

Preparation of Microporous Chlorinated Poly(Vinyl Chloride) Membrane in Fabric and the Characterization of Their Pore Sizes and Pore-Size Distributions

Jong Seok Kang, Ki Yoen Kim, Young Moo Lee

National Research Laboratory for Membranes, School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

Received 31 October 2001; accepted 17 January 2002

ABSTRACT: Chlorinated poly(vinyl chloride) (CPVC)/poly(vinyl pyrrolidone) (PVP) membranes were prepared by using the solvent system tetrahydrofuran (THF)/*n*-butyl alcohol (*n*-BA) to investigate the possibility of pore size and pore-size distribution control. The coagulation of CPVC/PVP solution was induced by the exposure to water vapor at 25 (± 0.5)°C. The average pore diameter, d_p , and the size distribution of pores on the surface of the membrane were quantified through the image analyzer from the images visualized by field emission scanning electron microscope (FE-SEM). Surface pore size and distribution of the prepared CPVC/PVP membrane were strongly affected by the relative humidity (RH) in the environment and the content of

PVP used as an additive. Particularly, in the case of CPVC membrane without PVP, the mean pore size was 0.15–0.2 μm , depending on the RH. The pore distribution became broad with the increase of the RH. The membranes had open pores as confirmed by the hydraulic permeation experiment. In addition, the water flux and membrane resistance (R_m) were greatly affected by the composition of polymer solution and the RH. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1195–1202, 2002

Key words: chlorinated poly(vinyl chloride) (CPVC) membrane; water vapor induced phase separation; membrane resistance; surface pore size

INTRODUCTION

Microfiltration, which covers the pore size ranging between 0.1 and 10 μm , has been widely used to separate liquid/liquid or liquid/solid mixtures.¹ Different membrane separation processes require different membrane structures to bring about good separation performance.² Also, separation property of microporous membranes is mainly determined by the pore diameter in the membrane surface as well as the surface chemical properties.^{3–5} Therefore, it is important to fabricate membranes with pore size suitable for the specific application.

Scanning electron microscopy is a tool used for direct observation of objects down to several microns in scale. Some tools, based on the image analysis, have already been developed to characterize porous media, especially in the field of metallurgy,⁶ ceramic and polymeric membranes,^{7,8} and other materials. In membrane technology, the observation of the surface or the cross-sectional morphology is common. The method presented here allows the treatment and the analysis of digital images by means of the image anal-

ysis program, which allows the pore size and frequency measurement.

Generally, it is a well-known fact that the pore sizes are affected by the concentration of the polymer solution and the relative humidity (RH) in the environment.^{9,10} However, this trend has not been consistent. In addition, no investigation has been reported for the combined effects of RH and polymeric additive on the pore size and distribution of membrane surface in the case of the water vapor induced phase separation.

The addition of organic components as an additive to a casting solution has been one of the important techniques used in membrane preparation. However, the role of various organic additives such as methyl cellulose, glycerin, poly(vinyl pyrrolidone) (PVP), and poly(ethylene glycol) in casting solution has been reported as a pore-forming agent enhancing permeation properties.^{11–16} Therefore, the surface morphology and permeation performance of membrane as functions of PVP concentration was observed at a given RH. Also, chlorinated poly(vinyl chloride) (CPVC), which had better mechanical and thermal properties than poly(vinyl chloride) (PVC), is a new microfiltration membrane material.

The objective of the present study is to investigate the effects of RH and the amount of PVP on the variation of average pore diameter, d_p , and the size distribution of pores on the surface of the membrane

Correspondence to: Y. M. Lee (ymlee@hanyang.ac.kr).

Contract grant sponsor: National Research Laboratory Program.

TABLE I
Characterization of CPVC Membranes and Their Permeation Properties

Sample code	RH ^a (%)	Content of PVP ^b (wt %)	Flux	Resistance
			(L/m ² h) <i>J_w</i> ^c	(10 ¹⁰ m ⁻¹) <i>R_m</i> ^d
CP9045		0	240	75.0
CP9145	45	1	1080	16.7
CP9245		2	3470	0.52
CP9345		3	4570	0.39
CP9060		0	550	32.7
CP9160	60	1	3221	0.56
CP9260		2	4104	0.44
CP9360		3	5800	0.31
CP9080		0	1790	10.1
CP9180	80	1	3530	0.51
CP9280		2	4830	0.37
CP9380		3	7262	0.25

^a Automatically controlled with error range of $\pm 2\%$.

^b Poly(vinyl pyrrolidone).

^c Deionized water flux.

