

Poly(vinyl alcohol) Gel Sublayers for Reverse Osmosis Membranes. I. Insolubilization by Acid-Catalyzed Dehydration

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SYNOPSIS

Both flat-sheet and tubular composite reverse osmosis (RO) membranes were prepared by depositing aqueous solutions of poly(vinyl alcohol) (PVA) and a dehydration catalyst on asymmetric poly(arylether sulfone) (PES) substrate membranes. The PVA coatings were insolubilized by heat treatment to create stable hydrophilic gel-layer membranes. The influence of variables such as PVA concentration, catalyst concentration, curing time, and curing temperature was investigated. It was shown that a simple manipulation of one or two variables could lead to membranes with widely differing salt retention and water permeability characteristics. The insolubilized PVA coatings were intended to serve as hydrophilic gel sublayers on which ultrathin salt-retention barriers could ultimately be formed by interfacial polycondensation. For this purpose, high-flux gel layers were required, whereas salt-retention capabilities were not regarded as important. However, the promising salt retentions obtained at 2 MPa (up to 85% NaCl retention and 92% MgSO₄ retention) showed that some of these PES-PVA composite membranes could function as medium-retention, medium-flux RO membranes, even in the absence of an interfacially formed salt-retention barrier. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Research Background

Several methods have been developed to make very thin synthetic membranes. Only two of these have become technologically important, namely, (i) the original approach of Loeb and Sourirajan¹ for the preparation of asymmetric membranes by the solvent-nonsolvent phase-inversion process, and (ii) the method of interfacial polymerization.² When carried out at one surface of a porous support material, this polymerization technique is widely used commercially as a means of producing thin-film composite reverse osmosis (RO) membranes.

During the last two decades, primary emphasis in nonpolysaccharide membrane research and de-

velopment has focused on aromatic polyamides and other related rigid nitrogen-containing hydrophilic heterochain polymers, e.g., aromatic polyhydrazides and polyureas.³ Although a wide variety of materials exist to choose from for RO applications, the various aromatic polyamides in integrally skinned (asymmetric) and interfacially formed composite membranes have, for many years, been the most attractive candidates on the basis of their performance and cost. These membranes exhibit water permeability and salt-rejection characteristics, as well as thermal, biological, and chemical resistance properties, superior to those of conventional asymmetric cellulose acetate membranes.

As a result of the inherent chain rigidity and a low extent of water-induced swelling, these aromatic backbone polymers exhibit low water permeabilities and, consequently, the membranes have to be operated at high transmembrane pressures (6–10 MPa) to obtain useful water fluxes. This makes them unsuitable for desalination of aqueous salt so-

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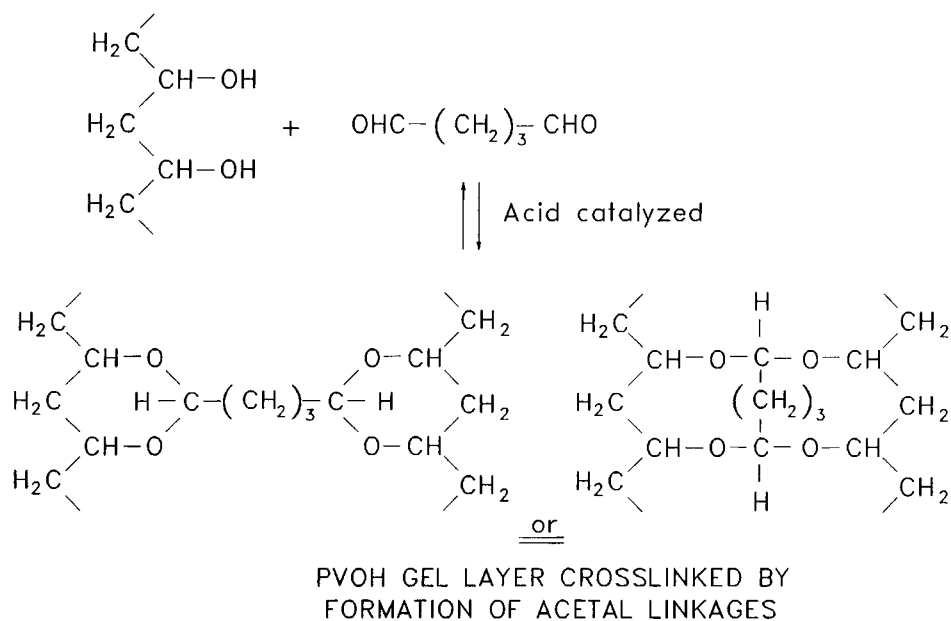
lutions with low osmotic pressures, such as brackish water and industrial wastewater, where permeate fluxes of at least 500 Lmd (liters per square meter per day) are required at low operating pressures of ≤ 2 MPa.

