Preparation of
Polymeric Membrane for pervaporation separation

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Abstract:

Poly (ether-block-amide) membranes were made via casting a solution on a non solvent surface. In this research, effects of different parameters such as ratio of solvent mixture (n-butanol / iso propanol), temperature and polymer concentration, on quality of the thin film membranes were studied. The results showed that the film quality enhances with increasing iso propanol ratio in the solvent mixture. This behavior can be related to reduction of solution surface tension and interfacial tension between solution and non solvent. Uniform films were made at a temperature rang of 70-80 ^{0}C and a polymer concentration of 4-7 wt%. Morphology of the membrane was investigated with Scanning Electronic Micrograph (SEM). Pervaporation of ethyl butyrate / water and iso propanol / 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. However, for iso propanol / water mixtures, it was found that by increasing iso propanol content in the feed, permeation flux enhances but separation factor diminishes. Increasing temperature in limited range studied resulted in decreasing separation factor and increasing permeation flux.

Keywords: Poly (ether block amide) membranes, Polymeric solution, Non solvent, Surface tension, PV;

1. 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 [1]. 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 [2]. The general chemical formula of PEBA is as follows [1]:

$$ HO \left[\begin{array}{c} C \\ \| \\ O \end{array} - PA - \begin{array}{c} C \\ \| \\ O \end{array} - O - PE \right]_n H $$
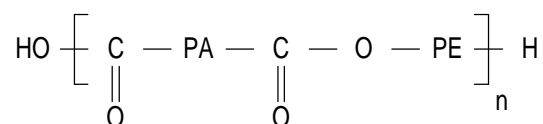
Where PA is a polyamide block and PE is a polyether block.
PV membrane has provided the method of separating liquid mixtures of volatile ingredients. The efficiency of PV has been approved by eliminating water from organic solutions, concentrating or

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recovering the organics from aqueous solutions, separation of organic mixtures, etc [3]. Aroma compounds in juice flavors such as esters, alcohols and aldehydes are very sensitive to heat; therefore conventional processes that involve evaporation may cause loss of these compounds and change the juice flavors. PV process can recover these aroma compounds without any loss.

In this work, PEBA membrane was prepared for separation of ethyl butyrate (ETB) and iso propanol from water mixtures. At first, effect of different parameters on film formation such as ratio of solvents, temperature and concentration of polymeric solution were studied. The SEM technique was used to investigate the membrane morphology. Prepared membrane showed good performance for separation of ETB and iso propanol from water.

2. Experimental

2.1. Materials

Poly (ether block amide) 1074 was provided by Arkema France Inc. in the form of granules. n-butanol and iso propanol (both from Merck chemical company) with a purity of 99.9% 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) and iso propanol with a purity of 99.9% were used in PV experiments.

2.2. 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. 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 polymeric membranes were formed. For providing mechanical strength of PEBA membranes in PV experiments, they were supported by polysulfone ultrafilteration membranes [4].

2.3. Pervaporation experiment

PV apparatus has used for recovery of ETB and iso propanol from water is presented in Figure 1. System was composed of a temperature controlled feed vessel, a circulating pump, a membrane test cell, a cold trap and a vacuum pump. During experiments, the upstream pressure was maintained at atmospheric pressure, while the downstream pressure was kept below 1 mbar using a vacuum pump. Permeation fluxes were determined by weighing the permeate collected over a given period of time in the cold trap.

Performance properties of a given PV membrane are defined by the permeate fluxes J and separation factor a :

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

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

Where m is weight of permeate, A is membrane area, t is PV time and C is concentration. Also, subscript x and y are organic permeating component and water, respectively.
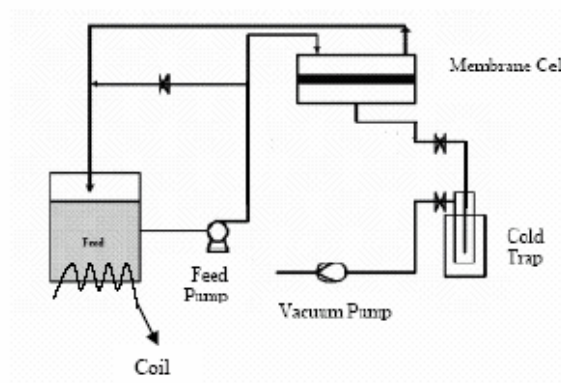

Figure 1: Scheme of the laboratory scale pervaporation setup

3. Results and discussion

3.1. Membrane formation

Because, surface tension of water (non solvent) 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 is spread spontaneously on the water surface. The polymer has a restricted solubility in water. Therefore, after mutual diffusion between water and the solvent, the polymer precipitates to form a polymeric thin layer floating on the water surface.

The ratio of solvents is an effective parameter on the film's quality. The best ratio of solvent (n butanol / iso propanol) can be obtained with determination of polymeric solution surface tension. 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.

