

Plasma Polymerization of Octafluorocyclobutane and Hydrophobic Microporous Composite Membranes for Membrane Distillation

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SYNOPSIS

In this paper, hydrophilic microporous cellulose nitrate membranes have been surface-modified by plasma polymerization of octafluorocyclobutane (OFCB). The microporous composite membranes with a hydrophilic layer sandwiched between two hydrophobic layers have been obtained. The obtained composite membranes have been used in a membrane distillation (MD) process and have exhibited good performance. The effects of polymerization conditions, such as glow-discharge power and deposition time, on the structures and MD performances of the obtained composite membranes have been investigated by SEM, X-ray microscopical analysis, and XPS. The polymerization conditions should be as mild as possible in order to prepare the hydrophobic composite membrane with good MD performance. The typical MD behaviors of the obtained hydrophobic composite membranes are in agreement with that of hydrophobic membranes directly prepared from hydrophobic polymeric materials, like PVDF, PTFE, or PP.

I. INTRODUCTION

Membrane distillation (MD) is a thermally driven membrane process. Because it has potential application in the production of high-purity water and for concentration of solutions, this process has obtained increased attention since Gore proposed in 1982 a spiral-type module named the "Gore-Tex membrane distillation."¹ However, lower flux prevents it from competing with other membrane process, for example, reverse osmosis, on the commercial scale. For this reason, to enhance the MD flux is still an open question. Besides module design, the property of the hydrophobic membranes used is the most important factor influencing the MD flux. Hydrophobicity and suitable microporous structure are two essential prerequisites for the membranes used for MD. Up to now, all hydrophobic microporous membranes used for MD have been directly prepared from hydrophobic polymeric materials, like PP,

PVDF, or PTFE.^{1,2} Production of hydrophobic microporous membranes is more difficult and less matured in comparison with production of hydrophilic microporous membranes, as the latter have been investigated for several decades. Therefore, it is easier to produce the hydrophilic microporous membranes with appropriate pore morphology for MD. Nevertheless, hydrophilic microporous membranes are not suitable for MD of aqueous solution because of their hydrophilicity. They have to be transformed into hydrophobic membranes by surface modification so that they can be used in the MD process for aqueous solution. This is a possible approach to enhance the MD flux.

The plasma technique is a useful tool in modification of surface properties for polymeric materials. Nowadays, more and more attention is being paid to its application in membrane separation science. The plasma technique has been applied so far to preparation of membranes used for reverse osmosis, pervaporation, and gas separation.³⁻⁵ But the application of the plasma technique in preparation of membranes for MD has not yet been reported. Compared with other plasma polymers, plasma

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polymer of fluorocarbon has much better chemical resistance, thermal resistance, and adhesivity to the substrate.⁶ Especially, the high hydrophobic plasma polymer film with a contact angle above 165° could be prepared from plasma polymerization of fluorocarbon.⁷ All these advantages of fluorocarbon plasma polymer are suitable for modifying the hydrophilic microporous membranes so that the high hydrophobic microporous membranes for MD can be produced.

The aim of this study was to investigate the possibility of preparation of hydrophobic microporous composite membranes for MD from hydrophilic microporous membranes. In this approach, the plasma polymerization technique was utilized to modify the hydrophilic microporous membrane so that the hydrophilic membrane could be turned into hydrophobic membrane for use in MD. Octafluorocyclobutane and cellulose nitrate microporous membrane were used as monomer and substrate membrane, respectively. The effects of polymerization conditions on the structures and MD performances of the obtained hydrophobic composite membranes have been studied. The typical MD performance of the obtained hydrophobic composite membranes were compared with that of hydrophobic membranes directly prepared from hydrophobic polymeric materials.

II. EXPERIMENTAL

2.1. Plasma Polymerization

The apparatus used for plasma polymerization in this study was a capacitively coupled reaction system

with external electrodes, as reported elsewhere.⁸ The distance between the two copper electrodes was 20 cm and the monomer inlet was located in the middle between the two electrodes.

