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Pervaporation through composite membranes with plasma treatment of porous support

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ABSTRACT

Composite membranes were prepared in independent stages. First, a polyethersulfone (PES) support porous membrane was synthesized by the phase inversion technique; a plasma pretreatment of the substrate surface using argon was followed by activated support coating with a layer of hydrophilic polymeric mixture of poly(vinyl alcohol) (PVA, 75 wt.%) and poly(acrylic acid) (PAA, 25 wt.%). Finally, thermal treatment of the composite membranes to promote crosslinking of the coated polymer was undertaken. Morphology was examined by electronic microscopy (SEM) for both, support membranes and the polymeric blend layer. Contact angles (θ) were measured and surface free energy (γ_S) and adhesion work (W_a) estimated, to evaluate the effect of plasma and hydrophilic polymer coatings. From infrared spectra with horizontal attenuated total reflectance (FT-IR/HATR), surface chemical composition of support membrane and incorporated hydrophilic groups, were analyzed. Composite membranes were investigated with water–ethanol (20/80 wt.%) mixtures performing pervaporation (PV) experiments at several temperatures (30, 40, 50 and 60°C). The membrane showed good performance for separation of water from ethanol. Fluxes, selectivity ($\alpha_{\text{water/Ethanol}}$) and permeation activation energy (E_{Ji}) are reported showing that the composite membranes were selective to water. Pervaporation separation index (PSI) ($\text{g m}^{-2}\,\text{h}^{-1}$) increased continuously with temperature.

Keywords: Composite membranes; Plasma treatment; Hydrophilic modification; Pervaporation

1. Introduction

Pervaporation is a separation process with increasing potential in several industries, particularly in biofuels production. A sorption-diffusion mechanism governs molecular transport through polymeric membrane and mass transfer rate grows linearly as dense membrane thickness decreases while mechanical resistance is affected in the opposite way. Therefore, pervaporation selective membranes usually need a suitable porous support to allow deposition of a dense polymeric film to produce a stable composite membrane with required selectivity and mechanical properties [1].

Among other techniques a composite multilayer membrane can be prepared by coating films of hydrophilic polymeric materials on a porous supporting membrane [2]. Thus, the film thickness can be reduced up to the point where the supporting surface is completely covered by the coating material. Same criterion must be applied for each successive layer deposited over the previously synthesized porous membrane. On the other hand, mechanical properties may be adequate through the suitable choice of the support porous membrane,

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which offers a negligible resistance to mass transfer when compared even with an extremely thin dense layer.

Poly(vinyl alcohol) (PVA) was chosen due to its hydrophilic character, good chemical stability, high temperature resistance and easy processability [3]. Moreover, poly(acrylic acid) (PAA) is greatly hydrophilic and also soluble in water. Therefore, while PVA is used to improve mechanical properties and to facilitate film formation, PAA should increase permeability of the formed coated film [4]. However, to achieve adequate chemical stability, a blend of PVA and PAA needs to be crosslinked before being used in pervaporation. As previously reported, a thermal process was found useful for this purpose [5,6].

Polyethersulfone (PES) membranes, synthesized by phase inversion—in immersed bath-technique, were used as porous support [7]. Their thermal properties allow heat treatment of the deposited film while hydrophobic character avoids polymer deposition within the porous structure.

Nevertheless to improve polymer adherence to the PES substrate, surface had to be modified by radiofrequency plasma treatment with non-polymerizable gas (argon) under vacuum conditions to increase hydrophilic character and reactivity [8].

Plasma treatment is a rapid, clean and flexible tool to modify surface properties of porous materials at room temperature while keeping bulk characteristics unaltered. Thus, it is particularly useful whenever surface adhesion and wettability has to be increased to deposit dense polymer films. It can produce changes by several mechanisms: ablation of weak supported compounds, production of active species such as functional groups, free radicals or highly reactive components and topological changes of the exposed surface [9,10].

