

Pervaporation Separation of Alcohol–Water Mixture Through 4-Vinylpyridine Chemical Modified Poly(4-methyl-1-pentene) Membrane

J. Y. LAI,^{1*} YIH-LANG YIN,¹ and KUEIR-RARN LEE²

¹Department of Chemical Engineering, Chung Yuan University, Chung Li, Taiwan 32023, and

²Department of Chemical Engineering, Nanya Junior College of Technology, Chung Li, Taiwan 32034, Republic of China

SYNOPSIS

For dehydrating separation aqueous alcohol solution by the pervaporation technique, a chemical modified poly(4-methyl-1-pentene) (TPX) membrane was synthesized with 4-vinylpyridine (4-VP). The morphology, crystallinity, and thermodegradation properties were investigated by scanning electron microscopy, X-ray, and thermogravimetric analysis, respectively. The modified TPX membrane possessed higher stability than that of the unmodified TPX membrane. The effects of feed temperature and poly(4-VP) (P4-VP) content of the modified TPX membranes on the performances of pervaporation were studied. A separation factor of 133 and a permeation rate of 115 g/m²h can be obtained for the TPX/P4-VP membrane with 3.0 wt % P4-VP content. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Separation and removal of water from an organic liquid and organic contaminants from wastewater by pervaporation technology were investigated.^{1–3} Recently, there has been much interest in the application of a polymer membrane to separating water from an ethanol aqueous solution.

According to the solution-diffusion theory, the permselectivity of a pervaporation membrane must be attributable to solubility and diffusivity. The solubility of permeant could be controlled by introducing functional moieties or chemical species that may cause a strong interaction. That can make it possible to separate such a specific permeant in preference to other components.⁴ Specific and selective separation of aqueous ethanol solution through membranes may be realized by incorporating a functional group into membranes such as the imide group, carboxylic acid moiety, pyridine moiety, and so on.^{2–5} The water-permselective membranes must be hydrophilic sub-

strates and allow water to permeate easily. To improve the hydrophilicity of the membrane substrates, several methods of membrane preparation may be used such as introduction of the cross-linking,^{6,7} block or graft copolymerization,^{8,9} and blending.¹⁰

Recently, to improve pervaporation performances, water-permselective membranes were prepared by introducing hydrophilic monomers such as hydroxyethyl methacrylate and vinyl acetate.^{11–15} Poly(4-methyl-1-pentene) (TPX), which has excellent mechanical strength, is regarded as a promising membrane material for gas separation.¹⁶ In the previous report, the modified poly(4-methyl-1-pentene) membrane was used for separation of acetic acid/water mixtures.¹⁷ In this study, the water-attractive 4-vinylpyridine (4-VP) monomer was introduced into TPX matrixes via a free radical polymerization. The morphology, crystallinity, and thermodegradation were investigated by scanning electron microscopy (SEM), X-ray, and thermogravimetric analysis (TGA). Pervaporation separation performances of aqueous alcohol solution through modified TPX membrane were discussed.

* To whom correspondence should be addressed.

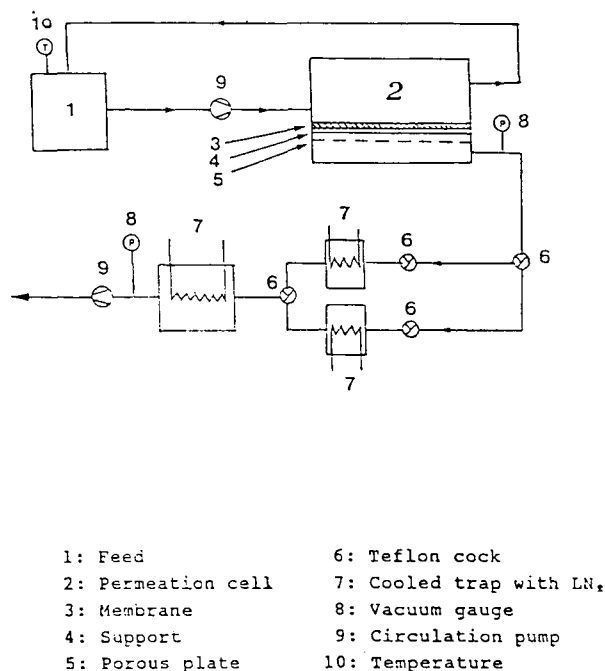


Figure 1 Schematic diagram of pervaporation apparatus.

