

Preparation of Chlorinated Poly(vinyl chloride)-g-Poly(*N*-vinyl-2-pyrrolidinone) Membranes and Their Water Permeation Properties

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ABSTRACT: Chlorinated poly(vinyl chloride) (CPVC) membranes for microfiltration processes were prepared with the combined process of a solvent evaporation technique and the water-vapor induced-phase-inversion method. CPVC membranes with a mean pore size of 0.7 μm were very hydrophobic. These membranes were subjected to surface modification by ultraviolet (UV)-assisted graft polymerization with *N*-vinyl-2-pyrrolidinone (NVP) to increase their surface wettability and decrease their adsorptive fouling. The grafting yields of the modified membranes were controlled by alteration of UV irradiation time and NVP monomer concentration. The changes in chemical structure between the CPVC membrane and the CPVC-g-poly(*N*-vinyl-2-pyrrolidinone) membrane and the variation of the topologies of the modified PVC membranes were characterized by Fourier transform infrared spectroscopy, gel permeation chromatography, and field emission

scanning electron microscopy. According to the results, the graft yield of the modified CPVC membrane reached a maximum at 5 min of UV exposure time and 20 vol % NVP concentration. The filtration behavior of these membranes was investigated with deionized water by a crossflow filtration measurement. The surface hydrophilicity and roughness were easily changed by the grafting of NVP on the surface of the CPVC membrane through a simultaneous irradiation grafting method by UV irradiation. To confirm the effect of grafting for filtration, we compared the unmodified and modified CPVC membranes with respect to their deionized water permeation by using crossflow filtration methods. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3188–3195, 2003

Key words: membranes; poly(vinyl chloride) (PVC); modification

INTRODUCTION

Many of the commercially available synthetic membranes in the field of microfiltration and ultrafiltration are made of hydrophobic polymers, such as polysulfone, polytetrafluoroethylene, poly(vinylidene fluoride), and polypropylene, because of their good mechanical properties. However, hydrophobic membranes are very susceptible to fouling by the adsorption of solutes in the feed, resulting in a decrease of flux.¹ It is possible to overcome this problem by the provision of hydrophilic character to the membrane surface. Surface properties are important because the interaction between a polymeric membrane and its environment occurs chiefly at the surface.²

The conventional grafting polymerization technique requires chemically reactive groups on the surface and on the membrane pore wall.^{1–5} For this reason, a series

of functionalization steps are necessary for covalent grafting. The surface functionalization techniques for grafting are ultraviolet (UV) irradiation,^{3,6,7} γ -ray irradiation,^{2,8,9} plasma,^{10,11} ion beams,¹² and chemical initiators.¹³ Among these techniques, the radiation grafting method is one of the more preferable methods because of its uniform and rapid generation of active radical sites without catalytic contamination in grafting materials.

Radiation grafting methods, such as preirradiation and simultaneous irradiation grafting, can introduce specific functional moieties to a polymeric substrate. In the former method, the polymer substrate is irradiated first in vacuum, nitrogen or air, and then, the subsequent monomer is grafted by peroxide radicals; in the latter method, the polymer substrate is simultaneously irradiated in the presence of monomers. If crystalline polymers are subjected to irradiation, the irradiation can crosslink polymer chains and cleave polymer bonds or form functional groups such as hydroxyls, carbonyls, or carboxylic acids on the surface. Consequently, when vinyl monomers are present, free-radical graft polymerization occurs at these reactive sites, resulting in the formation of polymer chains that are covalently bonded to the surface of

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the membrane. Therefore, radiation-induced grafting can be used to modify the chemical and physical surface properties of polymeric materials because it imparts desirable properties, such as blood compatibility,¹⁴ ion exchange,¹⁵ immobilization of bioactive materials,^{16,17} and protein filtration,^{2,18} to membranes.

In this study, *N*-vinyl-2-pyrrolidinone (NVP), known as a hydrophilic graft monomer,^{5,9} was used to improve membrane performance. Also, microporous chlorinated poly(vinyl chloride) (CPVC) membranes with a mean pore size of 0.7 μm were used to carry out the surface modification. The procedures used to prepare the CPVC membrane with submicron-scaled surface pores were detailed in a previous work.¹⁹ The objective of this study was to prepare CPVC membrane modified with hydrophilic NVP monomer by UV-assisted graft polymerization. The main goal was to examine the effects of hydrophilized CPVC membrane on the water flux under crossflow filtration.

