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Exploring Torlon/P84 co-polyamide-imide blended hollow fibers and their chemical cross-linking modifications for pervaporation dehydration of isopropanol

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Abstract

A research study has been conducted to fabricate and chemically modify Torlon® 4000T and Torlon/P84 co-polyamide-imide blended hollow fibers as new materials for the dehydration of isopropanol (IPA). It has been found that Torlon/P84 blends are miscible, as confirmed through the single glass transition temperatures (T_g s) detected by differential scanning calorimetry (DSC). Both pure and blended hollow fibers fabricated from the dry-jet wet-spinning process do not show sufficient resistance to suppress water and IPA induced swelling, whereas cross-linked pure Torlon hollow fibers show only marginal improvement. However, the Torlon/P84 blended fibers display enhanced separation performance after chemical cross-linking modification with the aid of *p*-xylenediamine. It is believed that the *p*-xylenediamine induced cross-linking reactions result in greater chain packing and the reduction of free volume. The highest separation factor obtained was 185 ± 8 for the 85/15 wt.% IPA/H₂O feed solution and the total permeation flux obtained was 1000 ± 45 g/m² h.

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Keywords: Torlon; Torlon/P84 co-polyamide-imide blends; Cross-linking; Dehydration of isopropanol; Hollow fiber

1. Introduction

Pervaporation is considered as one of the effective techniques to separate liquid mixtures, for instance: dehydration of organic compounds and separation of azeotropic mixtures, isomeric or heat sensitive liquid mixtures [1]. In pervaporation, the liquid feed mixtures are in direct contact with the polymeric membrane. Thus, appropriate selection of polymeric material, which has superior separation performance and minimal solvent-induced swelling, is a crucial parameter. Generally, four modification approaches have been proposed to improve membrane stability and obtain high separation efficiencies, such as: (1) chemical cross-linking/grafting [2–8], blending [9,10], heat treatment [2,3,11,12], and the introduction of robust inorganic fillers [13–15].

Studies on polyamide-imides (PAI) as polymeric membranes materials have received great interest lately because of their

proven resistance to various organic solvents. Since Torlon® is a relatively new commercial PAI, the study and investigation on its membrane applications are still limited. Although there are some research studies using Torlon as the polymeric membrane for gas separation, ultrafiltration and vapor permeation, only three studies have been reported using Torlon for pervaporation [12,16,17]. The earliest work on Torlon hollow fiber fabrication was reported by Takegami et al. [12] in 1993. After heat treatment at 265 °C (which is about the T_g of Torlon), the hollow fibers showed a high separation factor of water to ethanol. The best pervaporation performance of separation factor (600) and permeate flux (30 g/m² h) was obtained for 95 wt.% ethanol solution conducted at 60 °C.

Subsequently, Higuchi et al. [16] compared the vapor permeation and pervaporation performance for 2-propanol/water mixture and reported that Torlon membrane preferentially permeated water in both test apparatus. The calculated diffusivity selectivity was about 1.96, while the solubility selectivity was estimated by separation factor and diffusivity selectivity. According to their data, the dehydration selectivity of Torlon for 2-propanol/water mixture was about 100 if the

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Fig. 1. Chemical structure of polymer: (a) Torlon® 4000T polyamide-imide, (b) P84 co-polyimide and (c) cross-linking agent *p*-xylenediamine.

feed contains water above 10 wt.%. Lastly, Kononova et al. [17] demonstrated the formation, morphology and transport properties of a multilayer pervaporation membrane; it exhibited a superior performance with high permeation flux (14.5 kg/m² h) and separation factor (27,430). However, Torlon was only used as a microporous support, *not* the selective layer.

In the context of the above discussion, Torlon clearly appears to be a potential membrane material applicable to the dehydration of water miscible organics; however, our initial studies on Torlon hollow fiber membranes show a relatively low separation performance. Therefore, the purposes of this study are to fundamentally investigate if the Torlon hollow fiber membrane can be a suitable candidate for the dehydration of alcohols and to explore if any modification methods such as polymer blending and chemical cross-linking modification can enhance its separation efficiency. Heat treatment was not considered in this study because it may take a long time to anneal a hollow fiber to obtain the desired separation performance and it may not be practical in industrial scale up.