EXPERIMENTAL

Materials

TPX was purchased from Mitsui Co. (Japan). The 4-VP, cyclohexene, and chloroform were supplied

by Merck Co. The initiator, azobisisobutyronitrile (AIBN), was purified by conventional methods and the 4-VP monomer was distilled under reduced pressure in vacuum.

Synthesis

TPX/P4-VP [poly(4-VP)] was synthesized as follows: 1.0 g of TPX polymer and 20 mL of cyclohexene were placed in an ampule and dissolved at 50°C for 24 h with stirring. The mixture solution of 4-VP monomer and initiator was sealed in an ampule after dissolving entirely. The mixture solution, i.e. TPX, 4-VP, cyclohexene, and initiator, was frozen instantly by liquid nitrogen and simultaneously degassed by vacuum pump. Polymerization was carried out at 80°C for 2 h by shaking. The product of TPX/P4-VP was collected by precipitation. The P4-VP content in the products were measured by the weight method.

Membrane Preparation

The casting solution of TPX and cyclohexene was dissolved in an appreciable weighted ratio at 50°C for 24 h with stirring. The pure TPX membrane was prepared by casting the solution on a glass plate to a appropriate thickness and allowing the casting solvent to evaporate at 50°C for 40 min. Then, the glass plate was immersed in water for

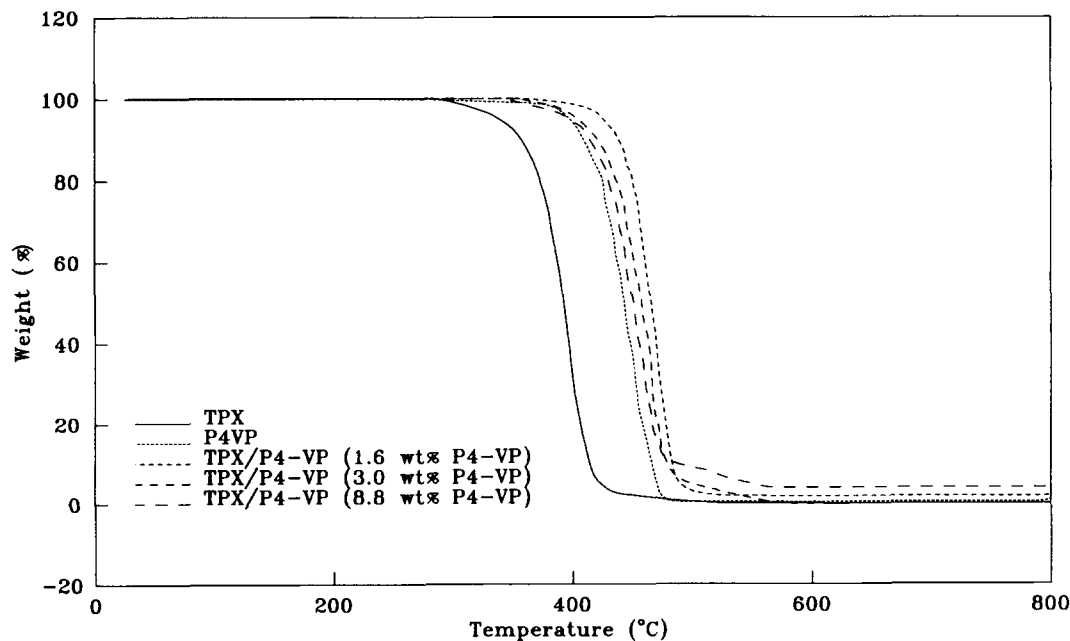


Figure 2 TG curves of the TPX, P4-VP, and TPX/P4-VP.