EXPERIMENTAL

Materials

CPVC (Nippon Carbide Ind. Co., Inc., Tokyo, Japan) with a chlorine content of about 63–68% was used as the base polymer for the preparation of the microporous membrane. NVP (Aldrich Chemical Co., Milwaukee, WI) was vacuum distilled to remove any inhibitor before use, was dissolved in methanol, and was then used as the grafting monomer. 1,1-Diphenyl-2-picrylhydrazyl (DPPH; Aldrich) was used for the quantification of peroxide concentration produced from UV irradiation. Methanol and toluene (J. T. Baker, Paris, KY) were reagent grade. Deionized water was produced by an ultrapure water system (Milli-Q Plus, Millipore, Bedford, MA).

Surface modification of CPVC membranes by UV irradiation

The grafting experiment was carried out by a simultaneous irradiation grafting method: NVP/methanol solution was purged with nitrogen for 12 h to minimize the presence of oxygen before the monomer solution was grafted. CPVC membranes were first dipped in NVP monomer/methanol solution (10, 20, 30, and 40 vol %) for 2 h before UV irradiation; then, the CPVC membrane was placed 10 cm from the UV source and irradiated in air with an unfocused medium-pressure mercury UV lamp (power = 450 W, Ace Glass Co., Vineland, NJ) with a mixed wavelength, where the main wavelengths were 303 and 363 nm, to graft the NVP monomer onto the surface of the CPVC membrane. After the grafting treatment, the grafted membrane [CPVC-g-poly(*N*-vinyl-2-pyrrolidinone) (PNVP) membrane] was washed in a vessel filled with deionized water at 65°C for 1 day to

remove unreacted monomer (NVP) and homopolymer (PNVP) remaining in the membrane. Deionized water was exchanged five times. After washing, all of the prepared membranes were dried completely in a vacuum oven. The graft yield was obtained gravimetrically with the following equation:

$$\text{Graft yield } (\mu\text{g}/\text{cm}^2) = \frac{w_g - w_0}{A}$$

where w_0 and w_g are the weights of the membrane before and after NVP grafting, respectively, and A is the effective area of the membrane surface.

Characterization of the CPVC-g-PNVP membrane

Determination of peroxide concentration

To obtain the optimal UV irradiation time, we quantified the amount of peroxide formed around the membrane after UV irradiation with DPPH.²⁰ The DPPH solution (1×10^{-4} mol/L) in toluene was degassed by a nitrogen gas purge for 30 min. The irradiated CPVC membrane was dipped into a DPPH/toluene solution at 65°C for 2 h in a shaking water bath to decompose the peroxides formed around the membrane. The amount of DPPH reacted with peroxides was measured with an UV-visible scanning spectrophotometer (Shimadzu UV-2101PC, Kyoto, Japan) at 520 nm. A calibration curve was obtained with five DPPH solutions of known concentration (0.0625, 0.125, 0.25, 0.5, and 1×10^{-4} mol/L). To investigate the relationship between the irradiation time and peroxide formation, we varied the irradiation times.

Fourier transform infrared spectroscopy (FTIR)

To investigate the changes in chemical structure between the unmodified and modified CPVC membranes and to confirm the grafting of NVP onto the membrane, we used a Fourier transform infrared spectrometer (Nicolet Magna-IR spectroscopy 550, Madison, WI).

Gel permeation chromatography (GPC)

The molecular weights (MWs) of the CPVC membranes grafted with NVP (CPVC-g-PNVP membranes) were determined by the elution time relative to monodisperse standard polystyrene from GPC (Waters, model 616 high performance liquid chromatograph (HPLC) pump, Milford, MA) with the Millennium software program. Four Styragel tetrahydrofuran (THF) columns (Waters HR1, 3, 4, and 5E; each 4.6 \times 300 mm) and a differential refractometric detector (R410, Waters) were used. The mobile phase was THF with a flow rate of 1 mL/min. The mobile injection volume was usually 100 μL of a stock solution. The

