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Hydrophilic/hydrophobic IPN membranes for the pervaporation of ethanol-water mixture

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SUMMARY

Pervaporation of ethanol-water mixture was examined on IPN membranes composed of hydrophilic polyurethane(PU) and hydrophobic polystyrene(PS). The IPN membranes showed preferential pervaporation of water over ethanol and revealed high permeation rate. As the content of hydrophobic PS was increased, the permeation rate decreased while the separation factor increased, indicating that the PS domains suppressed the swelling of the PU phase and reduced the plasticizing effect. The average diffusion coefficient, computed from the permeation rate and solubility, was highly dependent on the viscosity and concentration of the permeant in the membrane.

INTRODUCTION

Pervaporation is a membrane separation process which can be used with liquid mixtures. The feed mixture is circulated and is in contact with one side of a non-porous polymeric membrane and the permeate is removed in the vapor state from the opposite side, which is kept under vacuum or under a stream of inert gas. This process is potentially useful in areas where conventional distillation techniques are difficult to be applied , such as the fractionation of azeotropic or isomeric mixtures.

Much attention has been directed recently to the separation of water and ethanol mixture from biomass products by this method. A large portion of such studies was made using hydrophilic polymer membranes. However, too much hydrophilicity often leads to excessive swelling of the membrane in contact with the aqueous feed solutions, and results in a loss of the mechanical and selective properties of the membrane. To avoid such defects, several methods of membrane preparation may be used : modification of the membrane surface by introducing the hydrophilic polymer on the hydrophobic substrate, introduction of the crosslinking, block or graft copolymerization, and by polymer blending.

The polymer blends of the hydrophilic/hydrophobic component system generally exhibit a large degree of phase separation due to the incompatibility of the component polymers. Thus block(1,2) or graft(3-5) copolymers of hydrophilic/hydrophobic constituents have mainly been attempted for high performance membranes. The concept of the interpenetrating polymer network(IPN) may be applied to combine the hydrophilic and hydrophobic component because the physical interlocking between the polymer components, which is the characteristic feature of the IPN structure, can restrict the phase separation. Lee et al.(6,7) could control the morphology of hydrophilic/hydrophobic IPN membrane by varying the synthesis pressure, and described the effect of the synthesis pressure on the dynamic mechanical properties, swelling behavior and the pervaporation characteristics.

In this paper, IPN membranes of hydrophilic polyurethane(PU) and

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hydrophobic polystyrene(PS) were prepared during the simultaneous polymerization process. To reduce the incompatibility between the PU and PS, hydrophilicity of the PU phase was given after the IPN formation by quaternizing the amines of PU domain to obtain the hydrophilic/hydrophobic IPN membranes.

EXPERIMENTAL

Membrane Preparation

Hydrophilic PU and hydrophobic PS IPN's were prepared by the simultaneous polymerization method. The isocyanate-terminated PU prepolymer was prepared by reacting 2 equivalents of the polyol mixture containing tertiary amine groups with 3 equivalents of hexamethylene diisocyanate at 70°C in a four-neck flask under dry nitrogen. The polyol mixture was composed of poly(tetramethylene ether)glycol (MW=1000) and N-methyldiethanolamine in 1:3 molar ratio. The reaction was continued until the theoretical isocyanate content was reached. One equivalent of the PU prepolymer was mixed with one equivalent of triethanolamine(TEA) as the crosslinking agent using a high-torque stirrer, and the air bubbles entrapped during mixing were removed by applying vacuum.

The PU membranes were prepared by casting the above mixture in a glass plate mold at 80°C for 24 hours. The mold was made of two glass plates between which a poly(ethylene terephthalate) film spacer was placed. The PS networks were prepared by polymerizing the purified styrene monomer mixture containing 8.8 wt% of divinylbenzene(DVB) and 1 wt% of benzoyl peroxide(BPO). PU/PS IPN membranes were prepared by mixing PU prepolymer, TEA, styrene monomer, DVB and BPO. The homogeneous mixture was then cast in the mold used for the preparation of PU membrane and reacted at 60°C for 24 hours and 80°C for 24 hours.

Cationic charges were introduced to the PU networks by quaternization of tertiary amine groups to obtain hydrophilic PU networks. Quaternization was carried out by swelling to equilibrium in benzylchloride(BC) at 40°C for 24 hours. The resulting samples were immersed in acetone for 12 hours to extract the unreacted BC, and then dried under vacuum at 50°C for at least 3 hours.