^d The membrane resistance (R_m) was calculated by the measured deionized water flux (J_w) by using the classical resistance model ($J = \Delta P / \eta R_m$).

by using a field emission scanning electron microscopy (FE-SEM) and analysis program. The phase-inversion process was guided by coagulating the polymer dope solution with the water vapor. The topology of microporous CPVC membrane was controlled upon varying the amount of PVP (MW, 10 kDa) in the solution of CPVC in the solvent system [tetrahydrofuran (THF)/*n*-butyl alcohol (*n*-BA) 70 : 30 wt %], as well as by water vapor concentration. In addition, because the hydraulic flux is important in the filtration, the pure water flux was measured by using a dead-end filtration apparatus. The membrane resistance (R_m) was calculated from the hydraulic flux.

EXPERIMENTAL

Materials

A CPVC (Nippon Carbide Ind. Co. Inc., Tokyo, Japan) with a chlorine content of about 63–68% was obtained and used as the membrane-forming polymer. PVP (M_w , 10 kDa, Aldrich Chemical Co., Milwaukee, WI) was used as the additive polymer. CPVC and PVP were dried under vacuum at 50°C for 2 h to minimize the presence of water in the polymer prior to the preparation of the solution. THF and *n*-BA were used as received without further purification.

Preparation of dope solution

CPVC/PVP dope solutions were made by dissolving CPVC/PVP in the solvent system. The composition of solvent system was 70 (THF) to 30 (*n*-BA) (%w/w). Polymer dope solutions were prepared by increasing the concentration of PVP while the total concentration of CPVC in the solution was maintained at 9 wt %. The microporous flat membranes were prepared by exposing the casting solutions at RH of 45, 60, and 80%, respectively. The compositions of polymer solution were summarized in Table I.

Preparation of microporous CPVC membrane

Membranes were prepared inside a glove box (model SK-G001, JEIO Tech., Seoul, Korea) capable of controlling both the RH and the temperature in the accuracy limit of $\pm 2\%$. The dope solution was cast on a polyester fabric with a casting knife of 150 μm thickness inside the glove box, with the humidity kept in the range of 35–88% at $25 \pm 0.5^\circ\text{C}$. The CPVC/PVP solution deposited on the polyester fabric was kept for 2 h in the glove box to dry and then moved into the

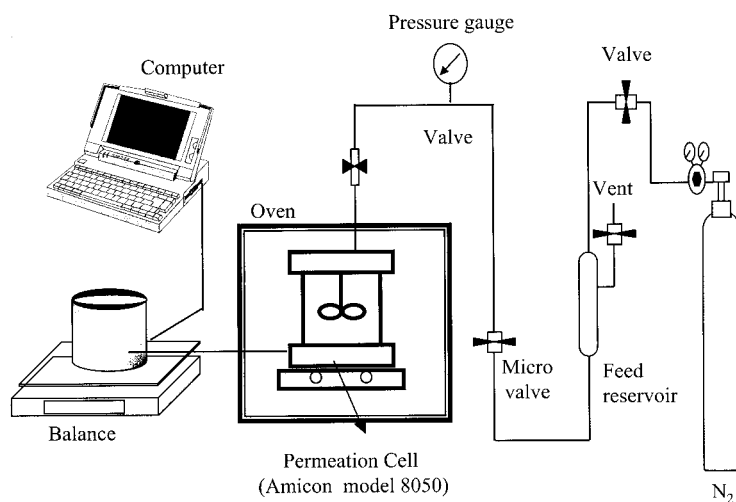


Figure 1 Schematics of dead-end filtration apparatus.

