

Permeation Characteristics of Poly(vinyl Alcohol)-Poly(vinyl Acetate) Composite Porous Membranes

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Synopsis

Poly(vinyl alcohol)(PVA)-poly(vinyl acetate)(PVAc) composite porous membrane has been prepared from PVAc latex film by extraction with acetone. The PVAc latex was prepared by emulsion polymerization of vinyl acetate in the presence of PVA, employing the hydrogen peroxide-tartaric acid system as an initiator. The extraction degree of PVAc could be controlled in a wide range by changing the addition method of the initiator, and, accordingly, PVA-PVAc composite porous membranes which had various void volumes were obtained. The maximum void volume attained was ca. 90%. Permeation characteristics of organic solvents were investigated on the membranes whose extraction degrees were 95.6% and 80.7%. The feeds were benzene, *n*-hexane, cyclohexane, and their mixtures. Neither swelling nor shrinkage in the appearance size of the membrane was observed in the feeds. *n*-Hexane and cyclohexane permeated very fast at 0.5 kg/cm², while benzene hardly permeated even at 20 kg/cm². The grafted PVAc in the membrane was removed or converted into grafted PVA by treatment with sodium methylate, and then the depression of benzene permeation was lost. The grafted PVAc was suggested to be localized on the cell wall, and was found to function as a valve which closes with benzene or a good solvent for PVAc and opens with *n*-hexane or a poor solvent for PVAc.

INTRODUCTION

Poly(vinyl alcohol) (PVA) has good film-forming, highly hydrophilic properties and, as such, has been studied as a membrane in various ways. As a reverse osmosis membrane, untreated PVA membrane¹ and radiation-crosslinked PVA membranes² showed low salt rejection, while the formalization endowed the PVA membrane with reasonably high water permeability, high salt rejection, and stability in the presence of acids and alkalis.³ Asymmetric PVA membranes were crosslinked with polyvalent metal ions, were exceptionally resistant to solvents, acids, and alkalis in the region between pH 0 to pH 14, and were found to have a selectivity for phenol.⁴ The permeation characteristics of alcohol/water systems and alcohol/benzene systems were investigated on the PVA membrane, which was bridged with monovalent alkali metal compounds, and the permeability of the permeating species and the permselectivities were discussed from the standpoint of the physicochemical natures of the permeating species and the polymer membranes.⁵ PVA membranes grafted with various vinyl monomers were investigated on the permeation of poly(ethylene glycol) solution and were found to have low rejection.⁶ Pervaporation was carried out on PVA membrane and grafted PVA membrane, and high permselectivity to water was observed in water-alcohol mixtures.^{7,8} PVA-acrylonitrile graft copolymer membranes⁹⁻¹² and vinyl alcohol-ethylene copolymer membranes¹³ were investigated in detail from the standpoint of hemodialysis and showed excellent

performances. These membranes are usually dense membranes or porous membranes of low void volumes.

The authors developed a novel method of preparing a PVA porous membrane of very high porosity (ca. 90%) by extracting poly(vinyl acetate) (PVAc) from a PVAc latex film which was obtained by casting PVAc emulsion latex polymerized under the presence of PVA.¹⁴ This porous membrane contains some amounts of PVAc grafted onto PVA.¹⁵ In this sense, this membrane can be called PVA-PVAc composite porous membrane. In this paper, some interesting permeation characteristics of the PVA-PVAc composite porous membranes will be shown to have resulted from the valvelike function of the grafted PVAc, which localizes on the inner surfaces of the pores.