The experimental procedure is described as follows: First, cellulose nitrate microporous membrane as the substrate membrane was placed under the monomer inlet. Then, the reaction system was evacuated down to a pressure of 0.39 Pa. The monomer was then introduced into the reactor until the pressure reached 12 Pa. Finally, glow discharge was initiated. The two surfaces of the substrate membrane were separately treated under the same condition.

Octafluorocyclobutane (OFCB) (99.9% in purity, from the experimental plant of the Shanghai Institute of Organic Chemistry, Academia Sinica) was used as monomer. The substrate membrane used was cellulose nitrate (CN) membrane ($0.45 \mu\text{m}$ nominal pore size, from the plant of the Beijing School of Chemical Technology).

2.2. Structure and Properties of the Modified Membrane

The contact angle was measured on a contact anglemeter Model G-II (Japanese Optical Co.). Surface morphology, distribution of the F element across the membrane, and surface element composition of the membrane were determined by SEM, X-ray microscopical analysis, and XPS, respectively.

2.3. Membrane Distillation

The MD was carried out in an apparatus of the direct-contact type. The apparatus is shown schematically in Figure 1. The warm and cold sides were

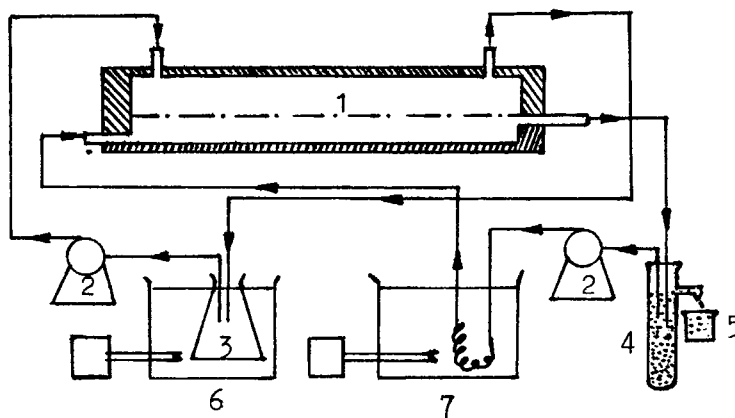


Figure 1 Schematic diagram of experimental apparatus of membrane distillation (MD): (1) membrane; (2) pump; (3) container of NaCl solution; (4) container of distillate; (5) beaker; (6) heating system; (7) cooling system.

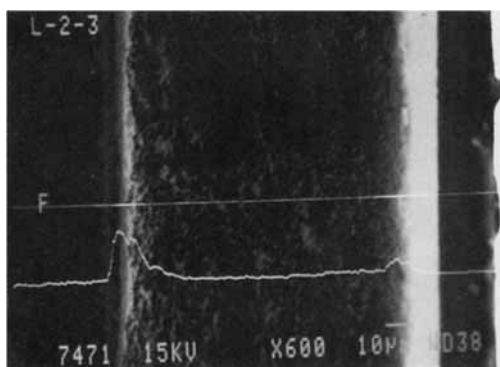


Figure 2 Distribution of F element across the CN MF membrane modified by plasma polymerization of OFCB.

filled with 0.5 M NaCl aqueous solution and distilled water, respectively. The flux was measured by weighing the distillate that overflowed from the distillate container. The retention coefficient was determined by measuring NaCl concentration of the distillate with a conductometer.

III. RESULTS AND DISCUSSION

3.1. Structure of the CN Membranes Modified by Plasma Polymerization of OFCB

The structure and properties of the membrane will be greatly altered if it is modified by plasma polymerization. In this study, the hydrophilic microporous CN membrane was transformed into hydrophobic microporous composite membrane after modification by plasma polymerization of OFCB.

