Wet Poly(vinyl Chloride) Membrane

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Synopsis

Wet, porous, and semipermeable poly(vinyl chloride) (PVC) membrane prepared from a binary system, PVC and dimethylformamide, by immersing in alcohols or ethers was studied. The pore dimensions of the wet PVC membrane were from 0.01 to 0.05 μm, calculated from hydrodynamic permeability by using experimental values such as water flux and water content. They agreed reasonably well with the dimension of the pores which prevented the protein passing through the membrane, observed by SEM photographs. Formation of the wet PVC membrane can be explained by slow phase separation and slow leaching of the casting solution immersed in alcohols and ethers such as methanol and ethylene glycol monomethyl ether.

INTRODUCTION

Many kinds of porous membranes such as ultrafiltration and reverse osmosis membranes have been prepared by various methods and subsequently applied to water treatment and biomedical materials.[1–3] A few of these porous poly(vinyl chloride) (PVC) membranes prepared under different membrane formation conditions have been developed by the authors.[4] Porous PVC membranes from a binary solution, PVC and dimethylformamide (DMF), were obtained by using the method of phase separation which was produced by absorption of aqueous vapor from the atmosphere. The membrane structure was closely related to the degree of phase separation just before leaching.

A membrane with a fingerlike structure was obtained by leaching a casting solution in water at an early stage, when the casting solution was still transparent. A network structure was obtained by leaching in water at the late stage, when the casting solution became opaque. In addition, a porous PVC membrane on which enzymes could be adsorbed was obtained by leaching the casting solution in methanol at the early stage. The porous PVC membrane was wet, due to water held in minute pores, and translucent in appearance; it was subsequently named "wet" PVC membrane to distinguish it from other porous membranes.

Wet and network PVC membranes have actually been applied as carriers for immobilized enzymes and filtration for water pollution, respectively. In particular, wet PVC membranes adsorbing glucose oxidase have been applied to enzyme electrodes.[5] The membrane adsorbs β-glucuronidase in steroid hormones analysis.[6,7]

In general, a carrier needs characteristics of porosity and proper hydrophilicity to promote effective enzymatic reactions under heterogeneous, water-swollen conditions.[8] Therefore, hydrophilic polymers such as polysaccharide,[9] polyacrylamide,[10] poly(vinyl alcohol)[11] and collagen[12] are of great use as carriers. PVC, a typical hydrophobic polymer, with wet PVC membrane has also been useful as carrier.

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The enzyme adsorbed by the wet PVC membrane gave high enzyme activity and rarely leaked out of the buffer solution during storage. But a detailed mechanism of the adsorption of enzyme on wet PVC membrane has not yet been elucidated.

The purpose of this article is to investigate the preparation and properties of wet PVC membrane in more detail, in order to understand the interaction between the wet PVC membrane and enzyme and to develop an appropriate carrier.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC; M_n 48,400) was a product of Kanegafuchi Chemical Co., Ltd. (Tokyo, Japan). Reagent-grade dimethylformamide (DMF) was purchased from Wako Junyaku Co., Ltd. (Tokyo, Japan) and was used as received. Proteins were purchased from Boehringer Mannheim GmbH.

Membrane Preparation

PVC solution in DMF (PVC 10 wt %) was cast approximately 400 μm thick on a glass plate (10 × 7 cm^2). The glass plate was left under evaporation conditions, i.e., at 25°C and 50% relative humidity, for a given evaporation time. The casting solution on the glass plate was leached in a gelation bath of water or organic solvents, and a porous PVC membrane was obtained. The organic solvent such as methanol replaced water in which the porous PVC membrane was kept. Membrane thickness obtained was ~180 μm.

Measurements of Membrane Properties

The volumetric water content ϕ of the wet PVC membrane was determined from the weight loss after drying under vacuum at 70°C and was defined as

$$\phi = \frac{W_1 - W_0}{AL\rho_w}$$

where W_1 is weight of the wet PVC membrane at 25°C (g), W_0 is weight of the PVC membrane dried (g), A is membrane area (cm^2), L is membrane thickness (cm), and ρ_w is density of water (g/cm^3).

