

# Synthesis and Characterization of Poly(ether-*block*-amide) Membranes for the Pervaporation of Organic/Aqueous Mixtures

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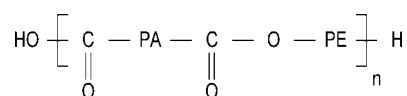
**ABSTRACT:** We made poly(ether-*block*-amide) membranes by casting a solution on a nonsolvent surface. The effects of the solvent ratio (*n*-butanol/isopropyl alcohol), temperature, and polymer concentration on the quality of the membranes were studied. The results show that the film quality was enhanced with increasing isopropyl alcohol ratio in the solvent. This behavior was related to the reduction of the solution surface tension and the interfacial tension between the solution and nonsolvent. Uniform films were made at a temperature range of 70–80°C and a polymer concentration of 4–7 wt %. The morphology of the membranes was investigated with scanning electron microscopy. The qualities of the films improved with increasing isopropyl alcohol ratio in the solvent. With these mem-

branes, the pervaporation of ethyl butyrate (ETB)/water and isopropyl alcohol/water mixtures was studied, and high separation performance was achieved. For ETB/water mixtures, with increasing ETB content, both the permeation flux and separation factor increased. However, for isopropyl alcohol/water mixtures, with increasing isopropyl alcohol content, the permeation flux increased, but the separation factor was diminished. Increasing temperature in a limited range resulted in a decreasing separation factor and an increasing permeation flux. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1917–1923, 2008

**Key words:** membranes; tension; synthesis; solution properties

## INTRODUCTION

Poly(ether-*block*-amide) (PEBA) is the general name for a class of thermoplastic elastomers in which the polyether soft segments are alternatively linked with rigid polyamide segments. The polyamide crystalline domains provide mechanical strength, and the polyether amorphous domains offer high permeability due to the high chain mobility of the ether linkage. The general chemical formula of PEBA is as follows:<sup>1</sup>



where PA is a polyamide block and PE is a polyether block. Through proper combinations, a wide range of PEBA grades can be obtained with different physical properties. Two types of PEBA materials were manufactured by Elf Atochem (Belgium): hydrophobic PEBA materials with poly(tetramethylene glycol) soft

segments and hydrophilic PEBA materials with poly(ethylene glycol) soft segments.<sup>2</sup> PEBA has attracted interests as a promising material for membrane preparation. Its solubility properties strongly depend on the amount of PE component in the block copolymer and on the polarity of the PE and PA backbone elements. PEBA membranes have shown excellent selectivity for the extraction of aroma compounds from water by pervaporation (PV), especially for the enrichment of esters from dilute aqueous solutions.<sup>3</sup>

PV membranes have provided a method for separating liquid mixtures of volatile ingredients. The efficiency of PV has been approved for the elimination of water from organic solutions, the concentration or recovery of organics from aqueous solutions, separation of organic mixtures, and so on.<sup>4</sup> More than 40 articles have been published on PV of aroma compounds, which represent experiments carried out on almost 60 different volatile organic compounds in aqueous mixtures.<sup>5</sup> Each group of aroma compounds, including esters, alcohols, and aldehydes, is responsible for a typical juice flavor. These compounds are very sensitive to heat; therefore, conventional processes that involve evaporation may cause the loss of aroma in compounds and change juice flavors. The PV process can recover these aroma compounds without any loss.

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In this study, PEBA membranes were prepared for the separation of ethyl butyrate (ETB)/water and isopropyl alcohol/water mixtures. First, the effect of different parameters, such as the ratio of solvents, temperature, and concentration of polymeric solution, on film formation were studied. Scanning electron microscopy (SEM) was used to investigate the membrane surface morphology. The prepared membrane showed good performance for the separation of ETB and isopropyl alcohol from water.

