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Poly(vinyl alcohol) Membranes Having an Integrally Skinned Asymmetric Structure

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Poly(vinyl alcohol) membranes, having integrally skinned asymmetric structures, were prepared by using 2-propanol and cosolvent composed of N-methyl-2-pyrrolidone and water, by phase inversion processes. In this work, the effects of cosolvent on the formation of integrally skinned structure of the asymmetric poly(vinyl alcohol) membranes were investigated and discussed from the morphological point of view. Experimental result indicated that the resulting membranes exhibited closely overall morphology change from a uniform cell structure to an asymmetric structure with a dense skin layer and a nonporous structure, by increasing the N-methyl-2-pyrrolidone ratio in the cosolvent. For this phenomenon, it was considered that as the N-methyl-2-pyrrolidone ratio in polymer solutions increased, due to a poor miscibility in between them, the inflow rate of 2-propanol decreased gradually, while the overall liquid-liquid demixing pattern between a cosolvent and 2-propanol depended on the outflow rate of the cosolvent during phase inversion.

Keywords: asymmetric membrane; cosolvent; phase inversion process; PVA

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INTRODUCTION

In hydrophilic polymers, poly(vinyl alcohol) (PVA) is well known membrane material with high tensile and impact strengths, high abrasion, good chemical resistance such as alkali, and an oxygen barrier property [1,2]. Therefore, PVA is especially superior to those of any known polymers in membrane separation process, such as nanofiltration, gas separation, and pervaporation. On the other hand, the separation performance of PVA membrane is things certain limitation because of its physicochemical properties. That is, as the cross-linking structure for the stability of PVA membrane introduces, the stability and the selectivity increases highly but the overall permeability exhibit to decreasing trends because of the compact structure of membrane, respectively.

In order to overcome the above-mentioned problems, several researchers have been investigated regarding the preparation of PVA membranes with an integrally skinned asymmetric structure. Among them, Peter and Chang *et al.* [3–5] have reported the results of the asymmetric PVA membranes using drying/precipitation procedures. Brannon and Dai *et al.* [6–8] have studied the mesh sized asymmetric membranes based on a gradient crosslinking and interfacial reaction.

However, most of asymmetric PVA membranes are still dependent on phase inversion method using the concentrated salt solution as a coagulant. Consequently, the purpose of this study has been focused to investigate an effective preparation method in relation to the asymmetric PVA membrane, and to develop integrally skinned asymmetric PVA membranes suitable for gas separation, vapor permeation and pervaporation process.

In general, integrally skinned membranes can be obtained in two ways. One is dry-wet phase inversion and another one is wet phase inversion. It is possible to prepare completely 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. Theoretically, these processes are capable of increasing the polymer concentration at the topside of casting solution, and correlates with a delayed onset of demixing.

In this respect, we considered that integrally skinned asymmetric PVA membranes can be prepared sufficiently by control the exchange rate between solvent and nonsolvent at the top layer in coagulation bath. The cosolvent systems, composed of *n*-methyl 2-pyrrolidone (NMP) and water, have been selected as a control method of the

demixing rate, and 2-propanol was chosen as a coagulant. The affinity between NMP and 2-propanol in the literature is low whereas 2-propanol has a high affinity for water.

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 31000–50000. The solvents used were *N*-methyl-2-pyrrolidinon (NMP) and ultra pure deionized water. NMP was purchased from Junsei Chemical Co. (Tokyo, Japan). 2-propanol also was purchased from Junsei Chemical Co. (Tokyo, Japan).

Membrane Preparation

100 g of a polymer solution with a mass ratio of 10 g PVA polymer and 90 g cosolvent mixture of water and NMP was prepared by refluxing in the round flask connected to a condenser at 80°C for 12 hours. A dissolved PVA solutions were kept for 4 hours in a given temperature condition for 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 minutes at 25°C. After coagulation, the membrane was dried in air at ambient temperature.

Characterization

The prepared membrane samples for scanning electron microscopy (SEM) study were first immersed in liquid nitrogen and fractured, and then sputtered with gold using a JEOL JFC-1100E Ion Sputtering Device. 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. 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.

RESULTS AND DISCUSSION

To estimate the effects of cosolvent, composed of NMP and water, on the formation of integrally skinned structure of the asymmetric poly(vinyl alcohol) membranes, the thermodynamic characteristics of polymer solutions, such as viscosity and coagulation value, were investigated. As shown in Figure 1, the overall viscosities of polymer solution increased gradually whereas the coagulation values decreased with the increase of NMP content in cosolvent system. In general, 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. According to the coagulation values, as can be seen in Figure 1, it can be suggested that with increasing the NMP content in the cosolvent, the phase behavior at the interface can induce a fast phase transition because the polymer solution becomes thermodynamically more unstable, whereas the overall exchange rate during membrane forming can also be delayed by decreasing of the miscibility between components. The reason is because NMP is not a good solvent for PVA whereas the miscibility of NMP with water is relatively good. Therefore, the increase of NMP content shows a significant increase of viscosity of a PVA/cosolvent solution by decreasing solvating power of the water for PVA.