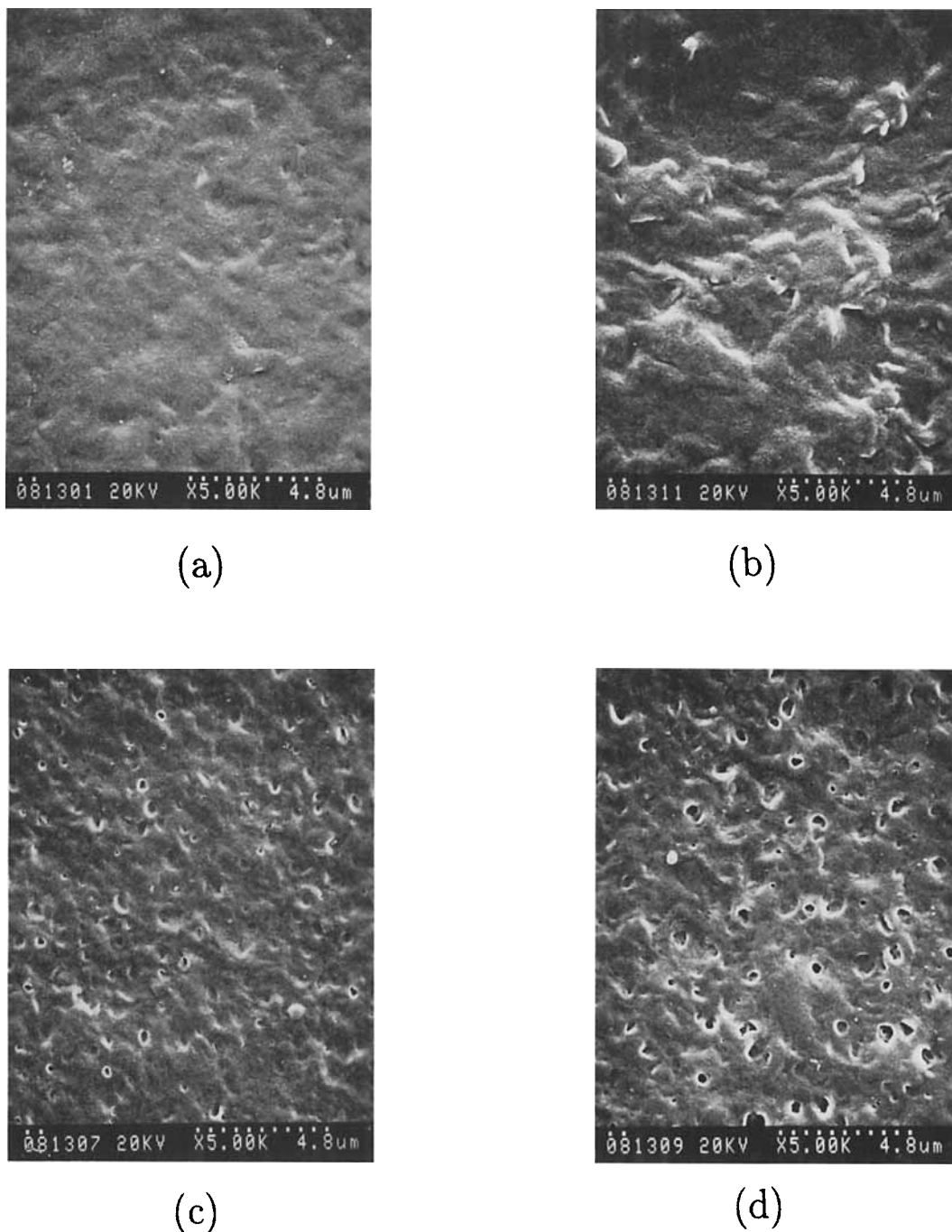


Figure 3 Surface views of SEM photograph for the TPX and TPX/P4-VP membranes. (a) TPX; (b)–(d) 1.6, 3.0, and 8.8 wt % P4-VP content of TPX/P4-VP.

2 h at 0°C. One gram TPX/P4-VP was dissolved in 26 mL chloroform at 50°C for 24 h with stirring. The TPX/P4-VP membrane was prepared by the same procedure as the TPX membrane. The thicknesses of the membranes were in the range of 19–25 μm .

