

Plasma-treated polyethersulfone coated with crosslinked poly(vinyl alcohol): composite membranes for pervaporation dehydration of ethanol

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Abstract Composite membranes with crosslinked poly(vinyl alcohol) matrix as selective layer coated on a polyethersulfone supporting porous layer were prepared aiming at separating ethanol/water mixtures by pervaporation. A polyethersulfone asymmetric microporous membrane was synthesized by the wet phase inversion process. The support membrane was then exposed to air plasma to activate the surface. The selective dense layer was obtained by coating of PVA and a crosslinking agent over the polyethersulfone substrate, followed by thermal treatment. The morphology was examined by scanning electron microscopy (SEM) for both, support membrane and the coated polymeric layers. Surface physicochemical properties were evaluated through measuring the contact angle (θ) and the estimation of surface free energy (γ_s) and adhesion work. The surface chemical composition of support membrane and coated hydrophilic layers were characterized by infrared spectra with horizontal attenuated total reflectance (FT-IR/HATR). The swelling degree of PVA dense membranes, and the pervaporation performance of the crosslinked PVA/PES composite membranes, manufactured with several coating steps, were evaluated with water/ethanol (20/80 wt%) mixtures at temperatures in the range of 30–60 °C. Results of the effective pervaporation dehydration of ethanol are discussed in terms of membrane morphology and the solution-diffusion transport mechanism.

Introduction

Pervaporation through membranes has potential advantages compared to the conventional separation technologies (distillation, adsorption, liquid–liquid extraction). These advantages include: lower energy consumption, separation efficiency, simplicity in operation, separation of heat sensitive components, easier removal of low concentration components, no chemical additives, minimum waste, compact industrial systems, and flexibility in process design when combination with other unit operations is indicated. Pervaporation has been mainly used in dehydration of organics and removal of low concentration organics from its aqueous mixtures. Operationally, the mixture to be separated is fed in the liquid state at atmospheric pressure, to a permeation cell or a module where the active dense layer promotes selective transport of the mixture components as a result of a sorption–diffusion mechanism and a driving force such as the difference of component partial pressures, maintained across the membrane [1].

Therefore, the morphology of the membrane and the chemical properties of the polymeric material affect the membrane performance. A composite membrane involves a deposited dense active layer on a porous support film. Thus, it combines a thin and selective skin with a thicker, thermally and mechanically stable substrate membrane. Further, the pervaporation performance of the composite membrane also depends on operational conditions (temperature, partial pressure gradient, feed composition, etc.).

In general, microporous polyethersulfone membranes have been used in membrane separation processes such as microfiltration and ultrafiltration. This polymer was selected as a support layer for the composite membrane because of its high resistance to heat, chemical resistance, light

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weight, good mechanical property, and film-forming properties [2].

Poly(vinyl alcohol) was chosen as active layer for the composite membrane due to its high hydrophilicity, good chemical stability, thermal resistance, film forming ability, and low cost [3–6]. However, to achieve an adequate swelling degree in contact with the feed mixture, the poly(vinyl alcohol) membrane needs to be crosslinked before being used in dehydration for pervaporation. As previously reported, chemical and thermal processes were found useful for this purpose. Poly(vinyl alcohol) can be insolubilized by heat treatment [7, 8], blended with poly(acrylic acid) and then cross-linked by heat treatment [3, 9], and using different types of crosslinking agents including glutaraldehyde [4, 10–13], maleic acid [14], tartaric acid [14], malic acid [5], sulfophthalic acid [15], borax [2], etc. Indeed, crosslinked poly(vinyl alcohol) membranes were tested in pervaporation to separate mixtures of ethanol/water [10], acetic acid/water [5], isopropanol/water [15], ethylene glycol/water [4, 12, 13], ethyl acetate/water [14], ϵ -caprolactam/water [11], methyl *tert*-butyl ether/methanol [9], dimethyl carbonate/methanol [3].

Furthermore, composite membranes have been prepared using poly(vinyl alcohol) as coating material for several porous substrates such as polyacrylonitrile [11, 14], polyethersulfone [12, 13], and polysulfone [16].

Different methods have been applied for surface modification to improve the interfacial interaction and to prevent peeling of layers in composite membranes: one can mention chemical interfacial crosslinking (e.g., with borax) [13] and physical plasma treatment (air) [17].

