

우수한 열적 특성을 갖는 Copolyimide 한외여과막의 투과 특성

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Permeation Properties of Copolyimide UF Membrane with Good Thermal Stability

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초록: 우수한 열적 특성을 갖는 한외 여과막의 투과 특성을 알아보기 위하여 copoly(bis[4-(3-aminophenoxy)phenyl] sulfone/bis(4-aminophenyl)1,4-diisopropylbenzene/pyromellite) imide(COPI)를 합성하여 상 분리방법으로 분리막을 제조하였다. 제조된 분리막은 운전 온도의 변화에 안정된 순수 투과유속과 용질 배제율을 나타내었다. 순수 투과유속에 대한 poly(ethylene glycol)(MW 2.0×10^4) 1000 ppm 수용액의 상대 투과 유속은 25 °C에서 90 °C로 운전 온도의 증가와 함께 0.15에서 0.55로 증가하였다. 또한 온도의 증가에 따른 막의 표면의 변화는 일어나지 않았다. 본 연구에서 COPI 한외 여과막은 우수한 열적 안정성을 나타내었으며, 극성 유기용매에 대한 COPI의 가용성으로 다양한 형태의 분리막 제조가 가능함을 알 수 있었다.

Abstract: Copoly(bis[4-(3-aminophenoxy)phenyl]sulfone/bis(4-aminophenyl)1,4-diisopropylbenzene/pyromellite) imide (COPI) was synthesized using an one-step imidization method. COPI exhibited excellent thermal stability and dissolved well in a number of aprotic polar solvents. COPI was used for the fabrication of membrane materials. COPI ultrafiltration (UF) membranes were prepared using a phase inversion method. Factors influencing the permeation properties and the thermal stability of the membrane were studied. The preparation conditions were determined to be important factors influencing the performance of the membrane. The thermal stability of the membrane was observed by measuring the shrinkage of area and the relative ratio of the permeate flux (J_t)/pure water flux (J_0). The relative flux for the poly(ethylene glycol) (MW 2.0×10^4) aqueous solution increased from 0.15 to 0.55 when temperature increased from 25 to 90 °C, respectively. The area of the membrane was unchanged under varying temperature. The membranes exhibited good thermal stability and were relatively simple to construct.

Keywords: ultrafiltration, membrane, copolyimide, thermal stability, relative flux.

Introduction

Membrane technologies have gained significant attention in a number of filtration applications because of their high efficiency and low environmental impact, saving energy and reducing overall operating costs. They have been widely used in pure water production as well as in wastewater treatment, in food and biotechnological fields, in electro-electronic industries, and especially, in a number of specific heat sensitive

industries. Their applications are still growing in many areas of separating fractionation and concentration.¹⁻³ In spite of their many advantages when applied to a host of industrial processes, cooling devices with relatively high associated costs are required for the stable operation of a number of such membranes. Generally, the temperature should be controlled to below 40~50 °C for the stable operation of membrane processes.^{4,5} For conventional applications, membranes can be generally engineered to possess high selectivity as well as good chemical and mechanical properties and compatibilities. The permeation properties of membranes are governed by the preparation conditions of the membrane, the operating terms, as well as the nature of the materials used in fabrication.^{2,4,6,7}

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The preparation conditions play an important role in determining the membrane's final structure. The relationships between the conditions of production and the final structure of membranes have provided the basis of many studies.^{2,4,8-11} In order to expand the application of membrane filtration technology, there has been a strong research interest in the development of thermally stable membranes. The chemical, thermal, and mechanical properties of membranes are necessarily related to the nature of the polymers which are used in membrane fabrication.^{2,4,6,12} For the practical application of membrane technology, the initial selection of membrane materials with suitable characteristics is very important. Polymers, such as polysulfone, polyamide, polyetherimide, CA, and so on, have been widely used in the fabrication of membranes, as they generally have outstanding mechanical and chemical properties for such processes.^{3,4,13-18} Among these polymers, polyimide derivatives are receiving a substantial degree of interest in many areas of application, as they have a relatively high degree of stability under various extreme environmental conditions, exhibiting outstanding chemical stability and excellent thermo-mechanical properties.¹⁸⁻²⁰ However, their practical applications are limited owing to their insoluble and infusible nature. Recently, several authors have reported the preparation of polyimide derivatives that are fusible and soluble in polar solvents.¹⁹⁻²³ We have previously synthesized many kinds of polyimide derivatives which dissolve well in aprotic polar solvents, and have applied them to the fabrication of membranes.^{19,24,25} Thermally stable membranes have many advantages over common membranes. Their advantages are based on their driving temperature range, heat recovery, sterilization, high temperature cleaning, enhancement of membrane lifetime, reduction of operation costs, and so on.^{5,26-28} The enhanced flux as well as the increased sieve effect in proportion to operating temperature are, perhaps, their most significant advantages, because the activity of the macromolecules in the feed solution is increased as a result, and hence, the viscosity of the feed solution is decreased, enhancing the efficacy of processes at a stable operating temperature.²⁷⁻³⁰ In this study, thermally stable copolyimide was synthesized using a one-step imidization process. It was determined to have outstanding thermal stability and dissolved well in a number of aprotic polar solvents such as NMP, DMAc, DMSO, and so on, resulting in a highly efficient and thermally stable ultrafiltration membrane. This paper focuses on the thermal stability of COPI UF membranes during filtration, and the effects of the preparation and filtration conditions on the permeate properties

