Synthesis and Characterization of Copoly(amide-imide) Derivatives and Ultrafiltration Membrane Performances II
- Permeation Properties of Copoly(amide-imide)s Ultrafiltration Membranes -

Jong-young Jeon and Jong-ho Kim

Department of Textile Engineering, Sangju National University, Sangju, Kyungbuk 711-742, Korea

Abstract : Ultrafiltration membranes base on copoly(amide-imide) derivatives were prepared by the phase inversion method and the factors determining the permeation characteristics of membrane were investigated. The permeation behavior was observed by the relative ratio of permeate flux (J_t)/pure water flux (J_0). The characteristics through membrane were measured using aqueous solution of poly(ethyleneglycol) (MW 2.0×10^4) over a temperature range of $10 \sim 90°C$. With increasing the operating temperature, the relative ratio of flux became high. All the membranes had good chemical stability. Copoly(amide-imide) membranes having various permeation properties could be obtained. Further, it was proved that the membrane performances could be determined from the preparation conditions as well as various operating conditions.

1. Introduction

Membrane processes have been represented one of the most effective and energy-saving means to the wide range of applications and are still growing [1-4]. The performances of the membrane processes for any specified application are dependent on the structure of membrane as well as the chemical natures of the membrane materials [5-8]. The structure mainly depends on the preparation conditions, such as composition of casting mixture, casting condition, and so on. The relationships between the structure and the preparation conditions have been studied. The chemical properties of the membrane materials relate to the chemical structure of polymers. The polymer suitable as membrane materials is necessary for the successful application of membrane technology in the specified area and much research has been done on new materials [5,8,9]. The polymers used for ultrafiltration (UF) membranes such as polysulfone, polyethersulfide, polyamide, poly(amide-imide), and so on were reported [10-12]. Among these polymers, copoly (amide-imide) derivatives have excellent thermal stability combined with good chemical stability and mechanical properties as well as good processibility [7,13].

The permeation properties of UF membranes made of copoly(amide-imide)s and the performance of the membrane according to the preparation and operating conditions are discussed in this paper.

[†] Author for all correspondences
(e-mail : jjy@sangju.ac.kr)

Table 1. Properties of Copoly(amide-imide) Derivatives[a]

Polymer	Viscosity (dL/g)	Tg (℃)	Strength (kg/mm²)	Elongation at break (%)	Solubility in NMP
CPAI-1	1.45	240	7.2	11.5	+
CPAI-2	1.21	220	5.2	17.5	+
CPAI-3	0.87	205	5.4	15.0	+
CPAI-4	1.30	225	6.3	16.0	+
CPAI-5	1.24	210	6.0	12.0	+
CPAI-6	1.03	200	4.2	19.0	+
CPAI-7	1.57	270	7.5	11.0	+
CPAI-8	1.52	240	5.8	16.5	+
CPAI-9	1.09	230	6.0	15.0	+
CPAI-10	1.54	245	6.5	14.5	+
CPAI-11	1.27	230	7.0	11.0	+
CPAI-12	1.10	220	4.8	14.0	+

[a] Data were obtained from reference 13.

Experimental

Materials

The copoly(amide-imide) derivatives (CPAI, prepared according to previous paper[13]) were used as membrane materials. Their properties are summarized in Table 1. The polymer solution in NMP was press-filtrated, followed by precipitation in a large quantity of methanol, and dried under reduced pressure before use. Poly(vinylpyrrolidone) (PVP, MW 1×10^4, Aldrich Chemical Co.) and poly(ethyleneglycol) (PEG, MW 2.0×10^4, Aldrich Chemical Co.) were dried under reduced pressure before use. Other laboratory grade reagents were used without further purification.

Preparation of Membrane

The mixture, which consisted of polymer, solvents, and additive with the specific composition, was doped on a non-woven polypropylene fabric and followed by hand casting in a thermohydrostatic chamber. The casting speed was about 5 cm/s and the thickness was in the range of 150~300 μm. The solvent was evaporated before immersion into coagulating bath. The phase inversion was occurred by immersing the cast membrane into gelation bath at about 4℃ for 24 h, then the membrane was washed free of used solvent with water.