In this work, crosslinked PVA-PAA/PES composite membranes, aiming at the separation media for ethanol–water are reported. Morphological changes and dense deposited films were observed with SEM. Physicochemical properties of the surface were investigated through measurements of θ (contact angles) and estimation of γ_S (surface free energy) and W_a (adhesion work) while the chemical nature of original and modified resulting surfaces were monitored by FT-IR/HATR. Pervaporation tests with ethanol–water mixture were performed, under different operating conditions, to measure fluxes and selectivity and to estimate pure components permeability and driving forces for mass transport through the membrane.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Mw~51,000 g/mol), was selected to synthesize porous membranes. Polyvinyl-pyrrolidone (PVP, Serva, Mw~25,000 g/mol) was added as soluble component to form porous structure while *N*,*N*-dimethylacetamide (DMA, Tedia) was chosen as solvent to prepare solution for the casting process. Distilled water was used as coagulating bath. Argon (Praxair, 99.9%) gas was fed into the reaction chamber of the plasma reactor to produce plasma radiation on porous membrane surface. Poly(vinyl alcohol) (PVA, Vetec, 80% hydrolyzed, Mw~72,000 g/mol) and poly(acrylic acid) (PAA, Aldrich, Mw~250,000 g/mol) were simultaneously applied on functionalized porous membrane surface to form composite pervaporation membranes. Deionized water and ethanol (Vetec, 99.8%, v/v) were employed to prepare the feed solution for dehydration experiments. All reagents were analytical grade and were utilized without further purification.

2.2. Dense blend membranes

Dense polymeric membranes were prepared by the casting technique from solution of 5% polymer dissolved in distilled water. Polymer composition included 75/25, 50/50, 25/75 wt.% PVA/PAA in addition to the pure polymers. All membranes were dried at room temperature and polymer blends were treated thermally at 150 °C for 3 h.

2.3. Porous membrane synthesis

Polyethersulfone membranes were synthesized through the well known inversion of phase process in a distilled water bath. First, a polymeric solution 15% PES, 7.5% PVP and 77.5% DMA, weight fractions, was prepared [11]. Then, it was spread over flat glass surface and exposed for 30 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 with distilled water.

2.4. Plasma treatment

A radio frequency reactor (Harry-Plasma-Inductive, 8–12 MHz) was used to perform plasma treatment. Porous PES membrane was set in the center of reactor chamber. The precursor gas was argon, fed at room temperature. Operating conditions were 300 mTorr chamber pressure and 29.6 W discharging power of the source. Exposure time was 15 min after a series of experiments to achieve best results.

2.5. Hydrophilic polymers coating

Dense hydrophilic skin was deposited by casting technique. Coating solution was 5 wt.% hydrophilic polymers dissolved in distilled water. Polymer composition was: 75% PVA and 25% PAA w/w. The first layer was deposited after 1 h of PES plasma treatment.

Then, the second layer was spread 24 h later. Composite membranes were dried at room temperature and crosslinking carried out by heating at 150 °C for 3 h.

2.6. 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°. Membrane surface hydrophilic character was investigated by measurements of contact angles (water drops of approximately 10 µl) 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 iterative procedure proposed by Neumann Eq. (1), [12]. The adhesión work was estimated through a combination of Young and Dupré equations [13]. For each membrane, five drops were placed at different locations and the average of these measurements is reported.

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_S}{\gamma_L}}\, e^{-\beta(\gamma_L-\gamma_S)^2} \qquad (1)$$

where θ° is contact angle, γ_L (mJ m^{-2}) and γ_S (mJ m^{-2}) are liquid tension and surface energy respectively, β is a parameter determined from experimental data, $\beta = 0.0001247$ (m^2 mJ^{-1})^2.

2.7. Sorption

The dry PVA-PAA dense membranes were weighed and immersed in pure water bath. Thus, they were maintained at 60°C for three days until swelling equilibrium. 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.

2.8. Pervaporation experiments

Permselective properties of crosslinked PVA-PAA/PES composite membranes were evaluated in a standard pervaporation lab set [14]. It was fed with a liquid mixture 20/80 wt.% basis water–ethanol. Membrane area of the flow cell in the experiments was 28.27 cm^2. 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), separation factor (α), and pervaporation separation index (PSI). Total permeation flux was calculated through Eq. (2):

$$J = \frac{W}{A \bullet t} \qquad (2)$$

where J, W, A and t denote flux (g m^{-2} h^{-1}), weight of the permeate (g), effective membrane area (m^2), and operation time (h), respectively. Separation factor, α, is estimated from Eq. (3):

$$\alpha_{\text{water}/\text{Ethanol}} = \frac{\dfrac{Y_{\text{water}}}{Y_{\text{Ethanol}}}}{\dfrac{X_{\text{water}}}{X_{\text{Ethanol}}}} \qquad (3)$$

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

Pervaporation separation index (PSI) (g m^{-2} h^{-1}] was calculated from Eq. (4):

$$\text{PSI} = J \bullet \alpha \qquad (4)$$

3. Results and discussion

3.1. Morphology

The photomicrograph of the support PES membrane shows the asymmetric structure obtained with the selected synthesis conditions (Fig. 1). A spongy region can be observed, in addition to macropores. Thickness of this membrane was approximately 230 µm.

