Separation of Aqueous Phenol through Polyurethane Membranes by Pervaporation. II. Influence of Diisocyanate and Diol Compounds and Crosslinker

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ABSTRACT: The influence of diisocyanate and diol compounds of polyurethane and crosslinking agent on the separation of phenol aqueous solution by pervaporation was investigated. Polyurethanes were prepared by polyaddition of diisocyanate and diol compounds and trimethylolpropane (TMP) using dibutyltindilaulate as a catalyst. The polyurethane membrane was prepared by a casting method and was sandwiched with a porous polypropylene membrane (Celgard[®] 2500). Pervaporation measurement was carried out under vacuum on the permeate side, and the permeant was collected with a liquid nitrogen trap. Little influence of diisocvanate compounds on the phenol permselectivity through diisocyanate-polytetramethyleneglycol [PTMG(1000)] membranes was observed since the influence on the solubility and the diffusivity was small. The phenol permselectivity was increased with an increase in the molecular weight of PTMG and polycaprolactone diol (PCL) for the 1,6-diisocyanato hexane (HMDI)-PTMG and HMDI-PCL membranes. It was considered that the increase in phenol diffusivity can be attributed to an increase in phenol selectivity. The permeability and selectivity of HMDI-[PTMG(2900)-TMP] membrane was relatively constant below the 2% TMP content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 439-448, 1999

Key words: pervaporation; polyurethane; phenol; diisocyanate; diol; crosslinker

INTRODUCTION

Membrane separation processes have been studied as an efficient method for liquid mixture separation.¹ Pervaporation, which is one of the membrane separation processes, has been investigated for alcohol dehydration, organic solvent separation from dilute aqueous solution, and recovery of useful aroma compounds.^{2–5} Furthermore, the alcohol dehydration plant has been available for industrial use. $^{\rm 6}$

We have also reported on polyacrylate, polymethacrylate, and polyurethane membranes for organic solvent separation from dilute aqueous solutions by pervaporation.^{7–9}

For the organic solvent separation from dilute aqueous solutions, we have focused on the separation of phenol dilute aqueous solution for the following reason: the phenol is a raw material used for the synthesis of phenolic resin, bisphenol-A, and other chemicals. Because a large quantity of wastewater containing phenol has been produced, its effective disposal is needed.¹⁰

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Polyether-*block*-polyamide (PEBA) membrane as phenol and other organics permselective membrane has been reported by many groups.^{11–14} But PEBA does not dissolve in the usual organic solvent at room temperature, so the membrane cannot be easily prepared by casting and coating of polymer solution; whereas the polyurethane shows high affinity to phenol and can be dissolved in the usual organic solvent by the selection of diisocyanate and diol compounds. Therefore, the homogeneous thin membrane can be easily prepared by casting or coating methods.

We have reported that the polyurethane, which was made from 1,6-diisocyanatohexane (HMDI) and polytetramethyleneglycol (PTMG), could be easily prepared for a composite membrane with a porous support membrane by the coating method, and it showed high phenol permselectivity.⁹

For the pervaporation separation with polyurethane membrane, the influence of diisocyanate and diol compounds has been reported.

H. Ohst et al.¹⁵ summarized the correlation between polymer parameter and membrane performance for the separation of a toluene-cyclohexane mixture. The amount of hard segment (consists from diisocyanate and chain extender) affected the flux, and there was no influence of chemical composition and crosslinking density of the hard segment on the flux. These parameters had no influence on the selectivity. The chemical composition, amount, crosslinking density, and glass transition temperature of the soft segment (consists from polyester and polyether diol) affected the flux. The influence of chemical composition and glass transition temperature of the soft segment on the selectivity was observed, and that of the other parameter was slight.

M. M. Cipriano et al.¹⁶ reported on the separation of ethanol-water mixture through polyurethane polymerized prepolymer, which was tolylene-2,4-diisocyanate-terminated polyethyleneglycol or polypropyleneglycol. The flux was increased with increasing molecular weight of the prepolymer, and there was no influence on the selectivity.

