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PREPARATION OF ASYMMETRIC POLYIMIDE MEMBRANES BY THE PHASE INVERSION PROCESS

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ABSTRACT

Preparation of asymmetric polyimide membranes by the phase inversion process was investigated to develop ultrafiltration, reverse osmosis and pervaporation membranes for organic solutions, using a commercially available solvent-soluble polyimide. The influences of the various factors such as the composition of a cast solution, casting conditions, gelating solutions and others on membrane structure and performance were studied in detail, and it was made clear that a wide variety of asymmetric polyimide membranes ranging from UF to RO for organic solutions could be prepared from the aromatic polyimide used. It was also found that the chemical stability and separation performance of the asymmetric polyimide membranes could be improved by annealing in a liquid or a vacuum at above 200 °C. The membrane annealed at 300 °C in a vacuum exhibited the separation factor $\alpha(H_2O/EtOH)$ of 900 with the flux of 1.0 $kg/m^2 \cdot h$ at 60 °C for an aqueous ethanol solution of 95 vol%.

1. INTRODUCTION

The pressure-driven membrane processes of ultrafiltration(UF) and reverse osmosis (RO) have been now widely used in various fields such as desalination, ultra-pure water production, waste water treatment, food processing, and others. However, almost all membranes which have been developed up to now can not be used in organic solutions owing to the poor solvent resistance, except for microfiltration(MF) membranes and the UF membrane developed by Nitto Denko Co., Ltd., and there has been no membrane which can be used for reverse osmosis of organic solutions.

So that, we investigated the preparation of asymmetric polyimide membranes by the phase inversion process to develop such membranes as UF, RO and pervaporation (PV) membranes for organic solutions, using a commercially available solvent-soluble polyimide.

The investigations were carried out at National Chemical Laboratory for Industry (NIMC, at present) in the "Jisedai Project" financially supported by the Agency of Industrial Science and Technology (AIST), MITI.

2. EXPERIMENTAL

Asymmetric polyimide membranes were prepared from the cast solutions composed of the polyimide, a solvent and an additive by the phase inversion process, using the semi-automatic apparatus for membrane preparation which was developed in our laboratory. The polymer used was the solvent-soluble aromatic polyimide (PI-2080) developed by Upjohn Co., Ltd.. The chemical structure of the polyimide is shown in Fig.1. A cold water or cold organic solvents were used as the gelating solutions.

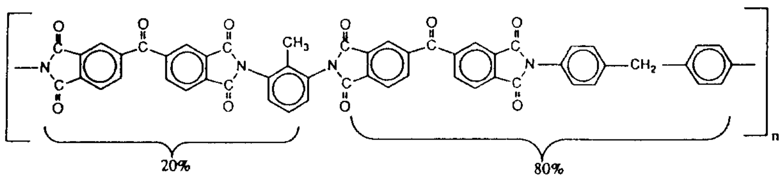


Fig.1 Structural formula of polyimide (PI-2080).

The Membranes prepared were evaluated by measuring UF, RO or PV performance using a flow type apparatus (UF and RO) and a batch type apparatus (PV). Aqueous or organic solutions of 0.3 wt% polyethylene glycol (PEG; M.W.= 200 - 100,000) and aqueous solutions of 0.5 wt% salts (Na_2SO_4, NaCl) were used as the feeds of UF or RO test. The concentration of PEG was measured by a GPC liquid chromatograph and that of salts by a electric conductivity meter.

Post treatment of the asymmetric polyimide membranes was conducted by heating in a liquid or a vacuum at above 200 °C for the improvement of their chemical stability and separation performance. The effects of the annealing were evaluated by their strength and performance.

A cross-section of membrane structure were observed by a scanning electric microscope (SEM).

3. RESULTS AND DISCUSSION

(1) Composition of Cast Solutions [1-3]

The composition of cast solution was first investigated. From the membrane preparation experiments using the cast solutions composed of the polyimide and solvents, N-methyl-2-pyroridone (NMP) was selected as the best solvent. It was, however, found that only ultrafiltration membranes could be prepared from the cast solutions of two component system. [1]

For further improvement of membrane performance, the effect of additives to the cast solution were studied, where the polyimide concentration was maintained at constant(20 wt%), NMP was used as the solvent, and various organic compounds or lithium salts were used as additives. Among more than ten kinds of additives, dioxane and acetone were found to be very effective. A part of the results was shown in Fig.2, where the arrow mark indicated the direction of better performance.