Another shortcoming that has limited the broader use of nitrogen-containing thin-film composite membranes in desalination applications is the lack of resistance to attack by chlorine and other oxidizing agents present in the feedwater. Over the years, several attempts have been made to develop chlorine-resistant membranes by using non-nitrogen-containing polymers as membrane materials. Properties such as chemical stability, film-forming ability, and high hydrophilicity make poly(vinyl alcohol) (PVA) an attractive material for production of RO membranes. However, the high hydrophilicity of PVA leads to permeation of both water and hydrated salts. To create stable membranes with good mechanical properties, and to improve the selective permeability to water and salts, the PVA must be insolubilized by cross-linking or other modification reactions.

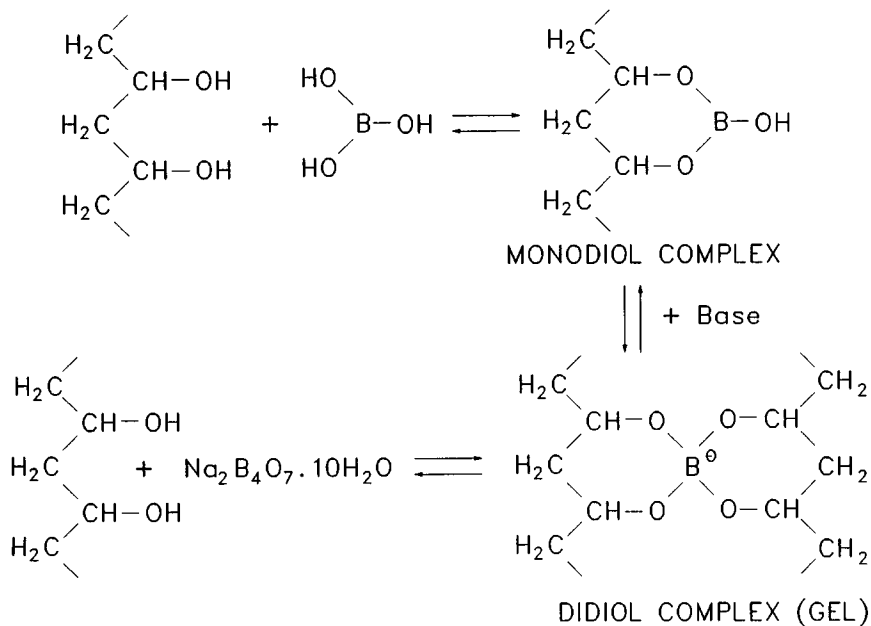
The insolubilization of PVA can be effected in a variety of ways. However, a survey of the available literature has shown that the reaction with dialdehydes and the formation of complexes with inorganic compounds and polyvalent metal ions have been studied in most detail. Insolubilization of PVA by cross-linking with dialdehydes, such as glyoxal, glutaraldehyde, and terephthalaldehyde, has been well

documented.⁴⁻¹² This type of reaction is also commonly used in the preparation of PVA-based alkaline battery separators.¹³⁻²⁰ Both inter- and intramolecular acetalization reactions are possible (Scheme 1). PVA forms many complexes, notably those with boric acid and sodium borate (borax), which result in the formation of monodiol and didiol complexes, respectively (Scheme 2). Gelation of PVA in the presence of boric acid and borax has been studied extensively.²¹⁻²⁷ Complex formation with metal ions, particularly with Cu^{2+} salts (Scheme 3), is commonly used to effect insolubilization of PVA.^{28,29} Unfortunately, all these complexes are sensitive to pH changes.