Membrane Performance

The membrane performance was determined by evaluating the flux and solute retention (SR). The experiment was conducted in a dead-ended stirred cell and the operating pressure was 1 kg/cm². They were calculated from the equations (1) and (2). The solute content was determined by using a high performance chromatography (Waters 410 C).

$$SR\ (\%) = (1 - C_p/C_f) \times 100 \tag{1}$$

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

$$Flux\ (L/m^2h) = \frac{Volume\ of\ permeated\ water\ (L)}{Effective\ area\ (m^2) \times time\ (t)} \tag{2}$$

The relative flux (RF) was obtained by using the equation (3) [14].

$$RF = J_t / J_0 \tag{3}$$

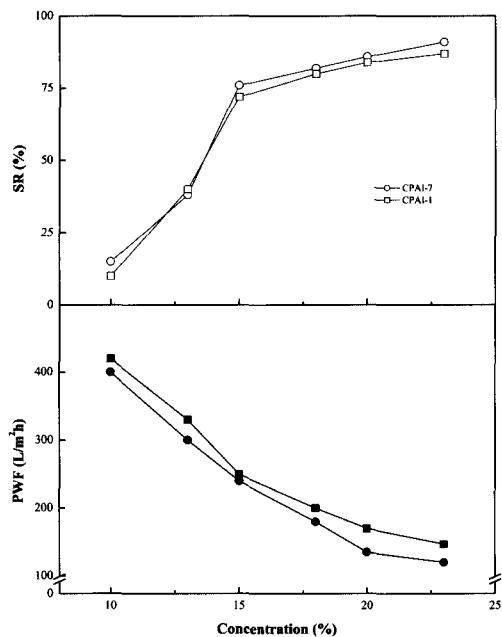where J_0 is the pure water flux and J_t is the permeate flux at a time t.

Fig. 1. The relationship between the permeation characteristics and the polymer concentration in dope solution.

Results and Discussion

Figure 1 shows the effect of polymer concen-

tration in dope solution on the performances of CPAI membrane and the permeation behaviors of CPAI membranes are summarized in Table 2. The membrane was prepared with different solid content ranging from 10 to 23%(w/w) in NMP. The concentration of polymer was made up the bases of the possibility of membrane formation and the permeation properties as UF membrane. When the membrane was prepared below 10%(w/w) polymer content in NMP, the result was not satisfactory and the membrane was unstable to hold its shape for continuous testing. From the result, the pure water flux (PWF) tended to decrease with increasing the content of polymer in NMP. On the other hand, the SR increased in proportion to the polymer concentration. The SR above 18%(w/w) was gradually increased and the value was to level off at a certain value. As the polymer content in the dope solution increased, the polymer density in the active upper layer became higher as well as a denser structure of support layer was formed [8,14]. It meant that the SR tended to increase, while the PWF decreased with increasing the density of the membrane. The variations of the performance diminished with the polymer concen

Table 2. Permeation Characteristics of CPAI Membranes with Different Polymer Content[a]

Membrane	PWF (L/m²h)					SR (%)[b]				
No	13	15	18	20	23	13	15	18	20	23
CPAI-1	330±10	250±10	200±5	170±5	145±5	<20	65±5	80±3	83±3	87±3
CPAI-2	360±10	270±10	210±5	175±5	160±5	<20	60±5	78±3	80±3	83±3
CPAI-3	400±10	290±10	230±5	190±5	180±5	<20	40±5	65±3	70±3	74±3
CPAI-4	320±10	250±10	205±5	185±5	155±5	<20	45±5	74±3	80±3	82±3
CPAI-5	340±10	270±10	210±5	180±5	160±5	<20	60±5	74±3	77±3	80±3
CPAI-6	340±10	290±10	210±5	190±5	175±5	<20	50±5	70±3	74±3	76±3
CPAI-7	310±10	240±10	180±5	135±5	120±5	<20	70±5	82±3	85±3	90±3
CPAI-8	320±10	240±10	190±5	165±5	140±5	<20	60±5	72±3	82±3	85±3
CPAI-9	350±10	270±10	200±5	165±5	150±5	<20	50±5	75±3	80±3	82±3
CPAI-10	320±10	220±10	190±5	145±5	130±5	<20	65±5	75±3	85±3	90±3
CPAI-11	360±10	260±10	195±5	160±5	135±5	<20	45±5	70±3	83±3	87±3
CPAI-12	390±10	270±10	210±5	170±5	150±5	<20	45±5	70±3	80±3	83±3

[a] Casting conditions: solvent, NMP; casting thickness, 200 μm; solvent evaporation time, 30s; solvent evaporation temperature, 25°C; RH, 65%.

[b] Feed solution: 1,000 ppm PEG (MW 2×10^4) aqueous solution.