The effect of dioxane concentration was shown in Fig.3. The rejection of PEG 14,000 increased with the concentration of dioxane, while the water flux decreased with it, and it was found that reverse osmosis type membranes could be prepared from the cast solution containing dioxane of above 40 wt%. In this case, the performance of the membranes was not appreciably affected by the evaporation time in the cast process. [2]

The effect of acetone as additive was also examined, but it was shown that the effect of dioxane was far superior to that of acetone. However, the reverse osmosis membranes with the rejection of above 97 % for NaCl could be obtained by increasing the polymer concentration up to 25 wt% in the cast solution.

Besides the effect of lithium salts as additive was studied in more detail, and it was found that the addition of LiCl to the cast solution was suitable for the preparation of UF membranes with large molecular weight cut-off characteristics or supporting membranes of composite ones.[3]

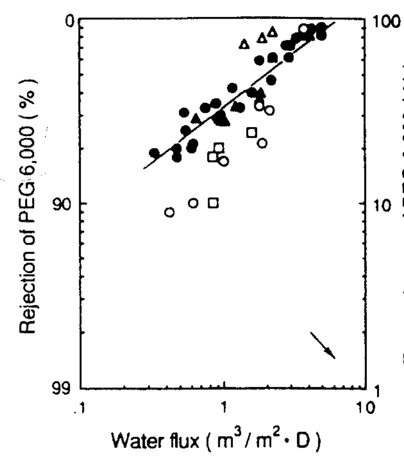


Fig.2 Effect of additives on membrane performance.
Additive: ●: None ▲: Acetamide □: Acetone
○: Dioxane △: LiCl

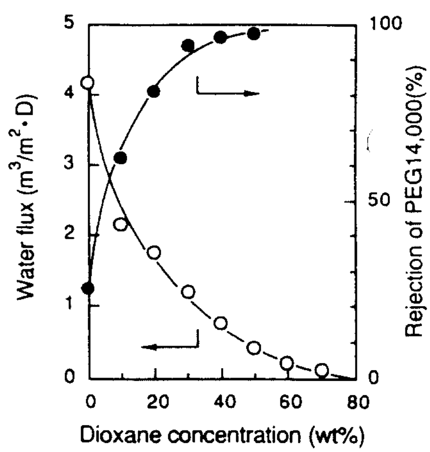


Fig.3 Effect of dioxane concentration of casting solution.
Casting solution: Polyimide of 20 wt%, NMP and Dioxane.
Evaporation time: 30 sec. at 25 ℃.

(2) Gelation Medium [2]

The effect of gelation medium on the membrane performance was studied by using several kinds of aqueous or organic solutions. The results obtained showed that the effect of acetone was superior to that of the others, as shown in Fig.4.

The heat of mixing of the solvent (NMP) and gelating solutions was measured by a microcalory meter. The results obtained were shown in Table 1, and showed that the excellence of acetone was attributable to a small exothermic heat in the mixing of NMP and acetone. This agreed with the results formerly reported by H.Strathmann. [4]

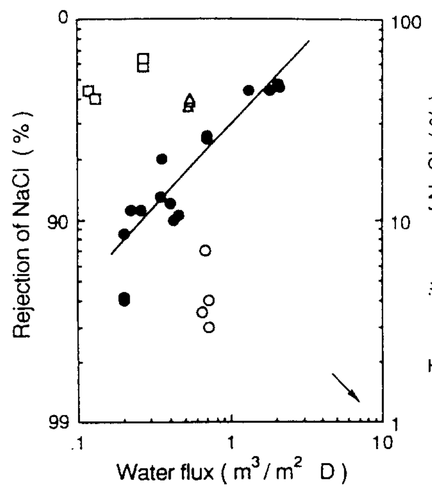


Fig.4 Effect of gelating solution on membrane performance .

Gelating solution: ●: Water ○: Acetone △: Methanol □: Benzene

Table 1 Mixing heat of solvents and gelating solution.