Apparatus and Measurements

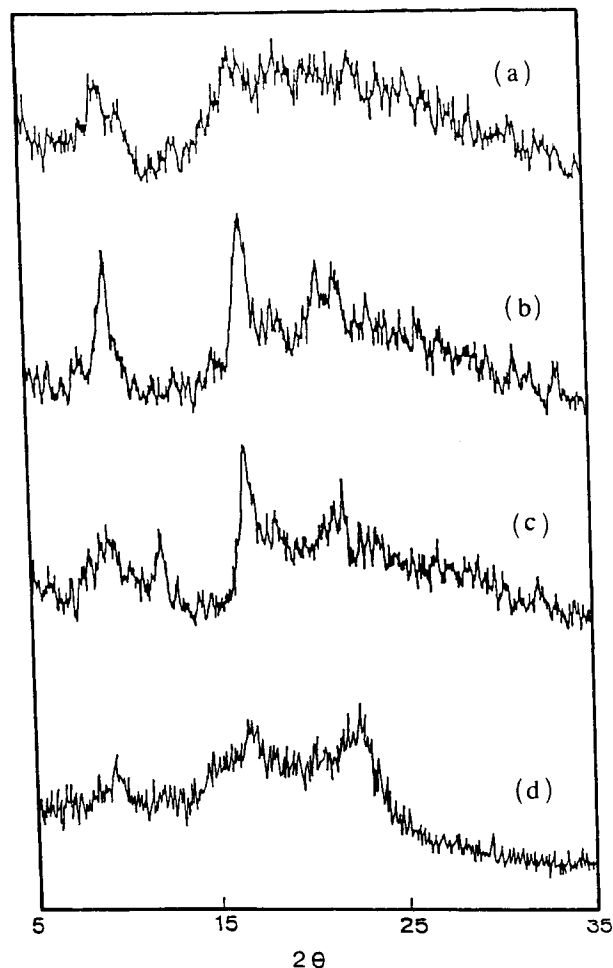
Pervaporation

Permeation of alcohol-water aqueous solution was carried out through a membrane by the ordinary pervaporation technique. The membrane area in

Table I Effect of P4-VP Content for TPX/P4-VP Membranes on Maximum Derivative Temperatures

P4-VP Content (wt %)	Maximum Derivative Temperature (°C)
0.0	397
1.6	472
3.0	463 526
8.8	456 534
100.0	449

contact with feed solution was 10.17 cm². The schematic diagram of pervaporation apparatus is shown in Figure 1. The permeation rate was de-

**Figure 4** X-ray diffraction patterns of the TPX and TPX/P4-VP membranes. (a) TPX; (b)–(d) 1.6, 3.0, and 8.8 wt % P4-VP content of TPX/P4-VP.**Table II** X-Ray Diffraction *d*-Spacing for TPX/P4-VP Membranes of Various P4-VP Content

P4-VP Content (wt %)	2θ (Degree)	<i>d</i> -Spacing (Å)
0.0	16.4	5.4
1.6	16.8	5.3
3.0	18.0	4.9
8.8	16.5	5.4

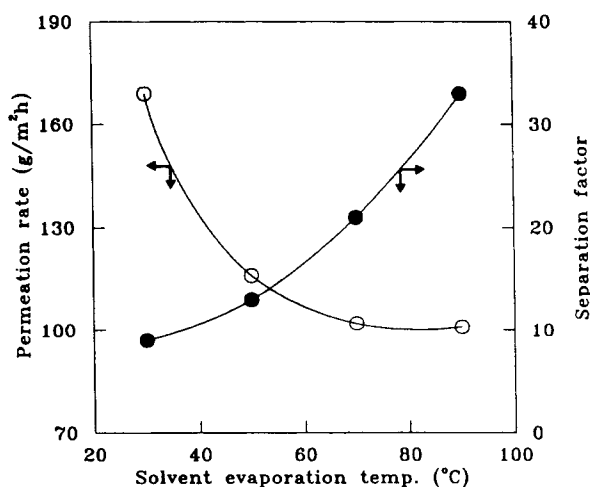
termined by measuring the weight of the permeate. The compositions of the feed solutions and permeates were analyzed by gas chromatography (GC, China chromatography 8700T). The separation factor was calculated from the following equation:

$$\alpha_B^A = (Y_A/Y_B)/(X_A/X_B)$$

where X_A , X_B , and Y_A , Y_B are the weight fractions of *A* and *B* in the feed and permeate (*A* being the more permeative species), respectively.

