# HTPB-H$_{12}$MDI based polyurethane IPN membranes for pervaporation

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## Abstract

Membranes of hydroxyl terminated polybutadiene (HTPB) and 4,4′-dicyclohexylmethane diisocyanate (H$_{12}$MDI) based polyurethane (PU) crosslinked with benzoyl peroxide (BPO) and then formed into an interpenetrating network (IPN) with 4-vinyl pyridine (4-VP) were utilized for the pervaporation separation of water–ethanol mixtures. Membranes of IPN with a content of 8.44 wt% 4-VP have a permeability of 1184 g/m$^2$ h and a separation factor of 4.11 at 90 wt% aqueous ethanol solution. The effect of hydrophilic–hydrophobic content variation and the crosslinking on the adsorption, transport and morphological properties were investigated. The hydrogen bonding index (HBI) and frequency difference as a measure of the phase segregation and the average strength of the interpolymer hydrogen bonds were utilized to study the sorption phenomenon and permselectivity of the prepared membranes. The change of the glass transition temperature and infrared spectra, which can be used to show the 4-VP content, were detected by DSC and FTIR, respectively. Thermal decomposition behaviors conducted by TGA were used to investigate the formation of IPN.

*Keywords:* Polyurethane membrane; Hydroxyl terminated polybutadiene; Interpenetrating networks; Pervaporation; Ethanol–water mixture separation

## 1. Introduction

The separation of water–ethanol by pervaporation has used polymer membranes such as cellulose acetate [1], silicone imide [2], polyurea-urethane [3], polyvinyl alcohol [4,5], asymmetric Nylon 4 [6], chitosan [7] and the IPN of PU membranes [8,9].

The crosslinking and IPN of PU polymers were usually obtained by the introduction of diol and triol mixtures to the PU prepolymer [8–13]. Alcohol permselective membranes from aqueous alcohol so-

lutions have been prepared by crosslinked polybutadiene [14,15] and divinyl benzene (DVB) modified styrene/butadiene/styrene (SBS) and styrene/ethylene-butylene/styrene (SEBS) [16]. The permeabilities of the above three modified membranes are small (1.2, 47.4 and 23.4 g/m$^2$ h, respectively) and they are permselective to alcohol and are suitable for the separation of dilute aqueous alcohol solutions.

The purpose of this study was to prepare the crosslinked HTPB based PU IPN membranes for the pervaporation process. The crosslinking between soft-soft HTPB segments were prepared by the introduction of BPO to the HTPB based PU membranes to increase the permeability and thermal stability. In order to increase water selectivity in concentrated

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aqueous alcohol solution, a hydrophilic vinyl monomer (4-VP), was used for the IPN preparation. The effects of crosslinking, hard segment content, 4-VP content of IPN, feed compositions, and feed temperature on the pervaporation performances of these membranes were studied. HBI values, frequency difference and shift used for the identification of phase segregation and the interpolymer hydrogen bonding behavior between proton-donating groups and pyridine nitrogen atom or carbonyl groups were measured by FTIR. Measurements of glass transition temperature by DSC and thermal degradation behaviors by TGA were used to characterize the formation of 4-VP/PU IPN.

## 2. Experimental

### 2.1. Materials

The chemicals used for this study were 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$, Desmodur W of Mobay Co.), hydroxyl terminated polybutadiene (equivalent weight 1370 g, average functionality of 2.3, R-45M of ARCO Co.), 1,4-butane diol (1,4-BD) was used as chain extender and dibutyltin dilaurate (DBTDL) as catalyst. Benzoyl peroxide (BPO) was used as initiator and DVB as crosslinking agent. 4-VP monomer was purified by vacuum distillation.

### 2.2. Membrane preparation

The two-stage polyurethanes were polymerized first by an –NCO terminated prepolymer and chain extended with 1,4-BD under 25 wt% solid content after the theoretical –NCO content was reached. It was diluted to 15 wt% solid content after the chain extended reaction had proceeded for 30 min. The reaction was terminated when the –NCO groups were completely consumed, as confirmed by the disappearance of the infrared (IR) absorption at 2280 $cm^{-1}$.

Crosslinked membranes were prepared by adding 1.0 wt% (based on PU solid content) of BPO to the PU solution and then reacted at 65°C for 6 h. IPN of HTPB based PU and poly(4-VP) were synthesized by sequential polymerization. BPO, 4-VP and DVB were added to the crosslinked PU solution and mixed homogeneously for about 20 min. The above two solutions were poured onto a glass plate to a thickness of 600 $\mu m$. Then the solvent in the casting solution was evaporated by vacuum pump at 60°C for 24 h. The dried membranes were peeled from the plate after it had been immersed in deionized ice water for several hours. The PU membranes were dried in a vacuum and stored at a relative humidity of 50% and 25°C for five days before testing.

