고분자 분리막에 관한 연구 :
3. 폴리술폰계 막의 제조 및 특성

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(1991년 3월 12일 접수)

Studies on the Polymeric Membranes for Separation :
3. Preparation and Characterization of Polysulfone Membranes

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(Received March 12, 1991)

요 약 : 습식 상전환법에 의한 한외여과용 폴리술폰막과 폴리에테르술폰막의 제조에 필요한 기초
적인 지식과 막 설계지침을 확립하고자, 막 제조시, 각종의 제막 변수들을 도입하여 제막 변수들이
막의 구조 및 투과 특성에 미치는 영향을 조사 검토하였다. 혼합 용매계에서 휘발성이 강한 조용
매의 함량비가 증가함에 따라, 수투과량은 점차 감소하였고, 용질배제율은 각각 조용매의 성질에
따라 다양하게 증가하는 것으로 나타났다. 투과유속과 용질배제율을 고려하였을 때, NMP-DCM
혼합 용매계가 가장 적절한 것으로 추측되었다. 폴리술폰막과 폴리에테르술폰막은 20,000 이상의
평균분자량 분획 특성을 보였다.

Abstract : This study was undertaken to establish the preparation condition of the flat sheet polysul-
fone and poly(ether sulfone)membranes for ultrafiltration application. Several membrane preparation
parameters were introduced to the membrane preparation process, and their effects on the morpho-
logy and performance of resulting membrane were investigated. Detailed studies on the permeation
characteristics and morphology of polysulfone membranes were undertaken through the various
mixed solvent system composed of N-methyl-2-pyrrolidone and more volatile cosolvent such as
tetrahydrofuran, chloroform, and dichloromethane. It is found that the pure water flux gradually
decreased with increasing the co-solvent portion in the mixed solvent system, while the solute rejec-
tion increased. Considering the pure water flux and solute rejection of the resulting membranes, the
NMP-DCM mixed solvent system was proved to be more preferable. The molecular weight cut-off
of the polysulfone and poly(ether sulfone)membranes developed in this study is more than 20,000.

INTRODUCTION

The primary role of a membrane is to act as a permselective barrier. The thin film in either solid or liquid state act as a permselective barrier for gaseous, liquid, or solid permeant. Strathmann[1] has defined a membrane as an interphase which restricts the transport of matter and/or energy between two adjacent outer phases in a very specific way. Lakshminarayanaiah[2] refers to a membrane as a phase that acts as a barrier to prevent mass movement but allows restricted and/or regulated passage of one or more species through it. Separation of a mixture is achieved when some components permeate the membrane more freely than others due to the permebility difference.

Although the synthetic polymeric membranes can be prepared in various ways, the majority of the commercially available membranes was produced by phase inversion method. Kesting[3] has defined that the phase inversion refers to the process by which a poymer solution inverts into a swollen three-dimensional macromolecular network or gel. Three different techniques are used for the membrane preparation by phase inversion : 1) thermal process, 2) dry or complete evaporation process, and 3) wet or combined evaporation-diffusion process. Membranes obtained by phase inversion can be classified as homogeneous(symmetric) or asymmetric membrane. The asymmetric membranes consist of an extremely thin layer (skin or active layer) on the top of a more or less porous sublayer.

In the case of asymmetric membranes, the porosity of the sublayer increases across the membrane from top to bottom. The separation characteristics are governed by the nature of the skin polymer or pore size and the mass transport rate mainly by the thickness. In general, the mass transport rate is inversely proportional to the thickness of the actual skin layer. The porous sublayer serves only as a support for the skin layer and has very little effect on the separation characteristics and mass transport rate of membrane.

The objective of this study was to describe the preparation. morphology, and permeation characteristics of the asymmetric membranes cast from polysulfone dope solution. In many works, the solvent system used in casting solution was aprotic solvent with high boiling point and low vapor pressure such as dimethylacetamide, dimethylformamide, and N-methyl-2-pyrrolidone. Therefore, in order to prepare the membrane having good performance, it was necessary that the solvent evaporation period prior to coagulation was prolonged and the solvent evaporation temperature was elevated.