Plasma treatment is a fast, easy, non-polluting, and flexible technique to modify surface properties of polymeric materials at room temperature while keeping bulk characteristics unaltered. Thus, it is particularly useful whenever surface adhesion and wettability have to be increased to deposit dense polymer films [17, 18].

In this study, crosslinked PVA/PES composite membranes were prepared to investigate the pervaporation performance aiming at separating ethanol/water mixtures, exploring surface activation by plasma treatment. The effect of membrane synthesis variables onto the morphology and transport properties were examined in order to get a better understanding of the involved phenomena.

Experimental

Materials

Polyethersulfone (PES, BASF, $M_w \sim 58000$ g/mol), was selected to synthesize porous membranes. Polyvinylpyrrolidone (PVP, SIGMA, $M_w \sim 40000$ g/mol) was added as

soluble component to promote porous structure while *N,N*-dimethyl formamide (DFM, MERCK) was chosen as solvent to prepare a solution for the casting process. Distilled water was used as coagulating bath. Poly(vinyl alcohol) [PVA, VETEC, 80 % hydrolyzed, $M_w \sim 72000$ g/mol] was the polymer selected for the dense (skin) layer of the composite pervaporation membranes. Deionized water and ethanol (VETEC, 99.8 %, v/v) were employed to prepare the feed solution for dehydration pervaporation experiments. All reagents were analytical grade and were utilized without further purification.

Porous membrane synthesis

Polyethersulfone membranes were synthesized through the well known wet phase inversion process in a distilled water bath. First, a polymeric solution 15 % PES, 7.5 % PVP, and 77.5 % DMF, weight fractions, was prepared [19]. Then, it was spread over flat glass surface and exposed for 20 s at ambient conditions allowing a partial evaporation of solvent. PES porous structure was achieved by precipitation in a water bath. Finally, it was carefully washed in three stages with distilled water, followed by ethanol and *n*-hexane.

Plasma treatment

A radio-frequency reactor (Harry-Plasma, Inductive, 8–12 MHz) was used for plasma treatment. Porous PES membrane was set in the center of reaction chamber. The precursor was atmospheric air, fed at room temperature. Operating conditions were 560 mTorr pressure in the chamber and 29.6 W discharging power of the source. Exposure time was 10 min after checking preliminary experiments to achieve an appreciable modification on the surface hydrophilicity.

Hydrophilic polymer coating

Dense hydrophilic skin was deposited by a casting technique. The coating solution was prepared with 5 wt% of hydrophilic polymer (PVA) and 0.5 wt% of crosslinking agent (maleic acid) dissolved in distilled water. The first layer was deposited on activated support after 1 h of plasma treatment and dried at room temperature for 24 h (first coating step). Then, each additional layer of equal liquid thickness was spread successively onto these coated membranes following the same procedure, and at intervals of 24 h (additional coating step). Composite membranes were dried at room temperature and crosslinking carried out by heating at 150 °C for 3 h.

Dense membranes

Dense PVA membranes were prepared by the casting technique from solution of 5 wt% polymer with 0.5 wt% of crosslinking agent dissolved in distilled water. These membranes were dried at room temperature and were treated thermally at 150 °C for 3 h.

Characterization

Cross-sections of membranes were observed by SEM (JEOL-JSM-6480 LV). Surface chemical characterization was deduced from IR spectrums with attenuated horizontal total reflectance technique (FT-IR/HATR, Perkin-Elmer, Spectrum GX) with a flat crystal of ZnSe at 45°. Surface hydrophilic character was investigated by the measurement of contact angle (water drops of approximately 10 μ L) with a Ramé-Hart goniometer, equipped with drop images capture and software to estimate surface energy and adhesion work. The surface energy was calculated by means of an iterative procedure proposed by Neumann [20]. The adhesion work was estimated through a combination of Young and Dupré equations [21]. For each membrane, five drops were placed at different locations and the average of these measurements was reported.

Gravimetric sorption measurements

The dry PVA dense membranes were weighed and immersed in a bath of water/ethanol (20/80 wt%). Thus, they were maintained at 30, 40, 50 and 60 °C for 3 days until swelling equilibrium was achieved. The sample was taken out of the immersion bath and the excess surface liquid was carefully removed with absorbent paper. The weight of the wet membrane sample was determined, and therefore, the liquid content.

