Pervaporation Separation of Methanol/Methyl *tert*-Butyl Ether with Poly(lactic acid) Membranes

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ABSTRACT: Poly(lactic acid), as a natural source polymer, was used to prepare pervaporation dense membranes. The performance of these membranes for the separation of the methanol (MeOH)/methyl *tert*-butyl ether (MTBE) mixtures was investigated. The effects of different operating conditions, including the feed concentration of MeOH, temperature, and flow rate, were examined. Several characterization tests were performed as well. The swelling results, scanning electron microscopy images, contact angles, and mechanical strength measurements are presented. These membranes were found to be selective to MeOH, particularly for traces of MeOH in MTBE with a separation factor of more than 30. There was a small decrease in the separation factor when the feed temperature was increased; meanwhile, the total flux increased to some extent. This could be explained with respect to the thermal motions of the polymer chains and the permeating molecules. With an increase in the feed flow rate, both the selectivity and total flux increased because the concentration and temperature polarizations decreased. At higher flow rates, the feed components were homogeneously distributed over the membrane surface, whereas there may have been a concentration or temperature gradient at lower flow rates. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1364–1371, 2010

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INTRODUCTION

In the chemical industry, a huge amount of energy is consumed in separation processes. Distillation, as a conventional, energy-intensive separation process, is highly expensive for the separation of close boiling liquids or liquids forming azeotropes. Pervaporation (PV) is considered as an energy-saving economic alternative for such separation processes. The other advantages of PV over traditional processes include its modularity, its ability to separate heat-sensitive components, and the lack of theoretical limitation in the final purity of product.[1]

To reduce air pollution from automobiles, lead-free or low leaded gasoline is recommended for use in many countries. Therefore, several fuel additives are currently added to maintain an adequate octane values in gasoline. Methyl *tert*-butyl ether (MTBE) has been used as an octane enhancer in gasoline and is produced by the reaction of methanol (MeOH) with isobutylene. It is often desirable to add MeOH in amounts up to 20% excess to improve the reaction conversion. However, the use of excess MeOH causes a purification problem because MeOH forms a minimum boiling azeotrope with MTBE at a composition of 14.3 wt % MeOH at atmospheric pressure.[2] For this reason, the possible application of PV, which is a more energy-efficient and lower cost process, has been considered as an alternative to distillation.

So far, different types of polymers have been used as membrane materials for the PV separation of MeOH/MTBE mixtures. These membranes mostly include cellulose-based membranes, mainly cellulose acetate,[2–5] poly(vinyl alcohol) (PVA)-based membranes,[6–9] and inorganic and mixed matrix membranes.[10–12] In a recent article by Sridhar et al.,[13] an extensive review on the properties, production, and separation processes used for an MeOH/MTBE system was presented. The performance of different PV membranes applied for this separation was highlighted, and an emphasis on prospective membrane materials for the future was made.

Different performances, including a wide range of separation factors from less than 2 (polyethylene-*co*-vinyl acetate, more than 10 Kg/m²h flux[14]) to more than a few thousand [PVA/poly(vinyl pyrrolidone) blend, around 10 g/m²h flux[7]] have been reported for polymeric membranes. Although there are many other materials and preparation methods studied for this particular PV separation, some of them focus on the membrane itself in evaluating this separation as a

case study. Because, to our knowledge, there has been no PV experience with poly(lactic acid) (PLA) polymer published, the aim of this study was to examine some aspects of this biodegradable polymer for MeOH/ MTBE separation. However, Friess et al. reported the potential of MeOH separation in PLA membranes with higher sorptions in comparison with other organic compounds (i.e., aliphatic and cyclic hydrocarbons).

Biodegradable polymers are a loosely defined family of polymers that are designed to degrade through the action of living organisms. They can be either natural (e.g., cellulose, chitin, chitosan, collagen) or synthetic (e.g., PVA, cellulose acetate, PLA). PLA is an aliphatic thermoplastic polyester obtained by the polycondensation of the acid or by the ring-opening of the lactide. Its mechanical performance is similar to that of polystyrene (PS). Lactic acid can be produced by the fermentation of coal, petroleum, or natural gas. Applications of PLA include bottles, thermoformed containers for food, films, and fibers.[16] PLA is produced from renewable resources, and it is expected to be a suitable replacement for numerous petroleum-based polymers in the future.[17]

Recently, new techniques that allow the economical production of high-molecular-weight PLA polymer have broadened its uses.[18,19] Most of the membrane studies carried out on PLA have been related to the gas permeation and separation properties of this polymer; this knowledge is necessary with respect to its barrier and food packaging applications.[20–24] In this study, the PV properties of PLA membranes were studied for MeOH/MTBE separation as a case study.