Swelling Experiments

A piece of membrane was immersed in a water-ethanol solution at 30°C. When sorption reached equilibrium, the membrane was rapidly removed from the solution, wiped with filter paper to remove the surface droplets and then weighed. The swelling ratio S is defined as

$$S = 100\ (W_s - W_d)\ /\ W_d$$

where W_d and W_s denote the weight of dry and swollen membrane, respectively.

Pervaporation

Pervaporation of aqueous ethanol solution through the IPN membrane was carried out by an ordinary pervaporation technique(8). The feed solution was circulated on the upper side of the membrane, and the downstream pressure was kept from 0.1 to 1.0 torr. The effective area of the membrane in contact with liquid was about 15.7 cm^2. Pervaporation experiments were carried out at a constant temperature of 30°C. The permeate was collected in a cold trap in liquid nitrogen. Composition of the permeate was analyzed by the gas chromatography (Hewlett Packard 5840A).

The permeation rate P was calculated by correcting the flux for the thickness of the membrane as in the following equation :

$$P = w \cdot l \,/\, a \cdot t$$

where w, l, a, and t denote the weight of the permeate, the membrane thickness, the surface area, and time, respectively.

The separation factor α was defined as

$$\alpha = \frac{Pw/Pe}{Fw/Fe} \qquad \text{w:water} \quad \text{e:ethanol}$$

where Pw/Pe and Fw/Fe denote the concentration ratio of water and ethanol in the permeate and in the feed, respectively.

Solvent Composition in the Membrane

The solvent composition in the membrane was determined by the extraction technique. Two or three grams of the membrane which was swollen in a given feed solution was immersed in about 50 ml of methanol to extract the solvent in the membrane. The concentration of water and ethanol in the methanol were determined using the gas chromatography.

RESULTS AND DISCUSSION

PU Membrane

Fig 1 shows the plot of swelling ratio as a function of ethanol composition in the feed solution for the PU membrane. The swelling ratio showed a maximum at around 70 wt% ethanol composition in the feed solution, as previously seen in the case of other hydrophilic polyurethane IPN's(6,7).

Fig 2 shows the effect of the feed composition on the permeation rate and the separation factor on the PU membrane. The permeation rate also becomes maximum at 70 wt% ethanol in the feed. According to this result, the sorption step seems to have an important contribution to the pervaporation process. On the other hand, the separation factor increased with increasing ethanol concentration in the feed.

Fig 3 shows the concentration of ethanol in the membrane at the equilibrium sorption condition and the concentration of ethanol in the permeate. The equilibrium sorption curve represents the contribution due to the "selective sorption" in the separation process. A significant difference between the sorption and pervaporation selectivity was observed. The preferential sorption of water decreased with decreasing ethanol concentration in the feed, and even an inversion in preferential sorption was observed at around 30 wt% ethanol in the feed. Considering that the permeation rate in pervaporation process is a function of solubility and diffusivity, the pervaporation selectivity of the PU membrane seems to be attributed mainly to the diffusion process.

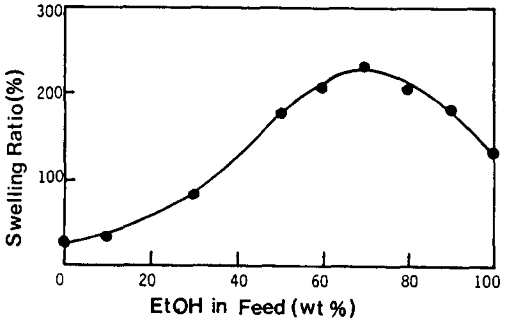

Fig 1. Swelling ratio of PU membrane as a function of EtOH composition.

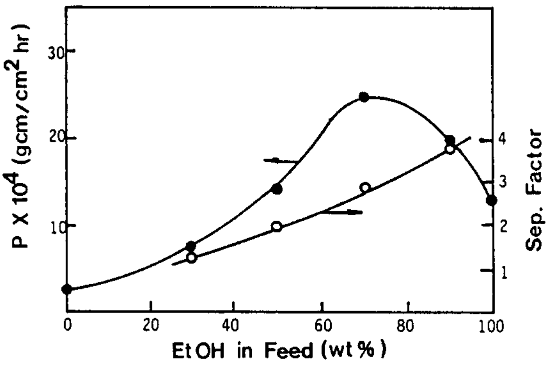

Fig 2. Effect of feed composition on permeation rate and separation factor in water-EtOH pervaporation through PU membrane.

