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졸-겔법에 의한 화학적 개질 공중합체막의 제조와 물-디옥산 혼합물의 투과증발분리법

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Preparation of Chemically Modified Poly(dimethylsiloxane-co-siloxane) Membranes by Sol-Gel Processes and Applications to Pervaporation of Water-Dioxane Mixtures

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요 약 : 세 종류의 개질 폴리디메틸실록산-실록산 공중합체막을 제조하고 디옥산-물 혼합물의 투과증발분리에 대한 이들 막의 응용성을 검토하였다. 화학적 개질은 투과증발분리 성능에 영향을 미치며 특히 chlorine을 포함하고 있는 작용기들이 디옥산의 선택적 투과성을 향상시킨다는 것을 실험결과로 확인할 수 있었다. 막을 통한 용매의 투과는 막재질과 용매간의 용해도 파라메타 차이로부터 예측될 수 있다.

Abstract : Three kinds of modified poly(dimethylsiloxane-co-siloxane) membranes were prepared and their applicability for pervaporation separation of dioxane-water mixtures was investigated. It was elucidated that the chemical modification affected the pervaporation properties and polymers containing the chlorine groups improve the selective permeability of dioxane. The permeation of solvents through the membrane could be predicted from the solubility parameter difference between the membrane polymer and solvent.

INTRODUCTION

Pervaporation[1] is a promising process in the field of membrane separation and much attention has been paid to find membranes available for separation of each component from close-boiling[2~5] and azeotropic mixtures.[6~9]

In a preceding paper,[9] the preparation of poly (dimethylsiloxane-co-siloxane) membranes (PDMS) by sol-gel processes and their application to the separation of dioxane from its aqueous solutions were reported. When tetramethoxysilane and

dimethyldiethoxysilane are used to react, the sol-gel process gives poly(dimethylsiloxane-co-siloxane), of which the structure of main chains is similar to that of silicone rubber prepared from oligo (dimethylsiloxane) in the usual procedure.[9]

On the other hand, the sol-gel process enables the preparation of a series of polysiloxanes with various substituents using various silane compounds.[10]

In this paper, the preparation of some polysiloxane membranes and their pervaporation behavior for dioxane-water mixtures were studied in order to obtain some informations about the relation of the chemical structure with the pervaporation properties.

EXPERIMENTAL

Materials

Dimethyldiethoxysilane(DMDES), tetramethoxysilane(TMOS), methylphenyl-diethoxysilane (MPDES), 2-chloroethylmethyldimethoxysilane (CEMDMS), 3-aminopropylmethyldiethoxylsilane (APMDES), which are products of Petrarch Systems Inc., were used without further purification. Diethylamine of Wako Co. was purified by distillation before use.

Preparation of Membranes

A mixed solution of DMDES-A-TMOS-C_2H_5OH, where A denotes one of MPDES, CEMDMS and APMDES, was mixed with an HCl- C_2H_5OH-H_2O solution under stirring at room temperature. Preparation conditions were summarized in Table 1.

When the mixed solution became viscous, it was spread onto a poly (tetrafluoroethylene) membrane filter (Toyo Roshi Co. Ltd., 25 mm in diameter, 65 μm in thickness, 0.2 μm in average pore size) on a glass plate. The membrane filter was fixed by a glass tube (24 mm in inner diameter, and 15 mm in height) in order to prevent for the solution from spreading over outside the membrane. In a few days the solution reacted to form a gel on the membrane filter and then the membrane was stripped off from the glass plate. The membrane was immersed in a large amount of ethanol for 1 day to get rid of unreacted compounds completely and then kept under a reduced pressure for 1 day at 110℃. The membranes thus prepared are flexible and rubber-like.

Pervaporation

Pervaporation experiments were carried out using the same glass cell in the same manner as described in the preceding paper.[9] All experiments were carried out at 30℃, and the permeates through the membranes were collected in a trap cooled by liquid nitrogen. The compositions and the permeation rates of the permeates were determined by measuring their refractive indices and weights.

