SEPARATION PERFORMANCE OF DVB CROSSLINKED POLYURETHANES

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Abstract—Polyurethanes (PUs) were prepared from hydroxyl-terminated polybutadiene (HTPB) and 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI) and 1,4-butane diol (1,4-BD) by step growth polymerization. The crosslinkage between the HTPB soft segment of PUs was formed by adding divinyl benzene (DVB) as crosslinking agent to the PU solution. The permeability and selectivity of an air or water/ethanol mixture of crosslinked PU membranes were investigated. The effect of hard segment content, DVB content, feed concentration and feed temperature on the gas and liquid separation were studied. The gas and liquid permeabilities of HTPB-based PU membranes with a suitable amount of crosslinking agent, which hindered the hard segment aggregation, were found to be higher than those of uncrosslinked ones. All the separation performances are explained by the flexibility of soft segments and aggregation of hard segments of PUs. The hydrogen bonding index (HBI) and frequency difference measured by FTIR, 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 glass transition temperature was determined by DSC, which can be used to show the degree of crosslinking of these membranes. The results of the FTIR and DSC measurements exhibit the degree of crosslinking with different DVB content and hence the gas and liquid permselectivities as well. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) and 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI) are viscous liquids which are easily used for the synthesis of polyurethane (PU) prepolymers and the preparation of membranes. The superior hydrolytic stability and high mechanical property performance of HTPB show surprising utility in many fields [1, 2]. HTPB-based PUs have been used for gas separation research because of their low temperature flexibility and high segregation between hard and soft segments [3, 4]. Pervaporation separation of ethanol/water mixtures [5] was also studied using HTPB-based PUs due to the high swelling behavior of the HTPB soft segment with ethanol.

The crosslinkage of PU polymers is generally obtained by the introduction of diol and triol mixtures to the PU prepolymer [6, 7]. Yoshikawa *et al.* [8] studied the crosslinking of polybutadiene (PB) membranes arising from the chemical reactions with the crosslinking agent bis(1-methyl-1-phenyl-ethyl) peroxide at sites of unsaturation in the polymer chain. Sun *et al.* [9] prepared divinyl benzene (DVB) crosslinked styrene/butadiene/styrene (SBS) and styrene/ethylene–butylene/styrene (SEBS) for alcohol permselective membranes. The permeabilities of the above three types of membranes are all small (1.2,

47.4 and 23.4 g/m².hr, respectively) and they are permselective to alcohol. These membranes are suitable for the separation of dilute alcohol aqueous solutions.

This study attempts to prepare crosslinked HTPB-based PUs by using DVB to crosslink between soft segments of butadiene. The gas permeability property and its relationship with HTPB/H_{12}MDI/1,4-BD compositions and the crosslinking agent content at various temperatures were investigated. The effect of hard segment content and DVB content on the gas separation or water/ethanol mixture were studied. The hydrogen bonding index (HBI), frequency difference and shift, used for the identification of phase segregation and the interpolymer hydrogen bonding behavior, were measured by FTIR. Measurements of glass transition temperature by DSC and the hydrogen bonding index by FTIR were used to identify the degree of crosslinking and hence to correlate this with the permselectivity behavior.

EXPERIMENTAL

Materials

The chemicals used were 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI, Desmodur W of Mobay Co.), hydroxyl-terminated polybutadiene (HTPB, equivalent weight 1333 g, R-45M of Arco Co.), 1,4-butanediol (1,4-BD) as chain extender and dibutyltin dilaurate (DBTDL) as catalyst. Dimethyl formamide (DMF) and toluene were used as solvents for the preparation of a PU solution. Benzoyl

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peroxide (BPO) was used as initiator for the preparation of divinyl benzene (DVB) crosslinked PUs.

Preparation of PU membrane

The two-stage PUs were polymerized first by an -NCO terminated prepolymer and then chain extended with 1,4-BD using 25 wt% solid content after the theoretical -NCO content had been reached. This was diluted to 15–20 wt% solid content after the chain extending reaction had proceeded for 30 min. The reaction was terminated as the -NCO groups were completely consumed, as confirmed by the disappearance of infrared absorption at 2280 cm^{-1}.

Uncrosslinked PU films were prepared by pouring the solution mixture on to a glass plate to a thickness of 600 μm. The solvent in the casting solution was evaporated by degassing at 65°C for 24 hr. The dried PU films were peeled from the plate after it had been immersed in the deionized water for several hours. The PU films were dried in a desiccator and stored at a relative humidity of 50% and 25°C for 5 days before testing.