## EXPERIMENTAL

### Materials

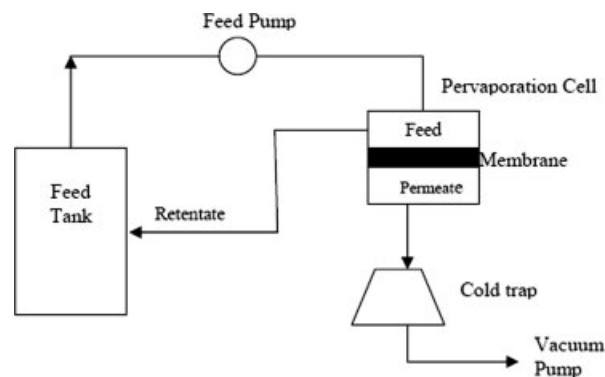
Hydrophobic PEBA was provided by Atochem as granules. Its properties are presented in Table I. *n*-Butanol and isopropyl alcohol with a purity of 99.9% (both from Merck Chemical Co., Germany) were used as solvents for the preparation of the PEBA membranes. The PEBA membranes were supported by microporous polysulfone (PS) membranes [ultrafiltration (UF) pHT20-6338], which were provided by Dow Denmark, Inc. ETB (from Merck Chemical Co., Germany), with a purity of 99.9%, and isopropyl alcohol were used in the PV experiments.

### Membrane preparation

PEBA membranes were prepared by the dissolution of the copolymer in the solvent or a mixture of the solvents. In polyamides (one of the copolymer parts), high intermolecular forces and strong hydrogen bonding forces make solubility difficult. Therefore, only polar solvents that interacted strongly with the polymer to break down the hydrogen bonds could be used. Polymeric solutions were stirred vigorously at a temperature near the boiling point of the solvents until a homogeneous solution was formed. One or two drops (0.01–0.03 g) of the polymeric solutions were dripped by capillary pipette on to the surface of deionized water. Because of the solvent exchange with the nonsolvent (water), thin membranes were formed. To provide mechanical strength to the PEBA membranes in the PV experiments, they were supported by PS UF membranes.<sup>6</sup>

**TABLE I**  
Properties of PEBA

PA segment	Polyamide 12 (nylon 12)
PE segment	Poly(tetramethylene glycol)
Composition (wt %)	57/43 PE/PA
Density (g/cm <sup>3</sup> )	1.01
Shore D hardness	55
Melting point (°C)	159



**Figure 1** Scheme of the laboratory-scale PV setup.

### PV experiment

A PV apparatus was used for the recovery of ETB and isopropyl alcohol from water and is presented in Figure 1. The system was composed of a temperature-controlled feed vessel, a circulating pump, a membrane test cell, a cold trap, and a vacuum pump. During the experiments, the upstream pressure was maintained at atmospheric pressure, whereas the downstream pressure was kept below 1 mbar with a vacuum pump. Permeation fluxes were determined by the weight of the permeate collected over a given period of time in the cold trap. The composition of the permeate mixtures was determined with gas chromatography. The performance properties of a given PV membrane were defined by the permeate fluxes ( $J$ 's) and separation factor ( $\alpha$ ):

$$J = \frac{m}{A \times t} \quad (1)$$

$$\alpha = \frac{(C_x/C_y)_{\text{Permeate}}}{(C_x/C_y)_{\text{Feed}}} \quad (2)$$

where  $m$  is the weight of the permeate,  $A$  is the membrane area,  $t$  is pervaporation time, and  $C$  is concentration. Subscripts  $x$  and  $y$  are the organic permeating component and water, respectively.

## RESULTS AND DISCUSSION

### Membrane formation

Because the surface tension of water (the nonsolvent) was greater than that of the polymeric solution and also the surface tension difference was large enough to overcome the interfacial tension between the two liquids, the polymeric solution was spontaneously spread on the water surface. The polymer had a restricted solubility in water. Therefore, after mutual diffusion between water and the solvent, the polymer precipitated to form a polymeric thin layer floating on the water surface. The membrane samples

**TABLE II**  
Surface Tension and Polarity of the Solvents  
and Water at 75°C (mN/m)<sup>8</sup>

	<i>n</i> -Butanol	Isopropyl alcohol	Water	PEBA
$\gamma$	19.95	16.10	72.00	55.00
$\gamma^p$	1.91	2.86	51.00	13.66
$\gamma^d$	18.03	13.23	21.00	41.34
$x^p$	0.09	0.18	0.71	0.25

were prepared five times in each condition, and the best one was cast on the support. Most samples were similar in appearance.

