일반강연 A-16

가용성 음이온, 양이온, 중성 공중합폴리이미드에 의한 통합형 나노막의 제조 및 특성평가

김인철, 이규호, 탁태문*
한국화학연구원 분리막다기능소재연구센터,
서울대학교 생물자원공학부*

Synthesis of integrally skinned nanofiltration membranes by soluble anionic, cationic and neutral copolyimides and its membrane performance

In-Chul Kim, Kew-Ho Lee, Tae-Moon Tak*
Membrane & Separation Research Center,
Korea Research Institute of Chemical Technology
Division of Biological resources and Materials Engineering,
Seoul National University*

1. Introduction

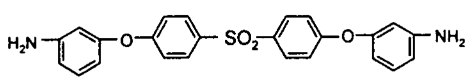
Aromatic polyimides are important engineering plastics due to their outstanding thermal stability, solvent resistance and mechanical properties. However, they have the drawback of poor solubility in organic solvents and being unprocessable.1-3 Polyimide membranes can be used in nanofiltration (NF) separation applications because of their outstanding chemical stability, their excellent strength and good thermal stability.4, 5 Commercially available polyamide composite NF membranes have good performance (high flux and rejection). However, the membranes are weak against chlorine and high pH. The coated materials of many NF membranes are unknown and difficult to correlate salt rejection with the surface material.

In order to have good performance for membrane application, hydrophilicity and charge property are important. In this study, polyimide membranes with different charges were prepared and compared with composite membranes of polyamide and poly(vinyl alcohol).

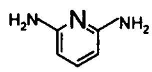
2. Experimental

A soluble polyimide from Bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-m) and pyromellitic dianhydride (PMDA) was prepared by the thermal two-step method. 4,4-oxyphthalic anhydride (ODPA) and 3,3,4,4-diphenylsulfone tetracarboxylic dianhydride (DSDA) were also used. Scheme 1 shows the molecular structures of the monomers.

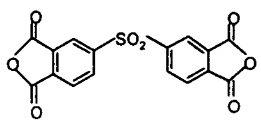
Scheme 1. Chemical structures of dianhydrides and diamines used in polymerization



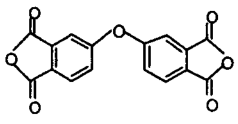
BAPS-m



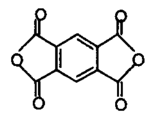
DAP



DSDA



ODPA



PMDA

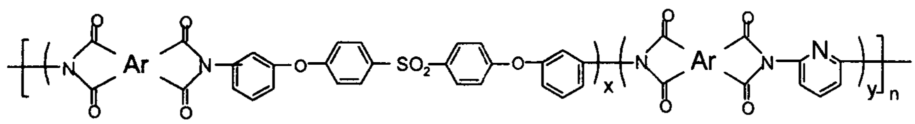
In order to synthesize anion-exchange copolyimides random copolyimides were firstly synthesized by using BAPA-m, diaminopyridine and PMDA. The copolyimide was modified homogeneously by treating an epichlorohydrin at moderate temperature (80 ℃). A cation-exchange polyimide was synthesized by reacting homopolyimide heterogeneously with sulfur trioxide.

Integrally skinned nanofiltration (NF) membranes were prepared by the typical phase inversion method using NMP as a solvent and diethyleneglycol dimethylether (DGDE) as a nonsolvent. The permeation rate and solute rejection rate (PEG 600 and various salts) were measured. The performance of integrally skinned NF membranes was compared to the thin film composite polyamide and poly(vinyl alcohol) NF membranes.

3. Results and Discussion

The conditions to prepare soluble copolyimides were controlled by changing the diamine ratio. Table 1 shows conditions for soluble copolyimides. The ratio of BAPS-m and DAP at which the resulting copolyimides was varied depending on the kind of dianhydride. DSDA increased solubility of the copolyimides compared to that of ODPA and PMDA. This resulted in increasing IEC.

Table 1. Molecular structures and molar ratios of soluble random copolyimides



Code	Ar	x
PI-1-a	DSDA	0.75
PI-1-b	ODPA	0.83
PI-1-c	PMDA	0.88

Table 2 shows the IEC and degree of substitution (DS). From the definition of IEC and DS, the relationship between IEC and DS could be calculated. All copolyimides were soluble in polar solvents. All copolyimides showed amorphous patterns because of less efficient packing of the chains and less regular structures. The thermal behavior of the copolyimides was evaluated. The neutral polyimide showed good thermal property. However, modified polyimide was degraded at around 260C. Integrally skinned asymmetric NF membrane was prepared by phase inversion method using DGDE as a nonsolvent. The pure water flux was in the range 85 to 96 L/m^2hr at $20Kg/cm^2$. The molecular weight cut-off (MWCO) was poly(ethylene glycol) 600. Anion-exchange copolyimides showed better salt retention of $CaCl_2$ than Na_2SO_4. Neutral