EXPERIMENTAL

Materials

PLA, with the trade name Nature Green 2100D [poly(L-lactic acid); PLA consists of two comonomers: L type and D type (D-isomer %) D% comonomer of up to 1.47 ± 0.2%; high crystalline], was supplied by Cargill-Dow, Inc. (Cargill Dow LLC, Minneapolis, MN) Chloroform was obtained from Carlo Erba (Milan, Italy) with a minimum assay of 99%. This product was stabilized with 0.6–1% ethyl alcohol. MeOH (99.8%) was purchased from Merck, (Darmstadtm, Germany) and *tert*-butyl methyl ether (99.7%) was obtained from Sigma-Aldrich; (Milan, Italy) these were used as feed components. All of the chemicals and the polymer itself were used as received without further purification.

Membrane preparation and characterization

PLA was dissolved in chloroform by stirring for at least 12 h at room temperature. A homogeneous solution of 7.5 wt % by polymer weight in a solvent was obtained. The solution remained untouched for at least 2 h for degassing. PLA films were cast on glass plates with a film applicator and slowly dried at 40°C for 48 h. The resulting dense membranes, which were detached in distilled water and dried, were transparent and had a thickness of around 23–28 μm. The measurement of thickness was performed with a digital micrometer (Mahr, 40E, Mahr GmbH, Göttingen, Germany) with an accuracy of ±4 μm and confirmed by scanning electron microscopy (SEM) micrographs (Cambridge Stereoscan 360, Cambridge Instruments, Ely, UK).

The contact angle for water on the surface of the membrane was measured at room temperature with an optical instrument (Nordtest srl, G-I, Serravalle Scrivia, Italy). Furthermore, mechanical strength tests were performed with a Zwick/Roell materials testing machine (BTC-FR2.5TN-D09, Ulm, Germany) to characterize the membranes. Several mechanical characteristics of the membranes were investigated before and after 1 week of immersion for the membranes in feed solutions with different MeOH concentrations.

Swelling experiments

Four small pieces of membranes ($\approx$10 cm^2) were weighed and immersed in liquid mixtures with different compositions of MeOH and MTBE at 30°C for 48 h to reach swelling equilibrium; they were then taken out of the mixtures. These membranes were quickly wiped with tissue paper to remove the excess free liquid on their surface and weighed with a digital balance (Gibertini, Crystal 500, Italy, Crystal 500, Gibertini Elettronica srl, Milan, Italy) with an accuracy of 0.001 g. The degree of swelling (DS) was calculated as follows:

$$DS = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

where W_s and W_d are the weights of the swollen and dry membranes, respectively.

PV experiments

A schematic of the experimental PV apparatus is shown in Figure 1. The volume of the double-jacket feed reservoir was around 300 mL. The temperature of the feed solution was maintained with a Thermo digital circulating bath (Neslab RTE-201, Newington, NH)) at ±0.01°C. The feed was pumped through a Verder gear pump (2035 Manual, Germany, Vleuten, Netherlands) with an adjustable flow rate to the membrane cell (Sempas, Membrantechnik GmbH, Sulzbach/Saar, Germany). The effective area of the membrane was approximately 60.7 cm^2. The remaining part of the feed was recycled back to the feed tank. The permeated vapor was condensed and collected *in vacuo* in a liquid nitrogen condenser and weighed with the balance (Gibertini, Crystal 500, Italy). The operating vacuum was maintained at 6 ± 1 mbar; this was done with a two-stage vacuum
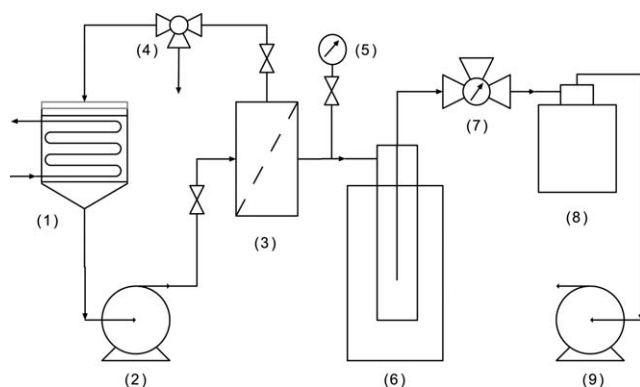
Figure 1 Schematic diagram of the PV apparatus: (1) double-jacket feed reservoir, (2) feed pump, (3) membrane cell, (4) three-way sampling valve, (5) digital vacuum meter, (6) liquid N_2 condenser, (7) vacuum purge valve, (8) cold trap, and (9) two-stage vacuum pump.

pump (RV5, Edwards, United Kingdom, Crawley, UK). This vacuum was measured with an Active Pirani Gauge (APG-M-NW16, Edwards) and could be read on a 5-Pascal digital vacuum meter (APG-A921, 5Pascal, Milan, Italy).