Polymer blending is potentially an easy and promising method to overcome material deficiencies and synergistically merge the desired properties of the individual components. Several studies involving the formation of Torlon blended systems have been reported [18–24]. Yoshikawa et al. [18] reported a vapor permeation of aqueous 2-propanol solution study by a gelatin/Torlon® 4000T system and found that the blended system significantly enhanced the separation performance. Other Torlon blends systems have also been studied, such as Matrimid® 5218 polyimide [19], polybenzimidazole [19], sulfonated and sulfamidated poly(ether-ether-ketone) [20–22], and poly(ether-imide) [23,24], but no pervaporation studies have been reported. P84 co-polyimide (BTDA-TDI/MDI) was chosen as a potential candidate material due to its excellent properties, for example: (1) superior

mechanical and physicochemical properties, (2) excellent thermal stability, (3) relative stability in most organic solvents, acid, fats and fuels, and (4) preference for water selectivity.

Chemical cross-linking modifications are also an effective method to enhance the membrane stability, reduce the interstitial chain space and further improve separation performance. *p*-Xylenediamine is selected as the cross-linking agent in this study because it has shown effectiveness for other polyimides such as fluoropolyimide [25,26] and Matrimid [27]. To the best of our knowledge, (1) T/P blended hollow fibers membranes fabricated for pervaporation and (2) the cross-linking effect of Torlon membranes on pervaporation dehydration of isopropanol (IPA) have not yet been reported.

2. Experimental

2.1. Materials

Torlon® 4000T polyamide-imide was provided by Solvay Advanced Polymers, while P84 co-polyimide (BTDA-TDI/MDI, co-polyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 80% methylphenylene diamine + 20% methylene diamine) was purchased from HP Polymer GmbH, Austria. The chemical structures for both polymers are shown in Fig. 1. The polymers were dried overnight at 120 °C under vacuum before use. The solvent *N*-methyl-2-pyrrolidinone (NMP) was purchased from Merck while solvent exchange agents, methanol and *n*-hexane, were provided by Tedia and Merck, respectively. In addition, the solvent IPA was supplied by Fisher Scientific and the cross-linking agent, *p*-xylenediamine, was purchased from Sigma–Aldrich. All chemical were used as received. Milli-Q ultra-pure water was produced in our laboratory.

Table 1
Spinning parameter of Torlon and T/P blended single-layer hollow fiber membranes

Spinning parameters	Values
Dope composition (wt.%)	Polymer blend/NMP: 27/73 (pure Torlon, T/P 9:1, T/P 7:3)
Dope flow rate (ml/min)	2.4
Bore fluid (wt.%)	NMP/water: 85/15
Bore flow rate (ml/min)	1.2
External coagulant (°C)	Tap water, 25 ± 1
Dope and bore fluid temperature (°C)	25 ± 1
Air gap (cm)	1.8
Room humidity (%)	65–70
Solvent exchange	3 days store in tap water, followed by 3 times methanol (30 min) and 3 times hexane (30 min)
Hollow fiber drying	Ambient temperature

2.2. Spinning process and modules fabrication

The dope was stirred to homogeneity and degassed for 24 h before loading into the syringe pump (ISCO 500D), followed by degassing for another 24 h before spinning. A mixture of 85/15 wt.% of NMP/water was employed as the bore fluid in order to form a porous inner structure and thus minimize the substrate resistance. Tap water was utilized as the external coagulant in order to obtain a dense-selective outer layer. Both dope and bore fluid were filtered through 15 μ m sintered metal filters before extruding through a spinneret at ambient temperature. Then, the nascent fibers went into the coagulation bath freely without additional drawing. Lastly, the hollow fibers were dried in air after solvent exchange. The spinning conditions are tabulated in Table 1.

