Macromol. Symp. **2008**, 264, 127–134 DOI: 10.1002/masy.200850420

Synthesis and Characterization of Poly(ether-*block*-amide) Membranes

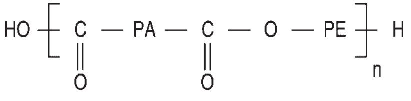
Toraj Mohammadi, Towan Kikhavandi, Mohammadreza Moghbeli*

Summary: Poly(ether-*block*-amide) membranes were made via casting a solution on a nonsolvent (water) surface. In this research, effects of different parameters such as ratio of solvent mixture (n-butanol/isopropanol), temperature, composition of coagulation bath (water) and polymer concentration, on quality of the thin film membranes were studied. The mechanism of membrane formation involves solution spreading, solvent–nonsolvent exchange, and partial evaporation of the solvent steps. Solvent- nonsolvent exchange is the main step in membrane formation and determines membrane morphology. However, at higher temperature of polymeric solution greater portion of solvent evaporates. The results showed that type of demixing process (mutual affinity between solvent and nonsolvent) has important role in film formation. Also, addition of solvent to the nonsolvent bath is effective on membrane morphology. The film quality enhances with increasing isopropanol ratio in the solvent mixture. This behavior can be related to increasing of solution surface tension, reduction of interfacial tension between solution and nonsolvent and delayed solvent-nonsolvent demixing. Uniform films were made at a temperature rang of 60–80 °C and a polymer concentration of 4–7 wt%. Morphology of the membranes was investigated with scanning electron micrograph (SEM). Pervaporation of ethyl butyrate/water mixtures was studied using these membranes and high separation performance was achieved. For ethyl butyrate/water mixtures, It was observed that both permeation flux and separation factor increase with increasing ethyl butyrate content in the feed. Increasing temperature in limited range studied resulted in decreasing separation factor and increasing permeation flux.

Keywords: poly(ether-*block*-amide) membranes; polymeric solution; PV; solvent-nonsolvent exchange

Introduction

Poly(ether-*block*-amide) (PEBA) is the general name for a class of thermoplastic elastomers that consist of linear chains of rigid polyamide blocks and flexible polyether blocks. The general chemical formula of PEBA is as follows:[1]



$$HO\left[\underset{\overset{\|}{O}}{C}-PA-\underset{\overset{\|}{O}}{C}-O-PE\right]_{n}H$$

where PA is a polyamide block and PE is a polyether block.

This copolymer depending on the PE block becomes hydrophobic or hydrophilic. The hydrophobic grades exhibit high selectivity for extraction of aromatic organic compounds from water by pervaporation (PV).[2] Each group of aroma compounds such as esters and alcohols is responsible for a typical juice flavor. These compounds are very sensitive to heat; therefore conventional processes that involve evaporation may cause loss of aroma compounds and change the juice flavors. PV process can recover these aroma compounds without any loss. Membrane PV is providing the method in separating liquid mixture of

---

Research Lab for Separation Processes, Faculty of Chemical Engineering, Iran University of Science and Technology, Narmak, Tehran, Iran
Fax: (+98) 21 77240495;
E-mail: torajmohammadi@iust.ac.ir

WILEY InterScience®

volatile ingredients. The efficiency of PV has been approved in eliminating water from organic solutions, concentrating or recovering the organics from aqueous solutions, separation of organic mixtures, etc.[3]

In this work, PEBA membrane was prepared for separation of ethyl butyrate (ETB)/water mixtures. At first, effect of different parameters on film formation such as ratio of solvents, temperature, composition of coagulation bath (water) and concentration of polymeric solution were studied. prepared membrane showed good performance for separation of ETB from water.