PV experiments were carried out for different feed concentrations, temperatures, and flow rates. After they reached the steady state, the permeates were collected for 1 h and analyzed with an Abbe 60 type direct reading refractometer (60/DR, Bellingham+Stanley, Ltd., Tunbridge Wells, UK) at 25°C for all of the samples and the feed. The permeate flux (J) was obtained with the following equation:

$$J = \frac{Q}{At} \qquad (2)$$

where Q is the amount of the permeate (g), A is the membrane area (m^2), and t is the operating time (h). The permeation selectivity [separation factor (α)] of MeOH was calculated from eq. (3) as follows:

$$\alpha = \frac{y_{MeOH}/y_{MTBE}}{x_{MeOH}/x_{MTBE}} \qquad (3)$$

where y_i and x_i are the weight fractions of component i in the permeate and the feed, respectively. The performance of the membrane was also evaluated in terms of the pervaporation separation index (PSI) and enrichment factor (β) as obtained from eqs. (4) and (5), respectively[25,26]:

$$PSI = J(\alpha - 1) \qquad (4)$$

$$\beta = \frac{y_{MeOH}}{x_{MeOH}} \qquad (5)$$

These are two other criteria that are applied to show the performance for a particular separation. Although the enrichment factor and the separation factor (selectivity) focus on the quality of separation, PSI also involves the quantity by the application of the permeation flux on selectivity. Because there are sometimes high separation factors reported with a really low flux, which make these membranes inapplicable for practical applications, PSI could be considered a more applicable criterion.

RESULTS AND DISCUSSION

Membrane characterization and swelling properties

An SEM micrograph of the cross section of PLA membrane is shown in Figure 2. Because the membranes were dry cast, we obtained dense transparent membranes. The homogeneity of the membranes was also confirmed by SEM. The contact angle for water on the surface of the membrane was around 74°. Therefore, the membranes were considered more hydrophilic, with an affinity for water and usually other polar molecules, including alcohols.

The swelling results are represented in Figure 3. DS and its variations at the different MeOH concentrations studied were very small. However, a slight increase at higher concentrations of MTBE was shown. There was also an insignificant increase in the opacity of the membranes after drying with respect to untreated transparent PLA membranes as the MTBE concentration increased. This behavior was probably due to a physical plasticization occurring at higher MTBE concentrations. The swelling trend could be explained by the solubility parameters of PLA, MeOH, and MTBE, as reported in Table I.[12,27] In general, the selection of polymers compatible with the mixtures for separation is based on the Hansen solubility parameter[28]:

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \qquad (6)$$

where δ_d, δ_p, and δ_h are the dispersive, polar, and hydrogen-bonding contributions to the solubility parameter. The solubility parameter value of PLA ($\delta_t = 21.73$) was closer to that of MTBE ($\delta_t = 16.73$) than that of MeOH ($\delta_t = 29.60$); this confirmed that the membranes swelled more at higher MTBE concentrations. The compatibility among the components and polymer was indicated by the following relationship as well[29]:

$$\Delta_{i,polymer} = \sqrt{\left[\left(\delta_{d,i} - \delta_{d,polymer}\right)^2 + \left(\delta_{p,i} - \delta_{p,polymer}\right)^2 + \left(\delta_{h,i} - \delta_{h,polymer}\right)^2\right]} \qquad (7)$$
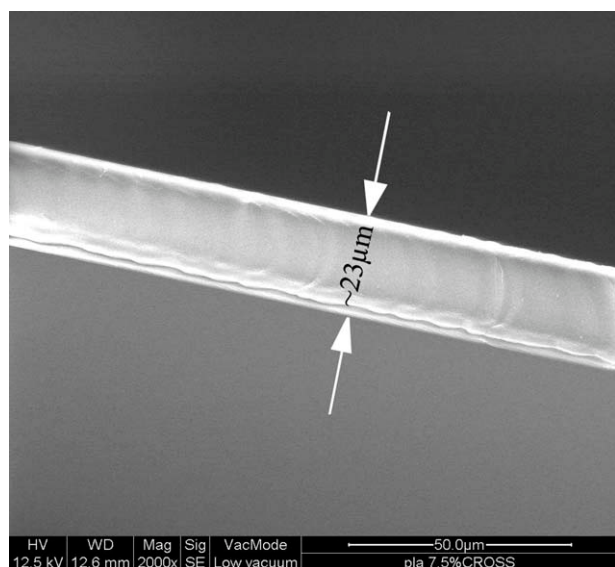
Figure 2 Cross-sectional SEM micrograph of the PLA dense membrane.