Crosslinked films were initially prepared by adding 0.5 wt% (based on solid PU content) of BPO to the HTPB-H$_{12}$MDI-1, 4BD-based PU solution (15 wt% solid content) in a closed vessel at room temperature for 30 min. Then 1.0, 2.0, 3.0 and 5.0 wt% of DVB (based on solid PU content) were added to the above PU solution at 65°C for 30 min and the solution then cooled to room temperature immediately. All the following film preparation steps were the same as those for uncrosslinked films.

Infrared spectroscopy

Infrared spectra of PU films were obtained using a Jasco FTIR-310E spectrometer. Spectra were collected at a resolution of 2 cm^{-1}. The peak due to hydrogen bonded C=O stretching is centered at 1700 cm^{-1} and that due to free C=O stretching is centered at about 1717 cm^{-1}. The peak of bonded -NH stretching is at 3320 cm^{-1} and that of free -NH stretching is at 3442 cm^{-1}. Hydrogen bonded carbonyl bands will correspond to those groups that are in the interior of hard segments, while the free bands may correspond to those groups in the hard segment domains or in the soft domains or at the interface [10]. In these butadiene-containing polyurethanes, hydrogen bonding occurs only between urethane segments, since the carbonyl groups in the urethane linkage and the urethane alkoxy oxygen are the only proton acceptors. The extent of the carbonyl absorption group participation in hydrogen bonding is expressed by the hydrogen bonding index (HBI), which is defined as the relative absorbance of the hydrogen bonded carbonyl peak ($A_{C=O,bonded}$) to that of the free hydrogen bonded carbonyl peak ($A_{C=O,free}$) [11]. The frequency difference is defined as $\Delta v = v_f - v_b$, where v_f and v_b are the frequencies of maximum adsorption for the free and hydrogen bonded -NH group, respectively. The frequency difference, Δv, is considered a measure of the strength of the hydrogen bond between molecules [5].

Property measurement

A DuPont 9000 instrument was used for DSC measurements, using liquid nitrogen for cooling and with a heating rate of 10°C/min in the temperature range −120–150°C. The oxygen and nitrogen permeabilities of membranes were determined using the Yanaco GTR-10 gas permeability analyzer. A detailed procedure for measuring the gas permeation was reported previously [12]. A traditional pervaporation apparatus was used in this study [13]. The permeability of the air or water/ethanol mixture was determined by the weight permeated per unit membrane area and time. The unit of gas permeability is expressed in barrer (cm$^2 \times 10^{10}$/sec.cmHg). The separation factor (α_{O_2/N_2}) of air was calculated as P_{O_2}/P_{N_2}, where P_{O_2} and P_{N_2} are the oxygen and nitrogen permeability, respectively. The separation factor of the water/ethanol mixture ($\alpha_{H_2O/EtOH}$)

was calculated as $(Y_{H_2O}/Y_{EtOH})/(X_{H_2O}/X_{EtOH})$, where Y_{H_2O}, Y_{EtOH}, X_{H_2O} and X_{EtOH} are the weight fraction of water and ethanol in the permeate and feed, respectively. The swelling ratio is defined as $(W_1 - W_0) \times 100\%/W_0$, where W_1 is the weight of the wet membranes, which have been dipped in the water/ethanol mixture and blotted with filter paper thoroughly, and W_0 is the weight of the dry membranes.

Crosslinking reaction

The mechanism for formation of DVB crosslinked PUs was as follows. BPO was decomposed first and an active site was produced by capturing the hydrogen atom nearest the double bonds of the HTPB soft segment. This active site reacted with DVB and then with other HTPB chains with or without an active site [8]. The crosslinkage between HTPB soft segments of PUs was formed.

RESULTS AND DISCUSSION

Gas separation of air

Effect of hard segment content. The higher the hard segment content, the lower is the oxygen permeability for all PU membranes, as shown in Fig. 1. Nitrogen permeability decreases with increase of hard segment content. Separation factors are slightly increased with increase of hard segment content. The latter two trends are not shown in the figure. These results for HTPB-based PU membranes are contradictory to those of conventional polyol-based PU membranes reported by Hsieh [14]. This phenomenon indicates that more carbonyl groups in PU membranes are hydrogen bonded with a higher hard segment content. The segregation between the nonpolar HTPB soft segment and hard segment decreases, which is due to fewer polar carbonyl groups being freely dispersed in the soft segment and the enlargement of hard segment aggregation. As is shown in Fig. 2, the HBI values increased with increase of hard segment content. The increase of HBI values indicates that the intermolecular attraction between hard segments increased.

