

## 아닐링된 폴리아크릴로니트릴 나노막의 성능

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### Performance of Annealed Polyacrylonitrile Nanofiltration Membrane

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**요 약:** 통합형 비대칭 폴리아크릴로니트릴(PAN) 한외여과막의 기공크기를 줄이기 위하여 아닐링을 하였다. 두 종류 PAN 고분자(단일중합체와 공중합체)의 화학적 구조가 아닐링에 미치는 영향을 조사하였다. PAN 고분자의 아닐링은 고분자의 화학적 구조에 큰 영향을 받는다. 공중합체가 단일중합체에 비해서 덜 강직한 구조를 지니므로 아닐링에 훨씬 큰 영향을 받는다. 아닐링을 실시하기 전에 고분자 내에 잔존하는 용매의 완벽한 제거를 위하여 분리막을 물 속에서 예열 처리하였다. 예열처리를 하지 않은 경우가 아닐링 효과가 더 컸다. 높은 온도에서 아닐링 하기 전에 예열을 하면 기공크기의 증가를 가져 왔다. 막의 표면은 약간 음전하를 띠었고 PAN 나노막의 염배제율은 다음과 같은 순서로 측정되었다:  $R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) > R(\text{MgSO}_4) > R(\text{CaCl}_2)$ . Donnan 평형과 전기중성도에 의해서 염제거 거동을 설명하였다.

**Abstract:** The integrally skinned asymmetric PAN ultrafiltration membranes were annealed for reducing the pore size. The effect of the chemical structure of two PAN polymers (homo- and copolymer) on annealing was investigated. The annealing of PAN polymer was strongly affected by the chemical structure of the polymer. In other words, the annealing effect of the copolymer was much larger than that of the homopolymer due to its less rigid structure of the main chain. Before annealing, the membranes were usually preheated in water in terms of the complete removal of remained solvents in the membranes. The annealing effect was bigger when no preheating. However, the preheating of the membrane before annealing at high temperatures leads to an increase in the pore size of membranes. The surface of the membranes was slightly negative and the salt rejection of PAN nanofiltration membrane was in the following order:  $R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) > R(\text{MgSO}_4) > R(\text{CaCl}_2)$ . This salt rejection behavior could be explained by the Donnan equilibrium and the electroneutrality

**Keywords:** annealing, polyacrylonitrile, copolymer, nanofiltration, Donnan equilibrium

### 1. Introduction

The phase inversion method, especially the immersion precipitation process has been used for the porous membrane preparation. In other words, a polymer solution containing polymer, solvent or another nonsolvent is immersed into a coagulation bath[1-3]. Many polymers such as polysulfone, cellulose acetate (CA), and poly-

acrylonitrile (PAN) soluble in solvents can be applied in this process. The pore size of these membranes can be reduced by several methods. The Changes of casting conditions[4-5], polymer solution compositions[6-8] and coagulation bath compositions[9] are good examples to controll the pore size. Among them, the addition of a second solvent in the casting solution is an effective way. Actually, we could succeed in reducing the pore size of the polyetherimide membrane significantly by adding nonsolvents or cosolvents such as 1,4-dioxane,

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diethylene glycol dimethyl ether, and acetic acid in the casting solution[10-12].

PAN is one of the versatile polymers because of its good solvent resistance. However, in case of PAN membranes, the addition of a second nonsolvent in the PAN solution has a limit to reduce the pore size due to poor solubility of PAN[13].

PAN membranes can be significantly shrunk by the annealing method[13]. The annealing method was first used for the preparation of the CA reverse osmosis membranes. The membrane was annealed at around glass transition temperature[14].

Many researchers have investigated the salt rejection behavior of various nanofiltration membranes with different charges in terms of the Donnan exclusion and the size exclusion[15-18]. The surfaces of the used membranes are highly charged or amphiphilic. Moreover, the membranes are nonporous. Therefore, the salt rejection rate of the membranes is dominantly explained by the Donnan exclusion theory. Our membranes are porous and moderately charged. It is important to explain the salt rejection rate of these membranes.