Experimental Part

Materials

Hydrophobic Poly(ether-block-amide) was provided by ATOCHEM in the form of granules. N-butanol and isopropanol with purity of 99.9% (both from Merck chemical company) were used as a solvent for preparing PEBA membranes. The PEBA membranes were supported by microporous polysulfone (PS) membranes (UF pHT20-6338) which were provided by Dow Denmark Inc. ETB (from Merck chemical company) with a purity of 99.9% was used in PV experiments. Properties of polymer and solvents are presented in Table 1 and 2, respectively.

Membrane Preparation

PEBA membranes were prepared by dissolving the copolymer in the solvent or a mixture of the solvents. Polymeric solutions were stirred vigorously at a temperature near the boiling point of solvents until a homogeneous solution was formed. The boiling points of n-butanol and isopropanol are 117.3 and 82.3 °C, respectively. Therefore, if temperature becomes more than 80 °C, the isopropanol that has a main ratio in the solvent mixture evaporates significantly and its concentration diminishes. Therefore, during solution preparation, using reflux system, solvent evaporation was minimized. One or two drops of the polymeric solutions were dripped by capillary pipette on to the surface of deionized water. Because of the solvent exchange with the non solvent, the thin membranes were formed. For providing mechanical strength of PEBA membranes in PV experiments, they were supported by polysulfone ultrafilteration membranes.[6]

Table 1.
Properties of PEBA.[2]

Polyamide (PA) segment	Polyamide 12 (nylon-12)
Polyether (PE) segment	Polytetramethyleneglycol (PTMG)
Composition (PE/PA) (wt. %)	57PE/43PA
Density (g/cm^3)	1.01
Shore D hardness	55
Melting point (°C)	159

Table 2.
Properties of solvents.[4,5]

Properties	isopropanol	n-butanol
Chemical formula	$CH_3CHOH\ CH_3$	$CH_3(CH_2)_3OH$
M_w (gr/mol)	60.10	74.12
Density (g/cm^3)	0.78	0.81
Boiling point (°C)	82.30	117.30
Viscosity (cP)	1.94	2.54
Solubility (%wt)		
In Water	∞	7.70
Water in	∞	20.10
Surface tension (mN/m)	20.93	24.57
Critical Temp. (°C)	235.20	289.93
Critical Pressure (kPa)	4760	4413

Pervaporation Experiment

PV apparatus used for recovery of ETB from water is presented in Figure 1. Performance properties of a given PV membrane are defined by the permeate fluxes J and separation factor α:

$$J = \frac{m}{A \cdot t} \tag{1}$$

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

where m is weight of permeate, A is membrane area, t is PV time and C is concentration. Also, subscript x and y are

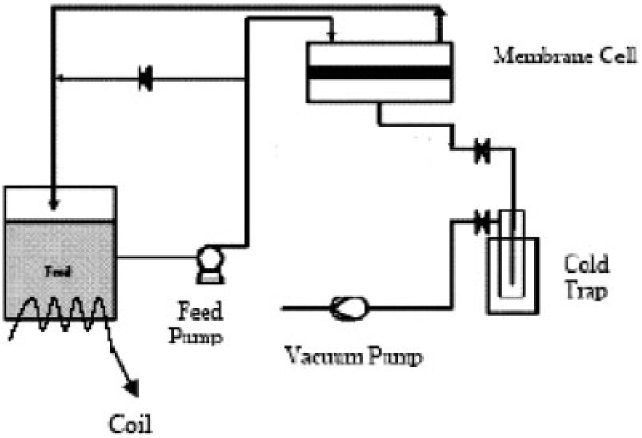


Figure 1.
Scheme of the laboratory scale pervaporation setup.

organic permeating component and water, respectively.

Each experiment was performed 3 times. Permeation fluxes were weighed using a digital balance (PRECISA M310) with an accuracy of about 0.001gr and analyzed using gas chromatography (GC-2010 Shimadzu).

