Preparation of Asymmetric PVA Membranes Using Ternary System Composed of Polymer and Cosolvent

Sang-Gyun Kim,[1] Yong-Il Kim,[1] Hyung-Gu Yun,[1] Gyun-Taek Lim,[2] Kew-Ho Lee[1]

[1]*Membrane and Separation Research Center, KRICT, P.O. Box 107, Yusung, Taejon 305-606, South Korea*
[2]*Department of Polymer Engineering, Chonnam Nat' l University, Gwang-Ju 500-757, South Korea*

Received 8 April 2002; accepted 27 June 2002

ABSTRACT: Integrally skinned PVA membranes have been prepared from PVA/NMP/water system by the phase inversion method in 2-propanol bath, and the pervaporation characteristics of these membranes were investigated. With an increase in the NMP content in the polymer solution, the formation of skin layer depended on the NMP content in the cosolvent, and the overall morphology of membranes changed from porous to dense structure. Particularly, PVA membranes showed an asymmetric structure composed of a dense skin layer and a porous sublayer with finger-like type and cellular structure in solvents of 50–60% NMP compositions. The experimental results from the pervaporation separation of MTBE and methanol mixtures were also in good agreement with the morphology for the formation of skin layer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2884–2890, 2003

INTRODUCTION

Most asymmetric PVA membranes have been prepared by the phase inversion method using the concentrated salt solution as a coagulant and followed by chemically crosslinking and heat treatment[1–6]. However, with these methods it is very difficult to prepare integrally skinned asymmetric membranes with thin and defect-free skin and open porous sublayer. Therefore, it is necessary to develop a more efficacious process for the preparation of asymmetric PVA membrane than the existing process. Integrally skinned membranes can be obtained in two ways[7,8]. One is the dry–wet phase inversion and another one is wet phase inversion. It is possible to completely prepare defect-free asymmetric membranes by introduction of an evaporation step before immersion in a nonsolvent bath or by immersion in nonsolvent with a low mutual affinity to the solvent[9]. Also, the addition of a nonsolvent, usually an organic nonsolvent, into the polymer casting solution is very important to obtain the optimal membrane structure and control the morphology of skin layer of the resulting membrane[10–13]. In a word, these processes are related to the polymer concentration at the topside of the casting solution and a delayed onset of demixing. Accordingly, integrally skinned asymmetric PVA membranes can be prepared sufficiently by controling the exchange rate between solvent and nonsolvent at the top layer in the coagulation bath. For that reason, in this study the cosolvent systems composed of *n*-methyl 2-pyrrolidone (NMP) and water are selected as a control method of the demixing rate, and 2-propanol is chosen as a coagulant to reduce the exchange time between cosolvent and nonsolvent. The pervaporation experiment for the separation of the methyl *t*-butyl ether (MTBE)/methanol mixture is used to probe the morphology of the skin layer and the separation performance of the resulting membranes. In addition, the aim of this study is developing integrally skinned asymmetric PVA membranes suitable for gas separation, vapor permeation, and pervaporation process.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (Aldrich) was obtained as a 99+% hydrolyzed powder with <0.1% residual acetate groups and a reported average molecular weight of 31,000–50,000. The solvents used were *n*-methyl-2-pyrrolidinon (NMP) and ultrapure deionized water. NMP was purchased from Junsei Chemical Co. (Tokyo, Japan). 2-Propanol with a 99% purity was purchased from Junsei Chemical Co. (Tokyo, Japan), and used as a coagulant without further purification.

Correspondence to: K.-H. Lee (khlee@krict.re.lcr).

Journal of Applied Polymer Science, Vol. 88, 2884–2890 (2003)

Membrane preparation

One hundred grams of a polymer solution with a weight ratio of 10 g PVA polymer and 90 g cosolvent mixture of water and *n*-methyl-2-pyrrolidinon (NMP) was prepared by refluxing in the round flask connected to a condenser at 80°C for 12 h.. Dissolved PVA solutions were kept for 4 h at a room temperature condition for the removal of air bubbles. The resulting solutions were cast on a glass plate at 25°C with a casting knife to give a film of appropriate thickness, and then the glass plate was immediately dipped into a 2-propanol bath during 20 min at 25°C. After coagulation, the membrane was dried in air at ambient temperature.