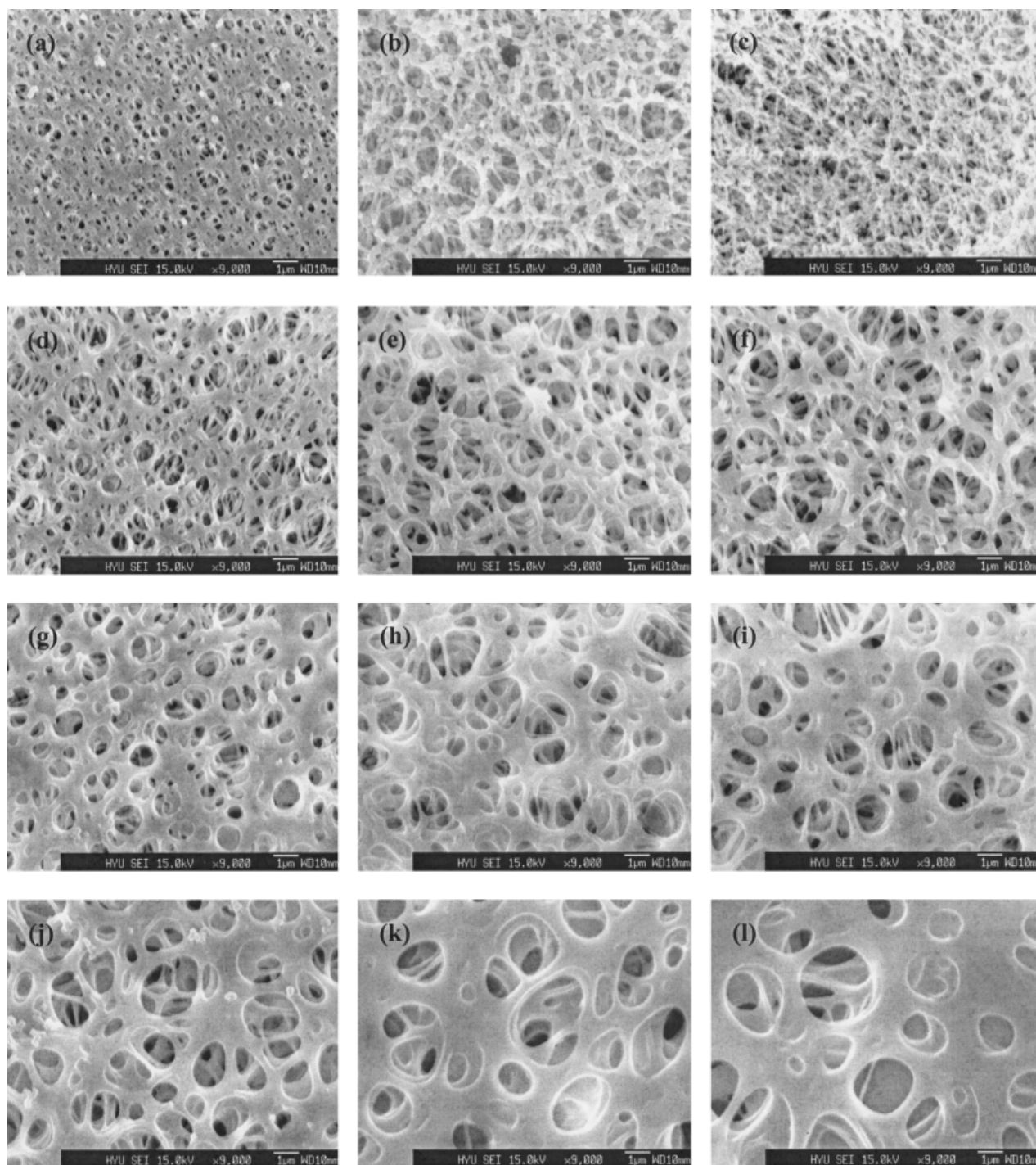


Figure 2 Photographs of the surface of CPVC membranes at a magnification of $\times 9000$. CP90 series without PVP: (a) CP9045; (b) CP9060; (c) CP9080; CP91 series with 1 wt % PVP: (d) CP9145; (e) CP9160; (f) CP9180; CP92 series with 2 wt % PVP: (g) CP9245; (h) CP9260; (i) CP9280; CP93 series with 3 wt % PVP: (j) CP9345; (k) CP9360; (l) CP9380.

convection oven at 30°C to eliminate the residual THF and solidify the membrane structure. This method of preparing membrane is a combined process of solvent evaporation technique and water vapor induced phase inversion. Therefore, the mechanism of membrane formation is complicated more by water-vapor adsorption and the solvent desorption (evaporation) on the surface of polymer solution.

Field emission scanning electron micrographs

The top surfaces of the membranes were observed by using FE-SEM (JEOL-6340F, Kyoto, Japan) at an accelerating voltage of 15 kV. The dried membrane was treated under cryogenic conditions by using liquid nitrogen to maintain the surface structure. The membrane specimens were coated with gold before FE-