PU143 represents the uncrosslinked PU membrane with equivalent ratio of HTPB/$H_{12}$MDI/1,4BD = 1/4/3. CPU143, CPU187 and CPU11211 represent crosslinked membranes with different equivalent ratio of HTPB/$H_{12}$MDI/1,4BD = 1/4/3, 1/8/7 and 1/12/11 or with hard segment content of 33.08, 50.56 and 60.79 wt%, respectively. The IPN membranes containing 1.36, 2.63, 8.44, 10.86, 17.42 and 25.35 wt% of 4-VP are designated as IPN-1.36, IPN-2.63, IPN-8.44, IPN-10.86, IPN-17.42 and IPN-25.35, respectively. The equivalent ratio of HTPB/$H_{12}$MDI/1,4BD of the PU solutions used for the preparation of IPN are 1/4/3.

### 2.3. Pervaporation experiments

A traditional pervaporation apparatus was used in this study [17]. A normal vacuum pervaporation apparatus consists of a cell made of stainless steel with circulation of the liquid over the membrane. The effective membrane area in contact with the feed solution was 10.2 $cm^2$. The membrane was supported by filter paper resting on a sintered stainless steel disk. A vacuum pump maintained the downstream pressure at 3–5 mmHg and the permeate was collected in a trap cooled by liquid nitrogen and analyzed by gas chromatography. The permeate rate was determined by the weight of the permeate. Most of the experiments were conducted at 25°C. The feed temperature was studied in the range of 25–65°C. The compositions of the feed solutions, permeates and solutions adsorbed in the membrane were measured by gas chromatography (GC China Chromatography, 8700T). The separation factor of sorption, $\alpha_{sorp}$, was calculated from:

$$\alpha_{H_2O/EtOH} = (Y_{H_2O}/Y_{EtOH})/(X_{H_2O}/X_{EtOH})$$

where $X_{H_2O}$, $X_{EtOH}$, and $Y_{H_2O}$ and $Y_{EtOH}$ are the weight fraction of water and ethanol in the feed and permeate, respectively.

## 2.4. Sorption measurement

Membranes were immersed in ethanol–water mixtures for 24 h. They were subsequently blotted between tissue paper to remove adherent solvent and placed in the left half of a twin tube setup. The system was evacuated while the left tube was heated with hot water and the right one was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by GC. The separation factor of sorption, $\alpha_{sorp}$, was calculated from:

$$\alpha_{sorp} = (Y_w/Y_e)/(X_w/X_e)$$

where $X_w$, $X_e$ and $Y_w$, $Y_e$ are the weight fractions of water and ethanol in the feed and permeate, respectively.

## 2.5. Infrared spectroscopy

Thin films for the infrared studies were prepared by 5% (w/v) polymer solution casting. The preparation procedures were the same as the above membrane preparation methods. Wet films were prepared by dipping membrane in ethanol or water for 24 h and then blotted with filter paper thoroughly. Infrared spectra of dry (no solvent adsorbed) and wet films were obtained with a BIO-RAD FTS-7 spectrometer. The frequency difference is defined as $\Delta\nu = \nu_f - \nu_b$, where $\nu_f$ and $\nu_b$ are the frequencies of maximum absorption for the free and hydrogen bonded N–H (or C=O) groups, respectively. The shift, $\Delta\nu$, in the stretching frequency is considered as a measure of the strength of the hydrogen bond. The hydrogen bonding index (HBI) is defined as HBI $= A_{C=O,b}/A_{C=O,f}$ or $A_{N-H,b}/A_{N-H,f}$, where $A_{C=O,b}$, $A_{N-H,b}$ and $A_{C=O,f}$, $A_{N-H,f}$ are the absorbance of bound and free C=O or N–H groups, respectively.

## 2.6. Differential scanning calorimetry (DSC)

The DSC measurements were made using a Du Pont 9000 thermal analyzer with liquid nitrogen for cooling and a heating rate of 10°C/min in the temperature range from $-120$ to 150°C.

## 2.7. Elemental analyzer and swelling test

A Perkin-Elmer 240C, 2400EA was used for the analysis of pyridine content in the 4-VP/PU IPN membranes. The swelling ratio is defined as $(W_1 - W_0) \times 100\%/W_0$, where $W_1$ is the weight of wet membranes thoroughly blotted with filter paper and $W_0$ is the weight of dry membranes.

## 2.8. Thermogravimetric analyzer (TGA)

TGA thermograms were obtained with a Du Pont 951 thermogravimetric analyzer with a heating rate of 20°C/min in the temperature range from 50 to 600°C under a continuous nitrogen flow of 30 ml/min.

# 3. Results and discussions

## 3.1. Effect of crosslinking and hard segment content on PU membrane

The permeability of a crosslinked membrane (CPU143) are higher than that of an uncrosslinked membrane (PU143) for all feed concentrations due to the more stretched HTPB soft segment chains as shown in Fig. 1. But their separation factors remain
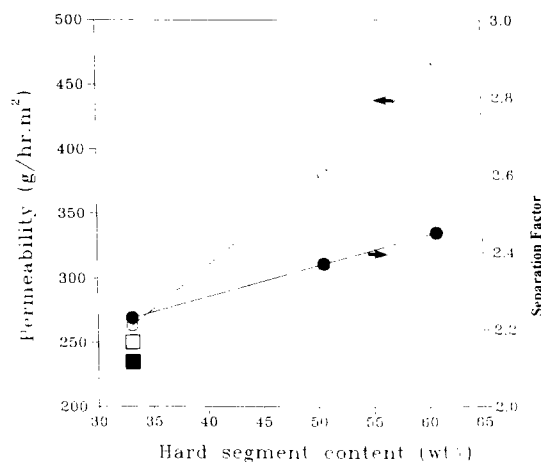


Fig. 1. Permeability and separation factor of uncrosslinked (PU) and crosslinked (CPU) membranes with different hard segment content at 90 wt% aqueous ethanol solution and 25°C operating temperature. Permeability of CPU (O) and PU (□); separation factor of CPU (●) and PU (■).

nearly constant owing to these two membranes having the same amount of urethane groups.