The pervaporation module was prepared by loading 2 pieces of hollow fibers membranes into a polypropylene module with the effective length of 15 cm for each module. Both ends were sealed by epoxy and cured for 48 h at ambient temperature. The membranes were chemically modified before module fabrication. At least two modules were tested for each membrane sample.

2.3. Chemical modification of membrane

The chemical modification was conducted by immersing hollow fibers in a 10% (w/v) *p*-xylenediamine/methanol solution for different cross-linking time intervals, followed by washing with fresh methanol immediately to wash away the residual solution on the membrane. After that, the hollow fibers were dried at ambient temperature in air for 1 day before evaluation.

2.4. Pervaporation experiments and data analysis

A laboratory scale pervaporation unit was employed and details of the apparatus have been published elsewhere [11]. The feed composition was fixed at IPA/water 85/15 wt.% and this was maintained constant throughout the duration of experiment. The pervaporation experiment was conducted at 60 °C. The feed flow rate was maintained at 0.5 L/min for each module and the

feed pressure was kept at 1.0 bar. The permeate pressure was maintained at 3–5 mbar by a vacuum pump. The feed solution flowed through the shell side of the hollow fibers and the permeate vapor was collected from the lumen side. The permeate vapor was condensed in a cold trap which was immersed in liquid nitrogen and the samples were weighed on a Mettler Toledo balance. The permeation flux, J (g/m² h) is determined using Eq. (1):

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

where Q (g) is the weight of collected permeate, A (m²) is the effective membrane area and t (h) represents the time interval. The feed compositions and permeate solutions were analyzed by a gas chromatography (HP 6890 Series GC System, USA) equipped with a thermal conductivity detector (TCD) and a HP-INNOWAX column (packed with cross-linked polyethylene glycol). The separation factor (β) for water/IPA is defined as follows:

$$\beta_{\text{water/IPA}} = \frac{y_{\text{water}}/y_{\text{IPA}}}{x_{\text{water}}/x_{\text{IPA}}} \quad (2)$$

where y and x refer to the weight and/or mole fraction of each component in the feed and permeate, respectively. Based on the solution-diffusion mechanism, the basic pervaporation transport equation is defined as:

$$J_i = \frac{P_i}{l} (P_i^f - P_i^p) = \bar{P}_i (p_i^f - p_i^p) \quad (3)$$

where P_i represents the membrane permeability, l is the membrane dense layer thickness, p denotes the partial vapor pressure, $\bar{P}_i$ corresponds to the permeance, while the superscripts f and p correspond to the feed and permeate. On the other hand, the partial vapor pressure (fugacity) of each component on the feed side can be calculated based on its concentration in the feed liquid mixture as:

$$P_i^f = x_i \gamma_i p_i^s \quad (4)$$

where the superscript s indicates the saturated state, and γ_i is the activity coefficient. In this study, p_i^s and γ_i were obtained from the HYSYS DISTIL software (version 5.0, provided by Hyprotech Ltd., Canada). By substituting Eq. (4) into (3), the permeance, $\bar{P}_i$ (g/m² h kPa) can be calculated based on the following equation [28]:

$$\bar{P}_i = \frac{J_i}{x_i \gamma_i p_i^s - p_i^p} \quad (5)$$

while the selectivity, α , of the hollow fiber can be calculated as:

$$\alpha = \frac{P_{\text{water}}/l}{P_{\text{IPA}}/l} = \frac{\bar{P}_{\text{water}}}{\bar{P}_{\text{IPA}}} \quad (6)$$

2.5. Characterization

The morphology of the resulting membranes was examined by field emission scanning electron microscopy (FESEM, JEOL JSM-5600LV). Samples were prepared in liquid nitrogen followed by platinum coating. The hollow fibers were also

Fig. 2. Morphology of the cross-section, inner surface and outer layer for (a) pure Torlon, (b) T/P 9:1 and (c) T/P 7:3 hollow fiber membranes.

characterized by FTIR (PerkinElmer FTIR Spectrometer Spectrum 2000) with a wave number range of $4000\text{--}400\text{ cm}^{-1}$ and a resolution of 4 cm^{-1} .