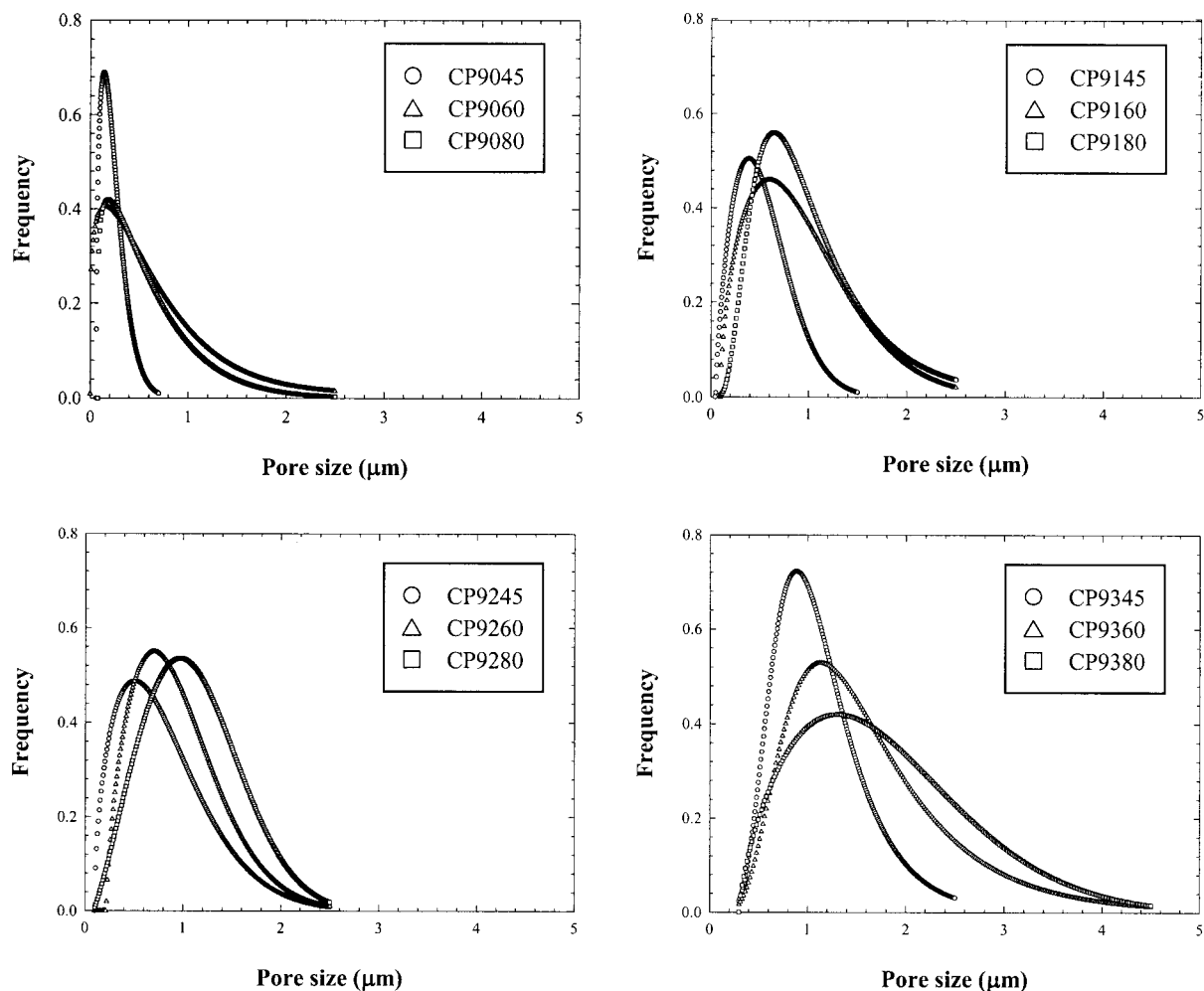


Figure 3 The effect of RH on the average number of pore size and distribution.

SEM photographs were taken. The average pore diameter, d_p , and the pore-size distribution at the surface of the membranes were investigated and determined from the image analyzer (BumMi Universe Co., Ltd., Ansan, Korea)

Optical observation

To investigate the formation of surface pores, optical microscopy was used to observe developments at the surface of casting solution during the formation of microporous membranes. The promotion of surface structure for cast solution was measured with an optical microscope (Nikon, Model Fax, Japan) which was installed in a glove box and taken at different time intervals.

Measurement of pure water flux and R_m

A dead-end stirred cell filtration system was used to measure the flux of deionized water of the membranes. Figure 1 shows the permeation apparatus. This

apparatus consisted of a 50-mL filtration unit (model 8050, Amicon Corp., W. R. Grace Corp., Beverly, MA), a 4000-mL feed reservoir, a permeate collection reservoir, a pressure gauge, and an electronic balance connected with a computer. The active membrane area was 13.4 cm². All filtration experiments were carried out at a constant transmembrane pressure of 0.05 MPa and a system temperature of 25 ± 1°C. All membranes were initially immersed into an isopropyl alcohol/H₂O (20/80 wt %) mixture at 0.3 MPa for 10 min before the test. The weight of permeate was measured every 30 s with an electronic balance and then automatically recorded on an on-line computer.