RESULTS AND DISCUSSION

Preparations of Membranes

The solidification rate of the membranes varies

Table 1. Preperation Conditions of Modified poly(dimethylsiloxane-co-siloxane) Membranes

Membrane CODE	A	DMDES/A/TMOS (molar ratio)	DMDES (g)	A (g)	TMOS (g)	H_2O (g)	HCl (g)	C_2H_5OH (g)
CEMDMS 1	CEMDMS	9/1/1	5.4	0.68	0.62	0.36	0.36	0.20
CEMDMS 2		8/2/1	4.8	1.37	0.62	0.36	0.36	0.20
MPDES 1	MPDES	9/1/1	5.4	0.85	0.62	0.36	0.36	0.20
APMDES 1	APMDES	9/1/1	5.4	0.77	0.62	0.36	0.36	0.20
APMDES 2		8/2/1	4.8	1.55	0.62	0.36	0.36	0.20

CEMDMS : 2-Chloroethylmethyldimethoxysilane, MPDES : Methylphenyldiethoxysilane,
APMDES : 3-Aminopropylmethyldiethoxysilane, DMDES : Dimethyldiethoxysilane,
TMOS : Tetramethoxysilane.

largely depending on the kind of silane compounds. APMDES and CEMDMS are ready to react and their membranes are obtainable with ease. On the other hand, MPDES reacts slowly so that it takes a prolonged time for preparation of membranes. We could not prepare the membrane of DMDES/MPDES/TMOS=8/2/1.

Pervaporation of Water-Dioxane Mixtures

Figs. 1 and 2 show the separation of water-dioxane mixtures through the CEMDMS and MPDES membranes. CEMDMS1 and CEMDMS2 membranes were prepared from the sol solutions with the composition DMDES/CEMDMS/TMOS= 9/1/1 and 8/2/1, respectively. The dioxane content of the permeate is high compared to that in the corresponding feed, and thus the preferential permeation of dioxane is confirmed. It is noted that the permeation of dioxane through the CEMDMS2 membrane is higher than that through the CEMDMS1 and PDMS membranes. This is clearly shown when the separation factors of dioxane vs. water are plotted against the composition of feed.

The separation mechanism which determines membrane selectivity consists mainly of (1) diffusion term and (2) solubility term, and the polymer-solute interaction is a predominant factor in determining the solubility term. The Hildebrand solubility parameter δ[11] provides a useful measure to estimate the interaction in liquids. Burrel[12] extended the solubility parameter to the polymer-solvent system : however, the accurate determination of δ for polymers is difficult when using the usual method and rather qualitative reference values have been reported.

Prediction of Solubility Parameter Components

The Hildebrand solubility parameters are divided into the following three components ; the dispersive forces contribution δ_d, the polar interaction δ_p, and the hydrogen bonding δ_h.

In this paper, we used group contribution of componenet to estimate the solubility paramenter δ of modified membranes.

The solubility parameter components from the prepared polymer membranes may be predicted