McBride *et al.* [15] reported that an increase in the hard segment content resulted in an increase in activation energy, which may explain the decrease of gas permeability. On the other hand, a restriction of
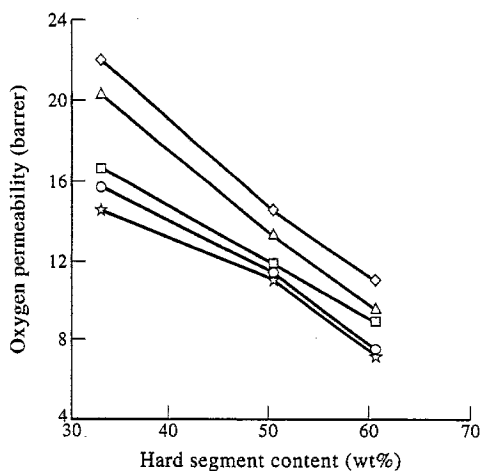

Fig. 1. Effect of hard segment content on the oxygen permeability of PUs with different DVB content (wt%): (○) 0; (□) 1.0; (△) 2.0; (◆) 3.0; (☆) 5.0.
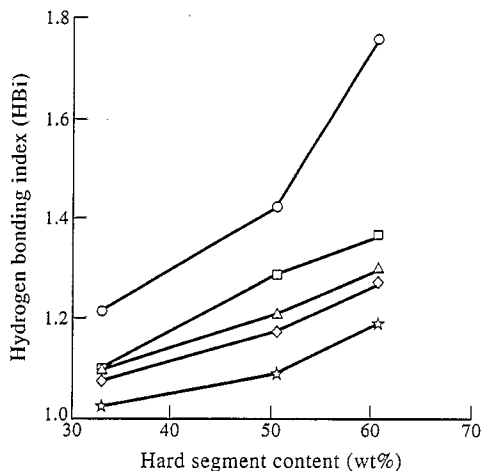
Fig. 2. Relationship between hard segment content and HBI value of PUs with different DVB content (wt%): (○) 0; (□) 1.0; (△) 2.0; (◆) 3.0; (☆) 5.0.
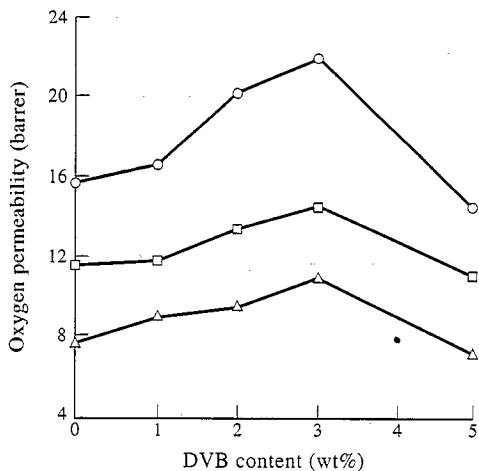

Fig. 4. Effect of DVB content (wt%) on the oxygen permeability of PUs with a different equivalent ratio of HTPB/H₁₂MDI/1,4-BD: (○) 1/4/3; (□) 1/8/7; (△) 1/12/11.

the movement of soft segments could be indicated by the increase of glass transition temperature of the soft segments (T_g values). Figure 3 shows that the T_g values increased as the hard segment content increased. The increase of T_g values indicated the decrease of soft segment mobility. The enlargement of the hard segment domain and the decrease in flexibility of soft segments may explain why the gas permeability decreased as the hard segment content increased.

Effect of DVB content. Maximum oxygen permeabilities were obtained for PU compositions of HTPB/H₁₂MDI/1,4-BD = 1/4/3, 1/8/7 and 1/12/11 with about 3 wt% of DVB content, as shown in Fig. 4. The addition of DVB might cause crosslinkage between soft segments and introduce benzene groups in the soft segment packing area. Crosslinkage usually results in a decrease in membrane permeability; however, this was not the case in this particular membrane. From the HBI measurements,

as shown in Fig. 2, we found that the HBI value decreased as DVB content increased. This indicates that the crosslinkage between soft segments hindered hydrogen bonding among hard segments, which might be the reason why the permeability increased after a suitable amount of DVB had been introduced. But when the DVB content was high enough, the mobility of soft segments was largely restricted and hence the decrease of oxygen permeability of PU membranes with higher DVB content. The DSC studies, as shown in Fig. 3, revealed that the glass transition temperatures of soft segments increased as the DVB content increased. This might explain why the separation factors (not shown in the figure) did not fall with the elevation of gas permeability.

Temperature effect. Figures 5–7 show that gas permeabilities all increased with increasing temperature. The gas permeabilities of membranes with a suitable amount of DVB were higher than those of uncrosslinked ones. The gas permeabilities of membranes with a high enough DVB content are lower than those of uncrosslinked ones. The separation factors of uncrosslinked membranes remain nearly constant or slightly increase for any composition compared with uncrosslinked membranes. Nitrogen permeability also increases with a suitable amount of crosslinking agent.

