Composite Membranes Formed by Plasma-Polymerized Acrylic Acid for Ultrafiltration of Bleach Effluent

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SYNOPSIS

Composite membranes were formed by deposition of plasma-polymerized acrylic acid (PPAA) films onto porous commercial membranes to improve the rejection, especially of chlorinated compounds, in ultrafiltration of E-stage bleach effluent. Although increased rejections were accompanied by reduced flux, in most cases, the reductions were not significant considering the extent of increased rejections. A good composite membrane showed the AOX removal of 94% (76% before the modification) and the chemical oxygen demand (COD) removal of 84% (67% before the modification) with 33% reduction of the flux. The permeate was optically clean. The improved rejection is attributed to the tightly cross-linked network of a plasma polymer film and its negatively charged surface. Ultrathin film thickness and the hydrophilic property of a plasma polymer film minimize the reduction of flux. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Bleaching processes to brighten pulps are the major sources of waste water from pulp and paper industries.[1] The waste water from bleaching processes, the bleach effluent, carries bleaching chemicals and color bodies derived from lignins, resins, metal ions, and noncellulose carbohydrates. Its dark color originating from long lignin chains and the presence of low molecular weight toxic compounds raise severe environmental problems. Chlorinated compounds of molecular weight lower than 1000 are found to be toxic to fish.[2]

Polymers and oligomers of high molecular weight in bleach effluents are successfully removed by ultrafiltration, which is one of the economically feasible methods for the treatment of bleach effluents.[3] However, it is rather difficult to remove low molecular weight compounds. In general, ultrafiltration is combined with a supplementary process such as chemical treatment, biological treatment, or reverse osmosis to achieve high rejection of low molecular weight compounds.

A simple way to increase the rejection of low molecular weight compounds maintaining adequate flux may be the use of a composite membrane that is composed of a thin dense film and a porous substrate. The nonporous dense film can provide high rejection without a significant reduction of the flux due to its thin film thickness. The flux of a permeate is inversely proportional to the film thickness of a membrane.[4]

For the formation of composite membranes, plasma polymerization is an excellent process. It has been extensively utilized to modify membranes for various membrane-separation processes.[5–15] Unique characteristics of plasma polymerization for thin-film coating and the highly cross-linked structure of plasma polymer films have led to the continuous development of membranes with high selectivities. Besides, functionalization on a film surface or a membrane surface *in situ* provides some additional effects such as improved wetting and antifouling.

In this study, improvement of the rejection, especially of chlorinated compounds, without significant reduction of the flux in ultrafiltration of bleach effluents was investigated. Composite membranes were formed by deposition of plasma-polymerized

acrylic acid (PPAA) films onto porous ultrafiltration membranes. Negatively charged functional groups were also provided on the surface of the composite membranes through control of the energy input for plasma polymerization.

EXPERIMENTAL

Membranes

Following commercial ultrafiltration membranes were used as a substrate membrane:

YM10 (cellulose acetate, molecular weight cutoff: 10,000, sodium azide added, product of Amicon);

NTR7410 (sulfonated polyether sulfone, molecular weight cutoff: 500–20,000 depending on pH, product of Nitto);

FS61PP (polyvinylidene fluoride, molecular weight cutoff: 20,000, packed in a glycerine solution, product of DDS);

Celgard 5511 (polypropylene, hydrophilic laminate of Celgard 2500 [effective pore size: 0.075 μ], product of Celanese);

Celgard 5410 (polypropylene, hydrophilic laminate of Celgard 2400 [effective pore size: 0.05 μ], product of Celanese).