Earlier work on PVA membranes focused on the water and salt permeability of dense (homogeneous) films, e.g., those prepared by heat treatment³⁰ and formalization of preformed PVA membranes.³¹ In recent years, there has been a great deal of interest in both asymmetric and thin-film composite PVA-based RO membranes. The separation and flow capabilities of asymmetric PVA membranes have been studied extensively by Peter and Stefan.³²⁻³⁶ They prepared asymmetric membranes from PVA and some of its derivatives by the classical phase-inversion method, using various types of precipitation solutions. The water-soluble membranes were insolubilized by cross-linking with solutions of organic compounds containing aldehyde, ketone, or carboxylic acid groups or with polyvalent metal ions, such as Cr^{3+} . The cross-linked membranes exhibited good



Scheme 1

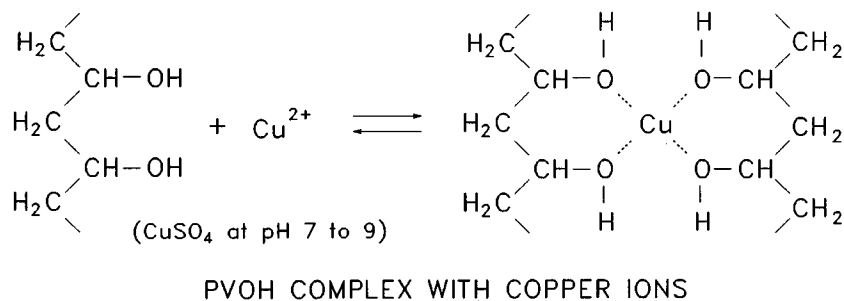


Scheme 2

chemical, mechanical, and thermal resistance and were designed for the removal of phenol and organic solvents from toxic industrial wastewater.

Katz and Wydeven³⁷⁻³⁹ studied the water and salt transport characteristics of asymmetric PVA membranes that were stabilized by ionizing radiation^{37,38} and heat treatment^{38,39} and proposed a method for preparing thin-skinned, high-flux PVA membranes. The characteristics of these asymmetric membranes were controlled by the casting conditions and by the posttreatment methods used. Chang⁴⁰ prepared asymmetric PVA membranes by the phase-inversion method, using various precipitation baths. The membranes were cross-linked with formaldehyde. The rejection of various mono- and divalent cations and anions by these membranes were investigated to determine which ions could be separated from wastewater.

Brannon and Peppas⁴¹ developed a new procedure for forming asymmetric PVA membranes by the phase-inversion method. Their membranes were formed by casting a PVA solution on a glass plate, drying the solution at 40°C, and pouring a precipitation solution, consisting of (NH₄)₂SO₄, ZnCl₂, Na₂SO₄·H₂O, and deionized water, over the PVA coating. The system was covered to prevent evaporation. The phase-inversion process was followed by cross-linking. For this purpose, the precipitation solution was poured off and replaced by a cross-linking solution consisting of H₂SO₄, glutaraldehyde, methanol, and acetic acid; the system was again covered and heated at 40°C for 4 h to facilitate cross-linking. The correlation between the structure of these asymmetric membranes and solute transport through them was studied using theophylline and vitamin B₁₂.



Scheme 3

Porous PVA-poly(vinyl acetate) (PVAc) composite membranes, although not with an asymmetric structure, were prepared by Hayashi et al.⁴² They extracted PVAc with organic solvents from PVAc latex films that were obtained by emulsion polymerization of VAc in the presence of PVA. Permselective asymmetric polymer blend membranes were prepared by Tsuchihara and co-workers,⁴³ using a mixture of aqueous PVA, PVAc emulsion, and LiCl. Tsuchihara et al.⁴⁴ also reported the use of blends of PVA and cyanoethylated PVA for membrane preparation.