In this study, the main object of investigation is preparation of a flat sheet membrane at mild experimental conditions, namely, a short solvent evaporation period at the room temperature. The asymmetric membranes were prepared by the wet process using polysulfone and poly(ethersulfone).

EXPERIMENTAL

Materials

Polysulfone(PSF, Udel P-1700, MW 30,000, Amoco) and poly(ether sulfone)(PES, Victrex4800P MW 22,400, ICI) were used as membrane materials without further purification. Poly(vinyl pyrrolidone)(PVP, MW 10,000, Aldrich) and lithium nitrate(LiNO$_3$, Aldrich) were used as additives.

The casting solvents used were N-methyl-2-pyrrolidone(NMP), tetrahydrofuran(THF), chloroform(CF), and dichloromethane(DCM). These were of analytical grade and were used without further purification. A major solvent used was NMP and all the other solvents were used as an co-solvent.

Preparation of Flat Sheet Membrane

All membranes were prepared by wet process method which is similar to that of our previous paper.[4,5] The homogeneous polymer solution consisted of polymer, solvent, and additive(s), with the specified composition. The nascent membranes were obtained by casting machine using Doctor's knife with a constant thickness in the thermohygrostatic chamber. The casting machine is shown schematically in Fig. 1. All membranes
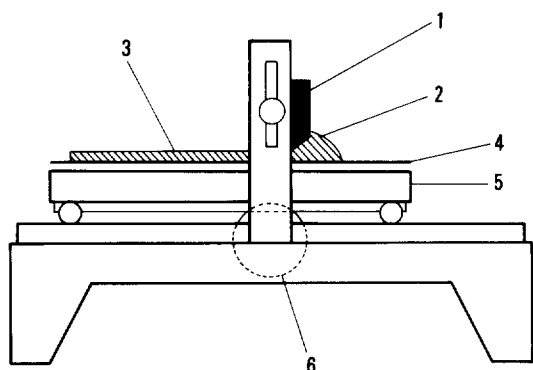
Fig. 1. Schematic diagram of casting machine : (1) doctor's knife, (2) casting solution, (3) nascent membrane, (4) polyester fabric, (5) moving board, (6) gear. (7) magnetic stirrer, (8) membrane, (9) graduated cylinder.
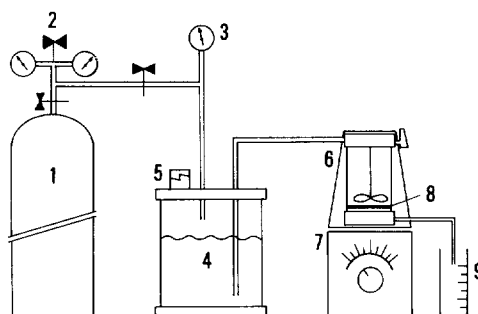

Fig. 2. Schematic flow diagram of ultrafiltration experiment apparatus : (1) N₂ bomb, (2) regulator, (3) pressure gauge, (4) reservoir, (5) safety valve, (6) UF cell, (7) magnetic stirrer, (8) membrane, (9) graduated cylinder.

were cast at 200μm thickness onto woven polyester fabric manufactured by SKI. The casting speed was 5cm/sec. The temperature and relative humidity of the membrane casting atmosphere were cotrolled at 25℃, 35± 5%, respectively. The solvent evaporation period prior to immerse into the coagulating medium was 30sec. In this experiment, distilled water was used as coagulating agent which was kept at 0~4℃. The residence period of the cast film in the coagulation bath was usually 2 hours, and then rinsed with running water at room temperature.

Characterization of Membrane Performance

The permeation characteristics of the membrane were determined with a Amicon 8050 ultrafiltration apparatus(the effective membrane area : 13.4 cm²). After the steady state of membrane against the operating pressure was attained, pure water flux(PWF) and solute rejection(SR) of membrane were measured by use of pure water and 1,000 ppm aqueous poly(ethylene glycol) (PEG MW 20, 000), poly(vinylpyrrolidone) (PVP MW 40,000), or Dextran(MW 87,000) solution, respectively. The solute concentrations in the feed and the permeate solutions were determined with the Waters Differential Refractometer Model R 401. The applied operating pressure used for performance evalua-

tion was 1kg/cm². All the experiments were carried out at 25℃ in the thermostatic chamber. The schematic flow diagram of experimental equipment is illustrated in Fig. 2.