Gelating solution / Solvent	Water	Methanol	Ethanol	Acetone
NMP	+45.4	+ 1.7	- 3.8	±0
Dioxane	+13.7	±0	-11.1	- 3.6

(cal / g)

Temperature : 30 ℃
Solvent : 3 cm^3
Gelation solution : 30 cm^3

Table 2 Polyimide membrane performance in reverse osmosis test.

Solvent	Flux (m^3 / m^2 D)	Rejection (%)		
		NaCl	PEG 200	PEG 400
Water	0.51	97	97	98
MeOH	0.43	---	85	95
Toluene	0.12	---	82	95

Applied pressure : 40 kg / cm^2
NaCl 5000 ppm
PEG 3000 ppm

(3) Characterization of the Developed Membranes [2]

Thus, it has become clear that a wide variety of asymmetric membranes ranging from UF to RO could be prepared from the aromatic polyimide (PI-2080) by the close control of the preparation conditions .

Fig.5 indicates the molecular weight (M.W.) cut-off characteristics of these membranes which are in the range of hundreds to ten thousand. The influence of the kinds of the solvent on PEG rejection were not fairly observed in the membranes with the M.W. cut-off characteristics of above 600. In the reverse osmosis membranes, however, the rejection of PEG 200 tended to differ from each other in aqueous, methanol and toluene solutions, as shown in Table 2.

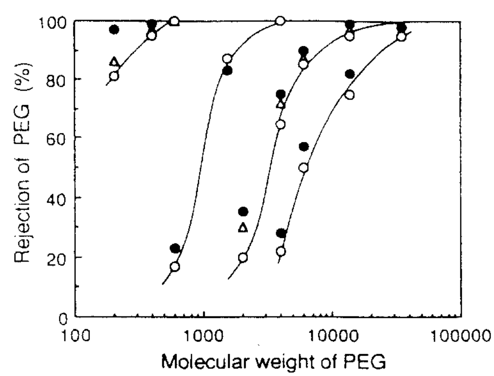
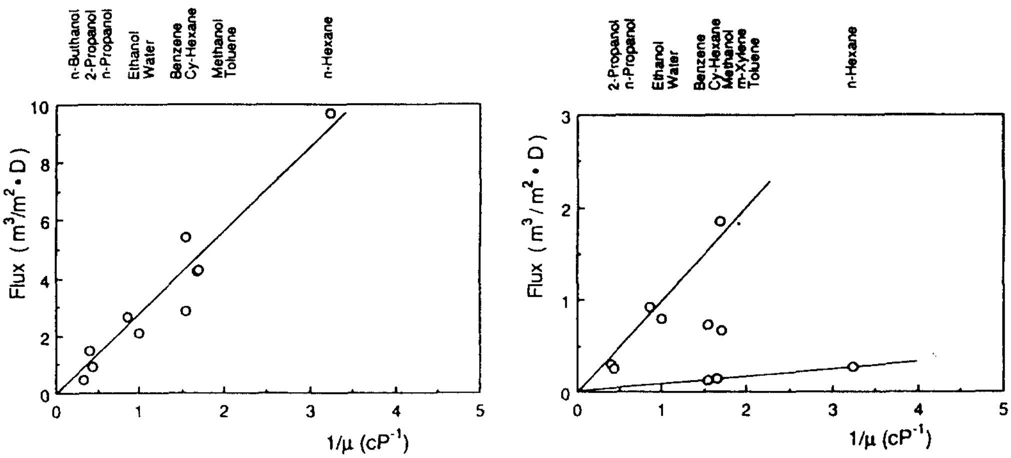


Fig.5 Molecular weight cut-off characteristics of polyimide membrane.

Test solution : ●: Water △: Methanol ○: Toluene

In order to know the interaction between permeates and the membrane, permeation behaviors of solvents were examined, and such results as indicated in Fig.6 were obtained. Fig.6(a) shows the results obtained in the typical UF membrane with the M.W. cut-off characteristic of 20,000, where the linear relationship was stood up between the flux of pure solvents and the reciprocal of the solvent viscosity. This means that the Hagen-Poiseuille equation was applicable to these results, and it could be considered that the permeation of solvents in the UF membrane of this type were mainly based on the capillary flow.