Results and Discussion

Mechanism of Membrane Formation

The mechanism of membrane formation involves solution spreading, solvent–nonsolvent exchange, and partial evaporation of the solvent. When drops of the polymeric solutions were dripped on water surface, the polymer solution spread on water surface rapidly. Spreading then stopped quickly after a short period of time. Because, surface tension of water (nonsolvent) is greater than that of polymeric solution and also surface tension difference is large enough to overcome the interfacial tension between the two liquids, polymeric solution spreads spontaneously on the water surface.

The initial procedure for membrane formation from ternary system (polymer+solvent+nonsolvent) is to prepare a homogeneous (thermodynamically stable) polymeric solution. Demixing occurs after addition of nonsolvent, and this makes the solution thermodynamically unstable. The solvent diffuses into the nonsolvent (coagulation bath) whereas the nonsolvent diffuses into the polymeric film. After a given period of time, the exchange of solvent and nonsolvent precedes so far that the solution becomes thermodynamically unstable and demixing takes place. Finally, a thin polymeric film floating on the water surface is obtained.

According to the fundamental thermodynamic equation, demixing can occur only because of the existence of positive interaction (enthalpy) term ($\Delta H_m > 0$):[7]

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{3}$$

When only dispersive or van der Waals forces are present and the entropic contributions are considered to be negligible, the enthalpy of mixing is always positive, or zero, which leads to unfavorable contributions to Gibbs free energy, and mixing. For a polymer and nonsolvent, the entropy of mixing is not so high and a small positive enthalpy of mixing can once more cause demixing. For a binary system (solvent or solvent+nonsolvent), ΔG_m is given by:[7]

$$\Delta G_m = RT(n_1 Ln\phi_1 + n_2 Ln\phi_2 + n_1\phi_2\chi) \tag{4}$$

Where ϕ_1, ϕ_2 are volume fraction of two component and χ is Flory-Huggins interaction parameter which is considered to be an excess parameter containing all non-idealities. In ternary systems, there are three interaction parameters, polymer-solvent, polymer-nonsolvent, solvent-nonsolvent. Interaction parameter between polymer and nonsolvent can be calculated using mixing term and elastic contribution:[7]

$$\left(Ln\phi_1 - \left(1-\frac{V_1}{V_2}\right)\phi_2 + \chi\phi_2^2\right) + \frac{V_1}{M_c V_2}\left(\phi_2^{1/3} - 0.5\phi_2\right) = 0 \qquad (5)$$

where M_c is average molecular weight of two crosslinks and ϕ_1, ϕ_2 are volume fraction of nonsolvent and polymer respectively. In case where the interaction between polymer and nonsolvent is relatively low (the weight increase is less than 30%) the elastic term may be neglected:[7]

$$\chi = -\frac{Ln(1-\phi_2) + \phi_2}{\phi_2^2} \qquad (6)$$

The used PEBA polymer was hydrophobic, therefore interaction between polymer and nonsolvent (water) is relatively low, and as a result, ϕ_2 could be estimated by determining the weight increase the volume fraction of polymer after immersion in the solvent.

The ratio of the solvents is an effective parameter on film's quality. This ratio determines some parameters such as solvent-nonsolvent exchange and surface tension of polymeric solution.

The solvent–nonsolvent exchange occured rapidly during the early stage of the membrane formation and then gradually slowed down. Rate of solvent-nonsolvent exchange was found effective on membrane structure. High mutual affinity between solvent and nonsolvent causes a porous membrane to be obtained, whereas in the case of lower mutual affinity, a nonporous membrane is obtained. In fact, two types of demixing processes result in two different types of membrane morphology can be distinguished: instantaneous solvent-nonsolvent demixing and delayed solvent-nonsolvent demixing. In delayed demixing some assumptions and considerations must be made:

- thermodynamic equilibrium is established at the film/nonsolvent interface.
- volume fluxes at the film/nonsolvent interface are equal (J_i (film) = J_i (bath)).
- diffusion in the nonsolvent (coagulation bath) is described by Fick's low.
- no convection occurs in the coagulation bath.

