폴리비닐클로라이드-그래프트-폴리스티렌 술폰산 복합 나노막 제조

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Preparation of Poly(vinyl chloride)-graft-poly(styrene sulfonic acid) Composite Nanofiltration Membranes

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요 약: 폴리비닐리덴플로라이드(PVDF) 지지체 위에 빗살모양의 술폰화된 공중합체를 코팅하여 나노 분리막을 제조하였다. 빗살모양의 공중합체는 원자전달 라디칼 중합법(ATRP)에 의해 제조하였으며, 폴리비닐클로라이드의 주사슬과 폴리스티렌 술폰산(PSSA)의 곁사슬로 구성되어 있다. 핵자기 공명법(^{1}H-NMR), FT-IR 분광학 그리고 WAXS 분석법에 의해 공중합체가 성공적으로 합성되었음을 확인하였다. PVC-g-PSSA로 구성된 복합 나노 분리막은 PSSA의 함량이 증가함에 따라 플럭스와 배제율 모두 증가하였다. 이러한 성능 향상은 분리막의 술폰산의 함량의 증가로써 설명할 수 있다. PSSA가 71 wt% 첨가된 나노 복합막의 배제율은 Na$_2$SO$_4$ 88%, NaCl 33%을 나타내었고, 플럭스는 Na$_2$SO$_4$ 26, NaCl 34 L/m^2 h을 각각 나타내었다.

Abstract: Nanofiltration membranes were prepared based on coating a sulfonated comb-like copolymer layer on top of a poly(vinylidene fluoride) (PVDF) support. The comb-like copolymer comprising poly(vinyl chloride) backbone and poly(styrene sulfonic acid) side chains, i.e. PVC-g-PSSA was synthesized by atom transfer radical polymerization (ATRP) using direct initiation of the secondary chlorines of PVC. The successful synthesis of graft copolymers were confirmed by nuclear magnetic resonance (^{1}H-NMR), FT-IR spectroscopy and wide angle X-ray scattering (WAXS). Composite nanofiltration membranes consisting PVC-g-PSSA as a top layer exhibited the increase of both rejections and solution flux with increasing PSSA concentration. This performance enhancement is presumably due to the increase of SO$_3$H groups and membrane hydrophilicity. The rejections of composite membranes containing 71 wt% of PSSA were 88% for Na$_2$SO$_4$ and 33% for NaCl, and the solution flux were 26 and 34 L/m^2 h, respectively, at 0.3 MPa pressure.

1. Introduction

Nanofiltration (NF) membranes have become the most important recent advance in membranes technology due to their increasing demand in separation process. NF is also attractive because of their advantages, such as low operation pressure, high flux, high retention of multivalent anion salt and organic molecule above 300 g/mol,

and relatively low operation and maintenance cost [1-9]. The separation characteristics of the NF membrane lie between those of reverse osmosis (RO) and ultrafiltration (UF) membranes.

The most common type of NF membranes is thin film composite membrane, which is prepared by coating a charged polymer on top of a porous substrate. Negatively charged polymers containing sulfonic acid groups such as sulfonated poly(phthalazinone ether sul-

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fone ketone) (PPESK) [1,2,5,6], poly(phenylene oxide) [3], poly(2,6-dimethyl-1,4-phenylene oxide) [4] are representative membrane materials for NF membranes. NF membranes have a looser skin layer structure enabling higher fluxes and lower operating pressures than RO membranes. Donnan effect is known to be responsible for a difference in rejection in salt separation [6]. Usually rejection is lower for monovalent ions and higher for divalent ions.

Here we synthesized a negatively charged graft copolymer from PVC via ATRP for composite nanofiltration membranes. The grafting of poly(styrene sulfonic acid) side chains (PSSA) from PVC backbone was performed to form PVC-g-PSSA graft copolymer [10,11]. The grafting and structures of PVC graft copolymer was characterized using ^{1}H-NMR, FT-IR spectroscopy, wide angle X-ray scattering (WAXS). Thin film composite nanofiltration membranes were prepared from PVC-g-PSSA as a top layer coated onto poly(vinylidene fluoride) (PVDF) ultrafiltration support membrane. Nanofiltration performance of membrane was tested for 1,000 mg/L Na_2SO_4, and NaCl, $MgSO_4$ and $MgCl_2$ aqueous solutions.