The domain structure in segmented urethanes is an unstable morphology with respect to temperature [16]. The degree of domain formation of uncrosslinked PUs apparently decreases upon heating and the domain structure was suggested to reform upon cooling. For the crosslinked PUs, the addition of DVB might cause crosslinkage between HTPB soft segments and introduce benzene groups in the soft segment packing area. Crosslinkage restricts the mobility of the HTPB soft segment. On the other hand, these molecular chains of the soft segment will be more extended and the interchain spacing increases as the temperature increases. There is competition between these two effects and the latter has the greater impact on gas permeability. This may
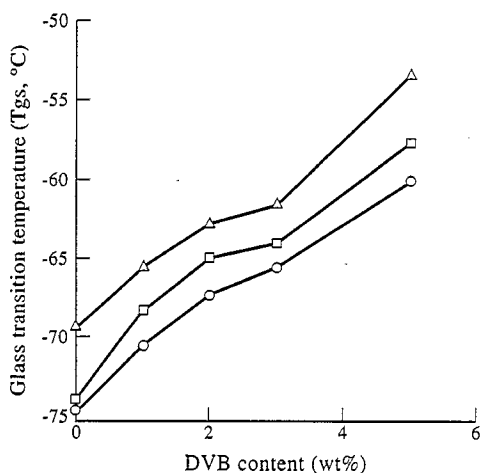

Fig. 3. Effect of DVB content on the glass transition temperature of soft segment of PUs with different composition: (○) 1/4/3; (□) 1/8/7; (△) 1/12/11.
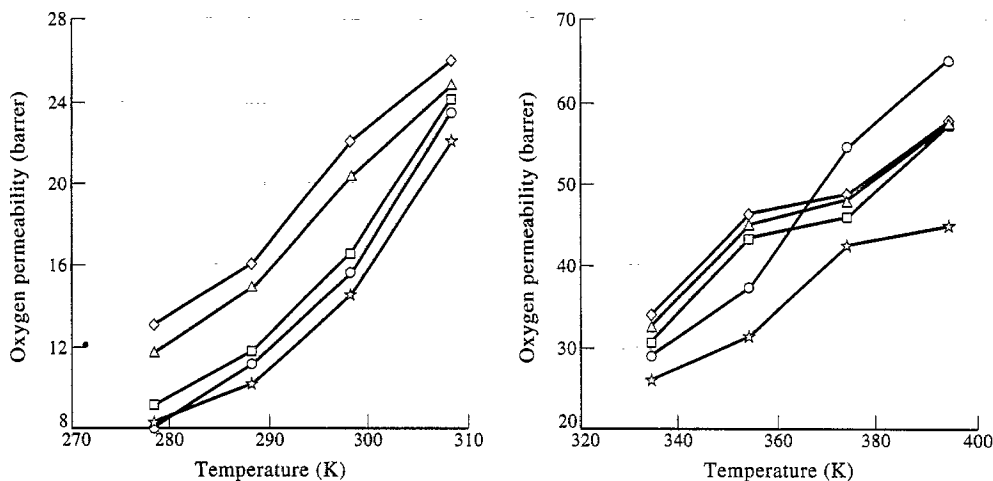
Fig. 5. Effect of operation temperature on the oxygen permeability of $HTPB/H_{12}MDI/1,4-BD = 1/4/3$
with different DVB content (wt%): (○) 0; (□) 1.0; (△) 2.0; (◆) 3.0; (☆) 5.0.

explain why the gas permeabilities increase as the temperature increases.

At higher temperature the interchain spacing of crosslinked PUs with higher DVB content is lower than that of uncrosslinked PUs or those with lower DVB content. PUs with higher DVB content possess a more rigid benzene ring structure in the soft segment and are more stable. This might explain why at higher temperature the gas permeabilities of membranes with the same composition decrease as the DVB content increases. On the other hand, the gas permeabilities of membranes with a high hard segment content were observed to be slightly higher than those of uncrosslinked membranes at a lower operating temperature. This may be due to a higher hard segment content and hydrogen bonding of the hard segment. Higher gas permeabilities of membranes with a lower hard segment content were obtained in the range 278–308 K. From this study, it is suggested that the crosslinking effect on the gas permeabilities of membranes decreases as the hard segment content increases.

Pervaporation separation of water/ethanol mixture

Effect of hard segment content and crosslinkage. The membranes used in this pervaporation study were dipped in the 90 wt% ethanol content water/ethanol mixture for 1 day, except uncrosslinked membranes which were dipped for 1 hr only due to their instability in this water/ethanol mixture. Figures 8 and 9 show that the permeabilities and the separation factors increase as the hard segment content increases. Earlier literature [17, 18] reported that the increase in hard segment content of PU elastomers induces an increase of sorption effect, predominantly changing the permeability for the water/ethanol mixture. The swelling behavior of the HTPB soft segment decreases as the hard segment content increases.

