

Preparation of Water-Swollen Hydrogel Membranes for Gas Separation

YOU-IN PARK, KEW-HO LEE

Membrane and Separation Research Center, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejeon, 305-606, South Korea

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ABSTRACT: Water-swollen hydrogel (WSH) membranes for gas separation were prepared by the dip-coating of asymmetric porous polyetherimide (PEI) membrane supports with poly(vinyl alcohol) (PVA)–glutaraldehyde (GA), followed by the crosslinking of the active layer by a solution method. Crosslinked PVA/GA film of different blend compositions (PVA/GA = 1/0.04, 0.06, 0.08, 0.10, 0.12 mol %) were characterized by differential scanning calorimetry (DSC) and their water-swelling ratio. The swelling behavior of PVA/GA films of different blend compositions was dependent on the crosslinking density and chemical functional groups created by the reaction between PVA and GA, such as the acetal group, ether linkage, and unreacted pendent aldehydes in PVA. The permeation performances of the membranes swollen by the water vapor contained in a feed gas were investigated. The behavior of gas permeation through a WSH membrane was parallel to the swelling behavior of the PVA/GA film in water. The permeation rate of carbon dioxide through the WSH membranes was 10^5 ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}$) and a CO_2/N_2 separation factor was about 80 at room temperature. The effect of the additive (potassium bicarbonate, KHCO_3) and catalyst (sodium arsenite, NaAsO_2) on the permeation of gases through these WSH membranes was also studied. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1785–1791, 2001

Key words: water-swollen hydrogel membrane; crosslinking; water-swelling ratio; poly(vinyl alcohol); glutaraldehyde

INTRODUCTION

Since the production of carbon dioxide, a major component among the greenhouse effect gases, is an international problem, interest in the separation and recovery of carbon dioxide has increased for many investigators. For the separation of carbon dioxide using a membrane, a liquid membrane containing an alkali salt or an amine compound have been studied due to the high selectivity toward carbon dioxide. But it is still difficult to

apply the liquid membrane for practical use yet because of the unstability of the liquid that should be contained in the formation of the liquid membrane.¹ Water-swollen hydrogel (WSH) membranes have been studied to solve such a difficulty without deterioration of their good selectivities. Ito² studied the permeabilities of O_2 , N_2 , and CO_2 in a moistened membrane as a function of various relative humidities. It was found for poly(vinyl alcohol) (PVA) and cellophane membranes that the permeability coefficients increased remarkably with an increase of water content in the membranes. Kamiya and Takahashi³ measured the permeability coefficients and diffusion coefficients of H_2 , He, and Ne in

Correspondence to: K.-H. Lee.

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moistened cellophane membranes prepared by a laminate method and found an extremely large increase in the permeabilities at above 60% relative humidity. Furthermore, Zhang et al.^{4,5} measured the permeability coefficients of O₂ and N₂ in swollen membranes using an improved apparatus attached with a bubble chamber and a water reservoir, which was developed to prevent water evaporation from the membrane. Recently, Ito et al.⁶ studied the permeabilities of N₂, CO₂, and CH₄ through a wet chitosan membrane and found the influence of the membrane preparation conditions and operating conditions on the separation performance of the wet chitosan membrane.

To investigate the transport mechanism, several groups studied the permeabilities of gases or solutes through WSH membranes. Yasuda et al.^{7,8} proposed an interpretation of the solute permeation through the membranes using a free-volume theory, by assuming that the water in the membrane is in a single state. Renkin⁹ suggested a pore theory based on the states of water in the membranes. Higuchi et al.^{10,11} measured the permeability coefficients and diffusion coefficients of several gases such as Ar, O₂, CH₂, CO₂, and C₂H₄ in water-swollen gel cellophane membranes and studied a transport mechanism of the gas through those membranes using a DSC analysis. He suggested that the water-swollen membranes are in two states and proposed a parallel permeation model. On the other hand, Ward and Robb¹² studied the facilitated transport separation of CO₂, SO₂, and O₂ in a modified cellulose acetate membrane, containing additives and catalysts such as KHCO₃, CsHCO₃ and Na₂SeO₃, NaASO₂, respectively. It was found that the performance increased remarkably with an addition of the additive and catalyst in the membrane. Okabe et al.¹ studied the permeability of mixture gases (CO₂, N₂) through the WSH membranes, containing K₂CO₃ or triethanolamine (TEA) and a complexing agent such as crown ether and analogous compounds.