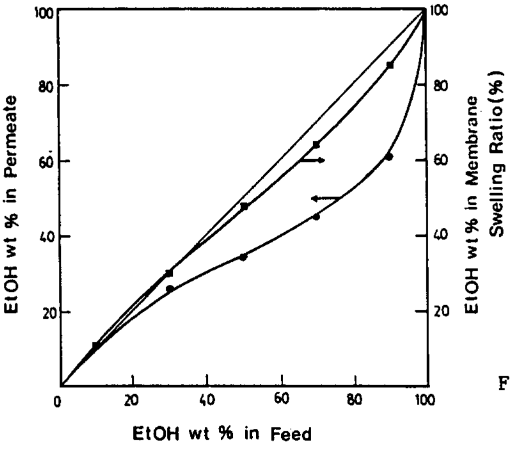

Fig 3. Relationship between the solvent composition in permeate, in the membrane and EtOH wt% in feed using PU membrane.

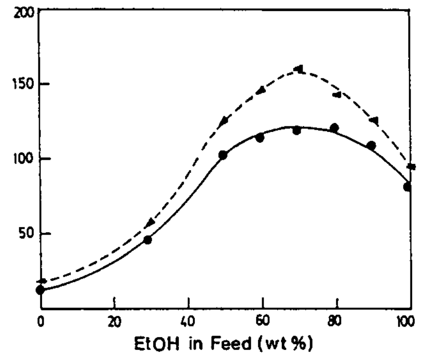

Fig 4. Swelling ratio of IPN membrane of PU/PS=70/30 as a function of EtOH composition. The dashed line is the calculated swelling ratio assuming no interpenetration.

PU/PS IPN membranes

Fig 4 shows the swelling behavior of the PU/PS=70/30 IPN membrane. The swelling ratio for the IPN membrane showed the same tendency as the PU membrane, but much lower values compared to that of the PU membrane. The swelling ratio of the IPN membrane was lower than the theoretical swelling ratio calculated from the composition of the IPN. This result suggests that the PS domain suppresses the swelling of the PU matrix. Similar restrictions in swelling was also observed in the PU/PS=50/50 IPN membranes.

Generally polymer blends containing hydrophilic and hydrophobic microdomains reveal that the hydrophobic domains act as the physical crosslinks when swollen in the aqueous solution. Lee et al.(6) reported that at the fixed IPN composition, IPN's containing the hydrophilic PU and hydrophobic PS showed decreased swelling ratio in water as the number of the dispersed PS domains increased as well as the degree of intermixing increased.

Fig 5 represents the results of the pervaporation experiment on the

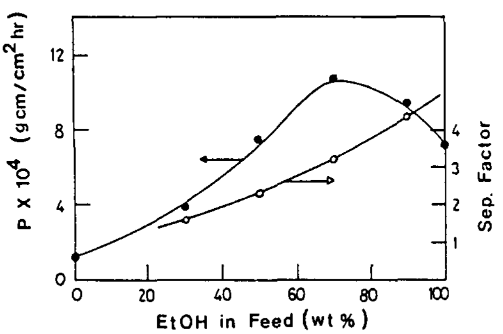

Fig 5. Effect of feed composition on permeation rate and separation factor in water-EtOH pervaporation through IPN membrane of PU/PS=70/30.

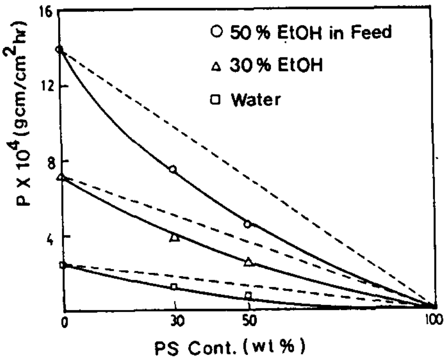

Fig 6. Effect of PS composition on permeation rate for PU/PS IPN membranes.