Fig. 1 shows that the permeability increases, while the separation factors remain nearly constant or slightly increase, as the hard segment content increases. The increase of hard segment content of PU elastomer induces the increase of sorption effect predominantly on the permeability of water/ethanol mixture [18,19]. Although the swelling behavior of HTPB soft segment decreases as the hard segment increases.

HBI and frequency difference were utilized in this study to discuss the hard segment content effect on the sorption phenomenon. The IR spectra indicate that the increase of interaction between water (or ethanol solvent) and C=O (or N–H groups) of these three CPU membranes are evidenced by the increase of absorbance intensity of bonded C=O (or N–H groups) relative to the free C=O (or N–H groups), HBI value. The frequency difference (134 cm$^{-1}$) of dipped in ethanol of N–H groups and frequency shift of bonded N–H groups (from 3331 to 3320 cm$^{-1}$) of CPU143 membrane are all larger than that of the C=O group. This could support a hypothesis that the hydrogen bond of N–H groups with ethanol or water molecules are stronger than that of C=O groups [19].

Coleman and co-workers [20] have used the frequency difference between free hydroxyl groups and those of the hydrogen bonded hydroxyl groups as a measure of the average strength of the intermolecular interactions. In this respect the average strength of the hydrogen bonds ($\Delta\nu$) between N–H groups and solvents (or C=O groups) of these dry and wet CPU membranes are in the order CPU11211 > CPU187 > CPU143, which shows that the sorption ability has a preferential effect on the increase of polyurethane elastomer as the increase of hard segment content. The hydrogen bond strength of these three membranes are in the order dipped in ethanol > dipped in water > non-solvent treated, which indicates that the sorption of ethanol is higher than that of water. The infrared study of bonded N–H groups frequency of these three CPU membranes shift to the lower frequency, when dipped in ethanol or water solvent, which means the interaction of N–H groups with ethanol and water molecules. But the water molecules are smaller than that of ethanol and the swelling degree is lower in the high hard segment polymer

(HTPB is the ethanol swelling component). From the above studies, their separation factors remain nearly constant or a slight increase as the hard segment content increases.

## 3.2. Effect of 4-VP content on IPN membrane

From the study of the above section, membranes of CPU have larger permeabilities than that of PU. But their separation factors are too low to the separation of water from concentrated ethanol aqueous solution. So that two component IPN of PU and 4-VP were prepared for high permeability and expected to be permselective to water from concentrated aqueous ethanol solution. The 4-VP contents were quantitatively detected by the elemental analysis and qualitatively by FTIR. Fig. 2 shows the characteristic infrared spectra of the pyridine groups at 1600 and 1643 cm$^{-1}$.

Fig. 3 shows that permeability increases, which is evidenced by the increasing swelling ratio in Table 1, as the hydrophilic 4-VP content increases. The hydrophobic HTPB soft segment has strong affinity with ethanol [14] and the affinity with ethanol decreases as the 4-VP content increases. This may be the reason for the increase of separation factor as the 4-VP content increases up to 8.44 wt% of 4-VP content and then decrease for higher 4-VP content. This also can be explained by frequency difference, HBI value and frequency shift of the interaction
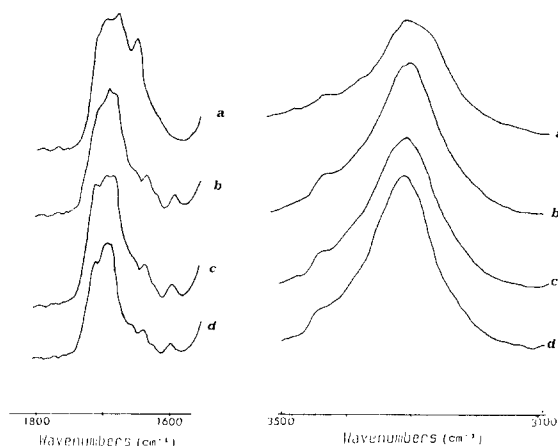