In this study, WSH membranes were prepared by dip-coating a PVA solution containing glutaraldehyde (GA) as a crosslinking agent¹³ on the asymmetric porous polyetherimide (PEI) supporters, followed by solution method crosslinking. The gas permeation behavior through the WSH membranes with different crosslinking degrees and under different operating conditions in the CO₂ separation process is discussed. The influence of the additive and catalyst on the separation performance of the WSH membranes are reported.

EXPERIMENTAL

Materials

PVA was purchased from the Aldrich Chemical Co. (Milwaukee, WI). The average molecular weight and the degree of saponification of the PVA were 50,000 and 99%, respectively. GA (25% content in water, EP grade), isopropyl alcohol (IPA) (guaranteed reagent), and hydrochloric acid (35% content, extrapure grade) were purchased from the Junsei Chemical Co. (Tokyo, Japan). PEI (Ultem-1000) and *N*-2-methylpyrrolidone (NMP) were purchased from the General Electric Co. (Indiana, USA) and the Junsei Chemical Co. (Tokyo, Japan), respectively. Ultrapure deionized water was used. Potassium bicarbonate (KHCO₃) and sodium arsenite (NaASO₂), used as an additive and catalyst, respectively, were purchased from the Aldrich Chemical Co. All chemicals were used without further purification.

Membrane Preparation

PVA solutions (3 wt %) were prepared by dissolving preweighed quantities of dry PVA in water and heating them for at least up to 6 h at 90°C. Then, the PVA solution and the GA solution were mixed to prepare PVA/GA mixture solutions with various compositions (PVA/GA = 1/0.04, 0.06, 0.08, 0.10, and 0.12 in mol %). PEI supporters were prepared by casting PEI solutions (composition of PEI/NMP = 25/75 in wt %) on glass plates using a Gardner knife with a predetermined drawdown thickness, followed by the immediate immersion of the glass plates into a coagulation bath containing ultrapure water. The PEI supporters prepared were kept in hot water for 24 h at 60°C and then dried for 3 h at 70°C. WSH membranes were prepared by dip-coating the dense layer of PEI supporters, which was fixed onto the glass plates using tapes, with the PVA/GA mixture solutions, followed by drying at room temperature for 24 h, and then the dry nascent WSH membranes were crosslinked by immersion for 10 min at 40°C in crosslinking solutions (IPA/water/HCl = 90/9/1 in wt %). In all cases, after the crosslinking reaction, the WSH membranes were taken out of the reaction solution, washed out several times with pure water, and immersed in pure water for 24 h at 40°C. The thickness of the coating layers and supporters of the WSH membranes were 0.8–1.2 and 180–200 μm, respectively.

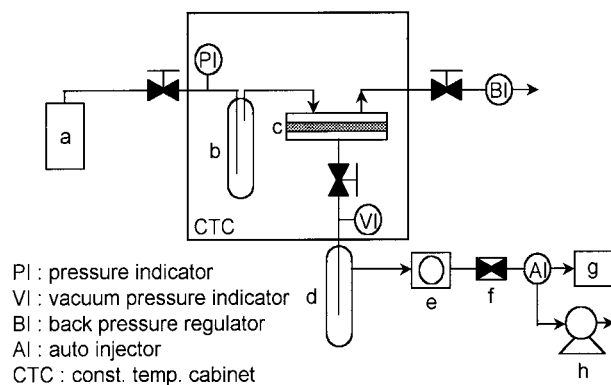


Figure 1 Schematic diagram of gas permeability measurement apparatus used in this study: (a) gas bomb; (b) water bubbler; (c) membrane cell; (d) cold trap; (e) vacuum controller; (f) mass flowmeter; (g) gas chromatography; (h) vacuum pump.

Addition of Additives into WSH Membranes

To put the additive ($\text{KHCO}_3/\text{NaASO}_3$) into the WSH membranes, the membranes were fixed to glass plates using tapes first, as mentioned under Membrane Preparation. Then, they were kept in the additive solution for 48 h at 40°C .