Consequently, it is presumed that the same influence exists in our work. In this study, the following investigations were carried out:

- 1. The influence of diisocyanate structure in diisocyanate-PTMG(1000) membranes;
- 2. The influence of PTMG molecular weight and polycaprolactone diol (PCL) molecular

weight in HMDI–PTMG and HMDI–PCL membranes; and

3. The influence of crosslinker.

EXPERIMENTAL

Synthesis of Polyurethane

Into a 500-cm³ flask equipped with a stirring motor and a reflux condenser with a CaCl₂ drying tube, diol compound, dibutyltindilaurate (DBTDL) as a catalyst, and ethylacetate were placed in an oil bath at 70°C under dry nitrogen atmosphere and stirred. After 1 h, diisocyanate compound was added, and the mixture was stirred 8 h at the same temperature. When the viscosity of the solution became high and did not stir enough, the solution was diluted with ethylacetate. After 8 h, 1-propanol was added and stirred for 15 min in order to react the residual isocyanate group and to stop the polyaddition reaction. Thus, polyurethane was obtained. The trimethylolpropane (TMP) as a crosslinker was added into the diol, catalyst, and ethylacetate mixture, and the polyaddition reaction was carried out in the same way as previously mentioned in preparing the crosslinked polyurethane. The TMP content (the ratio of hydroxy group of TMP to total hydroxy group) was 1, 2, and 3%.

The molecular weight of polyurethane was measured by size exclusion chromatography (SEC; standard, polystyrene), and the remnant isocyanate was confirmed by a Fourier transform infrared (FTIR) spectrometer.

In this study, HMDI, isophoronediisocyanate (IPDI), tolylene-2,4-diisocyanate (TDI), 4,4'- methylenebis (phenyl isocyanate) (MDI), and 4,4'- methylenebis (cyclohexyl isocyanate) (H₁₂MDI) as diisocyanate compounds, and PTMG (molecular weights, 650, 1000, 2000, and 2900) and PCL (molecular weights, 530, 1000, 3000, and 4000) as diol compounds were used.

The diol compounds were made by vacuum drying for 1 day. Other reagents were used without further purification.

For example, the polyurethane, which was made from HMDI, PTMG(2900), and TMP (content 1%), is represented as HMDI-[PTMG(2900)-TMP(99:1)].

Membrane Preparation

The membrane was prepared in the same way as in the previous work. $^{7-9}$



Figure 1 Pervaporation apparatus: (1) stirring motor, (2) pervaporation cell, (3) constant temperature water bath, (4) glass cock, (5) cold trap for collecting sample, (6) ball joint, (7) vacuum gauge, (8) cold trap, and (9) vacuum pump.

The ethylacetate solution containing 20–30 wt % polyurethane was coated on an exfoliatetreated polyethyleneterephthalate (PET) film and then dried at 100°C for 5 min. The polyurethane membrane was laminated with a porous polypropylene sheet, Celgard[®] 2500, and the PET film was displaced with Celgard[®]. Thus, a sandwiched-type composite membrane was prepared. The membrane thickness was from 60 to 90 μ m.

Pervaporation Measurement

A schematic diagram of the pervaporation measurement apparatus is shown in Figure 1. A permeation cell was assembled from two half-cells of stainless steel and fastened together by bolted clamps. A Viton[®] *o*-ring was used between the pervaporation cell's upper compartment and the membrane. The membrane was supported on a sintered stainless-steel plate with holes, and the effective membrane area was 14.55 cm². The feed liquid (1000 cm³) was circulated using a microtube pump. The downstream pressure was kept below 0.1 mm Hg, and the upstream pressure was maintained at atmospheric pressure. The permeate vapor was collected in a cold trap surrounded by liquid nitrogen.

The experimental procedure was as follows. The pervaporation cell, after setting the membrane, was placed in the constant temperature water bath maintained at 60°C. The downstream side of the membrane was under vacuum, and the feed liquid was circulated. After reaching a steady-state condition, the permeate vapor was collected. The phenol concentration in the feed liquid was measured by gas chromatographic analysis at the start and the end of the pervaporation measurement. The concentration of phenol and water in the permeate liquid and the flux were determined by gas chromatographic analysis and by measuring the weight of the collecting sample, respectively. The concentration of the phenol in the permeate liquid was high so that the permeant separated into two phases. The gas chromatographic analysis was then carried out by adding ethanol to make a uniform solution.