Pervaporation experiments

Permselective properties of crosslinked PVA/PES composite membranes were evaluated in a standard pervaporation lab set. It was fed with a liquid mixture of water/ethanol (20/80 wt%). Membrane area of the flow cell in the experiments was 28.27 cm². Temperature was controlled at 30, 40, 50, and 60 °C. The feed and permeate compositions were determined using a Perkin-Elmer (Clarus-500) gas chromatograph.

From experimental data, membrane performance can be assessed in terms of total permeation flux (J) and separation factor (α). Total permeation flux was calculated through Eq. 1:

$$J = \frac{W}{A \cdot t} \quad (1)$$

where J , W , A , and t denote flux ($\text{g m}^{-2} \text{h}^{-1}$), weight of the permeate (g), effective membrane area (m^2), and operation time (h), respectively. Separation factor, α , is calculated from Eq. 2:

$$\alpha_{\text{water/ethanol}} = \frac{\frac{Y_{\text{water}}}{Y_{\text{Ethanol}}}}{\frac{X_{\text{water}}}{X_{\text{Ethanol}}}} \quad (2)$$

where Y_{water} , Y_{Ethanol} are weight fractions of water and ethanol in the permeate, and X_{water} , X_{Ethanol} are weight fractions of water and ethanol in the feed. Partial permeation fluxes can be obtained from the total flux and the permeate concentration.

Results and discussion

Morphology

Figure 1a shows the photomicrograph of the support PES membrane where the top surface does not reveal an apparent porosity. An asymmetric structure with thickness of approximately 260 μm can be observed. The bottom porous surface morphology of this PES substrate is shown in Fig. 1b.

The morphologies of the crosslinked PVA/PES composite membranes obtained, when 2 and 4 coating steps with PVA, were spread on the activated support PES (air plasma, 29.6 W, 650 mTorr, 10 min), and are shown in Fig. 1c, d, respectively. The dense film thickness of the two steps-coated composite membrane is about 1 μm , whereas the four steps-coated membrane reaches approximately 5 μm .

From Fig. 1c, it can be seen that the cross-section morphology just below the top layer is a spongy region and evolves toward a finger-like structure in direction of the bottom face of the support membrane. The macropores average diameter evolves from approximately 2–5 μm , interconnecting and reaching a value diameter of 30–75 μm on the bottom face (Fig. 1b).

Contact angle, surface free energy, and adhesion work

Contact angle measurements provide information on the hydrophilicity of the membrane surface. The results of the contact angle measurements are given in Table 1. Although a PES dense membrane has a surface with hydrophobic character with contact angle of 82°, the PES porous support membranes present a value of $\theta = 66^\circ$ due to combined effects of porosity, roughness, and some traces of the hydrophilic additive (PVP) that probably remains trapped