Table 3. Permeation Properties of CPAI Membranes with Different Casting Thickness[a]

Thickness	PWF (L/m²h)		SR (%)[b]	
(μm)	CPAI-1	CPAI-7	CPAI-1	CPAI-7
150	230±5	220±5	74±3	75±3
200	200±5	180±5	80±3	82±3
250	155±5	130±5	83±3	85±3
300	110±5	110±5	87±3	90±3

[a] Casting conditions: solid content, 18%(w/w); solvent, NMP; solvent evaporation time, 30s; solvent evaporation temperature, 25°C; RH, 65%.
[b] Feed solution: 1,000 ppm PEG (MW $2×10^4$) aqueous solution.

tration in casting solution.

Table 3 represents the effect of casting thickness on the performances of CPAI membranes. The casting thickness mainly affected the physical structure of the support layer [14,15]. In proportion as casting thickness increased, the tortuosity in the membrane enlarged. Thus, the diffusion and permeability constants might be inversely proportional to the thickness. It was observed that as the casting thickness increased, the PWF through the membrane decreased, but the SR of PEG solution gradually increased. The SR of all the membranes varied between 74 and 90% for PEG (MW $2.0×10^4$). This behavior could relate to the fact that the SR was mainly influenced by the active upper layer of the membrane. On the other hand, the flux was dependent on the upper layer as well as the porous support layer. The variation of the flux was relatively larger than that of the SR. The casting thickness was selected at 200 μm for all further investigation.

The role of additive in the membrane formation was investigated. The amount of PVP (MW; 1.0 $×10^4$) as an additive was varied from 0 to 10.0%(w/w). PVP is hydrophilic in nature and has been used to change the formal structure of membrane [16-19]. The hydrophilic PVP in the membrane was dissolved and migrated out of the membrane during immersing in the coagulation bath and/or rinsing with flowing water. Therefore, the porosity of membrane increased. Figure 2 shows CPAI membrane performances with different amount of PVP in the casting solution. As the amount of additive in the casting solution
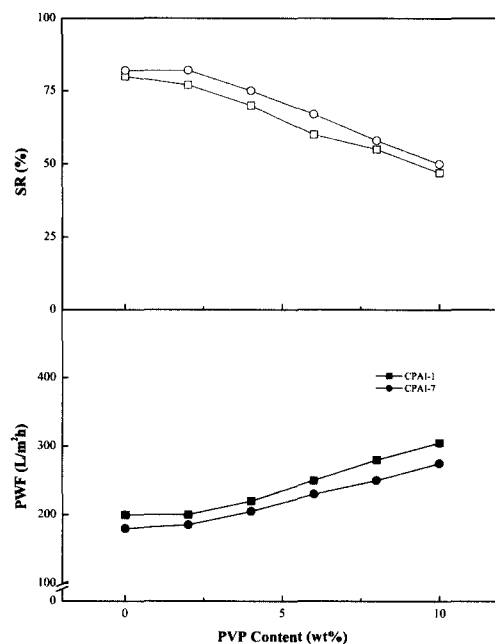

Fig. 2. The relationship between the permeation characteristics and the additive content in dope solution.

increased, the PWF increased, while the SR decreased. The variation of the SR was larger than that of the PWF. This result also related to the structure of the membrane. The SR was mainly dependent on the upper layer, where the pore size was probably enlarged by released additive in the layer. On the other hand, the flux was governed by the upper layer and the porous support that. In general, the support layer was less influenced by the additive as compared with the upper layer.

The relationship between the performance of

Table 4. The Relationship Between the Performance of Membrane and the Composition of Gelation Medium[a]

NMP/Water	PWF (L/m²h)		SR (%)[b]	
(wt ratio)	CPAI-1	CPAI-7	CPAI-1	CPAI-7
0/100	200±5	180±5	80±3	82±3
5/95	200±5	175±5	80±3	82±3
10/90	185±5	160±5	80±3	85±3
15/85	165±5	140±5	83±3	85±3
20/80	140±5	125±5	85±3	85±3
25/75	110±5	100±5	85±3	90±3
30/70	100±5	90±5	87±3	90±3

[a] Casting conditions: solid content, 18%(w/w); solvent, NMP; casting thickness, 200 μm; solvent evaporation time, 30s; solvent evaporation temperature, 25°C; RH, 65%.
[b] Feed solution: 1,000 ppm PEG (MW 2×10⁴) aqueous solution.