Figure 3 DS at different feed concentrations.

where Δ is the magnitude of the vectorial distance of the parameters and i represents each component. The greater the compatibility is between any component and polymer, the smaller will be the magnitude of Δ. These values were 16.83 and 6.82 for MeOH and MTBE, respectively. Therefore, we confirmed that the membrane should have swelled more in MTBE.

With respect to the mechanical strength tests, the polymer films had good mechanical properties for use in the PV experiments. The results, including those of Young's (elastic) modulus, maximum stress, and elongation at break, are represented in Figure 4. The mechanical properties of the PLA membrane before immersion in the feed solution is indicated by a base horizontal line. Both the Young's modulus and maximum stress values decreased with increasing MTBE content of the solution, whereas the elongation values increased. This trend, which was quite the same as the transparency change in the swelled membranes, indicated that the PLA films were more sensitive to MTBE than to MeOH. The plasticization of PLA in MTBE resulted in lower stress and higher strain values. The values of Young's modulus were comparable with the approximate value of other
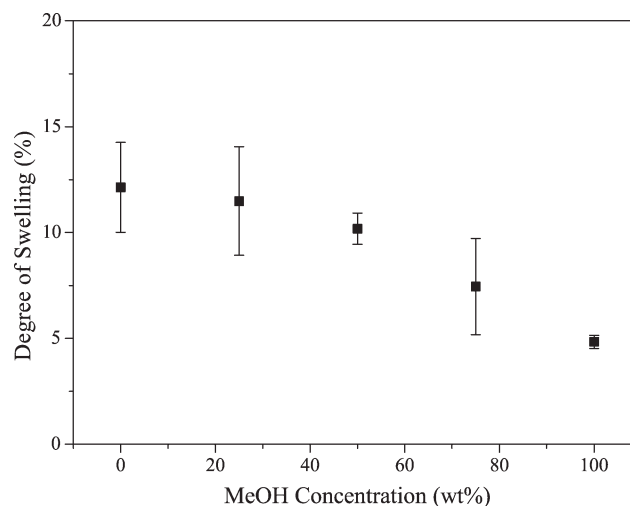
polymers, such as PVA (1900 N/mm^2), PS (3000–3500 N/mm^2), low-density polyethylene (200 N/mm^2), high-density polyethylene (800 N/mm^2), polytetrafluoroethylene (500 N/mm^2), and polypropylene (1500–2000 N/mm^2). However, the PLA membranes lost their initial strength during the experiments; even these membranes were still strong in comparison with many other PV membranes. This was in agreement with the results reported by Dorgan et al.,[30] in which the tensile and flexural moduli of PLA were higher than those of high-density polyethylene, polypropylene, and PS, but the Izod impact strength and elongation at break values were smaller than those for these polymers.

Effect of the feed concentration

New PLA membranes were used for each new PV experiment to prevent any possible effect on the performances by probable morphological changes once the membranes contacted the MeOH/MTBE solution. The separation factors and total fluxes are shown in Figure 5. The MeOH selectively permeated through the PLA membranes. There was a tendency of MeOH to separate from the feed, particularly at lower MeOH concentrations. The separation factor for 1% MeOH in feed was more than 35. However, it dropped drastically from 35 to 4 when the MeOH

