

표면 개질된 나노복합막의 투과 특성

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(2004년 8월 20일 접수, 2004년 9월 10일 채택)

Permeation Properties of Surface Modified Nanofiltration Membrane

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(Received August 20, 2004, Accepted September 10, 2004)

요약: 본 연구에서는 복합막의 제조공법으로 가장 광범위하게 쓰이는 계면중합법을 이용하여 나노복합막을 제조하였다. Monomer의 농도 및 조성, curing 조건, 후처리 조건과 같은 복합막 제조조건과, 운전압력, 공급액의 농도와 같은 운전 인자에 의한 막성능 변화를 조사하였고, 계면중합 과정에서 첨가제를 사용하여 막의 유효면적을 확대하여 투과유속을 증가시키고자 하였다. Monomer의 농도가 증가함에 따라 배제능은 일정하였지만 투과유속이 감소하였고, curing 온도가 증가함에 따라서는 오히려 안정적인 박막층의 형성이 저해되어서 배제능과 투과유속이 모두 감소하였고, curing 시간에 따른 막성능의 변화는 나타나지 않았다. Test solution의 농도가 올라감에 따라서 투과유속과 배제능 모두 감소하였으며, 운전압력이 증가함에 따라서는 배제능과 투과유속 모두 향상하는 경향을 보였다. 계면중합과정중에 사용하는 아민단량체 (amine monomer) 중 방향족 다이아민(aromatic amine)인 MPD의 함량을 높임에 따라서 배제능은 증가하였지만 투과유속은 현저하게 떨어졌다. 첨가제의 농도에 따른 표면 거칠기 증가 경향은 MPD가 포함된 amine 조성일 때가 더 높았지만 투과유속은 piperazine만 단독으로 사용하였을 때보다 떨어졌다.

Abstract: In this study, we prepared nanofiltration membrane by applying the interfacial polymerization method as a way of manufacturing composite membranes. We have examined the effects of various preparation factors such as monomer concentration and composition, thermal curing condition, post treatment condition. In addition to preparation conditions, we also monitored the effects of operation conditions such as feed solution concentration and operation pressure on the permeation properties of the resulting nanofiltration membrane. We intended to increase the permeation rate of nanofiltration membrane by the enlargement of effective surface area using additives during interfacial polymerization step. With increasing the monomer concentration, membrane permeation rate are decreased with maintaining almost constant rejection. With respect to curing condition, with increasing the curing temperature both permeation rate and rejection are decreased. With increasing the ratio of MPD in amine monomer composition, permeation rate decreased drastically with high rejection. With increasing the feed solution concentration, both permeation rate and rejection decreased. Both permeation rates and rejection increased with increasing the operating pressure. Nanofiltration membrane have higher surface roughness with increasing additive concentration in the case of using MPD contained amine composition than using piperazine alone. Permeation rates are much lower than the nanofiltration membrane prepared by piperazine.

Keywords: thin film composite membrane, interfacial polymerization polysulfone, nanofiltration, additive, surface roughness

1. Introduction

Membrane processes as a treatment alternative in the

water industry have drawn more attention. Membrane separation technologies are simple physical processes and have advantages such as susceptible system designation availability, easy to automate the processes. Especially, nanofiltration (NF) membranes can be em-

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ployed to produce high quality drinking water and to reclaim wastewater effluents. Nanofiltration membranes can separate various divalent ions and low molecular weight organic compound that the treated water can meet current and anticipated water quality requirements and standards. Comparing to conventional water treatment system, nanofiltration membranes have low economical cost in maintenance and operation the system.

Although membranes offer several advantages to conventional process, their most serious drawback is the pronsess to membrane fouling. Fouling can drastically reduce product flux, increase operation cost and eventually decrease membrane life. From these reasons, to develop fouling resistant and high permeation rates nanofiltration membranes is important to improve economical efficiency of nanofiltration equipments applied to drinking water treatment and wastewater effluents reclaim industry.

Permeation properties of the composite membranes depend on the characteristics of support and skin layer formation technologies. Ultrafiltration membranes used as supports need to have chemical stability and sufficient mechanical strength to maintain practical operation condition of nanofiltration equipment system and higher porosity to increase permeation rate of composite membrane. Additionally, to achieve higher separation performance, it is more important to modify properties of polyamide thin layer of NF membranes by controlling the interfacial polymerization conditions [1-4].