Table 5. The Relationship Between the Performance of Membrane and the Solvent Composition in Casting Mixture[a]

NMP/DCM	PWF (L/m²h)		SR (%)[b]	
(wt ratio)	CPAI-1	CPAI-7	CPAI-1	CPAI-7
82/0	200±5	180±5	80±3	82±3
77/5	160±5	130±5	85±3	90±3
72/10	110±5	85±5	95±3	> 95
67/15	90±5	70±5	> 95	> 97

[a] Casting conditions: solid content, 18%(w/w); casting thickness, 200 μm; solvent evaporation time, 30s; solvent evaporation temperature, 25°C; RH, 65%.
[b] Feed solution: 1,000 ppm PEG (MW 2×10⁴) aqueous solution.

membrane and the composition of gelation medium are represented in Table 4. It was observed that the SR slightly increased in proportion to the increase of the portion of NMP in a coagulation bath, while the flux gradually decreased with increasing the moiety of NMP. Above the composition ratio of 30/70(w/w) NMP/water, the results was not satisfactory and the procedure of phase inversion for forming membrane became very slow. This behavior related to the exchange rates of the solvent and non-solvent [1,5,19]. The exchange between the solvent and the non-solvent was occurred by the diffusion processes. Therefore, the rates of the solvent and the non-solvent through the membrane might be changed by the different composition of coagulating bath. The changed transfer rates could induce various structure of membrane because the rate of solvent exchange deter-

mined the procedure of a phase separation. As the portion of NMP in gelation bath increased, the rate of phase inversion was reduced and the membrane with denser support layer was probably formed. It was observed that the composition of coagulating bath played an important role in the formation of membrane structure.

Table 5 represents the influence of solvent composition on the membrane performance. The composition of solvent system in the casting solution played an important role in the structure of membrane [15,20]. As the amount of the evaporating solvent before phase separation increased, the density of polymer in the upper layer as well as porous layer might be increased. In this investigation, the solvent composed of NMP and volatile dichloromethane (DCM) as a co-solvent was used for leading to various structure of membrane. The flux decreased, while
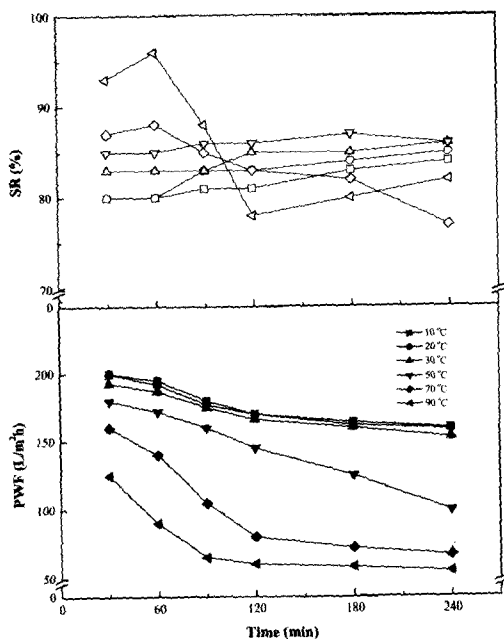
Fig. 3. The relationship between the permeation characteristics of CPAI-1 membrane and the solvent evaporating period at different temperature.

Fig. 4. The relative flux versus operating time of CPAI-1 membrane at different temperature.

the SR was gradually increased in proportion of DCM moiety. It was explained that as the amount of evaporating solvent in the nascent membrane increased, the gradient of solvent content between the surface layer and the inner layer induced higher. Therefore, the rate of solvent diffusion inside membrane to the surface of membrane was increased and the membrane with denser structure was made up.

CPAI-1 membrane was prepared at different evaporation periods in various temperatures and the results are represented in Figure 3. The membrane with shorter evaporation period became a more asymmetric structure, while that with longer evaporation time had compact and homo- geneous structure [5,15]. During the solvent evaporation, the active upper layer was formed in the first period. Then the structure of support layer was determined by the diffusing process of the solvent. The density of polymer in the membrane was governed by the solid content in casting solution and/or nascent membrane. The
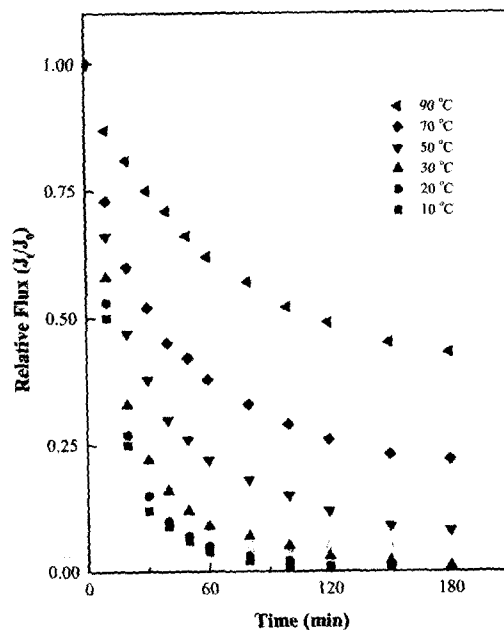
amount of evaporated solvent in the nascent membrane increased in proportion to evaporation time and temperature. Therefore, more dense membrane was induced. From the result, the flux through the membrane had a tendency to decrease but the SR gradually increased with increasing the evaporation period and temperature. Operation temperature also plays an important role for the performance of membrane. Figure 4 represents the relative flux of CPAI-1 membrane with different operation temperature. To observe the permeation behavior of the membrane, besides the PWF, the relative ratio of PWF and permeate flux was used. The permeation properties of the membrane were about PWF 200(L/m^{2}h) and SR 80(%) to PEG (MW 2×10^4). The flux at a constant pressure gradually reduced during the continuous filtration because of the formation of fouling and the concentration polarization on the surface of membrane [5,21,22]. The higher the value of the relative ratio, the better the antifouling in membrane. The relative flux for the PEG (MW 2×10^4) aqueous solution increased in proportion to the operating temperature. The