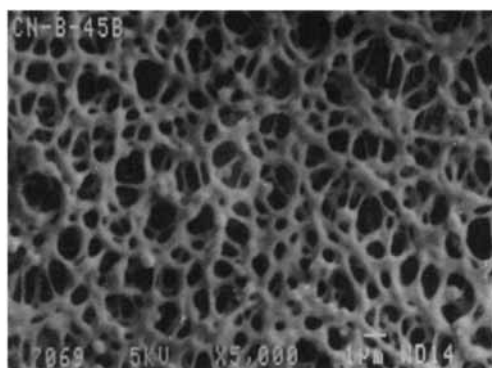
The water-contact angles of all the modified membranes in this paper were above 100°.

The structures of modified membranes were investigated by the SEM and X-ray microscopical analysis. Figure 2 shows the distribution of the F element across the modified membrane, and Figure 3 illustrates the scanning electron micrographs of surfaces of the original and modified membranes. As illustrated in Figure 2, in the process of modification, most of the plasma polymer was deposited on the surface of the CN microporous membrane; only a small amount of plasma polymer could be deposited in the micropores of the membrane. Globular polymer deposits could be observed clearly on the surface of the modified membrane, as shown in Figure 3.

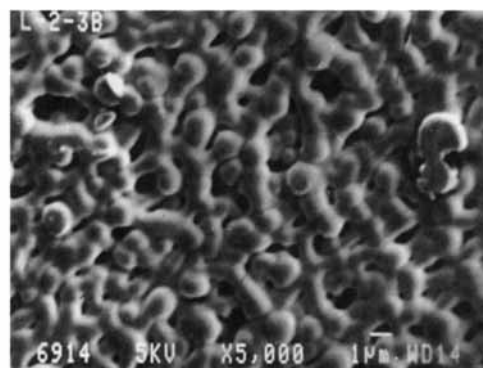
The above results show that a microporous composite membrane composed of a hydrophilic layer sandwiched between two thin hydrophobic layers has been produced after modification of hydrophilic CN MF membrane by plasma polymerization of OFCB.

3.2. Plasma Polymerization and Properties of the Modified CN Membrane

The essential requirements for the membrane used for MD are nonwettability and appropriate pore size. Because water-penetrating pressure through porous membrane is inversely proportional to the pore diameter, a certain pressure difference between the two sides of the membrane should be allowed in practical application. The larger the pore size is, the more easily water penetrates the pore, decreasing the retention coefficient, if not preventing the MD



a. original membrane



b. modified membrane

Figure 3 SEM of the surfaces of the original and modified CN MF membranes: (a) original membrane; (b) modified membrane.

process from continuing, whereas smaller pore size will result in lower MD flux. Thus, the membranes with high hydrophobicity, which provide the possibility of increasing the pore size of the membrane for MD, are prepared in order to enhance the MD flux. In the process of preparation of hydrophobic composite membrane by the plasma polymerization technique, the surface structures and properties of the modified membranes are significantly dependent on plasma polymerization conditions.

3.2.a. The Effect of Glow-Discharge Power on Properties of the Modified Membranes

Figure 4 shows scanning electron micrographs of the surfaces of the modified membranes prepared with different glow-discharge power at the deposition time of 5 min. It is clearly seen that the pore size of the modified membrane slightly depends on glow-discharge power.

The hydrophobicity of the modified CN membrane is contributed to by the fluorine-containing groups on the membrane surface, such as $-\text{CF}-$, $-\text{CF}_2-$, and $-\text{CF}_3$. The other groups containing oxygen and nitrogen on the surface of the membrane, like $-\text{OH}$ or $-\text{NO}_2$, decrease the hydrophobicity of the modified membrane. In the plasma polymerization process, the elemental composition of the obtained plasma polymer is significantly affected by the glow-discharge power. As a result, a suitable glow-discharge power should be selected so that the modified membranes with the plasma polymer layer that contains more fluorine element and fewer oxygen and nitrogen elements can be prepared. Therefore, the modified membranes with good hydrophobicity could be obtained.