Wide-angle X-ray diffraction (WAXD) was performed using a Bruker X-ray diffractometer at room temperature with a Cu K α radiation wavelength of $1.54\text{ \AA}$ to measure the d -spacing of resulting membranes. d -Spacing can be calculated from Bragg's rule as follows:

$$n\lambda = 2d \sin \theta \quad (5')$$

where d is the dimension spacing, θ is the diffraction angle, λ is the X-ray wavelength and n is an integer.

The thermal measurements were made using a PerkinElmer Pyris-1 differential scanning calorimetry (DSC). The apparatus was calibrated with high purity indium and zinc, and an on-line baseline subtraction was also used. The normal heating rate was $20\text{ }^{\circ}\text{C/min}$ and all the experiments were conducted under a nitrogen environment of 20 psig.

3. Results and discussion

3.1. Miscibility study of Torlon/P84 blends

Truly miscible Torlon/P84 blends are readily confirmed using DSC, whereby single glass transition temperatures (T_g) are

Fig. 3. Pervaporation performance for pure Torlon, T/P 9:1 and T/P 7:3 blended membranes.

Fig. 4. Possible chain morphology of *p*-xylenediamine cross-linked Torlon, P84, and T/P.

observed for the blends. In contrast, two distinct T_g s may be observed for immiscible blends [29]. The resultant Torlon/P84 membranes are transparent and homogeneous when observed using polarizing light microscopy at 50 $\times$ magnification. The T_g s for pure Torlon and P84 polymers are 274 and 317 $\pm$ 2 $^{\circ}$ C, respectively, which are in good agreement with the reports of Wang et al. [19] as well as Qiao and Chung [31]. Moreover, the T_g s increase with an increase in P84 composition; the T_g s for Torlon/P84 blends with weight ratios of 9:1, 8:2, 7:3 and 5:5 are 282, 288, 295 and 304 $^{\circ}$ C $\pm$ 2, respectively. This result apparently confirms the true miscibility of this blending system.

3.2. Morphology of Torlon and Torlon/P84 (hereafter referred as T/P) membranes

The micrographs in Fig. 2 show the morphology of pure Torlon, T/P 9:1, and T/P 7:3 single-layer hollow fiber membranes. It can be seen from the cross sections of these three membranes that they have relatively similar structures, which consist of two layers: a dense-selective layer and a porous substrate layer with finger- and sponge-like macrovoids. The solution viscosities determined by ARES Rheometric Scientific rheometer, of 27 wt.% for pure Torlon, T/P 9:1, T/P 7:3 blends and pure P84 in NMP solvent are 28,000, 31,000, 34,800 and 41,000 cP, respectively. These data clearly indicate that a higher percentage of P84 may lead to higher polymer dope viscosity and less macrovoid formation under the same spinning conditions. For T/P blended membranes, there are slightly fewer macrovoids on the supporting substrate which may provide slightly higher mechanical stability.

3.3. Pervaporation performance of Torlon and Torlon/P84 blended membranes

The pervaporation performance for pure Torlon and T/P blended membranes is illustrated in Fig. 3. The blended membranes show a relative enhancement in the flux, especially for the T/P 7:3 blend, which increase by $\sim$ 85% as compared to the pure Torlon membranes. Similar trends of increase can be observed for water permeances. Nevertheless, the systems display a relatively low separation factor/selectivity. This may arise from two possible causes: (1) the polymer blends may exhibit different phase inversion conditions during the spinning process which could create minor defects on the dense selectivity layer, and (2) greater interstitial space (i.e., more free volume and broader free volume distribution) may be induced among chains due to different chain packing and polymers adhesion. These phenomena may lead to a significant flux increase and selectivity drop. The poor pervaporation performance in T/P blended copolyamide-imide membranes is supported by a higher *d*-space value observed in XRD data (and will be discussed later).