2. Experimental

2.1. Materials

Poly(vinyl chloride), 4-styrenesulfonic acid sodium salt hydrate (SSA), copper(I) chloride (CuCl), 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA) and 1-methy-2-pyrrolidinone (NMP) were purchased from Aldrich. Methanol and dimethyl sulfoxide (DMSO) were purchased from J. T. Baker. All solvent and chemicals were regent grade, and were used as received.

2.2. Synthesis of PVC-g-PSSA Cpolymer

In a 250 mL round bottom flask, the various amounts of SSA was dissolved in DMSO at 70°C. 2 g of PVC was dissolved in 28 mL of NMP at 70°C separately. The SSA solution was added to the PVC solution. Then 0.04 g of CuCl and 0.1 mL of HMTETA were added to the solution. The green mixture solution was stirred un-

til homogeneous solution and purged with nitrogen for 20 min. The mixture solution was placed in a 90°C oil bath for 24 h. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. PVC-g-PSSA copolymer was obtained and dried in a vacuum oven overnight at room temperature.

2.3. Membrane Preparation

Composite membranes were prepared by coating a 2 m thick PVC-g-PSSA layer onto porous PVDF ultrafiltration membrane (Pall Corp. DV-20) using an RK Control Coater (Model 101, Control Coater RK Print-Coat Instruments LTD, UK) [12,13]. The resulting membranes were dried in a convection oven at 80°C for 24 h and further dried in a vacuum oven for 24 h at 120°C. The composite membranes were stored in water before use.

2.4. Nanofiltration Performance

The membranes were characterized in the module after pretreatment with pure water under 0.1~0.3 MPa pressure for 30 min [14]. The pure water flux and the rejection of 1,000 mg/L Na_2SO_4, NaCl, $MgSO_4$ or $MgCl_2$ solutions were measured under a pressure difference of 0.1~0.3 MPa at room temperature. The permeation flux, F, is calculated as Equation (1):
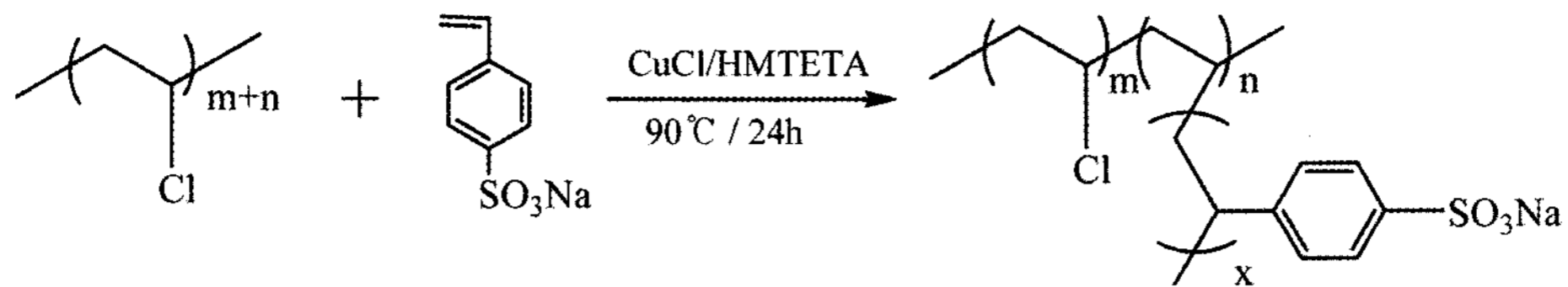
$$F = \frac{V}{At} \tag{1}$$

