Formalized Poly(vinyl Alcohol) Membranes
for Reverse Osmosis

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Synopsis

The permeation properties of formalized poly(vinyl alcohol) membranes are described. The interest of this work is centered on the properties relevant to desalination by reverse osmosis. These membranes, when properly prepared, showed reasonably high water permeability, high salt rejection, and stability in the presence of acids and alkalies.

INTRODUCTION

Considerable work has been carried out in the area of reverse osmosis since the discovery of cellulose acetate as a desalination membrane by Reid and Breton[1] and the subsequent improvement achieved by Loeb and Sourirajan.[2] When reverse osmosis membranes are used for desalination, sodium chloride can be rejected from aqueous solution to the extent of more than 99%, simply by forcing the saline water through a membrane under pressure.[3] The best reverse osmosis membranes so far prepared are from cellulose acetate. However, they have a number of disadvantages such as deterioration of the membrane performance at a pH which deviates appreciably from 5, decline of water flux under pressure, poor resistance to microbial actions, etc. The search for new and improved polymers has been continued with only moderate success.

In the present work, the permeabilities of water and salt through the membranes of formalized poly(vinyl alcohol) have been studied. These membranes, when properly prepared, showed high water permeability, high salt rejection, good chemical resistance, and good mechanical strength.

Few reported works have thus far been carried out on permeabilities of poly(vinyl alcohol) membranes. Since poly(vinyl alcohol) is highly hydrophilic, the unmodified membranes are highly permeable to both water and salt. The water flux is said to be directly proportional to the pressure, while the salt rejection decreases with the pressure.[4] The membranes of styrene-grafted syndiotactic poly(vinyl alcohol) are reported as water permeable as cellulose acetate, although much less selective.[5] With hollow fibers of poly(vinyl alcohol), Orofino[6] found that heat treatment and for-

malization improved both salt rejection and mechanical strength but drastically reduced water flux. The conditions of heat treatment appeared relatively severe, e.g., 80 hr at 90°C, 2-4 hr at 150°C, or 15 min at 225°C.

As has been demonstrated in this work, the membranes can be prepared with mild heat treatment or even without heat treatment, which exhibit relatively high water permeabilities without much sacrifice of salt rejection.

EXPERIMENTAL

Materials

Elvanol 71-30, a product of E. 1. du Pont de Nemours and Co., was used in this work. This is a 99.0-99.8% hydrolyzed poly(vinyl alcohol) whose 4% solution in water has a viscosity of 28-32 cps at 20°C by the Hoeppler falling-ball method. All chemicals were of commercial origin and were used without further purification. Formalin was used as a source of formaldehyde without removal of the additives.

Preparation of Membranes

Casting. 6-8% Solutions of poly(vinyl alcohol) in water were prepared by slurrying the polymer in cold water, heating to 90°C under agitation, and filtering through a glass filter. The solutions were spread on Plexiglas plates to a uniform thickness and dried in dust-free air at temperatures between 23° and 33°C for 5-10 days.

Heat Treatment. The dried membranes on the Plexiglas plates were placed in an oven set at the desired temperature for a given period of time.

Formalization. The formalization bath consisted of 20% H_2SO_4, 20% Na_2SO_4, and 5-7% HCHO. Although we do not claim that the membranes prepared in this study were chemically homogeneous, an attempt was made to attain membranes as close to homogeneous as possible. The membranes were immersed in the formalization bath at room temperature for at least 20 hr before raising the temperature to the desired level. This was to allow sufficient time for the reagents to penetrate the membrane and enable the reaction to take place throughout the membrane as uniformly as possible. The membranes thus prepared had a thickness generally between 15 and 25 μ.