Fig. 2. IR spectra of CPU and 4-VP/PU IPN membranes. (a) CPU143, (b) IPN-8.44, (c) IPN-10.86, (d) IPN-17.42.
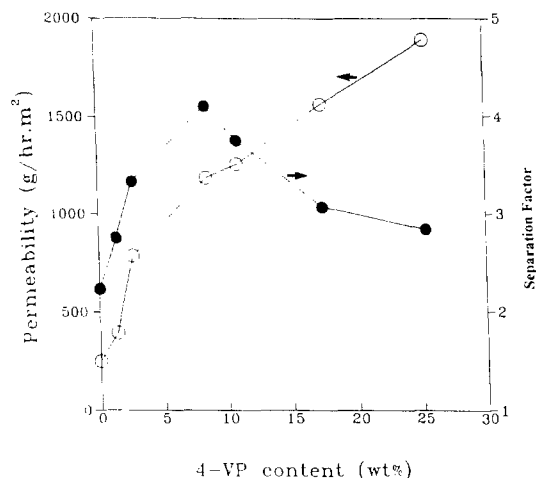
Fig. 3. Permeability (○) and separation factor (●) of different 4-VP content IPN membranes at 90 wt% aqueous ethanol solution and 25°C operating temperature.

Table 1
Swelling ratio of different 4-VP content polymer in 90 wt% ethanol aqueous solution at 25°C

| Composition | IPN-2.63 | IPN-8.44 | IPN-10.86 | IPN-17.42 |
|---|---|---|---|---|
| Swelling ratio | 5.31 | 20.85 | 29.74 | 43.57 |

between N–H, C=O, pyridine groups and ethanol or water in the following discussions.

4-VP/PU IPN polymers can form hydrogen bonds with proton-donating group through sharing the valence electrons of pyridine nitrogen atoms. The presence of pyridine rings in the polymer leads to a competition with carbonyl groups for hydrogen bonding with ethanol, water and N–H groups. In other words, the association between ethanol, water, N–H groups and pyridine prevails over those with carbonyl association [21]. Infrared studies of frequency shift from 3331 cm$^{-1}$ of dry CPU to 3318 or 3319 cm$^{-1}$ of three dry IPN membranes indicate that there is a strong intermolecular interaction between 4-VP and N–H groups. Fig. 4 shows that the infrared spectra of three 4-VP/PU IPN dry membranes and dipping in the water and ethanol, respectively. The interpolymer complexes are formed through intermolecular hydrogen bonding associations between N–H and pyridine nitrogen atom [22]. Fig. 5 shows that the average strength of the hydrogen bonds of three different dry 4-VP/PU IPN are in the order IPN-17.42 ($\Delta\nu = 136$ cm$^{-1}$) > IPN-10.86 ($\Delta\nu = 133$ cm$^{-1}$) > IPN-8.44 ($\Delta\nu = 131$ cm$^{-1}$). These three frequency differences are all larger than that of CPU 143 ($\Delta\nu = 101$ cm$^{-1}$).

The frequency differences ($\Delta\nu$) of three IPN membranes decrease from 131–136 cm$^{-1}$ of non-
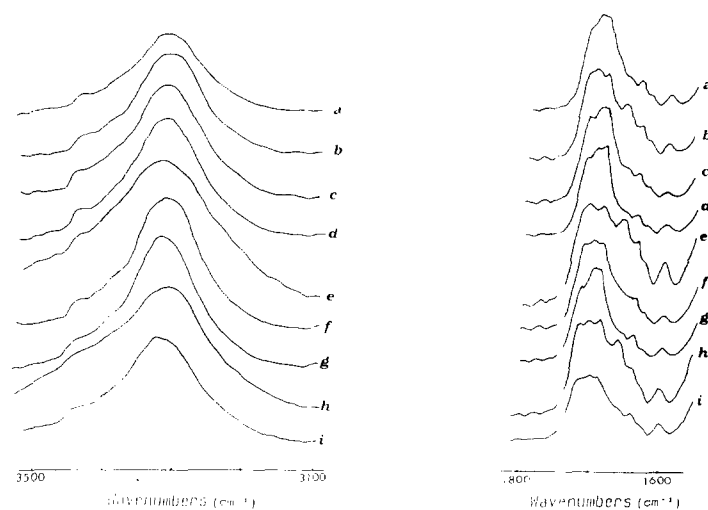


Fig. 4. IR spectra of three dry 4-VP/PU IPN membranes, then dipped in ethanol and water, respectively. IPN-8.44: (a) dry, (b) dipped in ethanol, (c) dipped in water; IPN-10.86: (d) dry, (e) dipped in ethanol, (f) dipped in water; IPN-17.42: (g) dry, (h) dipped in ethanol, (i) dipped in water.

solvent treated to 118–120 cm$^{-1}$ of dipped in water and 106–108 cm$^{-1}$ of dipped in ethanol. The hydrogen bond between ethanol and other electronegative groups is lower than that of water [22]. The frequency differences between water and other polar groups of CPU and three IPN membranes remain nearly the same. From the above studies, it indicates that the sorption of water in these three IPN membranes are higher than that of ethanol.