where V is the total volume of the water or solution permeated during the experiment; A represents the membrane area; and t denotes the operation time. Rejection, R, is calculated as Equation (2)
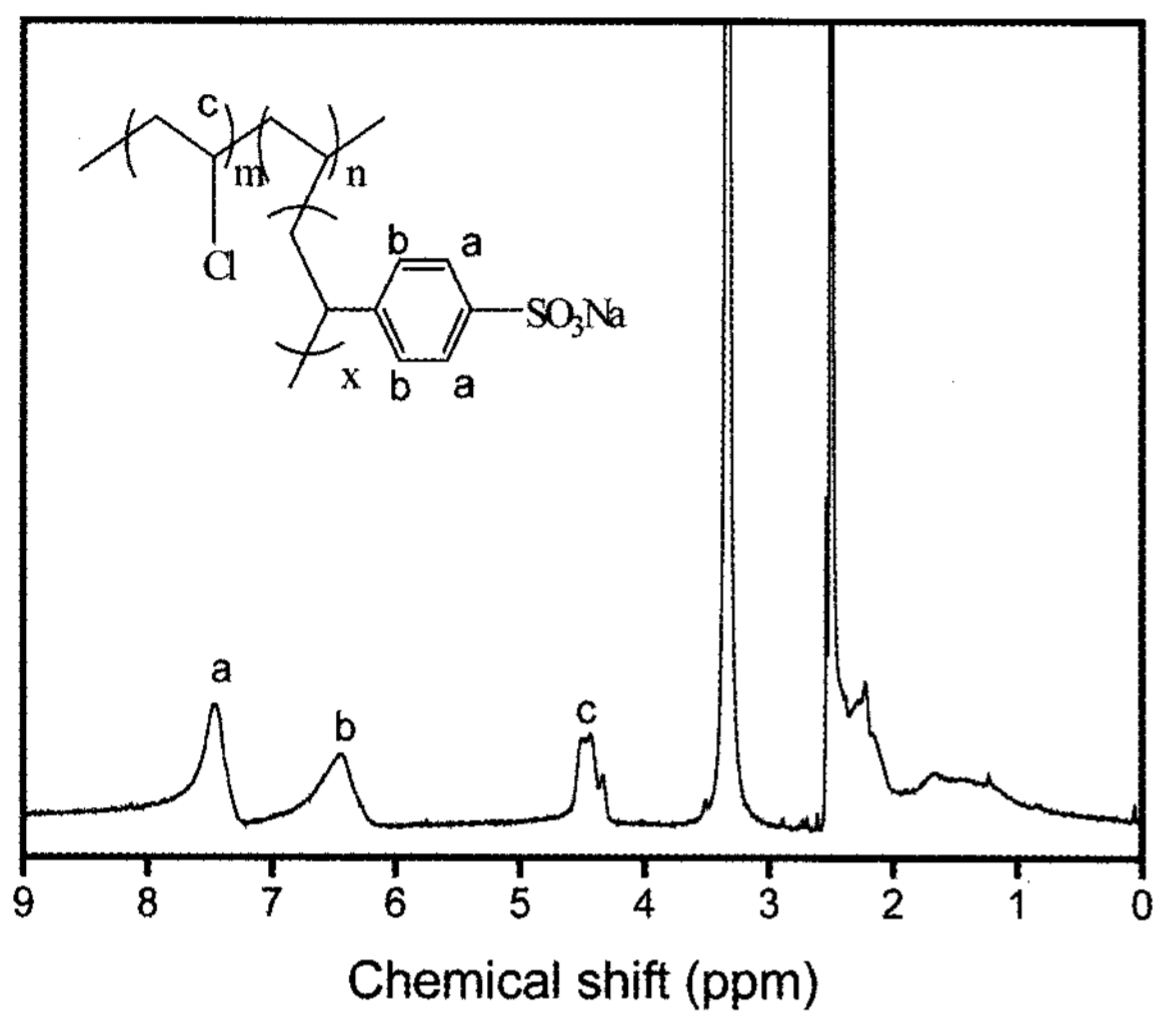
$$R = \frac{1 - C_p}{C_f} \tag{2}$$

where C_p and C_f are permeate concentration and feed concentration, respectively.

To determine concentration, a conductivity measure-

Scheme 1. Graft copolymerization of PSSA from PVC via ATRP.

Fig. 1. ^{1}H-NMR spectrum of PVC-g-PSSA graft copolymer.

Table 1. Composition of PVC-g-PSSA Graft Copolymers

Membrane	Added PVC : SSA wt ratio	Actual PSSA content (wt%)
PVC-g-PSSA14	1:3	14
PVC-g-PSSA32	1:5	32
PVC-g-PSSA44	1:7	44
PVC-g-PSSA71	1:9	71

PVC-g-PSSA copolymer electrolyte is presented in Scheme 1. PVC backbone was directly grafted with styrene sulfonic acid (SSA) at 90°C for 24 h through ATRP technique. The amphiphilic PVC graft copolymer is expected to molecularly self-assemble into continuous nanophase domains of semicrystalline PVC interweaved with hydrophilic proton conducting domains of PSSA brush layer, providing a mechanism for ion transport through the membranes [15,16].