#### Ratio of solvents

The ratio of solvents is an effective parameter of the quality of films. The best ratio of solvent (*n*-butanol/isopropyl alcohol) can be obtained with the determination of polymeric solution surface tension. The surface tension of water is constant; therefore, better solution spread can occur with a surface tension reduction in the polymeric solution. The surface tension of the polymer was also constant; therefore, the surface tension of the polymeric solution at constant temperature and concentration changed with the solvent ratio. The surface tension ( $\gamma$ ) could be separated into a dispersion component (nonpolar) and a polar component:<sup>7</sup>

$$\gamma = \gamma^d + \gamma^p \quad (3)$$

where  $\gamma^p$  is the polar component of surface tension (arising from various dipolar and specific interactions) and  $\gamma^d$  is the dispersion component of surface tension (arising from dispersion-force interactions). Polarity could be calculated as follows:<sup>7</sup>

$$x^p = \frac{\gamma^p}{\gamma} \quad (4)$$

where  $x^p$  is polarity of the solvents and the non solvents.

The surface tensions and polarity of the solvents, nonsolvent (water), and PEBA are listed in Table II. The quality of the films was enhanced with increasing temperature; therefore, the surface tensions were calculated at 75°C.

The surface tension of PEBA and its polarity were measured with a contact-angle technique with three liquids with different polarities (water, diiodo-methane, and formamide). The contact angle was measured with a goniometer 14° horizontal beam comparator (22-2000 series model 20-4200, Scherr Tumico, St. James, MN). From the contact angle of the mentioned liquids on the PEBA surface and with Young's method, the surface tension and polarity could be obtained.<sup>9</sup>

With the mixing rule,<sup>10</sup> the surface tensions of the solvents at a constant polymer concentration of 5 wt % were calculated. With this calculation, we tried to show the approximate variation of surface tension of solvents, and all contributions were assumed linear with concentration/mass fraction.

As shown in Table III, the surface tension of the solvents decreased with increasing the portion of isopropyl alcohol in the solvent, and this improved the quality of the film. However, pure isopropyl alcohol was a weak solvent, and the polymer could not be dissolved more than 3 wt %.<sup>11</sup> Therefore, solution 5 could not be obtained. For pure isopropyl alcohol as a solvent, because polymer chains did not extend into the solution and also because of very quick solvent-nonsolvent exchange (it had a very high solubility in water<sup>8</sup>), the polymer chains aggregated, and a thin membrane layer with an open net was formed. *n*-Butanol was a strong solvent but could not diffuse into water immediately (it had restricted solubility in water<sup>8</sup>). Therefore, with mixing, better isopropyl alcohol and *n*-butanol films could be obtained. Interfacial tension between the two liquids could be calculated as follows:<sup>7</sup>

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (5)$$

where subscripts 1 and 2 are the surface tensions of two liquids that are in contact with each other. The interfacial tension between the solution and the nonsolvent at different solvent ratios are listed in Table IV.

As shown in Table III, with increasing ratio of isopropyl alcohol in the solvents, the interfacial tension between the solution and nonsolvent decreased. This means that the adhesive between the molecules of

**TABLE III**  
Surface Tension of the Solvents

Solution number	Butanol/isopropyl alcohol (weight ratio)	$\gamma$	$\gamma^p$	$\gamma^d$	$x^p$
1	1/—	21.70	2.50	19.19	0.11
2	3/1	20.77	2.71	18.05	0.13
3	1/1	19.87	2.95	16.91	0.15
4	1/3	18.95	3.17	15.77	0.17
5	—/1	—	—	—	—

**TABLE IV**  
**Interfacial Tension Between the Solution and Nonsolvent at Different Ratios of the Solvents**

Solution number	Interface tension (Solution – nonsolvent)
1	44.06
2	43.65
3	43.24
4	42.98

the two liquids decreased, and the solution spread was enhanced on the water surface (nonsolvent).