It is commonly believed that the nanofiltration membrane fouling intensity is affected by surface morphological characteristics and surface charge. Recently, surface charge is regarded as a main factor of membrane fouling. Polyamide nanofiltration membranes have anioic surface charge caused by residual reactant of interfacial polymerization. Therefore, in the case of existence of divalent ions in raw water, they act as salt-bridge to organic materials regarded as a major membrane foulant. Consequently, they make severe membrane fouling by attaching to membrane surface. It is need to decrease surface charge density of nanofiltration membrane. How-

ever, decreasing surface charge density of nanofiltration membrane may lower fouling intensity and susceptibility, it also decreases permeation rate due to lower hydrophilicity of nanofiltration membrane. In order to overcome these defects, we intended to enlarge effective surface area by means of the increase of surface roughness, prepared by using additives during interfacial polymerization[5]. Previous studies shown that increase of surface roughness may usually increase the membrane fouling tendency in the case of the experiment using colloidal substances as a feed solution. However, recent studies have proposed that surface charge density affects membrane fouling mainly rather than surface roughness[6,7]. Therefore, we could confirm that surface roughness is not a main factor of composite membrane fouling.

In this study, we have examined the basis characteristics and permeation properties of nanofiltration membrane prepared by interfacial polymerization using polysulfone ultrafiltration membranes as a substrate. Membrane performance variation was investigated in respect to monomer concentration, monomer composition, coating conditions, operation conditions and types of additive [8,9].

2. Experimental

2.1. Materials

Polysulfone ultrafiltration membrane with a molecular weight cut-off (MWCO) 100,000 was used as a support membrane for the preparation of nanofiltration membrane. A support was prepared by typical phase inversion method in laboratory scale. Polysulfone was broadly used as support for preparation of composite membrane because of its higher chemical, thermal and mechanical stabilities. Piperazine (PIP), m-phenylenediamine (MPD) and trimesoyl chloride (TMC) as monomers from Aldrich Co. (Milwaukee, WI) and triethyl amine as a catalyst, from Tokyo Kasei Co. (Tokyo, Japan), were used for interfacial polymerization of PA active layer. Isol-C (SK Chem.) was used as a organic solvent. Dimethyl sulfoxide (DMSO), 2-ethyl-1,3-hexanediol, *p*-

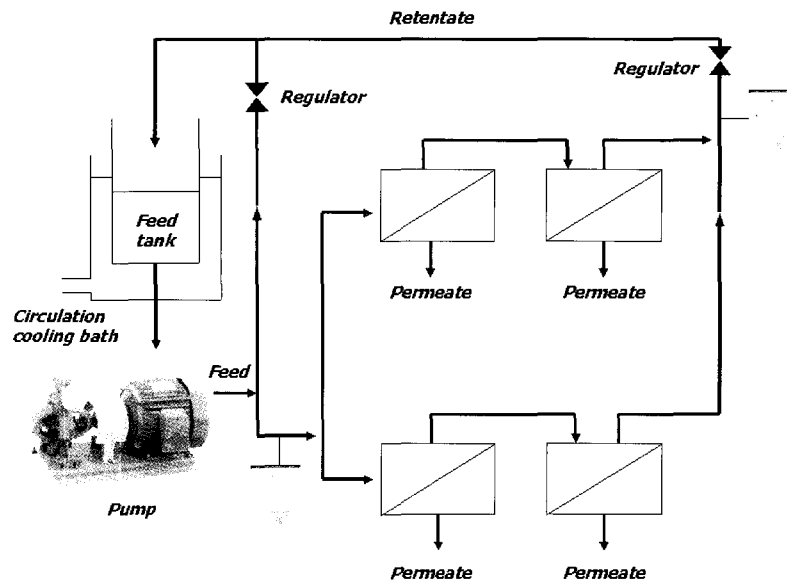


Fig. 1. Schematic diagram of membrane performance testing equipment.

toluenesulfonic acid monohydrate, camphour sulfonic acid from Aldrich Co. and diethylene glycol dimethyl ether, diethylene glycol hexyl ether from Jusei Co. were used as additives during interfacial polymerization. Poly(ethylene glycol) with a molecular weight of 600 g/mol, sodium chloride (NaCl) and magnesium sulfate ($MgSO_4$), bought from Daejung Co. were used as solutes of feed solutions. All chemicals and reagents were used as received from suppliers without further purification.

2.2. Preparation of the Nanofiltration PA Composite Membrane

Thin film composite nanofiltration membranes were prepared by the conventional interfacial polymerization of polyamide (PA) active thin layers on the surface of polysulfone support. Polysulfone supports were cleaned with deionized water, and then dipped into a amine monomer dissolved aqueous solution, in which TEA and other additives used as flux enhancing agent also dissolved, for 40 sec. To remove the excess amount of the aqueous solution, the surface of the supports were rolled with soft rubbery roller. After rolling, the supports were immersed in TMC solution in isoparaffin for 1 min for the interfacial polymerization of PA active layers. And then, it was dried in oven at an ele-

vated temperature to increase the stability of polymerized polyamide thin layer. Finally, membrane was dipped into the potassium carbonate solution as a post treatment to remove organic solvent residue existed on the membrane surface. The prepared polyamide composite membrane was kept in deionized water (DI) before membrane performance test.