The successful graft copolymerization of PSSA from PVC backbone was confirmed using ^{1}H NMR spectroscopy. A ^{1}H-NMR spectrum for PVC-g-PSSA with 1 : 7 wt ratio of added PVC:SSA amounts is presented in Fig. 1. The strong peaks at 2.6 and 3.5 ppm are due to DMSO and water, respectively. The peak at around 4.5 ppm is attributed to CHCl of PVC [17]. Grafting of PSSA to PVC produced additional new peaks at 7.5 and 6.5 ppm attributable to the aromatic bonding environments in the SSA [18]. This ^{1}H-NMR result presents the successful grafting of PSSA from the secondary chlorines of PVC units using ATRP. The grafting amounts of PSSA were determined from the integral ratio of the signals originated from the PSSA at 7.5 or 6.5 ppm, and the PVC at 4.5 ppm. The actual grafting contents of PSSA in the graft copolymer and the added amounts of PVC and SSA were summarized in Table 1.

Fig. 2 presents the FT-IR spectra of PVC and PVC-g-PSSA copolymer with PSSA concentrations of 14 and

ment (Orion 115 conductivity meters) was taken at the same time as sampling, and the feed cell conductivity was also measured. Then conductivities were converted to concentrations using a calibration curve.

2.5. Characterization

^{1}H-NMR measurement was performed with 600 MHz, high resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Bruker). FT-IR spectra of the graft copolymers were collected using Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency range of 4000 to 700 cm^{-1} using ATR facility. Wide angle X-ray scattering (WAXS) measurements were performed with a Rigaku D/max-RB apparatus (Tokyo, Japan) at rate of 1°/min.

3. Results and Discussion

3.1. Synthesis of PVC-g-PSSA Copolymer
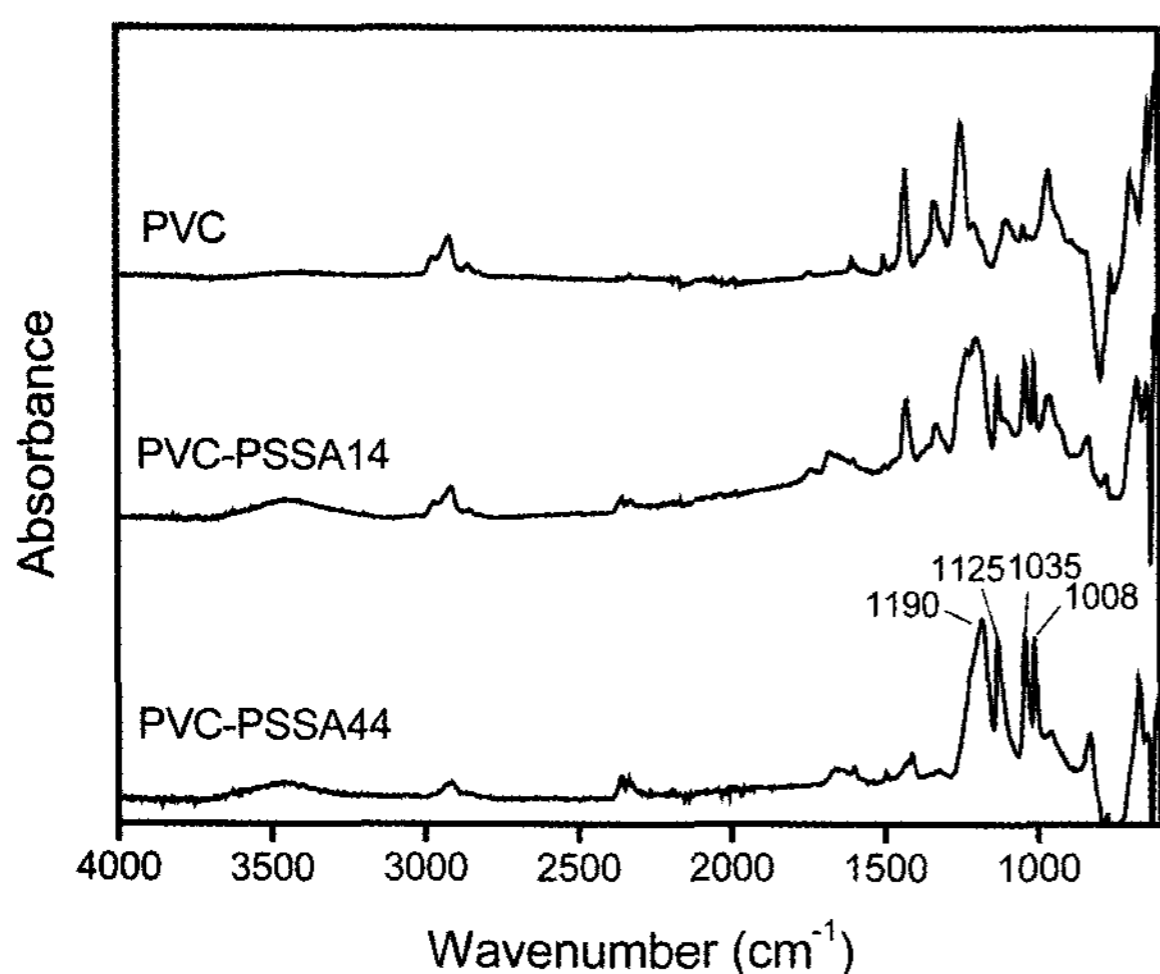
The schematic diagram illustrating the synthesis of