Fig. 5 shows the HBI values of $A_{N-H,b}/A_{N-H,f}$ of CPU and these three dry IPN membranes change from 1.3184, 1.4062, 1.4342 to 1.4735, as the 4-VP content increase from 0, 8.44, 10.86 to 17.42 wt%. Whereas the ratio of $A_{C=O,b}/A_{C=O,f}$ decreases from 1.1293, 1.1162, 1.0746 to 1.0453. The reason may be that part of the N–H groups form hydrogen bonds with the pyridine nitrogen atoms which induce the increase of bonded N–H groups and free bonded C=O groups. Higher HBI values of $A_{C=O,b}/A_{C=O,f}$ of three IPN membranes indicate that the segregation between polymer chains is small in the non-polar HTPB based PU membranes [23] and hence higher separation factor of IPN-8.44. The frequency of bonded N–H groups of these three wet IPN membranes are all higher than that of dry membranes respectively, which means that the interaction of N–H groups with pyridine groups is stronger than with water or ethanol molecules. The frequency shifts of bonded N–H groups of these three IPN mem-



Fig. 6. Effect of feed concentration (wt%) on the permeability (○) and separation factor (●) of IPN-8.44 membrane at 25°C operating temperature.

branes dipped in water are larger than that dipped in ethanol. The increase of swelling ratio and high sorption ability for water as the 4-VP content induced may be the reason of maximum separation factor of IPN-8.44.

HBI values, frequency difference and shift may be the reason for higher permselectivity toward water in the 4-VP/PU IPN membranes although these PU membranes contain non-polar HTPB soft segment.

## 3.3. Effect of feed concentration

The membrane of IPN-8.44 used for the following pervaporation study is due to its pervaporation separation index, which is the product of permeability and separation factor, of 4866 g/m$^2$ h is higher than that of CPU143 and other IPN membranes. Fig. 6 shows that the permeability and separation factor of IPN-8.44 membrane are all increased from dilute ethanol aqueous solution to concentrated solution. Selectivity of pervaporation toward water and the permeability were improved significantly by the 4-VP/PU IPN in comparison with the pervaporation results of the CPU membranes. This might be due to the known strong affinity of 4-VP for electrophilic nitrogen groups. Obviously, the hydrogen bonding ability of the C=O, N–H and pyridine groups is an important factor in the present pervaporation system as discussed in the above section.
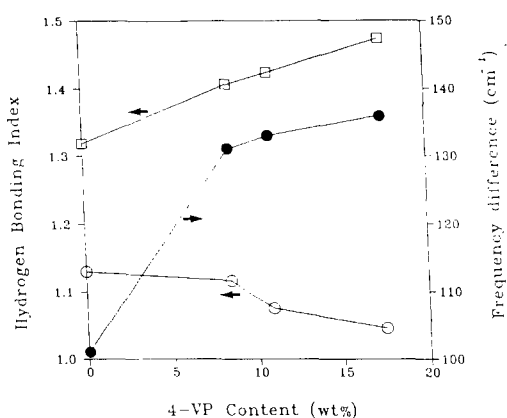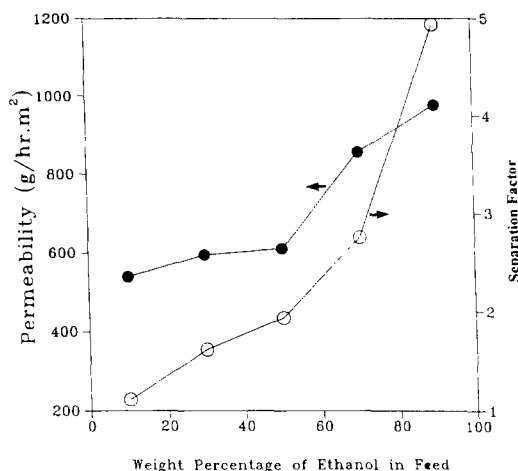


Fig. 5. Effect of 4-VP content on the HBI values (○, $A_{C=O,b}/A_{C=O,f}$; □, $A_{N-H,b}/A_{N-H,f}$) and frequency difference (●, $\Delta\nu$) between bonded and free bonded N–H groups of dry membranes.

Table 2
Swelling ratio of PU membranes in different weight percentages of ethanol in ethanol aqueous solution

| Wt% of ethanol | 10 | 30 | 50 | 70 | 90 |
|---|---|---|---|---|---|
| Swelling ratio (%) of CPU143 | 2.42 | 2.83 | 4.03 | 7.71 | 11.49 |
| Swelling ratio (%) of IPN-8.44 | 6.52 | 9.75 | 12.19 | 16.44 | 20.85 |

Swelling experiments carried out with various feed concentration have shown that the degree of swelling in ethanol is higher than in water. The increase of permeability as the increase of ethanol content in the feed concentration can be evidenced by the increase of swelling degree as shown in Table 2.