Water flux F was measured by the quantity of water that permeated through the membrane at 0.5 atm and 25°C.

Stress and strain at a fracture point were measured by an autograph machine (model IS-5000, Shimatsu Seisakusho, Kyoto, Japan). As shown in Figure 1, the experiments were carried out using a load cell of 400 g or 1 kg under the conditions of a load cell speed of 1 mm/min, load cell diameter of 15 mm, and PVC membrane diameter of 43 mm. The symbol "l" denotes the possible distance of the load cell in the vertical direction, and therefore represents elongation.

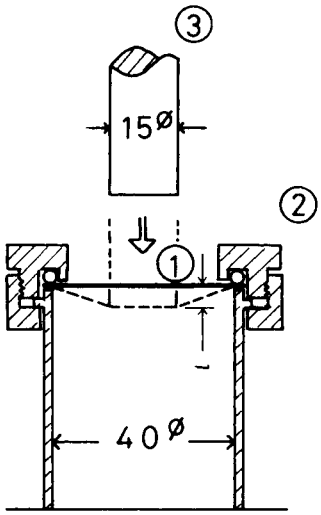


Fig. 1. Apparatus for measuring membrane strength: 1, wet PVC membrane (43 mm/diam.); 2, membrane holder; 3, load cell (15 mm/diam.).

Testing for Protein Rejection

The ultrafiltration cell used in this study was a Toyo Roshi-model UHP-43 (Toyo Roshi Co., Ltd., Tokyo, Japan) with a reservoir of 50 ml. The wet PVC membrane with diameter 43 mm was supported on a porous plastics disc and sealed by a rubber O-ring. A magnetic stirring bar helped to minimize product (proteins) built up at the membrane surface.

Fifty milliliters of 0.1% protein solution in deionized water was poured into the ultrafiltration cell. Half of the feed in the volume was passed through the membrane at 2.0 atm and 30°C. Apparent rejection efficiency E_{app} was the fraction of one species of molecules which was retained and was expressed as

$$E_{app} = 1 - (S_f/S)$$

where S_f is concentration of protein in the filtrate and S is initial concentration of protein. Weights of protein in the feed and the filtrate were determined by the method of Lowry et al.[13] with the use of crystalline serum albumin as a standard.

Annealing

Wet PVC membranes which were prepared from the casting solution of 8 wt % of PVC concentration were annealed in hot, deionized water at 70–95°C.

RESULTS AND DISCUSSION

Preparation of Wet Membranes

The PVC–DMF solution, which was initially transparent, became opaque (cloud phenomenon) after 20 min when the solution was cast on a glass plate under standard conditions, and phase separation during membrane formation

TABLE I
Typical Relationship between Membrane Formation Processes and Membrane Structure

Run no.	Membrane formation process[a]			Membrane structure
	Evaporation time, min	Before leaching	Leaching medium	
1	60	cloudy	water	network[b]
2	5	transparent	water	fingerlike[b]
3	60	cloudy	methanol	network
4	5	transparent	methanol	wet

[a] PVC membranes were prepared from 10 wt % PVC concentration under the evaporation conditions at 50% RH and 25°C.
[b] As in a previous report.[4]

was caused by absorption of aqueous vapor from the atmosphere, as described in a previous report.[4]

Table I shows the membrane structures obtained under various membrane formation conditions. Runs 1 and 2 were two typical examples taken from previous experiments. In runs 3 and 4, methanol as a leaching solvent was used. The cloud phenomenon, in run 3, was observed after 20 min of evaporation time in 50% RH as run 1. The cloudy solution was subsequently leached by methanol. The membrane structure in run 3 was a network structure and closely resembled that of run 1. In run 4, a "wet" membrane structure was obtained by leaching the casting solution in methanol after a short evaporation time, i.e., before it became cloudy. Therefore, there is no absorption effect of aqueous vapor on the phase separation during membrane formation when evaporation time is short.