In this article, we compared the possibility of the annealing process of homopolymer and copolymer. Moreover, the salt rejection behavior of annealed PAN membrane was investigated.

## 2. Experimental

### 2.1. Materials

Two polyacrylonitrile polymers were supplied from Han-il (H-PAN, Korea) and Tae-kwang (C-PAN, Korea) and used as membrane materials. The polymers were dried for three days at 60°C. N-methyl-2-pyrrolidone (NMP, Aldrich) was used as a solvent. Deionized (DI) water was used as a coagulation media. All the chemicals were used without further purification.

### 2.2. Polymer Characterization

Fourier-transform Infrared (FTIR) spectrum of PAN was recorded using a MIDAC model M2000, over a frequency range of 4000~400  $\text{cm}^{-1}$ . DSC (DSC 2910)

was conducted under nitrogen at a heating rate of 20°C/min. All DSCs were run twice and the second run was taken for data.

### 2.3. Membrane Preparation

15 and 18 wt% of PAN were dissolved in NMP at 60°C while stirring. Air bubbles in the casting solution were removed by use of an ultrasonicator and then, the casting solution was kept at room temperature for at least 24 hr. The casting solution was cast on a polyester non-woven fabric with a doctor knife having 200  $\mu\text{m}$  thickness. The nascent membrane was immersed in a DI water coagulation bath within 10 sec. After the immersion, the remaining solvents were removed by keeping them in tap water for at least 24 hr.

The PAN membrane was annealed in boiling water (70~96°C). The annealed membrane was soaked in water at the room temperature. In order to investigate the effect of preheating on membrane performance before annealing, the membrane was preheated at relatively low temperature (40~70°C). And then, the preheated membrane was annealed at high temperature (96°C).

### 2.4. Zeta Potential Measurements

Surface zeta potentials of membranes were measured by using a zeta-potentiometer (electrophoretic method, Otsuka). The concentration of the electrolyte solution was 0.01 M NaCl at pH 7.0.

### 2.5. Membrane Performance Measurement

The PEG 600 solution flux was measured at 200 psi, 2.5 L/min of flow rate and 25°C. The solute rejection rate of PEG 600 was measured at the same condition as above. In order to investigate the salt rejection behavior, NaCl,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{Na}_2\text{SO}_4$  were used. The ionic strength of the salts was 0.017 M in pure water. The feed concentration was 1000 ppm in pure DI water. The permeated sample was collected to measure the permeate concentration. The concentration was measured by HPLC (Waters Co.) equipped with a refractometer.

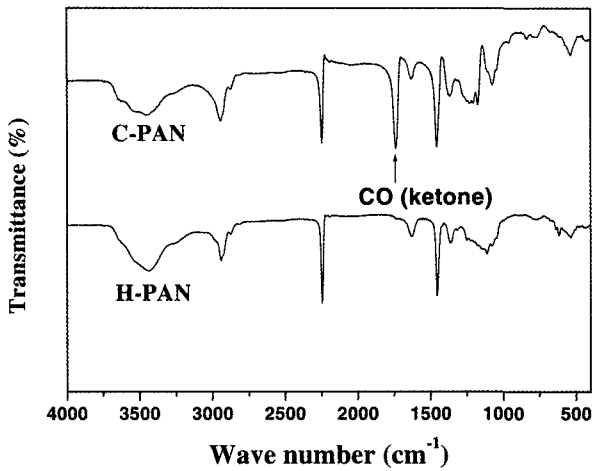


Fig. 1. FTIR spectra of PANs of homopolymer and copolymer.