The pure water flux through the membrane is directly proportional to the applied hydrostatic pressure:

$$J_w = \frac{\Delta P}{\eta R_m} \quad (1)$$

where J_w is the hydraulic flux, R_m is the hydrodynamic resistance of the membrane, ΔP is the pressure differ-

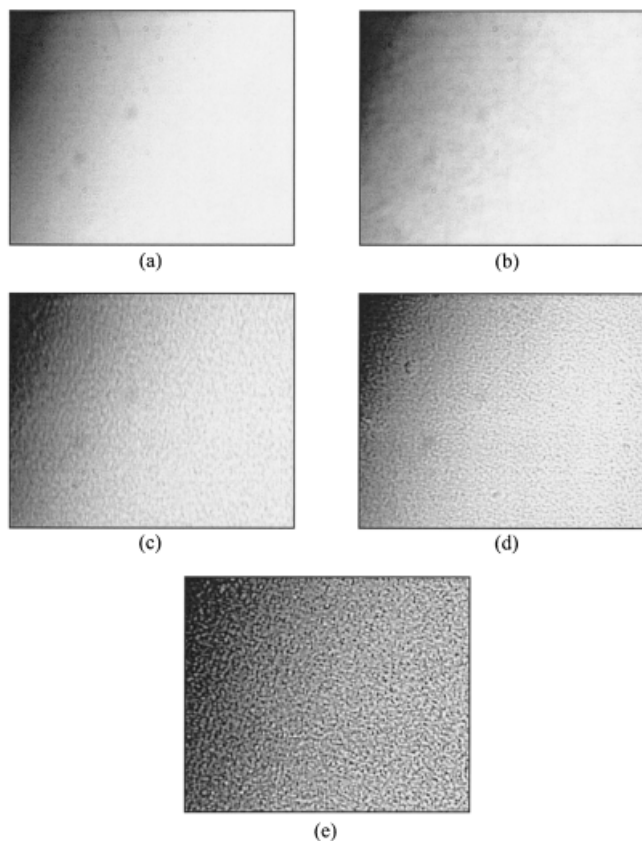


Figure 4 Evolution of the surface of casting solution during the formation of membranes with surface pores. The CPVC solution with 2 wt % PVP was investigated under RH 80% at 24°C. (a) 0 s; (b) 5 s; (c) 8 s; (d) 15 s; (e) 34 s.

ence between the feed and the permeate side of the membrane, and η is the viscosity of water (~ 1 cp). R_m can be calculated from the hydraulic flux (J_w), which is the intrinsic property related to the geometry of the membrane.

RESULTS AND DISCUSSION

Surface morphology of CPVC membranes

The SEM images of surface morphology of CPVC membranes, solidified by drying at 30°C in a convection oven after quenching in water vapor, were shown in Figure 2. Membranes produced by coagulating the polymer solution in a liquid nonsolvent media exhibited in general a more or less dense surface morphology, whereas the membranes made by water vapor induced phase separation showed a microporous surface morphology. Considering that the activity of water in a vapor phase is similar to that in a liquid phase, membrane through the water vapor induced phase separation should show a similar morphology with one coagulated by liquid water because the thermodynamic state of all the other components are the same. Therefore, the difference in the two cases seems

not to be originated from the differences of thermodynamic terms, but from the differences of kinetic terms. Up to now the mechanism of the formation of surface morphology has not been completely understood.

Only recently it was reported that when the hydrophobic polymer solution containing the hydrophilic additives was exposed to air containing water vapor, the pore size of membrane surface could be tailored by controlling the growth of the nuclei of emulsion drops generated according to whether the water vapor was drawn onto the surface of casting solution.¹⁷

As shown in Figure 2, the pore size of the top surface morphology of the membrane was strongly affected by the RH in the environment as well as the content of PVP used as an additive. It was clear that the pore size increased as both the RH and the content of PVP increased. It could be seen from the vertical comparison of the surface morphologies in Figure 2 that the polymer-casting solution with a higher content of PVP always resulted in the larger pores at the same RH and showed the coarser porous surface structure, although the decrease of PVP content brought about the small pore size ($<0.8 \mu\text{m}$) and fine surface structure. The detailed description for the variation of pore size and distribution would be presented in the next section.

Effect of the RH on the pore size and distribution

The average pore diameter, d_p , and the size distribution of pores on the surface of the membrane were quantified through the image analyzer from image visualized by FE-SEM. It was very clear that when the RH increased, the pore size of membrane top surface increased and the pore-size distribution broadened. Similar trends were observed in all the experimental results. Note that for polymer solution without PVP as shown in Figure 3(a), the mean pore size varies within a narrow range of 0.15–0.22 μm when the RH increases to 45, 60, and 80%, respectively. However, for polymer solutions with PVP as shown in Figure 3(b–d), as the RH increased, the mean pore size became larger than that of membranes prepared from polymer solution without PVP (CP90 series). For example, when the membranes were prepared from the CPVC solution containing 3 wt % PVP at different RH conditions of 45, 60, and 80%, the mean pore size of CPVC membrane surface was about 0.8, 1.2, and 1.4 μm , respectively. Meanwhile, the pore-size distribution became broad with the increase of the RH, regardless of the addition of PVP.