Table 6. Evaluation of Organic Solvent Resistance on PWF of CPAI Membranes[a]

Solvent[b]	PWF (L/m²h)					Remarks
	CPAI-1	CPAI-3	CPAI-6	CPAI-9	CPAI-12	
Water	200±5	200±5	200±5	200±5	200±5	
Acetic acid	200±5	200±5	200±5	200±5	200±5	
Benzene	200±5	200±5	200±5	200±5	200±5	
Chloroform	200±5	200±5	200±5	200±5	200±5	
EtOH	200±5	200±5	200±5	200±5	200±5	
MeOH	200±5	200±5	200±5	200±5	200±5	
pH 3-HCl$_{aq}$	200±5	195±5	200±5	195±5	195±5	
pH 11-NaOH$_{aq}$	205±5	210±5	200±5	205±5	205±5	
Py	–	–	–	–	–	swell
NMP	–	–	–	–	–	dissolve
DMAc	–	–	–	–	–	dissolve
DMSO	–	–	–	–	–	dissolve
H2SO4	–	–	–	–	–	dissolve
m-Cresol	–	–	–	–	–	dissolve

[a] The membranes were immersed in each solvent at room temperature for 48 h before testing.
[b] NMP, N-methyl-2-pyrrolidone; DMAc, N,N'-dimethylacetamide; DMSO, dimethylsulfoxide; Py, pyridine; EtOH, ethanol; MeOH, methanol.

behavior might relate to the solute activity and the viscosity of solute. The activity of PEG had a tendency to increase with increasing temperature, while the viscosity of solute decreased [5,23]. Therefore, both the dispersion of solute from the polarization layer and the absorption on the membrane surface might be influenced by the operating temperature.

The comparison between CPAI membranes treated organic solvents and their original membrane was investigated and the results are represented in Table 6. The permeation characteristics of the membranes were adjusted to about PWF 200(L/m²h) and SR 80(%) to PEG (MW 2×10⁴). The membrane was immersed in the various organic solvents, allowed to stand for 48 h, and then washed several times with deionized water to be free of solvent before observing the PWF of UF membrane. As showed result, the PWF of CPAI membrane treated common organic solvents was nearly unchanged. On the other hand, the membrane, which was immersed in some polar solvents such as NMP, DMAc, DMF, and so on, was unstable to hold its

surface shape and the permeation properties were drastically changed. The performance of membrane immersed in pH 11 NaOH and pH 3 HCl aqueous solutions was slightly changed, but there was within the limits of an error. Those results related to the membrane materials. The CPAIs as membrane materials have excellent thermal and high-temperature mechanical properties and favorable balance of physical and chemical properties [7,13]. The CPAI membranes could have the advantage for a processing and an enhanced applications of various areas.

Conclusions

The membranes using copoly(amide-imide)s as a membrane materials for UF membrane were prepared by the phase inversion methods. The membrane performances were governed by the differently prepared conditions and operating conditions. The prepared conditions played an important role in determining the physical structure of the membrane. The relative flux was increased with increasing operation temperature.

The temperature might influence the activity of solute and the viscosity of that. All the membranes showed good chemical stability to the common organic solvents. The CPAI membranes could have the advantage for a processing and an enhanced applications of various areas because of the following characteristics; (1) good thermal and chemical stability because the CPAIs as membrane materials are an outstanding thermal and chemical stable polymer; (2) easy membrane formation having various structures because the membrane materials dissolve well in some polar solvents and the structure is governed by prepared conditions.

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