Determination of Swelling Ratio

Dry PVA/GA film strips (thickness: $10\text{--}20\ \mu\text{m}$; dimension: $3 \times 3\ \text{cm}$) were immersed in water or the additive solution thermostated for 48 h at 40°C to allow the strips to reach equilibrium sorption. After measuring the swollen weight of a strip at equilibrium sorption, the strip was dried at room temperature for 24 h under a vacuum and the dry weight was measured. Swelling ratios of the PVA/GA film were determined using the following equation:

$$\text{SR} = [(W_w - W_d)/W_d]$$

where W_d is the weight of the dried films and W_w is the weight of the swollen films.

Differential Scanning Calorimetry

To characterize the effect of the different blend compositions (PVA/GA) on the crosslinking degree variation of the PVA/GA films, the thermal analysis of the PVA/GA crosslinked films were carried out with a DuPont 2000. Sample weights ranged from 5 to 7 mg. The samples were heated from 30 to 300°C at a heating rate of $10^\circ\text{C}/\text{min}$.

The intercept point of the slopes was taken as the glass transition temperature, T_g .

Permeation Measurement

The apparatus used in this study is illustrated in Figure 1. The apparatus consisting of a water bubble chamber was attached to a permeation cell, a gas vessel, a pressure gauge, an autoinjector, a gas chromatography (GC), a vacuum pump, a vacuum controller, and a temperature-controlling cabinet as the main elements. Then, the mixture gas with saturated water vapor in the upstream was controlled by using a needle valve and a back-pressure controller. The degree of the vacuum in the permeation side was controlled by using a vacuum controller. Water vapor in the permeation side was collected in a cold trap jar. Permeation rates and compositions of the permeates were determined using a GC. A calibration curve of the permeation rate was prepared by using the data obtained from the GC and a mass flowmeter at the standard state. A purity of the mixture gas ($\text{N}_2/\text{CO}_2 = 80/20, 90/10$) used in this study was 99.5%.

RESULTS AND DISCUSSION

Physical Properties of Coating Materials

Figure 2 shows the effect of the GA content used as a crosslinking agent on the water-swelling ra-

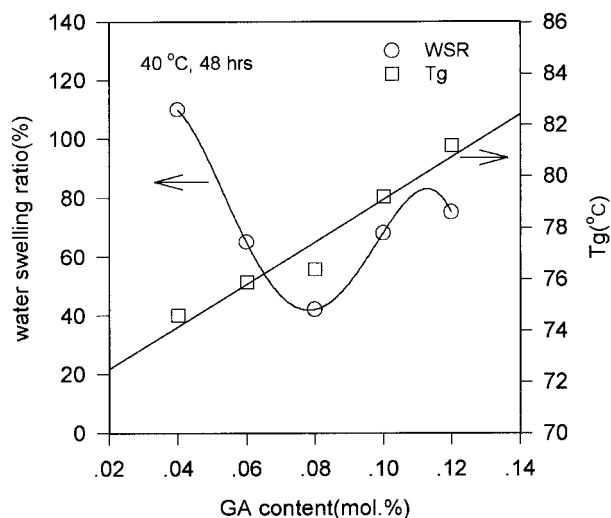


Figure 2 Water-swelling ratio and glass transition temperature of PVA/GA as a function of GA content in the film.

tio and the glass transition temperature, T_g 's, of the crosslinked PVA/GA films. With an increasing GA content, the swelling ratio of the film decreased rapidly until 0.08 mol % and then increased slowly. However, the T_g 's of the film increased with the GA content. Usually, as a crosslinking density of a polymeric material increases, the polymeric material has a less chain mobility and a more compact network, leading to a lower swelling ratio in the liquid and a higher T_g . So, it is clear that the decrease in the swelling ratio and the increase in the T_g of the PVA/GA films resulted from an increase in the crosslinking density of the film below 0.08 mol % of the GA. On the other hand, as the GA content increased further above 0.08 mol %, in spite of increasing T_g 's, the water-swelling ratio increased.

This result can be explained through the mechanism of the crosslinking reaction between PVA and GA and the swelling behavior of crosslinked PVA/GA film in the water and acetic acid which Yeom and Lee postulated.¹⁴ They reported two types of chemical structure created as a result of the crosslinking reaction between the hydroxyl group of PVA and the aldehyde group of GA as follows: structure **I**, the acetal ring group or ether linkage, which is the result of the crosslinking reaction,^{15,16} and structure **II**, the pending aldehyde group, formed by the monofunctional reaction of GA. According to the report, structure **I** makes the film less swollen while structure **II** makes the film more swollen in the water. GA is miscible in water, indicating that the aldehyde group has an affinity to water. So, it can be suggested that, as the GA content was above 0.08 mol %, the reason that the water-swelling ratio of the film was increased was due to the significant formation of structure **II** and that the T_g 's of the film were increased was due to an increasing bulky side group such as a pending aldehyde group.