As shown in Table 2, isopropanol is miscible with water, therefore it is very quickly and instantaneously exchanged with nonsolvent and membrane with open net is formed. Furthermore, since isopropanol is a poor solvent and polymer chains do not extend in the solution, therefore polymer chains aggregate and the membrane with high quality can not be obtained. N-butanol is a strong solvent but the mutual solubility between n-butanol and water is poorer than that between isopropanol and water. Restricted solubility of n-butanol in water and poor solvent-nonsolvent exchange result in partial precipitation of the polymer during the solution spreading. Spreading processe occurs so fast but because of slow phase inversion, the integrity that is required for PV membranes can not be obtained. With mixing isopropanol and n-butanol, phase inversion modified and films with high quality can be formed. Figure 2 shows ratio of the measured solvent concentration (C) to the limiting concentration ($C\sim$) obtained when the solvents completely dissolved in water, in different solvent ratios (iso propanel/n-butanol).

As shown, pure isopropanol is very quickly exchangable with water and membranes with open net can be obtained. On the other hand, pure n-butanol causes partial precipitation and a ragged structure is formed. With mixing isopropanol and n-butanol, delayed solvent-nonsolvent exchange occures and the quality of films improves. High quality films can be obtained with a ratio of 3 isopropanol/1 n-butanol as solvent.

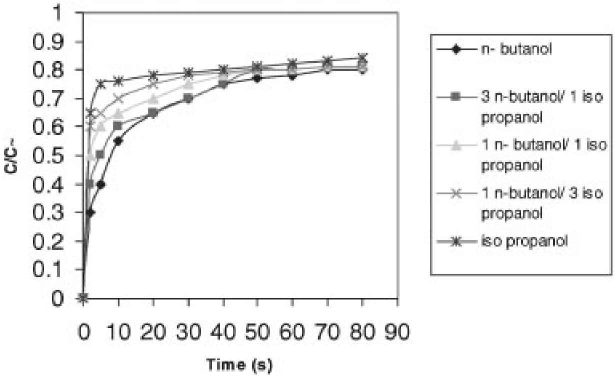


Figure 2.
Solvent- non solvent exchange in different solvent ratio and at 75 °C.

Surface tension is another parameter that has effective role in film formation. The surface tension of water is constant; therefore, better solution spread can occur with surface tension reduction of the polymeric solution. Surface tension of the polymer is also constant; therefore, surface tension of polymeric solution changes with solvent ratios. As shown in Table 2, surface tension of isopropanol is greater than n-butanol, therefore; surface tension of polymeric solution decrease with increasing the portion of isopropanol in the solvent and this makes quality of the film to improve. With increasing the ratio of isopropanol in the solvents, interface tension between solvent and nonsolvent decreases. It means that the adhesive between molecules of the two liquids decreases and solution spread enhances on the water surface (nonsolvent).

Composition of the coagulation bath (water) can change the morphology of the membrane. This changing results in a delayed onset of solvent-nonsolvent demixing. Increasing solvent content in the water reduces the polymer concentration in the film at the interface. In fact, two opposing effects appear to operate: delayed mixing tends to produce non porous films, whereas low interfacial polymer concentration tends to produce more open net films. Therefore; due to these opposing effects, in this research, the composition of coagulation bath also taken constant (pure water) and the other parameters were changed to obtain defected-free membranes.

Polymer concentration range of 4–7% causes uniform films to be made. Lower concentrations causes open net films to obtain. Higher concentrations causes viscosity of polymeric solution to increase, and as a result, the solution spreading becomes so difficult. In polyamides (one of the copolymer parts), high intermolecular forces and strong hydrogen bonding forces are made solubility difficult. Therefore; high polymeric concenteration can not prepared. Furthermore, pure isopropanol is a weak solvent and the polymer can not be dissolved more than 3%wt in this solvent.[8]