are also discussed.

Experimental

Materials. Pyromellitic dianhydride (PMDA) (Aldrich Chemical Co., USA) was recrystallized from 4-methyl-2-pentanone. Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS, Wakayama Seika Kogyo Co., Japan) and bis(4-aminophenyl)-1,4-diisopropylbenzene (BADB, Tokyo Kasei Co., Japan) were purified by recrystallization in methanol. Poly(vinylpyrrolidone) (PVP, MW 1×10^4 , Aldrich Chemical Co., USA) and poly(ethylene glycol)(PEG, MW 2.0×10^4) (Aldrich Chemical Co., USA) were dried under reduced pressure prior to use. All other reagents were of laboratory-grade, and were used without any further purification.

Preparation of Copolyimide (COPI). COPI was synthesized according to a previously described method.¹⁹ A four-neck round flask containing BAPS, BADB, and NMP, was equipped with a sealed stirrer, nitrogen gas inlet-tube and reflux condenser that had a vessel for receiving water, and a thermometer. Under flowing nitrogen, an equivalent amount of PMDA was added to the flask at 20 °C, and the solid content was kept at 20 wt%. When the reaction was completed, the mixture was heated to 180 °C until no more liberated water in the nitrogen gas flow, and the polymer was then separated in methanol, filtered off, and dried *in vacuo* at 70 °C.

Preparation of Membrane. COPI membranes were fabricated through an immersion-phase inversion method which included a solvent evaporation period. COPI was purified according to a previously described method.⁸ The casting solution, which was composed of the polymer, solvents, and additive, was doped on a non-woven polypropylene fabric and was continuously cast by hand. The casting speed and thickness were about 5 cm/s and 200 μ m. After the solvent was evaporated, the nascent solution-state membrane was immersed in a coagulation bath at about 4 °C for 24 h, and the corresponding solid-state membrane was then thoroughly rinsed with water to remove any residual solvent and additive.

Measurements. **Characterization of COPI:** Synthesized COPI was characterized according to the below methods. FTIR spectrum was recorded on film using a thermo scientific FTIR spectrometer (Nicolet 380). Thermal properties were measured using differential scanning calorimetry (DSC, Dupont 910) and thermogravimetric analysis (TGA, Dupont 951). The viscosity was measured for a 0.5 g/dL NMP solution at 25 °C in an Ubbelohde suspended viscometer. To determine

solubility, the polymer film was immersed in the solvent, and was then shaken at room temperature for 24 h.

The Solute Retention and The Flux: The solute retention (SR) and the flux were obtained from eq. (1) and (2), respectively. The solute content was calculated using HPLC (Waters 410C). The experiment was conducted in a dead-ended magnetic stirred cell (effective area: 28.7 cm², Millipore Model 8200) and the operating pressure was kept constant at 1 kg/cm². Each membrane was firstly compacted for 30 min at 1 kg/cm² prior to the experiment.

$$SR(\%) = (1 - C_p/C_f) \times 100 \quad (1)$$

where C_p and C_f are solute concentration in the permeated solution and in the feed solution, respectively.

$$\text{Flux(L/m}^2\text{h)} = \text{Vol of permeated water(L)} / (\text{Effective area (m}^2) \times \text{time(h)}) \quad (2)$$

The Relative Flux: The relative flux (RF) was determined according to eq. (3).

$$RF = J_t/J_0 \quad (3)$$

where, J_0 is the pure water flux (PWF) and J_t is the permeated flux at time t .