The infrared study of bonded -NH group frequency of these crosslinked PU (CPU) membranes shows a shift to lower frequency when dipped in ethanol or water solvent, which means the interaction of -NH groups with ethanol and water molecules. The infrared spectra indicate that the
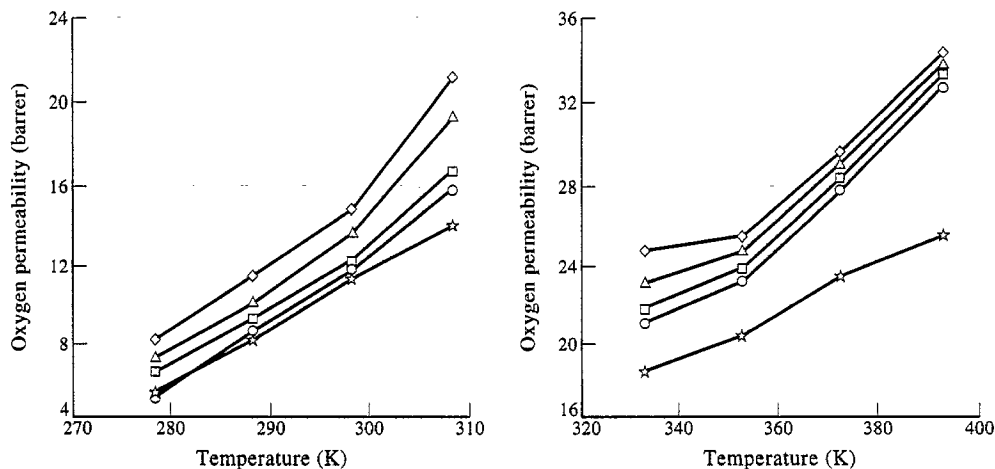

Fig. 6. Effect of operation temperature on the oxygen permeability of $HTPB/H_{12}MDI/1,4-BD = 1/8/7$
with different DVB content (wt%): (○) 0; (□) 1.0; (△) 2.0; (◆) 3.0; (☆) 5.0.

Fig. 7. Effect of operation temperature on the oxygen permeability of HTPB/H₁₂MDI/1,4-BD = 1/12/11 with different DVB content (wt%): (○) 0; (□) 1.0; (△) 2.0; (◆) 3.0; (☆) 5.0.
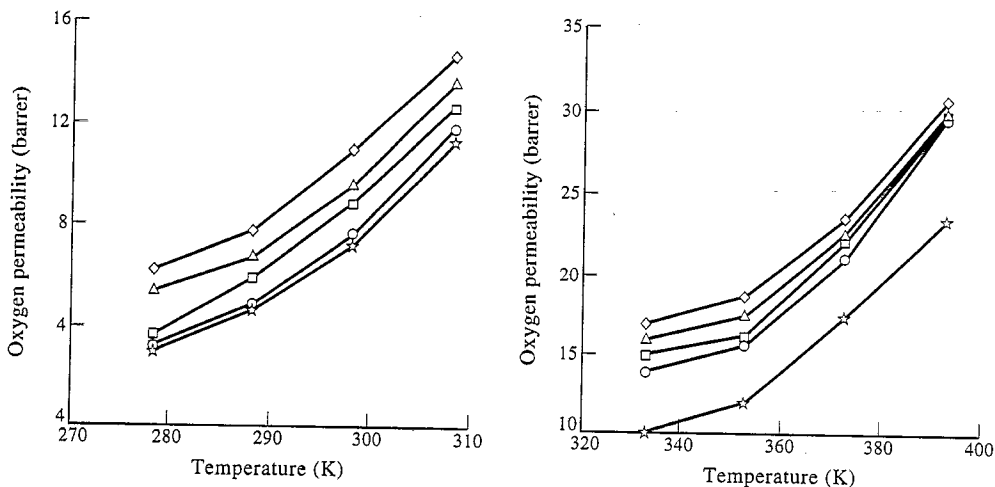
increase in interaction between water (or ethanol solvent) and C=O (or -NH groups) of these CPU membranes is evidenced by the increase of absorbance intensity of bonded C=O (or -NH groups) relative to free C=O (or -NH groups), which is defined as the HBI value. The frequency difference between the -NH groups and solvents (or C=O groups) of these dry and wet CPU membranes varies in the order: CPU11211>CPU187>CPU143, which shows that the sorption ability has a preferential effect on the increase of PU elastomer with increase of hard segment content.