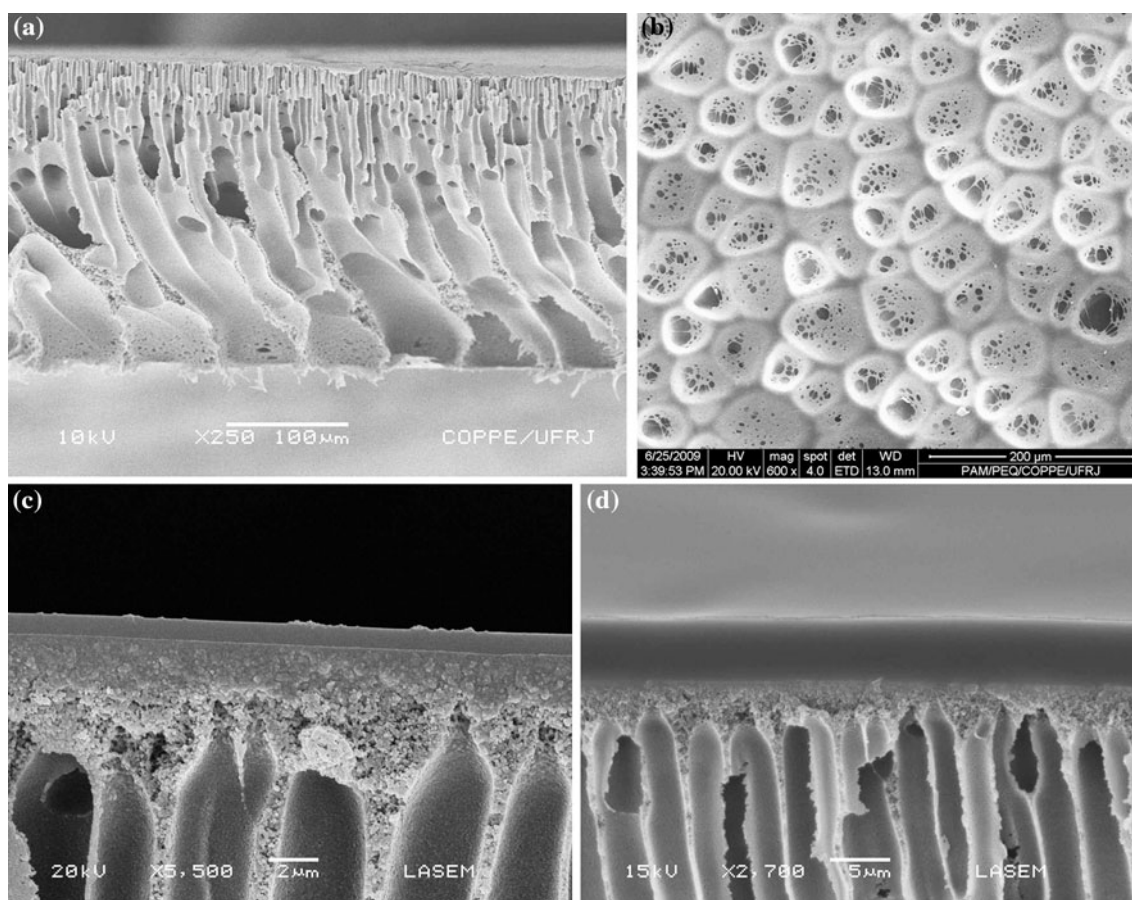


Fig. 1 **a** Cross-section of the PES support membrane prepared by phase inversion technique (magnification: $\times 250$). **b** Bottom surface of the PES support membrane (magnification: $\times 600$). **c** Cross-section of

the crosslinked PVA/PES composite membrane with two coating steps (magnification: $\times 5.5$ k). **d** Cross-section of the crosslinked PVA/PES composite membrane with four coating steps (magnification: $\times 2.7$ k)

Table 1 Effect of plasma treatment time on surface physico-chemical properties of the support PES membranes (Air, 650 mTorr, 29.6 W)

Plasma treatment (min)	θ ($^{\circ}$)	γ_s (mJ/m 2)	W_a (mJ/m 2)
0	66	42.32	99.50
2	51	52.84	118.04
5	45	56.83	124.07
8	31	64.02	135.23
10	24	67.02	139.05
15	21	68.30	140.60
20	19	69.01	141.12
25	18	69.39	141.95

Bold values indicate the initial support membrane and the final plasma-treated PES (coated with PVA)

in the polymeric matrix. On the other hand, the air plasma treatments modify the chemical behavior of this surface also creating hydrophilic properties. According to the observed results, the contact angles value decreased from

66° to 24° after of plasma exposure for 10 min (29.6 W, 650 mTorr). Therefore, surface energy and adhesion work also showed important changes after of plasma treatment. Surface energy values increased from 42.32 to 67.02 mJ/m 2 , corresponding to an enhancement of approximately 40 % for the adhesion work. This high surface energy exhibits aging due to re-arrangement of surface groups. Thus, the diluted polymeric solution was spread over the activated membrane surface after 1 h had elapsed from the end of the plasma treatment. The crosslinked PVA/PES composite membranes have a hydrophilic skin with $\theta = 53^{\circ}$, $\gamma_s = 51.68$ mJ/m 2 , and $W_a = 116.34$ mJ/m 2 . This hydrophilic character showed no changes with time.

