

Permeabilities of Water, Several Alcohols, and Water/Alcohol Mixtures through Thin Films of Syndiotactic-Rich Poly(vinyl Alcohol)

KAZUO YAMAURA, SHUICHI KIRIKAWA, NOBUHIRO SAKUMA,
TETSUYA TANIGAMI, and SHUJI MATSUZAWA, *Faculty
of Textile Science and Technology, Shinshu University,
3-15-1 Tokida, Ueda-City, Nagano-Prefecture 386, Japan*

Synopsis

The permeabilities of liquids through syndiotactic-rich poly(vinyl alcohol) (*s*-PVA) very thin films (about 0.3 μm) scooped up from the interface of air/aqueous solution were compared with that of casting *s*-PVA films (about 15 μm). The permeability of water decreased with time and the volume of permeate leveled off after 4 or 5 days in both films. In the case of the very thin films, the permeabilities of alcohols decreased with the increase in the molecular weight of alcohol, whereas, in the case of casting films, the permeability of methanol was lower than that of ethanol. In the case of the very thin films, the permeabilities of any water/alcohol (= 50/50) mixtures were lower than those of pure water and alcohols. These results were correlated to rearrangement of *s*-PVA molecules, formation of bound water, hydrophobic interaction, and clusterization of small molecules.

INTRODUCTION

Many studies for the permeation of liquids through the films of atactic poly(vinyl alcohol) (*a*-PVA) derived from vinyl acetate have been reported.¹⁻¹⁰ In the case of the permeation of water, the annealed,^{4,8-10} esterified,^{3,4} or crosslinked *a*-PVA films⁵⁻⁷ with water resistance were used. The permeation of water has been reported recently to be dependent on the degree of swelling of *a*-PVA film.⁹ The permeation of organic liquids through *a*-PVA films has been examined and the maximum molecular length and the molecular cross section of the permeating species have been shown to control the rate of permeation.² The separating ability of water/alcohol mixture has also been studied.² However, the rates of permeation of water and organic liquids were very low, because the thickness of these films used were more than 25 μm .

The authors have reported that poly(vinyl alcohol) (*s*-PVA) derived from vinyl trifluoroacetate had strong water resistance¹¹ and was adsorbed very easily on air/aqueous solution interface,¹² and that the very thin films of *s*-PVA were prepared by the frame (film thickness: 0.18 μm) or bubble (0.026 μm) methods using the adsorption.^{13,14} Although these films were very thin, they had the water resistance and were used as a permeation membrane of water.¹⁴ The rate of permeation of water lowered with the increases in thickness of film and annealing temperature.¹⁴ The effect of the thickness of film on the permeation of water has been explained by the model of three phases in which the intermediate phase prevented the permeation of water. In this study, the permeation

behaviors of water for the casting *s*-PVA film and the *s*-PVA thin film prepared by the frame method were compared. Furthermore the permeabilities of alcohols of different molecular lengths and water/alcohol mixtures were examined for the films which were prepared by the frame and casting methods. The relation between the order of polymer chains in the films and the permeabilities of liquids, and the interaction between the polymer chains and the liquid molecules were investigated.

EXPERIMENTAL

Sample and Films

The *s*-PVA used was prepared by ammonolysis reaction of diethylenetriamine and the polymers obtained by bulk polymerization of vinyl trifluoroacetate (VTFA) at 60°C using benzoyl peroxide as an initiator. The degree of polymerization (*DP*) and the syndiotactic diad content [*s*-(diad) %] were 1970 and 58.0%. The *DP* was determined from the intrinsic viscosity number [η] of benzene solution of acetylated *s*-PVA using $[\eta] = 8.91 \times 10^{-3} DP^{0.62}$ (dL g⁻¹, 30°C) and *s*-(diad) % were determined from the absorbance ratio of D_{916}/D_{849} by the use of the infrared method described previously.¹⁵ Ultrathin films were prepared scooping out from the air/solution interface of 0.6 g/dL *s*-PVA aqueous solution using the metallic circular frames by the method described previously.¹⁴ The films with thicknesses of about 0.3 μm were obtained. The casting films with thicknesses of about 15 μm were prepared using 1.25 g/dL aqueous *s*-PVA solution.