The surface elemental compositions of the modified membranes analyzed by XPS and the water-contact angles of the membranes are listed in Table I as a function of discharge power. The N/C ratio

increased with increasing discharge power. When discharge power was less than 150 W, the F/C ratio decreased and the O/C ratio increased with increasing discharge power. When the discharge power was greater than 150 W, the F/C ratio increased and the O/C ratio decreased with increasing discharge power. The minimum value of the F/C ratio and the maximum value of the O/C ratio were observed at discharge power of 150 W. The water-contact angles of the modified membranes also varied with the glow-discharge power. Compared with the modified membranes prepared at a discharge power of 60, 175, and 200 W, the water-contact angles of the modified membranes at a discharge power of 100 and 150 W were smaller because of the lower fluorine contents and higher oxygen and nitrogen contents on the surfaces of the modified membranes. The modified membranes prepared at a discharge power of 60, 175, and 200 W showed high hydrophobicity.

In the modification process of CN membrane by plasma polymerization of OFCB, the CN membrane is exposed to the bombardment of energetic particles in plasma and gradually degraded. The degradation products of the CN membrane are gaseous fragments containing oxygen and nitrogen. Some of these gaseous fragments are polymerized again under the influence of plasma and deposited on the membrane. The degradation rate of the CN membrane is greatly dependent on the discharge power. The higher the discharge power, the higher the degradation rate is and the more gaseous fragments containing nitrogen produced. As a result, the plasma polymer film deposited on the surface of CN membrane contains more nitrogen element, as shown in Table I.

The effect of discharge power on the F/C ratio and O/C ratio presented in Table I can be interpreted as follows: The mechanism of plasma polymerization in the glow discharge is a process of competitive ablation and polymerization (CAP).⁹ The deposition rate, structure, and properties of the

Table I Surface Elemental Composition and Water-Contact Angles of Modified Membranes Prepared at Different Discharge Powers^a

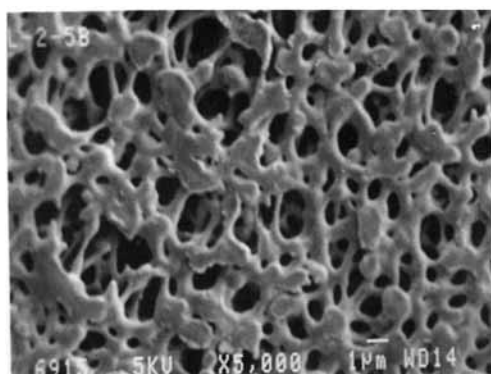
	Discharge Power (W)				
	60	100	150	175	200
Elemental composition					
F/C ratio	1.12	0.500	0.278	1.03	1.05
O/C ratio	0.100	0.319	0.331	0.197	0.154
N/C ratio	0.0374	0.0474	0.0589	0.0521	0.0869
Water contact angle (°)	113	101	100	120	120

^a Deposition time, 5 min.

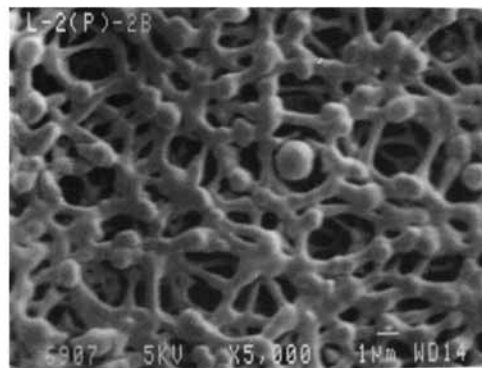
plasma film are significantly affected by the balance of polymerization and ablation. For the case of using CN membrane as substrate, the effect of discharge power on the ablation rate and the deposition rate of OFCB plasma differs from that noted by Yie and Chen.⁹ The degradation products of CN membrane can capture active fluorine particles in plasma to lower the ablation rate of OFCB plasma. When discharge power was less than 150 W, the degradation rate of CN membrane was less than the generation rate of the active fluorine particles in OFCB plasma. The concentration of the active fluorine particles in plasma increased with increasing discharge power, so the ablation rate of OFCB plasma increased and deposition rate of OFCB plasma polymer decreased with increasing discharge power. Therefore, the F/C ratio and O/C ratio decreased and increased with increasing discharge power, respectively. On the contrary, when the discharge power was greater than

150 W, the degradation rate of the CN membrane was greater than the generation rate of active fluorine particles with increasing discharge power. More and more active fluorine particles were captured by degradation products of the CN membrane. The ablation rate of OFCB plasma was decreased and deposition rate of OFCB plasma polymer was increased. Thus, an increase of F/C ratio and a decrease of O/C ratio were observed.