TABLE I
Molecular Properties of the Solvents and the Polymer

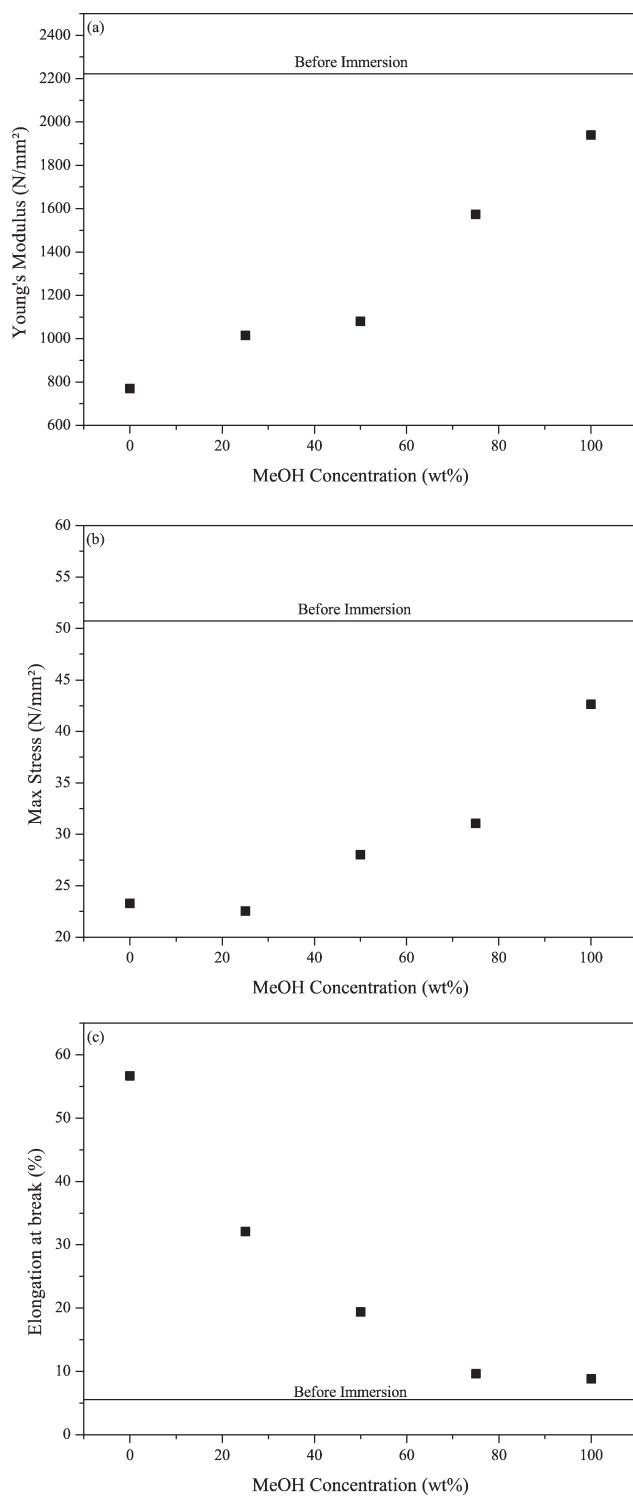| Solvent or polymer	Solubility parameters (MPa$^{1/2}$)				Vectorial distance (MPa$^{1/2}$)	Molar volume (cm^3/mol)	Molecular kinetic diameter (nm)
	δ_d	δ_p	δ_h	δ_t			
MeOH	15.13	12.27	22.29	29.60	16.83	40.7	0.40
MTBE	15.48	3.63	5.22	16.73	6.78	119.12	0.62
PLA	18.5	9.7	6	21.73			

Figure 4 Mechanical strengths of the PLA membrane before and after 1 week immersion in feed solution: (a) Young's elastic modulus, (b) maximum stress, and (c) elongation at break.

concentration increased to more than around 10%, and then, it remained constant. Despite swelling increases at higher concentrations of MTBE, because the molecular size of MeOH was much smaller (Table I), it could selectively penetrate through the

membrane. In other words, MTBE molecules made the membrane swell but not enough to allow their passage through the membrane, whereas the smaller size of the MeOH molecules was favored by the swelled membrane. Furthermore, the polar contribution of the solubility parameter of PLA (9.7 $MPa^{1/2}$) was much closer to that of MeOH (12.27 $MPa^{1/2}$) than to that of MTBE (6 $MPa^{1/2}$), despite the hydrogen bounding contribution (Table I). Because MeOH/MTBE PV was categorized as a polar/non-polar separation, the polar contribution may be of more importance in comparison with the other contributions.

The general trend of total flux was an increase with the MeOH concentration in the feed; this was expected because of the greater number of MeOH molecules. The simultaneous increase in the amount of small penetrating MeOH molecules and the decrease in the amount of MTBE molecules, together with the decreasing swelling effect, resulted in a rather constant separation factor for higher MeOH concentrations.