On the other hand, a typical SEM image of a crosslinked PVA-PAA/PES composite membrane, prepared

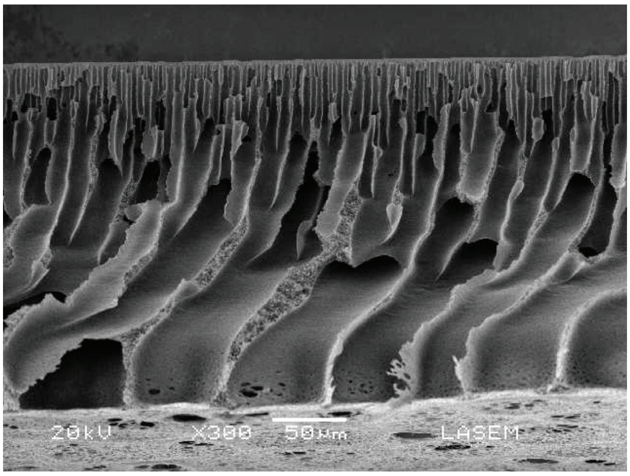

Fig. 1. Cross-section of the PES support membrane (magnification: 300×).

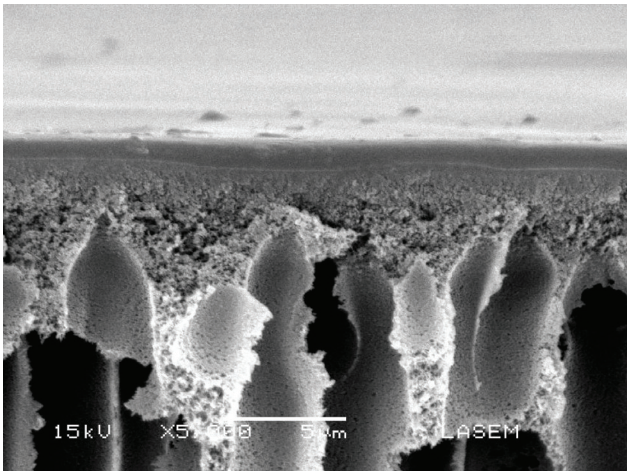

Fig. 2. Cross-section of the PVA-PAA/PES composite membrane (magnification: 5000×).

with technique described above, can be seen in Fig. 2. Dense film thickness of coated polymers is about 1.2 µm.

During the coating process, diluted polymeric solution can subtly penetrate in pores located close to the PES surface. However, SEM images could not identify the extent this intrusion phenomena. Nevertheless, a clear interface between PES surface and dense polymer film can be noticed.

3.2. Contact angle, surface free energy and adhesion work

Porous support PES membranes have a surface with hydrophobic character. Argon plasma treatments modify the chemical behavior of this surface creating hydrophilic properties. As a matter of fact, surface energy values increased from 48.06 to 67.92 mJ/m^2 after plasma exposure for 15 min (300 mTorr, 29.6 W), as well as adhesion work was enhanced approximately 30% (Table 1). This behavior facilitated the adhesion of a dense polymer film, of hydrophilic nature, onto the porous support surface modified by plasma treatment.

Table 1
Effect of plasma treatment time on surface properties of the support PES membranes, (Argon, 300 m Torr, 29.6 W)

Treatment time	θ (°)	γ_s (mJ/m^2)	W_a (mJ/m^2)
0	**60**	**48.06**	**109.18**
2	53	51.70	116.07
5	47	55.35	122.23
10	38	60.45	130.18
15	**23**	**67.92**	**139.06**
20	22	68.05	140.21
25	21	68.54	140.70
30	19	68.97	141.95

Contact angle also showed an important change from 60° to 23° after 15 min of plasma treatment. Although it must be pointed out that this hydrophilic character decays with time [8]. Therefore, diluted polymeric solution was spread over activated membrane after 1 h of plasma treatment. The crosslinked PVA-PAA/PES composite membranes have a stable hydrophilic skin with θ 51°, γ_S = 52.80 mJ/m^2 and W_a = 118.27 mJ/m^2. This hydrophilic character is permanent with time.

After 15 min of plasma treatment (Argon, 300 m Torr, 29.6 W), the contact angle changes are less pronounced (Table 1). A plasma treatment for longer times can damage the surface of the membrane [15,16].

3.3. Surface chemical nature

A comparison between FT-IR/HATR spectra of PES and the composite membranes is presented in Fig. 3. The strong presence of bands assigned to O–H (3305 cm^{-1}) and C=O (1703 cm^{-1}) confirm the observed hydrophilic character in the composite membranes [17]. It should also be stressed that in the range of 1600–600 cm^{-1} the penetration depth of IR beam is larger, going beyond the polymer skin [18]. Thus, bands of the PES porous membrane can also be seen in this spectrum region.