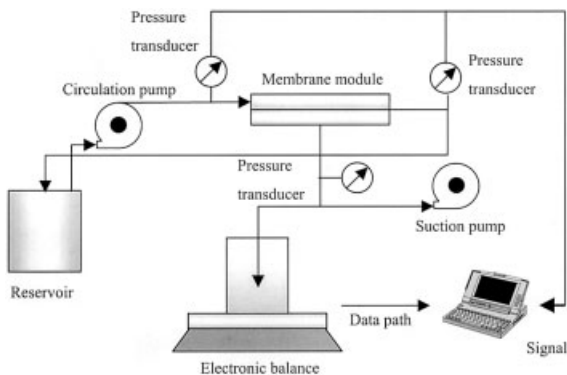


Figure 1 Schematic diagram of the crossflow filtration apparatus.

calibration curve was prepared before measurements with 15 standard polystyrenes (374–2,160,000 g/mol, polydispersity index = 1.03–1.09).

Field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM)

The surfaces of the unmodified and modified CPVC membranes were observed by FESEM (Jeol-6330F, Kyoto, Japan). Also, to observe the detailed physical properties of the membrane surfaces, we used an AFM apparatus (Digital Instruments, NanoScope III, Santa Barbara, CA) in air in the tapping mode to obtain images of the membrane surface topography. The tapping frequency was 380.4 kHz, the scan rate was 3 Hz, and the size was $5 \times 5 \mu\text{m}$. Differences in membrane surface topography can be expressed in terms of various roughness parameters such as the root mean square (RMS) of the Z values, the mean roughness, and the maximum height. Among these methods, the RMS roughness was used. The RMS of Z is the standard deviation of the Z values between the reference markers and is calculated by the following equation:

$$\text{RMS} = \sqrt{\frac{\sum (Z_i - Z_{\text{ave}})^2}{N}}$$

where Z_i and Z_{ave} are the current Z value and the average of the Z values between the reference markers, respectively, and N is the number of points between the reference markers.

Wettability measurement

The sessile drop method was used to determine the polarity of the unmodified and modified CPVC membranes. Deionized water ($0.1 \mu\text{L}$) was dropped with a microsyringe onto a dry membrane in air, and the contact angle was measured with a goniometer (CA-X, Kyowa, Kaimenkagaku Co., Tokyo, Japan) as soon as possible. The reported values are the means of at least 10

experiments, and the standard deviation was within about $\pm 7\%$. The $\cos \theta$ of the contact angle has been termed as the wettability of the membrane surface.²¹

Crossflow filtration experiment

A crossflow filtration system was used to characterize the filtration performances of the unmodified and modified CPVC membranes. Figure 1 shows the schematic diagram of a crossflow filtration apparatus. The crossflow filtration apparatus consisted of a crossflow module cell ($170 \times 100 \times 50 \text{ mm}$, effective membrane area = 16 cm^2), a circulation pump (Masterflex L/S model 77310-01, Cole-Parmer Instruments, Vernon Hills, IL) for a stable feed supply, a peristaltic pump (Minipuls3, Gilson, Middleton, WI) for a constant suction performance, a pressure transducer (model 626A13TAE, MKS instruments, Andover, MA) for detection of the pressures of upstream and downstream in the module, a 2000 mL feed reservoir, a permeate collection reservoir, and an electronic balance connected with a computer. In the crossflow test, the crossflow velocities was 22 and 44 cm/s. We increased the suction pressure every 150 s by increasing the rotations per minute of the suction pump. All of the membranes for the crossflow filtration test were initially immersed into an isopropylalcohol/ H_2O (2/8 wt %) mixture for 10 min before the test. The weight of permeate was measured every 30 s with an electronic balance and was then automatically recorded by an online computer.

RESULTS AND DISCUSSION

Determination of UV irradiation time

The DPPH titration method and GPC were utilized to determine the optimal UV irradiation time. Free rad-

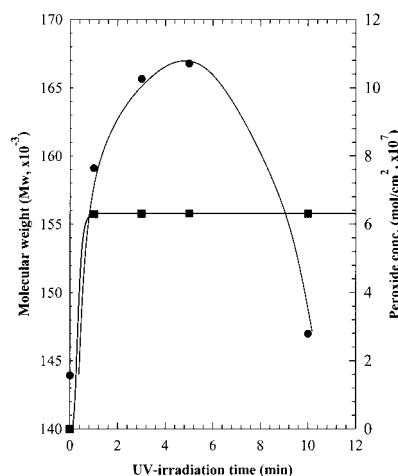


Figure 2 Variation of the (●) MW of the CPVC membrane and (■) peroxide concentration generated with UV irradiation time.