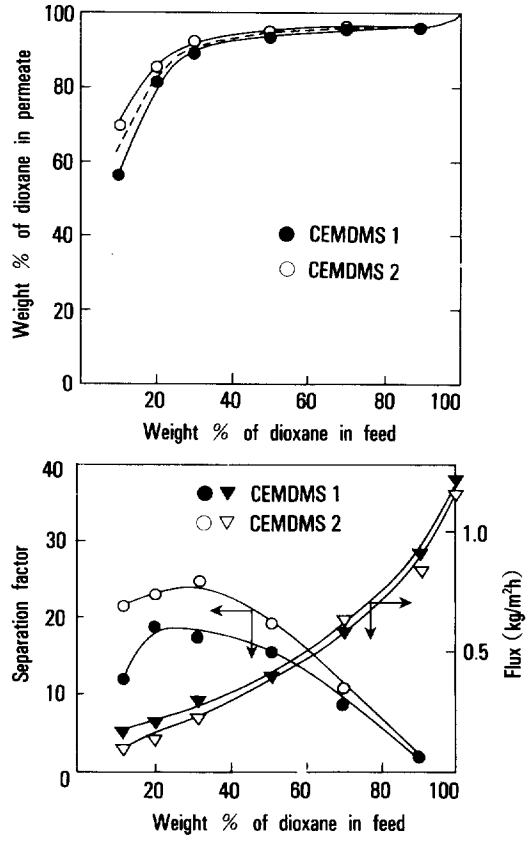

Fig. 1. Composition in permeate vs. composition in feed. Pervaporation was carried out with the CEMDMS membranes at 30℃. A dotted line represents the separation curve of the PDMS membrane reported in reference 9. The notations CEMDMS1 and CEMDMS 2 mean the membranes made from DMDES/CEMDMS/TMOS=9/1/1 and 8/2/1 solutions, respectively, (See Table 1).

from group distributions using the following equations[13] ;

$$\delta_d = \frac{\Sigma F_{di}}{V}$$

$$\delta_p = \frac{\sqrt{\Sigma F^2_{pi}}}{V}$$

$$\delta_h = \sqrt{\frac{\Sigma E_{hi}}{V}}$$

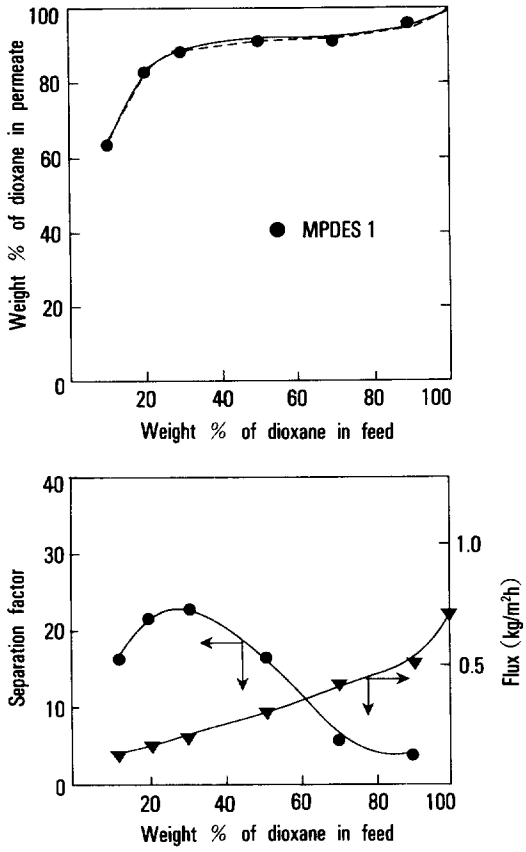

Fig. 2. Composition in permeate vs. composition in feed. Pervaporation was carried out with the MPDES membranes at 30℃. A dotted line represents the separation curve of the PDMS membrane.

where : F_{di} : dispersion component of the molar attraction constant.
F_{pi} : polar component of the molar attraction constant.
E_{hi} : hydrogen bonding energy
V : The molar volume of prepared polymer figment.

The group contribution F_{di}, F_{pi} and E_{hi} for a number of structural groups are given in Table 2.

Table 3 shows the solubility parameters of water and dioxane together with those of phenyl, chloroethyl and aminophenyl, which give respectively the values of reference for characteristic groups

Table 2. Solubility Parameter Component Group Contributions.

Sturctural Group	F_{di} ($J^{\frac{1}{2}}.m^{\frac{3}{2}}.mol^{-1}$)	F_{pi} ($J^{\frac{1}{2}}.m^{\frac{3}{2}}.mol^{-1}$)	E_{hi} (J/mol)
*−C(−)(−)	-70	0	0
$-CH_3$	420	0	0
$-CH_2-$	270	0	0
-Cl	450	550	400
-O-	100	400	3000
$-NH_2-$	280	—	8400

*We cannot know the correct values of −Si(−)(−) group, we had to adopt an approximate −C(−)(−) group.