EXPERIMENTAL

Emulsion Polymerization. Vinyl acetate (VAc) of commercial grade was distilled before use. PVA (Kuraray PVA-110), whose average degree of polymerization and degree of saponification were ca. 1000% and 99%, respectively, was obtained from Kuraray Co., Ltd., and used without further purification. Hydrogen peroxide (HPO) and tartaric acid (TA) were extra-pure grade chemicals from Wako Pure Chemical Industries, Ltd., and were used without purification. Polymerizations were carried out in a 1-L five-necked separable flask equipped with a thermometer, a reflux cooler, a VAc dropping funnel, and a stirrer. Total weight of the ingredients in the polymerization flask was adjusted to 500 g. In practice, the temperature of 250 g of 10% PVA aqueous solution was raised to 70°C, and then 0.5 g of TA was charged as an aqueous solution, being followed by intermittent addition of HPO and by dropwise addition of 200 g of VAc. The VAc was added dropwise in 3 h. The total amount of HPO was 2 mL in 30% aqueous solution. A certain amount of HPO was charged right after the starting of VAc addition, and then one sixth of the rest amount of HPO was added every 30 min. The polymerization was completed in 3.5 h, and the conversion determined gravimetrically was ca. 99% in all cases. Polymerization was performed in the other way, too. In this case, PVA aqueous solution and VAc were all charged at one time, and the temperature of the mixture was raised to 70°C; then the whole amount of HPO-TA was charged. The polymerization was completed within 1 h, and the conversion easily reached over 99%.

Preparation of Composite Porous Membranes. PVAc latex obtained was casted on a polyethylene film fixed on a thermostated glass plate, and was dried at 30°C. A latex film thus obtained was extracted with acetone in a Soxhlet extractor for 20 h. After the extraction of PVAc, the film changed from a semitransparent film into a paperlike white porous membrane. The membrane was immersed in *n*-hexane for solvent exchange right after the extraction, being followed by dry air flushing, and was kept in a desiccator.

Alkaline Methanolysis. A sheet of membrane was immersed in a methanol solution of sodium methylate purchased from Wako Pure Chemical Industries, Ltd., and kept at 50°C for 1 h. After methanolysis, the membrane was thoroughly rinsed in methanol, being followed by the foregoing solvent exchange and drying process. The membrane thus prepared was served for measurements.

Measurements. Void volume and swelling degree of the membrane were determined by pycnometry.¹⁶ Viscosity measurements of the feed solutions were

TABLE I
Characterization of Poly(vinyl Alcohol)-Poly(vinyl Acetate) Composite Porous Membranes

Initial amount of initiator ^a	Extraction degree(%)	Void volume (%)		Swelling degree in length	Flux of <i>n</i> -hexane (mL/cm ² -s) at 0.5 kg/cm ²
		<i>n</i> -Hexane	Benzene		
1 (all charged)	95.6	87.0	87.6	0.98	5.58 × 10 ⁻² 2.20 × 10 ⁻² ^b 4.89 × 10 ⁻⁵ ^c 1.03 × 10 ⁻³ ^d
1/2	80.7	78.5	76.9	0.95	1.69 × 10 ⁻²
1/4	35.9	12.6	77.4	1.42	0
0	16.3	4.90	69.7	1.44	0

^a Shown as the fraction of the total amount of initiator.

^b Flux of cyclohexane measured at 0.5 kg/cm².

^c Flux of benzene measured at 0.5 kg/cm².

^d Flux of benzene measured at 20 kg/cm².

carried out with Ubbelohde viscometer at 30°C. Density of a solution which was necessary to estimate the absolute viscosity was measured at 30°C by employing a Lipkin type pycnometer. Permeation was measured by using RO-3 type reverse osmosis filter (Bioengineering Co., Ltd.) at ambient temperature. Benzene (Bz), *n*-hexane (*n*-H), cyclohexane (*c*-H), and their mixtures were employed as the feed solutions.

RESULTS AND DISCUSSION

Some membranes prepared were characterized and tabulated in Table I. The extraction degree considerably depended on the initial amount of initiator in the emulsion polymerization. The smaller the initial amount of initiator, the lower the extraction degree, void volume, and the flux of *n*-H, and the higher the swelling degree in Bz. The highest extraction degree, 95%, was attained for the membrane prepared by the all charged method. The membrane whose extraction degree is *x*% will be denoted *x*% membrane in this paper. Although there is some controversy on the graft efficiency conventionally defined as (100-*x*)%, it can be taken as a qualitative measure.^{15,17-22} Therefore, unextracted or residual PVAc may be considered grafted onto PVA for convenience. The void volumes shown in Table I were measured in *n*-H and Bz. As *n*-H is a poor solvent and did not cause any swelling for both PVA and PVAc, the void volumes measured in *n*-H are reasonable values while those in Bz must be seriously affected by the swelling of the grafted PVAc in the membranes. On membranes containing abundant grafted PVAc, for instance, 35.9% and 16.3% membranes, the effect of the PVAc swelling could not be negligible and the enlargements of the membranes were observed in Bz. However, 95.6% and 80.7% membranes did not show any enlargements in Bz, but rather little shrinkages, which might result from the nature of PVA,²³ were observed. The fluxes of *n*-H at 0.5 kg/cm² were measurable in 95.6% and 80.7% membranes, but no permeation was detected in 35.9% and 16.3% membranes, suggesting that pores did not pass through the membranes in the latter two cases, in which the fluxes were not detected even at 20 kg/cm². On the 95.6% membrane, the fluxes of Bz were much smaller even