TABLE I
Characterization of the Modified Membranes

Sample code	NVP concentration (vol %)	UV exposure time (min)	Grafting yield ($\mu\text{g}/\text{cm}^2$) ^b	Wettability ($\cos \theta$) ^c	MW ^d
CPVC ^a	—	—	—	-0.39	143,923
CN10	10	5	95.35	0.19	176,000
CN20	20	5	117.23	0.36	182,000
CN30	30	5	95.50	0.20	177,000
CN40	40	5	57.26	-0.09	172,000

^a CPVC membrane without UV exposure.

^b Grafting yield ($\mu\text{m}/\text{cm}^2$) = $(w_g - w_0)/A \times 100$, where A is the area of the specimen and w_0 and w_g are the weights of membrane before and after the grafting reaction, respectively.

^c The average estimated error for $\cos \theta$ was ± 0.05 .

^d Measured by GPC.

icals generated in the original CPVC membrane without dipping into the NVP monomer solution after UV irradiation could be used to initiate the grafting reaction. The amount of peroxide was determined by measurement of the concentration of consumed DPPH molecules that reacted with free radicals generated after UV irradiation. The effect of UV irradiation time on the radical concentration generated on the CPVC surface after UV irradiation is shown in Figure 2. The concentration of peroxides remained almost constant (6.292×10^{-7} to 6.315×10^{-7} mol/cm²) for 10 min. Also, the MWs of the original CPVC doping solution increased up to 5 min of exposure time as the UV exposure time increased. However, if the exposure time exceeded 5 min, the MWs of the original doping solution decreased because polymer chains were cleaved off by UV irradiation.²² Although the concen-

tration of radicals under UV irradiation for 10 min was almost constant, the coupling (recombination) mainly occurred for 5 min, and then, chain scission continued. Therefore, an exposure time of 5 min was regarded as the optimal UV irradiation time for this study.

Preparation of the CPVC-g-PNVP membranes and their wettability

The grafting polymerization of NVP onto the CPVC membranes was conducted by alteration of the concentration of NVP monomer at a fixed UV exposure time of 5 min, as summarized in Table I. GPC measurement was used to confirm the MWs of the CPVC-g-PNVP membranes prepared from NVP monomer contents of 10, 20, 30, and 40 vol %. Contact angle measurements have been commonly used to charac-