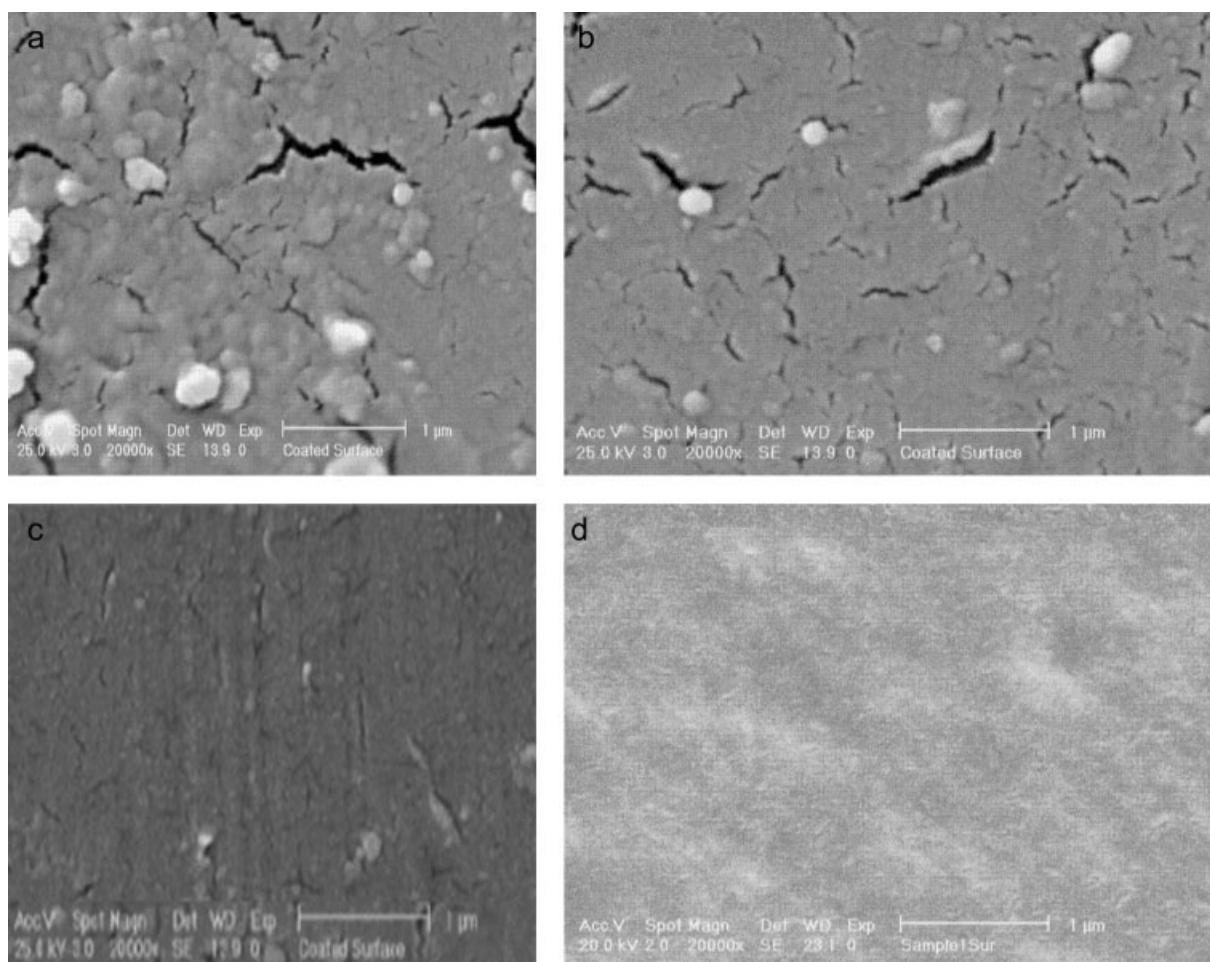
SEM photographs of the membranes made with different ratios of the solvents (isopropyl alcohol/*n*-butanol) at 75°C are presented in Figure 2. Figure 2(a) demonstrates the membrane made with pure *n*-butanol as the solvent. As shown, the membrane surface had a lot of cracks and polymer aggregations. As shown in Figure 2(b), the addition of isopropyl alcohol improved the surface quality, but some cracks were still observed. The membrane surface quality still improved, as shown in Figure 2(c),

but it was not yet perfect. With a 1/3 *n*-butanol/isopropyl alcohol ratio [Fig. 2(d)], defect-free membranes were obtained, and a high separation performance was achieved.

The solubility parameters of the solvents are presented in Table V. As shown, the solubility parameter of isopropyl alcohol was higher than that of *n*-butanol, and its difference with solubility parameter of water was less. Therefore, with increasing isopropyl alcohol concentration in the solvent mixture, mutual diffusion between water and the solvent occurred faster, and partial precipitation of the polymer was not observed.

An SEM photograph of the membrane cross section is presented in Figure 3. As shown, a dense selective layer (PEBA) was made on the microporous support (PS UF membrane). The thickness of the selective layer was about 4–5 μm.

From the results [SEM photographs and calculations (Tables III and IV)], we concluded that the film quality improved with increasing isopropyl alcohol ratio in the solvents.