Morphology of Flat Sheet Membrane

In order to reveal the relationship between the membrane structure and its performance, the structure of the resulting membranes was observed employing AKASHI-DS-130 scanning electron microscope. The cross-sections of the membranes were obtained by fracturing the sample under liquid nitrogen. After removing water within the membrane by freezing-dryer, the samples were coated with gold under high vacuum and examined with the scanning electron microscope.

RESULTS AND DISCUSSION

Effect of PVP as an Additive in Casting Solution

PSF membranes obtained from the casting solution consisting of more than 20wt% PSF with NMP solvent only (in case of PES membrane : >25 wt%) were hardly permeable. In order to increase the water flux, PVP was added to the casting solution. PVP is a quite hydrophilic polymer and has been used as a perferable additive to prepare polysulfone hollow fibers.[6]

Table 1. Effect of PVP Amount in Casting Solution on the Performance of Polysulfone Membranes

PSF Conc. (wt%)	NMP Conc. (wt%)	PVP Content* (wt%/ PSF wt)	Pure Water** Flux (L/m²hr)	Solute Rejection(%)*** Dextran (MW 87,000)
20	80	25	141.4	49
		50	214.9	45
		75	220.1	26
		100	235.7	31

Solvent evaporation period ; 30sec.

Solvent evaporation temp. ; 25℃

Relative humidity ; 35 ± 5%

Doctor's knife thickness ; 200μm

*PVP content ; wt% against PSF weight

**Applied operation pressure ; 1Kg/cm²

***Feed solution concentration ; 1,000ppm aqueous solution

Table 2. Effect of PVP Amount in Casting Solution on the Performance of Poly(ethersulfone) Membranes

PSF Conc. (wt%)	NMP Conc. (wt%)	PVP Content(wt%/ PSF wt)	Pure Water Flux (L/m²hr)	Solute Rejection(%) PEG (MW20,000)
25	75	20	147.9	90
		40	207.4	87
		60	230.5	89
		80	262.1	84

Experimental conditions are the same as shown in Table 1.

Tables 1 and 2 show the results about the effect of PVP in the casting solution on the PSF and PES membrane performance, respectively. As shown in tables, the pure water flux increased while the solute rejection decreased with increasing PVP content in the casting solution.

It means that the porosity of membrane is increased with the increase of PVP content in the casting solution. In other words, when the nascent membrane is immersed in the coagulation bath, the PVP will be dissolved in water (coagulating agent) and flowed out toward co-agulation bath, and hence induce to form pores within the final membrane.

Judging from the experimental data, 50%(against PSF wt.) of PVP in the PSF membrane and 60%(against PES wt.) in the PES membrane, were proved to be most proper concentration, respectively.

Effect of Composition of Mixed Solvent System

In general, it is well known that the solute rejection depends upon the polymer density of the uppermost surface layer in membrane. With increasing the polymer density in the upperlayer, polymer molecules will be aggregated more compactly to increase the solute rejection of resulting membranes. It is necessary that the gradient of solvent concentration in the upperlayer must become smaller than that in the sublayer of membrane. This is achieved by the vigorous solvent evaporation from the surface of the nascent membrane prior to coagulation.

In this study, the various mixed solvent systems composed of non-volatile solvent NMP and more volatile co-solvent were introduced to increase the amount of solvent loss during evaporation period. THF, CF, and DCM were chosen as co-solvents of the mixed solvent system on the consideration of their volatility, miscibility with water and NMP, and solubility against polymer.

The results of permeation characteristics of PSF membranes prepared from the various mixed ratios of NMP and co-solvents are shown in Tables 3~4. It is found that the pure water flux gradually tended to be decreased with increasing co-solvent portion in the mixed solvent system, while the solute rejection tended to be increased.