The variation of the permeate concentration of MeOH with its feed concentration and the enrichment factor data at 30°C are represented in Figure 6(a,b), respectively. The concentration of MeOH in the permeate increased with a rather constant slope with respect to its concentration in the feed up to 50%. The enrichment factor, which is the concentration ratio of MeOH in the permeate to that in the feed, decreased sharply from more than 26 at 1% MeOH to around 2 at 18% MeOH and then slightly decreased. The PSI values are also depicted in Figure 7. Because of the high permeation flux of the membranes, these values were generally high. Particularly, at lower MeOH concentrations, because the
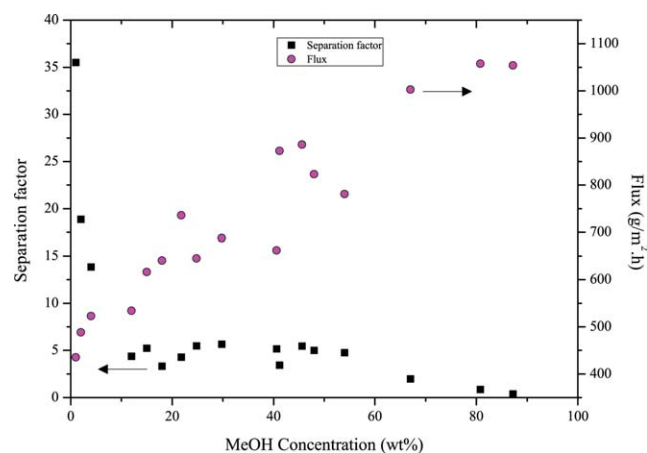

Figure 5 Separation factors and permeate fluxes for different MeOH concentrations in feed (feed temperature = 30°C, feed flow rate = 50 L/h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
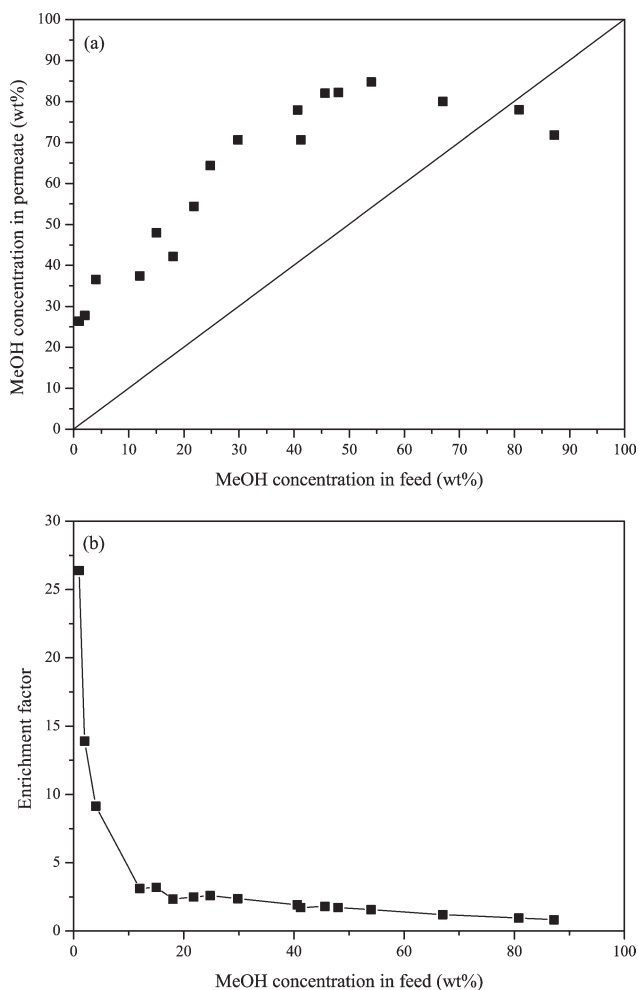
Figure 6 MeOH concentrations in the feed and permeate: (a) variation of permeate concentration of MeOH with its feed concentration and (b) enrichment factor.

Figure 7 PSI for different feed concentrations.

Figure 8 Effect of the feed concentration and flow rate on the (a) separation factor and (b) flux (g/m^2 h) at 30°C (concentrations = 4, 15, and 27 wt %; flow rates = 5, 17, 29, 40, and 50 L/h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]

separation factors were also high, the PSI values were in the range of 10,000 g m^{-2} h^{-1}.

Effect of the feed flow rate

Figure 8(a,b) shows the dependence of the MeOH separation factor and total flux, respectively, with feed flow rate at different feed concentrations. The feed temperature was constant at 30°C. The MeOH concentrations used to generate these figures were 4, 15, and 27 wt % at different flow rates of 5, 17, 29, 40, and 50 L/h.