Permeation

The experiments of permeation were carried out using an apparatus consisting of 2 detachable cells (cell I and cell II) made of glass.^{1,14} The films were clamped between the cells with filter paper supports. The permeation experiments for thin film was carried out as follows. One side cell (cell I) separated by the film was filled with water and was stood for 15 min. Then water permeated was removed (cell II) and cell I was filled with water again. After 10 min water permeated was separated, the volume was measured and water permeated was added to cell I. This process was repeated at 10 min intervals. The maximum pressure was 0.0153 atm. The pressure was generated under the gravitation of liquids.

The permeation experiments for a casting film were carried out under the pressure ΔP in the range of 0.02–0.7 atm and the permeation experiment similar to that for thin film was also carried out. The pressure ΔP is the difference of those between both sides of film. The pressure except the gravitation of liquids was given by N₂ gas (ca. 0.10–0.58 atm). Methanol, ethanol, and *n*-propanol were a special grade from Wako Pure Chemical Industries, Ltd.

RESULTS AND DISCUSSION

Permeation of Water

Figure 1 is the cumulative volume of permeated water, *Q*, through the thin film at 30°C as a function of time. *Q* is represented as the volume per unit area

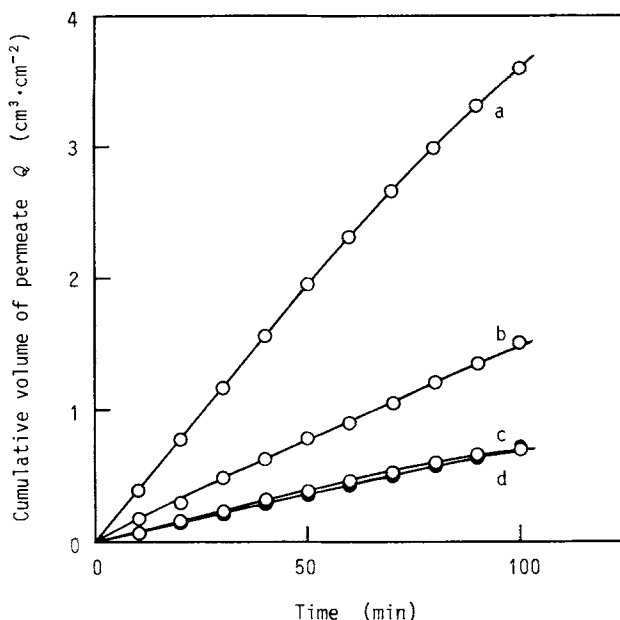


Fig. 1. Relations between cumulative volume of permeate and time for *s*-PVA thin film. (a) The cell was filled with water at 30°C and the measurement was instantly initiated after 15 min, (b) after 15 h, (c) after 62 h, and (d) after 85 h (●).

(Q : $\text{cm}^3 \text{cm}^{-2}$). Figure 1 shows that the rate of permeation, J_w , decreased with time and leveled off after 3 or 4 days ($J_w = 6.5 \times 10^{-3} \rightarrow 1.0 \times 10^{-3} \text{ cm}^3 \text{cm}^{-2} \text{ s}^{-1}$). The unannealed casting *s*-PVA film began to swell after 10 s dipping in water at 30°C to reach to the swelling equilibrium after 5 min.¹⁶ We expected, therefore, that the permeability of water was independent of time after 15 min at 30°C. No expected result was obtained. This suggests that, in this film, absorbed free water was gradually transformed into bound water combined with PVA molecules or that the free chain segments between junctions were arranged to make new junctions. The combination of free polymer chains are considered to narrow the channels of permeants to decrease the rate of permeation. In the case of casting films, though the rate of permeation was very slow under the gravitation of liquids ($J_w = 1.1\text{--}3.3 \times 10^{-5} \text{ cm}^3 \text{cm}^{-2} \text{ s}^{-1}$), the tendency was similar to that of thin film.