Surface tensions and polarity of the solvents and non solvent (water) are listed in Table1. It should be noted that the quality of the films enhances with increasing temperature, therefore surface tensions are calculated at 75 ^{0}C.
Interface tension between two liquids can be calculated   as follows [5]:

$$g_{12} = g_1 + g_2 - \frac{4g_1^d g_2^d}{g_1^d + g_2^d} - \frac{4g_1^p g_2^p}{g_1^p + g_2^p} \tag{3}$$

Subscript 1 and 2 are surface tension of two liquids that are in contact with each other.
solvent and non solvent decreases. It means that the adhesive between molecules of the two liquids decreases and solution spread enhances on the water surface (non solvent). However, it should be noted that, pure iso propanol is a weak solvent and the polymer can not be dissolved more than 3%wt [6], therefore, solution No.5 could not be obtained.

Table 1: Surface tension and polarity of the solvents and water at 75 ^{0}C (mN/m) [7]

	n-Butanol	Iso propanol	Water	PEBA
g	19.95	16.10	72.00	55.00
g^{p}	1.91	2.86	51.00	13.66
g^{d}	18.03	13.23	21.00	41.34
x^{p}	0.09	0.18	0.71	0.25

Table 2: Surface tension of the solvents

Solution number	Butanol/ iso propanol (weight ratio)	g	g^{p}	g^{d}	x^{p}	g_{12} (solvent –water)
1	1/-	21.70	2.50	19.19	0.11	44.06
2	3/1	20.77	2.71	18.05	0.13	43.65
3	1/1	19.87	2.95	16.91	0.15	43.24
4	1/3	18.95	3.17	15.77	0.17	42.98
5	-/1	-	-	-	-	-

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. Temperature of the 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 ^{0}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 ^{0}C cause the solution to gel and this also makes spreading impossible.
SEM photographs of the membrane surface and cross section are presented in figure 2-3. As shown, dense selective layer (PEBA) was made on the microprose support (UF polysulfone membrane). Thickness of selective layer is a bout 4-5 mm.
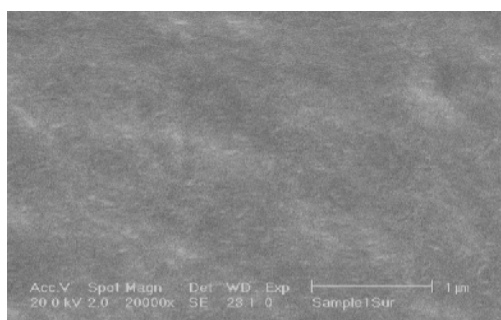

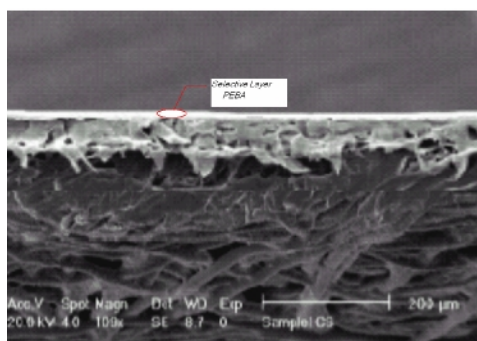Figure 2. SEM photograph of the membrane

Figure 3. SEM photograph of the membrane cross section

3.2. Pervaporation

PV experiments were carried out with ETB / water and iso propanol / water mixtures. Effects of feed concentration on permeation flux and separation factor at a constant temperature for ETB / water and iso propanol / water are shown in Figures 4 and 5, respectively. ETB permeation flux and its separation factor increase because of the enhancement of liquid activity and driving force for ETB transport across the membrane, however, water permeation flux decrease with increasing ETB concentration in the feed. For iso propanol / water mixture, with increasing iso propanol concentration in the feed, the amorphous domains of the membrane swells, therefore organic and water fluxes increase, and as a result, permeation flux increase but separation factor decreases.

Effect of temperature on permeation flux and separation factor for ETB / water and iso propanol / water mixtures are illustrated in Figures 6 and 7, respectively. As seen in two systems, permeation fluxes enhance with increasing temperature. This phenomenon can be described with increasing the mobility of polymer chains; therefore, permeation through the membrane increases. This increases organic and water fluxes, as a result, the membrane selectivity decreases.
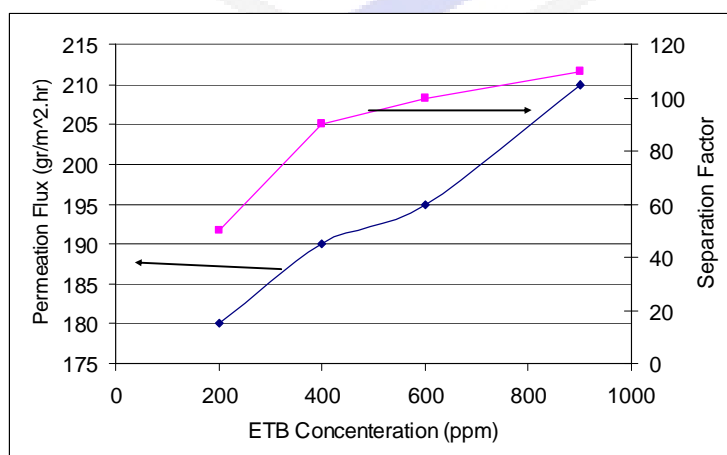