It was reported that membranes with microporous surface pores can be fabricated by evaporating the polymer solution.¹⁸ Because THF has higher volatility than *n*-BA in the used cosolvent, the *n*-BA/THF ratio increases during the evaporation stage. Therefore, it might be suspected that an increase of the *n*-BA/THF

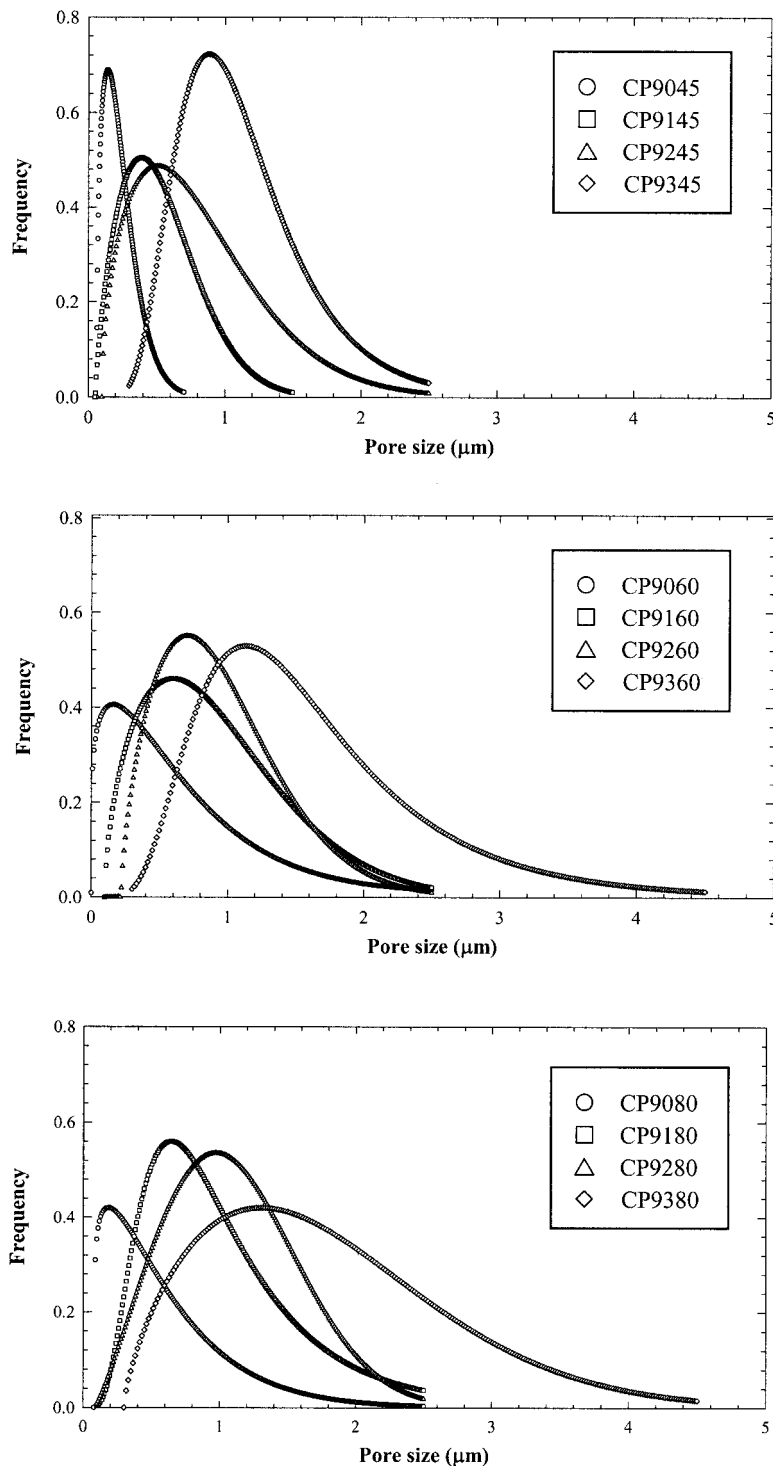


Figure 5 The effect of the amount of PVP on the average number of pore size and distribution.

ratio during solvent evaporation causes phase separation in casting solution and generates the pores on the membrane surface. However, in the present case, the membrane-formation mechanism is not simply elucidated because of the combined process of solvent evaporation and water vapor adsorption.