Membrane characterization

A JEOL JSM-80A instrument was used for the investigation of the PVA membrane morphology. The viscosities of casting solution were determined by Brookfield digital viscometer (Model DV-II), which was calibrated from standard solutions at 25°C.

Light-scattering and coagulation value measurement

To investigate the kinetics of phase separation, a light-scattering (LS) measurement was carried out using a similar experimental apparatus introduced by Smolders group,[14] and the scattering profile was recorded as a function of time. The coagulation value for each polymer solution was visually detected by a titration method at 25°C, and estimated for their thermodynamic stability. In each case, 2 g of polymer was dissolved in 98 g of cosolvent. 2-propanol was slowly added into the homogenous polymer solution by a syringe, stirring it constantly, until the solution yielded the first permanent turbidity. The coagulation value in each case was determined by measuring the amount of 2-propanol, causing the first permanent turbidity in the polymer solution.

Permeation experiments

The schematic pervaporation apparatus is shown in Figure 1. The membrane cell is made of a stainless steel. A feed mixture enters the cell through the center opening, flows radically through the thin channel, and leaves the cell through the side opening, which allows relatively high-fluid velocity parallel to a membrane surface. The effective membrane area was 19.6 cm^2. The feed mixture was circulated from the feed tank having a capacity of 2.5 L through the membrane cell. The feed tank was wrapped with the heating tape to heat the feed mixture. The feed mixture temperature was controlled by PID (proportional-integral-derivative) temperature controller with an accuracy of 0.5°C. The permeation vapor was collected in a cold trap by liquid nitrogen with a given time interval, heated up to room temperature, and weighed to determine the flux. Separation analysis was carried out by gas chromatograph (Model Shimadzu GC-14B) equipped with a column packed with Porapak-Q and with a thermal conductivity detector. Separation factor (α) was calculated by the following equation:

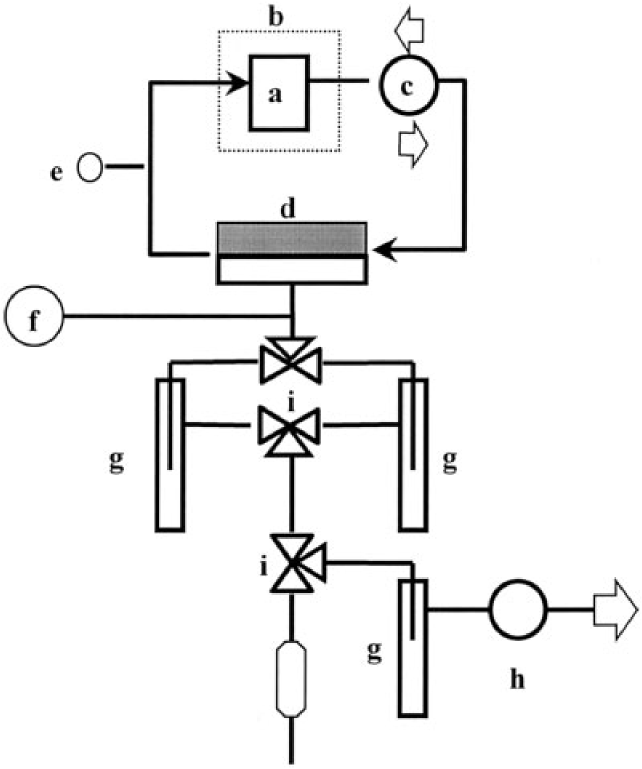

Figure 1 Schematic representation of the prevaporation device: (a) feed tank, (b) heating controller, (c) pump, (d) prevaporation cell, (e) temperature indicator, (f) pressure indicator, (g) cold trap, (h), vacuum pump, (i) three-way vacuum valve.

$$\alpha_{\text{methanol/MTBE}} = \frac{Y_{\text{methanol}}/Y_{\text{MTBE}}}{X_{\text{methanol}}/X_{\text{MTBE}}}$$

where X and Y are the weight fractions of each component in feed and permeate, respectively.