For each condition, the previous pervaporation measurement was conducted three times, and it was confirmed that the flux and the concentration of phenol and water in the permeate liquid were constant. The flux was calculated from the following equation:

Flux (g m⁻² hr⁻¹) =
$$\frac{Q}{A \cdot t}$$
 (1)

The separation factor of permeation, α_P , was expressed as follows:

$$\alpha_{P(\text{phenol/water})} = \frac{C_{\text{phenol}}^2 / C_{\text{water}}^2}{C_{\text{phenol}}^1 / C_{\text{water}}^1}$$
(2)

Sorption and Degree of Swelling Measurement

The polyurethane membrane without a porous substrate was prepared by the same method as the pervaporation membrane. The polyurethane membrane piece, whose weight was previously measured, was immersed in the aqueous phenol solution for 48 h at 60°C. The solution on the membrane surface was wiped off, and the weight of the membrane was measured. The polyurethane piece was sandwiched with polyethyleneterephthalate mesh sheet for the swelling mea-



Figure 2 Desorption apparatus: (1) glass vessel, (2) swollen membrane piece, (3) cold trap for collecting sample, and (4) temperature controlled heater.

Table I Molecular Weight of Polyurethane

Polymer	$\begin{array}{c} M_n \\ (\times \ 10^4) \end{array}$	$M_w \ (imes 10^4)$
HMDI–PTMG(650)	1.67	2.93
HMDI–PTMG(1000)	1.83	3.01
HMDI-PTMG(2000)	3.68	6.82
HMDI-PTMG(2900)	6.36	13.8
TDI-PTMG(1000)	1.83	3.79
IPDI-PTMG(1000)	4.64	9.57
MDI-PTMG(1000)	3.91	8.25
H ₁₂ MDI–PTMG(1000)	1.85	3.51
TDI-PTMG(2900)	5.21	11.2
IPDI-PTMG(2900)	3.38	6.26
MDI-PTMG(2900)	3.77	7.53
$H_{12}MDI-PTMG(2900)$	4.24	8.15
HMDI–[PTMG(2900)–TMP(99 : 1)]	11.7	38.2
HMDI-[PTMG(2900)-TMP(98:2)]	9.73	27.6
HMDI-[PTMG(2900)-TMP(97:3)]	11.2	42.5
HMDI-PCL(530)	4.01	8.36
HMDI-PCL(1000)	1.91	4.37
HMDI-PCL(3000)	5.10	10.6
HMDI-PCL(4000)	5.77	12.3

surement because of an adhesiveness of the polyurethane.

The degree of swelling was calculated as follows:

Degree of swelling (%) =
$$\frac{W_W - W_D}{W_D} \times 100$$
 (3)

The concentration of the absorbate was measured with the apparatus shown in Figure 2.

After weighing the swollen membrane for the degree of swelling measurement, the membrane piece was frozen in a glass vessel with liquid nitrogen. The glass vessel and a cold trap were under vacuum, and then the glass vessel was heated after removing the liquid nitrogen. The absorbate was vaporized and collected in the cold trap with liquid nitrogen. The pressure of the glass apparatus was made atmospheric by opening a leak cock attached to a calcium dichloride drying tube. The concentration of phenol and water was determined by measuring the collected liquid in the same way as for the pervaporation.

The separation factor of partition, α_K , was expressed as follows:

$$\alpha_{K(\text{phenol/water})} = \frac{K_{\text{phenol}}}{K_{\text{water}}} = \frac{C_{\text{phenol}}^3 / C_{\text{phenol}}^1}{C_{\text{water}}^3 / C_{\text{water}}^1} \qquad (4)$$

RESULTS AND DISCUSSION

Synthesis of Polyurethane

The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) for the synthesized polyurethanes are summarized in Table I. The degree of polyaddition of each polyurethane was enough to prepare the membrane.

The FTIR spectra of HMDI–PTMG(2900), HMDI, and PTMG(2900) are shown in Figure 3.