Water Content: Water content was calculated according to eq. (4). Using an electronic balance, membranes were weighed in their wet state after wiping the free surface water. The membranes were then dried in an oven at 80 °C for 24 h, and were again weighed in its dry state.

$$\text{Water content(\%)} = (1 - W_{\text{dry}}/W_{\text{wet}}) \times 100 \quad (4)$$

where W_{dry} and W_{wet} are the membrane weights of the dry and wet membranes, respectively.

Shrinkage: Membrane shrinkage was obtained by measuring the area of the membrane before and after immersion in a water bath at temperatures ranging from 25 to 90 °C for 24 h.

$$\text{Shrinkage(\%)} = (1 - A_T/A_{25}) \times 100 \quad (5)$$

where A_{25} and A_T are the areas of membrane immersing in water bath at 25 and at T °C for 24 h, respectively.

Table 1. Properties of COPI

Polymer	Monomer (mol ratio)			Thermal properties (°C)			Viscosity ^a (dL/g)	Solubility ^b	
	PMDA	BAPS	BADB	T_g	T_{10}	T_{max}		Dissolve	Swell
COPI	1	0.7	0.3	305	545	650	0.93	NMP, DMSO, DMF, DMAc	Pyridine

^aMeasured with 0.5 g/dL in NMP at 25 °C. ^bDMSO: dimethylsulfoxide; DMF: *N,N'*-dimethylformamide; DMAc: *N,N'*-dimethylacetamide.

Results and Discussion

The formation of COPI was confirmed based on its FTIR spectrum. Figure 1 shows a typical FTIR spectrum of COPI. The spectrum revealed the characteristic peaks of imide groups at around 1780 and 1710 cm⁻¹, which are related to the stretch vibration of the C=O linkage of cyclic imide, and at about 1370 and 725 cm⁻¹, which are due to the -C-N stretch vibration of the imide group. However, the absorption peaks that identified polyamide and/or polyamic acid with amide I, II, and III at around 1650, 1520, and 1300 cm⁻¹ were not observed.³⁰ Other properties of the polymer are summarized in Table 1. The 10% weight-loss temperature (T_{10}) and the maximum rate of decomposition (T_{max}) observed on TGA. As shown in Table 1, COPI showed good thermal stability. It dissolved well in aprotic polar solvents, thus presenting advantages for application as membrane materials.

The permeation of pure water was generally diminished as the polymer content in the casting solution and the nascent solution membrane was increased.^{2,4,26,31} The increase of polymer moiety in the casting solution and/or the nascent membrane intimated a higher volume fraction of polymer, leading to a lower porosity, a higher density, and a higher tortuosity. Consequently, the permeation of pure water was decreased.

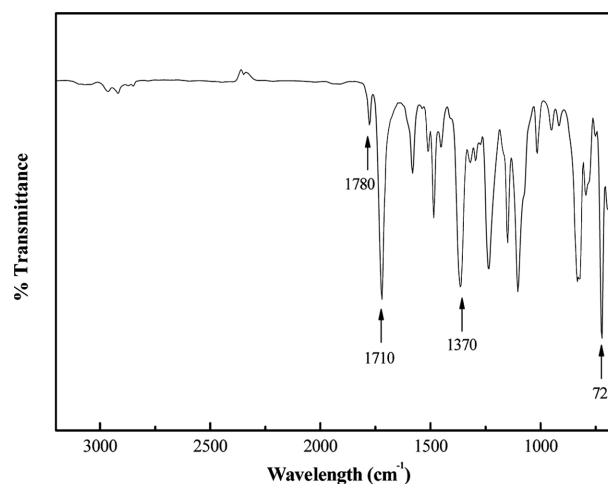


Figure 1. FTIR spectrum of COPI.