RESULTS AND DISCUSSION

Figures 2 and 3 show the results of SEM study for the resulting membranes prepared from PVA/cosolvent/2-propanol systems with varying NMP/water ratios. These membranes showed closely overall morphology change from a uniform cell structure to an asymmetric structure with a dense skin layer and a nonporous

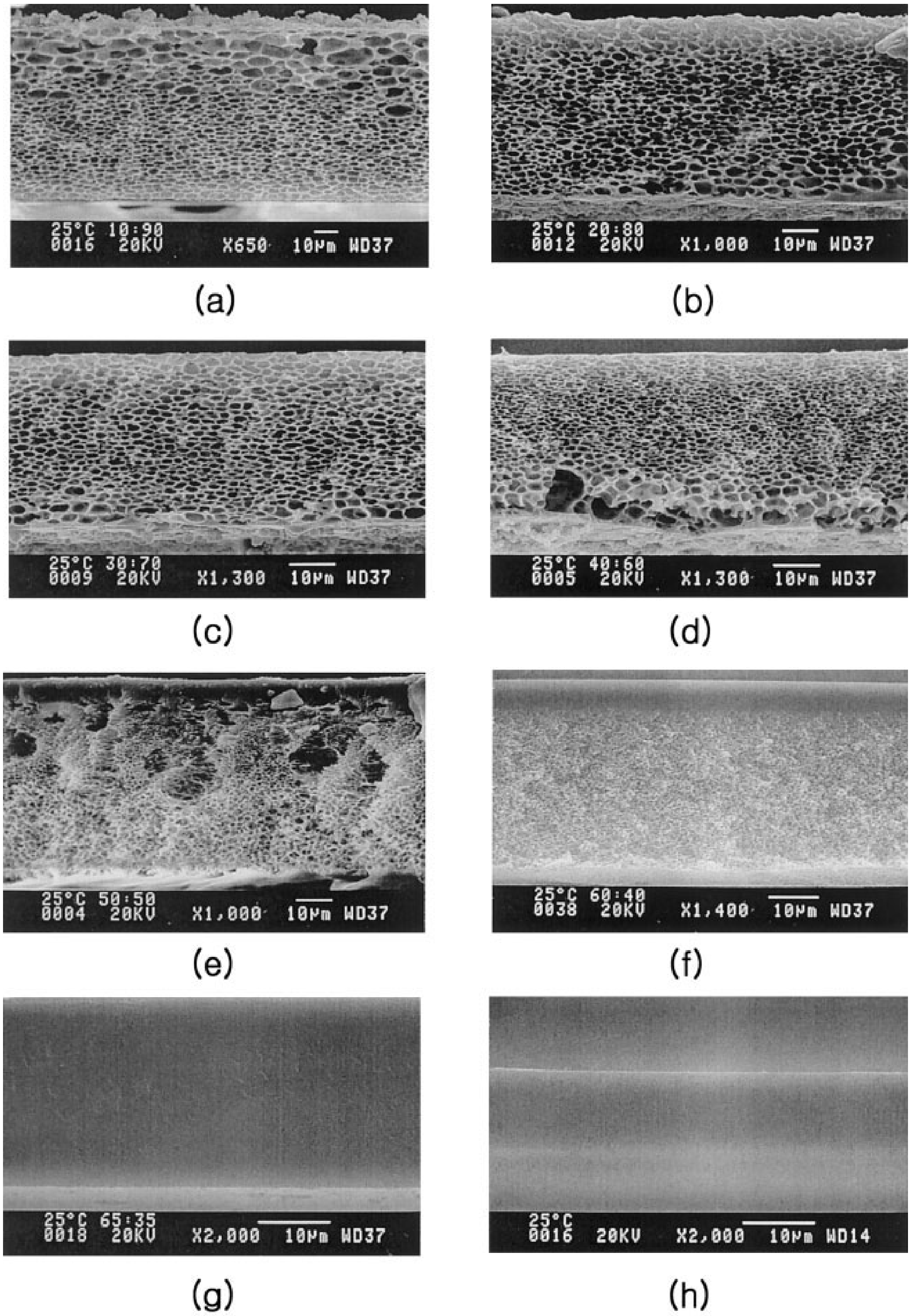

Figure 2 Cross-sectional SEM photographs of PVA membranes prepared as a function of the NMP/water ratio: (a) 10/90 wt %, (b) 20/80 wt %, (c) 30/70 wt %, (d) 40/60 wt %, (e) 50/50 wt %, (f) 60/40 wt %, (g) 65/35 wt % (h), 70/30 wt %.