Fig.6(b) shows the results obtained in the RO type membrane with the M.W. cut-off characteristic of 1,000, where the quite different behaviors were observed in the solvent permeation. Especially, the permeation behaviors of hydrocarbons were considerably different from that of alcohols. It was considered that the solvent permeation was much affected by the interaction of the solvent and membrane (material) in the case of such diffusible permeation.



(a) 20,000 molecular weight cut-off membrane

(b) 1,000 molecular weight cut-off membrane

Fig.6 Correlation of flux and viscosity of solvent.

The solvent resistance of the membranes prepared was examined by immersion in the various solvents for one week and measuring the changes in their size caused by swelling. As shown in Table3, the membranes were almost stable in such common solvents as alcohols and hydrocarbones but unstable in such polar solvents as nitrobenzene and dioxane, within the scope of this experiment. It was, however, thought that the chemical stability of the polyimide membranes needed further improvement.

Table 3 Effect of organic solvent on membrane swelling.

Solvent	Diameter (mm)	Shirinkage (%)	Observation
Acetone	49.7	0.6	Unchange
Benzene	50.4	-0.8	Unchange
Chloroform	47.6	4.8	Unchange
Dioxane	--	--	Destroyed
Ethanol	50.1	-0.2	Unchange
Formamide	49.9	0.2	Harden
Glycerin	50.0	0.0	Unchange
n-Hexane	50.0	0.0	Unchange
cy-Hexane	49.9	0.2	Unchange
Methanol	49.3	1.4	Unchange
Nitrobenzene	--	--	Destroyed
n-Propanol	50.0	0.0	Unchange
2-Propanol	50.0	0.0	Unchange
Tetrahydrofran	50.3	-0.6	Harden
Toluene	50.1	-0.2	Harden

Casting solution : Polyimide of 20 wt% and NMP of 80 wt%

(4) Improvement of Asymmetric Polyimide Membranes [5-6]

Post-treatment of the asymmetric polyimide membranes was studied to improve their chemical stability and separation performance. It was found that polyimide membranes could be improved by heating them in a liquid or a vacuum at above 200°C. Various solvents of high boiling point were examined for the applicability to the liquid medium, and dioctyl sebacate was found out as the best solvent for curing the polyimide membranes. As shown in Table4, the solvent resistance of the polyimide membranes could be considerably improved by the annealing in this solvent. The separation performance was also improved. It was thought that the annealing in the solvent was suitable for the improvement of solute separation membranes, because it resulted moderate shrinkage.[5]

It was also found that the annealing in a vacuum was very effective to improve the solvent resistance and PV performance of the polyimide membranes. The results are partially shown in Table 5. It has been said that the high performance of gas separation or PV membranes are mainly resulted in the chemical structure of their membrane materials, and a high performance RO membrane needs not only the preferable chemical structure of the membrane material but also the appropriate fine structure of the membrane. However, the results of Table 5 suggested that a high performance PV membrane also needed the appropriate fine structure of the membrane in analogy with an RO membrane.

The asymmetric polyimide membrane heated at 300 °C in a vacuum exhibited the separation factor $\alpha(H_2O/EtOH)$ of 900 with the flux of 1.0 kg/m^2• h at 60°C for an aqueous ethanol solution of 95 vol%.[6]

Table 4 Effect of annealing on solvent resistance of membrane.

Solvent	Strength (kg f / cm^2) Before	Strength (kg f / cm^2) After
Toluene	42	212
Chloroform	54	171
Dioxane	--	158
Aniline	--	18
Nitrobenzene	--	77

Annealing condition : 3hours at 250 ℃ in Dioctyl sebacate.

Table 5 Effect of annealing in vacuum (300 ℃) on membrane performance.

Memb.	Before annealing: UF · RO performance (PEG rejection)	After annealing in vacuum: PV performance*** $\alpha(H_2O/EtOH)$	After annealing in vacuum: PV performance*** Flux Q (kg/m^2/h)
A	85% (PEG 6,000)*	10	0.35
B	97% (PEG 6,000)* (PV, α=3, Q=6.5)***	60	0.22
C	96% (PEG 600)**	480	0.18
D	99% (PEG 200)**	120	0.02

*UF 3 kg/cm^2, **RO 40 kg/cm^2, ***PV 95 vol% EtOH, 25 ℃

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