Properties Measurements

The structure of the prepared membranes was examined by a Hitachi S-570 Scanning Electron Microscope. Wide-angle X-ray diffraction (WAXD) scans were generated by a Shimadzu XD-5 diffractometer operating with monochromatized copper radiation. Thermal analysis was measured

**Figure 5** Effect of solvent evaporation temperature for the TPX membranes on the (○) permeation rate and (●) separation factor.

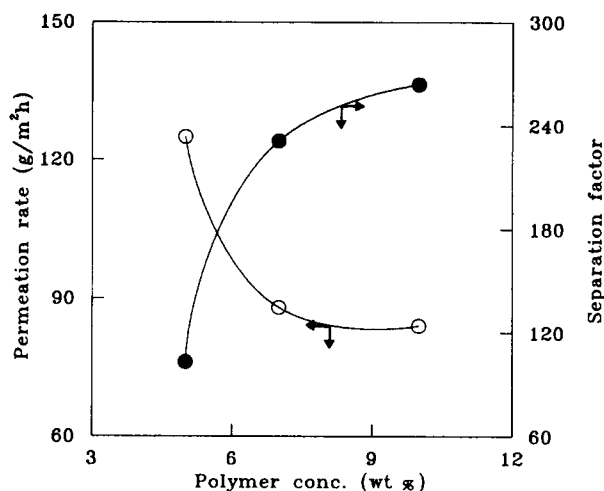


Figure 6 Effect of polymer concentration for the TPX membranes on the (○) permeation rate and (●) separation factor.

by a DuPont Thermal Gravimetric Analyzer Model 9900. The analysis was performed at a heating rate of 20°C/min under a stream of nitrogen.

RESULTS AND DISCUSSION

Thermal Characterization

The TG curves for the thermal degradation show about 7 mg of different P4-VP contents in TPX/P4-VP membranes (Fig. 2). The thermal degradation temperature in TPX/P4-VP membranes

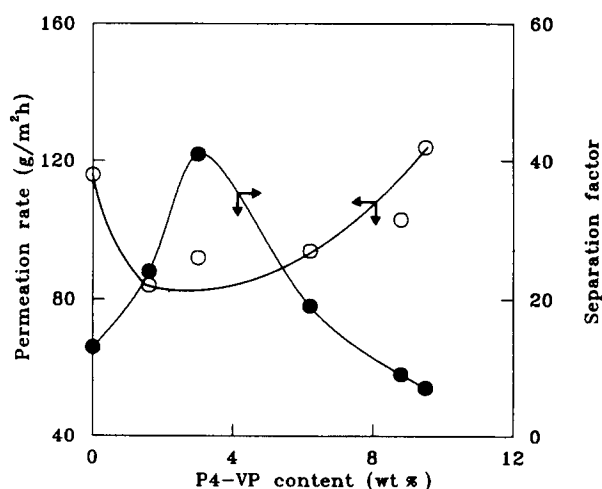


Figure 7 Effect of the P4-VP content in the TPX/P4-VP membranes on the (○) permeation rate and (●) separation factor.

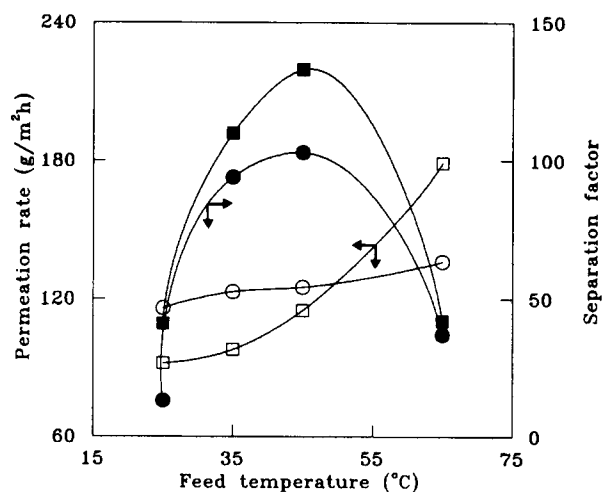


Figure 8 Effect of feed temperature of 90 wt % ethanol-water mixture for TPX and TPX/P4-VP membrane (P4-VP content: 3.0 wt %) on the permeation rate and separation factor. (○, ●) TPX membrane; (□, ■) TPX/P4-VP membrane.