structure by increasing the NMP ratio in the cosolvent. However, from above 65 wt % NMP ratio, the final structure after phase inversion does not show an asymmetric structure. In general, the mutual affinity of NMP and 2-propanol is poor compared with that of water and 2-propanol, whereas the miscibility of NMP with water is very good, as can be seen from in Table I. This suggests that the in-flow rate of 2-propanol into

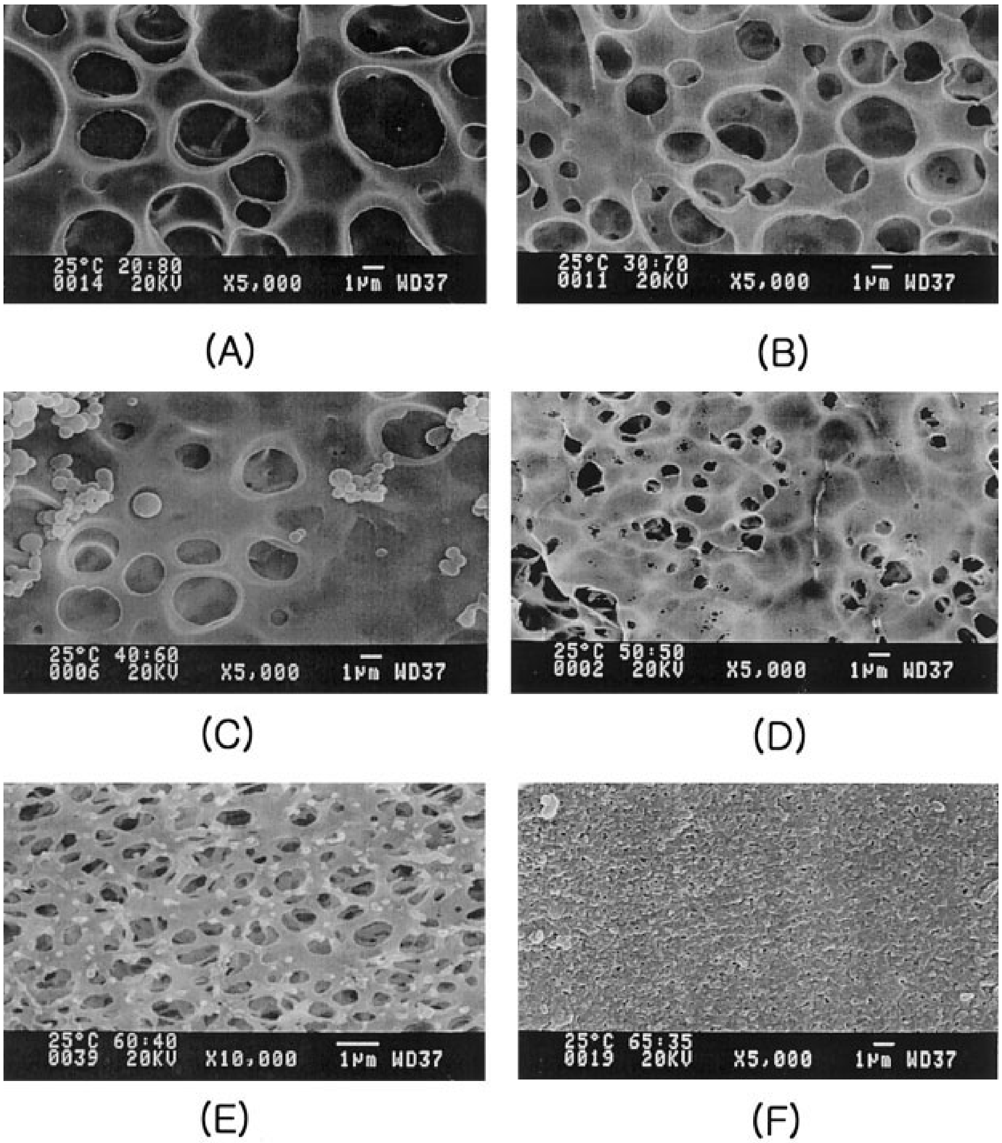

Figure 3 Bottom SEM photographs of VPA membranes prepared as a function of the NMP/water ratio: (a) 20/80 wt %, (b) 30/70 wt %, (c) 40/60 wt %, (d) 50/50 wt %, (e) 60/40 wt % (f) 63/35 wt %.

