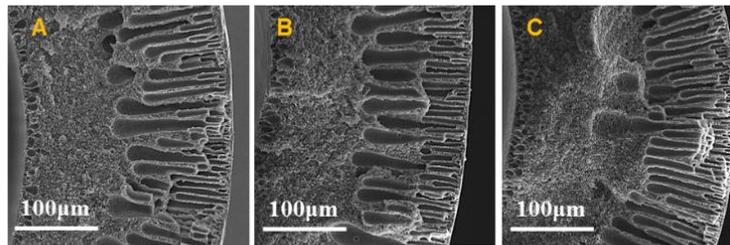


Fig. 11. 3D AFM view of the PEI and PEI/PVA blend membrane formed using different external coagulant.

**Cross-section:**



**Outer surface:**

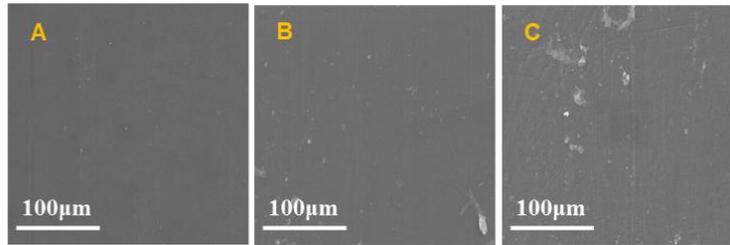


Fig. 12. SEM images HF1-B hollow fiber membranes in different external coagulant flow rate (A: 0.2ml/min; B: 0.5ml/min; C: 1ml/min).

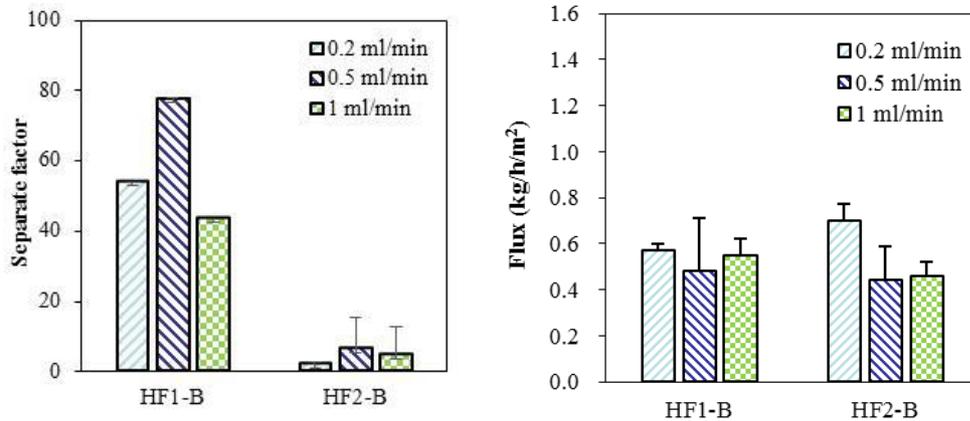


Fig. 13. The pervaporation performance of hollow fibers HF1-W, HF1-B, and HF2-B formed with different flow rate of 1st coagulant (The feed solution: ethanol/water (85/15 wt. %) mixture; the operating temperature: 60 °C).

**Table 3**

The flux and the separation for the PEI/PVA hollow fiber membranes with different crosslinking conditions ( The feed solution: ethanol/water (85/15 wt. %) mixture; the operating temperature: 60 °C).

Crosslinking solution	Crosslinking duration (h)	Crosslinking temperature (°C)	HF2-W		HF2-B		HF3-W		HF3-B	
			Flux (kg/m <sup>2</sup> /h)	Separation factor						
2% MA in ethanol	4	60	-	-	0.33	11.2	-	-	-	-
2% MA in water	4	95	3.4	1.0	0.36	28.7	0.61	17.4	1.2	9.7
		60	-	-	0.53	18.6	-	-	-	-

The effect of the external coagulation flow rate on membrane performance is also investigated. Three *n*-butanol flow rate selected are 0.2 ml/min, 0.5 ml/min, 1 ml/min.

Figure 12 exhibits the FESEM images of the surface and cross-section morphologies for these hollow fiber HF-1. It is observed that there exist some differences in the morphology. With higher flow rate of *n*-butanol, the finger-like macrovoids becomes shorter and narrower. No obvious difference is observed with the external surface. The performance of these hollow fiber are compared in Figure 13. It seems that the intermediate flow rate delivers higher separation factor, but has no patterned influence on the flux. It is thought that higher flow rate may prolong the effect of *n*-butanol on membrane formation, due to the thicker *n*-butanol layer attaching to the external surface of the freshly extruded hollow fiber.

### 3.2.4. Effect of crosslinking

The performance of PEI/PVA hollow fibers with different crosslinking conditions are tabulated in Table 3(a). Two different solvents (i.e. water and ethanol) for MA and two temperatures (i.e. 60 and 95 °C) are selected for the crosslinking. As could be observed, crosslinking does not improve the performance of HF1-W, probably due to its more defective selective structure. The other hollow fibers show different degree of enhancement in their separation properties towards the crosslinking treatment. The separation factor of HF2-B is raised from around 4.4 to 28.7, when crosslinked with MA aqueous solution at 95 °C for 4 h, and that for HF3-W from about 9.8 to 17.4 under the same conditions. The reason for the performance change may be that the crosslinking has tightened the overall membrane skin layer structure. In addition, it probably acts as a sealing procedure to remove or reduce the defects.