The strong absorption in the $2260-2280 \text{ cm}^{-1}$ region (asymmetric —N=C=O stretch) of HMDI disappeared. The peak of C=O stretch or Amide I (near 1720 cm⁻¹), which was not observed on HMDI and PTMG(2900), was observed.¹⁷ The same change in the peaks was observed on the other polyurethanes. Thus, it is concluded that the polyaddition reaction progressed sufficiently.



Figure 3 FTIR spectrum of HMDI–PTMG(2900), PTMG(2900), and HMDI.

	Pervaporation			Sorption			
Membrane	Phenol in permeate (wt %)	$\begin{array}{c} Flux \\ (g \ m^{-2} \ h^{-1}) \end{array}$	α_P	Thickness (µm)	Phenol in Membrane (wt %)	Degree of Swelling (%)	α_K
HMDI-PTMG(1000)	22.8	121.0	29.6	89.1	71.1	43.3	243
TDI-PTMG(1000)	20.9	137.9	30.8	85.1	79.9	49.6	393
MDI-PTMG(1000)	23.8	146.2	33.2	80.6	82.1	51.9	455
IPDI-PTMG(1000)	21.3	121.5	26.7	81.7	74.7	45.3	292
$\rm H_{12}MDI{-}PTMG(1000)$	25.2	115.3	26.2	83.3	77.0	40.4	331

Table II Influence of Diisocyanate on the Pervaporation and Sorption at 60°C

Diisocyanate Compounds

The influence of diisocyanate compound structure on the separation and sorption of phenol aqueous solution is summarized in Table II.

There was little influence on the pervaporation and sorption measurement results. The flux of TDI-PTMG(1000) and MDI-PTMG(1000) membranes was greater than that of the other membranes. The concentration of phenol in the membrane and the degree of swelling for these membranes are also greater.

The apparent mean diffusion coefficient (diffusion coefficient), which was calculated from the results of the pervaporation and the sorption measurement using equations (5), (6), and (7), is listed in Table III.⁹

$$J_i = \frac{P_i}{l} C_i^1 \tag{5}$$

$$P_i = D_i \cdot K_i \tag{6}$$

$$K_i = \frac{C_i^3}{C_i^1} \tag{7}$$

The diffusion coefficient of phenol $(D_{\rm phenol})$ for the HMDI–PTMG(1000), TDI–PTMG(1000), and MDI–PTMG(1000) membranes was greater than that of IPDI–PTMG(1000) and H₁₂MDI–PTMG-(1000) membranes, and that of water $(D_{\rm water})$ for the TDI–PTMG(1000) and MDI–PTMG(1000) membranes was greater than the other membranes.

The flexibility of the molecular chain increased with the increase in degree of swelling.^{18,19} The degree of swelling for TDI–PTMG(1000) and MDI–PTMG(1000) membranes was greater than the others. Therefore, it is considered that the $D_{\rm phenol}$ and $D_{\rm water}$ of the TDI–PTMG(1000) and MDI–PTMG(1000) membranes were greater than the other membranes. Therefore, the flux of the TDI–PTMG(1000) and MDI–PTMG(1000) membrane should be higher due to an increase in the diffusivity of these membranes.

PTMG Molecular Weight

The effect of PTMG molecular weight on the phenol aqueous solution separation for HMDI–PTMG membranes is shown in Figure 4.

The phenol concentration in the permeate solution increased from 22.2 to 33.1 wt %, and the

Table III Influence of Diisocyanate on the Apparent Mean Diffusion Coefficient at $60^{\circ}C$

Membrane	$D_{ m Phenol} \ (imes \ 10^{13} \ { m m}^2 \ { m s}^{-1})$	$D_{ m Water} \ (imes \ 10^{13} \ { m m}^2 \ { m s}^{-1})$
HMDI–PTMG(1000)	9.71	80.0
TDI-PTMG(1000)	9.79	124
MDI-PTMG(1000)	9.88	137
IPDI-PTMG(1000)	7.76	85.8
$H_{12}MDI-PTMG(1000)$	7.30	91.7



Figure 4 Effect of PTMG molecular weight on the separation of phenol through HMDI-PTMG membranes at 60°C, with 1 wt % phenol aqueous solution.

flux also increased from 113 to 206 g m⁻² h⁻¹ with increasing PTMG molecular weight.