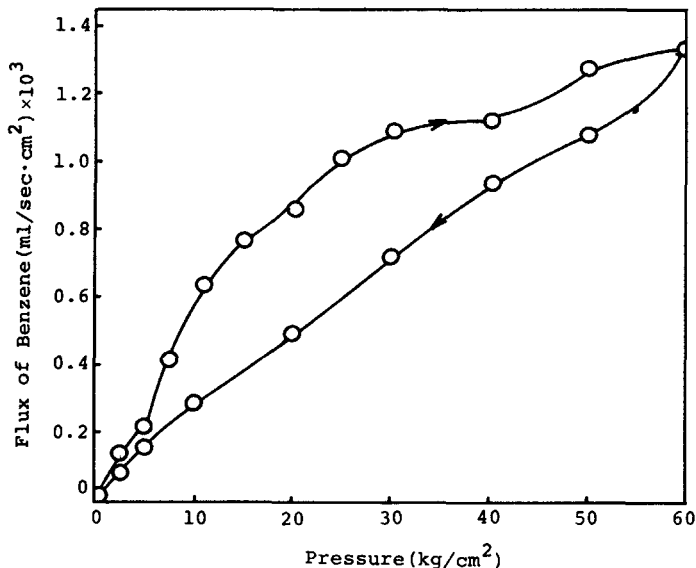


Fig. 1. Pressure hysteresis of 95.6% membrane.

at 20 kg/cm² than those of *n*-H and *c*-H, as shown in Table I. Further investigation was carried out on 95.6% and 80.7% membranes. The pressure hysteresis of the 95.6% membrane is shown in Figure 1. The compaction proceeded irreversibly, and the thickness of the membrane changed from 1.054 mm to 0.946 mm. The compacted membrane indicated the flux with the good reproducibility at the pressures lower than 2 kg/cm² in the successive operations. The membranes which were not exposed under higher pressures than 2 kg/cm² also showed excellent reproducibility, suggesting no compaction proceeds under the conditions. In Figure 2, pressure dependences of the fluxes for various feeds were shown on the 80.7% membrane. The fluxes changed proportionally with the pressure irrespective to the feed composition when the pressure is less than 2 kg/cm². This was so in the case of the 95.6% membrane, too. The proportionality suggests that the pore sizes and their distributions, which were determinant factors of the flux of the membrane, do not change under the experimental conditions, and hence the Hagen-Poiseuille law can be assumed to be valid on these permeations. Then the effect of the viscosity of the feed on the flux can be excluded by multiplication of the flux by the viscosity according to the following equation²⁴:

$$\eta \cdot J = \frac{r^2 \cdot V \cdot \Delta P}{8 \cdot d}$$

where η , J , r , V , ΔP , and d are the viscosity of the feed, the flux, the radius of the pore, the void volume, the charged pressure, and the thickness of the membrane, respectively. The relative flux corrected on the viscosity can be defined as

$$\text{relative flux} = \frac{(J \text{ for the feed}) \cdot (\eta \text{ of the feed})}{(J \text{ of } n\text{-H or } c\text{-H}) \cdot (\eta \text{ of } n\text{-H or } c\text{-H})}$$