Figure 2 shows the relations between the rate of permeation of water, J_w ($\text{cm}^3 \text{cm}^{-2} \text{ s}^{-1}$), and the pressure difference between of both surfaces of film, ΔP (atm), for casting film. The volume of permeate was measured after standing the cell with film at 30°C for 4 days in water. The change in J_w with the rise of pressure was determined at 30°C and then every 10°C. J_w increased with the rise in temperature, especially rising steeply at the temperatures above 60°C. Therefore, this result was not able to be analyzed using the Arrhenius plots. The result corresponded to that for the swelling of *s*-PVA films in water.¹⁷ Moreover, though J_w increased with the rise of pressure, no proportionality was recognized. This might be due to the insolubility of small junctions at 30°C which were broken by the rise of pressure. Kojima et al. have found a linear relationship between the J_w and the pressure for the swollen *a*-PVA film.⁹ The

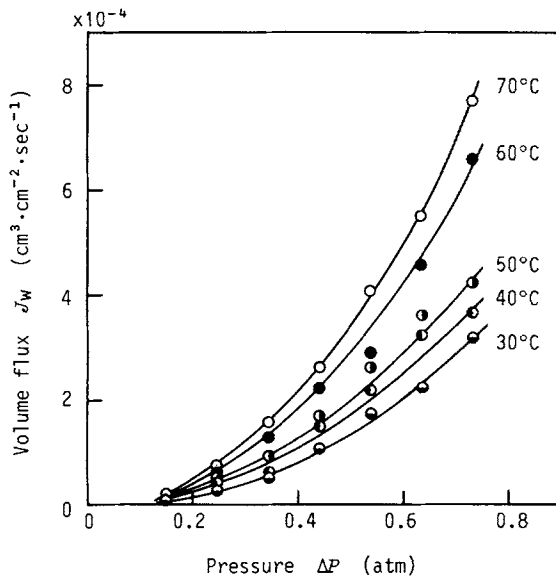


Fig. 2. Volume flux of water J_w vs. applied pressure at various temperatures for s-PVA casting film pre-swollen at 30°C in water.

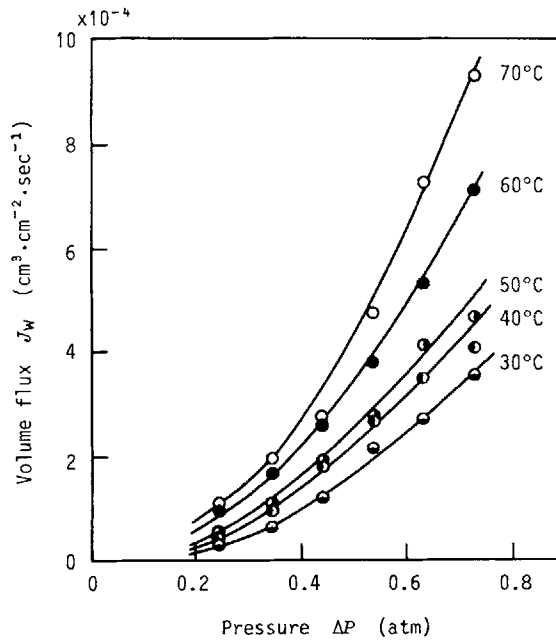


Fig. 3. Volume flux of water J_w vs. applied pressure at various temperatures for s-PVA casting film pre-swollen at 70°C in water.

difference of results in both thin *s*-PVA and thick *a*-PVA casting films is considered to be due to the increment of permeation area by stretching of thin film and the decrement of permeation path by compression of thick film under high pressure.