The structures and properties of PVC membranes obtained by using various

TABLE II
Porous PVC Membranes Obtained by Using Various Organic Solvents as Leaching Media

Leaching medium[a]	Membrane Structure	Filtration rate, ml/min/cm^2[b]	Molecular cutoff[c]
Methanol	wet	0.14	85,000
Ethanol	wet	0.07	130,000
n-Propanol	wet	0.055	60,000
Isopropanol	wet	0.055	80,000
n-Butanol	wet	0.024	40,000
t-Butanol	wet	0.050	85,000
DGME[d]	wet	0.14	180,000
Glycerol	not obtained	—	—
n-Dodecane	not obtained	—	—
Methanol/water (9:1)	fingerlike	0.40	>480,000
Methanol/acetone (8:2)	wet	0.30	140,000

[a] The experiments were carried out under the following conditions: PVC concentration, 10 wt %; evaporation time, 5 min; 50% RH; 25°C.
[b] Differential pressure was 2 kg/cm^2.
[c] When protein rejection of 50% was observed.
[d] Diethylene glycol monomethyl ether.

organic solvents are summarized in Table II. Organic solvents that are poor for PVC and soluble for DMF, such as alcohols, ethers, glycols, and *n*-paraffins, were chosen in this study. An organic solvent in which the casting solution was leached controlled the membrane structure obtained.

Leaching in alcohols and diethylene glycol monomethyl ether led the casting solution to the wet PVC membrane. The wet PVC membrane was not obtained when glycerol and *n*-dodecane were used as leaching solvents. DMF in the casting solution could rarely be leached by the above organic solvents, because glycerol was too viscous and *n*-dodecane was slightly soluble in DMF.

A methanol–water (9:1) mixture made a fingerlike membrane from the casting solution. A methanol–acetone (8:2) mixture led the casting solution to a wet PVC membrane. Only acetone could not fix the casting solution thoroughly.

Properties and Structures of Wet PVC Membranes

The effect of PVC concentration of the casting solution on water flux and water content of the wet membrane is shown in Figure 2. Both water flux and water content decreased with increase in PVC concentrations. This shows that the interstitial matrix of the wet PVC membrane plays an important role in its permeability. Wet PVC membrane prepared from a PVC concentration of less than 4 wt % was not self-existing in mechanical strength because of its interstitial matrix of large pore size.

Stress and strain at the fracture point of the wet PVC membrane are summarized in Table III. The wet PVC membrane had a higher strength and elongation than collagen membranes, which have shown potential and practical application in enzyme electrodes.[12] Fracture strength increased with increasing PVC concentration of the casting solution. This was because the interstitial matrix of the wet PVC membrane is formed with minute pores as PVC concentrations increase. Membrane thicknesses were almost constant.

Figure 3 shows protein rejection curves by the wet PVC membrane prepared from the various PVC concentrations. All three membranes showed the ability to reject proteins. The molecular cut-off became lower when using wet PVC membrane prepared from a higher PVC concentration. Shown in Figure 4 are

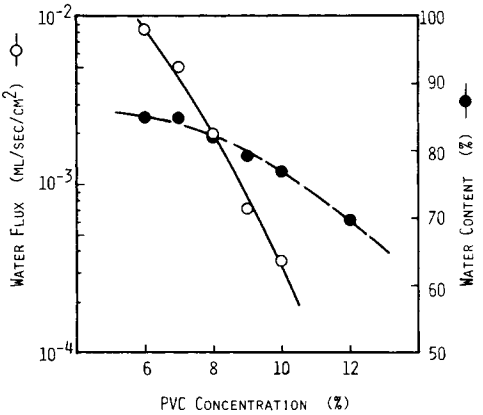


Fig. 2. Water flux and water conent vs. PVC concentration of the casting solution from which the wet PVC membrane was made: (○) water flux; (●) water content.