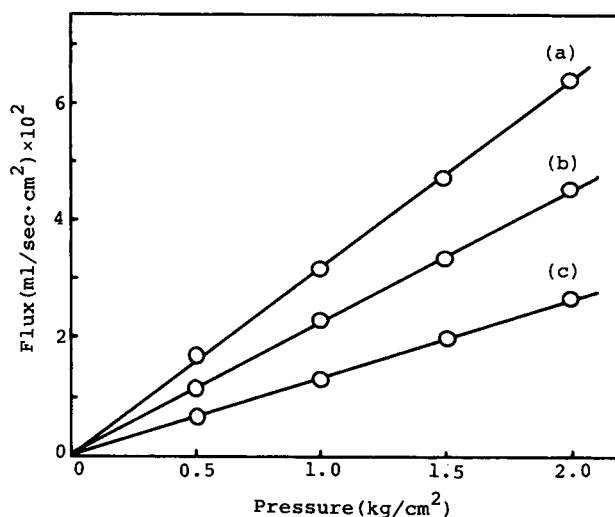


Fig. 2. Dependence of flux on pressure: 80.7% membrane; feed composition (*n*-hexane/benzene by volume) = (a) 10/0; (b) 6/4; (c) 4/6.

The dependence of the relative flux on the feed composition is depicted in Figure 3. The relative flux decreased with the increase of Bz content of the feed slowly up to 60% and drastically above 60%, and this feature is common to the three cases. There can be found little difference between the (*n*-H)-Bz system and the (*c*-H)-Bz system, suggesting the changes in the relative fluxes did not result

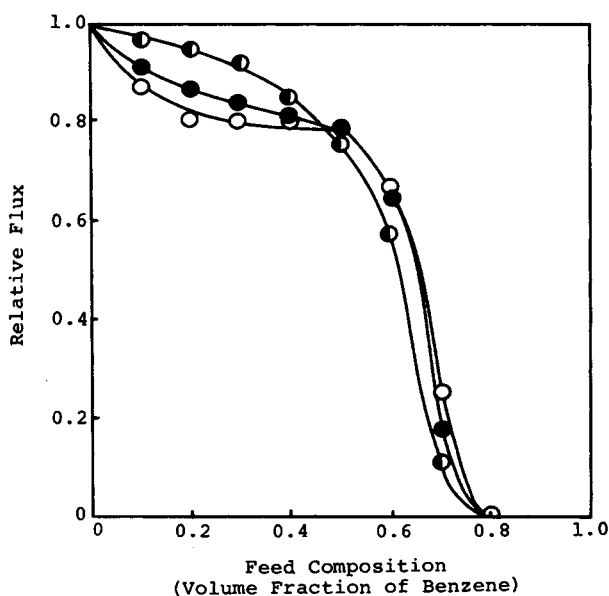


Fig. 3. Dependence of relative flux on feed composition: (O) 95.6% membrane, *n*-hexane/benzene system; (●) 95.6% membrane, cyclohexane/benzene system; (●) 80.7% membrane, *n*-hexane/benzene system.

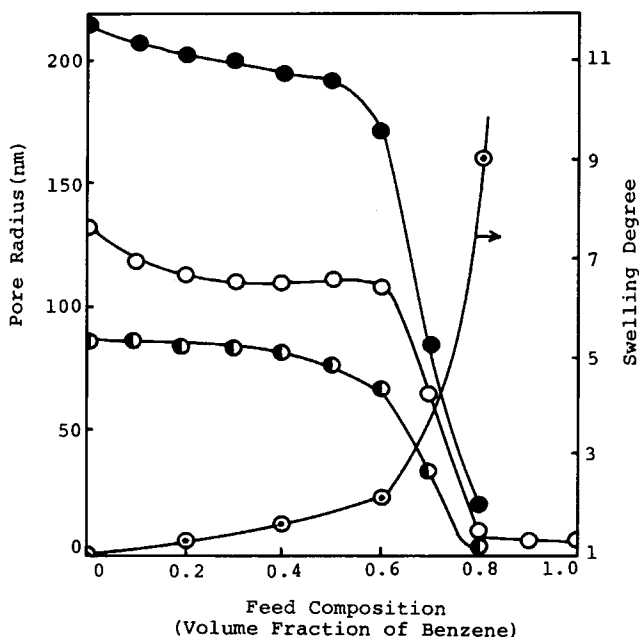


Fig. 4. Dependence of pore radius and swelling degree of PVAc on feed composition: (●) pore radius of 95.6% membrane which was not exposed under higher pressure than 2 kg/cm²; (○) pore radius of 95.6% membrane which suffered compaction; (◐) pore radius of 80.7% membrane which was not exposed under higher pressure than 2 kg/cm²; (⊙) swelling degree of PVAc.

from the feed and its viscosity. Differences in the extraction degree did not affect the relative flux so much, either, as shown in Figure 3, although the flux of the 80.7% membrane was less than one-third that of the 95.6% membrane, as shown in Table I.