2.3. Permeation Testing of Nanofiltration PA Composite Membrane

Typical NF test equipment was used for membrane performance estimation and the operating pressure was controlled from 125 to 325 psi. Membrane performance was determined by the broadly used method[14]. Fig. 1 shows schematic diagram of membrane performance testing system. The flux was evaluated from the weight of the permeate during some pre-determined period of time, and the rejection was calculated from the following equation, $\text{rejection (\%)} = 100 \times (C_f - C_p) / C_f$, where C_f and C_p represent the conductivity or concentration of the feed solution and permeate, respectively. To maintain constant temperature at 25°C during permeation testing, circulation cooling chiller was used and the feed solution cross flow velocity was maintained at 2.0 L/min. Conductivity was measured by conductivity me-

Table 1. Permeation Properties of Nanofiltration Membrane Prepared by Various Monomer Concentration

	2% + 0.1% (piperazine + TMC)		1% + 0.05% (piperazine + TMC)		0.5% + 0.025% (piperazine + TMC)	
	Before	After	Before	After	Before	After
Flux (LMH)	76.7	64.2	98.8	66.7	107.5	52.9
Rejection (%)	98.8	94.5	98.7	88.2	97.3	85.9
Flux reduction (%)	-19.4%		-48.1%		-203.1%	
Rejection reduction (%)	-4.6%		-11.9%		-13.2%	

Applied Pressure : 225 psi, Feed solution : 2000 ppm MgSO₄ aqueous solution

ter (ORION RESEARCH, Inc. model 115, U.S.A) and high-performance liquid chromatography (HPLC) equipment (Waters-410, Milford, MA, U.S.A) attached to a differential refractometer was used to determine the concentration of each solutions.

2.4. Characteristics of Nanofiltration PA Composite Membrane

A scanning electron microscopy (SEM, Jeol, JSM 5410V, Japan), was used to observe the surface morphological characteristics of PA nanofiltration membranes, the membrane was cryogenically fractured in liquid nitrogen and then coated with gold. With a atomic force microscopy (AFM, Park Science Instrument, Autoprobe CP, U.S.A), the AFM images of PA composite membrane were observed for the measurement of the correlation between membrane performance and surface roughness variation caused by using additives during interfacial polymerization. The AFM studies were conducted on a tapping mode. The detail AFM study techniques were given elsewhere and the root mean square roughness is the mean value of surface relative to the imaginary center plane[10,11].

3. Result and Discussion

3.1. Chemical Stability

Membrane fouling is serious drawback in most membrane processes. Therefore, it is inevitable to clean membrane periodically in order to maintain membrane performance. Membrane cleaning strategies can be classified as physical method such as back flushing,

rotating vibrational module and chemical method using cleaning agents such as sodium hypochloride, hydrochloric acid, and sodium hydroxide[12]. Though the latter has higher cleaning efficiency compared to the former, it is known to decrease membrane life cycle. Therefore, we prepared nanofiltration membranes with diverse piperazine and TMC concentration, and then examine the stabilities of nanofiltration membranes to chemical reagent used in membrane cleaning process. We compared the membrane performance after dipping the nanofiltration membrane in 0.2% sodium hydroxide solution for 7 days. As shown in Table. 1, nanofiltration membrane prepared from higher monomer concentration composition exhibits lower permeation flux and higher rejection compared to those prepared from lower monomer concentration composition. Permeation flux decreases because more denser polyamide thin layer formed with the increase of monomer concentration. In the case of piperazine, more monomer could take part in interfacial polymerization reaction owing to the increase of diffusing monomer concentration to organic phase across the initially formed polyamide layer and in the case of trimesoyl chloride, higher monomer concentration enabled highly crosslinked network structure of thin layer. Membrane rejection increases because of higher surface charge density caused by higher monomer concentration.

Chemical stability of nanofiltration membrane is superior in the case of prepared by higher monomer concentration. All membranes show lower rejection and permeation flux after immersing in 0.2% sodium hydroxide solution for 7 days. This is contradictory result