In addition, membrane swelling also plays an important role which is attributed to the high flux but low separation factor/selectivity in the as-spun fiber. This is due to the fact that the dense-selective layer prepared by the phase inversion process is in a state of thermodynamic non-equilibrium because of the rapid gelation and precipitation. The quenched and non-relaxed polymer chains have non-equilibrium molecular configurations [31], which have strong tendency toward the thermodynamic equilibrium via densification, configuration rearrangement or chain packing if energy (i.e., thermal treatment) is provided or if the friction among chains is reduced due to the sorption of

Fig. 5. Proposed mechanism for the chemical cross-linking modification of pure Torlon and P84.

penetrants among polymer chains. Therefore, the direct contact of the as-spun membrane with the feed solution may swell and soften polymer chains. The sorption amounts of P84 dense membranes in pure water and IPA are 0.034 and 0.006 g/g dry

membrane, respectively [30]. A similar study has also been conducted in our laboratory for Torlon, where the sorption data in pure water is 0.058 g/g dry membrane but there is undetectable sorption in pure IPA solvent after 1 month. Therefore, the sorption data apparently suggest that both Torlon and P84 dense

Fig. 6. ATR-FTIR spectra of pure Torlon with p -xylenediamine cross-linked hollow fiber membranes.

Fig. 7. WAXD spectra of Torlon and T/P 7:3 blended membranes with different cross-linking time.

membranes have preferential affinity with water, which may be the main cause of loosening the chain packing and inducing more free interstitial space for permeate diffusion through the membranes.

Furthermore, the asymmetric structure may generate an uneven transition in membrane morphology when the as-spun membrane is exposed to the water penetrant. An asymmetric swelling across the outer selective dense layer to the inner porous substructure would be developed. As a result, the dilation and relaxation phenomena will be locally different, which may bring about defects and reduce separation factor and selectivity.

3.4. Characterization of Torlon and T/P blended membranes cross-linked with *p*-xylenediamine

Since as-spun Torlon and T/P blended membranes have relatively low separation performance for IPA dehydration, post treatments with the aid of *p*-xylenediamine cross-linking agent was explored to enhance the pervaporation performance. The resultant chain morphology for the *p*-xylenediamine cross-linked Torlon PAI and P84 polyimide was simulated by the Amorphous Cell procedure developed by Material Studio™. The most stable energy-minimized configuration between Torlon, P84, T/P, and *p*-xylenediamine structure is illustrated in Fig. 4. Obviously, Torlon chemical structure has a polar bond (amide and ether groups) which may result in less linearity of the chemical backbone as well as a lesser degree of molecular packing compared with the P84 structure. Moreover, the proposed mechanism of the chemical cross-linking modification of pure Torlon and P84 is shown in Fig. 5.

Fig. 6 represents the ATR-FTIR spectra of the original Torlon and *p*-xylenediamine cross-linked membranes as a function of immersed time. The spectrum of the imide functional group is characterized by bands at 1774 cm^{-1} ($\nu_{\text{C=O}}$ of $-(\text{OC})_2\text{N}$ -asymmetric stretch), 1703 cm^{-1} ($\nu_{\text{C=O}}$ of $-(\text{OC})_2\text{N}$ -symmetric stretch) and 1344 cm^{-1} ($\nu_{\text{C-N}}$ of $-(\text{OC})_2\text{N}$ -stretch), while amide group is characterized at 1642 cm^{-1} ($\nu_{\text{C=O}}$ of $-\text{CONH}-$) and 1532 cm^{-1} ($\nu_{\text{C-N}}$ of $-\text{CNH}-$). Since Torlon is a polyamide-imide component, the spectra for the original Torlon derive from a combination of these two structures. The intensities of imide characteristic peaks 1774 , 1703 and 1344 cm^{-1} are found to gradually decrease, whereas the characteristic peaks of amide group intensify with an increase in immersion time. Thus, this observation confirms that the amidation reaction (conversion of imide groups into amide groups) has been successfully obtained via the simple cross-linking method. Similar patterns of ATR-FTIR spectra also can be observed in the T/P blended membranes (which are not shown here).