Plasma Reactor

The plasma reactor used in this study is a homemade cylindrical reactor. The design of the reactor is shown in Figure 1. It consists of a large glass vessel (i.d. = 15 cm, length = 65 cm), a double-stage rotary pump (Lebold Heraeus Model D 40 B), a radiofrequency (125–375 kHz) power generator (ENI model HPG-2), two external copper electrodes (3 cm wide, 10 cm apart), a pressure transducer (MKS
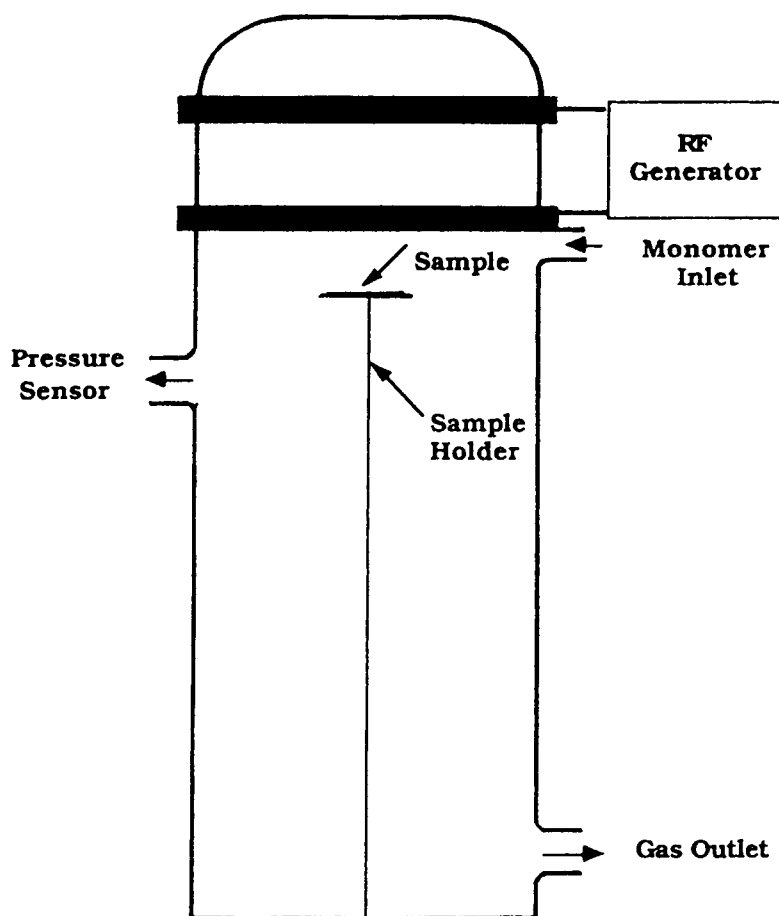

Figure 1   Schematic diagram of the plasma reactor: i.d., 15 cm; length, 65 cm.

Model 127A), and flow control systems (LH, HI-TEC and manual controllers). A stainless-steel sample holder, of which the length is adjustable, is located at the center.

Formation of Composite Membranes

Composite membranes were formed by deposition of plasma-polymerized acrylic acid (PPAA) films onto porous substrate membranes. Samples were placed 10 cm below the side monomer inlet. The reactor was evacuated to at least 5 mTorr, followed by introduction of acrylic acid vapor for plasma polymerization. Plasma polymerization was carried out at a flow rate of 5.0 SCCM and a monomer pressure of 26 mTorr. After plasma polymerization, samples were taken out of the reactor after 5 min evacuation by breaking vacuum with air.

Test and Analysis

Modified membranes were characterized by means of electron spectroscopy for chemical analysis (ESCA, LH 2000) or scanning electron microscopy (SEM, Philips SEM 515). The thickness of a PPAA film was estimated with a thickness monitor (IN-FICON, Model XTC) placing a quartz crystal at the position of a substrate. The PPAA films were assumed to have a density of 1 g/cm^3 when converting the deposited weights into the film thicknesses.