Comparison of the NMP-THF and the NMP-CF Solvent System : The volatility of THF is similar to that of CF, but the miscibility of THF with water is better than CF. The effects of the addition of co-solvent in the mixed solvent system on the resulting membrane performances are illustrated in Fig. 3.

The decreasing trend of pure water flux of membranes prepared with NMP-THF system is more drastical than that of prepared with NMP-CF system. On the other hand, the solute rejection

Table 3. Permeation Characteristics of Polysulfone Membranes Prepared with NMP-THF Mixed Solvent System in Casting Solution
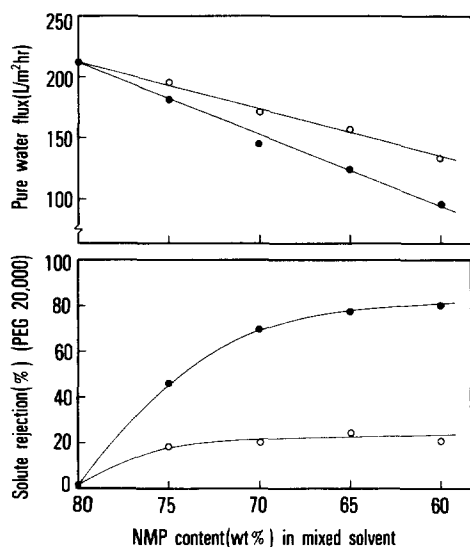
PSF Conc.	PVP Content	NMP Conc.	THF Conc.	PWF	Solute Rejection(%)	
(wt%)	(wt%/PSF wt)	(wt%)	(wt%)	(L/m²hr)	PEG 20,000	PVP 40,000
20	50	75	5	180. 1	46	90
		70	10	145. 2	69	96
		65	15	124. 9	77	96
		60	20	93. 9	79	95

Experimental conditions are the same as shown in Table 1.

Table 4. Permeation Characteristics of Polysulfone Membranes Prepared with NMP-CF Mixed Solvent System in Casting Solution

PSF Conc.	PVP Content	NMP Conc.	CF Conc.	PWF	Solute Rejection(%)	
(wt%)	(wt%/PSF wt)	(wt%)	(wt%)	(L/m²hr)	PEG 20,000	PVP 40,000
20	50	75	5	196. 0	19	84
		70	10	173. 3	20	90
		65	15	153. 5	26	92
		60	20	136. 6	20	89

Experimental conditions are the same as shown in Table 1.

Fig. 3. Comparison of NMP-THF system and NMP-CF system : (●) PSf membranes prepared from NMP-THF, (○) PSf membranes prepared from NMP-CF.

results showed opposite trends. These trends may be resulted from the properties of co-solvent such as miscibility with water and specific gravity.

The casting solution prepared by the NMP-THF

solvent system exhibits rapid depletion of solvents compared with the NMP-CF system when it immersed in the coagulation bath, because THF is miscible with water(coagulating agent) and has a low specific gravity. Cabasso[7] have reported that the instant depletion and removal of solvent follows a solidification of the polymer molecules into a dense membrane. As a result, the upperlayer of final membrane prepared from the NMP-THF mixed solvent system will be formed more dense than that from the NMP-CF system.

Comparison of the NMP-CF and the NMP-DCM Solvent System : The performance of membranes prepared from NMP-CF and NMP-DCM mixed solvent system is described in Fig. 4. Both CF and DCM are high specific gravity and immiscible with water. However, the volatility of DCM is higher than that of CF.

As shown in Fig. 4, with increasing co-solvent portion in the mixed solvent system, the pure water flux decreased with similar trends in both cases of the NMP-CF and the NMP-DCM. While the solute rejection of membranes prepared from the NMP-DCM solvent system increased rapidly.