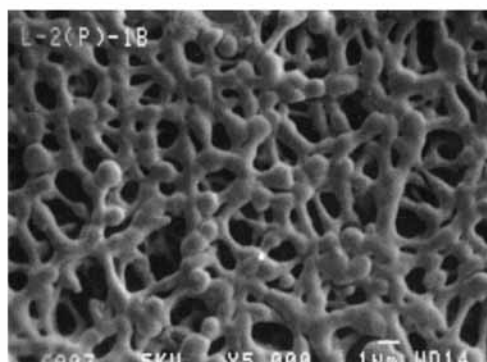
The MD performances of the modified membranes were decided by the structures and the surface properties of the membranes. The factors affecting the MD performance of the modified composite membrane include the hydrophobicity, pore size, pore size distribution, and thickness of the plasma polymer layer of the membrane. As shown in Figure 4, the membrane pores were large for the modified membranes at the deposition time of 5 min. In consequence of this, high hydrophobicity and



a. 60 W



b. 150 W



c. 200 W

Figure 4 SEM of the surfaces of the modified composite membranes prepared at different discharge powers; duration of deposition 5 min: (a) 60 W; (b) 150 W; (c) 200 W.

thick deposited plasma polymer layers were required for the modified composite membranes to prevent water from penetrating into the membrane pores.

The thickness of the plasma polymer layer of the modified membrane was decided by the deposition rate of OFCB plasma polymer. For the modified membranes at discharge power of 100 and 150 W, the lowest deposition rates of OFCB plasma polymer resulted in the thinnest plasma polymer layers. For the modified composite membrane at the discharge power of 175 W, the deposition rate of the OFCB plasma polymer was lower when compared with the membranes prepared from discharge power of 60 and 200 W. Therefore, the deposited plasma polymer layer of the modified membrane at discharge power of 175 W was thinner than that of the modified membranes at discharge power of 60 and 200 W. MD performances of the modified membranes at the deposition time of 5 min are tabulated in Table II as a function of discharge power. For the modified membranes prepared at the discharge power of 100 and 150 W, the MD process could not be carried out because both the hydrophobicity and the thickness of the deposited plasma layers of the modified membranes were not enough to prevent water from entering the membrane pores. The membranes at discharge power of 60 and 200 W presented higher MD flux and retention coefficients because of the high hydrophobicity and the thick deposited plasma polymer layers of the membranes. Although the modified composite membranes at discharge power of 175 W had good hydrophobicity, its thin deposited plasma layer was not able to prevent water from entering parts of the large pores of the modified membrane. This would decrease the retention coefficient of the membrane. When some of the pores of the membranes used in MD were entered by water, the effective membrane area for vapor transportation was decreased. Besides this, the distillate would

flow toward the NaCl solution side through water-entered pores due to the osmosis pressure. The above two reasons could cause the decrease of the MD flux. Therefore, the modified membranes at discharge power of 175 W presented low MD flux and retention coefficients.

The results demonstrate that the MD performance of the modified membrane is significantly dependent on the glow-discharge power, by which the hydrophobicity of the membrane is greatly affected. To prepare the modified membrane with good MD performance, the discharge power should be as low as possible as long as glow discharge could be initiated. This condition is necessary to decrease the degradation rate of the membrane and the ablation rate of OFCB plasma so that the deposition rate of OFCB plasma is dominant. As a result, the very hydrophobic modified membrane can be obtained.