Membranes were tested by ultrafiltration of bleach effluents at the alkaline extraction stage (E-stage). Ultrafiltration was carried out with a stirred cell apparatus, shown in Figure 2, for a model of the
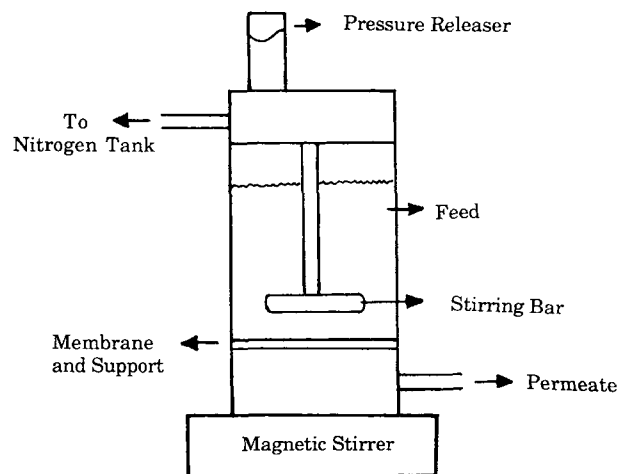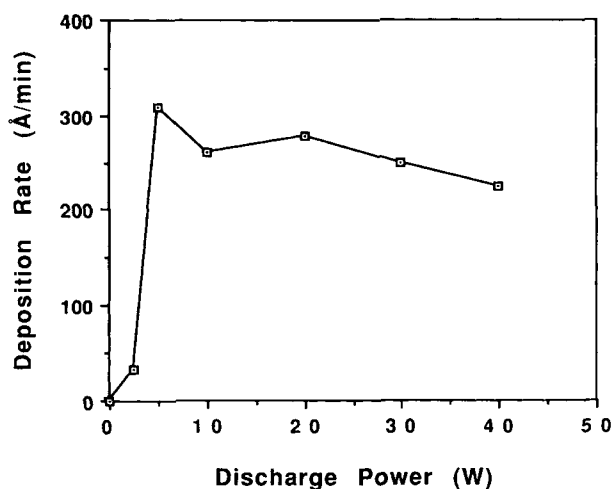
Figure 3 Deposition rates of plasma-polymerized acrylic acid as a function of discharge power: monomer flow rate, 5 SCCM; monomer pressure, 26 mTorr.

plate and frame unit. It was operated at a pressure of 3 bars and at room temperature. The stirrer was rotated at a speed of 300 rpm to reduce concentration polarization. Bleach effluent, 180 mL, was filtered in each batch operation with the concentration factor of 2.

The permeate was analyzed by means of UV/visible spectroscopy (Perkin-Elmer Lambda 6), COD, or AOX measurement. Light absorbances were measured at wavelengths from 200 to 700 nm. Chemical oxygen demand (COD) was analyzed by the Dr Lange cuvette test 114 on a Lasa Aqua spectrophotometer (Dr Lange).[16] Adsorbable organic halogens (AOX) were analyzed by acidification of the sample with nitric acid, and its organic constituents were adsorbed on activated carbon. The carbon was combusted with oxygen in a quartz tube at a temperature of 1000°C. The hydrogen chloride formed was absorbed in an electrolyte solution and determined by microconlometric titration.[17]

RESULTS AND DISCUSSION

Characteristics of PPAA films

Some characteristics of PPAA films have been investigated in a previous study.[18] A PPAA film showed a linear structure with a high density of carboxyl groups when polymerized at a low-energy input (5 W, 4 SCCM, 17 mTorr, W/FM = 2.3 × 10^7 J/kg). It was highly wettable by water (water contact angle of 15°). As the discharge power increased, however, the structure became cross-linked with a

Figure 2 Schematic diagram of a stirred cell apparatus for ultrafiltration.

lowered density of carboxyl groups and lowered wettability (42° at 20 W and 55° at 50 W). The deposition rate sharply increased until 5 W and became saturated.

The deposition rate of PPAA films at the condition of this study (5 SCCM, 26 mTorr) showed the same trend but with increased rates. Deposition rates of PPAA films are shown in Figure 3. Except for at a very low discharge power (2.5 W), the deposition rates are rather saturated for discharge powers in the range between 5 and 40 W.

The surface morphology of composite membranes depended on the size of pores in a substrate membrane, as shown in Figures 4 and 5. Figure 4 shows SEM pictures of an NTR7410 membrane surface before and after the deposition of a PPAA film for

7 min. The composite membrane shows a smooth surface with complete coverage of pores. Figure 5 shows SEM pictures of a Celgard 5410 membrane surface, which has larger pores, before and after the deposition of a PPAA film for 10 min. Even with a thicker film, the pores are not completely covered, and the surface is rough.