Direct Osmosis Tests

A piece of the membrane was supported between two perforated, stainless steel plates which, in turn, were fastened between two cylindrical Plexiglas chambers. A 1-molar solution of NaCl was placed in one chamber and distilled water in the other. Both sides were stirred during the experiment. The entire apparatus was placed in a constant-temperature water bath kept at 25°C. Water permeability P_w was obtained by measuring the rate of increase in solution volume on the brine side; a calibrated capillary tube was used. Salt permeability P_s was determined by monitoring the

electrical conductance of the water side. The following equations were used for the calculation of P_w and P_s:

$$P_w = \frac{J_w RTd}{v_w \Delta \pi}$$

$$P_s = \frac{J_s d}{\Delta C}$$

where J_w and J_s are the flux of water and salt, respectively; $\Delta \pi$ is the osmotic pressure difference; ΔC is the salt concentration difference, d is the thickness of the membrane; v_w is the molar volume of water; T is the absolute temperature; and R is the gas constant.

Filtration Tests

Filtration tests were carried out using a stainless steel filter unit made by Gelman Instrument Co., Ann Arbor, Michigan. A membrane was supported by a sintered porous stainless steel disc and clamped between two halves of the filter unit. The area of filtration was 13.4 cm². The inlet was connected to a water reservoir which, in turn, was pressurized by nitrogen gas. The rate of filtration was measured by following the rise in liquid level in a calibrated vertical tube attached to the outlet of the filter unit.

Reverse Osmosis Tests

The Abcor Reverse Osmosis Test Cell, a product of Abcor, Inc., Cambridge, Massachusetts, was used. The membrane was supported by a sintered porous stainless steel disc covered with filter paper. Continuous agitation just above the membrane surface was provided by a magnetic stirrer suspended from a Teflon bearing. The tests were run batchwise under 600 psi of nitrogen pressure, employing a 0.1-molar NaCl solution. For the calculation of P_w, the same equation as was used in the direct osmosis test was employed, except that $\Delta \pi$ was replaced by $\Delta P - \Delta \pi$, where ΔP is the hydrostatic pressure difference.

RESULTS AND DISCUSSION

Degree of Formalization as a Function of Reaction Time

As stated in the experimental section, the formalization was carried out with preformed membranes. Conceivably the maximum degree of formalization attainable by this type of heterogeneous reaction should be greatly dependent on the morphological structure of the membrane. Poly(vinyl alcohol) easily forms crystallites which are less susceptible to reaction such as formalization. All membranes prepared in this study had a degree of formalization lower than 50%. This was true even with the membranes which were made without heat treatment.
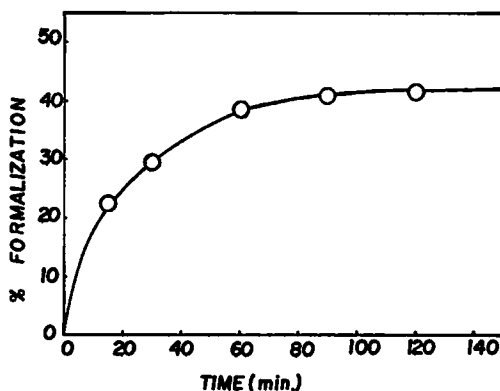
Fig. 1. Degree of formalization vs. reaction time in the formalization of the nonheat-treated poly(vinyl alcohol) membranes at 60°C.

For the measurement of the degree of formalization, 1.5–2.0 g of the membranes were hydrolyzed under reflux with 100 ml of $0.5N$ H_2SO_4 for 2 hr, followed by steam distillation. The distillate was collected in a flask which contained 50 ml of $1N$ Na_2SO_3 solution that had been neutralized in advance with $0.1N$ HCl using thymol phthalein as the indicator. The distillate which was collected in the Na_2SO_3 solution was titrated with $0.5N$ HCl. To calculate the degree of formalization, it was assumed that every mole of HCHO liberated by hydrolysis corresponded to two formalized hydroxy groups of the polymer.

Figure 1 illustrates the degree of formalization versus the time of reaction, for the nonheat-treated membranes of poly(vinyl alcohol) formalized at 60°C. The formalized membranes were 15–20 μ thick.

The degree of formalization almost reached a maximum of 42% after 2 hr of reaction. In another experiment, 8 hr of reaction gave 45.2% for the degree of formalization. The unexpectedly low degree of formalization suggests that considerable amounts of crystallites were formed during the course of drying which were less susceptible to formalization than the amorphous regions.