Fig. 2. FT-IR spectra of pristine PVC and PVC-g-PSSA graft copolymers with various amounts of PSSA.

Fig. 3. WAXS data of PVC and PVC-g-PSSA graft copolymer.

44 wt%. Compared to the pristine PVC, the PVC-g-PSSA graft copolymer exhibited the strong absorption bands at 1190, 1125, 1035, 1008 cm^{-1}. These bands result from the stretching vibrations of phenyl rings substituted with sulfonate groups and sulfonate anions attached to phenyl ring [19]. The broad absorption band at around 3435 cm^{-1} is attributed to the water bounded to ionic groups of the membranes. These FT-IR spectroscopic results also support the successful graft copolymerization via ATRP from secondary chlorine atoms on the PVC backbone.
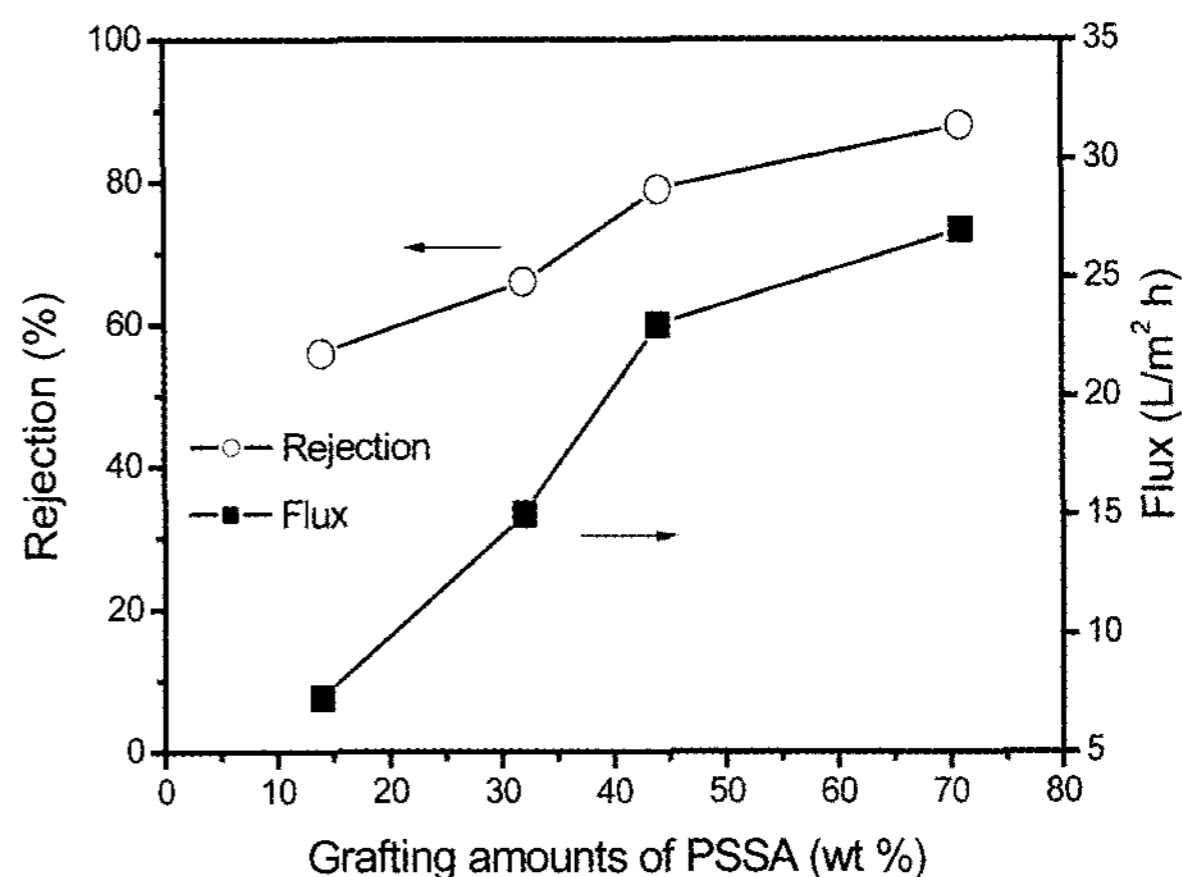
The structural change of a polymer by grafting polymerization was investigated by WAXS pattern. The WAXS curves for the pristine PVC and its graft copolymer with PSSA are shown in Fig. 3, where the intensity of X-ray scattering is plotted against the diffraction angle, 2θ. The grafting of PSSA from the PVC alters the resulting molecular structure and physical network, leading to a decrease in its crystallinity. This can be explained by the fact that the randomness of the amorphous phase in the graft copolymers is enhanced by introducing sulfonic acid groups, which gives rise to a perturbation of long-ranged spacing between the chains [20].