When the membranes are immersed in the water–ethanol mixture, the ethanol molecules are absorbed on the polymer chains of HTPB soft segment. The polymer interacts with the hydrophobic moiety of the ethanol and the OH groups of the ethanol remain exposed on the surface. This hydrophilisation of the somewhat hydrophobic membrane by the ethanol is probably responsible for the selectivity for water [24]. In this study, the addition of 4-VP into the PU polymer for the strong affinity with water in the membrane increases the permselectivity toward water in the membrane.
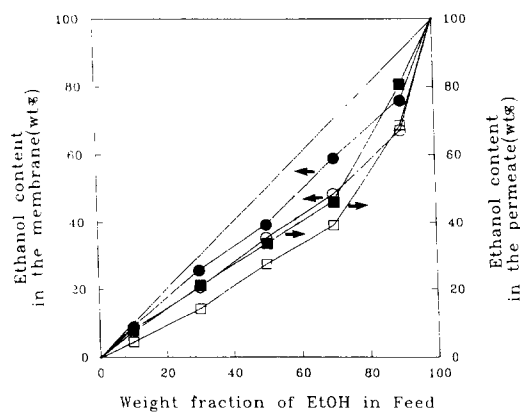
According to the solution-diffusion model, the



Fig. 7. Ethanol concentration in membrane (O) and in permeate (□) of IPN-8.44 membrane and ethanol concentration in membrane (●) and in permeate (■) of CPU143 membrane at feed concentration at 25°C.
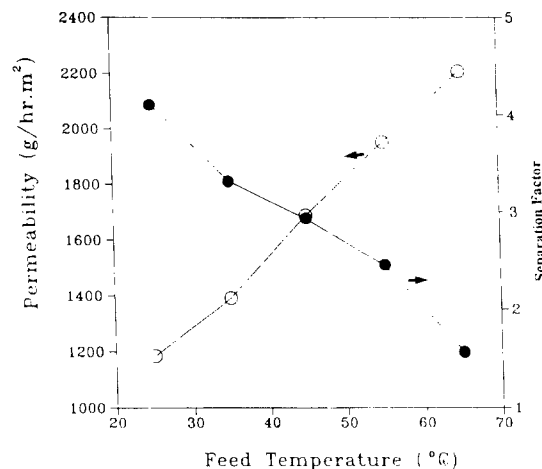


Fig. 8. Effect of feed temperature for IPN-8.44 membrane on permeation rate (●) and separation factor (O) at 90 wt% aqueous ethanol solution.

effect of solubility plays an important role in the permselectivity of elastomeric membranes. The sorption experiments for the CPU143 and IPN-8.44 membranes were conducted as shown in Fig. 7. The curve of ethanol content in the membrane and permeate of these two membranes are all below the diagonal line. This suggests that water molecules are selectively dissolved into these two membranes. Larger deviation of permeate from the diagonal line than that in the membrane indicates that higher permselectivity of permeate. At 90 wt% aqueous ethanol solution, the ethanol content in the permeate is higher than that in the membrane of CPU143, which may be due to the higher swelling ratio at this concentration.

## 3.4. Effect of feed temperature

For IPN-8.44 membrane, the permeability increases and the separation factor decrease with the increase of feed temperature as shown in Fig. 8. These results are due to the fact that a higher feed temperature, causing an increase in chain mobility and the swelling of membrane matrix and hydrogen bonds decay as the increase of feed temperature, induces a higher permeability of IPN membranes. When the feed temperature reaches 55–65°C, which is the glass transition temperature of the hard segments of the IPN-8.44 membrane, the free volume of
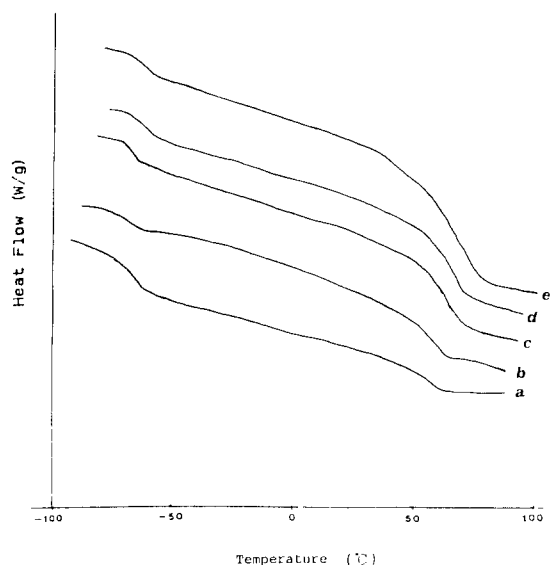
Fig. 9. DSC thermogram of CPU143 and 4-VP/PU IPN membranes. (a) CPU143, (b) IPN-8.44, (c) IPN-10.86, (d) IPN-17.42, (e) IPN-25.35.

membrane largely increases and hence the separation factor decreases appreciably.

## 3.5. Characterization of PU membranes

### 3.5.1. Infrared spectroscopy

The existence of 4-VP in the 4-VP/PU IPN membranes can be evidenced by the infrared spectra and the strength of hydrogen bonds [25], which are detected by FTIR. Fig. 2 shows the characteristic spectra of the pyridine group at 1643 and 1600 cm$^{-1}$ in the three pyridine containing PU polymer. While at 1660 cm$^{-1}$ of N–H deformation only appear in the CPU membranes, which may be due to the strong hydrogen bonding between nitrogen atom of pyridine and N–H group, induces the disappearance of this band in the 4-VP/PU IPN membranes.