Coleman and co-workers [19] have used the frequency difference between free hydroxyl groups and hydrogen bonded hydroxyl groups as a measure of the average strength of the intermolecular interactions. The hydrogen bond strength of these CPU membranes varies in the order: dipped in the ethanol>dipped in water>not solvent treated, which indicates that the sorption of ethanol is higher than that of water. When the membranes are immersed in the water/ethanol mixture, the ethanol molecules absorbed in the membranes are selectively absorbed upon the polymer chain of the HTPB soft segment. The polymer interacts with the hydrophobic moiety of the ethanol and the -OH groups remain exposed on the surface. This hydrophilization of the somewhat hydrophobic membrane by the ethanol is probably responsible for the selectivity for water [20]. In addition, the water molecules are smaller than those of ethanol and the degree of swelling is lower in the high hard segment content PU polymer (HTPB and DVB are the ethanol swelling components). From the above studies, the separation factors of these membranes slightly increase as the hard segment content increases. From the above explanations, HBI value, frequency difference and shift can be used to see the effect of hard segment content on the sorption phenomenon, which is superior to the increase of permeability of these PU membranes.

Effect of DVB content. The effect of the amount of DVB included in the membrane of equivalent ratio of HTPB/H₁₂MDI/1,4-BD = 1/12/11 on the pervaporation performance of a 90 wt% ethanol content
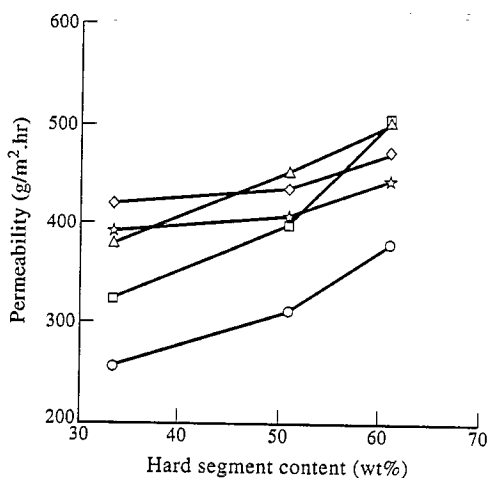

Fig. 8. Effect of hard segment content on the permeability of water/ethanol mixture of PUs with different DVB content (wt%): (○) 0; (□) 1.0; (△) 2.0; (◆) 3.0; (☆) 5.0.
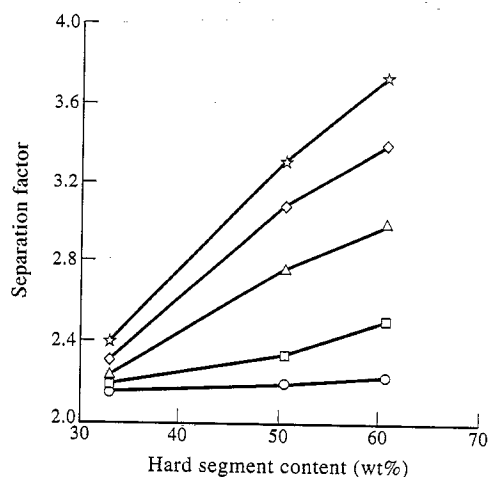
Fig. 9. Effect of hard segment content on the separation factor of water/ethanol mixture of PUs with different DVB content (wt%): (○) 0; (□) 1.0; (△) 2.0; (◆) 3.0; (☆) 5.0.
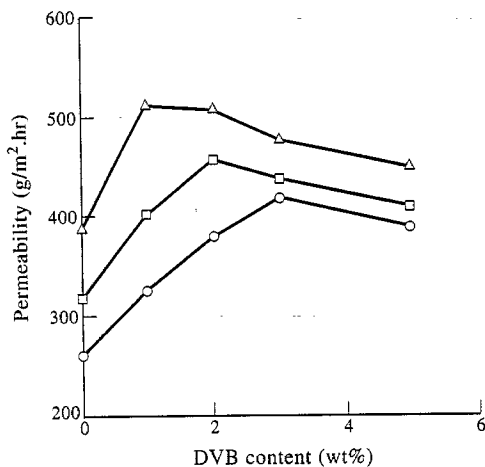
Fig. 10. Effect of DVB content (wt%) on the permeability of water/ethanol mixture of PUs with a different equivalent ratio of HTPB/H₁₂MDI/1,4-BD: (○) 1/4/3; (□) 1/8/7; (△) 1/12/11.