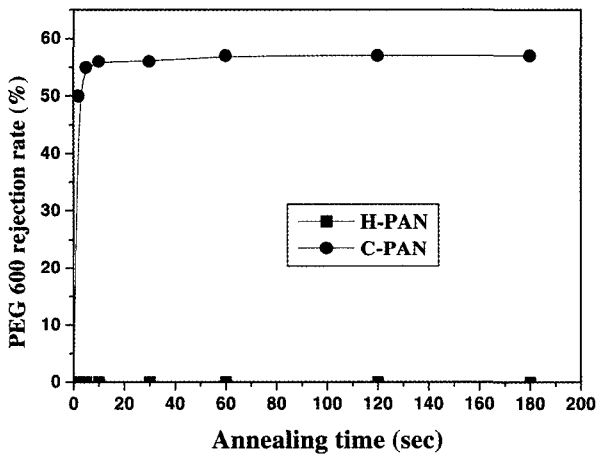


Fig. 2. Effect of annealing on membrane performance of homopolymer and copolymer.

### 3. Results and Discussion

#### 3.1. Effect of Annealing on Membrane Performance

Fig. 1 shows the FTIR spectra of two PAN polymers. As shown, the PAN from Han-il was homopolymer (H-PAN) and the PAN from Taekwang copolymer (C-PAN). The peak around  $1700\text{ cm}^{-1}$  indicates that the C-PAN has a group of acrylate. The Taekwang Company did not disclose the composition ratio of acrylonitrile and acrylate. Therefore, we could not confirm the structure of the C-PAN, except that the polymer contains the acrylate group.

Fig. 2 shows the effect of the annealing process on

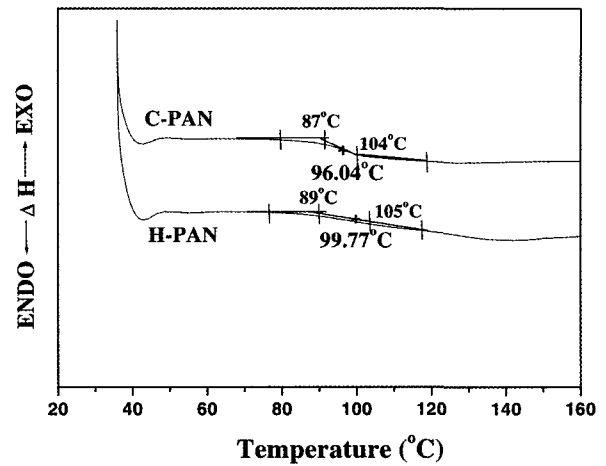


Fig. 3. DSC thermograms of homopolymer and copolymer.

two polymers at different temperatures. Even though the addition of a second solvent in the casting solution is a very effective way to reduce the pore size of the membrane, it was very difficult to reduce the pore size of the PAN membranes by adding a second solvent in the casting solution due to the limited solubility of the PAN polymer. Another post treatment such as the annealing process could significantly reduce the pore size. The effect of annealing on C-PAN (copolymer) was much larger than that on H-PAN (homopolymer). The annealed C-PAN membrane could reject small molecular PEG 600 up to 60%, while the annealed H-PAN could not reject PEG 600.

As shown in Fig. 3, the glass transition temperatures of the two PAN polymers were similar. We got  $100^\circ\text{C}$  and  $96^\circ\text{C}$  for H-PAN and the C-PAN, respectively.

In general, PAN molecules containing bulky polar cyanide (-CN) side groups can be hindered sterically and repulse each other during annealing around the glass transition temperature due to the polar character of the cyanide group. That makes the molecule rod-like and therefore PAN molecules can fit into a fairly regular crystalline structure. In other words, stereo-regular polar PAN polymers may pack slightly well. The shrinkage that takes place by annealing may be partially responsible for reduction in pore sizes. The fast coagulation of PAN in water makes the membrane very porous because polymer chains of the unannealed