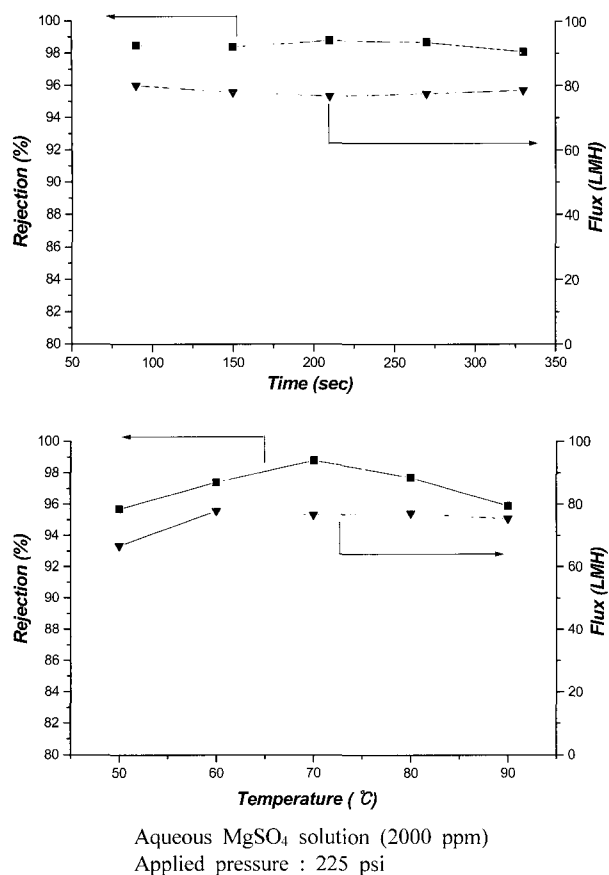


Fig. 2. Membrane performance as a function of different curing time and curing temperature.

comparing to typical trade-off relation between flux and rejection. Hydrolysis of amide linkage may loose the crosslinked network structure, as a result it decreases the solute rejection and membrane flux also decreased because of the pore blocking caused by a portion of hydrolyzed amide oligomers. We maintained monomer concentration constant at 2% piperazine and 0.1% trimesoyl chloride at further experiment because that composition represents superior chemical stability.

3.2. Effect of Coating Condition

Polyamide thin film prepared by interfacial polymerization reaction was stabilized through the thermal curing which enable to form crosslinked network structure[13]. As illustrated in Fig. 2, it shows that there was no significant variation in membrane performance in according to curing time. This is contradictory to

the result of A. Prakash *et al*[13]. They stated that the decrease of the curing time during interfacial polymerization increases the membrane flux with almost constant rejection due to the thickness reduction of the polyamide thin film layer. However, in this study isoparaffin was used as a organic solvent with high volatility, so the minimum curing time of 90 sec was regarded as sufficient time to stabilized the polyamide thin film. Consequently, there was no variation in membrane performance according to curing time because the polyamide chain form fully stabilized structure even at the short curing time.

Meanwhile, curing temperature affects significantly on membrane performance. We regarded the reasons of these results as follows. At first, below 70°C organic solvent residue caused by insufficient evaporation prevent the flow of feed solution to the membrane surface so decreased the membrane flux and loosely cross-linked network structure of polyamide thin film layer decreased rejection. In contrast, above 70 flux remains almost constantly and rejection decreased because the curing temperature was above the boiling point of organic solvent so evaporation was finished before polyamide thin layer had tightly crosslinked network structure[13]. Additionally, there was no change in thermal properties of polyamide layer in the curing temperature range, because the polyamide has sufficient thermal stability. Thus, the organic solvent used in interfacial polymerization can have a major effect on the membrane performance.

Post treatment was performed after curing step in order to remove organic solvent residue and non-reactive monomer existed on membrane surface. Fig. 3, represents the membrane performance variations according to different post treatment conditions. Membrane flux decreases due to prevention of feed water approach to membrane surface caused by residual barriers on membrane surface in case of no post treatment. However, there was no differences in membrane rejection because post treatment had no effect on chemical structure of polyamide layer. As increasing the concentration of potassium carbonate post treatment solution

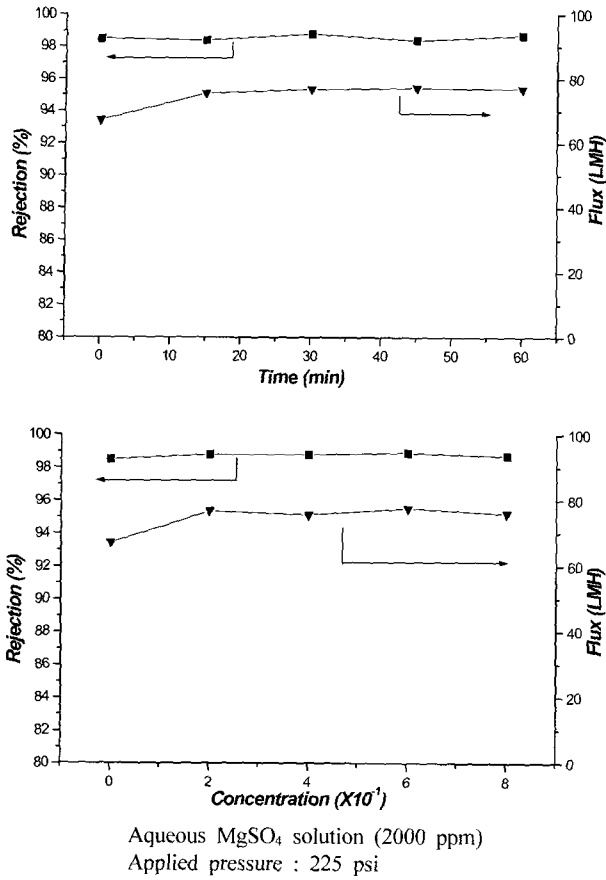


Fig. 3. Membrane performance as a function of different post treatment condition.

and treatment time, membrane performance maintains in whole applied experimental range. Thus, considering the efficiency of manufacturing process and economical cost, it is favorable to lower the post treatment concentration and treatment time at critical value.