Fig. 12. Swelling ratio of HTPB/H₁₂MDI/1,4-BD = 1/12/11 with different DVB content.
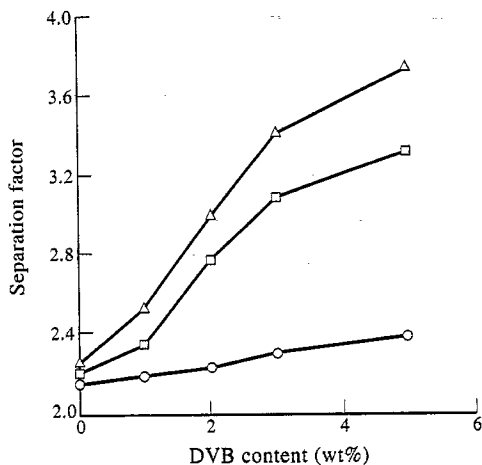

Fig. 11. Effect of DVB content (wt%) on the separation factor of water/ethanol mixture of PUs with a different equivalent ratio of HTPB/H₁₂MDI/1,4-BD: (○) 1/4/3; (□) 1/8/7; (△) 1/12/11.
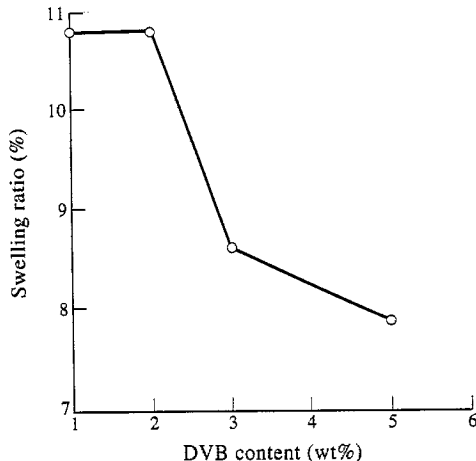
ethanol/water mixture is shown in Figs 10 and 11. The permeability of these membranes increases with increasing amounts of DVB, attaining a maximum and then decreasing as shown in Fig. 10. The separation factors increase as the DVB content increases as shown in Fig. 11.

It was suspected that two effects may be introduced by the addition of DVB. One effect was the enlargement of soft segments, which could be shown by the change in HBI and T_g values, by the rigid benzene structure of DVB. The DSC studies, as shown in Fig. 3, revealed that the glass transition temperature of soft segments increased after DVB addition. From the measurement shown in Fig. 2, we found that the HBI values decreased after DVB was introduced and decreased as the DVB content increased. These results indicate that the crosslinkage between soft segments hindered the hydrogen bonding among hard segments, which might be the reason why the permeability increased after DVB was introduced. But when the DVB content is high enough, there is competition between the above two effects, and rigidity has the greater influence on the permeability and hence a maximum permeability for any PU composition is attained. The maximum swelling ratio occurs with between 1 and 3 wt% of DVB content, which is shown in Fig. 12, and this may explain the maximum permeability of the 1/12/11 equivalent ratio PU membrane with about 1–3 wt% DVB content.

The packing among hard segments of PUs with DVB becomes looser and the polar groups of free hydrogen bonded C=O or -NH induce the increase in sorption effect on the permselectivity of the water/ethanol mixture [17, 18]. On the other hand, modification of the membranes by the inclusion of DVB probably increases the hydrophobicity. The hydrophobic moiety of the ethanol interacts with the soft segment of PUs, and the -OH groups remain exposed on the surface, and have more affinity with the water than with ethanol [20]. This hydrophiliza-tion is probably responsible for the increase of separation factor as the DVB content increases.

Feed concentration. The membrane of HTPB/ H₁₂MDI/1,4BD = 1/12/11-based PUs with 5 wt% DVB content was used for the following study due to its pervaporation separation index (the product of permeability and separation factor) of 1696 g/m².hr, which is the highest among these PUs. Figure 13 shows that the permeability and separation factor increase from a dilute ethanol aqueous solution to a concentrated solution. Swelling experiments carried out with various feed concentrations have shown that the degree of swelling in ethanol is higher than in water. The strong interactions between these membranes of HTPB soft segments and ethanol, shown by the increase in degree of swelling seen in Fig. 14, may be the reason for the increase of permeability as the ethanol content in the feed increases.