Temperature is an effective parameter on film formation. Temperature of polymeric solution should be high; otherwise, the hydrogen bonding makes the solution to gel. The suitable temperature range for spreading the polymeric solution on water surface was found to be 60–80 °C. In this case, surface tension difference between the solution and non solvent is large enough to obtain high quality films. Higher temperatures, close to the boiling points of solvents causes evaporate and this makes solution spreading impossible. As mentioned, lower temperatures than 60 °C cause the solution to gel and this also makes spreading impossible. It should be noted that, with increasing the tempreature

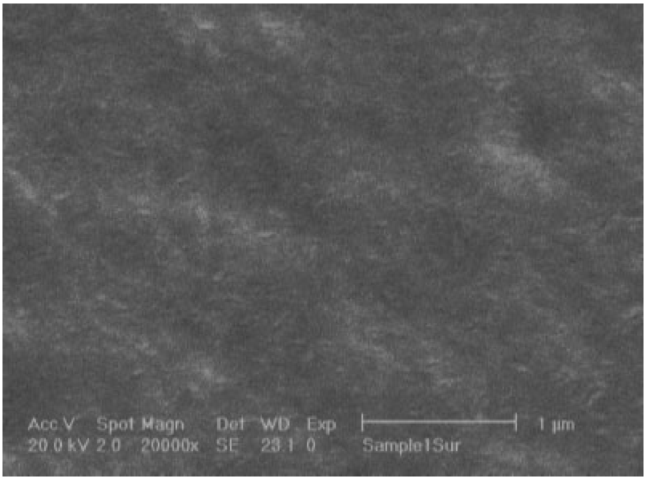


Figure 3.
SEM photograph of the membrane surface after coating.

of polymeric solution, the role of partial evaporation in film formation becomes important and the more portion of solvents evaporates.

SEM photographs of the membrane after coating surface and membrane cross section are presented in Figure 3–4. As shown, dense selective layer (PEBA) was made on the microporous support (UF polysulfone membrane). Thickness of selective layer is ~4–5 μm.

Pervaporation Experiments

PV experiments were carried out with ETB/water mixtures. Effect of operation parameters (feed concentration and temperature) on permeation flux and membrane selectivity was also investigated.

Effects of feed concentration and temperature on permeation flux and separation factor at for ETB/water mixture are shown in Figure 5 and 6, respectively. With increasing feed concentration, ETB permeation flux and its separation factor increase because of the enhancement of liquid activity and driving force for ETB transport, however, water permeation flux decrease with increasing ETB concentration in the feed.

As shown in Figure 6, permeation flux enhance with increasing temperature. This phenomenon can be described with increas-

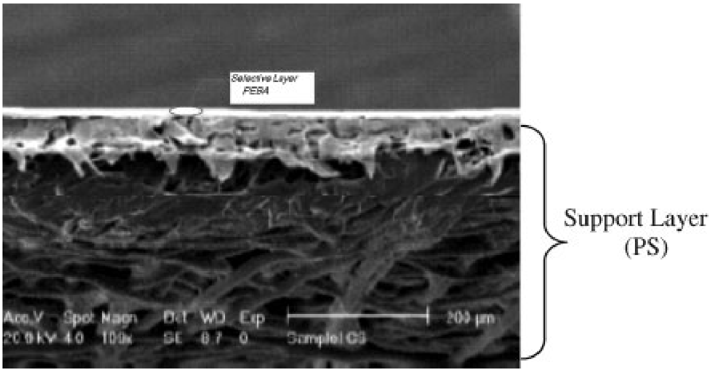


Figure 4.
SEM photograph of the membrane cross section.