Surface chemical nature

A comparison between the FT-IR/HATR spectra of dense PVA membrane with maleic acid, before and after the heat treatment is presented in Fig. 2. The main characteristic peaks of PVA, the O–H stretch vibration (3300 cm $^{-1}$), the

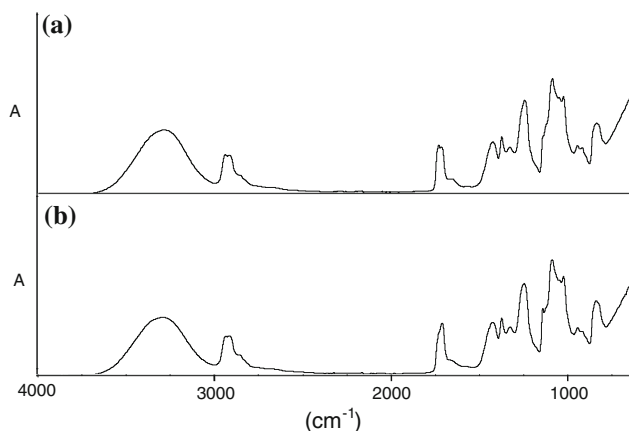


Fig. 2 FT-IR/HATR spectra of dense PVA membrane containing crosslinking agent maleic acid: *a* before heat treatment and, *b* after heat treatment

C–H stretch vibration (2936 and 2911 cm^{-1}), the C–H deformation vibration (1420 and 1328 cm^{-1}), the C–O stretching vibration (1241 and 1090 cm^{-1}), and the O–H bending (917 cm^{-1}) can be observed [22–24].

In addition, for partially hydrolyzed PVA, the absorption bands of C=O associated with acetate groups are found in the regions of 1735 – 1710 cm^{-1} (Fig. 2a). Further, absorption in the region of 1730 – 1710 cm^{-1} is also produced by C=O stretching vibration of maleic acid (Fig. 2a).

Differences can be seen at 1725 cm^{-1} , and in the regions of 1160 – 1150 (Fig. 2a, b). Thus, absorption peak detected around 1725 cm^{-1} in the spectrum of PVA after the heat treatment indicated that the crosslinking reaction between hydroxyl groups of PVA and carbonyl groups of maleic acid had indeed occurred, corroborated by the vibration of resulting ester groups (–COO–), as represented in Fig. 3 and according to the literature [5, 25, 26].

Also, the increase of the band intensity from 1150 to 1160 cm^{-1} (Fig. 2b) can be attributed to C–O of the alcohol, ether and ester groups, after heat cross-linking [25].

Furthermore, thermally induced intermolecular PVA chains crosslinking may also have occurred, resulting in the formation of ether bonds (C–O–C), observed at 1255 cm^{-1} , (Figs. 4, 5).

When the PVA dense membrane is crosslinked, its loose flexibility with decrease of chain mobility and a color change is observed, from transparent to light brown.

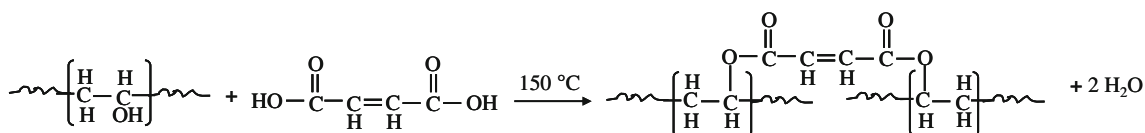


Fig. 3 Chemical reaction of the crosslinking of PVA with maleic acid and heat treatment

The resulting composite membrane structure consists of a thin layer supported by porous substructure. Penetration depth of IR/HATR beam (dp), changes with wavelength [27]. If dp is larger than the deposited top layer thickness, chemical groups belonging to the PES support membrane will also be detected.

The spectra of the prepared membranes are shown in Fig. 6 for PES support and Fig. 7 for crosslinked PVA/PES composite membranes.

Extraction of PVP additive from a PES membrane produced by phase inversion usually is not complete, and lead to the permanent entrapment of PVP molecules in the polymeric matrix. Therefore, the peak located at 1640 cm^{-1} in the PES spectrum (Fig. 6) can be assigned to the presence of C=C–N group of this hydrophilic additive.

Unlike the spectrum of crosslinked dense PVA membrane (Fig. 2b), the spectrum of the final composite membrane (Fig. 7) shows two bands located at 1577 and 1485 cm^{-1} that may be associated with the aromatic stretching for PES [28, 29]. Such differences confirm that the skin layer is coating the PES membrane.