3.3. Effect of Operation Condition

Membrane performance was evaluated according to operation factors such as operation pressure and feed concentration. Fig. 4, shows that at constant operation pressure 225 psi, with increasing the feed concentration, flux and rejection decrease simultaneously. Osmotic pressure, solution mole fraction, solution viscosity increase with feed concentration. Thus, with increasing the feed solution concentration, effective net pressure decreases by previously described factors such as increase of osmotic pressure, solution mole fraction and feed solu-

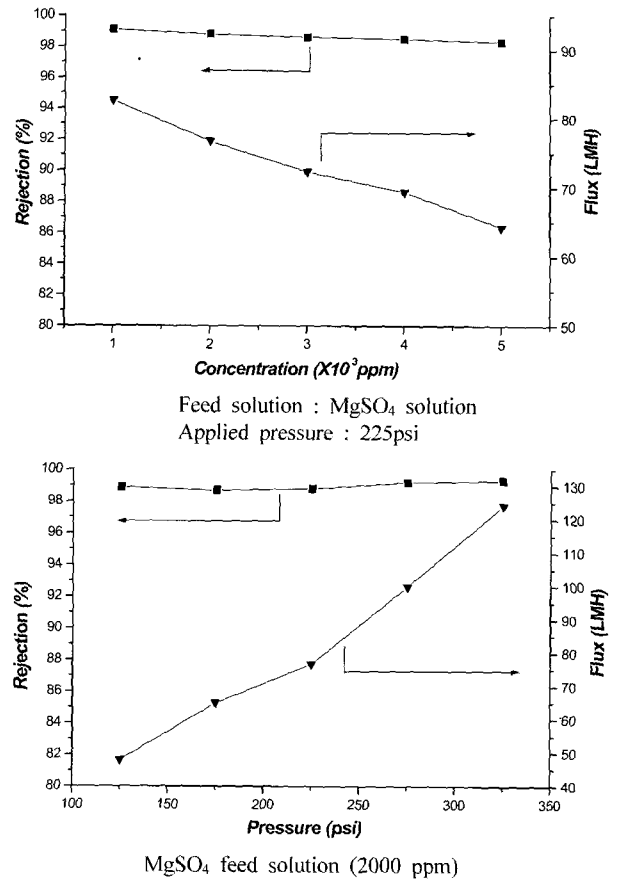


Fig. 4. Membrane performance as a function of operation condition.

tion viscosity at constant operation pressure so permeation flux decreases. Additionally, solute rejection slightly decreases due to increase of solute concentration on membrane surface[14].

With increasing operation pressure, both the membrane flux and rejection increase. Solvent flux is mainly affected by operation pressure so it increases in proportion to effective net pressure. Whereas, solute flux is independent on operation pressure, it rather relates to solute concentration on membrane surface. Dissolved solutes diffuse through the membrane by concentration gradient. With increasing operation pressure solvent pass through the membrane more than solute at constant feed concentration. As a result, rejection slightly decreases because permeate concentration relatively lower at higher operation pressure. Previous study also showed similar results when NaCl, Na_2SO_4 , $CaCl_2$ solution used

Table 2. Permeation Properties of Nanofiltration Membrane Prepared by Various Amine Monomer Composition

PIP	MPD	PEG 600		NaCl		MgSO ₄	
		Flux (LMH)	Rejection (%)	Flux (LMH)	Rejection (%)	Flux (LMH)	Rejection (%)
100	0	90.1	94.6	129.3	17	76.7	98.8
80	20	37.4	97.8	54.2	59	30.1	99.2
50	50	18.2	97.7	35.6	78	13.6	99.0
20	80	12.5	97.8	24.9	89	8.3	99.4
0	100	6.2	97.8	8.7	96	3.6	99.6

Applied Pressure: 225 psi, Feed solution concentration: 2000 ppm

Table 3. Permeation Properties of Nanofiltration Membrane Prepared with Various Additives

	EHD*		DGDE**		DGHE***		DMSO****		<i>p</i> -toluene sulfonic acid		Camphour sulfonic acid	
concentration (%)	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6	0.3	0.6
Flux (LMH)	84.2	95.8	78.8	84.3	112.9	145.8	87.5	100.4	87.1	98.3	96.3	101.7
Rejection (%)	96.7	92.3	96.6	95.4	86.7	48.1	94.6	91.8	98.5	98.7	98.6	98.7

Monomer composition: Piperazine (2%) + TMC (0.1%), Applied Pressure: 225 psi, Feed solution: 2000 ppm MgSO₄ aqueous solution EHD*; 2-ethyl-1,3-hexanediol, DGDE**; Diethylene glycol dimethyl ether, DGHE***; Diethylene glycol hexyl ether, DMSO****; Dimethyl sulfoxide

as feed of reverse osmosis membrane operation[15].