Table 3. Solubility Parameters[13]

Substance	Index	δ_d	δ_p	δ_h	Δ1-i	Δ2-i	Δ1-i/Δ2-i
Dioxane	1	9.30	0.9	3.6	–	–	–
Water	2	6.0	15.3	16.7	–	–	–
-CH	3	8.779	3.986	8.176	5.544	14.436	0.384
$-CH_2CH_2Cl$	4	9.308	3.848	7.513	4.899	15.049	0.325
	5	10.403	3.146	7.236	4.413	16.021	0.275
$-CH_2CH_2$ CH_2NH_2	6	9.874	3.344	9.354	1.277	14.556	0.43

Δi-j : Distance between substances i and j.

involved in the MPDES, CEMDMS, and APMDES membranes. The interaction between respective characteristic groups of membrane and solvent determines the relative value of solubility of the solvent in respective membranes against the original PDMS membrane.[14]

According to Cabasso,[15] if a solubility parameter space is constructed by setting three components of solubility parameter as the rectangular coordinates, the distance between the points referring to two substances in the space is a useful index to determine the mutual miscibility. If one is a polymer and another is a solvent, this value is useful to predict the preferential absorption of the solvent into the polymer and the smaller value of the dis-

tance means the higher extent of absorption.

In the present case, the major part of the membrane matrix consists of the chains of poly(dimethylsiloxane), of which the methyl groups are partly replaced by phenyl, chloroethyl, or 3-aminopropyl groups. These modifications cause small deviations from the original PDMS membrane and the extent of deviations could be measured by the solubility differences from the original PDMS membrane. Thus the distance between two related substances were calculated and these as well as the relative ratios of the distances were given in Table 3.

Here, we intend to explain the increasing tendency of separation factor with the increasing content of chloroethyl group in the CEMDMS membrane. It is clear from Table 2 that the relative ratio of the distance $\Delta 1\text{-}4/\Delta 2\text{-}4$ is smaller than $\Delta 1\text{-}3/\Delta 2\text{-}3$ and, therefore, preferential absorption of dioxane would take place in the chloroethyl-substituted PDMS. This explains the increasing tendency of the separation factor of dioxane vs. water as shown in Fig. 1. Similarly the membrane modified with phenyl groups should exhibit preferential separation of dioxane in comparison with original PDMS membrane. But the difference between the separation curves for MPDES1 and PDMS membranes shown in Fig. 2 is hardly noticeable. Figure 2 shows that MPDES 1 membrane modified with phenyl groups has smaller selectivity than CEMDMS has.

This is similar to the tendency of the values calculated in Table 3.

Although the amino groups in the APMDES membranes interact strongly through hydrogen bonding, the distance between water or dioxane gives the similar ratio to the cases of (pheny and chloroethyl) groups, as shown in Table 3. But the separation curves for APMDES 1 and APMDES 2 membranes are quite different from others. This is probably because of the existence of ammonium groups, which are formed by quaternarization of amino groups with hydrochloric acid used as a catalyst for membrane preparation. The absorption

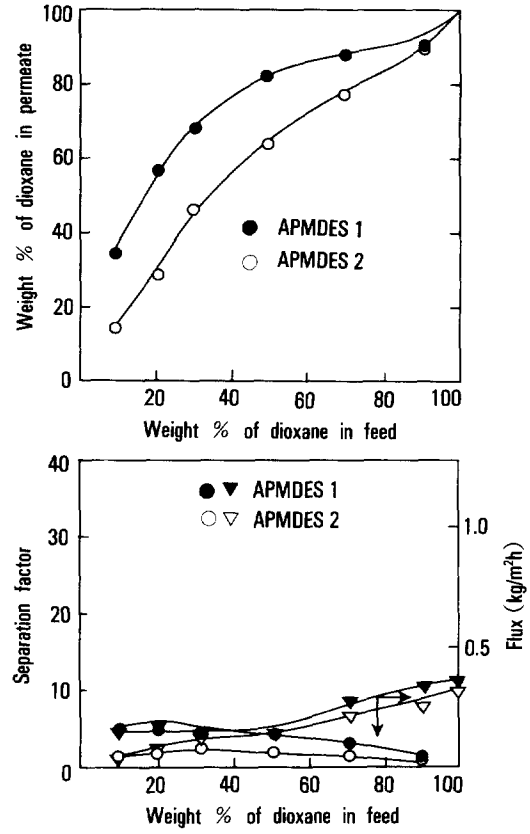

Fig. 3. Composition in permeate vs. composition in feed. Pervaporation was carried out with the APMDES membranes at 30℃.

of water into the membrane takes place predominantly in the ammonium-rich domains and, therefore, the separation of dioxane becomes poor as the content of APMDES increases.