These results may be due to the volatility difference of between CF and DCM used as a co-solvent. During solvent evaporation period, the solvent loss from the surface of the nascent membrane might be greater in the NMP-DCM system than in the
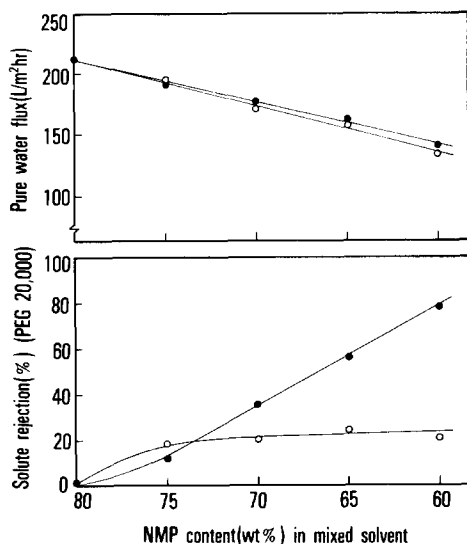
NMP-CF system. This means that the polymer density of the upperlayer in the nascent membrane is relatively higher in the NMP-DCM system than in the NMP-CF system. Subsequently, the upperlayer of membranes prepared from NMP-DCM system is more densely formed. It can be presumed that the solute rejection of membrane prepared from the NMP-DCM solvent system is higher than that of membrane from the NMP-CF solvent system.

Membrane Morphology : With the objeci of elucidating structurally the previous results, the cross section of the membranes was observed with scanning electron microscope. Photographs in Fig. 5 are SEMs of PSF membranes prepared from the various mixed solvent systems.

Generally, it can be seen that the upperlayer of the resulting membranes was gradually thicker with the increase of co-solvent portion in all of the mixed solvent system. In special, the NMP-THF case is more denser than any other one. In addition, it can be found that the upperlayer of membrane perpared from the NMP-CF system is more porous than that from the NMP-DCM system. These facts correspond with results of membrane performance shown in Tables 3~5.
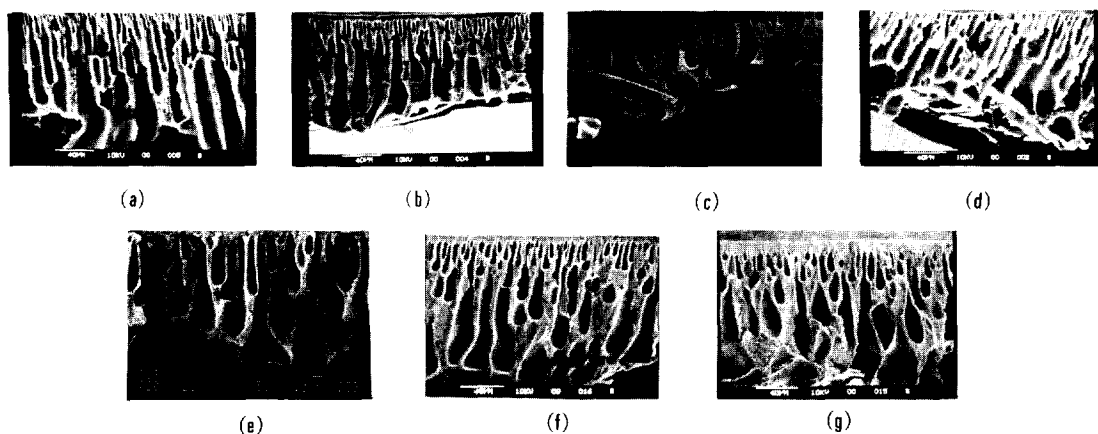

Fig. 4. Comparison of NMP-CF system and NMP-DCM system : (○) PSF membranes prepared from NMP-CF, (●) PSF membranes prepared from NMP-DCM.
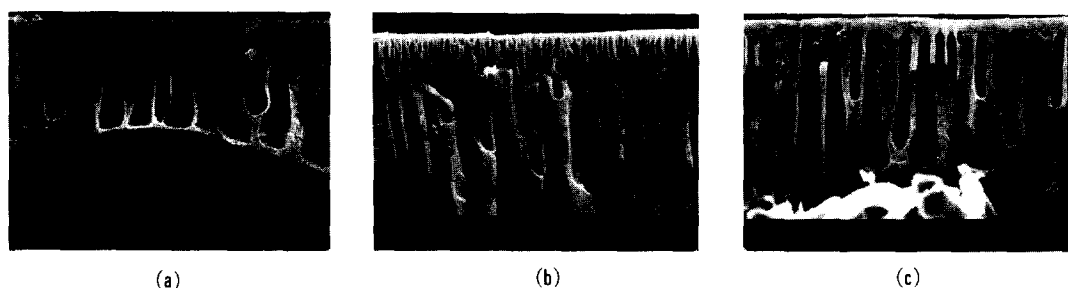