Gas Permeation

Figure 3 shows the CO_2/N_2 mixed-gas permeation results of the WSH membrane swollen by the saturated water vapor in the feed at 25°C. The permeation data are plotted versus the GA content in the coating layer of the WSH membrane. The behavior of the gas permeation properties of the WSH membrane were parallel to the swelling behavior of the PVA/GA film in the water. The results can be explained by the gas mainly passing through the free volume of the coating layer that was filled by the water. Usually, for the WSH

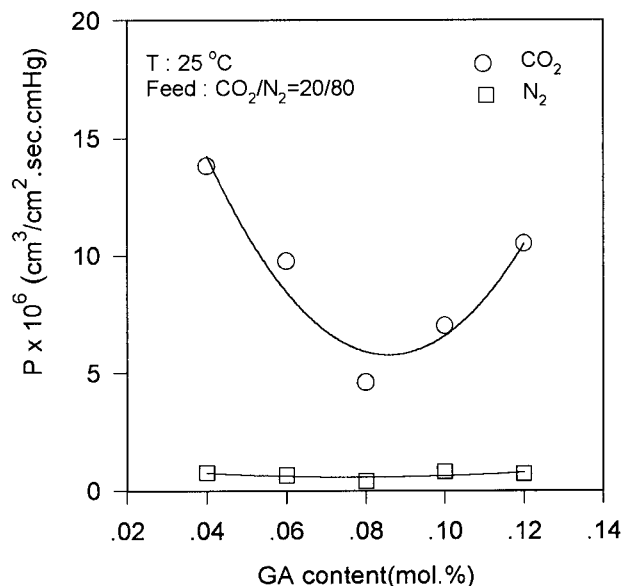


Figure 3 Gas permeation rate of WSH membranes as a function of GA content in the coating layer of the WSH membrane: upstream pressure: 179 cmHg; Downstream pressure: 0.4 cmHg; measurement time: 10 h.

membrane swollen by water, the water absorbed into the coating layer acted like plasticizer and increased the intermolecular distance of the polymer molecules of the coating layer and increased its free volume.

Figures 4 and 5 show the plots of the gas permeation rates and CO_2/N_2 separation factors of the WSH membrane, respectively. The permeation data are plotted versus the different downstream pressure at 179 cmHg of the upstream pressure. As shown in the figures, when the downstream pressure (3.4 cmHg) is above the saturation pressure (about 2.2 cmHg) of water at room temperature, the performance of the WSH membrane is higher.

In the membrane process, usually, with an increasing driving force, the permeation rate increases proportionally. However, in this case, in spite of the decreasing driving force, the permeation rate of the WSH membrane increased. This result can be explained like this: As the downstream pressure increases at a fixed upstream pressure (in other words, the driving force decreases), the amount of water absorbed into the coating layer increases. Therefore, as mentioned before, the water absorbed into the coating layer acts like a plasticizer and makes the polymer chains more mobile and the diffusion rate of the permeate can be increased. However, the reason

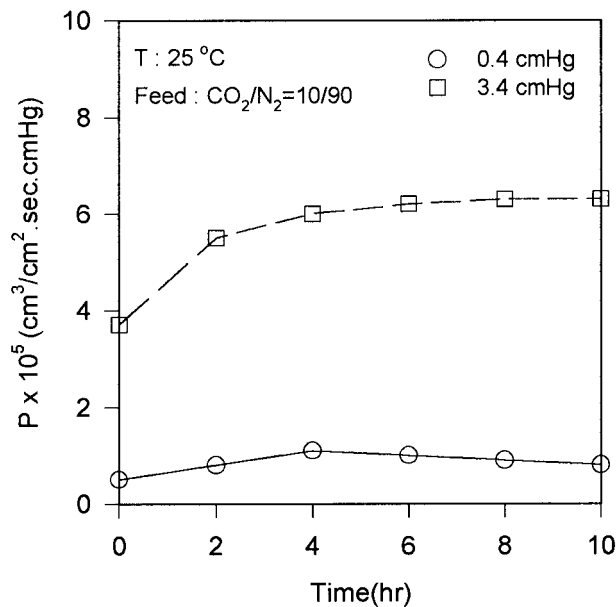


Figure 4 Effect of downstream pressure on the gas permeation rate through the WSH membrane: coating layer: PVA/GA = 1/0.04 mol %; upstream pressure: 179 cmHg.