3.2.b. Effect of Deposition Time on the Structure and Properties of the Modified Membrane

As mentioned above, the modified CN composite membrane with high hydrophobicity is able to be prepared by the correct choice of glow-discharge power, but the pore size of the modified membrane slightly depends on the glow-discharge power. The control of the pore size of the modified membranes can be realized by the regulation of deposition time. Figure 5 shows the scanning electron micrographs of the surfaces of modified membranes prepared at different deposition times. As shown, with increasing deposition time, the pore size of modified membranes was gradually decreased until 90 min, at which time the pores are almost covered with plasma polymer.

The MD performances of the modified membranes are illustrated in Figure 6 as a function of deposition time. The MD flux of the modified membrane decreased with increasing deposition time, since both pore diameter and number of the pores of the modified membrane decreased with increasing deposition time. When the deposition time was less than 30 min, the decrease of pore size of the modified membrane resulted in the increase of nonwettability of the modified membranes while deposition time was increased. Therefore, the retention coefficient showed a rapid increase. When the deposition time was more than 30 min, the pore size of the modified membrane was small enough to prevent water from entering the pores of the membranes and the retention coefficient asymptotically approached 100%. The further increase of deposition time just caused the decrease of the MD flux.

Table II Membrane Distillation (MD) Performances of Modified Membranes Prepared at Different Discharge Powers^a

	Discharge Power (W)				
	60	100	150	175	200
Flux (kg/m ² ·h)	32.0	—	—	12.0	31.5
Retention coefficient (%)	92.1	0	0	89.6	92.0

^a Temperature of warm side, 70°C; temperature of cold side, 25°C.