with 1.6 and 3.0 wt % P4-VP content is higher than that of unmodified TPX membrane. That is, the heat stability of such TPX/P4-VP membrane is higher than that of the unmodified TPX membrane. These phenomena might be due to the fact that the rigid ring structure of the pyridine ring of P4-VP and the entanglement among these two polymer chains result in the increase of the thermal stability.¹⁸

It can be seen from Figure 2 that the thermal degradation temperature for the pure TPX, P4-VP, and 1.6 wt % P4-VP content of TPX/P4-VP membranes occur in one stage in a nitrogen atmosphere. However, two stages of thermal degradation appeared when the P4-VP content was higher than 1.6 wt %. These phenomena may be

Table III Effect of Feed Alcohol Solutions on Pervaporation Performances

Kinds of Alcohols	Molar Volume (mL/mol)	TPX/P4-VP	
		α	Q
Ethanol	58.68	133	115
1-Propanol	75.14	148	73
<i>t</i> -Butanol	94.88	281	61

Operation temperature: 45°C; feed concentration: 90 wt % alcohols; unit: Q (g/m²h); TPX/P4-VP membrane: P4-VP content 3.0 wt %; initiator: AIBN.

due to the fact that the membrane voids increase and the crystallinity decreases with increasing the P4-VP content in TPX/P4-VP membrane. The SEM graph confirms these results very well as shown in Figure 3.

Phase separation occurred in the TPX/P4-VP membrane when the P4-VP content was larger than 3.0 wt %. As a criterion of heat stability for the TPX/P4-VP membrane, we recorded the temperature of the maximum rate of weight loss at a heating rate of 20°C/min under a stream of nitrogen. The results are presented in Table I. The thermal degradation temperature of maximum weight loss for the pure TPX and P4-VP are 397 and 449°C, respectively. A higher heat stability modified TPX membrane was obtained, that is, TPX/P4-VP membrane with a 1.6 wt % P4-VP content. Nevertheless, the thermal degradation temperature decreased when the P4-VP content further increased. These phenomena might be due to the phase separation between the TPX and P4-VP.

WAXD Analysis

In general, the crystallinity and d -spacing can be measured by WAXD analysis. The WAXD patterns of the pure TPX and the TPX/P4-VP membranes with various P4-VP contents are shown in Figure 4. The peaks at $2\theta = 9.4^\circ$, 12° , and 16.4° are assigned as the typical peak of TPX.¹⁹ The intensity of the diffraction at $2\theta = 9.4^\circ$, 12° , and 16.4° increased with increasing content of P4-VP, up to 1.6 wt %. When the P4-VP content of the modified TPX membrane exceeded the limit (1.6 wt %), the intensity of diffraction began to decrease. These phenomena may be due to the polymer chain entanglement of these two materials. A decrease in peak intensity of TPX/P4-VP was exhibited at 3.0 wt % P4-VP content; however, these characteristic peaks decrease simultaneously at 8.8 wt % P4-VP content. These phenomena were also observed by Lee et al.¹⁰

In addition, the d -spacings, as shown in Table II, are evaluated with Bragg's equation,²⁰ $n\lambda = 2d \sin \theta$. The value of d -spacing decreased from 5.4 to 4.9 Å as 2θ increased from 16.4° to 18.0° , caused by the increase of P4-VP content in the TPX/P4-VP membranes. This implies a general increase in the crystalline region. However, because of the intensity decrease of any obvious peaks, the TPX/P4-VP membranes may have an increase in amorphous structure with a P4-VP content up to 8.8 wt %. The reasons may be the increase of phase separation, as evidenced by TGA and SEM in the latter section,

and entanglement with the increase of P4-VP content.