**Figure 2** SEM photographs of the membranes with different solvent ratios at 75°C: (a) *n*-butanol, (b) 3/1, (c) 1/1, and (d) 1/3 *n*-butanol/isopropyl alcohol.

**TABLE V**  
Solubility Parameters of the Solvents<sup>12</sup>

Solvent	$\delta_d$ (J/cm <sup>3</sup> )	$\delta_p$ (J/cm <sup>3</sup> )	$\delta_h$ (J/cm <sup>3</sup> )	$\delta$ (J/cm <sup>3</sup> )
Isopropyl alcohol	7.7	3	8	11.50
<i>n</i> -Butanol	7.8	2.8	7.7	11.31
Water	7.6	7.8	20.7	23.39

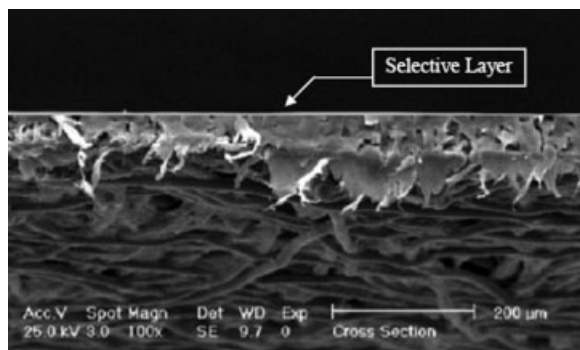
$\delta_d$  = dispersion component of the solubility;  $\delta_p$  = polar component of the solubility;  $\delta_h$  = hydrogen bonding component of the solubility.  $\delta^2 = \delta_p^2 + \delta_d^2 + \delta_h^2$ .

### Polymer concentration

A polymer concentration range of 4–7% caused uniform films to be made. Lower concentrations caused open-net films to be obtained. Although the PEBA solubility was difficult, a higher concentration of the polymeric solutions was impossible to use. Also, higher concentrations caused the viscosity of the polymeric solution to increase, and as a result, the solution spreading became difficult or even impossible.

### Temperature

The temperature of the polymeric solution should have been high; otherwise, the hydrogen bonding would cause the solution to gel. A suitable temperature range for the spreading of the polymeric solution on the water surface was found to be 70–80°C. In this case, the surface tension difference between the solution and the nonsolvent was large enough to obtain high-quality films. Higher temperatures, close to the boiling points of the solvents, caused evaporation, and this made solution spreading impossible. As mentioned, temperatures lower than 70°C caused the solution to gel, and this also made spreading impossible. In addition, the best temperature for film formation was a temperature close to the boiling point of the solvents. The boiling points of *n*-butanol and isopropyl alcohol were 117.7 and 82.3°C, respectively. Therefore, if the temperature was more than 80°C, isopropyl alcohol, which had a higher concentration in the solvent mixture, evaporated signifi-



**Figure 3** SEM photograph of the membrane cross section.

cantly, and its concentration diminished. As a result, the temperature could not exceed 80°C. Furthermore, during solution preparation, a reflux system was used, and as a result, solvent evaporation was minimized. Due to the same reason, membrane casting (film formation) was performed immediately (within 2–3 s), and after that, solvent evaporation caused the membrane synthesis to be completed.