Figure 2 shows the cross-sectional and bottom photographs of phase inversion membranes prepared from PVA/cosolvent/2-propanol

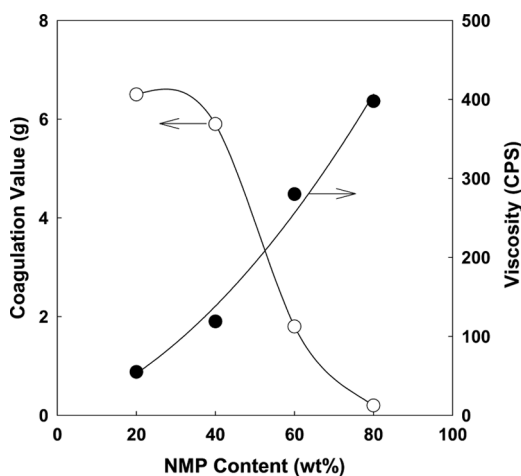


FIGURE 1 Viscosities and coagulation values as a function of NMP content in polymer solution.

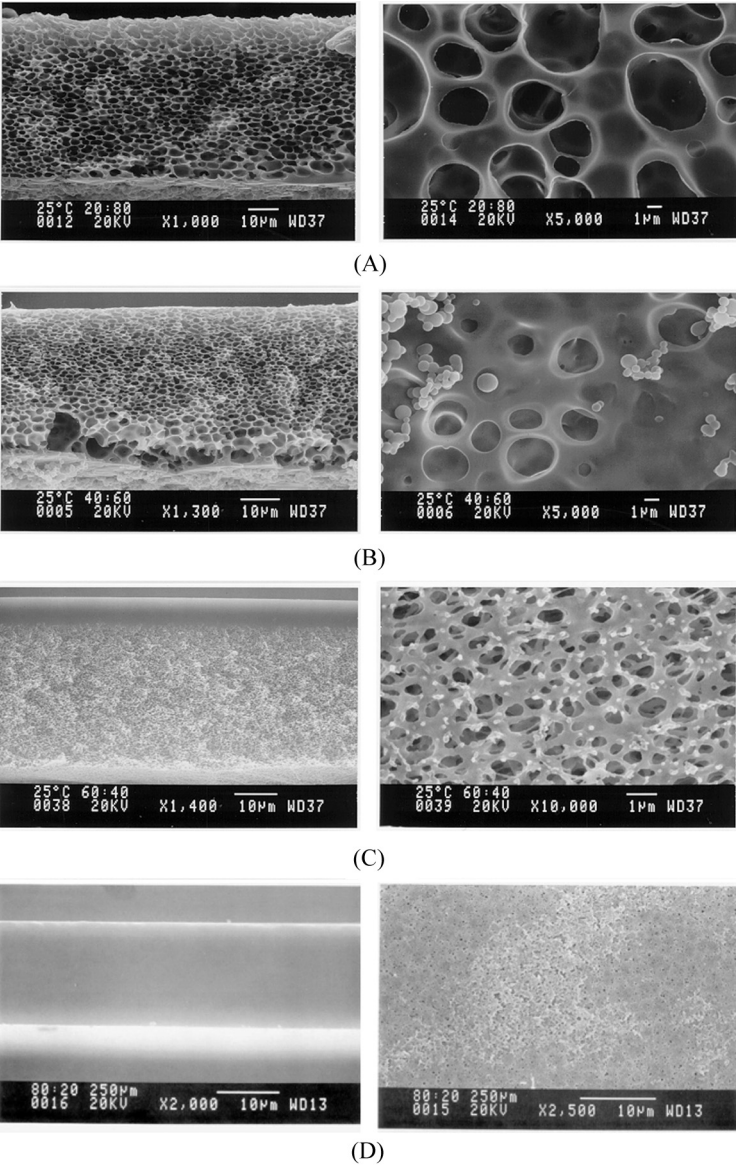


FIGURE 2 Cross-sectional (left) and bottom (right) SEM photographs of PVA phase inversion membranes prepared as a function of NMP content in the cosolvent: (A) 20 wt%, (B) 40 wt%, (C) 60 wt% (D) 80 wt%.