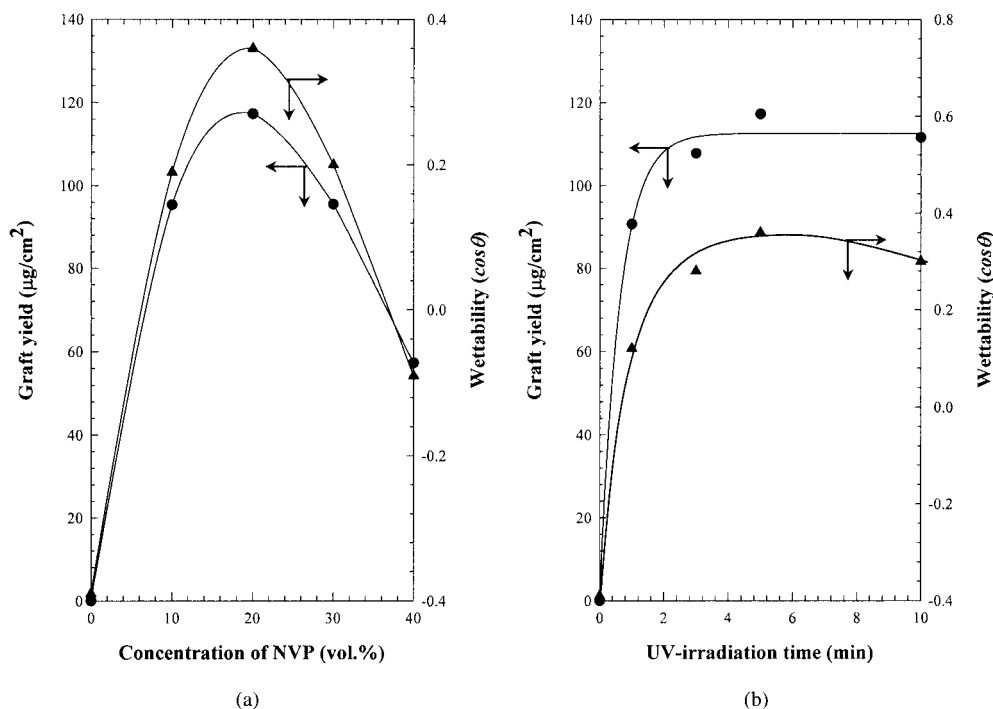


Figure 3 Effect of (a) NVP concentration and (b) UV irradiation time on the grafting yield and wettability, respectively.

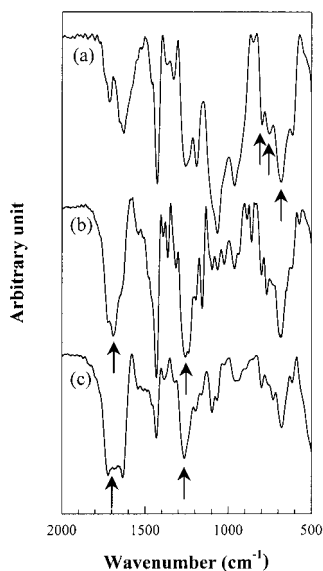


Figure 4 FTIR spectra of membranes: (a) unmodified CPVC membrane, (b) CN20, and (c) CN30.

terize the polarity or the surface energy of polymeric surfaces.^{23–25} However, such measurements are difficult to interpret for synthetic membranes because of capillary forces within pores, contraction in the dried state, heterogeneity, roughness, and restructuring of

the surfaces. Nevertheless, the relative hydrophilicity or hydrophobicity of each sample can be easily obtained by this measurement. As shown in Table I, the GPC results of CPVC-*g*-PNVP membranes were exactly in accordance with the results of grafting yields based on gravimetric analysis.

The effect of NVP concentration on the wettability and the graft yield was investigated and is shown in Figure 3(a). The modified membrane (CN20) had the highest grafting yield, as indicated by the largest MW. Therefore, because the NVP monomer had hydrophilic properties, the CN20 membrane with the highest grafting yield showed the maximum wettability. The wettability of the highest grafted membrane (CN20) was almost twice that of the unmodified membrane. In the case of CPVC-*g*-PNVP membranes, as the graft yield increased up to 20% NVP concentration, the wettability of membranes increased because of the hydrophilicity of the grafted PNVP. However, above 20 vol % NVP, the wettability gradually decreased. We deduced that excessive use of the NVP monomer accelerated the formation of homopolymer, PNVP, without reaction with the substrate of the CPVC membrane. Figure 3(b) shows the graft yield and the wettability of membranes prepared as a function of UV irradiation time at NVP concentration of 20 vol %.