3.2. Nanofiltration Performance
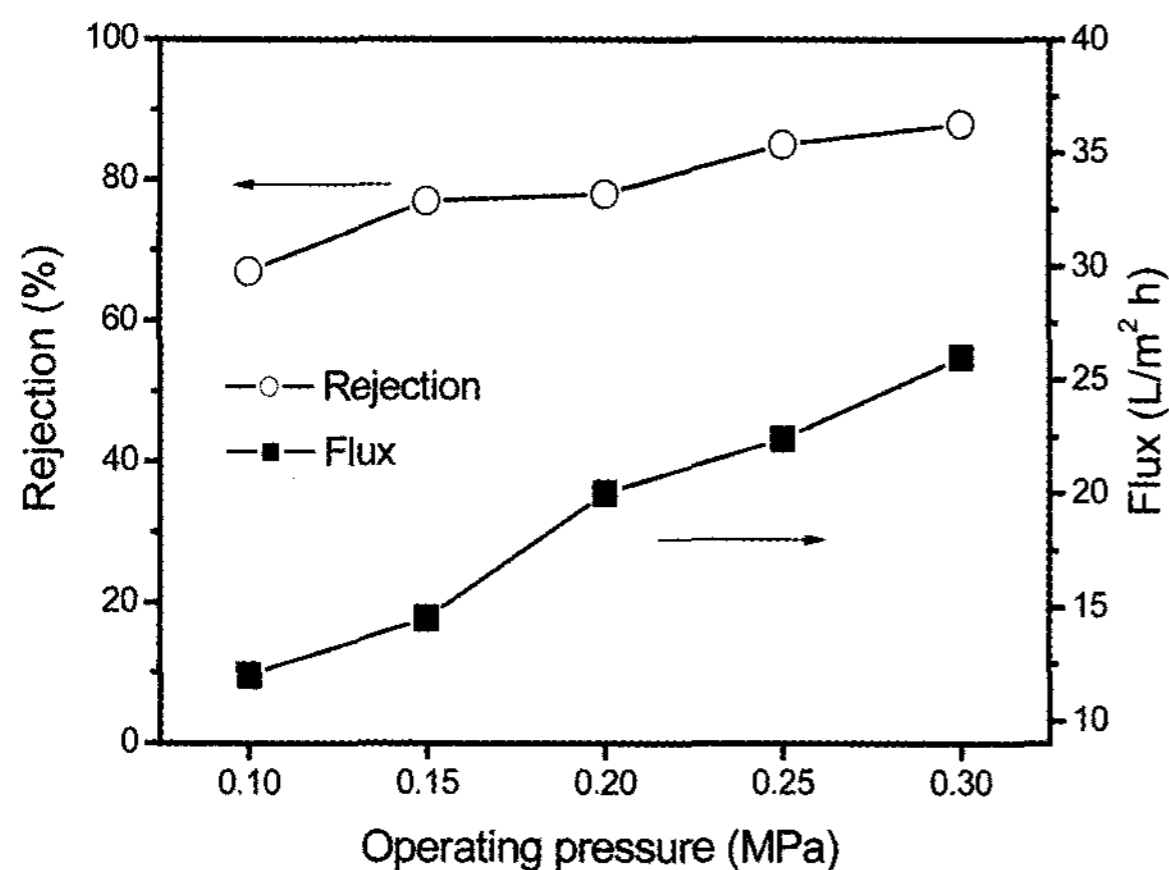
Nanofiltration performances of PVC-g-PSSA compo-