A PPAA film deposited at 5 W showed cation exchangeability in an alkaline solution, indicating the presence of acid groups. After immersion in $0.1 M$ NaOH solution for 48 h at room temperature, one sodium atom per six $—C(O)O—$ type carbon atoms was detected by ESCA. $—C(O)O—$ type carbons were 6% of the total carbons, which is much lower compared to the amount in the film (27%) without immersion in $0.1 M$ NaOH solution. The
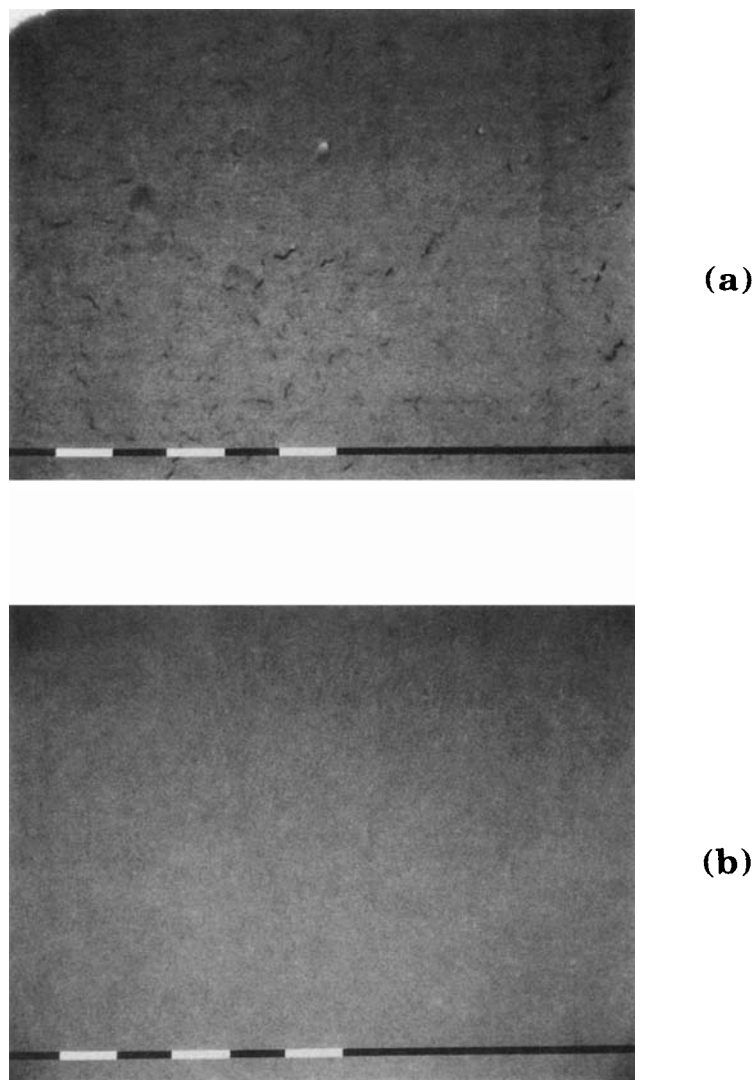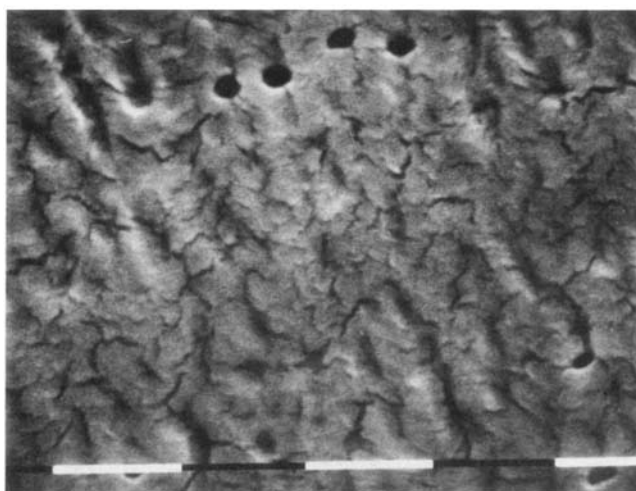

(a)

(b)

Figure 4 SEM pictures (×10,000) of an NTR7410 membrane surface (a) before and (b) after deposition of a PPAA film (4 min at 20 W and 3 min at 5 W).