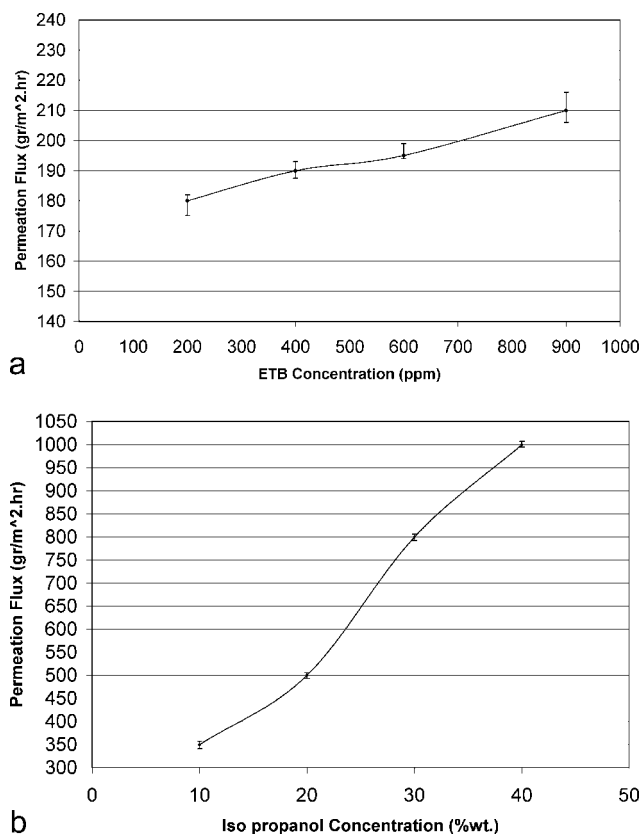
### PV

PV experiments were carried out with ETB/water and isopropyl alcohol/water mixtures. The effects of the operation parameters (feed concentration and temperature) on permeation flux and membrane selectivity were also investigated.

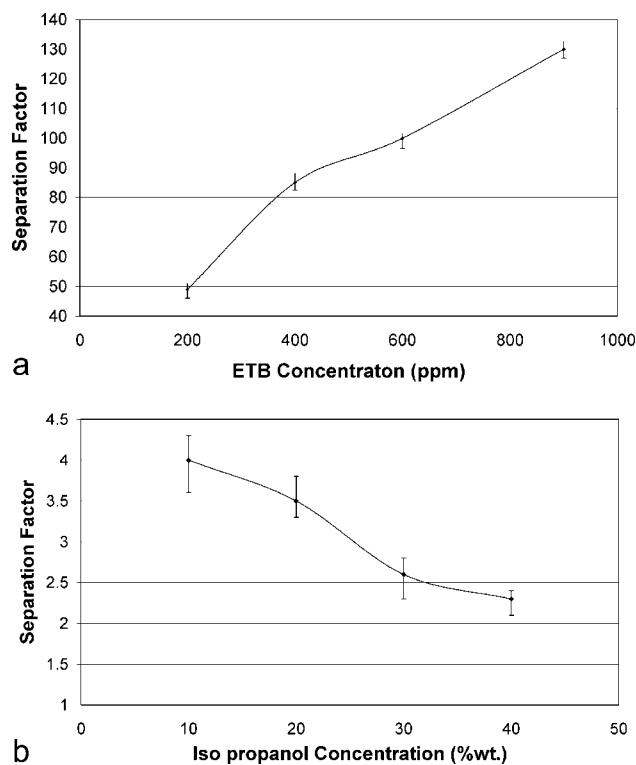
Each experiment was performed three times. The permeates were weighed with a digital balance (PRECISA M310) (Switzerland) with an accuracy of about 0.001 g and were analyzed with gas chromatography (GC-2010 Shimadzu, Columbia, MD).

### Effect of the feed concentration

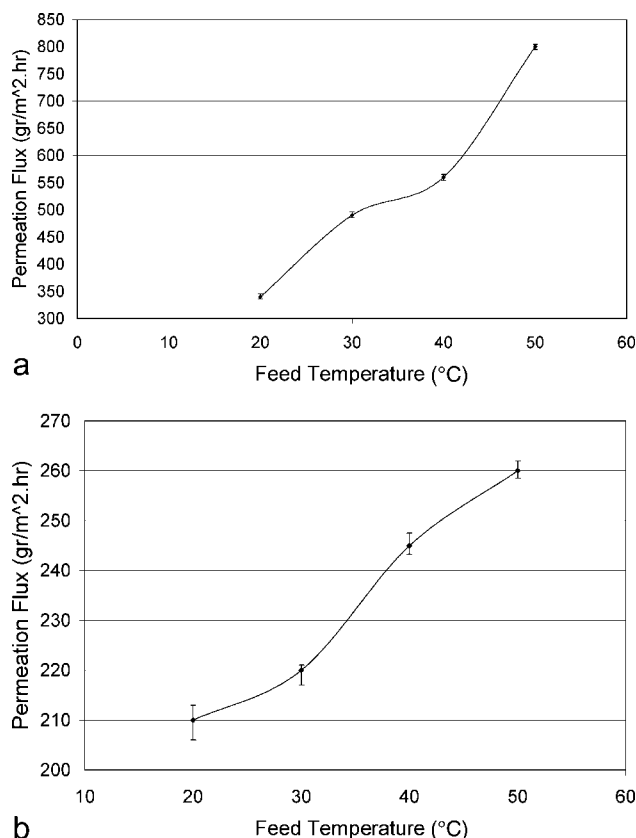
The effects of feed concentration on the permeation flux and separation factor at a constant temperature



**Figure 4** Effect of the feed concentration on the permeation flux: (a) ETB/water and (b) isopropyl alcohol/water (at 25°C).