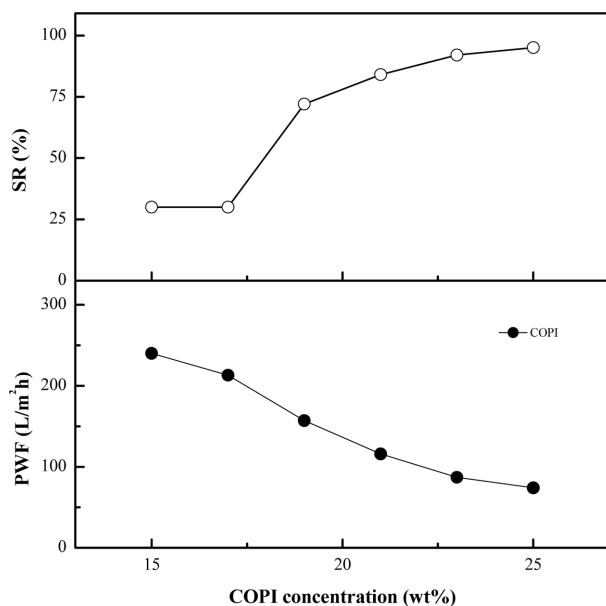


Figure 2. Relationship between the permeation behaviors and COPI concentration in dope solution. The accuracy of PWF and SR was less than 2 L/m²h and 2%, respectively.

Figure 2 represents the permeation properties according to COPI content in the casting solution. The PWF was decreased from 240 to 74 L/m²h, but the SR was increased from below 30 to 95% as the concentration of polymer in the casting solution was increased from 15 to 25 wt% in NMP. The rate of declination of the PWF was reduced as the polymer content was increased. The SR was first enhanced, and then reached a steady value. These behaviors were similar to those observed in previous papers.^{4,15,25} The PWF was affected by the surface layer, as the sieve layer, as well as by the internal sub-layer. On the other hand, the SR was strongly influenced by the structure of the selective surface layer.^{4,31} As to result, an explanation was possible with density and tortuosity. The densities of both the upper surface and the inner sub-layer were increased in proportion to the concentration of polymer in the casting solution. The tortuosity of the membrane might be directly proportional to the density of the membrane. Increased tortuosity induced that the migration of water through the membrane became longer. The PWF was much more influenced by the concentration of polymer than by that of the SR. An additive was applied to the casting solution to form a membrane with high porosity.^{4,14,31} The amount and type of additive were selected according to general methods, which are used to prepare membranes of various structures. Appropriate additives must be soluble in both solvent and coagulation liquid in order to ensure that they are miscible with the polymer, and must

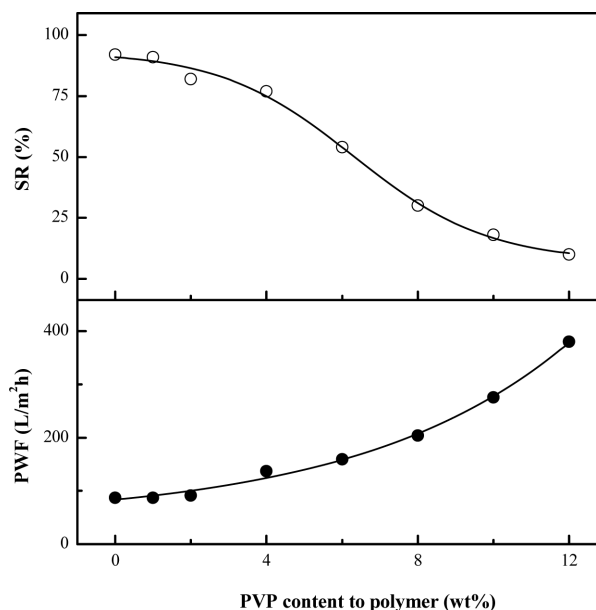


Figure 3. Effect of PVP content on the performance of COPI UF membrane. The accuracy of PWF and SR was less than 2 L/m²h and 2%, respectively.

easily come out from the inside of the membrane to external of that during soaking in the solidification bath and/or rinsing with water. Figure 3 shows the permeation properties of membranes with different amounts of PVP as an additive. PVP dissolves well in both NMP and water, and is miscible well with COPI. The PWF was gradually increased, while the SR was significantly decreased from 92% to below 30%, as the amount of PVP was increased from 0% to 12% with respect to COPI. The various additions resulted in alterations of the porosity of the fabricated membrane. PVP is a hydrophilic polymer which easily admixes with membrane material, and dissolves well in NMP. While the nascent solution membrane was phase inversion to the corresponding solid-state that in the solidification bath and solid-state membrane was rinsing with water, PVP dissolved in water and flowed out of the membrane. Consequently, pores formed in the active surface as well as within the inner sub-layer. The water content of membranes according to the amount of added PVP is shown in Table 2. The water content of membranes with PVP additions of 0% to 12% increased from about 68% to 78%. In general, the porosity of membranes are inversely proportional to their water content.^{29,32} As shown in Table 2, it was observed that membranes prepared with PVP had higher porosity values than those prepared without PVP. As mentioned previously, the PWF was substantially influenced by both the sieving upper surface layer and the porous inner layer. On the other hand, the SR mainly