On the other hand, WAXD was employed to characterize the chain packing for unmodified and *p*-xylenediamine cross-linked membranes, as shown in Fig. 7. *d*-Space is an average interstitial space for a polymer chain; a tighter polymer chain normally has a relatively lower *d*-space. The pure Torlon, T/P 9:1 and T/P 7:3 membranes possess *d*-spaces value of 4.19, 4.21 and $4.26\text{ \AA}$, respectively, suggesting that the *d*-space for T/P blends is shifted toward pure P84 which has a value of $4.87\text{ \AA}$ [3]. It is certainly clear that the *d*-space of the resultant membranes

decrease after cross-linking (i.e. 4.16, and $4.10\text{ \AA}$ for T/P 7:3 *p*-xylenediamine cross-linked at 1 and 10 min, respectively). The shift of these peaks evidently indicates an increase in polymer chain packing. A possible explanation is that the cross-linking agent occupies the inter-spaces between the polymer chains, tightens and rearranges the chain configuration. As a result, a decrease in the interstitial space and alteration of the free volume distribution are clearly induced by the chemical modification.

Fig. 8 illustrates the morphology of the outer layer for the cross-linked Torlon, T/P 9:1 and T/P 7:3 membranes. By further augmenting *p*-xylenediamine immersion time, all three membranes demonstrate an increase in their dense layer thicknesses, clearly suggesting that the hydrophilic diamine successfully cleaves the imide rings because of the amidation reaction, thus leading to a stronger intermolecular bonding and tighter chemical structure. Compared to the pure Torlon membrane, the T/P blended membranes show a significant growth in the thickness of densified skin layer.

3.5. Pervaporation performance of Torlon and Torlon/P84 blended membranes cross-linked with *p*-xylenediamine

The pervaporation performance of the *p*-xylenediamine cross-linked Torlon and T/P membranes are summarized in Tables 2 and 3. It is obvious that the cross-linking increases the separation factor/selectivity gradually in the beginning and then rapidly with an increase in immersion time. The highest separation factor is the T/P 7:3 sample with 5 min chemical cross-linking time. It enhances the separation factor from 7 ± 1 (no cross-linking) to 185 ± 8 , while maintaining a reasonable high flux ($1000 \pm 45\text{ g/m}^2\text{ h}$). Moreover, the effect of cross-linking modification on flux decline is much severer in the cross-linked T/P 7:3 sample compared to both cross-linked Torlon and T/P 9:1 samples. The flux drop is $\sim 67\%$ after 10 min cross-linking for the T/P 7:3 system, whereas it is only ca. 29% for the other two membranes. This difference may arise from the fact that the dense-selective layer of the as-spun T/P 7:3 fiber has bigger interstitial space than the other two systems, as discussed previously in Section 3.4. As a result, the *p*-xylenediamine cross-linking agent can diffuse easily within the polymer chains and induce a higher degree of chemical cross-linking, leading to a greater chain tightening and freed volume reduction. However, the degree of permeability reduction is comparable to those of other cross-linked pervaporation membranes published elsewhere [2,3].

A comparison of flux/permeance and separation factor/selectivity results among these three membranes reveals that the cross-linked T/P blends have higher separation performance than the cross-linked Torlon. Clearly, both the cross-linking and blending methods play important roles for the performance enhancement. Introducing a small amount of P84 not only creates wider interstitial space in the first place, but also contributes more imide groups that are available for cross-linking reactions. Even though the incorporation of *p*-xylenediamine into polyimide chains may occupy some free volume, the wide interstitial space induced by P84 may offset this effect. As a result, the subsequent cross-linking modification still results in blended

Fig. 8. Morphology of the outer layer for (a) pure Torlon, (b) T/P 9:1 and (c) T/P 7:3 hollow fiber membrane *p*-xylenediamide at different immersion time intervals.

membranes with high flux and high separation factor if the degree of cross-linking reactions is not high.