**Figure 5** Effect of the feed concentration on the separation factor: (a) ETB/water and (b) isopropyl alcohol/water (at 25°C).

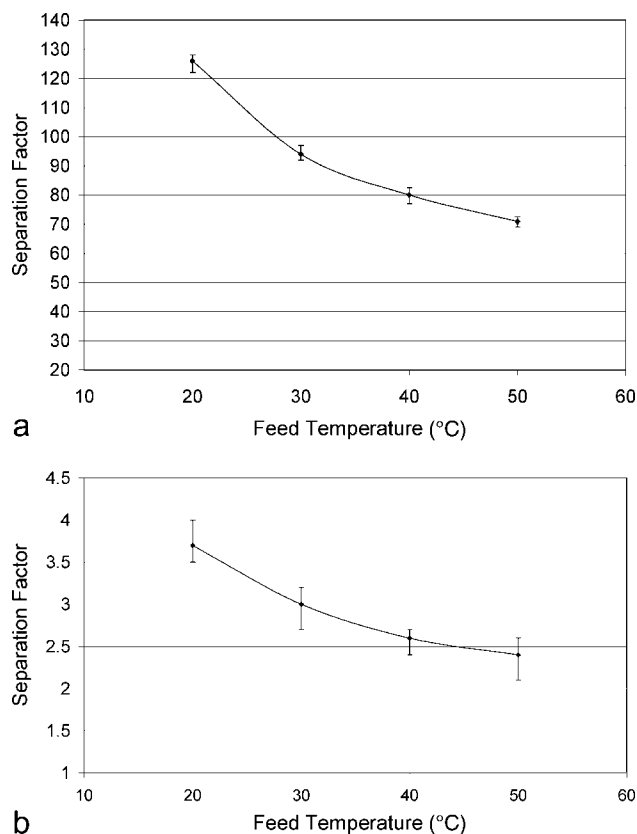


**Figure 6** Effect of the feed temperature on the permeation flux: (a) ETB/water (900 ppm) and (b) isopropyl alcohol/water (10 wt %).

for ETB/water and isopropyl alcohol/water are shown in Figures 4 and 5, respectively. ETB permeation flux and its separation factor increased because of the enhancement of liquid activity and the driving force for ETB transport; however, water permeation flux decreased with increasing ETB concentration in the feed. Isopropyl alcohol was used as one of the solvents for the preparation of PEBA membranes. Although, it was a weak solvent, for the PV of isopropyl alcohol/water mixtures, with increasing isopropyl alcohol concentration in the feed, the amorphous domains of the membrane slightly swelled; therefore, the organic and water fluxes increased, and as a result, the separation factor decreased.

#### Effect of temperature

The effects of temperature on the permeation flux and separation factor for ETB/water and isopropyl alcohol/water mixtures are illustrated in Figures 6 and 7, respectively. As seen in the two systems, the permeation fluxes were enhanced with increasing temperature. This phenomenon could be described by the increasing mobility of the polymer chains; therefore, permeation through the membrane increased. This



**Figure 7** Effect of the feed temperature on the separation factor: (a) ETB/water (900 ppm) and (b) isopropyl alcohol/water (10 wt %).

increased the organic and water fluxes; as a result, the membrane selectivity decreased.

### CONCLUSIONS

In this research, the synthesis and characterization of PEBA membranes was studied. The effects of different parameters on film formation were investigated. High-quality films were obtained in a 3/1 ratio of isopropyl alcohol/*n*-butanol, a temperature range of 70–80°C, and a polymer concentration range of 4–7 wt %. The recovery of ETB and isopropyl alcohol from water was carried out with the PEBA membrane, and high performance was achieved. With increasing ETB concentration in the feed, both the permeation flux and separation factor increased; however, with increasing isopropyl alcohol concentration in the feed, the permeation flux increased, and the separation factor decreased. At higher temperatures, the mobility of the polymer chains increased; therefore, in the two systems, the permeation flux was enhanced, but the membrane selectivity was diminished.

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