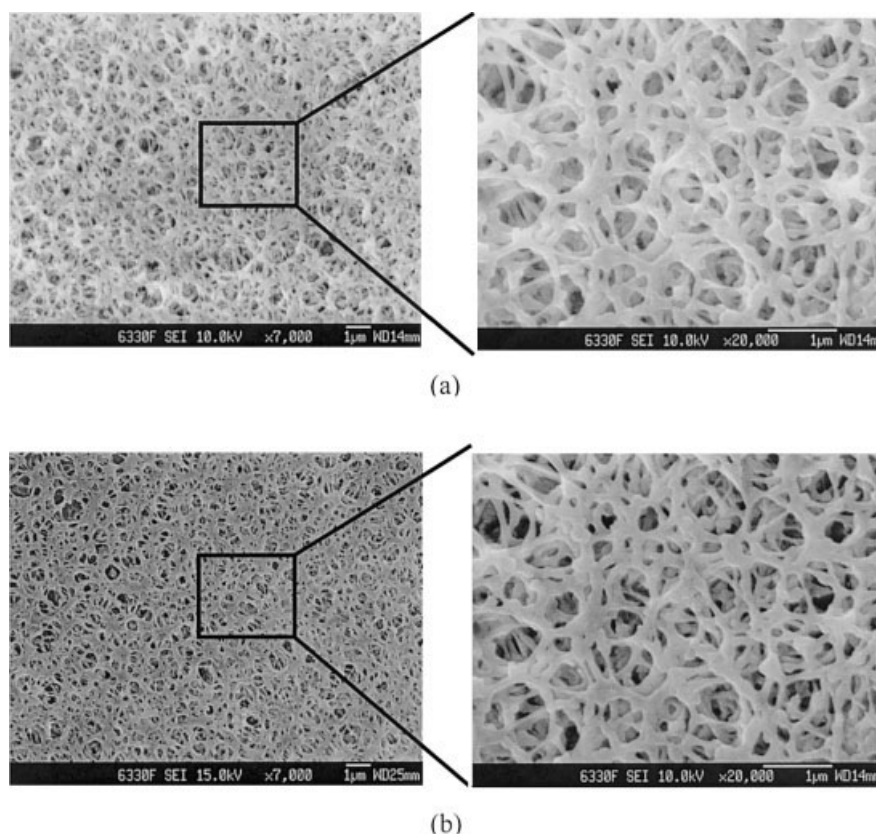


Figure 5 FESEM photographs of membrane surfaces: (a) unmodified CPVC membrane and (b) CN20.