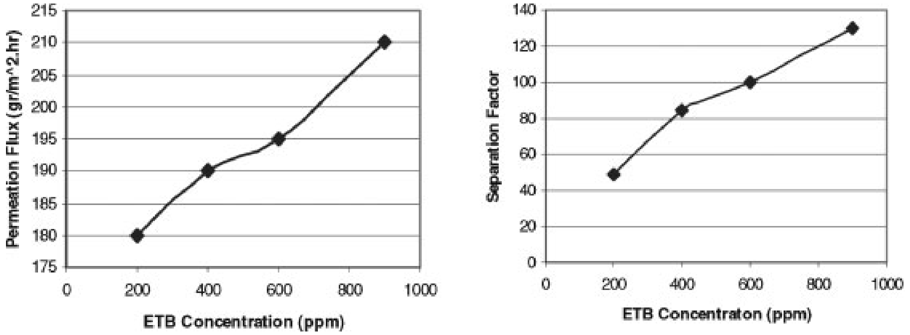


Figure 5.
Effect of feed concentration on permeation flux and separation factor for ETB/water (at 25 °C).

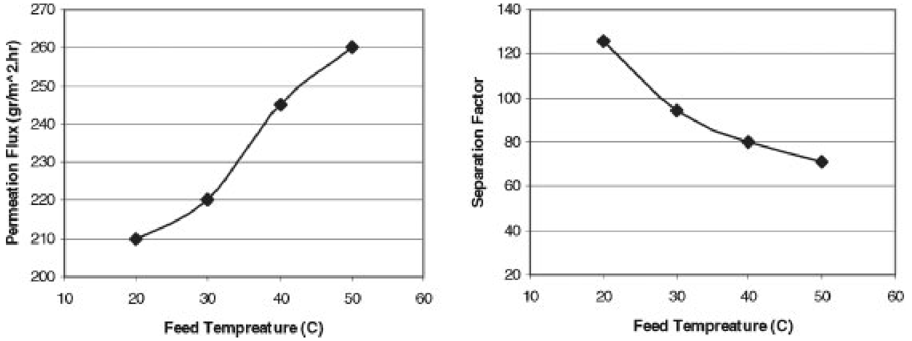


Figure 6.
Effect of feed temperature on the separation factor for ETB/water (900 ppm).

ing the mobility of polymer chains, therefore, permeation through the membrane increases. This increases organic and water fluxes, and as a result, the membrane selectivity decreases.

Conclusions

In this research, synthesis and characterization of Poly(ether-*block*-amide) membranes for pervaporation processes was studied. Effect of different parameters on film formation was investigated. High quality films were obtained in a (3/1) ratio of isopropanol/n-butanol, a temperature range of 60–80 °C and a polymer concentration range of 4–7 wt%. Recovery of ETB from water was carried out using the PEBA membrane and high performance was achieved. It was found that with increasing ETB concentration in the feed, both permeation flux and separation factor increase. At higher temperatures mobility of the polymer chains increases, therefore, in this system, permeation flux enhances but membrane selectivity diminishes.

[1] PEBA-Polyether Block Amide, Elf Atochem Technical Document.
[2] M. Kaddour, Q. T. Nguyen, R. Clement, Y. Germain, Pervaporation of aqueous ester solutions through hydrophobic poly (ether-block-amide) copolymer membranes, Journal of Membrane Science (1998), 146, 125–133.

[3] B. K. Zhu, X. Z. Tian, Y. Y. Xu, Recovering ethyl acetate from aqueous solution using P (VDF-co-HFP) membrane based pervaporation, *Desalination* **2005**, *184*, 71–78.

[4] A. Riddick, *Organic Solvents*, 3th ed., Wiley, New York **1970**.

[5] B. P. Whim, P. G. Johnson, *Directory of solvents*, Chapman & Hall, **1996**.

[6] L. Li, C. Amit, X. Feng, Anovel method of Preparing Ultrathin Poly(ether-block-amide) membrane, *Journal of Membrane Science* **2004**, *235*, 43–52.

[7] M. Mulder, ‘‘*Basic Principles of Membrane Technology*’’, Kluwer Academic Publishers, Dordrecht, the Netherlands **1996**.

[8] l. Blume, l. Pinnau, Composite membrane, method of preparation and use, US patent 4,963,165, **1990**.