Figure 5 SEM pictures (×20,000) of a Celgard 5410 membrane surface (a) before and (b) after deposition of a PPAA film (10 min at 20 W).

large reduction of —C(O)O— type carbons after storing under humid conditions or immersion in water is common, possibly due to a hydrogel effect.[18]

Composite Membranes on Various Substrate Membranes

Composite membranes were prepared on various kinds of substrate membranes. The conditions for plasma polymerization of acrylic acid and results after ultrafiltration are shown in Table I. The rejection was evaluated by light absorbances of permeates at wavelengths between 400 and 700 nm, which is used for simple color detection. The absorbances increased monotonically from 700 to 400 nm.

Absorbances at 400 nm are listed in Table I for convenience.

Composite membranes showed better rejection than did substrate membranes in all cases, as expected. The reductions of light absorbance were high for substrate membranes with lower molecular weight cutoff or smaller pores and for higher discharge power. A pronouncing result obtained by composite membranes may be that reduction of the flux is quite small even with a highly reduced absorbance (YM10 and NTR7410 membranes).

## Effect of PPAA Film Structure

The effect of the PPAA film structure on the rejection was studied by depositing PPAA films onto

Table I   Flux and Light Absorbances (at 400 nm) of Permeates after Ultrafiltration of E-Stage Bleach Effluent

Membrane	Power (W)	Time (min)	Flux (l/m² h)	Absorbance at 400 nm
	Plasma Condition			
Original bleach effluent				5.00
YM10	Unmodified		54.0	2.20
	5	5	49.2	1.63
	20	5	48.4	0.98
FS61PP	Unmodified		94.7	2.95
	20	5	94.7	2.29
Celgard 5511	Unmodified		69.2	3.76
	5	10	75.0	3.52
	20	10	34.6	2.78
Celgard 5410	Unmodified		No practical flow	
	20	10	11.4	0.39
NTR7410	Unmodified		50.7	1.06
	5	7	41.4	0.47
	20	7	23.8	0.12

YM10 membranes at various plasma discharge powers (5–30 W). After ultrafiltration, light absorbances of permeates at 262.5 nm were measured, for the simple measurement of AOX levels, as well as at 400 nm. The permeates of E-stage bleach effluent showed a characteristic peak at 262.5 nm, as shown in Figure 6, and the absorbances were linearly dependent on the AOX values with a little deviation at high absorbances (see Fig. 7). Results after ultrafiltration of E-stage bleach effluent are shown in Table II.

It is clear that the structure of a PPAA film plays an important role in improving the rejection. As the
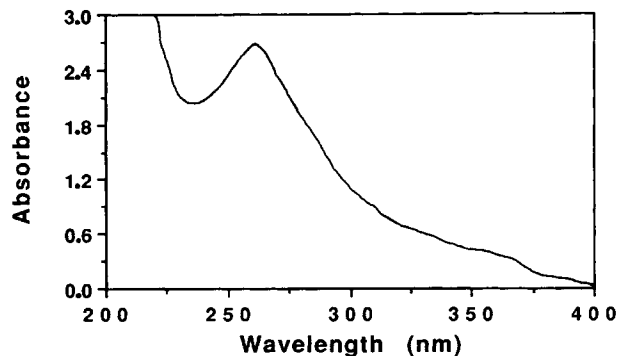
Figure 6   Typical UV absorption curve of ultrafiltrated E-stage bleach effluent.
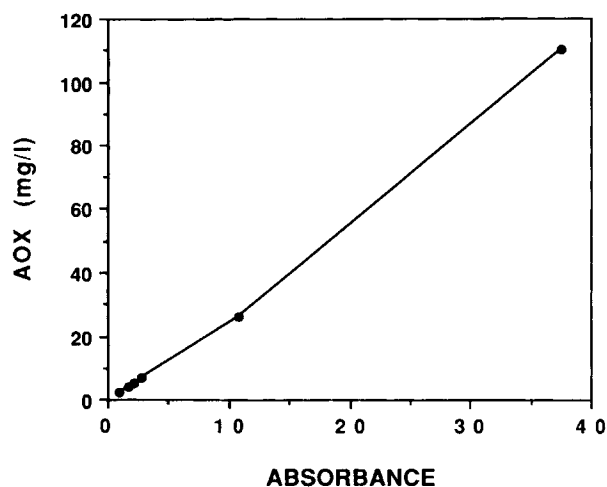
Figure 7   AOX value vs. UV absorbance at 262.5 nm of ultrafiltrated E-stage bleach effluent.