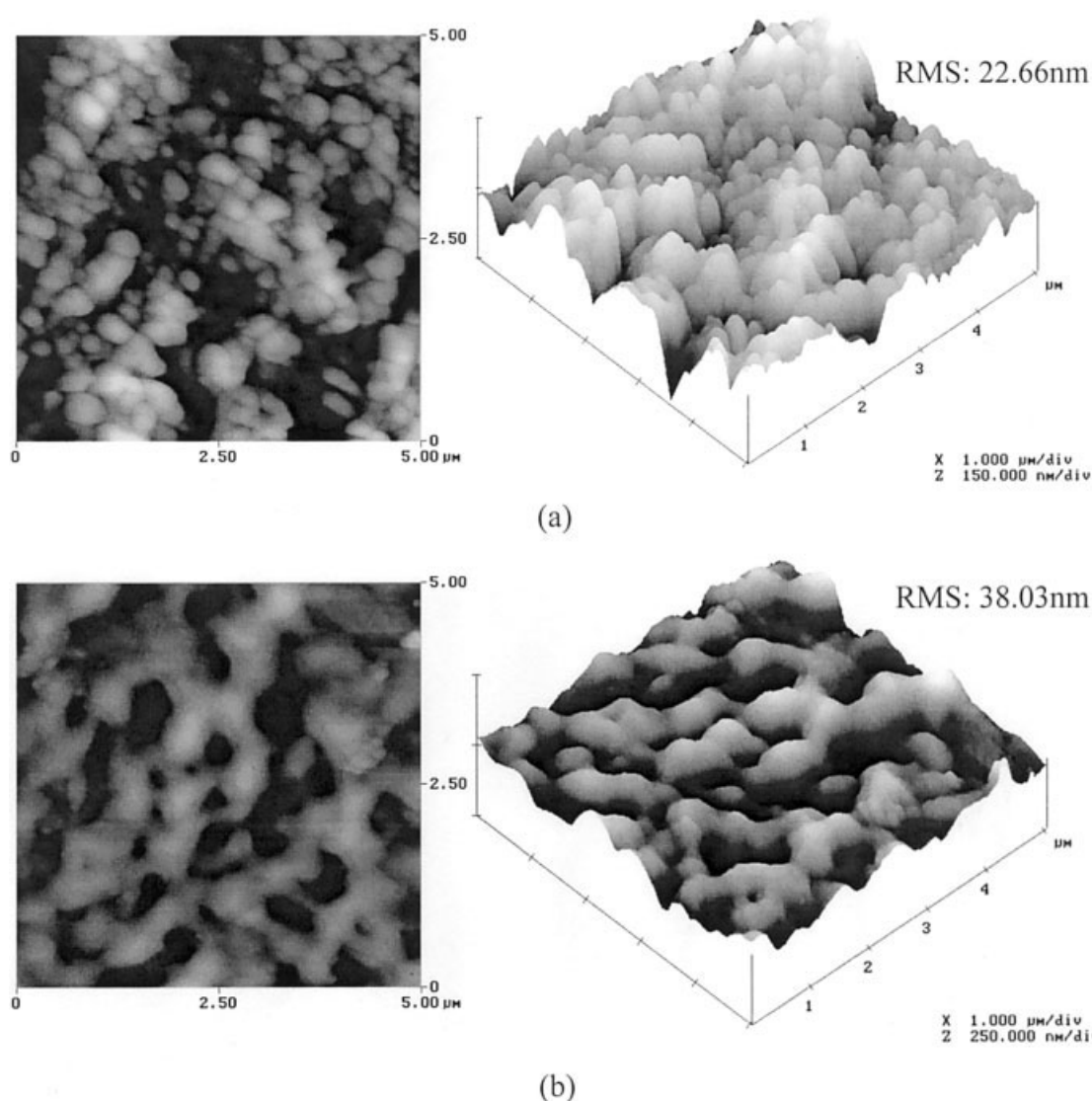


Figure 6 AFM images of membrane surfaces: (a) unmodified CPVC membrane and (b) CN20. The scanning speed was 2.5 $\mu\text{m/s}$, and the area was $5 \times 5 \mu\text{m}^2$, respectively.

FTIR spectra of the modified CPVC membrane

FTIR spectra of the unmodified CPVC membrane [Fig. 4(a)] and the CPVC membranes modified with NVP grafting [Fig. 4(b,c)] are shown in Figure 4. The most significant change in the spectra of the CPVC-g-PNVP membranes was the appearance of a redshifted 1350 cm^{-1} absorption band due to the C—N stretching vibration of NVP into about a 1230 cm^{-1} band without the variation of the 1730 cm^{-1} stretching band representing the C=O of NVP. Also, the major characteristic peaks for CPVC appeared at 800 , 750 , and 720 cm^{-1} , representing C—Cl stretching bands. This confirmed the grafting of NVP onto the CPVC membrane surface.

Topology of the CPVC-g-PNVP membranes

The topographical changes of CPVC membrane before and after the grafting reaction were observed by

FESEM and AFM, respectively. The representative images of the unmodified CPVC membrane and the grafted CPVC membrane (CN20) are presented in Figure 5(a,b). As shown in Figure 5, we did not observe a visible change in the pore shape and pore size of membrane surface after the grafting reaction of the NVP monomer through UV irradiation. It appears that most of the reaction formed homopolymer, and little occurred on the surface. However, the morphological changes of the unmodified and the modified CPVC membranes were confirmed by AFM pictures.

Figure 6 shows the surface topographical images of the original CPVC membrane [Fig. 6(a)] and CN20 [Fig. 6(b)]. As shown in Figure 6, the RMS roughness of the grafted CPVC membrane (CN20) was higher than that of the unmodified CPVC membrane, and the surface RMS roughness of the modified CPVC mem-