Pervaporation

Effect of Solvent Evaporation Temperature on Pervaporation Performances

The TPX membrane used for separation of the water-alcohol solution by the pervaporation process has not been reported in the literature, so it was studied first. The effect of the solvent evaporation temperature on the permeation rates and separation factor for pervaporation of 90 wt % aqueous ethanol solution through 5 wt % pure TPX membrane is shown in Figure 5. The permeation rates and separation factors are in the range of 170–100 g/m²h and 9–33, respectively, for solvent evaporation temperatures of 30–90°C. The separation factor increased and the total permeation rate decreased with an increase in the solvent evaporation temperature. The higher evaporation rate of solvent in the casting solution was caused by the higher temperature, so that the packing density of the TPX polymer chain increased. Hence the increase of solvent evaporation temperature induced the more dense structure, the increase of separation factor, and the decrease of permeation rate.²¹ In addition, the membrane formation at the higher evaporation rate results in the reduction in pore size accompanying the shrinkage that takes place. The solvent evaporation temperature is probably responsible for the separation factor increase and the permeation rate decrease.

Effect of Polymer Concentration on Pervaporation Performances

The effect of polymer concentration on the pervaporation performances of a 90 wt % of aqueous ethanol solution through the TPX membrane is shown in Figure 6. The permeation rate decreased and separation factor increased with increasing polymer concentration of casting solution from 5 to 10 wt %. These results might be due to the fact that the polymer chain can be packed more tightly when the solvent evaporates at higher polymer concentration. Thus the separation factor increases and the permeation rate decreases. The poor membrane formation was observed for polymer concentration higher than 10 wt %.

Effect of 4-VP Content in TPX/P4-VP Membrane on Pervaporation Performances

Accordingly the TPX membrane could be applied to the dehydration from aqueous ethanol solution by the pervaporation separation process. However, a lower separation factor was obtained. Thus, in the hope of further increasing the permselectivity properties of pervaporation, a hydrophilic monomer, (4-VP), was used to modify the TPX membrane. Figure 7 shows that the pervaporation performances of a 90 wt % of aqueous alcohol solution through the TPX/P4-VP membrane are significantly influenced by the P4-VP content. The separation factor increased with the P4-VP content up to 3.0 wt % then decreased. In addition, the permeation rate has a minimum value (84 g/m²h) at the 1.6 wt % P4-VP content in the TPX/P4-VP membrane. These phenomena might be due to the factors that the interaction of hydrogen bonding between feed solution and the membrane and crystallinity of the prepared membrane are increased by the addition of P4-VP. The separation factor decreases with increasing P4-VP content because of the increase of the phase separation and decrease of crystallinity. The results indicated in Figures 2–4 confirm the results.

Effect of Feed Composition on Pervaporation Performances

The effect of feed solution temperature on the total permeation rate and separation factor for 90 wt % aqueous ethanol feed solution in pervaporation is shown in Figure 8. The separation factor has a maximum at about 45°C. According to the free volume theory,²² the thermal motion of the polymer chain in the amorphous regions produces more free volume. As the temperature increases, it frequently results in a larger free volume and an increasing activity of permeating molecules while the amplitude of the chain jumping increased. Therefore, the separation factor increases with the feed solution temperature up to 45°C. The decrease of the separation factor at temperatures higher than 45°C is attributed to the plasticizing effect of the permeants and the interaction between the permeant and polymer. The increase of the total permeation rate is because of an increase in motion of the permeants and the polymer chain.

Moreover, compared with an unmodified TPX membrane, the TPX/P4-VP membrane with 3.0 wt % P4-VP content effectively increases the separation factor for the water-ethanol mixtures on pervaporation separation. This result is attributed to

the TPX/P4-VP membrane becoming denser and the interaction of hydrogen bonding between water and the membrane increasing with adding more hydrophilic P4-VP. Similar results were obtained by Uragami and Shinomiya.²³

Effect of Feed Aqueous Alcohol Solution on Pervaporation Performances

The pervaporation performances of a 90 wt % of aqueous alcohol solution through the TPX/P4-VP membrane are shown in Table III. An increase in the separation factor and a decrease in the permeation rate occurs as the molar volume in the alcohol increases. These results can be explained by the molecular size.

CONCLUSIONS

The heat stability of TPX/P4-VP membrane is higher than that of the unmodified TPX and P4-VP. The crystallinity of the membrane depends on the P4-VP content for the TPX/P4-VP membrane. Pervaporation results show that the water is preferentially permeated over the entire concentration range when using the TPX/P4-VP membrane. A separation factor of 133 and a permeation rate of 115 g/m²h can be obtained for the TPX/P4-VP membrane with a 3.0 wt % P4-VP content.

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