Sorption of crosslinked PVA dense membranes

The thickness of the crosslinked PVA dense membranes were of approximately $50\text{ }\mu\text{m}$. The total swelling in a 20/80 water/ethanol mixture is still quite pronounced as shown in Fig. 8 where little dependence on the temperature in the range 30 – $60\text{ }^\circ\text{C}$ can be observed. This can be due to the increase of mobility of the polymer chains, the relaxed structure of the membrane, which allows more incorporation and rearrangement of penetrant species in the polymeric matrix.

It is expected that crosslinking of PVA will lead to dense layers with swelling degrees suitable for pervaporation membranes. In the composite membranes, the support also should contribute to limit the swelling of the active layer bound to the porous substrate through a good adhesion. The plasma treatment with air raised the surface energy of the support surface, increasing the interfacial interactions between both materials.

Pervaporation results

It is also expected that the performance of crosslinked PVA/PES composite membranes can be modified with the

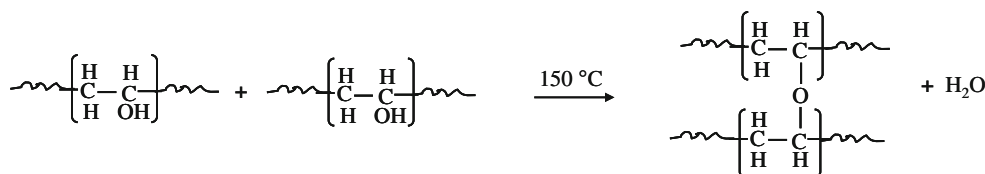


Fig. 4 Schematic illustration of thermally induced PVA chains crosslinking

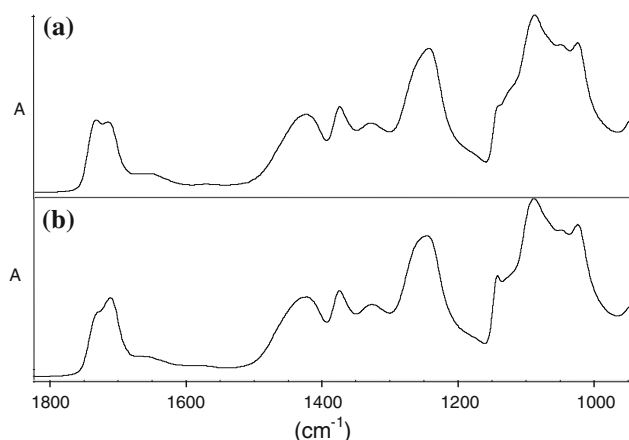


Fig. 5 Detailed FT-IR/HATR spectra at lower wavenumbers of dense PVA membrane containing the crosslinking agent maleic acid: *a* before heat treatment and *b* after heat treatment