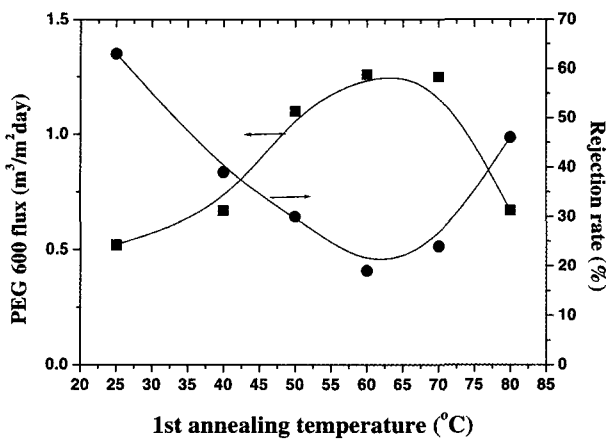


Fig. 4. Effect of preheating on annealing.

membrane are fixed in a form of very loose structure. However, by the thermal annealing process, the conformation of the polymer chains appears to be affected. The pore structure is rearranged and constricted.

The reason for the greater effect of the annealing on the C-PAN membrane than on the H-PAN membrane can be seen in the chemical structure difference between the two polymers. The cyanide group of the H-PAN can restrict the free rotation of the main chain due to its rigid structure. In contrast, acrylate group of the C-PAN can rotate better than the cyanide group of the H-PAN. In other words, the results of the annealing can be affected by the chemical structure. The rigid cyanide group prevents the polymer molecules from fitting into a regular crystalline structure. By incorporation of less rigid groups like the acrylate group into a rigid polymer, the polymer chain may rearrange easily and fit into a regular crystalline structure due to the annealing process.

With an increase in the polymer concentration of the casting solution, the annealing effect (reduction in pore size) was observed at lower temperatures than for membranes prepared from low concentrated casting solution.

### 3.2. Effect of Preheating on Annealing

Fig. 4 shows the results of preheating at low temperature (40~80°C) before annealing. In order to increase the reduction in pore size, the membrane was

preheated at a low temperature (first annealing) before the actual annealing (second annealing) at a high temperature (96°C). By prereducing the pore size of the membrane in the first annealing step, the total annealing effect will be larger. However, unexpected results were revealed. As a result of annealing after preheating the membrane, the rejection rate of the membrane for PEG 600 was lowered. Without preheating the membrane the rejection rate of the membrane became higher after annealing. The preheated (first annealing) membrane will not change the pore size during the second annealing. The membrane will partially arrange in a crystalline structure in the preheating step, a further rearrangement into an even more regular structure in the annealing step is not possible. That is the reason why by preheating the rejection rate cannot be higher. With an increase in the preheating temperature up to 60°C, the phenomena were apparent. In other words, by increasing the preheating temperature, the rejection rate was lowered. With increasing the preheating temperature, a crystalline structure, which was set before the second annealing acts as a resistance against building of a crystalline structure in the second annealing. A preheating temperature above 60°C leads to a higher rejection rate during the second annealing. The first annealing can explain the result. By preheating at 70°C and 80°C, the annealing effect can be shown. However, the annealing effect on the rejection rate of PEG 600 was lower for the preheated membranes than for the membranes annealed without preheating. Once again, the reason may be explained by the presetting of the crystalline structure.

### 3.3. Salt Rejection Behavior

Table 1 shows the salt rejection data of various membranes with different surface zeta potential. The C-PAN membrane and the NTR-7410 are moderately negative. The polyamide TFC membrane is highly negative. The surface of the PVA membrane is neutral. Many researchers have investigated the salt rejection behavior of various nanofiltration membranes with different charges (negative, positive, and neutral). The

**Table 1.** Effect of Surface Charge on Salt Rejection Rate

Membrane	Zeta potential (mV) <sup>a</sup>	Salt rejection (%)				PEG 600 Rejection (%)
		NaCl	Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	CaCl <sub>2</sub>	
C-PAN	-26	34	73	27	2	65
TFC polyamide <sup>b</sup>	-67	8	99	93	2	93
PVA <sup>c</sup>	-5	20	93	78	36	93
NTR-7410 <sup>d</sup>	-42	12	29	5	3	0