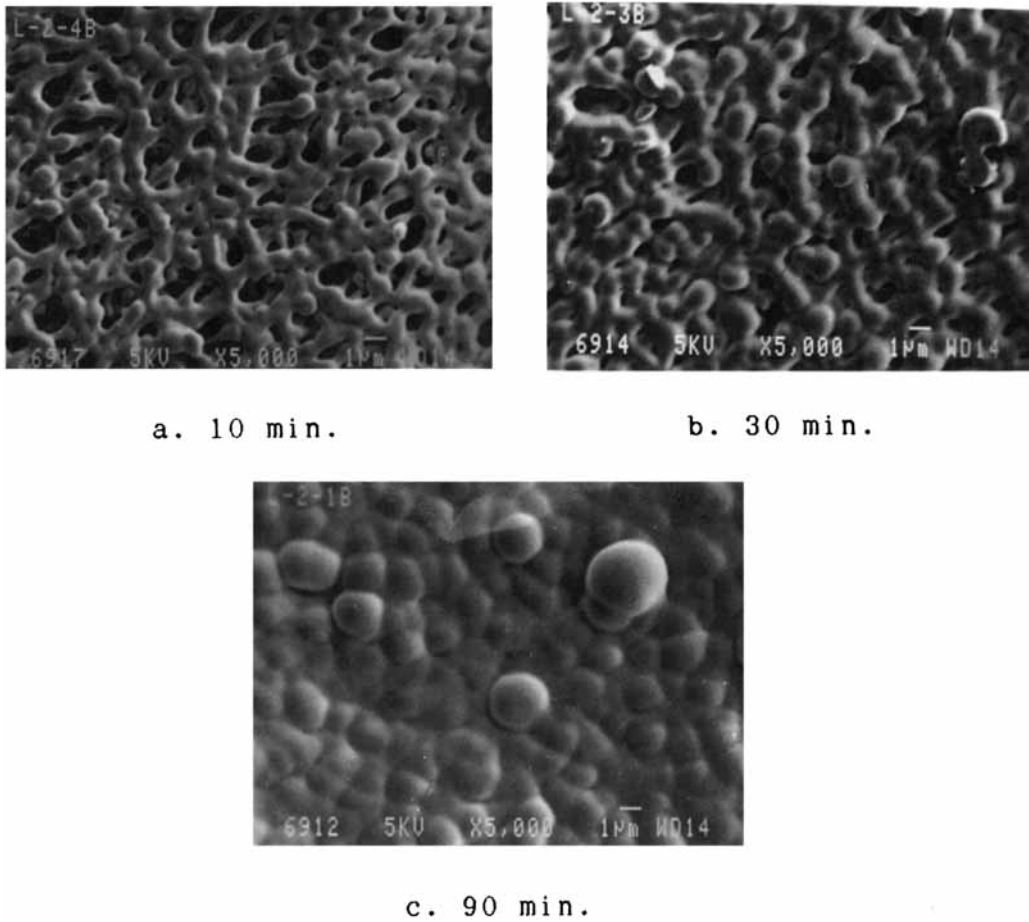


Figure 5 SEM of the surfaces of the modified membranes prepared with different deposition times at the discharge power of 60 W: (a) 10 min; (b) 30 min; (c) 90 min.

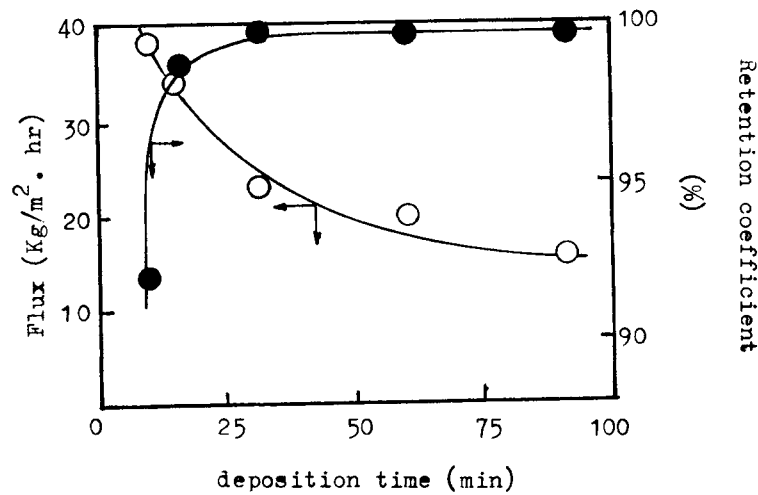


Figure 6 MD performances of the modified composite membranes prepared with different deposition time at the discharge power of 60 W.

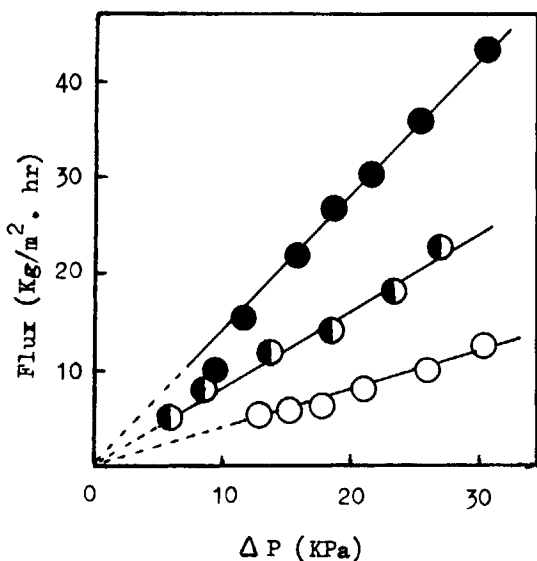


Figure 7 Relationship between MD flux and vapor pressure difference across the membrane for the modified composite membranes prepared at discharge power of 60 W; deposition time: (O) 90 min; (D) 30 min; (●) 10 min.