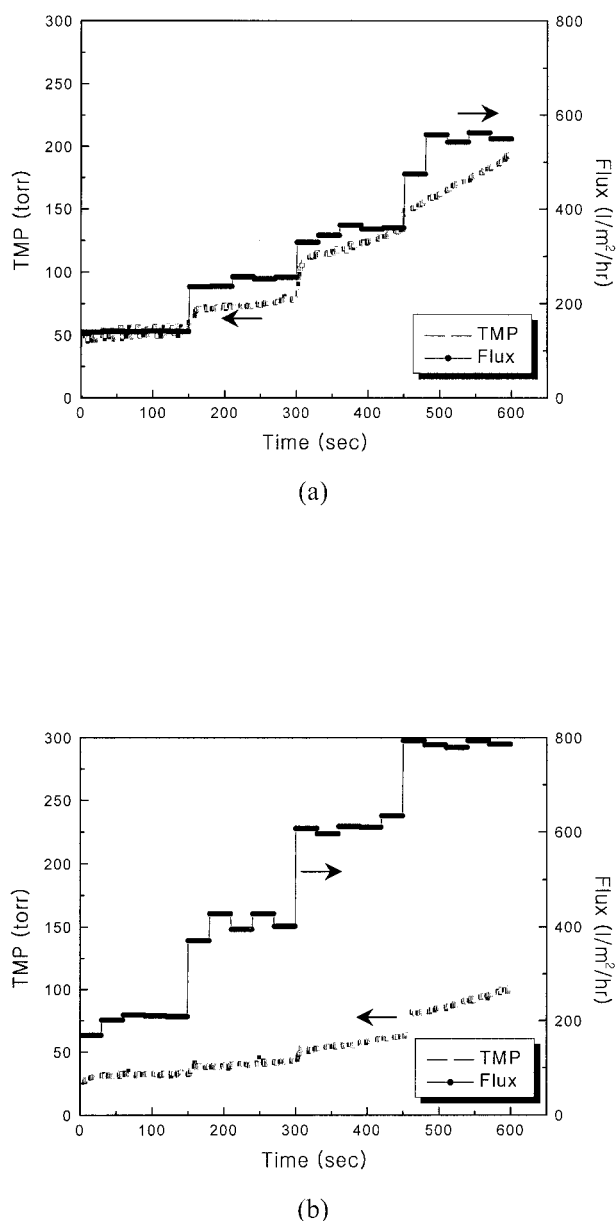


Figure 7 Effects of NVP grafting on the crossflow water permeation and TMP for the (a) unmodified CPVC membrane and (b) CN20 at a circulation flow velocity of 22 cm/s.

brane increased as the grafting yield of the NVP monomer increased.

Crossflow filtration experiment

To investigate the effect of NVP grafting on the membrane performance, we carried out the crossflow filtration of deionized water with the unmodified and the modified CPVC membranes (CN20). The crossflow filtration process is usually operated under the driving force of transmembrane pressure (TMP). In this study, we increased TMP every 150 s by increasing the speed of the suction pump. This means that the permeate

flow rate was controlled only by the speed of the suction pump.

Figure 7 shows the TMP and the flux of the unmodified [Fig. 7(a)] and the modified membranes [Fig. 7(b)] at a circulation flow velocity of 22 cm/s. Even though the initial conditions of this crossflow experiment, such as the suction pressure and circulation flow velocity, remained the same, there were differences in the TMP and the flux of the unmodified membrane and the modified membrane. During the initial period (0–150 s), the TMP of the modified membrane was lower than that of the unmodified membrane, whereas the flux of the modified membrane was higher than that of the unmodified membrane. After the initial period, the difference in TMP between the unmodified and the modified membrane (CN 20) became remarkably larger. The gradual increase in the TMP for the modified membrane was noticeably smaller than that of the TMP for the unmodified membrane. That is, if the crossflow filtration experiment were carried out under a constant TMP, the difference of flux between the unmodified and the modified membranes (CN20) would become greater. Consequently, the water flux of the modified membrane was obviously higher than that of the unmodified membranes during the crossflow filtration test because the membrane resistance was reduced by the increase in hydrophilicity caused by the grafting of NVP. We concluded from these results from the crossflow filtration test that the introduction of hydrophilic PNVP to the microporous CPVC membrane improved the membrane performance, as indicated by the low TMP and high water flux.

CONCLUSIONS

We used a surface modification technique on a CPVC membrane by grafting NVP using UV-assisted polymerization and varying UV exposure time and the concentration of NVP monomer. The graft yield was at a maximum at $117.23 \mu\text{g}/\text{cm}^2$ at a UV exposure of 5 min and 20 vol % NVP. NVP was effectively grafted on the CPVC membrane surface, which was confirmed by FTIR, GPC, wettability, and AFM. Also, we executed crossflow filtration of deionized water using the unmodified and the modified CPVC membranes. Even though the initial conditions of this crossflow experiment remained the same, the permeation properties of the modified membrane were superior to those of the unmodified membrane. The modified CPVC membrane, CPVC-g-PNVP, showed a higher water flux throughout the filtration test. These phenomena were caused by the increased hydrophilicity of the membrane surface induced by the grafting of NVP. Therefore, we can conclude that by grafting hydrophilic NVP monomer on the microporous CPVC

membrane, we easily improved the performance of the CPVC membranes.

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