The data in Table 3(b) implies as well that MA aqueous solution is more efficient in promoting membrane performance. Water has smaller diameter, compared with ethanol; its solubility parameter is closer to that of PVA additionally. With these conditions, it is easier for water to approach the PVA structure and cause swelling, which paves the way for MA molecules accessing PVA chain and inducing crosslinking. It is also found that 95 °C generates higher degree of performance increase than 60 °C. At elevated temperature, the thermal motion of the polymer chains becomes more intensive, which has two aspects of impact. Firstly, the more open interstitial space inside the polymer matrix presents lower resistance towards penetration of crosslinking solution; secondly, the more flexible polymer chains have the tendency to relax and rearrange. Both changes are leading to densified chain packing favoring preferential transport of smaller molecules.

### 3.3. Long term pervaporation performance

For industrial applications, it is necessary that membrane can perform consistently over an extended period of time. A longer operational life of a membrane means reduced operating cost and enhanced economic feasibility of the pervaporation process. Among all the hollow fibers, the HF2-B-w4 and PEI exhibit more sound pervaporation performance, and are singled out for this test. Figure 14 shows the result of their long-term operation in pervaporation dehydration of 85 wt.% ethanol/H<sub>2</sub>O solution at 60 °C. The test terminated overnight with simply stopping the feed circulation and gas sweep. The modules were left mounted on the system without drying or other special treatment.

It is observed that both batches of hollow fibers maintained a relatively stable flux. Their separation factors, however, exhibit different variation pattern. For neat PEI membrane, its separation factor gradually degraded from around 50 to 20, during the 200-hr operation. In contrast, the HF2-B-w4 hollow fiber membranes show a relatively good stability in separation factor

during this long-term operation. This higher stability is very likely due to the crosslinking of PVA by MA. The slight enhancement in separation factors of the blend membrane during the pro-longed test is attributed to the thermal annealing that rearranges the polymer, compounded by the crosslinking of residual MA inside the membrane matrix. Table 4 summarizes the ethanol dehydration performance of different membranes. Obviously, the performance of the hollow fibers in this study is relatively low, which was attributed to the non-compatibility of the two types of membrane materials.

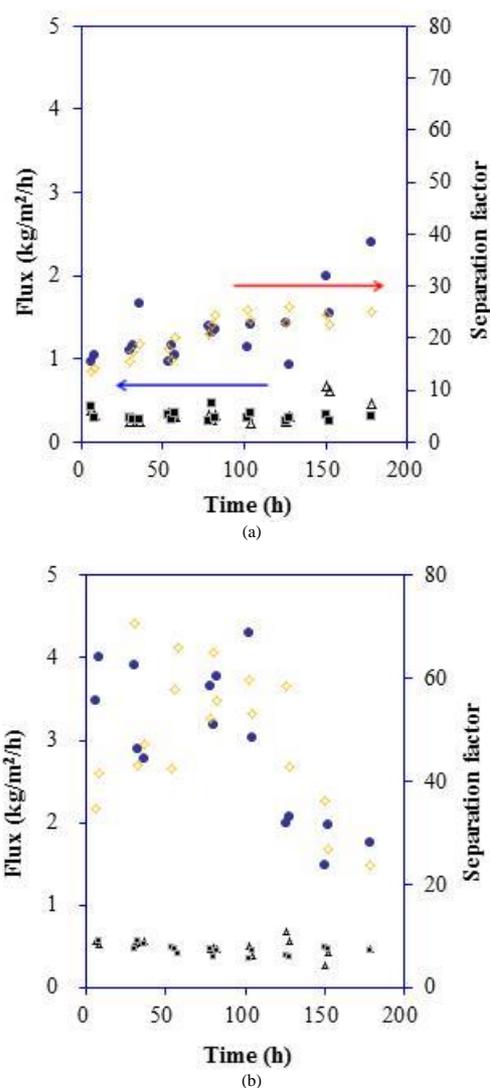


Fig. 14. The long-term pervaporation performance of hollow fibers in dehydration of 85 wt. % ethanol-H<sub>2</sub>O solution at 60 °C. (a) HF2-B-w4 membrane, (b): HF1-B.

**Table 4**  
PV Comparison of different membranes with current work in terms of performance for ethanol dehydration.

Membrane	Type	Feed composition H <sub>2</sub> O/Ethanol	Temperature (°C)	Flux (g/m <sup>2</sup> h)	Separation factor	Reference
PTFE-PVP	Dense	5.7/94.3 wt.%	25	1.59	18.4	56
PAN-PVP	-	5.9/94.1 wt.%	20	0.64	10.4	57
Composite PVA	Asymmetric	6/94 wt.%	50	0.6	28	58
PVA/PAN	Composite	20/80 wt.%	60	0.04	1320	59
PVA-g-ST/MA	Composite	50/50 wt.%	30	0.95	24	60
PVA-g-AN	-	50/50 wt.%	30	4	0.7	61
PEI/PVA crosslinking by maleic acid (MA)	Integrally-skinned asymmetric	15/85 wt.%	60	0.36	28.7	This study

#### 4. Conclusions

Hollow fibers of partially miscible PEI/PVA blend were fabricated for pervaporation dehydration. The effects of PVA loading, coagulant type and chemical crosslinking on the membrane performance were investigated. The results show that using weak coagulant (i.e. n-butanol) can significantly enhance the neat PEI hollow fiber performance. For blended membrane, the effect of external coagulant coordinates with PVA loading to determine the membrane performance. Due to the microphase inversion of the dopes, the separation properties of hollow fiber using blend is generally low. Chemical crosslinking using maleic acid dissolved in aqueous solution obviously enhances the separation factors of the PEI/PVA blend membranes by tightening the overall polymer matrix and reducing the defects. In addition, one batch of the crosslinked PEI/PVA blend membrane exhibits good stability during a 200-hr pervaporation test, while the separation factor of neat PEI hollow fiber gradually deteriorates in the same test. Future work will attempt to identify methods to enhance the miscibility of PVA with PEI.

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