When the membranes are immersed in the water/ethanol mixture, the ethanol molecules absorbed in the membrane are selectively adsorbed
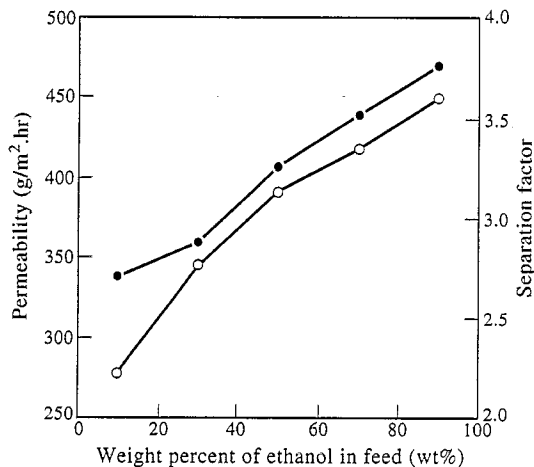
Fig. 13. Effect of feed concentration on the permeability (O) and separation factor (●) of HTPB/H₁₂MDI/1,4-BD = 1/12/11 with 5 wt% DVB content.
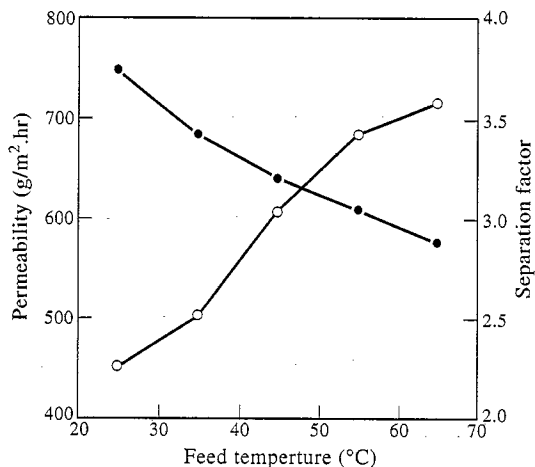

Fig. 15. Effect of feed temperature on the permeability (O) and separation factor (●) of HTPB/H₁₂MDI/1,4-BD = 1/12/11 with 5 wt% DVB content.

upon the polymer chains of the HTPB soft segment. The polymer interacts with the hydrophobic moiety of the ethanol, and the -OH groups remain exposed on the surface. This hydrophilization of the somewhat hydrophibic membrane by the ethanol is probably responsible for the selectivity for water [20]. In this study, the addition of DVB into the PU polymer for the increase of hydrophilization with ethanol induces a slight increase in the separation factor of these membranes.

Feed temperature. For the HTPB/H₁₂MDI/1,4BD = 1/12/11-based PUs with 5 wt% DVB content, the permeabilities increase and the separation factors decrease with increase of feed temperature, as shown in Fig. 15. These results are due to the fact that a higher temperature, causing an increase in chain mobility and swelling of the membrane matrix and hydrogen bond decay, induces an increase in permeability of DVB crosslinked PU membranes. A

slight change in permeability and separation factor occurred for a higher feed temperature. This may be due to the introduction of the rigid benzene structure, which is stable at high temperatures.

CONCLUSION

HTPB-based PUs crosslinked with a suitable amount of DVB provide higher gas and water/ethanol mixture permeability than uncrosslinked membranes. A membrane with a higher hard segment content has lower gas permeability, while possessing higher water/ethanol mixture permeability. All the above results can be explained by the flexibility of soft segments and aggregation of hard segments. The degree of crosslinking can be determined by the change of glass transition temperature and infrared spectra. HBI values increased with the increase of hard segment content, while they decreased after DVB was introduced. This indicates that the crosslinkage between soft segments hinders the hydrogen bonding among hard segments. Higher HBI values represent increased participation of carbonyl groups in hydrogen bonding and the lower degree of segregation between hard and soft segments. HBI value, frequency difference and shift of hydrogen bonded -NH groups can be used to explain the sorption phenomena and interpolymer hydrogen bonds with different DVB contents. The results of FTIR and DSC measurements show the effect of DVB content on crosslinking degree and hence the gas and water/ethanol mixture permeability.

Fig. 14. Effect of feed concentration on the swelling ratio of HTPB/H₁₂MDI/1,4-BD = 1/12/11 with 5 wt% DVB content.

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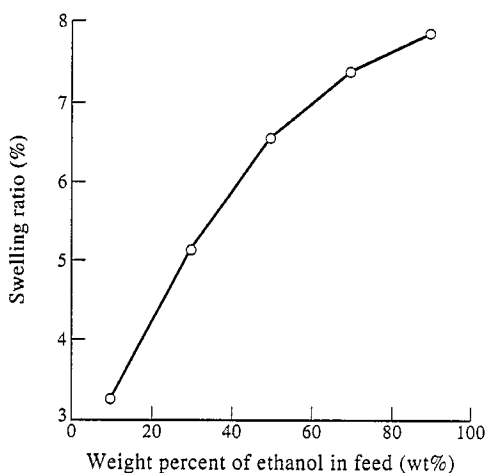3. Huang, S. L. and Lai, J. Y., *J. Appl. Polym. Sci.*, 1995, **58**, 1913.

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