polymer solution decreases with increasing the NMP ratio in the polymer solution, and the overall demixing pattern depends on the outflow rate of the cosolvent during phase inversion. Accordingly, the polymer solutions of the small NMP ratio exhibit a fast demixing pattern by liquid–liquid phase separation than gelation due to a higher efflux of water. When the efflux of NMP having a low affinity for 2-propanol is faster than water, the polymer solution shows a delayed demixing pattern by gelation rather than liquid–

TABLE I
Physical Properties of Solvent and NonSolvent Used in This Study

	δ ((cal/cm^3)$^{1/2}$)	*V* (cm^3/mol)	η (cp)	BP (°C)	σ (dyn/cm)
Water	23.49	18.0	0.90	100	72.5
2-Propanol	23.6	76.50	1.90	82	21.7
NMP	11.21	97.19	1.69	202	40.7

δ: Solubility parameter; *V:* Molar volume; η: density; Bp: boiling point; σ: surface tension.

liquid phase separation. Therefore, with increasing NMP ratio in polymer solution, the skin layer of the resulting membranes becomes denser and thicker by decreasing the inflow rate of 2-propanol at the skin region.

On the other hand, even if the miscibility of NMP with water is good, NMP is not a good solvent for PVA. Therefore, the increase of NMP ratio, as shown in Table II, shows a significant increase of viscosity of a PVA solution by decreasing solvating power of the water for PVA. Finally, the miscibility of the 2-propanol/cosolvent/PVA system decreases with the increase of the NMP ratio, and the phase inversion of the skin layer can be advanced by a delayed demixing. The resulting effects can be easily observed from the pore size of bottom morphology of Figure 3 and the coagulation value of each polymer solution of Figure 4. The coagulation value is defined as the amount of nonsolvent causing phase separation and yields the first persistent turbidity in a homogeneous polymer solution, and is related to the miscibility of the nonsolvent/solvent/polymer system. As shown in Figure 4, it can be suggested that with increasing the NMP ratio in the polymer solution the phase behavior at the interface can induce a fast phase transition because the polymer solution becomes more unstable, whereas the overall exchange rate during membrane forming can also be delayed by decreasing of the miscibility between components. As it were, it can be considered that when the water ratio to NMP in cosolvent is larger, the resulting membranes, as shown in Figure 2(a)–(d), yield more porous structures because the in-flow of 2-propanol is more predominant than the outflow rate of solvent during the coagulation process, and conversely, the membranes obtained from the polymer solution in which NMP ratios are greater than water, which yield a dense skin and a supporting substructure with large macrovoids or a whole dense structure due to the dominant outflow of solvent, as shown in Figure 2(e)–(h). In addition, the light scattering results of Figure 5, also appears to agree with the above-mentioned phase separation results shown by the cross-sectional morphology and coagulation value. That is, Figure 5(a) results from the progress in a fast phase transition at the interface under a facile inflow of 2-propanol, while Figure 5(b) is gradually delayed because the outflow of solvent and the viscous property of solution play an important role for demixing. From the above results it can be concluded that the dense skin layer of the asymmetric PVA membranes can be controlled sufficiently by kinetic factors, such as the ratio of outflow of the solvent/inflow of coagulant and the ratio of outflow of NMP/out flow of water.

TABLE II
Viscosity of PVA Polymer Solution Prepared by Charging NMP/Water Ratio

Composition of PVA/water/NMP (wt %)	Viscosity (cps)
10/90/10	38.2000
10/80/20	54.9200
10/70/30	73.2000
10/60/40	118.8500
10/50/50	140.2800
10/40/60	280.0600
10/30/70	290.8900
10/20/80	397.6700

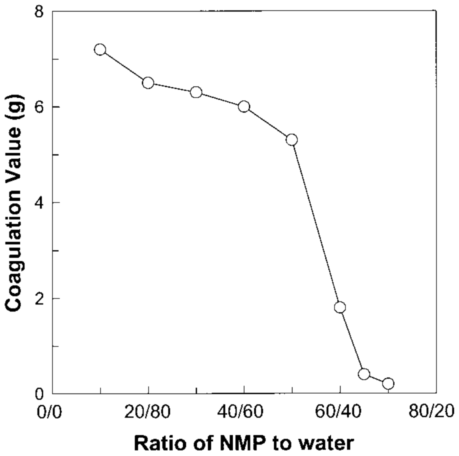

Figure 4 Coagulation values of PVA polymer solution prepared by changing the NMP/water ratio.