According to the Hagen-Poiseuille law, the pore radii can be estimated, and the results are shown in Figure 4. Dependence of the swelling degree of a PVAc film on the Bz content is also shown in Figure 4. Low extraction degree and compaction caused the decrease of the pore radius. The estimated pore radius decreased slowly with the increase of Bz content below 60% and drastically above 60%. Over 80% of Bz content the pore radius did not change so much. The swelling degree of PVAc, on the other hand, increased slowly with Bz content up to 60% and then quickly above 60%. The swelling behavior of PVAc corresponded very well to the decrease of the pore radius. In Figure 5, the effect of the alkaline methanolysis on the permeation was shown on the 95.6% membrane. The weight of the membrane decreased somewhat by this treatment. The magnitude of the weight loss was over 80% of the grafted PVAc by weight. The appearance size of the membrane was not affected by the treatment. Before methanolysis, the permeation of Bz was undetectable under the experimental condition, but it increased remarkably after the treatment, indicating nearly the same flux as that observed for *n*-H when the difference in the viscosity of the feed was taken into account. The results in Figure 4 together with those in Figure 5 show the origin of the permeation characteristics of the membranes. The grafted PVAc in the membrane swells with Bz-rich feed to depress the permeation by narrowing or closing the pathways. Actually, the amounts of the grafted

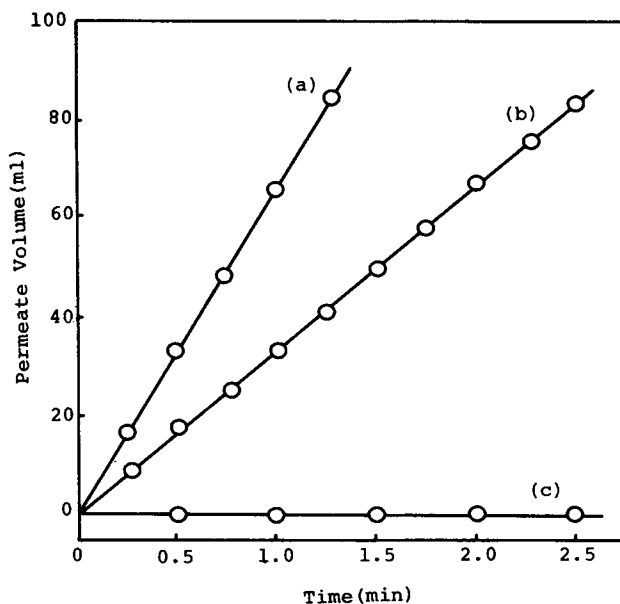


Fig. 5. Effect of alcoholysis on permeation: (a) *n*-hexane, after alcoholysis; (b) benzene, after alcoholysis; (c) benzene, before alcoholysis; 95.6% membrane.

PVAc in the membranes are 60.7% and 26.0% by weight for 80.7% and 95.6% membranes, respectively, and can be considered enough to indicate the foregoing behavior. The swelling of the grafted PVAc, however, did not cause the changes in the appearance sizes of the membranes for 80.7% and 95.6% membranes (Table I). It means the volume increase induced by the swelling of the grafted PVAc is absorbed by the inner rooms of pores, and this is possible as it was suggested from the results in Figure 5 that the grafted PVAc localized on the inner surfaces of the pores. Thus, it is concluded that the grafted PVAc localized on the surface of the pore of the membrane plays a critical role and behaves like a valve which closes with Bz or a good solvent for PVAc and opens with *n*-H or a poor solvent for PVAc.

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Received February 25, 1983

Accepted April 18, 1983