The increase in the hydrophilic groups is observed in the PVA-PAA dense membranes. The absorbance of O–H peak increases with the PVA concentration, while the absorbance of C=O peak increases with the content of PAA (Fig. 4).

3.4. Sorption

The thickness of the PVA-PAA dense membranes were of approximately 40 µm. The swelling behavior

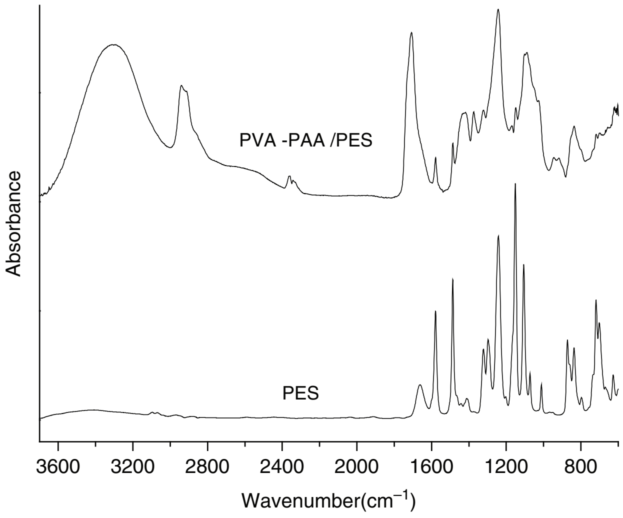

Fig. 3. FT-IR/HATR spectra of PES support membranes and PVA-PAA/PES composite membranes.

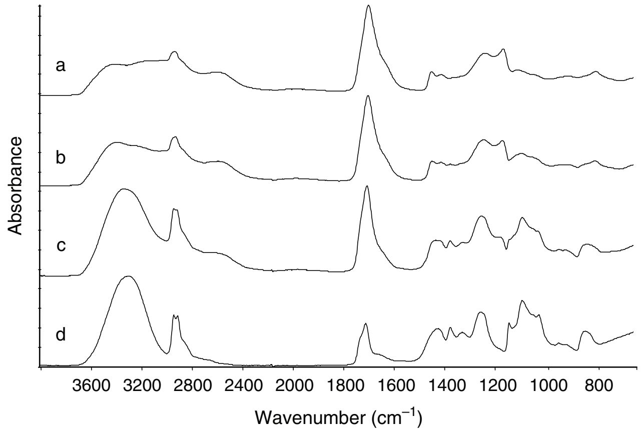

Fig. 4. FT-IR/HATR spectra of PVA-PAA dense membranes and pure PVA; (a) 25%PVA-75%PAA, (b) 50%PVA-50% PAA, (c) 75%PVA-25% PAA, (d) pure PVA.

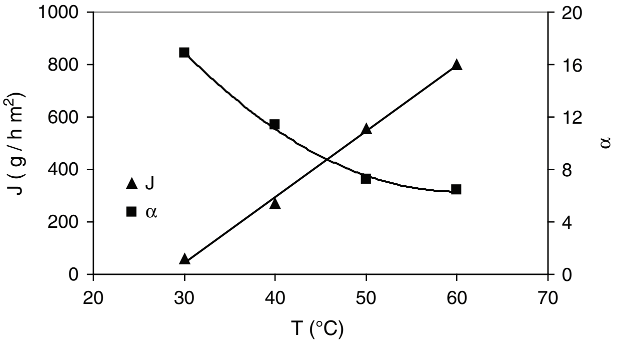

Fig. 5. Effect of feed temperature on total flux and separation factor of the PAA-PVA/PES composite membrane for the pervaporation of a 20/80 wt.% water–ethanol mixture.

Table 2
Pervaporation separation index (PSI) of PVA-PAA/PES membranes for a 20/80 wt% water/ethanol feed

T (°C)	PSI (g m^2 h^{-1})
30	1013
40	3061
50	4029
60	5127

is very sensitive to the polymers ratio. The equilibrium swelling increases with the PAA content in the membranes. This is due to the contribution of hydrophilic groups, to the decrease of the crystalline portion in the PVA-PAA membrane and the reduced crosslinking among the polymers.

The membrane of pure PVA resulted excessively swollen. Introducing PAA promotes crosslinking with the thermal treatment. Similar results are reported in the literature when blends of PVA-PAA in the range of 15–20 wt.% PAA were thermally crosslinked [19]. When % PAA is increased, the dense membranes lose flexibility after the thermal treatment, and the PAA membrane is very brittle.