The results show that both variables increased with increasing feed flow rate. However, the separation factors did not significantly change at higher MeOH concentrations. This could be explained by means of the concentration and temperature polarization phenomena. During the PV tests, the concentration trend of MeOH on the membrane surface decreased gradually, whereas the MTBE concentration increases. Furthermore, the permeating compo-
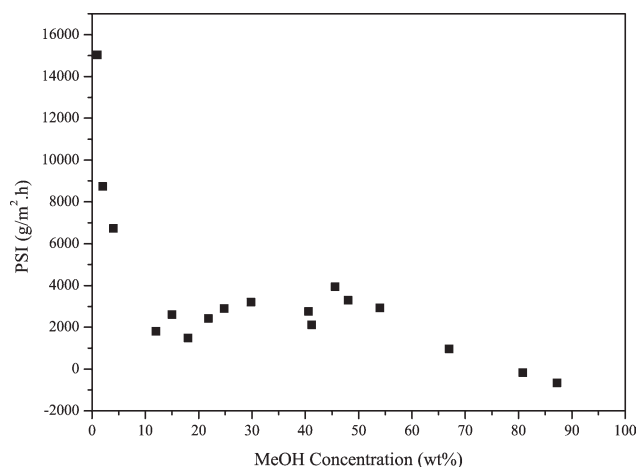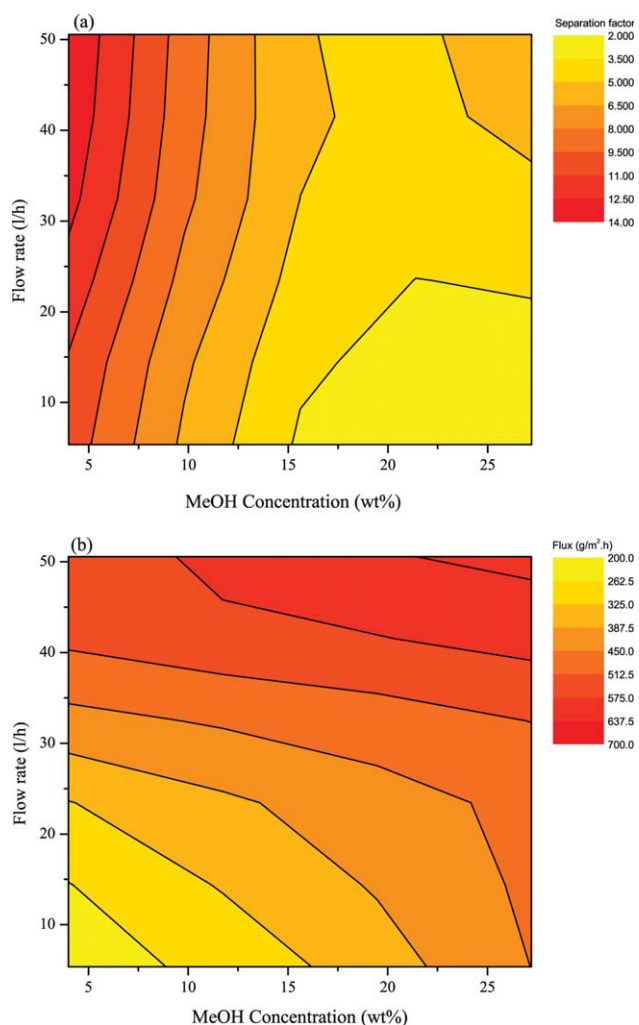
Figure 9 Effect of the feed concentration and temperature on the (a) separation factor and (b) flux (g/m² h) at 50 L/h (concentrations = 4, 15, and 40 wt %; temperatures = 30, 40, and 50°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