Figure 3 shows the pressure dependency of the permeability of water for the casting film swollen for 1 h in water at 70°C. The permeation experiments were initiated after standing the swollen film at 30°C for 4 days in water. The J_w of the film swollen at 70°C was higher than that of the film swollen at 30°C at the same pressure and the curve for former became somewhat straightened in the pressure range above $\Delta P = 0.5$ atm. This may be due to the higher swelling at 70°C. The degree of swelling (film length at equilibrium swelling/film length before swelling) for *s*-PVA film in water at 70°C was 1.6 which was fairly higher than that in water at 30°C and 1.2.¹⁷ The unstable small junctions were dissolved completely in the former swollen film. In the latter films, many weak junctions which are easily destructed by pressure still remain after swelling. The steep increment of the rate of permeation with pressure at low pressure range (0.25 ~ 0.4 atm) might be due to releasing of the water molecules combined with PVA chain by weak interaction by pressure. This result is similar to that found by Kojima et al. for *a*-PVA film of the thickness of 200 μm .⁹ They found that as the degree of hydration became higher, the activation energy of water permeation became lower.

Permeation of Alcohols

Figure 4 shows the permeabilities of several alcohols at 30°C for the thin films. Though no forced pressure was given, the thin films permeated alcohols

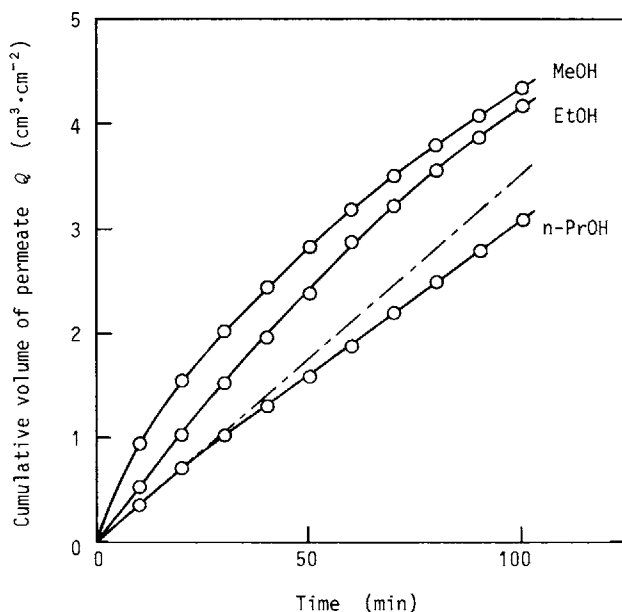


Fig. 4. Relations between cumulative volume of permeate of various alcohols and time at 30°C for *s*-PVA thin film. Difference in pressure between both the surfaces of film: methanol/0.0154 atm, ethanol/0.0153 atm, *n*-propanol/0.0173 atm.

which were poor solvent for PVA. PVA films were not swollen at all by these alcohols. The rate of permeation decreased with the increase in the molecular weight of alcohol and the permeation of alcohols became gradually hard to permeate with time. Uragami et al. studied the permeabilities of methanol, ethanol, and *n*-propanol to the atactic PVA films crosslinked by sodium hydroxide.⁶ These alcohols barely permeated at high pressure and the permeability decreased with the increase in the molecular length.⁶ The results shown in Figure 4 are analogous to those of Uragami et al. The ratio of the cumulative volume of permeate estimated from the initial slope of each curve in Figure 4 to the measured one after 100 min were 0.70, 0.80, and 0.89 for methanol, ethanol, and *n*-propanol, respectively. This means that the rate of permeation became independent of time with the increase in molecular weight of alcohols. At the initial stage, alcohol of lower molecular weight permeate easily through channels in the film. However, the hydrophobic interaction between the alcohol and the PVA increases with time to narrow the channels.

Figure 5 shows the pressure dependency of the permeabilities of three kinds of pure alcohols (methanol, ethanol, and *n*-propanol) for the casting film at 30°C. The pure alcohols permeated through the very thin films in the cell without external pressure, whereas in the casting films these permeated with external pressure. J_w of pure alcohols increased with pressure in the pressure range over 0.2 atm. Although the methanol molecule is smaller than ethanol molecule, J_w was low at any pressure. The result was contrary to that of the