3.4. Effect of Amine Monomer Composition

As shown in Table 2 amine monomer composition has major influence on permeation properties of nanofiltration membrane. With increasing the ratio of piperazine in amine monomer solution, flux increases and rejection decreases drastically. Piperazine is more flexible monomer because of its aliphatic alkyl chain structure. Thus, it is suitable to form bigger size pore and make high free volume in polyamide layer. Comparing to MPD which has aromatic ring structure, piperazine has more flexible aliphatic (C-C) structure. Additionally, chair structure of piperazine prevent tight packing of polymer chain so that it provides higher free volume in polyamide layer[16]. These properties need to be considered in preparing nanofiltration membrane with enhanced flux. Namely, it is more favorable using piperazine in preparing higher flux nanofiltration membrane in order to maintain moderate rejection when using additives as flux enhancing agent during interfacial polymerization.

3.5. Effect of Various Additives on Membrane Properties

Membrane performance variation with additive spe-

cies was evaluated and its flux enhancing behavior according to amine monomer composition was also monitored. These additives are primarily used in preparing flux enhanced composite reverse osmosis membranes. However, reverse osmosis membranes mainly prepared by MPD as a amine monomer, so there were no previous results about effect of additives on piperazine based nanofiltration membrane. Thus, we tried to find additives suitable to apply the preparation of nanofiltration membrane by testing general additives used in preparation of reverse osmosis membrane.

In respect to membrane performance improvement, flux enhancement accompanied with rejection decline is unfavorable. Therefore, we evaluated membrane performance variation according to various additives by using them a small portion in amine monomer solution. Additives were dissolved in amine monomer solution during interfacial polymerization. As shown in Table 3 additives can be divided as an inappropriate ones for flux enhancing agents which enhance flux accompanied with serious rejection decrease, or suitable ones for flux enhancing agents which increase flux with maintaining moderate rejection. Therefore, as shown in Table 4 we observed membrane performance variations with increasing concentration of additives suitable for

Table 4. Permeation Properties of Nanofiltration Membrane Prepared with Various Additive Concentration

concentration (%)	<i>p</i> -toluenesulfonic acid						Camphoursulfonic acid					
	0.3	0.6	0.9	1.2	1.5	1.8	0.3	0.6	0.9	1.2	1.5	1.8
Flux (LMH)	87.1	98.3	106.7	111.7	142.1	183.9	96.3	101.7	111.7	121.7	122.5	127.1
Rejection (%)	98.5	98.7	98.4	94.8	89.7	82.1	98.5	98.7	98.9	98.6	98.2	96.4

monomer composition: Piperazine (2%) + TMC (0.1%), Applied Pressure: 225 psi, Feed solution: 2000 ppm MgSO₄ aqueous solution