Fig. 5. SEMs of cross-sections of PSF membranes prepared with various mixed solvent systems in casting solution : (a) NMP only, (b) NMP : THF=70 : 10, (c) NMP : THF=60 : 20 (d) NMP : CF=70 : 10 (e) NMP : CF=60 : 20 (f) NMP : DCM=70 : 10 (g) NMP : DCM=60 : 20.

Table 5. Permeation Characteristics of Polysulfone Membranes Prepared with NMP-DCM Mixed Solvent System in Casting Solution

PSF Conc. (wt%)	PVP Content (wt%/PSF wt)	NMP Conc. (wt%)	DCM Conc. (wt%)	PWF (L/m²hr)	Solute Rejection(%)	
					PEG 20,000	PVP 40,000
20	50	75	5	193.0	10	92
		70	10	176.7	35	90
		65	15	160.7	56	93
		60	20	140.2	79	92

Experimental conditions are the same as shown in Table 1.

(a) (b) (c)

Fig. 6. SEMs of cross-sections of PES membranes prepared with different composition ratios of DCM-NMP system in casting solution : Mixed ratios of NMP : DCM are : (a) 75 : 0, (b) 65 : 10, (c) 55 : 20.

Table 6. Effect of NMP-DCM Mixed Solvent System in the Casting Solution on the Performance of Poly (ethersulfone) Membranes

PSF Conc. (wt%)	PVP Content (wt%/PSF wt)	NMP Conc. (wt%)	DCM Conc. (wt%)	PWF (L/m²hr)	Solute Rejection(%)	
					PEG 20,000	PVP 40,000
25	60	75	0	230.5	89	96
		70	5	199.7	90	99
		65	10	167.2	96	99
		60	15	151.4	99	99
		55	20	129.5	99	99

Experimental conditions are the same as shown in Table 1.

Application of the NMP-DCM Mixed Solvent System to PES Membranes

From the previous results, the NMP-DCM mixed solvent system was preferable on the consideration of pure water flux and solute rejection of resulting membranes. Therefore, the performance of PES membranes prepared using the NMP-DCM mixed solvent system was investigated.

As shown in Table 6, higher DCM fraction in the mixed solvent system produces lower pure water flux. When the DCM content in the casting solution is more than 10wt%, the solute rejection showed higher than 96% against aqueous PEG 20,000 solution.

Fig. 6 exhibits the SEM photographs of the cross-section of PES membranes prepared from the various mixing ratio of NMP-DCM solvent system. With increasing DCM content in the casting solution, the overall thickness of membrane was thinned and the upperlayer was densed. These re-

sults are, as stated above, due to the vigorously solvent evaporation from the nascent membrane surface prior to immersion into coagulation bath. That is, as more DCM is lost, the polymer concentration in the upper layer of the cast film increases and molecular rearrangement results in a close-packed configuration of the polymer molecules. Consequently, the dense upperlayer is formed and the overall thickness is thinned. Above results agree with the permeation behavior that the pure water flux increases and the solute rejection decreases with increasing DCM content in the casting solution.(see Table 6)

Effect of Temperature of Casting Atmosphere

Solvent evaporation temperature affects the final membrane structure and its performance significantly because the loss amount of volatile solvent will be changed according to the evaporation temperature. This fact implies that the loss amount of solvent from the surface of the nascent membrane during evaporation period can be vigorously increased by elevating evaporation temperature.