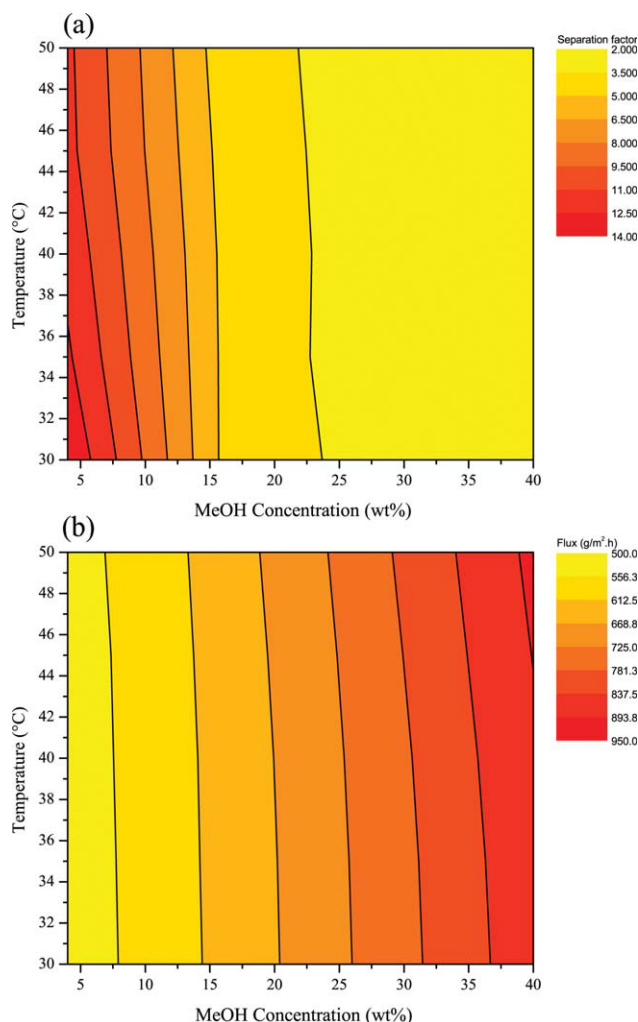nents needed some energy to transfer into the vapor phase; this decreased the feed temperature on the membrane. Both the temperature polarization and, particularly, the concentration polarization led to a decrease in the PV performance. These phenomena decreased with increasing feed flow rate; this allowed us to obtain an increase of total flux and selectivity to some extent.[31,32]

Effect of the feed temperature

As shown in Figure 9(a,b), increasing the temperature led to a decrease in the separation factors and an increase in the total flux. However, there was no significant change in the separation factors at higher temperatures or at higher concentrations. In these experiments, the flow rate was kept constant at 50 L/h, whereas the MeOH concentrations and feed

temperatures were varied as 4, 15, and 40 wt % and 30, 40, and 50°C, respectively.

The temperature enhancement acted in two ways: increasing the mass transfer and the mobility of polymer molecules. The driving force in the PV process was the chemical potential, which was based on the partial vapor pressure differences of the permeating components in the feed and permeate sides. The vapor pressure of the feed side increased with increasing temperature, whereas the vapor pressure of the permeate side did not change significantly. Therefore, the driving force of mass transfer was enhanced.[33] In addition, during PV tests, the permeating molecules diffused through the free volumes of the membrane. Thermal motions of the polymer chains in the amorphous regions randomly produced free volumes. As the temperature increased, the frequency and amplitude of the polymer jumping chains increased. As a result, the free volume of the membrane increased. An increase in the side chain mobility in the polymer and consequent enlargement of the free volume inside the membrane facilitated the permeation of larger MTBE molecules. Therefore, MeOH selectivity decreased on the contrary of the total flux.[34,35]

CONCLUSIONS

The feasibility of using PLA membranes in PV was studied for MeOH/MTBE separation and quantified by means of the separation factor, total flux, PSI, and enrichment factor. Unmodified PLA membranes were able to selectively separate low concentrations of MeOH from MTBE with a selectivity of more than 30 (35.5 for 1 wt %). The separation factors dropped drastically and became almost constant (ca. 5) at an MeOH concentration higher than around 10 wt %. The enrichment factors and permeation separation indices showed similar behavior. However, because of the high permeation flux, the PSI values were high (15,000 g m⁻² h⁻¹ for 1 wt %).

In addition to the effect of the feed concentration on the performance, the effects of other operational conditions, such as the feed temperature (30–50°C) and flow rate (5–50 L/h), was also investigated. We observed that an increase in the feed temperature led to a higher total flux but a lower selectivity because of the increasing of free volume inside the polymer and also mass transfer. However, this effect was not significant at higher temperatures. Increasing the feed flow rate enhanced both the flux and selectivity and decreased the temperature and concentration polarizations on the membrane surface.

The mechanical strength of the PLA membranes decreased with contact with the MeOH/MTBE solution. The Young's modulus for the untreated membrane was 2224 N/mm². This value decreased to 770

and 1939 N/mm^2 for membranes immersed in pure MTBE and MeOH, respectively. However, the change in the mechanical properties of the PLA membranes did not compromise the PV tests in the MeOH/MTBE concentration range of interest.

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