However, a further increase in the cross-linking time results in a severe reduction in both the high flux and separation factor obtained. As displayed in Fig. 8, an increase in cross-linking duration (i.e., the degree of cross-linking) results in a thicker dense-selective layer as well as a denser substructure. Clearly, the interstitial space among chains, chain mobility, and free volume would decrease with an increase in cross-linking duration. Previous cross-linking studies on 6FDA-Durene using *p*-xylenediamine indicated a 70–80% reduction in gas permeability and diffusion coefficient if the cross-linking time was about 15 min [25], whereas 6FDA-2,6-DAT using *p*-xylenediamine and *m*-xylenediamine reported a decay of ~70%

in gas permeability and ~30% lower in CO₂/N₂ selectivity after only a 5 min cross-linking time [26]. As a consequence, the low separation performance is mainly resulted from extended cross-linking time because it induces high substructure resistance for the diffusion of water and IPA molecules, thereby reducing the overall separation performance, as predicted by Pinnau and Koros [32]. One must optimize the chemical modification in order to produce membranes with a balanced degree of cross-linking against swelling and substructure.

Table 4 summarizes the separation performance of commercial cross-linked polyvinyl alcohol (PVA) flat sheet membranes (Sulzer) and cross-linked polymeric hollow fibers by recent studies for pervaporation dehydration of alcohols. Although the overall performance of the first-generation cross-linked

Table 2

Pervaporation performance of the original and *p*-xylenediamine cross-linking Torlon hollow fiber membranes

Membrane ID	Permeate water concentration (wt.%)	Total flux (g/m ² h)	Separation factor	Permeance ^a		Selectivity ^b
				Water	IPA	
Original Torlon	69.8 ± 1.4	815 ± 15	12 ± 1	16.6 (0.92)	3.4 (0.06)	5 (16)
Torlon-PXD-1 min	78.1 ± 2.9	698 ± 43	20 ± 1	16.4 (0.91)	2.1 (0.03)	8 (26)
Torlon-PXD-5 min	78.0 ± 3.1	634 ± 24	21 ± 1	15.4 (0.85)	1.9 (0.03)	8 (28)
Torlon-PXD-10 min	81.5 ± 1.2	615 ± 26	26 ± 1	15.6 (0.86)	1.5 (0.03)	10 (34)
Torlon-PXD-15 min	81.8 ± 2.5	514 ± 15	25 ± 1	12.6 (0.70)	1.3 (0.02)	10 (33)
Torlon-PXD-20 min	82.3 ± 1.3	469 ± 19	26 ± 1	12.1 (0.67)	1.2 (0.02)	10 (34)
Torlon-PXD-30 min	73.4 ± 4.1	434 ± 30	15 ± 1	9.6 (0.53)	1.6 (0.03)	6 (20)

^a Permeance: g/m² h kPa (mol/m² h kPa).

^b Selectivity calculated: Based on mass term (based on molar term).

Table 3

Pervaporation performance of the original and *p*-xylenediamine cross-linking T/P blended hollow fiber membranes