Table 2. Water Content and Shrinkage of COPI UF Membranes

Membrane	PVP ^a (wt%)	Water content (%)	Temperature ^b (°C)	Shrinkage ^b (%)
COPI	0	68	25	0
	4	70	50	0
	8	75	70	0
	12	78	90	<0.01

^aPVP added was wt% against polymer weight.

^bThe membrane was soaked in water bath with each temperature during 24 h before testing.

depended on the surface and the upper denser layer. Thus, the PWF was more influenced by the added amount of added PVP than the SR.

The efficacy of membrane filtration is strongly influenced by the membrane structure, which is mainly determined by the conditions of preparation. Solvent evaporation period and temperature before immersing in the coagulation bath are two of the most important factors influencing membrane structure. Several authors have studied the effect of solvent evaporation period and temperature on membrane characteristics.⁹⁻¹¹ In general, a longer evaporation period before soaking in the solidification bath results in an increased moiety of polymer in the nascent solution membrane, which results in a membrane structure of greater density.^{4,31,33} In Figure 4, the PWF gradually decreased in proportion to the evaporation period, and the SR slightly increased at first, and then becoming constant. The variation of the SR was within the range of experimental error. The results related to both the structure of the sieve-surface, that of the actual function-layer for separation, and that of the internal porous layer. While solvent in the casting solution-state was evaporated from the nascent solution membrane, the surface was first formed, and subsequently the formation of the supporting inner layer was determined by the solvent diffusion from the internal area to the surface of the membrane. The influence of the solvent evaporation period on membrane morphology suggested that the membrane prepared with a longer solvent evaporation period had a more dense and homogeneous inner structure.⁴ The volume fraction of polymer in the nascent solution state increased in proportion to the amount of evaporated solvent, which resulted in a membrane with a more dense structure. As mentioned earlier, the PWF was influenced by the denser upper layer as well as by the sub-layer, while the SR was mainly influenced by the functional surface. Consequently, the PWF was affected to a greater degree by the sol-

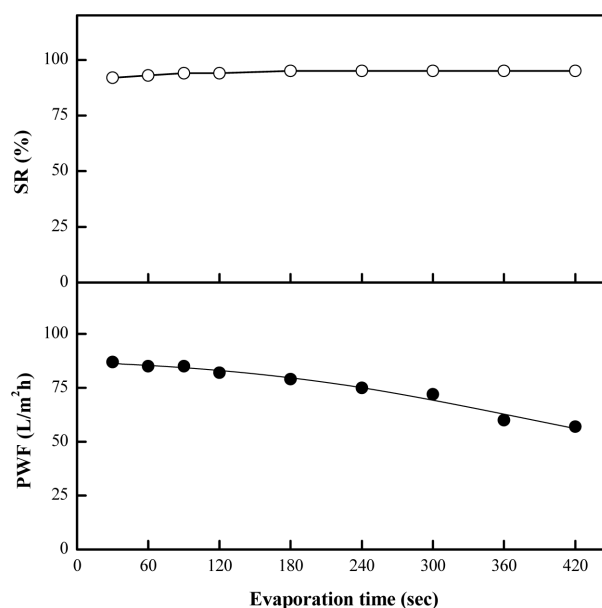


Figure 4. Effects of solvent evaporation period on the permeation properties of COPI UF membrane. The accuracy of PWF and SR was less than 2 L/m²h and 2%, respectively.

vent evaporation than by the SR.