The composition 75% PVA-25% PAA was then selected for the production of the selective skin of the composite membrane and application to pervaporation of water–ethanol (20/80 wt.%).

It is expected that in the composite membranes, the support contributes to limit the swelling of the active layer stuck into the porous substrate, justifying why a good adhesion is a key point. The plasma treatment with argon raised the surface energy of the support surface, increasing the interfacial interaction with the active layer.

3.5. Pervaporation

Crosslinked PVA-PAA/PES composite membranes showed a good hydrophilic selective behavior during the pervaporation experiments. Their performance and stability, comparable to average values reported in the literature, within the range of temperature investigated (30–60°C), can be seen in Fig. 5. Calculated PSI values, also presented in Table 2, increase fivefolds with temperature.

It was observed that flux of both components rises with temperature while selectivity ($\alpha_{\text{water/Ethanol}}$) decreases. In order to explain the results, one can attribute the flux behavior to the increase of both, the driving force across the composite membrane and the molecular mobility within the crosslinked polymeric structure. Moreover, selectivity reflecting the relative magnitudes of the fluxes of each component, may have been reduced by a compensation of activation energies and also possibly due to a coupled diffusional transport of water and ethanol molecules.

Driving forces for mass transport across the membrane can be estimated by the fugacity difference between the bulk feed and the permeate as follows [20]:

$$f_i^b - f_i^p = p_i^S x_i \gamma_i - p^P y_i \tag{5}$$

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

The effect of temperature on the driving force shown in Fig. 6 confirms that ethanol driving force grows faster. On the other hand, with the plotted data in Fig. 7, one can assume the conventional Arrhenius relationship,

$$J_i = J_{i0} \exp\left(-\frac{E_{Ji}}{R \bullet T}\right) \tag{6}$$

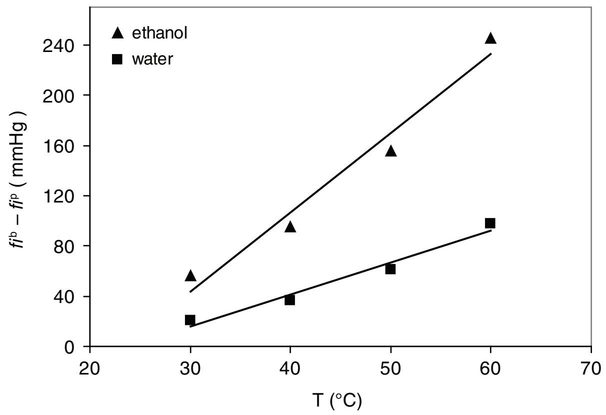

Fig. 6. Effect of feed temperature on driving forces (f_i^b–f_i^p) for mass transport in the pervaporation of a 20/80 wt.% water–ethanol mixture.

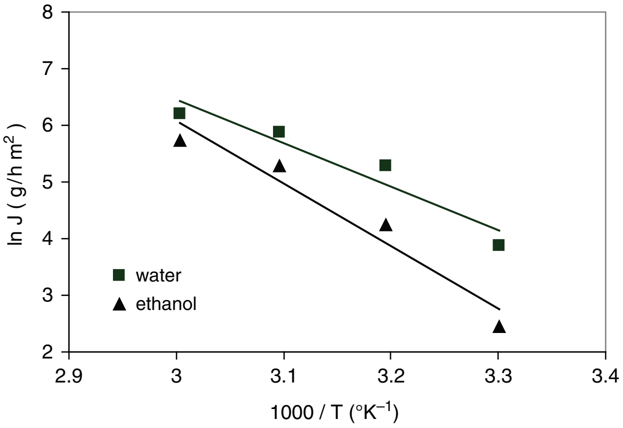

Fig. 7. Effect of feed temperature on permeation fluxes of water and ethanol (feed mixture water–ethanol, 20/80 wt.%).

where J_i and E_{Ji} denote flux and apparent activation energy for component i, respectively. R is the gas constant and T is the Kelvin temperature. From this model, the calculated apparent activation energy for water and ethanol were 15 and 22 kcal/g mol, respectively, reflecting the variation of the driving forces and the consequent reduction in selectivity.

4. Conclusions

The PES substrates revealed a marked reduction of contact angle after the plasma treatment with argon. The resulting increasing surface energy was used to deposit a diluted solution of polymer mixture. A PVA-PAA dense skin could be formed and well characterized. Thus starting from a porous hydrophobic support it was ended with a very stable hydrophilic membrane with properties shared from both polymers. Dehydration of a 20/80 wt.% water–ethanol mixture by pervaporation resulted in good flux-selectivity performance and indicates good prospects for future explorations of the technique.

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