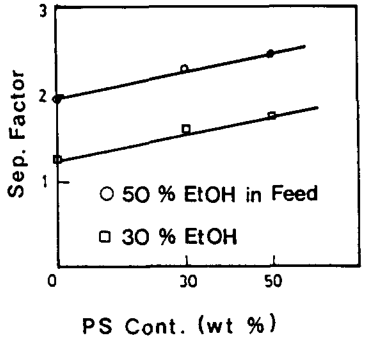

Fig 7. Effect of PS composition on separation factor for PU/PS IPN membranes.

PU/PS=70/30 IPN membrane. Comparing the results of the IPN and the pure PU membranes, we noticed that both curves showed practically the same behavior, while the IPN membrane exhibited higher selectivity and lower permeability than the PU membrane. These results imply that for the IPN membrane, decreased swelling ratio reduces the permeation rate and suppresses the plasticization of the membrane, thus improving the selectivity.

The effect of the PS composition in the IPN membrane on the permeation rate and separation factor is given in Fig 6 and Fig 7, respectively. The permeation rate decreased with increasing the PS content in the IPN membrane, and showed lower values than those calculated by simple additivity rule. On the other hand, the separation factor increased with an increase in the PS composition as seen in Fig 7. This result is reflecting the fact that the hydrophobic PS domains suppressed the plasticizing effect as the result of the restricted swelling ratio, and consequently the diffusivity ratio of water and ethanol through the IPN membranes increased.

Average Diffusion Coefficient

The data obtained from the sorption and pervaporation experiment on PU and PU/PS=70/30 IPN membranes were used to compute a average diffusion coefficient($\bar{D}$) employing the following equation

$$P = \bar{D}(C_u - C_d)$$

where P is the permeation rate and C_u and C_d are the permeant concentration at the upstream and downstream surfaces of the membrane. In pervaporation, where C_d is assumed to be zero and C_u to be the concentration of the solvent at the equilibrium sorption condition, $\bar{D}$ can be simply calculated from

$$\bar{D} = P/C_e$$

where C_e is the equilibrium concentration of the permeant as determined in the swelling experiments. The $\bar{D}$ values were computed for the water-ethanol mixture as a permeant.

For the permeation of a liquid through a swollen membrane, the diffusion coefficient usually depends on the concentration of the permeant, because it often acts as a plasticizer of the membrane. The concentration dependence of diffusion coefficient is often approximated by an exponential equation(9). Paul et al.(10,11) and Hamaya et al.(12,13) reported that the permeation rate is dependent on the viscosity, since the diffusion coefficient is inversely proportional to the permeant viscosity.

To substantiate above discussions, a semilog plot of the product of $\bar{D}$ and the viscosity of liquid mixture(η) vs. concentration of permeating liquid mixture, shown in Fig 8, was made. An exponential relationship was indicated by the nearly straight line. Therefore, we may conclude that in this system, the diffusion coefficient is strongly dependent on the viscosity of the liquid permeant as well as on the concentration of the permeant in the membrane. It was also suggested that the PS domains in the IPN membrane acted as inert fillers and hardly participated in permeation, since the data points of PU and IPN membrane in Fig 8 fall about a single straight line.

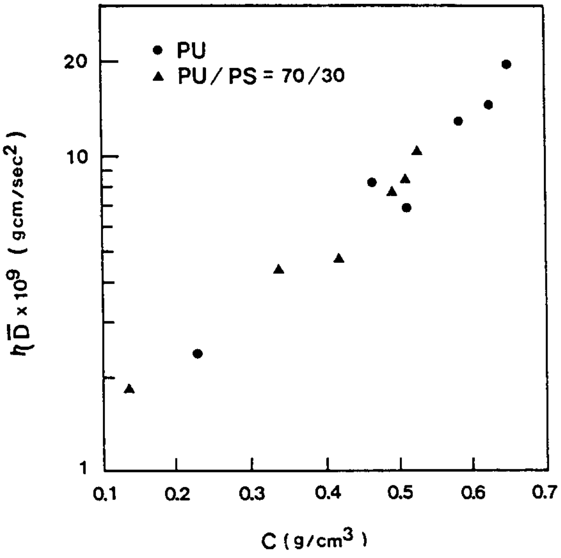

Fig 8. Correlation of $\eta\,\bar{D}$ with permeant concentration at the membrane's upstream interface. The symbol η refers to the viscosity of liquid mixture.

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