for the increasing separation factor with an increasing downstream pressure is not clear, but one of the reasons would be related to the variation of the thickness of the swollen zone in the

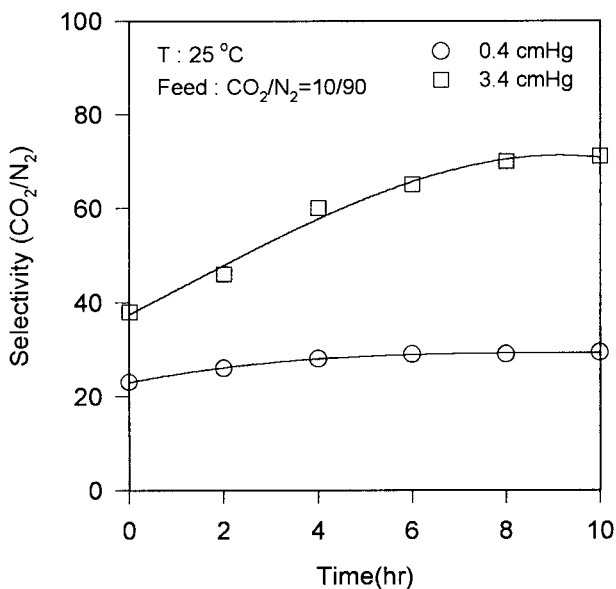


Figure 5 Effect of downstream pressure on the gas (CO₂/N₂) separation factor in the WSH membrane: coating layer: PVA/GA = 1/0.04 mol %; upstream pressure: 179 cmHg.

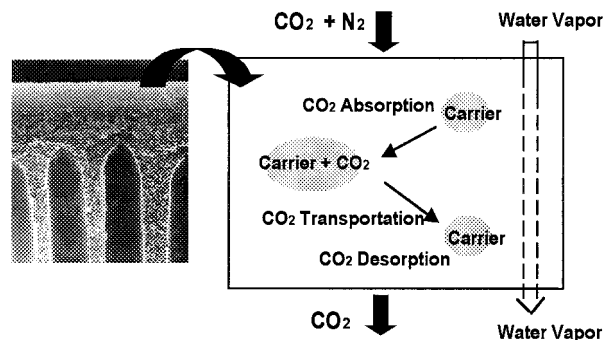


Figure 6 Schematic representation of facilitated transportation of CO₂/N₂ separation through the WSH membrane.

coating layer with different downstream pressures. In other words, when the downstream pressure is lower than the water-saturation vapor pressure, the dried zone will be developed in the coating layer and the thickness of the dry zone will increase toward the upstream side and with a further decreasing downstream pressure. Such an increasing dried zone will naturally induce a decrease of the wet layer in the coating layer and result in a poor separation factor. Usually, it is well accepted that during the operation the coating layer of the WSH membrane is in a swollen state by the saturated water vapor, and the water in the coating layer induces a higher permeability and a higher separation factor, indicating that the water should be involved in the gas separation, and without the water in the coating layer, the WSH membrane cannot show a good permselective performance.

Figure 6 presents a schematic diagram of the mechanism of the expected facilitated transportation as an additive is added into the WSH membrane. Figures 7 and 8 show the effect of the additives on the permeation properties. As shown in Figures 7 and 8, not as expected, after treatment with the additives, the permeability decreased and the separation factor toward CO₂ slightly increased. To determine the reason for this result, the variation of the swelling ratios as a function of the concentration of KHCO₃ and NaASO₂ of the PVA/GA films that have the same degree of crosslinking as that of the coating layer of the WSH membrane was studied. From Table I, it is found that with an increasing concentration of the additives the swelling ratio decreases drastically. This result may be due to the difference in the solubility of the film in the aqueous solutions of KHCO₃ and NaASO₂ with different concentra-