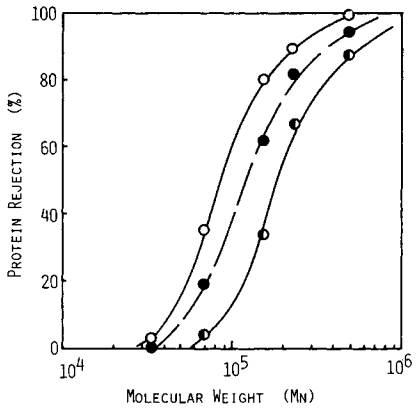


Fig. 3. Protein rejection curves by using the wet PVC membrane prepared from the various PVC concentrations: (◐) 6 wt %; (●) 8 wt %; (○) 10 wt %.

protein rejection curves by using the various membrane thicknesses. The molecular cutoff decreased with increasing membrane thickness. This means that the whole wet PVC membrane contributed to the retention of proteins. In addition, the inside of the wet PVC membrane became red after experiments with hemoglobin rejection. Therefore, the wet PVC membrane was semipermeable and different from commercial ultrafiltration membranes in which a skin layer mainly rejects protein due to an asymmetric membrane.

The effect of annealing on water flux is shown in Figure 5. At more than 80°C of annealing temperature, water flux decreased with increasing annealing time. Protein rejection was almost unchanged by annealing. The wet PVC membrane shrank and became thin with annealing. SEM photographs of the surface of the wet, annealed membrane are shown in Figure 6. Micropores of the surface of the membrane remained unchanged. It is thought that annealing at more than 80°C softened the PVC matrix and that the micropores were blocked with this softening of the PVC matrix. Glass transition temperatures T_g of pure PVC and wet membrane were identical at 80°C when observed by DSC.

Annealing drastically improves the separation properties of membranes such as cellulose acetate membranes,[14,15] and polymer alloy membranes.[16] However, annealing did not improve the separation property when used for protein rejection as in this experiment.

TABLE III
Mechanical Properties of Wet PVC Membranes

PVC concn., wt %	Membrane thickness, μm	Fracture point	
		Strength, kg/cm²/cm[a]	Elongation, cm[b]
8	35	0.396	0.43
10	32	0.716	0.58
12	34	0.912	0.68
10	143	0.617	0.69

[a] Observed stress/contact area of the load cell/membrane thickness.
[b] Possible distance of the load cell in the vertical direction (l in Fig. 1).

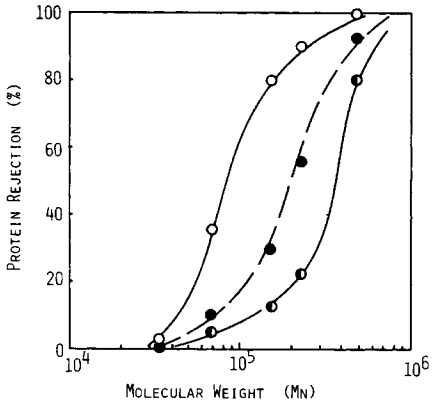


Fig. 4. Protein rejection curves by using the various membrane thicknesses: (◐) 40 μm; (●) 80 μm; (○) 180 μm.

DISCUSSION

It has been demonstrated that the PVC membrane prepared from the PVC–DMF casting solution and leached into methanol is wet, porous, and semipermeable. Some characteristics of the wet PVC membrane are elucidated (Figs. 2–4, Table III).

One should note that the membrane structure is determined by the state of phase separation just before leaching, as previously mentioned. In general, two important features of phase separation are the correlation length of the concentration fluctuation in the early stage and the rate of separation throughout. They are basically determined by thermodynamic stability and mobility.