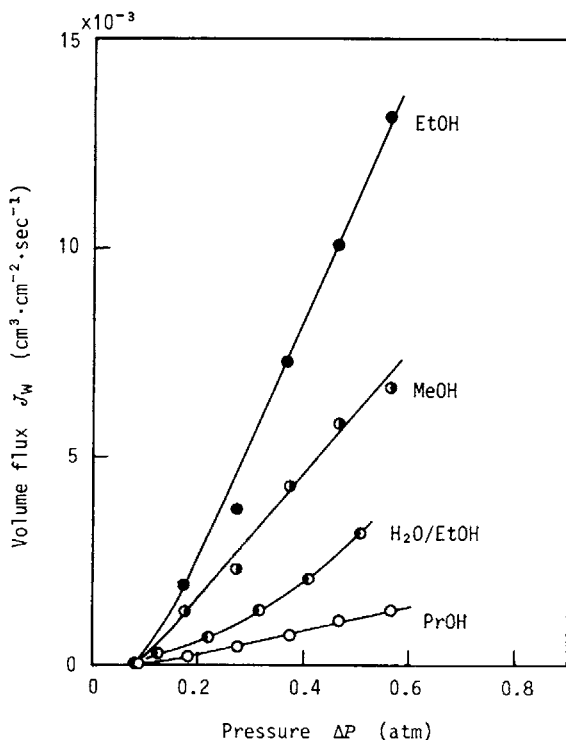


Fig. 5. Volume flux J_w of various alcohols and water/ethanol mixture vs. applied pressure at 30°C for *s*-PVA casting film.

thin film. It may be caused by the thickness of the intermediate phase in the film.¹⁸ PVA films were considered to consist of three layers, that is, two adsorbed layers and one middle layer.^{13,14,18} The degree of crystallization of thin film with less intermediate phase was lower than that of casting film with more intermediate phase.^{13,14} Therefore, casting films are considered to have a denser structure and narrower channels than thin films. In addition, since the hydrophobic interaction between PVA and methanol is stronger than that between PVA and ethanol, it is considered that the channel of permeates became narrow by the hydrophobic bond between methanol and PVA in the intermediate phase and the rate of permeation of methanol became lower than that of ethanol. The rate of permeation increased with the increase in pressure in accord with the concave curve under low pressure (below about 0.2 atm). The weak junctions or the hydrophobic bonds between alcohol and PVA are considered to be broken by pressure leading to complete destruction at about 0.2 atm. At the pressure above 0.2 atm, the rate of permeation increased in proportion to pressure.

Permeation of Water/Alcohol Mixtures

Figure 5 also shows the pressure dependency of the permeability of water/ethanol 50/50 mixture for the casting film at 30°C. J_w of the water/ethanol mixture were lower than that of pure ethanol and higher than that of pure water (see Fig. 2), and the curve was analogous to that of water (see Figs. 2 and 3). The refractive indices of the 50/50 mixture and the permeate liquid was equal. The permselectivity was not recognized.

Figure 6 shows the permeability of the water/ethanol 50/50 mixture for the thin film at 30°C compared with the permeabilities of pure water and ethanols.

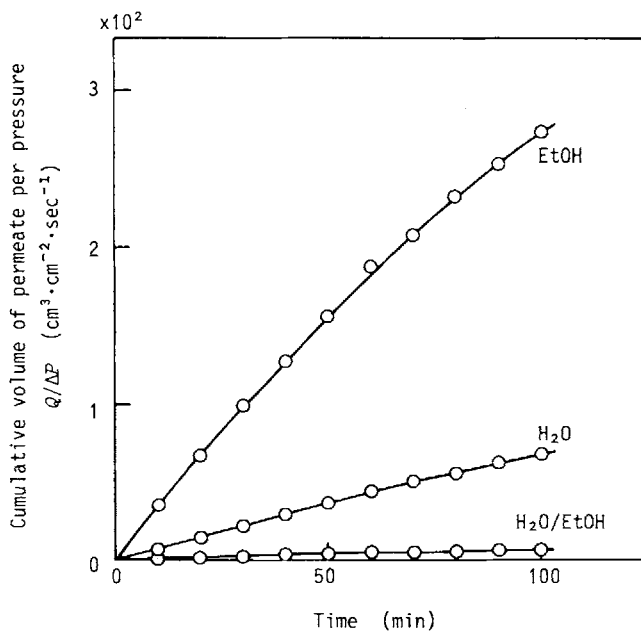


Fig. 6. Relations between cumulative volume of permeate per pressure of ethanol, water, and water/ethanol mixture and time at 30°C for *s*-PVA thin film.