<sup>a</sup> pH 7.0, 0.01 M NaCl<sup>b</sup> interfacially polymerized from piperazine (1%) and trimesoyl chloride (0.05%)<sup>c</sup> coated by poly(vinyl alcohol) of 0.05% and cross-linked by glutaraldehyde<sup>d</sup> coated with sulfonated polyethersulfone (Nitto Denko Company)

surfaces of the membranes are composed of a dense film. The salt rejection behavior of membranes with pores has not been reported yet. In addition, most of the membranes are highly ionic. Therefore, the Donnan equilibrium theory was dominantly used for understanding the salt rejection behavior. In case of the highly negative charged PA-TFC membrane, bivalent co-ions such as sulfate ions can be rejected more than monovalent anions such as chloride ions on the membrane surface. Due to the electroneutrality, a salt with divalent co-ions (Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>) can be rejected more than one with monovalent co-ions (NaCl and CaCl<sub>2</sub>). If the salt rejection behavior of Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> is compared, the Na<sub>2</sub>SO<sub>4</sub> can be rejected slightly better than the MgSO<sub>4</sub>. The divalent counter-ion (Mg) becomes richer than the monovalent counter ion (Na) near the membrane surface. Moreover, the diffusion coefficient of Na<sub>2</sub>SO<sub>4</sub> is higher than that of MgSO<sub>4</sub>. Despite of these facts, the difference of rejection rate between Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> is not large due to the significant repulsion of the divalent co-ion by the charge of the membrane surface. The Donnan equilibrium and the electroneutrality can also explain the lowest rejection rate of CaCl<sub>2</sub> due to the richness of divalent counter-ions (Ca) near the membrane surface.

In case of the neutral or the amphiphilic membrane, the rejection rate has not been explained by the Donnan equilibrium but by the diffusion coefficient. The rejection sequence of Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> and NaCl could be explained. However, considering also MgSO<sub>4</sub>, the explanation of rejection sequence by the diffusion

coefficient alone is not enough. As can be seen in Table 1. Although the diffusion coefficient of MgSO<sub>4</sub> is lower than that of Na<sub>2</sub>SO<sub>4</sub>, the rejection sequence is reversed. In terms of the diffusion coefficient and the size of the salts[16,17] the rejection rate of MgSO<sub>4</sub> is expected to be the highest. The reason for this phenomenon is not yet clear.

In case of a slightly negative charged membrane (C-PAN and NTR-7410), the effect of the Donnan equilibrium on the salt rejection becomes less. The sequence of salt rejection of Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> and NaCl of this membrane is the same as the one of the highly negative charged membrane. However, the rejection rate of MgSO<sub>4</sub> became less than that of Na<sub>2</sub>SO<sub>4</sub> and that of NaCl. This is due to a lower counter-ion charge for Na<sub>2</sub>SO<sub>4</sub> and for NaCl. The salts with a higher counter-ion charge like MgSO<sub>4</sub> and CaCl<sub>2</sub> are less retained. From the results, it seems that for slightly negative charged membrane the rejection rate is mainly determined by the counter-ion charge and the co-ion charge seems to be less important. Due to the possibility of less retained divalent co-ion because of the slight negative charged membrane, the divalent counter-ion becomes rich near the membrane surface. Therefore, the concentration of counter-ions of the membranes surface seems to determine the rejection rate of salts.

#### 4. Conclusions

The annealing process could prepare the integrally skinned asymmetric polyacrylonitrile (PAN) membranes

with small pore size. Even though the glass transition temperature and the molecular weight of two polymers (homo- and copolymer) were similar, the effect of annealing on the copolymer was much larger than on the homopolymer due to the more flexible structure of the copolymer. By annealing at high temperature without preheating at relatively low temperature, the pore size was significantly reduced. However, preheating of the membrane before annealing at high temperature lead to a comparatively large pore size of the membrane. By preheating the membrane, the structure of the polymer cannot be affected during the second annealing. The surface of the membranes was slightly negative. The salt rejection was in the order:  $R(\text{Na}_2\text{SO}_4) > R(\text{NaCl}) > R(\text{MgSO}_4) > R(\text{CaCl}_2)$  despite of large size of hydrated  $\text{MgSO}_4$  and  $\text{CaCl}_2$  salts. The Donnan equilibrium and the electroneutrality could explain the salt rejection behavior.