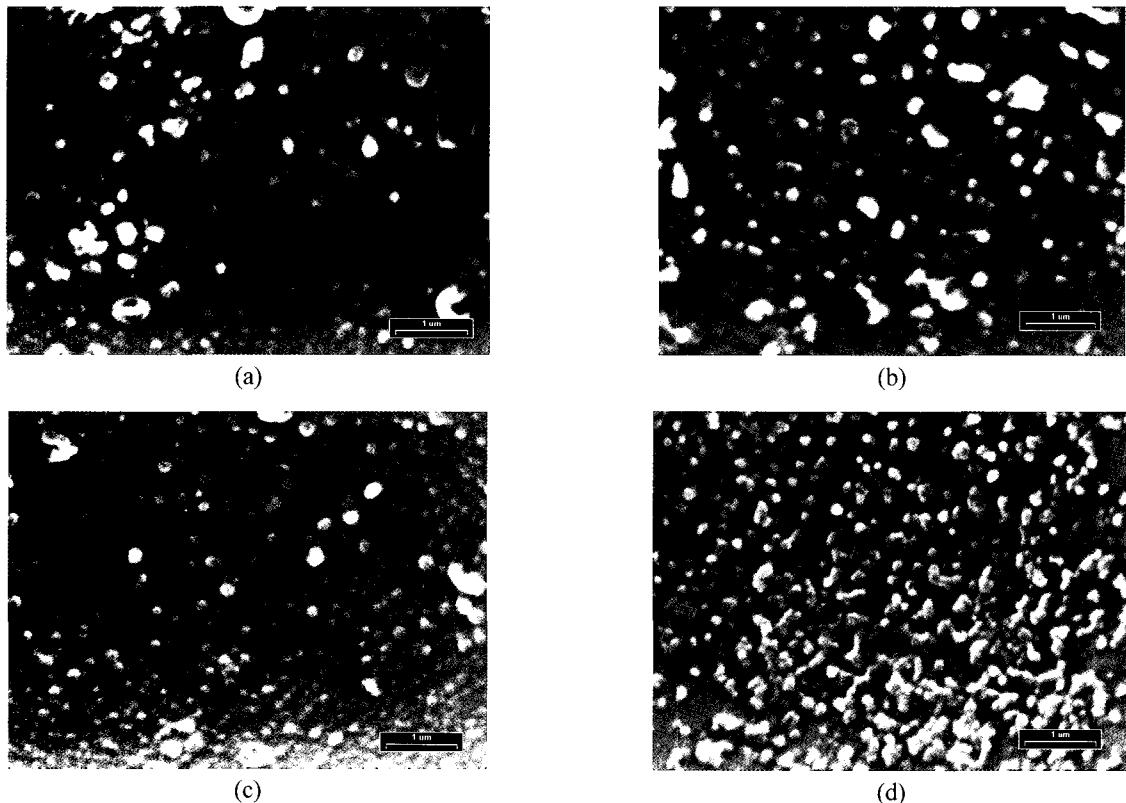


Fig. 5. SEM photographs of membrane surfaces prepared by interfacial reaction of piperazine and camphorsulfonic acid with TMC. (a) No additive (2% piperazine + 0.1% TMC), (b) Camphorsulfonic acid 0.6%, (c) Camphorsulfonic acid 1.2%, (d) Camphorsulfonic acid 1.8% (X20,000).

flux enhancing agents. In the case of *p*-toluenesulfonic acid, it maintains susceptible rejection above 97% till 0.9% additive concentration and at this point flux is 106.7 LMH. Whereas, in case of camphoursulfonic acid, it shows 98.2% rejection with 122.5 LMH flux at 1.5% additive concentration. We regarded 1.5% additive concentration as optimal point because rejection started to decrease with maintaining almost constant rejection above 1.5% additive concentration. As increasing additive concentration above the optimal point, additive prevents formation of defect free polyamide layer during interfacial polymerization. Namely, it acts as impurities

during thin layer forming interfacial polymerization. Therefore, we select camphoursulfonic acid as additive for preparation of piperazine base enhanced flux nanofiltration membrane. To investigate the correlations of membrane performance improvement with membrane surface characteristics, we have examined the surface properties of nanofiltration membrane prepared from various camphoursulfonic acid concentration.

As depicted in Fig. 5 membrane surface roughness increases with the concentration of camphorsulfonic acid used as the flux enhancing agent. We compare these surface characteristics change obtained by visual

Table 5. RMS Roughness of Membrane Prepared from Various Camphoursulfonic Acid Concentration

Additive concentraion (%)	No additive	0.3	0.6	0.9	1.2	1.5
RMS roughness (\AA)	157	197	220	303	514	649

monomer composition: Piperazine (2%) + additive + TMC (0.1%)

Table 6. Permeation Properties of Nanofiltration Membrane Prepared with Various Additive Concentration

concentraion (%)	No additive	Camphoursulfonic acid				
		0.3	0.6	0.9	1.2	1.5
Flux (LMH)	47.9	54.6	62.1	69.6	94.6	105.4
Rejection (%)	99.4	99.2	98.9	98.5	98.8	98.7

monomer composition: Piperazine + MPD (9:1) 2% + TMC 0.1%, Applied Pressure: 225 psi, Feed solution: 2000 ppm MgSO_4 aqueous solution