### 3.5.2. Differential scanning calorimeter

The change of glass transition temperatures give evidence for the existence of 4-VP in the 4-VP/PU IPN membranes. Fig. 9 presents DSC curves for a number of different 4-VP/PU IPN and CPU membranes. Table 3 shows that the glass transition temperature of soft segment ($T_{gs}$) and hard segment ($T_{gh}$) increased as the 4-VP content increased. Larger posi-

Table 3
Glass transition temperature of soft and hard segments of CPU143 and different 4-VP content PU membranes

| Composition | $T_{gs}$ (°C) | $T_{gh}$ (°C) |
|---|---|---|
| CPU143 | −74.2 | 58.5 |
| IPN-8.44 | −70.6 | 63.3 |
| IPN-10.86 | −68.2 | 66.8 |
| IPN-17.42 | −67.3 | 70.6 |
| IPN-25.35 | −66.2 | 80.7 |

tive deviation in $T_{gh}$ values than that in $T_{gs}$ values observed indicates the stronger interactions between 4-VP and hard segment of PU.

### 3.5.3. Thermogravimetric analysis

In most cases, the thermograms of the IPN fall in between those of two components [26]. TGA curves can be used to manifest the formation of 4-VP/PU IPN membranes, as reproduced in Fig. 10.

A three-step degradation was observed in all these membranes. It is stable up to 300°C and the polymer remains almost intact in the first step. The quantity of gaseous components, mainly water released in this step, is relatively small.
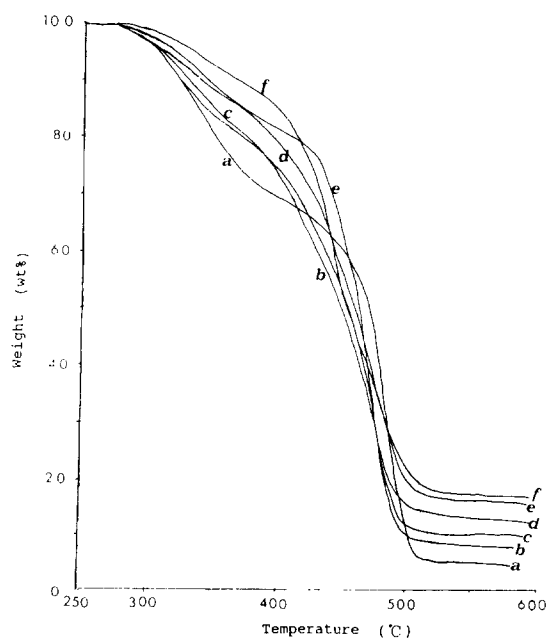


Fig. 10. TGA thermogram of CPU143 and 4-VP/PU IPN membranes. (a) CPU143, (b) IPN-2.63, (c) IPN-8.44, (d) IPN-10.86, (e) IPN-17.42, (f) IPN-25.35.

A rapid weight loss starts at approximately 300 up to 500°C, the main quantity of gaseous components, e.g. water, carbon monoxide and methane were split off. Decomposition of step 2 corresponds to the urethane bonding (i.e. hard segment) breaking and step 3 is the polyol decomposition [27]. Membranes of CPU have the lower 2nd decomposition temperature, higher 3rd decomposition temperature and lower residue. However, the 2nd decomposition temperature of the 4-VP/PU IPN membranes increase as the 4-VP content increases, due to higher thermal degradation temperature of 4-VP. With lower oxygen atom content of hard segment and higher carbon atom content in the molecular structure of 4-VP/PU IPN, these membranes have higher residue remains after TGA analysis.

## 4. Conclusions

The pervaporation permeabilities and separation factors of CPU membranes are all higher than that of PU membranes and increase as the increase of hard segment content. The best performance of 4.11 separation factor and 1184 $g/m^2$ h permeability can be obtained by the IPN membrane with 8.44 wt% of 4-VP content. Permeability increases as the 4-VP content increases and decreases as the feed temperature increases. Separation factor has an appreciable decrease at the feed temperature of 55–65°C, which is the $T_{gh}$ of the IPN-8.44 membrane. The HBI value, frequency difference and shift of free and hydrogen bonded N–H groups were measured by FTIR and hence well explain the sorption phenomena and interpolymer hydrogen bonds with different 4-VP content. The change of glass transition temperature and infrared spectra, which can be used to manifest the 4-VP content, was detected by DSC and FTIR, respectively. Thermal decomposition behaviors conducted by TGA were used to manifest the formation of IPN.

## Acknowledgements

## References

[1] E. Nagy, O. Borlai and A. Vjhidy, Membrane permeation of water–alcohol binary mixtures, J. Membrane Sci., 7 (1980) 109.

[2] J.Y. Lai, S.H. Li and K.R. Lee, Permselectivities of polysiloxaneimide membrane for aqueous ethanol mixture in pervaporation, J. Membrane Sci., 93 (1994) 273.

[3] M.M. Cipriano, A. Diogo and M.N. de Pinho, Polyurethane structure design for pervaporation membranes, J. Membrane Sci., 61 (1991) 65.

[4] C.K. Yeom and R.Y.M. Huang, Modelling of the pervaporation separation of ethanol–water mixtures through crosslinked poly(vinyl alcohol) membrane, J. Membrane Sci., 67 (1992) 39.