It is considered that the membrane modified with 3-aminopropyl group has the smallest separation for dioxane as shown in Fig. 3, due to the high ratio of $\Delta 1\text{-}6/\Delta 2\text{-}6(0.43)$.

To confirm this, diethylamine was allowed to react with the 2-chloroethyl groups in the CEMDMS 1 and CEMDMS 2 membranes to form quaternary ammonium cations. Freshly distilled diethylamine was dissolved in anhydrous ethanol to prepare 0.1 N solution. The CEMDMS membranes were immersed in ethanol for 24 hr to swell suffi-

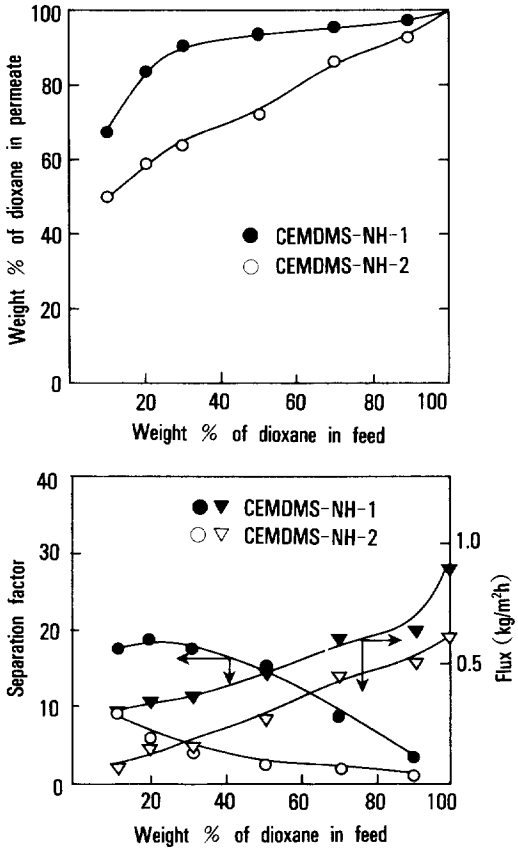

Fig. 4. Composition in permeate vs. composition in feed. Pervaporation was carried out with the CEMDMS-NH membranes at 30℃. CEMDMS-NH-1 and and CEMDMS-NH-2 represent the membranes prepared by reactions of diethylamine with the CEMDMS1 and CEMDMS2 membranes, respectively.

ciently and then put in an excess amount of the diethylamine solution for 24 hr. After washing, the membranes were kept under air at room temperature for 12 hr, and put in an oven to dry under a reduced pressure for 24 hr at 110℃.

The membranes were used in the pervaporation experiments and the results are shown in Fig. 4. The notations CEMDMS-NH-1 and CEMDMS-NH-2 indicate the membranes prepared by the reaction of diethylamine with the CEMDMS 1 and CEMDMS 2 membrane, respectively. The separation of dioxane becomes poorer compared to the cases of the original CEMDMS membranes, as being expected. In summary, the pervaporation performance of membranes could be related with the polymer-solute interation by estimation the solubility parameter distances.

CONCLUSIONS

A series of modified PDMS membranes were prepared and the separation of dioxane-water by the pervaporation process was studied. It is clarified that the extent of separation is affected by chemical modifications of the membranes and the results are properly explained by means of the solubility parameter distance approach. The introduction of chloroethyl groups in the membrane improves the selectivity of dioxane, while the existence of ammonium groups increases the permeability of water.

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