To investigate more clearly the formation process of surface pores, optical microscopy was used to observe

the surface of casting solution during the formation of microporous membrane. It was found that when the RH in air was $< 30\%$, the generation of crumples on the surface of casting solution (CPVC solution with 2 wt % PVP) was observed after at least 2 min. Meanwhile, crumples appeared within several seconds at a RH of 80%, as shown in Figure 4. Obviously, the introduction of a large amount of water vapor into the

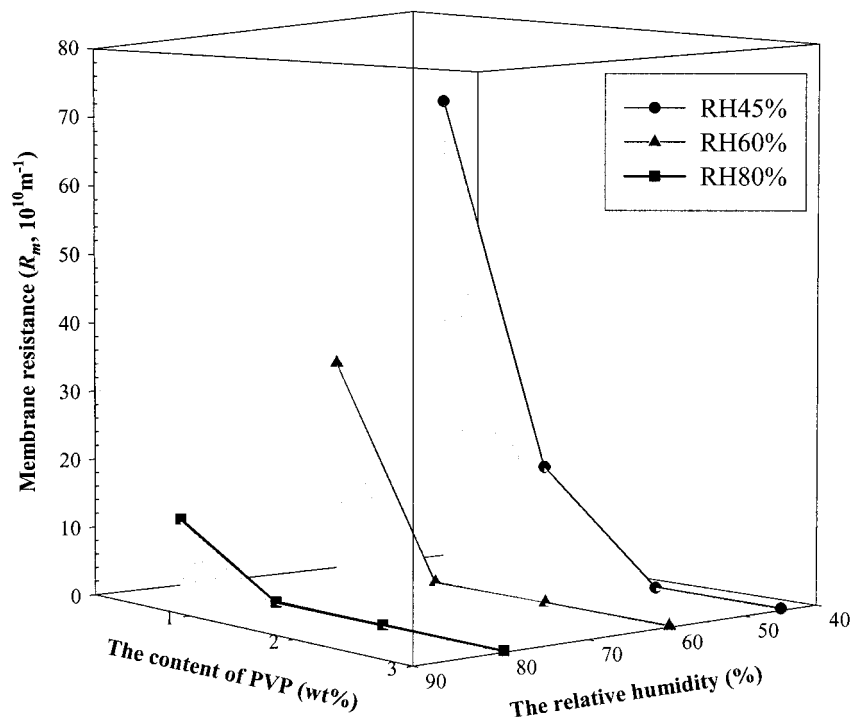


Figure 6 The conjugated effect of relative humidity and the content of PVP on membrane resistance.

surface of polymer solution caused the polymer solution to be readily separated into two phases, and as a result, the pore size of membrane surface formed increased. Moreover, the hydrophilic additive (PVP in this case) was required to draw water vapor onto the casting solution to initiate spontaneous phase separation. Therefore, the formation of surface pores is strongly related to the content of water vapor in air. This suggests that the increase of PVP content in polymer solution caused the fast phase separation and the formation of large pore size on the membrane surface.

Effect of PVP on the pore size and distribution of membrane surface

The surface topologies of typical membranes prepared were investigated from FE-SEM and image analysis. It was obvious from the observations in Figure 5 that the pore size of the membrane top surface became large and the pore-size distribution became broadened with increasing PVP concentration. When the content of PVP in polymer solution was 0, 1, 2, and 3 wt %, the mean pore size of membrane surface prepared at RH of 45% was about 0.2, 0.4, 0.5, and 0.8 μm , respectively. Also, when the RH was 80%, the mean pore size of the membrane surface was about 0.2, 0.8, 1.2, and 1.4 μm for the PVP content of 0, 1, 2, and 3 wt %, respectively. Therefore, this result showed that the content of PVP played a crucial role in the pore size of membrane surface prepared. As already mentioned in the previous section, the introduction of hydrophilic

PVP in CPVC solution accelerated the incorporation of water vapor in air into the casting solution, resulting in an increase of surface pore size due to spontaneous phase separation.

Pure water permeation and R_m

The hydraulic permeation of pure water was measured by using the permeation apparatus shown in Figure 1 to investigate the interconnectivity of pores and R_m , because the final performance of membrane was strongly affected by the geometry of the membrane, which was controlled by the preparation process. As summarized in Table I, the pure water flux increased with the increase of RH and the content of PVP in polymer solution. The membranes (CP9060, CP9160, CP9260, and CP9360) prepared from CPVC solution with PVP showed the water flux of 550, 3221, 4104, and 5800 $\text{L}/\text{m}^2 \text{ h}$ (LMH) at the feed pressure of 0.05 MPa, respectively. Therefore, as the content of PVP in CPVC solution increased, the membranes prepared at a given RH exhibited increased pure water fluxes. Also, the membranes (CP9345, CP9360, and CP9380) prepared from CPVC solution with 3 wt % PVP showed the water flux of 4570, 5800, and 7262 LMH with an increase of RH of 45, 60, 80%, respectively.