The results of the sorption measurement and the swelling measurement are plotted in Figure 5.

The degree of swelling increased, and the phenol concentration in the membrane slightly decreased with an increase in the PTMG molecular weight.

The urethane group, which generates the hydrogen bond, in unit length of the polymer chain decreased with increasing PTMG chain length. It is thought that the degree of swelling increased because the polymer chain became more flexible with a decrease in the hydrogen bond between the urethane groups. Because the uptake of water, whose affinity to the membrane was low, was increased with an increasing degree of swelling, the phenol concentration in the membrane should decrease slightly.



Figure 5 Effect of PTMG molecular weight on the sorption and swelling for HMDI–PTMG membranes at 60° C, with 1 wt % phenol aqueous solution.

Figure 6 shows the effect of the PTMG molecular weight on the diffusion coefficient, which was calculated using equations (5), (6), and (7).⁹

The diffusion coefficient of phenol increased from 7.89×10^{-13} to 2.51×10^{-12} m² s⁻¹, and that of water was relatively constant. The flexibility of the polymer chain was increased with increasing the degree of swelling.^{18,19} It seems that the increase in the flexibility of polymer



Figure 6 Molecular weight of PTMG dependence on the apparent mean diffusion coefficient for HMDI– PTMG membranes at 60°C, with 1 wt % phenol aqueous solution.



Figure 7 Effect of PCL molecular weight on the separation of phenol through HMDI-PCL membranes at

60°C, with 1 wt % phenol aqueous solution.

chain contributes to the decrease in the diffusion resistance of the permeant. Therefore, the diffusivity of phenol should be increased due to the decrease in the diffusion resistance. For water, the molecular size is smaller than that of phenol. The decrease in the diffusion resistance due to an increase in the flexibility should be little affected. Consequently, it is considered that the change in D_{water} was very small. The increase in the phenol selectivity and flux with increasing PTMG molecular weight should be attributed to increase in the phenol diffusivity.

PCL Molecular Weight

The effect of PCL molecular weight on the phenol aqueous solution separation through HMDI–PCL membranes is shown in Figure 7.



Figure 8 Effect of PCL molecular weight on the sorption and swelling for HMDI–PCL membranes at 60°C, with 1 wt % phenol aqueous solution.

The phenol concentration in the permeate liquid was increased from 10.4 to 23.6 wt % with an increasing PCL molecular weight. The phenol partial flux was also increased to about three times, and the increase in the total flux was mainly that of the phenol partial flux. Whereas the influence of the PCL molecular weight on the water partial flux was slight.

Figure 8 shows the influence of PCL molecular weight on the sorption and degree of swelling for the HMDI–PCL membranes.



Figure 9 Molecular weight of PCL dependence on the apparent mean diffusion coefficient for HMDI–PCL membranes at 60°C, with 1 wt % phenol aqueous solution.



Figure 10 Influence of TMP content on the separation of phenol through HMDI–[PTMG(2900)–TMP] membranes at 60°C, with 1 wt % phenol aqueous solution.

The phenol concentration in the membrane was decreased from 46.5 to 41.9 wt %, and the degree of swelling was increased from 59.2 to 73.0% with increasing PCL molecular weight.

The apparent mean diffusion coefficient of each component, which was calculated using equations (5), (6), and (7), is shown in Figure 9.⁹

The influence of the PCL molecular weight on $D_{\rm water}$ was very slight, whereas the value of $D_{\rm phenol}$ was remarkably increased from 6.17×10^{-13} to 2.12×10^{-12} m² s⁻¹ with an increase in the PCL molecular weight. It seems that the influence of PCL molecular weight on the diffusion coefficient and membrane performance was similar to that of PTMG molecular weight. The hydrophilicity of the ester group is greater than that of the ether group. It seems that the affinity of PCL to water is

also greater than that of PTMG. Therefore, the difference in the membrane performance between the HMDI–PTMG membrane and HMDI–PCL membrane should be attributed to the difference in the hydrophilicity between PTMG and PCL.

Crosslinking Agent

The influence of crosslinking agent (TMP) content on the separation of the phenol-water mixture is shown in Figure 10.