When the casting solution is leached in water at the early stage of phase separation, the structure of the demixed solution just before leaching, which should be minute, is broken by water leaching and turns out to be the fingerlike structure since water is a strong leaching solvent, giving a rapid and severe change to the solution. As a result, water leaching at the early stage gives a fingerlike membrane having the relatively large pore dimensions of the fingerlike PVC membrane shown in Figure 7.[17] This is also the case in methanol leaching before phase separation because phase separation and leaching occur almost simulta-

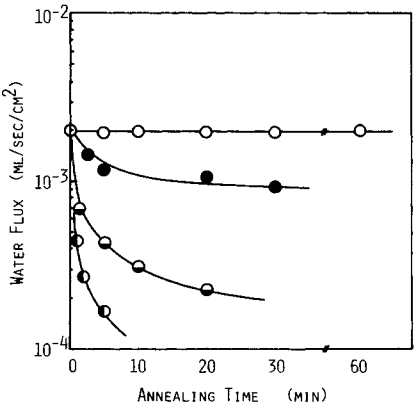
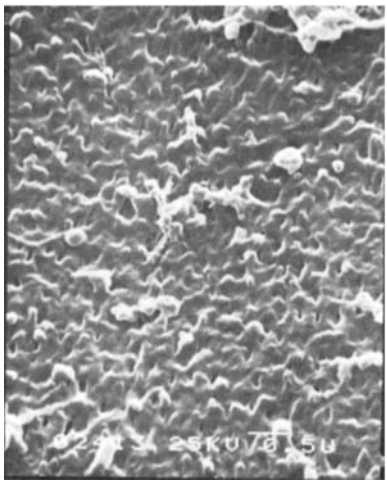
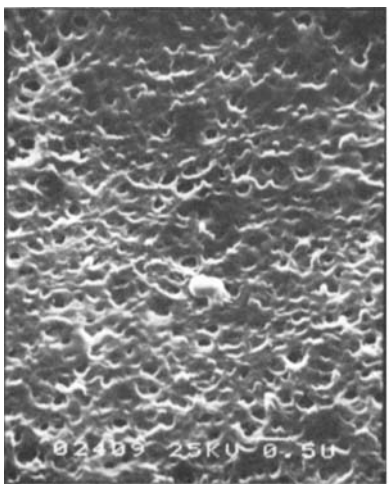


Fig. 5. Effect of annealing time on water flux: (○) 70°C; (●) 80°C; (◒) 85°C; (◐) 90°C.



(a)



(b)

Fig. 6. SEM photographs of the surface of the membrane (PVC 8 wt %) before (a) and after (b) annealing at 80°C for 30 min.

neously. But if the porous matrix were fixed in the fashion used in the slow phase separation process, in other words, at the early stage, without severe change, the smaller pore dimensions of the porous membrane could be manipulated by controlling the nature of phase separation. It can be considered that the solvent systems such as alcohols and glycol ethers in these experiments fit the above rules. Therefore, the pore dimensions of the wet PVC membrane are relatively small compared with the pore dimensions obtained in Figure 7.

The pore dimensions are estimated on the hypothesis that water penetrates

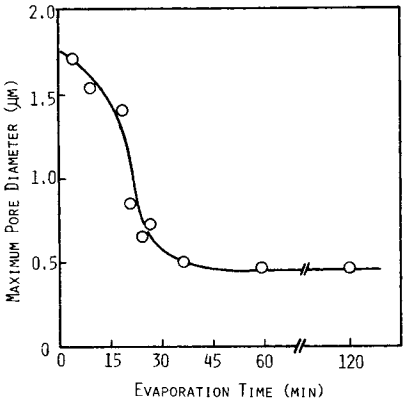


Fig. 7. Effect of evaporation time on maximum pore diameter (PVC concn. 8 wt %).

TABLE IV
Apparent Pore Dimensions of Wet PVC Membranes

PVC concn.[a]	6 wt %	8 wt %	10 wt %
F, cm^3/sec/cm^2	8.33×10^{-3}	2.00×10^{-3}	3.50×10^{-4}
ϕ	0.85	0.82	0.77
r,[b] cm	0.51×10^{-5}	0.25×10^{-2}	0.11×10^{-5}
n,[b] cm^{-2}	1.1×10^{10}	4.1×10^{10}	20.6×10^{10}

[a] PVC concentration in the casting solution.