Finally, to evaluate the performance of PVA membranes having a dense skin layer, the pervaporation separation of a 50/50 wt % methyl *tert*-butyl ether (MTBE)/methanol mixture was carried out. Figure 6 shows the permeation fluxes and MTBE concentrations in the permeate side for the different membranes prepared by changing the NMP ratio in the cosolvent. As expected, these membranes show that both the permeation fluxes and MTBE concentrations decrease gradually with an increase of the NMP content. In this experiment, MTBE is nonpolar and has a molecule size of maximum 5.4 Å, while methanol is very polar and has a molecular size of 2.8 Å. Therefore, as the thickness and density of the skin layer increases, MTBE molecules can hardly penetrate to the permeate side, and these results were consistent with SEM results shown in Figure 2.

CONCLUSIONS

In this study, the cosolvent systems composed of NMP and water have been selected as a control method of the demixing rate at the surface region, and asymmetric PVA membranes having a dense skin layer were prepared by immersion in the 2-propanol coagulant. Their morphology was controlled by the interrelation between the ratio of out-flow of the water to inflow of

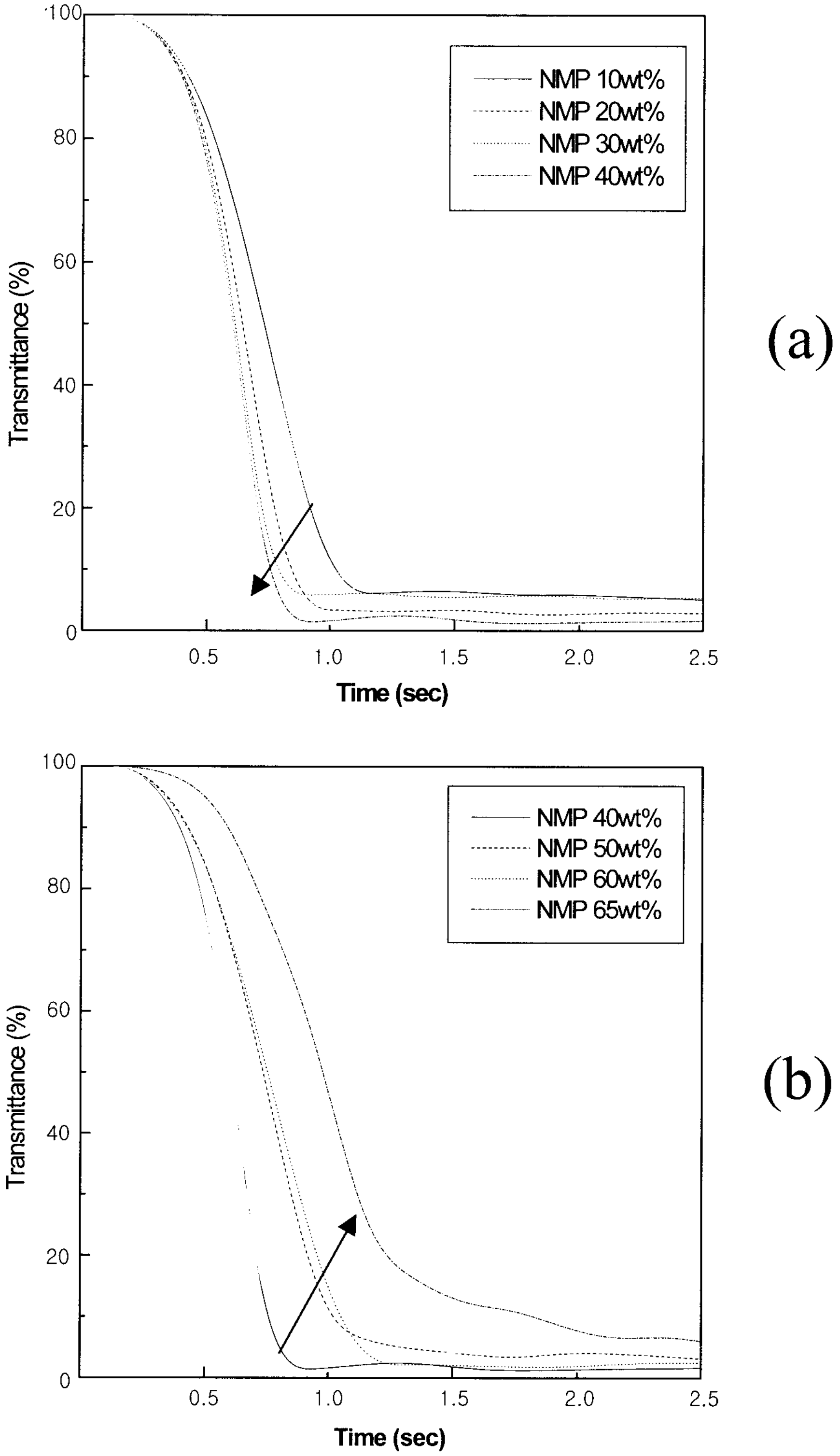

Figure 5 Light-scattering curves of PVA polymer solution prepared by changing the NMP/water ratio: (a) NMP: 10–40 wt %, (B) nmp: 40–65 wt %.