discharge power, thus, the degree of cross-linking, increased, the rejection significantly increased up to 20 W, indicating a molecular sieving effect of the cross-linked structure. The rejection decreased again at 30 W. This may be explained by the fact that highly cross-linked films are brittle and easily deformed under aqueous environments due to internal stress.[18] Lowered rejections for thicker films deposited at 20 W support this explanation. Internal stress of a plasma polymer film increases with the film thickness.

Despite good rejections, cross-linked structures gave almost no influence on the flux of a permeate. This is due to the ultrathin film thickness and good wettability. The thickness of films deposited for 5 min are under 1500 Å. Water-contact angles ranged

Table II   Flux and Light Absorbances of Permeates after Ultrafiltration of E-Stage Bleach Effluent with YM10 Composite Membranes

Power (W)	Time (min)	Flux (l/m² h)	At 262.5 nm	At 400 nm
Plasma Condition			Absorbance	
Unmodified		54.0	31.2	2.20
5	5	49.2	18.5	1.63
10	5	48.4	14.1	1.22
20	5	50.7	11.8	0.98
	7	48.8	14.4	1.14
	10	40.9	13.6	1.09
30	5	50.0	15.8	1.31

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between 10° and 45° on PPAA films deposited at discharge powers between 5 and 30 W.

Effect of Negatively Charged Surface

Table I shows that the most efficient improvement was achieved when a composite membrane was prepared on a YM10 membrane (20 W) considering both the extent of the improved rejection and reduction of the flux. However, NTR7410 composite membranes were much better in terms of the absolute value of rejections (light absorbances), although the flux was reduced to some extent. Since the main objective of this study was to obtain the highest possible rejection, especially of chlorinated compounds, as long as an adequate flux is maintained, further improvement was investigated with NTR7410 membranes.

A PPAA film was deposited by the combination of two different conditions for plasma polymerization: deposition at a higher discharge power (20 W) for a cross-linked film followed by deposition at a lower discharge power (5 W) for a negatively charged surface. This type of a film can provide the composite membrane with a dual effect of molecular sieving and electric charge repulsion.

The repulsion effect of a negatively charged surface is shown in Table III. A composite membrane prepared by the combination of 20 W (4 min)/5 W (3 min) is better, in both the rejection and the flux, than is a composite membrane prepared at 20 W alone for 7 min. This indicates that the charge repulsion between a negatively charged surface and negatively charged chlorinated compounds in bleach effluent contributes to increase the rejection. How-

ever, just charge repulsion is not sufficient enough for good rejection, since it is efficient only in low molecular weight compounds. The result obtained with a composite membrane prepared at 5 W (7 min) alone shows this fact. Although relatively high flux was obtained, due to absence of a cross-linked layer, rejection was much lower than in the membranes described above. The difference was more pronounced when the rejection was evaluated by the absorbance at 400 nm (four times) than by the absorbance at 262.5 nm (double). Inefficient rejection of large molecules by charge repulsion brings such a larger difference in the absorbance at 400 nm. It is believed that molecules with longer chain lengths are more responsible for the absorption at 400 nm and molecules with shorter chain lengths are more responsible for the absorption at 262.5 nm.

The results with composite membranes of some other combinations are also shown in Table III. More improvements were achieved in the rejection but with corresponding reductions of the flux. As a whole, the removal of AOX (94–98%) was more efficient than the removal of COD (78–86%). It is a general trend in ultrafiltrations of bleach effluents except that the difference is a little bit larger due to the effect of a negatively charged surface. The AOX value is only part of the COD value, which is the measure of amount of organics including molecules that do not carry negative charge.