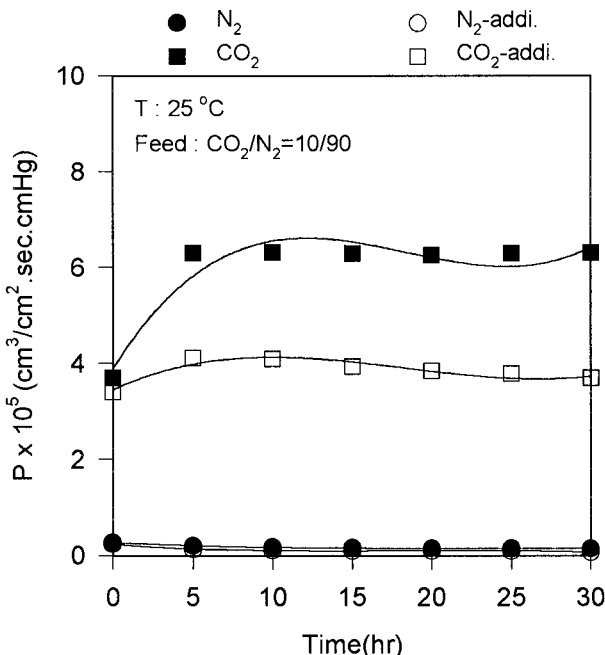


Figure 7 Effect of additive on the gas permeation rate through the WSH membrane: additive: 2N KHCO_3 ; catalyst: 0.5N NaASO_2 . upstream pressure: 179 cmHg; downstream pressure: 3.4 cmHg.

tions. Since the solubility of the film in the additive solution is much lower compared with that in pure water, the swelling ratio decreases drasti-

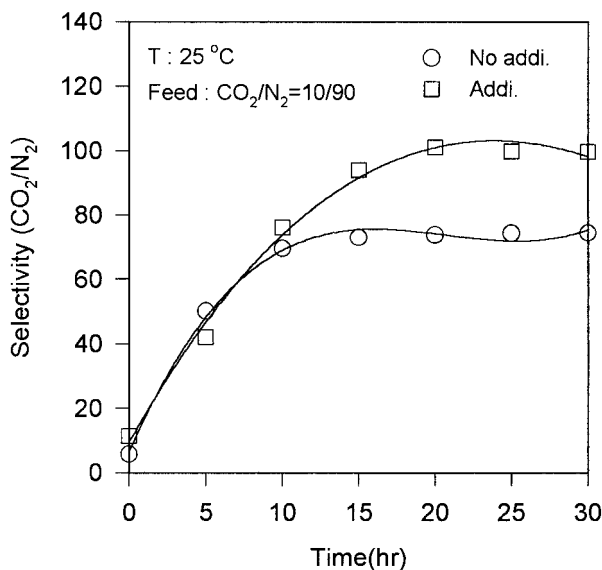


Figure 8 Effect of additive on the gas (CO_2/N_2) separation factor through the WSH membrane: additive: 2N KHCO_3 ; catalyst: 0.5N NaASO_2 . upstream pressure: 179 cmHg; downstream pressure: 3.4 cmHg.

Table I Swelling Ratio of the PVA/GA Film as a Function of the Additive Concentration

Additive Solution Concentration (N)	Swelling Ratio (%)
0N ^a	108
1N KHCO_3 + 0.25N NaASO_2	80
2N KHCO_3 + 0.50N NaASO_2	61
3N KHCO_3 + 0.75N NaASO_2	48

PVA/GA film (PVA/GA = 1/0.04 mol %). Immersion time, temperature: 48 h, 40°C.

^a Pure water.

cally in proportion to the concentration of the additives in aqueous solutions. It was reported by Ward and Robb¹² in a previous article that the concentration of the additive should be higher than 1N to expect the facilitated transport. Therefore, the decrease in the permeability, as an additive solution was used instead of pure water, can be explained by the decreasing amount of water in the coating layer that resulted from the shrinkage of the coating layer due to the additive.

CONCLUSIONS

WSH membranes for gas separation were prepared by dip-coating asymmetric porous PEI supports with the PVA-GA solution, followed by the crosslinking of the coating layer by a solution method. From this work, several important observations can be summarized as follows:

1. With increasing GA content of the coating solution, the swelling ratios of the coating layer decreased rapidly up to 0.08 mol % and then increased after that. However, the T_g 's of the coating layer increased with the GA content.
2. The behavior of gas permeation properties of the WSH membranes was parallel to the swelling behavior of the coating layer in water.
3. Additives did not affect on the gas permeation properties of the WSH membranes because they were not soaked into the coating layer sufficiently.

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