coagulant and the ratio of outflow of NMP to out flow of water. To estimate the formation of dense skin layer, the pervaporation experiment of MTBE/methanol mixture was carried out additionally. The results showed that overall flux and MTBE concentration in the permeate side were decreased simultaneously, which was an identical behavior with a morphology change of dense skin layer.

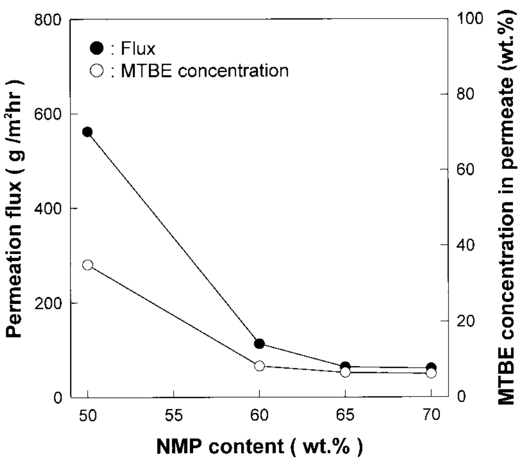

Figure 6 Permeation fluxes and MTBE concentrations in the permeate side of the prepared membranes as a function of the NMP/water ratio: feed composition: 50/50 wt % MTBE/methanol mixture, operating temperature: 30°C.

References

1. Peter, S.; Hese, N.; Stefan, R. Desalination 1976, 19, 161.
2. Peter, S.; Stefan, R. ACS Symp Ser 1981, 154, 281.
3. Chang, H. N. Desalination 1982, 42, 63.
4. Brannon, M. L.; Oeppas, N. A. J Membr Sci 1991, 57, 257.
5. Li, R. H.; Barbari, T. A. J Membr Sci 1994, 88, 115.
6. Dai, W. S.; Barbari, T. A. J Membr Sci 1999, 156, 67.
7. Strathmann, H.; Kock, K.; Amar, P. Desalination 1975, 16, 179.
8. Mulder, M. Basic Principles of Membrane Technology; Kluwer Academic: Dordrecht, 1991.
9. Pinnau, I. Ph.D. Dissertation, The University of Texas at Austin, 1994.
10. Wijmans, J. W.; Kant, J.; Mulder, M.; Smolders, C. A. Polymer 1985, 26, 1539.
11. Kim, J. H.; Lee, K. H. J Membr Sci 1998, 138, 153.
12. Kim, S. R.; Lee, K. H.; John, M. S. J Membr Sci 1996, 73, 259.
13. Park, J. S.; Kim, S. K.; Lee, K. H. J Ind Eng Chem 2000, 6, 93.
14. Reuvers, A. J.; Smolders, C. A. J Membr Sci 1987, 34, 67.