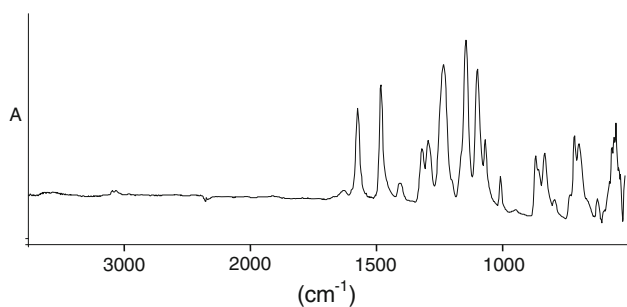


Fig. 6 FT-IR/HATR spectrum of PES support membrane

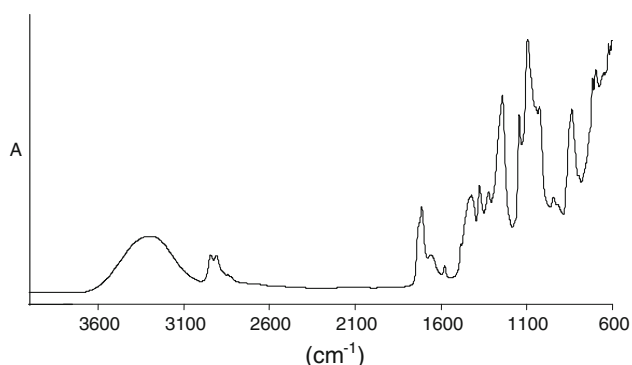


Fig. 7 FT-IR/HATR spectrum of crosslinked PVA/PES composite membrane

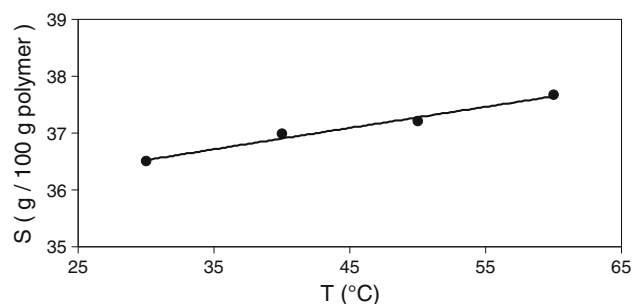


Fig. 8 Effect of feed temperature on total sorption of the crosslinked PVA dense membrane for a 20/80 wt% water/ethanol mixture

deposited dense layer thickness. This effect as well as the influence of operation temperature were evaluated for the pervaporation of a water/ethanol (20/80 wt%) mixture.

In Fig. 9, total fluxes of composite PVA/PES membranes with several coating steps are shown as function of the temperature. As data reported in Fig. 10, these membranes are quite selective towards water, with relatively high separation factors, reaching values of almost 30. As expected, the total flux gradually decreases with skin thickness. A higher pervaporation temperature favours a higher flux (reaching approximately 700 g/h m²), and even with the decrease of selectivity, a separation factor in the range of 12–15 is still sustained.

If a sorption–diffusion transport mechanism in the deposited PVA dense layer is assumed, while mass

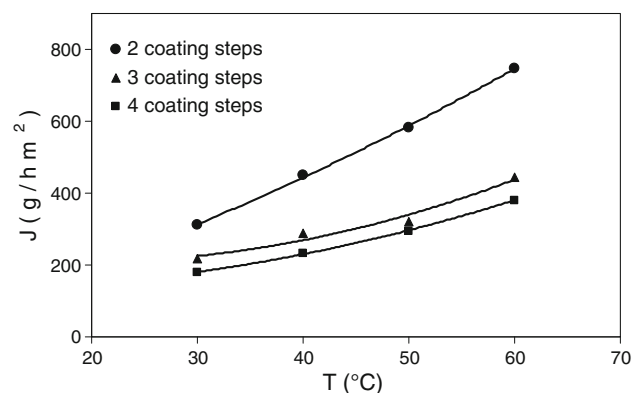


Fig. 9 Effect of feed temperature on total flux of the crosslinked PVA/PES composite membranes for the pervaporation of a 20/80 wt% water/ethanol mixture

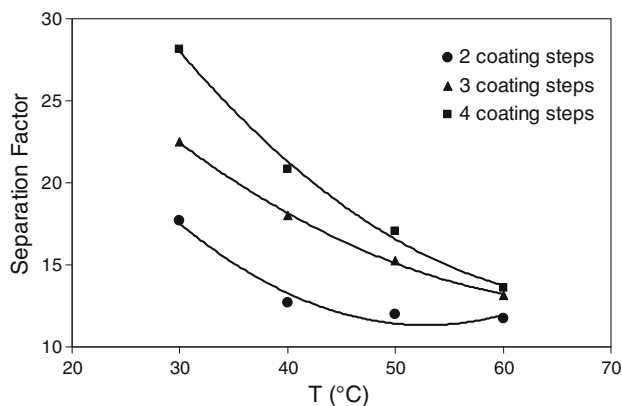


Fig. 10 Effect of feed temperature on the separation factor of the crosslinked PVA/PES composite membranes for the pervaporation of a 20/80 wt% water/ethanol mixture

transport resistance is considered negligible in the PES support membrane, the results of the temperature dependence may be attributed mainly to the increase of the driving force across the composite membrane and the molecular mobility within the crosslinked polymeric structure, excluding therefore sorption contributions, as its temperature dependence is quite reduced.