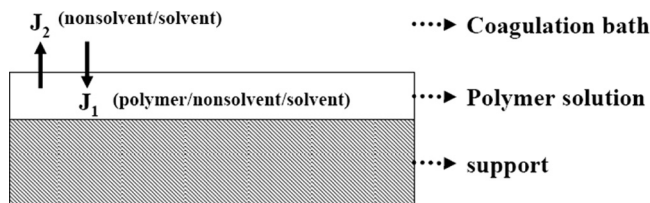


FIGURE 3 Schematic representation for liquid-liquid demixing between a coagulant (influx, J_1) and a cosolvent (efflux, J_2) during phase inversion.

system with varying NMP content in the cosolvent. With increasing the NMP content in cosolvent system, the overall morphologies change from a uniform cell structure (Fig. 2A) to an asymmetric structure with a dense skin layer (Fig. 2C). In addition, from above 80 wt% NMP content, the final morphology after phase inversion does not show an asymmetric structure as shown in Figure 2D, and exhibit a dense structure in the whole cross-section.

For this result, it considered that as an additive of NMP component induced a significant increase of viscosity of polymer solutions as shown in Figure 1, the overall mass transfer between a cosolvent and 2-propanol such as the liquid-liquid demixing shows gradually a delayed pattern and gelation behavior. 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 as shown in Figure 3. 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-liquid phase separation. Therefore, with increasing NMP content in polymer solution, the top layer of the resulting membranes becomes denser and thicker by decreasing the inflow rate of 2-propanol at the interface.

TABLE 1 Physical Properties for Cosolvent and Nonsolvent Used in this Study

Component	Physical properties			
	Hydrophilic surface area (cm ² /mol × 10 ⁹)	Hydrophilic surface area (%)	Polar surface area	Surface tension (dynes/cm)
Water	2.19458	100.00	31.50	72.5
NMP	7.04273	88.51	23.47	39.2
2-Propanol	1.43157	22.70	20.23	22.4

TABLE 2 Solubility Parameters for a Cosolvent and 2-Propanol Used in this Study. (δ_d : Dispersion Force, δ_p : Polar Force, δ_h : Hydrogen Bonding)

Component \ Solubility parameter	δ (MPa ^{1/2})	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})
PVA	26.5	15.8	8.8	19.4
Water	47.8	15.6	16.0	42.3
NMP	23.0	18.0	12.3	7.2
2-Propanol	23.4	15.7	6.9	15.9

Actually, it can be considered that the mutual affinity of NMP for 2-propanol are a poor comparison to that of between water and 2-propanol, whereas the miscibility of NMP for water is very good, from the viewpoint of the hydrophilic and polar properties as shown in Table 1.

To estimate the miscibility in between PVA and solvent in details, the solubility parameter and the interaction parameter between them is calculated by group contribution method and from Hansen's equation by using the calculated values in Table 2. As expected, the affinity or miscibility in PVA/solvent system is increasing in order of PVA/water > PVA/NMP > PVA/2-propanol as shown in Table 3, while the miscibility of 2-propanol for NMP is respectively better than that for water. Therefore, with increasing NMP content in polymer solution, the rate of 2-propanol inflow into polymer solution decreases gradually, and the overall demixing pattern is affected by the rate of cosolvent outflow. Accordingly, when the water content in cosolvent is larger, as shown in Figures 2A and B, the resulting membranes yield more porous structures because the in-flow of 2-propanol is more

TABLE 3 Interaction Parameters (χ_H) for PVA-Solvent and Cosolvent-IPA

System	χ_H
PVA/Water	0.17974
PVA/NMP	0.76298
PVA/2-propanol	1.06371
2-Propanol/Water	2.54386
2-Propanol/NMP	1.05815

$$\chi_H = \frac{V_1}{RT} [(\delta_{d1} - \delta_{d2})^2 - (\delta_{p1} - \delta_{p2})^2].$$

V : molar volume of solvent, 1: solvent, 2: polymer, R : gas constant, T : temperature.

predominant than the outflow rate of solvent during the coagulation process. 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 Figures 2C and D. 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.

CONCLUSIONS

PVA membranes with an integrally skinned structure were prepared by immersion precipitation in phase inversion process, by using cosolvent systems composed of NMP and water, as a control method of the demixing rate at the surface region. When the increase in NMP contents in polymer solution increased, the dense layer at the surface increased because the increase of the matrix viscosity as well as the decrease of the rate of 2-propanol inflow at the skin region, and then, the cell sizes in bottom also should decreased slowly. From the above results, it was considered that the dense skin layer can be controlled sufficiently by thermodynamic relationship between components, such as the out flow of the solvent/inflow of coagulant and the outflow of NMP/its ratio to water outflow.

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