[5] J.W. Rhim, M.Y. Sohn, H.J. Joo and K.H. Lee, Pervaporation separation of binary organic aqueous liquid mixtures using crosslinked PVA membranes. I. Characterization of the reaction between PVA and PAA, J. Appl. Polym. Sci., 50 (1993) 679.

[6] J.Y. Lai, Y.H. Chu, S.L. Huang and Y.L. Yin, Separation of water–alcohol mixtures by pervaporation through asymmetric Nylon 4 membrane, J. Appl. Polym. Sci., 53 (1994) 999.

[7] Y.M. Lee and E.M. Shin, Pervaporation separation of water–ethanol through chitosan membranes. IV. Phosphorylated chitosan membranes, J. Membrane Sci., 64 (1991) 145.

[8] Y.K. Lee, T.M. Tak, D.S. Lee and S.C. Kim, Cationic/anionic inter-penetrating network membranes for the pervaporation of ethanol–water, J. Membrane Sci., 52 (1990) 157.

[9] Y.K. Lee, I.S. Sohn, E.J. Jeon and S.C. Kim, IPN membranes for the pervaporation of ethanol/water mixture, Polym. J. 23(5) (1991) 427.

[10] S.S. Shyu, D.S. Chen and J.Y. Lai, Polycarbonate-polyurethane semi-interpenetrating polymer networks: $T_g$ behavior and morphology, J. Appl. Polym. Sci., 34 (1987) 2151.

[11] P. Zhou, H.L. Frisch and H. Ghiradella, Interperetrating polymer networks of poly(carbonate-urethane) and polyvinylpyridine, J. Polym. Sci., Part A, Polym. Chem., 30 (1992) 835.

[12] V. Choudhary and R. Gupta, IPN from hydroxyl terminated polybutadiene based polyurethane and poly(methyl methacrylate), J. Appl. Polym. Sci., 50 (1993) 1075.

[13] B. Das, T. Gangopadhyay and S. Sinka, Physical, mechanical and morphological behavior of sequential polybutadiene-poly(methyl methacrylate) IPN, J. Appl. Polym. Sci., 54 (1994) 367.

[14] M. Yoshikawa, T. Wano and T. Kitao, Speciality polymeric membranes. 1. Modified polybutadiene membranes for alcohol separation, J. Membrane Sci., 76 (1993) 255.

[15] M. Yoshikawa, T. Wano and T. Kitao, Speciality polymeric membranes. 2. Pervaporation separation of aqueous solutions through modified polybutadiene, J. Membrane Sci., 89 (1994) 23.

[16] F. Sun and E. Ruckenstein, Membranes of block copolymer poly(divinyl benzene) blends for the pervaporation of alcohol–water mixtures, J. Membrane Sci., 90 (1994) 275.

[17] K.R. Lee and J.Y. Lai, Dehydration of acetic acid–water mixtures by pervaporation with a modified poly(4-methyl-1-pentene) membrane, J. Polym. Res., 1 (3) (1994) 247.

[18] M.H.V. Mulder, J.O. Hendrikman, H. Hegeman and C.A. Smolders, Ethanol–water separation by pervaporation, J. Membrane Sci., 16 (1983) 269.

[19] L. Di Landro, M. Pegoraro and L. Bordogna, Interactions of polyether polyurethanes with water vapour and water–methane separation selectivity, J. Membrane Sci., 64 (1991) 229.

[20] E.J. Moskala, D.F. Varnell and M.M. Coleman, Concerning the miscibility of poly(vinyl phenol) blends. FTIR study, Polymer, 26 (1985) 228.

[21] L.C. Cesteros, J.R. Isasi and I. Katime, Hydrogen bonding in poly(4-vinyl pyridine) and poly(vinyl acetate-co-vinyl alcohol) blends. An infrared study, Macromolecules, 26 (1993) 7256.

[22] J. Dai, S.H. Goh, S.Y. Lee and K.S. Siow, Interpolymer complexation between poly(p-vinyl phenol) and pyridine-containing polymers, Polymer J. 26(8) (1994) 905.

[23] S.L. Huang and J.Y. Lai, On the gas permeability of HTPB based PU membrane, J. Membrane Sci., 105 (1995) 137.

[24] E. Ruckenstein and F. Sun, Anomalous sorption and pervaporation of aqueous organic mixtures by poly(vinyl acetal) membranes, J. Membrane Sci., 95 (1994) 207.

[25] G. Spathis, M. Niaounakis, E. Kontou, L. Apessis and C. Christodoulides, Morphological changes in segmented PU elastomers by varying the N–CO/OH ratio, J. Appl. Polym. Sci., 54 (1994) 831.

[26] S.C. Kim, D. Klempner, K.C. Frisch and H.L. Frisch, PU IPN's V. Engineering properties of polyurethane-poly(methyl methacrylate) IPN's, J. Appl. Polym. Sci., 21 (1977) 1289.

[27] P.D. Nair, M. Jayabalam and V.N. Krishramurthy, Polyurethane-polyacrylamide IPN's. I: Synthesis and characterization, J. Polym. Sci., Part A, Polym. Chem., 28 (1990) 3775.