Table 7 summarized the effect of solvent evapo-

ration temperature on the performances of the resulting membranes prepared from the NMP-DCM solvent system. As shown in Table 7, with the elevating solvent evaporation temperature, the pure water flux tended to be decreased. Particularly, the solute rejection of polysulfone membrane is drastically increased. It is presumed that the polymer density of membrane upperlayer will be relatively increased due to increase the amount of solvent loss.

From these results, it is possible to prepare a high performance membrane with a relatively short solvent evaporation period.

Effect of Lithium Nitrate as an Additive

The permeation characteristics of PES membranes obtained with $LiNO_3$ are presented in Table 8. As shown in Table 8, the pure water flux was increased gradually with increasing $LiNO_3$ content in the casting solution, while the solute rejection is decreased.

These phenomena are explained as follows. During coagulation in water, Li^+ ions in the nascent membrane will be aggregated by water molecules.

Table 7. Effect of Evaporation Temperature on the Performance of Polysulfone and Poly(ethersulfone) Membranes

Polymer (wt%)	Solvent(%) NMP : DCM	PVP Content (wt%/polymer wt)	Evaporation temp.(℃)	PWF (L/m²hr)	Solute Rejection(%) PEG 20,000
PSF 20	70 : 10	50	25	176.7	35
			30	149 : 3	92
PES 25	65 : 10	60	25	167.2	96
			30	143 : 4	99

Experimental conditions are the same as shownin Table 1.

Table 8. Effect of Adding $LiNO_3$ in Casting Solution on the Performance of Poly(ethersulfone) Membranes

Solution Composition(g)			$LiNO_3$ Content	PWF	Solute Rejection (%)	
PES	NMP : DCM	PVP	(g)	(L/m²hr)	PEG 20,000	PVP 40,000
25	65 : 10	15	0	167.2	96	99
			1	208.3	32	96
			2	227.7	28	95
			3	240.0	25	96

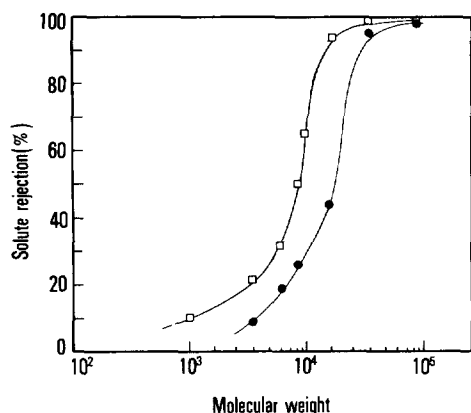Experimental conditions are the same as shownin Table 1.

Fig. 7. Molecular weight cut-off characteristics of PES membranes : (□) PES : NMP/DCM : PVP = 25 : 65/ 10 : PVP without LiNO$_3$, (●) PES : NMP/DCM : PVP = 25 : 65/10 : PVP with LiNO$_3$ 3gr.

This complex ions may weaken the coagulating power of water. Thus gelation of nascent membrane will be retarded. Therefore, the resulting membrane prepared with LiNO$_3$ will be more porous.[5,8]

Characterization of Molecular Weight Cut-Off

In order to determine the molecular weight cut-off characteristics of PES membranes prepared with or without LiNO$_3$, the solute rejections against PEG, PVP, and Dextran were investigated. The molecular weight cut-off characteristics are illustrated in Fig. 7. The molecular weight cut-off of PES membrane without LiNO$_3$ is 20,000 and the membrane with LiNO$_3$ in 40,000.

CONCLUSION

The asymmetric membranes developed in this study were suitable for ultrafiltration. In the preparation of the membranes, with the increase of additives content in the casting solution, the pure water flux tended to be increased while the solute rejection decreased. It is found that the pure water flux gradually decreased with the increase of the co-solvent portion in the mixed solvent system, while the solute rejection increased. Also it can be seen that the upper-layer of the resulting membranes was gradually thickened with increasing the co-solvent portion in all of the mixed solvent system. Considering the pure water flux and solute rejection of resulting membranes, the NMP-DCM mixed solvent system was proved to be more preferable. The molecular cut-off of PSF and PES membrane in more than 20,000.

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