The R_m calculated from the measured pure water fluxes are presented in Figure 6. It is very important that the desired membrane structure and performance

for microfiltration could be readily controlled through the conjugated effect of RH and PVP content. Figure 6 shows that when the PVP content of 2–3 wt % is utilized for the preparation of membrane, the R_m are steeply decreased in the range of 0.25×10^{10} to 0.52×10^{10} (m^{-1}), independent of RH. This result shows that the addition of PVP during the preparation of microporous CPVC membrane is more effective in reducing the R_m . From these results, it is reasonable that the increase of surface pore size directly affects the increase of the flux of pure water and that the PVP in polymer solution and water vapor in air greatly assist pore interconnectivity, thereby reducing R_m .

CONCLUSION

Microporous CPVC membranes were prepared by water vapor induced phase inversion technique. Note that the amount of PVP and RH plays a significant role in the control of surface pore size in membrane preparation. When the RH increases, the pore size of the membrane top surface increases and the pore-size distribution broadens. However, in the case of CPVC solutions without PVP, the mean pore size varies within a narrow range of 0.15–0.22 μm , although the RH increased to 45, 60, and 80%, respectively. As the amount of PVP in CPVC solution increases, the pore size of membrane surface increases and the pore-size distribution broadens. Therefore, hydrophilic PVP in CPVC solution accelerates the incorporation of water vapor in air into the casting solution, resulting in an increase of surface pore size due to spontaneous phase separation. From the hydraulic flux measurements, we conclude that the increase of surface pore size directly affects the increase of pure water flux and that the PVP in the polymer solution and water vapor in air greatly increases pore interconnectivity, resulting in reduced R_m . When a PVP of 2–3 wt % is utilized for the preparation of CPVC membrane, the R_m steeply decreases in the range of 0.25×10^{10} to 0.52×10^{10} (m^{-1}),

independent of RH. These results show that the addition of PVP during the preparation of microporous membrane was more effective in producing submicron scale surface pores.

Jong Seok Kang and Ki Yeon Kim are grateful to the Han-yang Brain Korea 21 program sponsored by the Korean Ministry of Education for a scholarship. This work is supported by the Korea Institute of Science and Technology Evaluation and Planning (KISTEP) under the National Research Laboratory Program in the year 2001.

References

1. Kesting, R. E. *Synthetic Polymeric Membranes: A Structure Perspective*, 2nd ed.; Wiley: New York, 1985.
2. Kesting, R. E. *J Appl Polym Sci* 1990, 41, 2739.
3. Kang, J. S.; Shim, J. K.; Huh, H.; Lee, Y. M. *Langmuir* 2001, 17, 4352.
4. Shim, J. K.; Lee, Y. B.; Lee, Y. M. *J Appl Polym Sci* 1999, 74, 75.
5. Kang, J. S.; Won, J.; Park, H. C.; Kim, U. Y.; Kang, Y. S.; Lee, Y. M. *J Membr Sci* 2000, 169, 229.
6. Aliotti, A. *Spectra 2000 Analyse* 1996, 25, 34.
7. Oshida, K.; Kogiso, K.; Matsubayashi, K.; Takeuchi, K.; Kobayashi, S.; Endo, M.; Dresselhaus, M. S.; Dresselhaus, G. *J Mater Res* 1995, 10, 2507.
8. Kim, K. J.; Fane, A. G.; Fell, C. J. D.; Suzuki, T.; Dickson, M. R. *J Membr Sci* 1990, 54, 89.
9. Park, H. C.; Kim, Y. P.; Kim, H. Y.; Kang, Y. S. *J Membr Sci* 1999, 156, 169.
10. van de Witte, P.; Dijkstra, P. J.; van den Berg, J. W. A.; Feijin, B. J. *J Membr Sci* 1996, 117, 1.
11. Kim, J. H.; Lee, K. H. *J Membr Sci* 1998, 138, 153.
12. Young, T. H.; Chen, L. W. *Desalination* 1995, 103, 233.
13. Munori, S.; Bottino, A.; Capannel, G.; Moretti, P.; Petit Bon, P. *Desalination* 1988, 70, 265.
14. Kesting, R. E.; Fritzsche, A. K.; Murphy, M. K.; Cruse, C. A.; Handermann, A. C.; Malon, R. F.; More, M. D. *J Appl Polym Sci* 1988, 35, 1769.
15. Kraus, M. A.; Nemas, M.; Frommer, M. A. *J Appl Polym Sci* 1979, 23, 445.
16. Chuang, W. Y.; Young, T. H.; Chiu, W. Y.; Lin, C. Y. *Polymer* 2000, 41, 5633.
17. Wang, D. M.; Wu, T. T.; Lin, F. C.; Hou, J. Y.; Lai, J. Y. *J Membr Sci* 2000, 169, 39.
18. Kawai, T.; Lee, Y. M. *Polymer* 1997, 36, 1631.