Membrane ID	Permeate water concentration (wt.%)	Total flux (g/m ² h)	Separation factor	Permeance ^a		Selectivity ^b
				Water	IPA	
Original T/P 9/1	49.2 ± 4.0	992 ± 40	6 ± 1	14.7 (0.82)	6.8 (0.11)	2 (7)
T/P 9/1–PXD-1 min	61.5 ± 1.2	916 ± 20	9 ± 1	17.2 (0.96)	4.7 (0.08)	4 (13)
T/P 9/1–PXD-5 min	64.5 ± 2.9	805 ± 36	10 ± 1	15.0 (0.83)	4.0 (0.07)	4 (13)
T/P 9/1–PXD-10 min	95.0 ± 1.3	702 ± 32	111 ± 5	20.5 (1.14)	0.5 (0.01)	43 (144)
T/P 9/1–PXD-15 min	75.4 ± 3.0	443 ± 18	16 ± 1	9.7 (0.54)	1.5 (0.03)	6 (21)
Original T/P 7/3	53.9 ± 3.4	2076 ± 95	7 ± 1	33.1 (1.84)	13.1 (0.22)	3 (8)
T/P 7/3–PXD-1 min	94.4 ± 1.8	1418 ± 60	99 ± 4	41.0 (2.28)	1.1 (0.02)	39 (128)
T/P 7/3–PXD-5 min	97.1 ± 1.4	1000 ± 45	185 ± 8	28.7 (1.60)	0.4 (0.01)	72 (241)
T/P 7/3–PXD-10 min	91.5 ± 1.2	683 ± 23	58 ± 2	18.0 (1.00)	0.8 (0.01)	23 (75)
T/P 7/3–PXD-15 min	75.5 ± 3.0	516 ± 20	18 ± 1	12.0 (0.67)	1.7 (0.03)	7 (24)

^a Permeance: g/m² h kPa (mol/m² h kPa).^b Selectivity calculated: Based on mass term (based on molar term).

Table 4

Separation performance of commercial cross-linked PVA flat sheet membranes and cross-linked polymeric hollow fiber membranes for pervaporation dehydration of alcohols

Membrane material	Test temperature (°C)	Feed alcohol (wt.%)	Total flux (g/m ² h)	Separation factor
Commercial cross-linked PVA flat sheet membranes				
Cross-linked PVA/polyacrylonitrile (PAN—supporting layer) membranes (PERVAP 2201) [33]	60	IPA 85%	300	600
		EtOH 85%	200	90
Cross-linked PVA/PAN (PERVAP 2201) [34]	80	IPA 85%	750	2600
Cross-linked PVA/PAN (PERVAP 2510) [34]	60	IPA 85%	857	1053
Cross-linked polymeric hollow fiber membranes				
Chitosan dip-coated cellulose acetate [35]	25	IPA 90%	170	809
		EtOH 90%	234	36
Cross-linked carboxymethyl chitosan (CMCS)/polysulfone (PS) [36]	45	IPA 87.5%	39	3238
Cross-linked P84/PES dual-layer [2]	60	IPA 85%	454	953
Cross-linked T/P 7/3 (this work)	60	IPA 85%	1000 ± 45	185 ± 8

Torlon/P84 membranes are not as good as commercially available cross-linked flat PVA membranes [33,34], it shows comparable separation performance with those hollow fiber membranes made from other materials [2,35,36] when comparing them in terms of pervaporation separation index (i.e., $PSI = \text{flux} \times \text{separation factor}$) [37]. To expand the Torlon hollow fiber membrane in pervaporation applications, one must further reduce its swelling, enhance its separation factor and reduce the dense-selective layer thickness.

4. Conclusions

Torlon and T/P blended single-layer hollow fibers have been fabricated by the phase inversion process for the dehydration of IPA. The true miscibility of T/P blends has been confirmed through the appearance of single T_g s detected by DSC.

Both pure Torlon and T/P blends have poor membrane separation performances, due to the extensive swelling. Cross-linked Torlon membranes show low permeation flux possibly because of inherently tight interstitial space and severe substructure resis-

tance. However, Torlon/P84 blended membranes which were cross-linked with *p*-xylenediamine had an enhanced water selectivity with comparatively high permeation flux.

The amidation reaction between the cross-linking agent and the polymer imide rings was verified by ATR-FTIR and a tighter chain packing after chemical modification was clearly observed by XRD spectra. For the dehydration of 85 wt.% IPA aqueous solution, 5 min cross-linked Torlon/P84 7:3 hollow fiber membranes possess a total permeation flux of 1000 ± 45 g/m² h and a separation factor of 185 ± 8 . Both the membrane characterization and pervaporation experiments confirm that blending a small amount of P84 with Torlon can effectively improve the separation performance after a relative short *p*-xylenediamine cross-linking duration (~5 min).

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