As might be expected, evaporation temperature played an important role in the evaporation of solvent from the casting solution membrane.¹⁰ In order to study the relationship between the temperature during solvent evaporation and the resultant permeate properties of the membrane, the solvent was evaporated at temperatures ranging from 25 to 90 °C. As has been previously mentioned, the structure of the membrane was determined by the moiety of the polymer in the nascent solution membrane prior to phase inversion. The moiety of the polymer in the casting membrane was enhanced with greater solvent evaporation, and thus, a membrane with a more dense structure was formed. From Figure 5, it can be seen that both the SR and the PWF first remained at almost constant values, after which the PWF decreased a little and the SR increased slightly with increasing evaporation temperature. These behaviors were due to the fact that NMP that has low vapor pressure: 4 mmHg at 60 °C, and high boiling point: 204.3 °C.³² Below 90 °C, only a small amount of NMP was evaporated, as NMP has a relatively low vapor pressure. The influence of the solvent, having a high boiling temperature and a low vapor pressure, only affected the permeation properties of the membrane to a very small degree.

Figure 6 displays the relationship between the permeation properties and the solvent composition at different solvent evaporation temperatures. The solvent system also played an

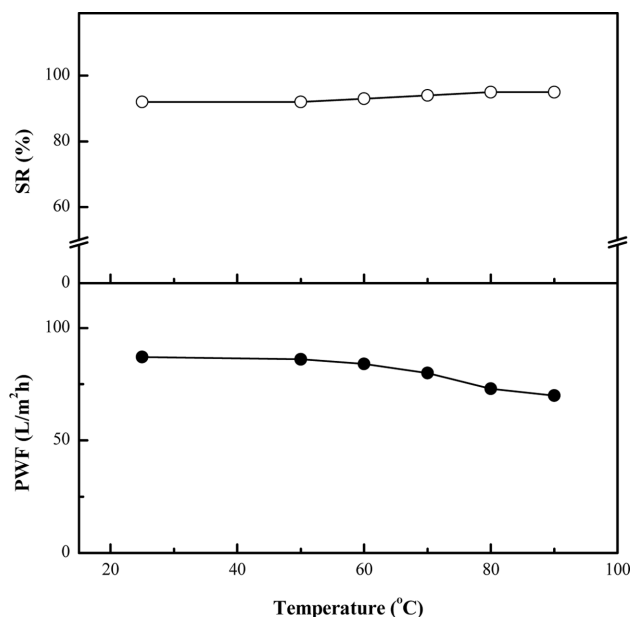


Figure 5. Effects of solvent evaporation temperature on the performance of COPI UF membrane. The accuracy of PWF and SR was less than 2 L/m²h and 2%, respectively.

important role in the determination of membrane properties.^{15,33} The rate of solvent evaporation from the nascent solution membrane influences the membrane properties. While solvent was evaporated from the surface of the casting membrane, the functional surface was first formed in the presence of solvent with a gradient concentration between the surface and the inner homogeneous solution state, and subsequently, the solvent diffused from the inner layer to the surface. The rate of diffusion was increased by increasing the gradient of solvent concentration, and hence, a more dense membrane was formed. In this study, dichloromethane (DCM, b.p: 39.6 °C, and vapor pressure: 352 mmHg at 20 °C) and ethanol (EtOH, b.p: 76 °C, and vapor pressure: 43.7 mmHg at 20 °C), with a relatively low boiling point compared to NMP, were introduced to the solvent system. Below boiling point, Figure 6 shows that the PWF declined and the SR slightly increased and became constant as the moiety of co-solvent in the solvent system enhanced. On the other hand, above boiling point, the PWF increased substantially, whereas the SR showed a significant decline. These results related to the amount of evaporated solvent and the evaporation rate of solvent in the casting solution membrane. In this solvent system, both the amount of evaporated solvent and the evaporation rate increased with increasing addition of DCM or EtOH as well as with increasing temperature. The evaporation of solvent led to dry phase inversion slightly at the surface of the casting solution mem-

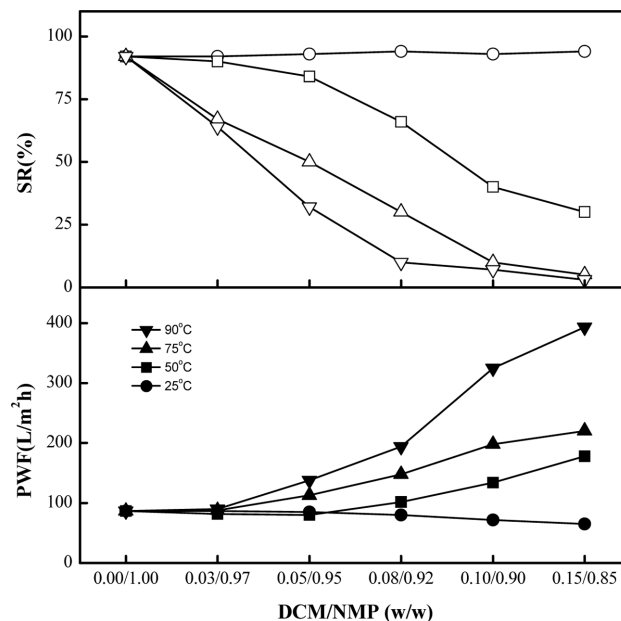


Figure 6-1. Effects of DCM/NMP solvent system on the performance of COPI UF membrane at different solvent evaporating temperature. The accuracy of PWF and SR was less than 2 L/m²h and 2%, respectively.