Effect of Heat Treatment on Permeabilities

The dried poly(vinyl alcohol) membranes were heat treated in an oven at a given temperature for 10 min and then formalized at 80°C for 10 min. The membranes swollen in water were 20–25 μ thick. Table I gives water absorption, permeabilities P_w and P_s, both obtained by direct osmosis, and the ratio P_w/P_s, which is an indicator of salt rejection. As anticipated, with increased temperature of heat treatment, both P_w and P_s decreased, accompanied with an increase in P_w/P_s. It should be noted that the non-heat-treated membrane also gave a relatively high salt rejection. Since heat treatment drastically reduces water permeation, it would be desirable to prepare a membrane with reasonably high salt rejection with only mild

TABLE I
Influence of Temperature of Heat Treatment on Permeabilities

Temperature of heat treatment, °C	Water absorption, %	P_w, cm²/sec	P_s, cm²/sec	P_w/P_s
120	16.8	7.0×10^{-8}	3.1×10^{-11}	2260
140	16.5	5.4×10^{-8}	2.5×10^{-11}	2160
160	16.0	4.6×10^{-8}	1.2×10^{-11}	3830
180	14.5	2.6×10^{-8}	1.0×10^{-11}	2600
200	12.3	3.0×10^{-8}	1.0×10^{-11}	3000
—	22.4	1.8×10^{-7}	3.8×10^{-10}	470

heat treatment or even no heat treatment at all. The above experiment appears to indicate such possibilities.

Effect of Formalization on Permeation

The dried poly(vinyl alcohol) membranes were heat treated at 110°C for 10 min, followed by formalization under the conditions given in Table II. The membranes had thicknesses between 20 and 25 μ. Table II gives the results of direct osmosis tests together with water absorption. The prolonged formalization resulted in decreased P_w and P_s and increased salt rejection. For the practical application to reverse osmosis, formalization at 50°C for 2 hr or at 60°C for 1–2 hr seemed appropriate.

In the light of the very low P_w/P_s ratio of the nonformalized membrane, the formalization had an essential influence on permselectivity. This was in striking contrast with the influence of heat treatment.

Effect of pH on Permeabilities

The permeselectivity of cellulose acetate membranes is known to deteriorate in the presence of base or even acid and constitutes one of the main

TABLE II
Effect of Formalization on Permeabilities

Formalization Temp., °C	Time, hr	Water absorption, %	P_w, cm²/sec	P_s, cm²/sec	P_w/P_s
50	1	22.8	1.55×10^{-7}	2.18×10^{-10}	7110
50	2	19.5	8.26×10^{-8}	5.12×10^{-11}	1610
50	3	18.6	5.36×10^{-8}	1.64×10^{-11}	3270
50	4	18.4	4.79×10^{-8}	7.22×10^{-12}	6630
60	1	17.7	8.27×10^{-8}	5.90×10^{-11}	1400
60	2	16.6	5.15×10^{-8}	2.31×10^{-11}	2230
60	3	16.3	5.22×10^{-8}	1.76×10^{-11}	2960
60	4	15.4	4.12×10^{-8}	6.58×10^{-12}	6260
—	—	—	5.40×10^{-7}	2.60×10^{-8}	21

drawbacks which must be overcome for practical application.[7,8] Formalized poly(vinyl alcohol) is quite stable against base, but may undergo hydrolysis in the presence of a small amount of acid.

The membranes were heat treated at 105–110°C for 10 min and formalized at 60°C for 3 hr. They were then rinsed in running distilled water for 24 hr and stored in distilled water for five months before the tests. The membranes were immersed in Beckman standard buffer solutions of various pH values; for pH 2, a mixture of 0.2N KCl and 0.2N HCl was used. After a certain number of days of immersion, the membranes were rinsed thoroughly in distilled water and then subjected to the direct osmosis tests. The thicknesses of the swollen membranes were between 15 and 20 μ.