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### References

1. M. Mulder, "Basic principles of Membrane Technology", Kluwer, London (1996).
2. K. Scott and R. Hughes, "Industrial Membrane Separation Technology", Chapman & Hall, London (1996).
3. R. E. Kesting, "Synthetic Polymeric Membranes", Wiley, NY (1985).
4. I. Pinnau and W. J. Koros, "A qualitative skin layer formation mechanism for membranes by dry/wet phase inversion", *J. Polym. Sci. Polym. Phys.*, **31**, 419 (1993).
5. H. Kawakami, M. Mikawa, and S. Nagaoka, "Gas permeability and selectivity through asymmetric polyimide membranes", *J. Appl. Polym. Sci.*, **62**, 965 (1996).
6. D. Wang, K. Li, W. K. Teo, D. Bo, and J. Kun, "Polyethersulfone hollow fiber gas separation membranes prepared from NMP/alcohol solvent systems", *J. Membrane Sci.*, **115**, 85 (1996).
7. H. Yanagishita, T. Nakane, and H. Yoshitome, "Selection criteria for solvent and gelation medium in the phase inversion process", *J. Membrane Sci.*, **89**, 215 (1994).
8. F. C. Lin, D. M. Wang, C. L. Lai, and J. Y. Lai, "Effect of surfactants on the structure of PMMA membranes", *J. Membrane Sci.*, **123**, 281 (1997).
9. P. Radovanovic, S. W. Thiel, and S. T. Hwang, "Formation of asymmetric polysulfone membranes by immersion precipitation. Part II. The effects of casting solution and gelation bath compositions on membrane structure and skin formation", *J. Membrane Sci.*, **65**, 231 (1992).
10. I.-C. Kim, K.-H. Lee, and T. M. Tak, "Preparation and characterization of integrally skinned uncharged polyetherimide asymmetric nanofiltration membrane", *J. Membrane Sci.*, **183**, 235 (2001).
11. I.-C. Kim, H. G. Yoon, and K.-H. Lee, "Formation of integrally skinned asymmetric polyetherimide nanofiltration membrane by phase inversion process", *J. Appl. Polym. Sci.*, **84**, 1300 (2002).
12. I.-C. Kim and T. M. Tak, "Synthesis of soluble anion-exchange copolyimides and nanofiltration membrane performances", *Macromolecules*, **33**, 2391 (2000).
13. I.-C. Kim, H. G. Yoon, and K.-H. Lee, "Preparation of asymmetric polyacrylonitrile membrane with small pore size by phase inversion and post-treatment process", *J. Membrane Sci.*, **199**, 75 (2002).
14. H. Strathmann, P. Scheible, and R. W. Baker, "A rationale for the preparation of Loeb-Sourirajan type cellulose acetate membrane", *J. Appl. Polym. Sci.*, **15**, 811 (1971).
15. J. M. M. Peeters, J. P. Boom, M. H. V. Mulder and H. Strathmann, "Retention measurements of nanofiltration membranes with electrolyte solutions",

- J. Membrane Sci.*, **145**, 199 (1998).
16. J. Schaep, B. Van der Bruggen, C. Vandecasteele, and D. Wilms, "Influence of ion size and charge in nanofiltration", *Sep. Purif. Technol.*, **14**, 155 (1998).
  17. X. L. Wang, T. Tsuru, S.-I. Nakao, and S. Kimura, "The electrostatic and steric-hindrance model for the transport of charged solutes through nanofiltration membranes", *J. Membrane Sci.*, **135**, 19 (1997).
  18. I.-C. Kim, H. G. Yoon, and K.-H. Lee, "Post treatment of asymmetric polyacrylonitrile membrane prepared by phase inversion", *International congress on membranes and membrane processes Supplementary book of abstracts*, 50 (2002).