The rate of permeation of water/ethanol mixture was obviously less than that of water and ethanol. The mixture became a poorer solvent to PVA due to the interaction between water and ethanol molecules and the association or the clusterization between water and alcohol. For the casting film, the volume of permeated mixture could not be measured under gravitation force of liquid in cell.

Figure 7 shows the permeability of water/*n*-propanol 50/50 mixture for the thin film at 30°C compared with the pure liquids. The result is analogous to that of the water/ethanol mixture, though the rate of permeation of water was lower than that of ethanol. This may be due to the larger size of associated and clustered molecules in water/*n*-propanol mixture than that in the water/ethanol. The maximum values of the difference in the refractive indices of the water/alcohol 50/50 mixture and the permeate liquid were 0.0103 for the water/ethanol mixture and 0.0085 for the water/*n*-propanol mixture. These differences indicate that water permeated about 10% more than ethanol or *n*-propanol.

CONCLUSIONS

The rate of permeation of water for *s*-PVA casting films decreased with standing time and became constant after 4 or 5 days. Therefore, the rearrangement of PVA chains or the addition of water as the bound water during the permeation were supposed.

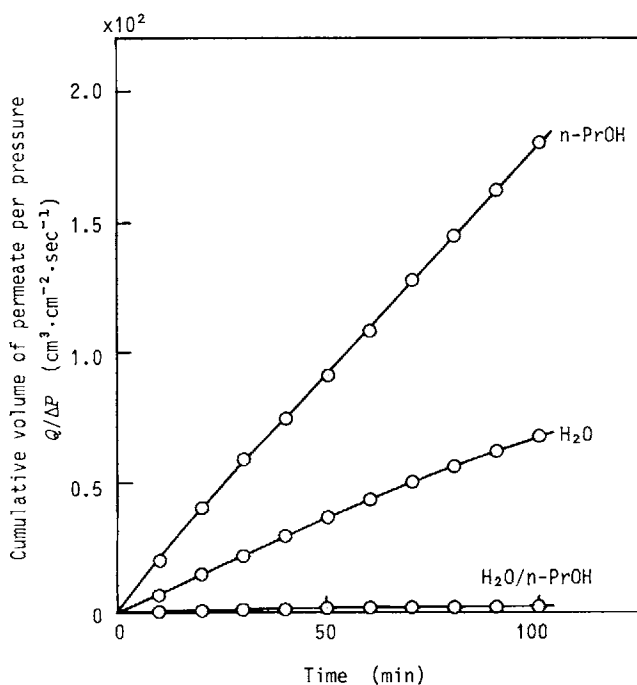


Fig. 7. Relations between cumulative volume of permeate per pressure of *n*-propanol, water, and water/*n*-propanol mixture and time at 30°C for *s*-PVA thin film.

In the case of the thin film, the time dependence of the rate of permeation of alcohols vanished with the increase in the molecular weight of alcohol. At the initial stage of permeation, alcohol of lower molecular weight permeated easier than that of higher molecular weight. At the second stage the hydrophobic bonds between alcohols and PVA are considered to be formed. In the case of the alcohol of lower molecular weight, the rate of permeation decreased with time. In the case of the casting film, the rate of permeation for methanol was lower than that for ethanol and the inverse relation was observed in the case of the thin film. In the thin film, the permeability of water/alcohol 50/50 mixtures were lower than that of pure water or alcohols. The mixtures may be a poor solvent for the PVA due to the interaction between water and alcohol molecules¹⁹ and become large by the association or the clusterization between water and alcohol molecules. In the casting films, J_w of water/alcohol 50/50 mixture was lower than that of alcohol and larger than that of water. Both of the casting and thin films had lower permselectivity.

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