The selectivity of phenol was maintained at less than 2% of TMP content and decreased for 3% TMP content in the membrane. The total flux was slightly decreased with an increase in the TMP content. The decrease in total flux was mainly due to a decrease in the phenol partial flux.

The results of sorption and degree of swelling measurement are shown in Figure 11. The concentration of phenol in the membrane was increased from 60 to 71 wt %, and the degree of swelling was decreased from 86 to 52% with an increasing TMP content in the membrane.

It seems that the swelling of the membrane was inhibited by decreasing the flexibility of the molecular chain with an increase in the crosslinking density. The distance between polymer chains became narrow with a decrease in the degree of swelling so that the interaction between the water molecule, whose affinity to the membrane is slight, and the polymer chain should become large. Therefore, it is thought that the uptake of water into the membrane was depressed by a decrease in the degree of swelling.



Figure 11 Influence of TMP content on the sorption and swelling for HMDI-[PTMG(2900)-TMP] membranes at 60°C, with 1 wt % phenol aqueous solution.



Figure 12 TMP content dependence on the apparent mean diffusion coefficient for HMDI–[PTMG(2900)–TMP] membranes at 60°C, with 1 wt % phenol aqueous solution.

Figure 12 shows the influence of TMP content on the $D_{\rm phenol}$ and $D_{\rm water}$. The $D_{\rm water}$ was relatively constant, whereas the $D_{\rm phenol}$ was decreased from 2.51×10^{-12} to $1.28\times10^{-12}~{\rm m}^2~{\rm s}^{-1}$ with an increase in the TMP content of the membrane. The flexibility of the polymer chain was decreased with an increase in the TMP content of the membrane (that is, an increase in the crosslinking density). Consequently, the intermolecular space should become small; this is supported by the results of the degree of swelling measurement. Comparing the molecule size of phenol with that of water, the former is larger than the latter. The diffusion of phenol should be more effective by decreasing the distance between the polymer chains. On the other hand, there was little influence on the diffusivity of the water molecule by the narrowness of the distance between the polymer chains over the range studied. Though the concentration of phenol in the membrane was increased, the diffusivity of phenol was decreased. Consequently, it is considered that the phenol selectivity and phenol partial flux decreased with increasing TMP content.

CONCLUSIONS

The separation of phenol dilute aqueous solution was studied using the polyurethane membranes, which were prepared by polyaddition of various diisocyanates, diol compounds, and crosslinker. These membranes showed phenol permselectivity.

For the various diisocyanate compounds– PTMG(1000) membrane, the influence of the diisocyanate structure on the phenol permselectivity was small due to the slight influence on the diffusivity and the solubility.

The phenol permselectivity was increased with increasing the PTMG and PCL molecular weight for HMDI–PTMG and HMDI–PCL membranes. This should be attributed to an increase in the phenol diffusivity due to the increase in the flexibility of the polymer chain.

The diffusivity of phenol was decreased, and the concentration of phenol in the HMDI– PTMG(2900) (that is, solubility of phenol) was increased with increasing the TMP content. Therefore, the phenol selectivity and the flux (total and partial) were relatively constant below the 2% TMP content. The phenol permselectivity was decreased in the high-TMP-content region due to an increase in the diffusion resistance of phenol.

NOMENCLATURE

A	effective membrane area	
C	concentration	
$C_{\rm phenol}$	concentration of phenol	
$C_{\rm water}$	concentration of water	
D	diffusion coefficient	
$D_{\rm phenol}$	apparent mean diffusion coeffi-	
*	cient of phenol	
D_{water}	apparent mean diffusion coeffi- cient of water	
J	flux per unit time and per area	
K	partition coefficient	
$K_{ m phenol}$	partition coefficient of phenol	
$K_{ m water}$	partition coefficient of water	
l	membrane thickness	
Р	permeability coefficient	
Q	weight of permeate liquid	
t	measuring time	
W_D	dried membrane weight	
W_W	swollen membrane weight	
α_K	separation factor of partition	
α_P	separation factor	
Subscript i	component i	
Superscript 1	quantities concerning the bulk	
	feed solution	
Superscript 2	quantities concerning the perme- ate side of the membrane	
Superscript 3	quantities concerning the mem-	
	brane interior	

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