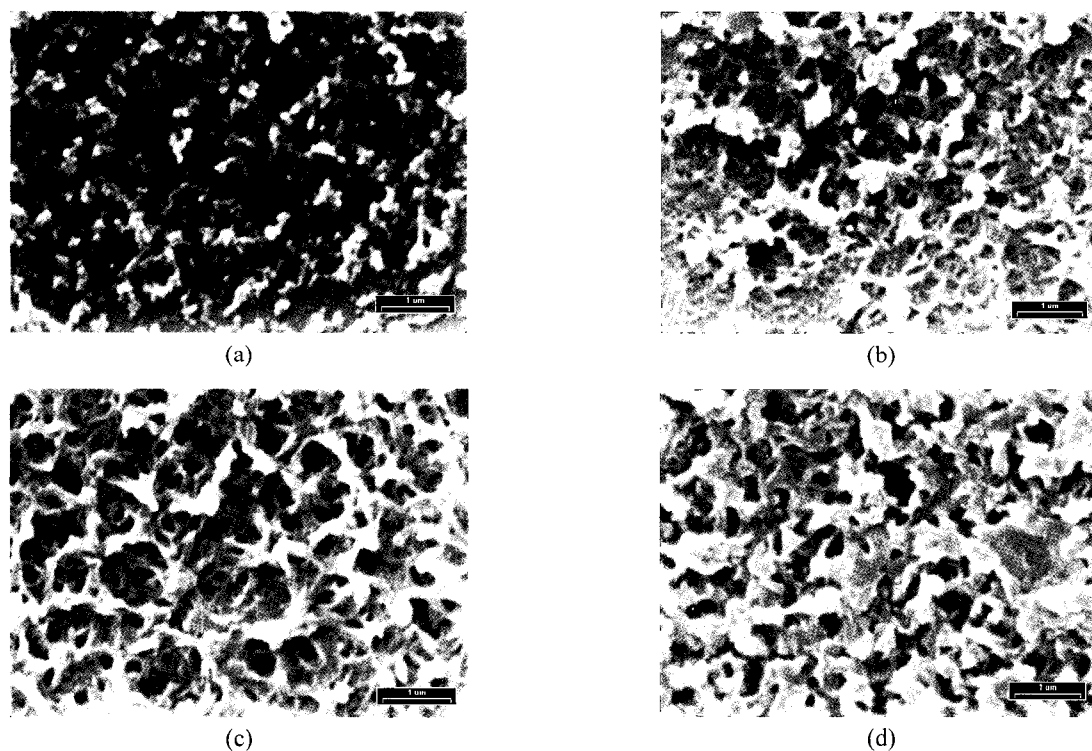


Fig. 6. SEM photographs of membrane surfaces prepared by different camphoursulfonic acid concentration monomer composition: Piperazine + MPD (9:1) 2% + TMC 0.1%. (a) No additive, (b) Camphoursulfonic acid 0.6%, (c) Camphoursulfonic acid 1.2%, (d) Camphoursulfonic acid 1.5% (X20,000).

SEM images with the surface roughness value measured from AFM images. As shown in Table 5 we could confirm numerically that membrane surface roughness increases with increasing the concentration of additive. Therefore, we can confirm that there is an evident relation between enlargement of effective membrane area and enhanced permeation flux.

3.6. Effect of Additive on Membrane Properties Prepared by Different Amine Monomer Composition

To investigate the effect of additive according to amine monomer composition, we established piperazine and MPD composition in the ratio of 9 to 1. And then we observe membrane performance and surface characteristics variation according to same experimental con-

Table 7. RMS Roughness of Membrane Prepared from Various Camphoursulfonic Acid Concentration

Additive concentraion (%)	No additive	0.3	0.6	0.9	1.2	1.5
RMS roughness (Å)	234	294	329	485	826	1024

Monomer composition: Piperazine: MPD (9:1) 2% + additive + TMC 0.1%

dition adopted to prepare higher flux piperazine base nanofiltration membrane. As shown in Table 2 with increasing the ratio of piperazine in amine monomer solution, flux increases and rejection decreases. Therefore, we use camphoursulfonic acid which verified as superior flux enhancing agent to prepare higher flux piperazine base nanofiltration membrane.

As shown in Table 6 in the case of using no additive, the flux decreases drastically with slight increase in rejection compared to piperazine based membrane. We can confirm this result from Table 2 which shows that amine monomer composition has major influence on permeation properties of nanofiltration membrane. According to SEM images of Fig. 6 and surface roughness from Table 7, nanofiltration membrane prepared from piperazine and MPD mixture has much higher surface roughness. However, the flux is much lower than piperazine-based membrane in spite of almost twice surface roughness. Namely, nanofiltration membrane have higher surface roughness with increasing additive concentration in the case of using MPD contained amine composition than using piperazine alone. Permeation rates are much lower than the nanofiltration membrane prepared by piperazine. The characteristics of MPD as a secondary amine affect more dominantly even at low content in amine monomer composition[17].

4. Conclusions

We prepared nanofiltration membrane by applying the interfacial polymerization method as a way of manufacturing composite membranes. We have examined the effects of various preparation factors and operation conditions. Both chemical stability and rejection increased as the concentration of monomer increased, however permeation rates decreased. As the ratio of

MPD increased in amine monomer solution, permeation rates decreased drastically with a slight increase of rejection. Membrane performance varies sensitively according to curing temperature. As the concentration of feed solution increased, both permeation rates and rejection decreased. Both permeation rates and rejection increased, as the operating pressure increased. Nanofiltration membranes have higher surface roughness with increasing additive concentration in the case of using MPD contained amine composition than using piperazine alone. Permeation rates are much lower than the nanofiltration membrane prepared from piperazine.

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