Figure 4. Effect of feed concentration on permeation flux and separation factor for ETB / water mixtures
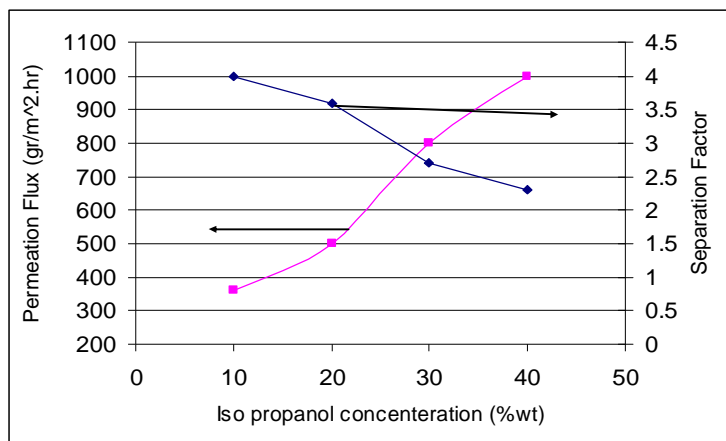
(at 25^0C)

Figure 5. Effect of feed concentration on permeation flux and separation factor for iso propanol / water
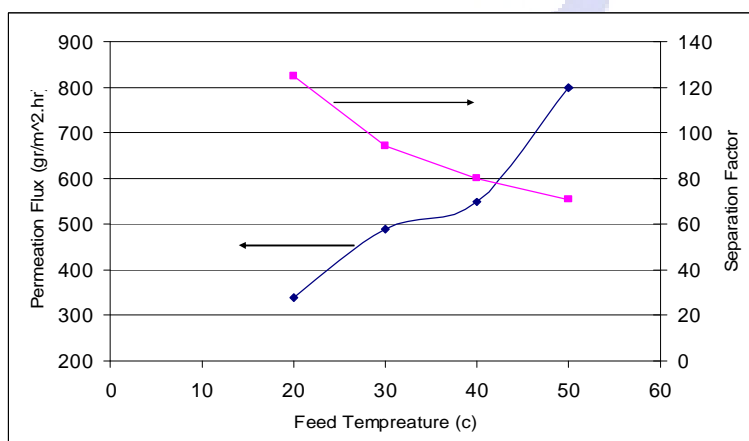
mixtures (at 25^0C)

Figure6. Effect of feed temperature on permeation flux and separation factor for ETB / water mixtures (at 900 ppm)
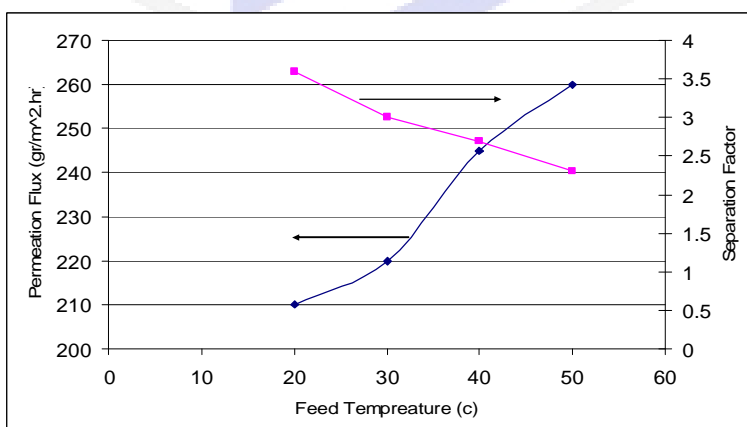

Figure 7. Effect of feed temperature on permeation flux and separation factor for iso propanol / water mixtures (at 10%wt)

4. Conclusions

In this research, synthesis and characterization of poly (ether block amide) membranes, was studied. Effect of different parameters on film formation was investigated. High quality films were obtained in a (3/1) ratio of Iso propanol / n-butanol, a temperature range of 60-80 ^{0}C and a polymer concentration range of 4-7 wt%. Recovery of ETB and iso propanol 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, however, with increasing iso propanol concentration in the feed, permeation flux increases and separation factor decreases. At higher temperatures mobility of the polymer chains increases, therefore, in the two systems, permeation flux enhances but membrane separation factor diminishes.

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