3.3. Typical MD Behaviors of Hydrophobic Microporous Composite Membrane

For the hydrophobic membranes prepared directly from hydrophobic polymeric materials, the typical experimental phenomenon of MD is that the MD flux is proportional to the vapor pressure difference across the membrane ($J = Km \times P$), characterized by a straight line through the origin.¹⁰ For the hy-

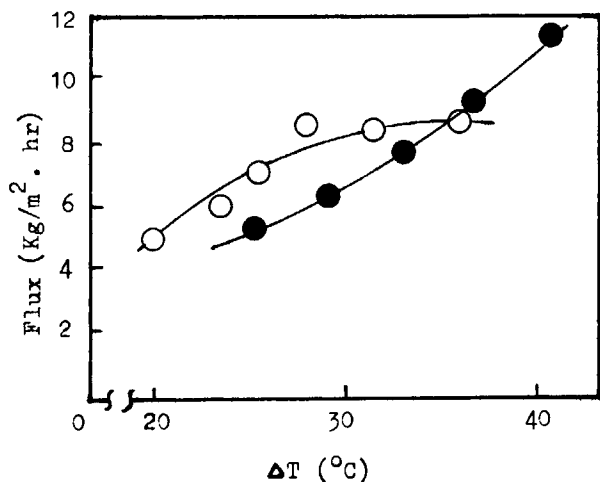


Figure 8 Relationship between MD flux and temperature difference across the membrane for the modified membrane prepared at discharge power of 60 W and deposition time of 60 min: (O) temperature of the warm side is 55°C; (●) temperature of the cold side is 20°C.

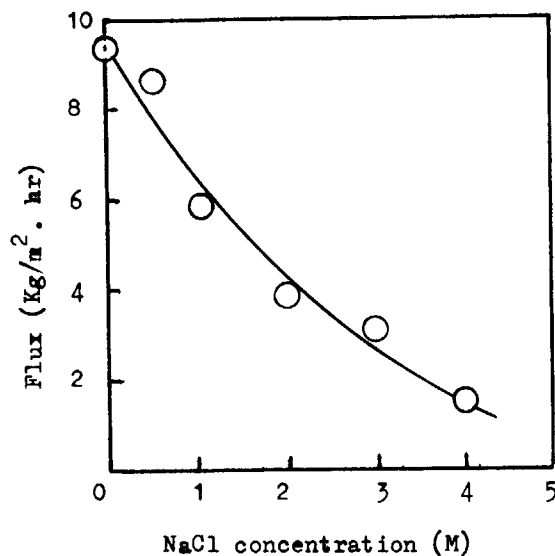


Figure 9 Relationship between MD flux and NaCl concentration in warm aqueous solution for the modified composite membrane prepared at discharge power of 60 W and deposition time of 60 min; temperature of warm side, 55°C; temperature of cold side, 25°C.

drophobic CN microporous composite membranes modified by plasma polymerization of OFCB, the MD fluxes are plotted as a function of vapor pressure difference across the membrane in Figure 7. Straight lines through the origin were obtained. The MD fluxes of the modified membranes were all proportional to the vapor pressure difference across the membrane, in accordance with the typical behavior of MD. The experimental results for the modified hydrophobic composite membrane are shown in Figures 8 and 9 in terms of MD flux as a function of temperature difference across the membrane and solute concentration in warm aqueous solution. As illustrated in Figure 8, the MD flux increased nonlinearly with an increasing temperature difference across the membrane due to the nonlinear relationship between MD flux and temperature difference across the membrane. The increase of solute concentration in warm aqueous solution resulted in the decrease of vapor pressure difference across the membrane, and, in consequence, the MD flux decreased with increasing solute concentration in warm aqueous solution, as shown in Figure 9.

IV. CONCLUSIONS

1. The hydrophobic microporous membrane composed of a hydrophilic layer sandwiched

between two hydrophobic layers has been prepared from cellulose nitrate (CN) MF membrane by modification with plasma polymerization of OFCB.

2. The hydrophobic microporous composite membrane obtained have been applied to the membrane distillation (MD) process and the typical MD behaviors of the modified hydrophobic composite membrane were in accordance with that of the hydrophobic membranes directly prepared from hydrophobic materials. The modified hydrophobic composite membranes showed good MD performances.
3. To prepare the hydrophobic microporous CN composite membranes with high hydrophobicity, the plasma polymerization conditions of OFCB should be as mild as possible. The pore size of the modified composite membranes could be controlled by the adjustment of deposition time.

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