Fig. 4. Nanofiltration performance of PVC-g-PSSA composite membrane with different grafting amounts of PSSA for a 1,000 mg/L Na₂SO₄ solution at 0.3 MPA.

site membrane were investigated by varying the grafting amounts of PSSA under 0.3 MPA for a 1,000 mg/L Na₂SO₄ solution. Fig. 4 shows that both the flux and the rejection of PVC-g-PSSA composite membranes increased with increasing PSSA concentration. This increase is presumably attributable to the increase of hydrophilicity and negatively charged properties of membranes, respectively [5,6]. Because the PVC-g-PSSA composite membrane containing 71 wt% of PSSA exhibited the highest nanofiltration performance, this membrane was subjected to be tested for the separation of various salts. The nanofiltration performance of PVC-g-PSSA71 composite membrane was tested under 0.3 MPa

Fig. 5. Effect of operating pressure on nanofiltration performance of PVC-g-PSSA71 composite membrane for a 1,000 mg/L Na$_2$SO$_4$ solution.

Table 2. Nanofiltration Performance of PVC-g-PSSA71 Composite Membrane for a 1000 mg/L Solution at 0.3 MPA

	Na$_2$SO$_4$	NaCl	MgSO$_4$	MgCl$_2$
Rejection (%)	88	33	23	12
Flux (L/m^2 h)	26	34	17	29

pressure for a 1000 mg/L feed solution and the results were listed in Table 2. The membrane exhibited higher rejections for Na$_2$SO$_4$ (88%) than NaCl (33%) and MgSO$_4$ (23%) than MgCl$_2$ (12%), demonstrating that rejection for divalent anions is higher than that for monovalent anions [5,6]. However, the rejection for Na$_2$SO$_4$ (88%) was higher than MgSO$_4$ (23%) and that for NaCl (33%) was higher than MgCl$_2$ (12%), demonstrating that rejection for cations has the reverse order as in the case of anions. Thus, the rejection for various salts is arranged in the order: Na$_2$SO$_4$ > NaCl > MgSO$_4$ > MgCl$_2$ for PVC-g-PSSA71 composite membranes. The flux for NaCl was higher than those for other salts [6].

Nanofiltration performance of P(VDF-CTFE)-g-PSSA71 composite membrane was investigated by changing operating pressure for 1000 mg/L Na$_2$SO$_4$ solution. Fig. 5 shows that both the solution flux and the rejection of membranes increased almost linearly with increasing operating pressure. The effect of operating pressure on nanofiltration performance may be explained by the solution-diffusion model based on the previous work [6]. It has been demonstrated that salt rejection is related to

the interface properties of membrane surface and the exerted pressure drives water molecules to permeate through the membrane [6].

4. Conclusion

PVC-g-PSSA graft copolymers with various amounts of PSSA were synthesized via ATRP technique for composite nanofiltration membranes. The synthesis involved the direct graft copolymerization of PSSA side chains onto PVC backbone, which served as a macroinitiator for ATRP. Synthesis of PVC-g-PSSA graft copolymer was successful via grafting from method, as confirmed by ^{1}H-NMR, FT-IR spectroscopy and WAXS analysis. PVC-g-PSSA71 composite membrane showed that the rejections were 88% for Na$_2$SO$_4$ and 33% for NaCl, and the solution flux were 26 L/m^2 h for Na$_2$SO$_4$ and 34 L/m^2 h for NaCl at 0.3 MPa pressure.

Acknowledgement

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