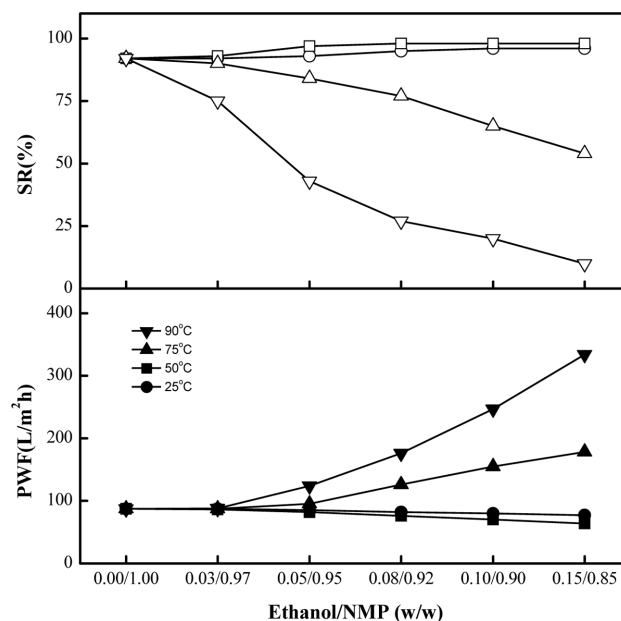


Figure 6-2. Effects of ethanol/NMP solvent system on the performance of COPI UF membrane at different solvent evaporating temperature. The accuracy of PWF and SR was less than 2 L/m²h and 2%, respectively.

brane, which had the greatest contact with air. The surface was weakly state. If the amount of evaporated solvent on the surface was less than that which migrated from the inner solution

state, the surface of the membrane, which was weakly solidified, obstructed solvent evaporation. Therefore, the surface became more unstable due to solvent diffusion from the interior of the membrane. As the moiety of solvent in the upper layer declined, the gradient of solvent concentration between the inner solution-state membrane and the surface was increased, and, consequently, the process of solvent diffusion to the surface was enhanced. These factors might induce a slight solidification of the sub-layer, lead to a greater aggregation of the polymer, and affect the overall structure of the membrane. The vigorous evaporation of co-solvents resulted in the generation of a membrane with an unstable surface as well as a porous sub-layer, as co-solvent rapidly migrated from the inner layer to the surface at above its b.p. From the results, the use of various solvents played an important role in determining the permeation properties of resultant membranes, and the relatively low b.p. of the co-solvent was strongly influenced by evaporation temperature.

In order to determine the thermal stability of the membrane during filtration, operating temperatures ranging from 25 to 90 °C were applied. The thermal property of membrane was mainly influenced by its polymer nature. Thermal stability was characterized based on SR and the relative flux. The relative flux (J_t/J_0) is the ratio of the permeate flux for a 1000 ppm PEG (MW 2.0×10^4) aqueous solution. Before measuring at different temperatures, the membrane was stabilized for 60 min at each operating temperature. From Figure 7, it can be seen that the SR slightly increased and the PWF remained almost unchanged with increasing operating temperature. The variation of the permeation properties was caused by the enhanced activity of the feed solution at higher temperatures. The values were within the range of experimental error. As shows in Figure 8, the relative flux of the PEG aqueous solution remarkably reduced during continuous filtration, and the rate of reduced that was slow down in proportion to the operating temperature, while under constant pressure. The relative flux was increased from 0.19 to 0.55 with increasing temperature from 25 to 90 °C at 240 min. When constant pressure was applied as a driving force, the permeation rate of solution, containing macromolecules through the membrane generally diminished throughout the operational period. This behavior was related to the concentration polarization of the solute as well as the fouling, irreversible absorption, on the surface of the membrane. Both the concentration polarization and the fouling contributed to congregation and/or irreversible absorption of macromolecules on the surface of the membrane. In