[b] r and n were calculated from hydrodynamic permeability, using the following values: $\eta = 0.00895$ poise, $L = 0.018$ cm, $\Delta P = 4.9 \times 10^5$ dyn/cm^2

only through straight capillaries in wet membranes according to Hagen–Poiseuille's law,[18] although the real membrane structure shown in Figure 6 is quite different from that in the above capillary model. According to this model, the radius of capillary, r (cm), and the capillary number density per unit area, n (cm^{-2}), are expressed as follows:

$$r = \left(\frac{8\eta L}{\Delta P} \cdot \frac{F}{\phi}\right)^{0.5}$$

$$n = \frac{\phi}{\pi r^2}$$

where η, L, ΔP, F, and ϕ express the viscosity of water (poise), the membrane thickness (cm), the pressure difference (dyn/cm^2), the water flux (cm^3/sec/cm^2), and volumetric water content, respectively.

The apparent pore dimensions of wet PVC membranes are summarized in Table IV. The pore dimensions calculated also agree very well with those observed from SEM photographs. Not only in the membrane formation process leaching in water or methanol at the late stage but also in leaching in methanol at the early stage, the pore dimensions are determined by mobility such as the PVC concentration in the casting solution.

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References

1. S. Sourirajan, *Reverse Osmosis and Synthetic Membranes,* National Research Council of Canada, Ottawa, 1977, chap. 7.

2. C. E. Rogers and S. Sternberg, in *Permselective Membranes,* C. E. Rogers, Ed., Marcel Dekker, New York, 1971, pp. 189–205.

3. R. E. Kesting, in *Biomedical Polymers,* A. Rembaum and M. Shen, Ed., Marcel Dekker, New York, 1971, pp. 161–170.

4. S. Hirose, A. Shimizu, and T. Nose, *J. Appl. Polym. Sci.,* **23,** 3193 (1979).

5. S. Hirose, M. Hayashi, N. Tamura, S. Suzuki, and I. Karube, *J. Mol. Catal.,* **6,** 251 (1979).

6. S. Hirose, M. Hayashi, N. Tamura, S. Suzuki and I. Karube, *J. Mol. Catal.,* **9,** 115 (1980).

7. S. Hirose, E. Yasukawa, M. Hayashi, N. Tamura, A. Kanai, S. Suzuki, and I. Karube, *J. Appl. Biochem.,* **2,** 45 (1980).

8. W. R. Vieth and K. Venkatasubramanian, *Chemtech,* 677 (Nov. 1973).

9. T. Tosa, T. Sato, T. Mori, Y. Matsuo, and I. Chibata, *Biotechnol. Bioeng.,* **15,** 69 (1973).

10. S. J. Updike and G. P. Hicks, *Nature,* **214,** 986 (1967).

11. H. Maeda, H. Suzuki, and A. Yamauchi, *Biotechnol. Bioeng.,* **15,** 607 (1973).

12. S. Suzuki, I. Karube, and I. Satoh, in *Biomedical Applications of Immobilized Enzymes and Proteins,* T. M. S. Chang, Ed., Plenum, New York, 1977, pp. 177–189.

13. O. H. Lowry, N. J. Rosebrough, A. L. Farr, and R. J. Randall, *J. Biol. Chem.,* **193,** 265 (1951).

14. S. Loeb and S. Sourirajan, *Adv. Chem. Ser.,* **38,** 117 (1962).

15. S. Manjikian, *Ind. Eng. Chem., Prod. Res. Dev.,* **6,** 23 (1967).

16. I. Cabasso and C. N. Tran, *J. Appl. Polym. Sci.,* **23,** 2967 (1979).

17. S. Hirose and A. Shimizu, *Kobunshi Ronbunshu,* **35,** 435 (1978).

18. Y. Mizutani and M. Nishimura, *J. Appl. Polym. Sci.,* **14,** 1847 (1970).

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