Driving forces for mass transport across the membrane can be estimated by the fugacity difference between the bulk feed and the permeate [30]. The fugacity of a component at the bulk feed is proportional to the saturated vapor pressure (which increases with temperature) (Eq. 3). The fugacity of a component at the permeate is proportional to the permeate mole fraction (Eq. 4).

$$f_i^b = p_i^s x_i \gamma_i \quad (3)$$

where f^b is fugacity at the bulk feed, p^s is the saturated vapor pressure, x is the feed mole fraction, and γ is the activity coefficient in the liquid feed phase. The saturated vapor pressures were determined from the Antoine's equation and the activity coefficients were calculated using Wilson's equations.

$$f_i^p = p^p y_i \quad (4)$$

where f^p is fugacity at the permeate, y is the permeate mole fraction, and p^p is the permeate pressure.

The ethanol driving force grows faster than the water driving force with temperature. Figure (11) shows the effect of feed temperature on driving forces for a crosslinked PVA/PES composite membrane with three coating steps (Fig. 11).

Therefore, selectivity may have been reduced with increasing temperature possibly due to a coupled diffusional transport of water and ethanol molecules.

Assuming an Arrhenius relationship for the correlation of the water and ethanol fluxes with temperature (Fig. 12),

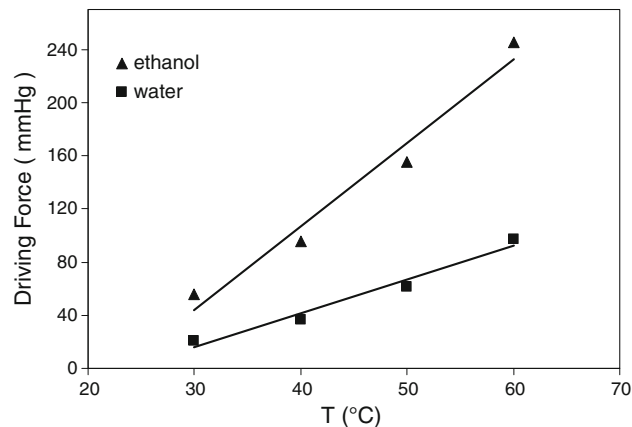


Fig. 11 Effect of feed temperature on driving forces for mass transport in the pervaporation of a 20/80 wt% water/ethanol mixture for a crosslinked PVA/PES composite membrane with three coating steps

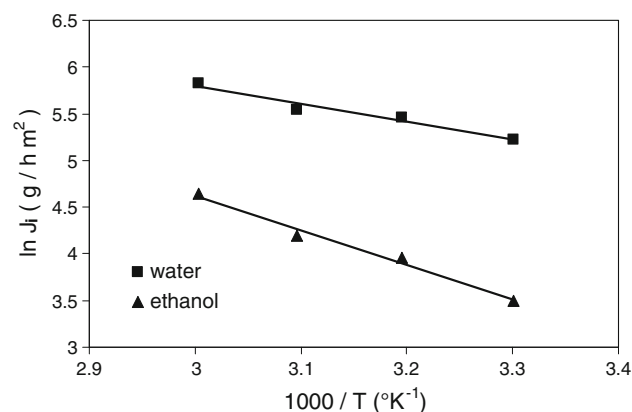


Fig. 12 Effect of feed temperature on permeation fluxes of water and ethanol (feed mixture water/ethanol, 20/80 wt%) for a crosslinked PVA/PES composite membrane with three coating steps

their estimated apparent activation energies were 3.8 and 7.3 kcal/g mol, respectively, for the pervaporation of the same feed through a crosslinked PVA/PES composite membrane with three coating steps. As the permeation flux of ethanol increases faster than water flux, a consequent reduction in selectivity is observed (Fig. 12).

Conclusions

Crosslinked PVA/PES composite membranes with controlled skin thickness ranging from 2 to 5 μm were successfully prepared and characterized. The hydrophilicity of the porous support membrane surface was significantly improved by plasma treatment (air, 29.6 W, 650 mTorr, 10 min), which contribute to an effective interaction of the active dense layer with the PES support. The FTIR spectra of PVA membranes showed that thermally induced maleic

acid chemical crosslinking of the PVA membrane occurred through an esterification reaction. The separation factor increases with increasing number of coating steps with PVA at the expenses of total flux. The crosslinked composite membrane of three coating steps exhibited a pervaporation performance with a total flux of 444 ($\text{g m}^{-2} \text{h}^{-1}$) and a separation factor of 13, at 60 °C, when the feed water content was 20 wt%. Pervaporation evaluation of the membranes indicated promising prospects for dehydration applications.

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