Table 2. The relationship between ion-exchange capacity (IEC) and degree of substitution of soluble ion-exchange copolyimides

Code	IEC(meq/g)[a]	IEC(meq/g)[b]	DS[c]	DS[d]
PI-2-a[e]	0.33	0.365	0.226	0.25
PI-2-b	0.18	0.255	0.160	0.17
PI-2-c	0.18	0.201	0.107	0.12
PI-3-a[f]	0.18	-	0.14	-
PI-3-b	0.13	-	0.09	-
PI-3-c	0.22	-	0.14	-

[a]measured by Fisher and Kunin method; [b]predicted values when all of the pyridine rings are substituted. PI-2-a: IEC=1000 · DS/(754-278 · DS); [c]the following equation could be used for predicting DS with IEC values. PI-2-a: DS=(0.75 · 754+0.25 · 431) · IEC/(1000-45 · IEC); [d]DS values of the unmodified copolyimides.; [e]anion-exchange PI; [f]cation-exchange PI.

copolyimides showed better salt retention of Na_2SO_4 than NaCl. By using DSDA and ODPA dianhydrides instead of PMDA, a salt rejection could be increased due to higher IEC of DSDA or ODPA-based copolyimides. Hydrophilicity of modified membrane was increased. This resulted in higher flux. Figure 1 shows the rejection behavior of salts and PEG of different charged membranes. By using DGDE as a nonsolvent, a membrane has a dense skin and a porous sponge support structure. Figure 2 shows the SEM photographs of a membrane prepared by using DGDE in the casting solution.

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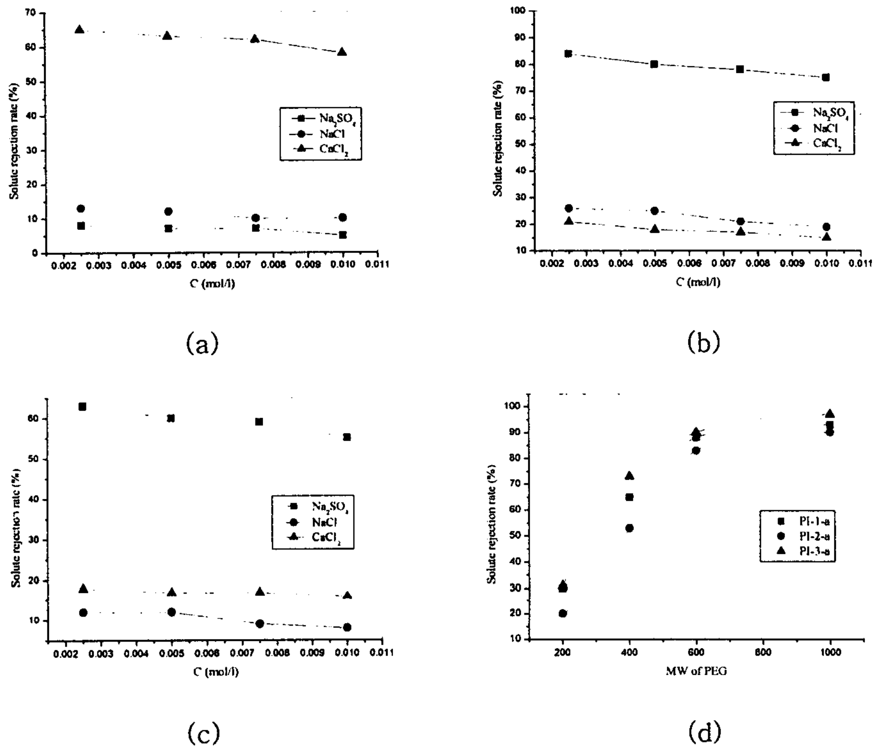

Figure 1. Retention rates of different salts (a-c) and PEG 600 (d) for various membranes. (a) cationic (b) anionic (c) neutral (d) PEG 600

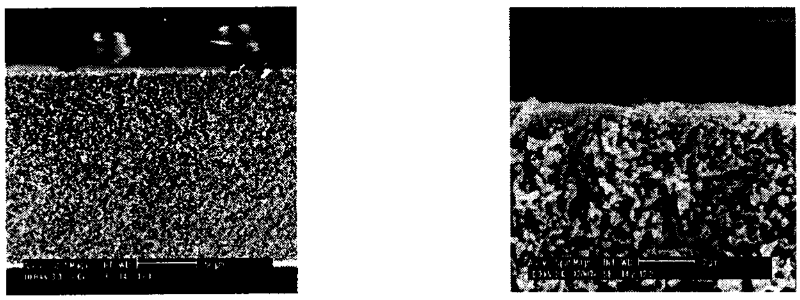

Figure 2. SEM photographs of a membrane prepared by using a DGDE as a nonsolvent