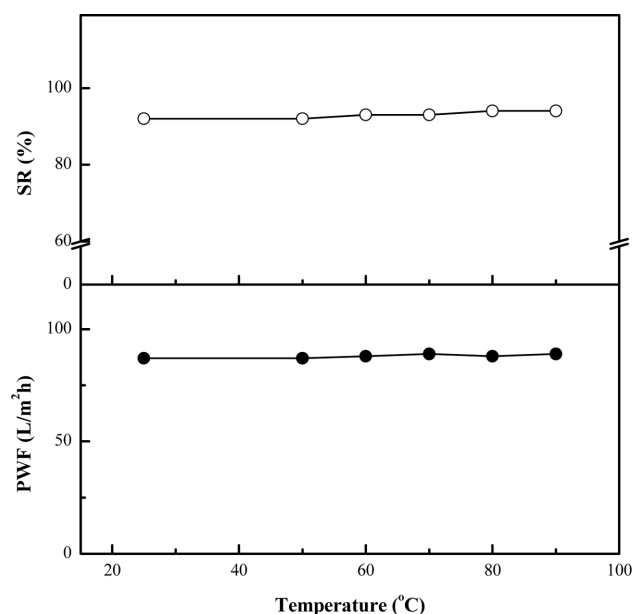


Figure 7. Effects of operation temperature on the performance of COPI UF membrane. The accuracy of PWF and SR was less than 2 L/m²h and 2%, respectively.

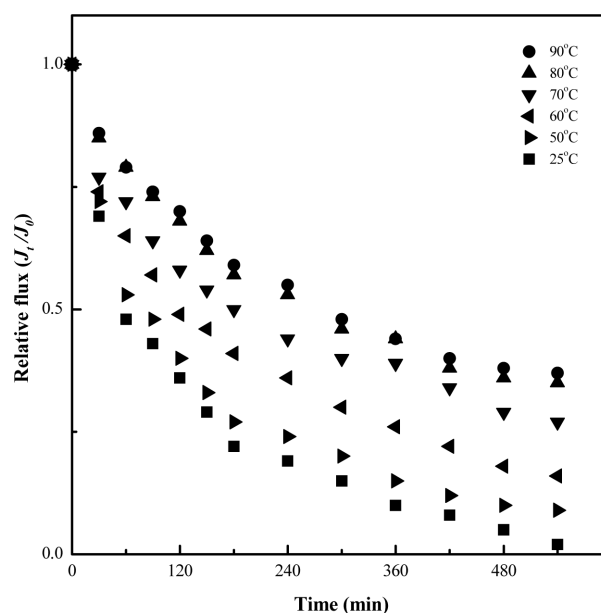


Figure 8. Relative flux *versus* operating period at the different temperature.

generally, the viscosity of the solution decrease and the activity of solute in solution has a tendency to increase in proportion to increasing temperature. Thus, the more that concentration polarization and fouling were reduced, the higher the relative flux became. As shown in Table 2, the area of COPI membranes nearly unchanged. From observations of the permeation behavior and the shrinkage at different temperatures, the oper-

ating temperature is likely a substantial influence on the permeation properties, and the COPI membranes were determined to have good thermal stabilities.

Conclusions

COPI was synthesized using one-step imidization process, and it exhibited outstanding thermal stability. COPI dissolved well in a number of aprotic polar solvents, resulting in a simplification of the membrane fabrication process. COPI UF membranes were made using a conventional phase inversion method. Factors, which influence the membrane properties, were investigated. The SR was enhanced, but the PWF was diminished with increasing polymer content in the casting solution. Increased PVP additive resulted in a higher PWF and a lower SR. The composition of the solvent system as well as the solvent evaporation period and evaporation temperature also played important roles in determining the permeability of the resultant membrane. The co-solvent, having a relatively low b.p., is more sensitive to solvent evaporation temperature than NMP with a high b.p. Both the PWF and the SR had almost the same value at different operation temperatures. While, the relative flux of the PEG aqueous solution was gradually increased from 0.15 to 0.55 in proportion to the filtrating temperature from 25 to 90 °C. The area of the membrane unchanged according to different treatment temperatures in the water bath. The operating conditions and stability of the membrane were most strongly attributed to the nature of the membrane materials.

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