As Table III indicates, within the range of pH and the duration of the immersion in this test, no distinctive decline in membrane performance was observed.

TABLE III
Influence of pH on Permeabilities

pH	Immersion time, days	P_w, cm²/sec	P_s, cm²/sec	P_w/P_s
2.00	14	4.22×10^{-8}	$<6 \times 10^{-12}$	>7000
4.01	12	3.94×10^{-8}	9.07×10^{-12}	4340
7.00	6	3.44×10^{-8}	5.36×10^{-12}	6420
10.00	13	3.81×10^{-8}	9.15×10^{-12}	4150
12.45	10	4.55×10^{-8}	8.40×10^{-12}	5420

Filtration Tests

The membranes were prepared by formalizing the dried poly(vinyl alcohol) membranes at 50°C for 2 hr. No heat treatment had been carried out before the formalization. The membranes were stored in distilled water for one month before the test. The thickness of the swollen membranes was 23 μ. The test was run at 600 psi. Figure 2 illustrates the water flux in gfd as a function of time. The water flux decreased to 90% in 24 hr. The water permeability, calculated on the basis of the flux after 24 hr and the initial thickness of the swollen membrane, was 7.95×10^{-8} cm²/sec, in comparison with 8.72×10^{-8} cm²/sec obtained by the direct osmosis test.

Reverse Osmosis Tests

The membranes prepared under the same conditions as those used for the filtration tests showed the reverse osmosis performance illustrated in Figure 3. The thickness of the swollen membrane was 6 μ. This series of membranes gave $6.0–9.0 \times 10^{-8}$ cm²/sec for P_w and 93–97% salt rejec-
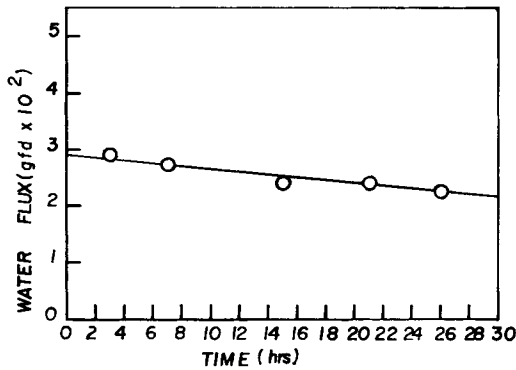
Fig. 2. Time dependence of water flux of a formalized poly(vinyl alcohol) membrane in the filtration test at 600 psi.

tion in reverse osmosis tests. The P_w was in good agreement with the value of 8.72×10^{-8} cm²/sec obtained by direct osmosis and 7.95×10^{-8} cm²/sec obtained by the filtration test.

CONCLUSIONS

It has been shown that membranes of formalized poly(vinyl alcohol) can be prepared which have the properties desired for reverse osmosis. The utilization of these membranes for the purpose of desalination will involve the preparation of high-flux membranes without sacrifice of permeselectivity and mechanical strength. This is a separate problem involving the manipulation of delicate morphologic structures. The important conclusion of this work, however, is that the formalized poly(vinyl alcohol) membranes, when properly prepared, showed sufficiently encouraging performance to warrant further investigation.
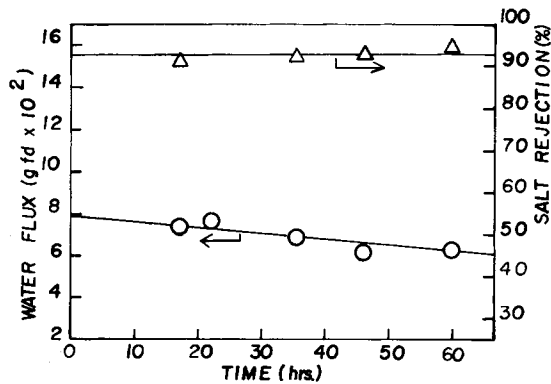

Fig. 3. Time dependence of water flux and salt rejection of a formalized poly(vinyl alcohol) membrane in the reverse osmosis test using $0.1N$ NaCl under 600 psi.

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