Fouling and Cleanability

One of the important factors in membrane-separation processes is fouling and cleanability, which determines the efficiency of a process and the lifetime

Table III   Results after Ultrafiltration of E-Stage Bleach Effluent with NTR7410 Composite Membranes

Plasma Condition			Absorbance			
Power (W)	Time (min)	Flux (l/m² h)	At 262.5 nm	At 400 nm	AOX (mg/L)	COD (mg/L)
Original bleach effluent			37.5	5.00	110	3180
Unmodified		50.7	10.8	1.06	26	1060
5	7	41.4	6.7	0.47		
20	7	23.8	3.05	0.12		
20/5[a]	4/3	33.8	2.75	0.085	6.7	520
20/5	7/3	19.5	1.68	0.045	4.2	450
30/5	4/3	9.1	0.88	0.023	2.2	690
30/5	2/1	24.0	2.1	0.056	5.1	480
30/5	1/1	16.4	1.62	0.038		

[a] 4 min deposition at 20 W followed by 3 min deposition at 5 W.
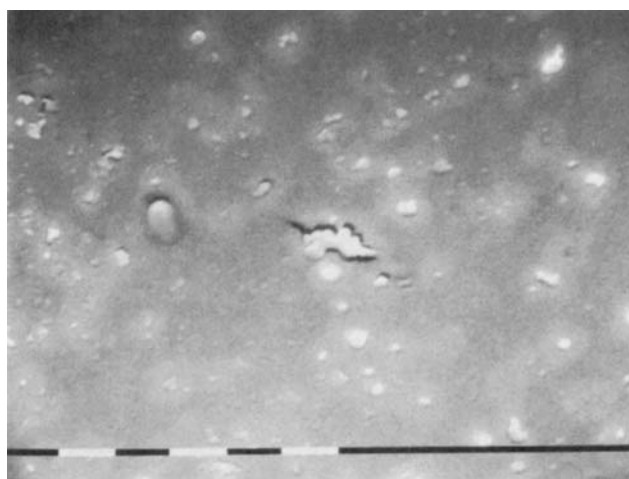
(a)
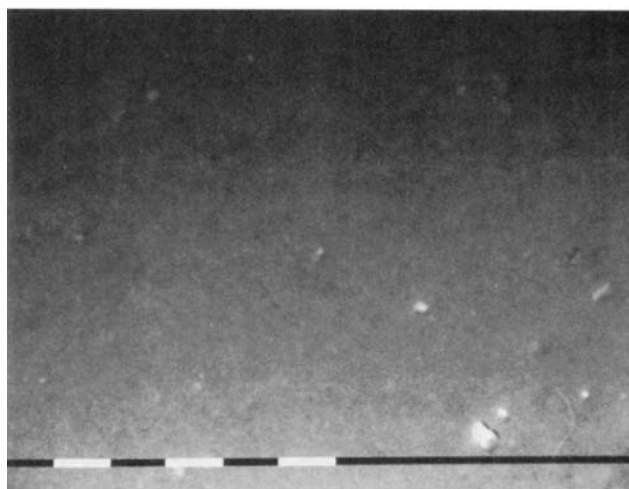
(b)

Figure 8   SEM pictures (×10,000) of (a) an NTR7410 membrane surface and (b) an NTR7410 composite membrane surface after ultrafiltration of E-stage bleach effluent.

of a membrane. Although fouling after a long run was not investigated in this study, SEM pictures after ultrafiltration and water rinse showed a large difference in cleanability between an NTR7410 membrane and an NTR7410 composite membrane. As shown in Figure 8, the number of particles left was much smaller on the surface of a composite membrane. SEM pictures were taken on the spot with the largest number of particles.

CONCLUSIONS

From this study, the following can be concluded:

1. Plasma polymerization is a highly efficient process for the formation of composite mem-

brane. An ultrathin nonporous film can be deposited uniformly on a porous substrate membrane if the size of pores is not so large. The structure and the functionality of a film can be controlled. The film is defect-free.

2. Composite membranes prepared by deposition of a PPAA film improves the rejection, especially of chlorinated compounds, in ultrafiltration of bleach effluent with small reduction of the flux.

3. Composite membranes with a film of dual functionality, molecular sieving by a cross-linked structure and charge effect, are more efficient than are composite membranes with a homogeneous film.

4. The composite membranes are easy to clean with water.

5. Membranes with smaller pores are better for a substrate membrane to form composite membranes.

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