Cadotte et al.⁴⁵ investigated the preparation of thin-film composite RO membranes by *in situ* cross-linking of PVA coatings on porous polysulfone supports. Aldehyde cross-linking agents, such as formaldehyde, glyoxal, acrolein, and terephthalaldehyde, as well as compounds such as hexamethoxymethyl melamine and 2-formyl-5-furansulfonic acid were used. The RO properties of these membranes were tested at very high operating pressures on 3.5% synthetic sea water. Koyama et al.⁴⁶⁻⁴⁸ prepared interpolymer anionic composite RO membranes by depositing a solution of PVA (as membrane matrix) and poly(styrene sulfonic acid) (as polyelectrolyte) on a microporous polypropylene support, evaporating the solvent and heat-curing the membrane at 120°C. Infrared spectra of the heat-cured membranes suggested that cross-linking occurred by formation of R—O—SO₂—R bonds between the two polymers, as well as by intermolecular dehydration of PVA during heat-curing in the presence of poly(styrene sulfonic acid). The rejections of NaCl,⁴⁶ polar organic solutes, e.g., alcohols, phenols, monocarboxylic acids, amines, and ketones,⁴⁷ and phenolic derivatives⁴⁸ by these thin-film composite membranes were studied.

Jian and Ming⁴⁹ reported the formation of thin-film composite RO membranes by coating a polysulfone support with aqueous solutions of PVA, containing aliphatic dicarboxylic acids (e.g., oxalic, malonic, succinic, and citric acids) and H₂SO₄ as catalyst, and cross-linking the PVA membranes by heat treatment at 90–120°C. Wojciak and Voelkel⁵⁰ previously reported that, in the absence of H₂SO₄ catalyst, dense PVA membranes could not be cross-linked with malonic or succinic acids in the temperature range 80–120°C. Heat-resistant composite semipermeable membranes were prepared at Nitto Electric Industrial Co.⁵¹ by coating a microporous polytetrafluoroethylene support with an aqueous solution of PVA and H₂SO₄ catalyst, heating the membrane at 150°C, then coating it with an aqueous solution of poly(acrylic acid) and H₂SO₄ catalyst, and heating it again at 160°C. This composite

membrane exhibited high NaCl rejections and relatively low water fluxes at an operating pressure of 40 kg cm⁻².

Linder et al.⁵² prepared thin-film composite desalination membranes by coating a microporous polypropylene support with a solution of PVA, or vinyl alcohol copolymers, which had been treated with a reactive dye. The composite membrane was dried and heated in a Na₂CO₃ solution to cross-link and fix the dye-modified PVA membrane. Researchers at Toray Industries⁵³ made thin-film composite RO membranes by coating an aqueous solution, containing PVA, hydroquinone, and sodium lauryl sulfate (as surfactant), on a porous polysulfone support and contacting the PVA/hydroquinone coating with an organic solution of trimesoyl chloride to give an interfacially polymerized membrane. After drying and heat treatment, the membrane was coated with a 20% aqueous PVA solution and heated again to give a high-rejection, low-flux composite membrane useful for sea water desalination (3.5% NaCl feed).

Ikehata et al.⁵⁴ prepared composite membranes by coating a porous polypropylene support with an aqueous solution of PVA and NaOH and heating the PVA membrane at 80°C for 5 h to form a water-insoluble PVA coating. This composite membrane exhibited very high water permeability and was used for ultrafiltration purposes. Thin-gel composite membranes for bioseparations were reported by Li and Barbari.⁵⁵ They coated PVA solutions on a porous cellulose acetate support and cross-linked the PVA interfacially by reacting it with an organic solution of isophthalaldehyde. Himeshima and Uemura⁵⁶ made semipermeable composite membranes, used in low-pressure desalination applications, by cross-linking PVA with divinylsulfone on a porous polypropylene support.

In the preparation of chlorine-resistant PVA-based membranes for low-pressure desalination of brackish water and industrial wastewater, the most successful approach so far has been that of preparing thin-film composite membranes comprising (i) a porous substrate, (ii) an ultrathin salt-retention barrier formed by interfacial cross-linking and polymerization of PVA and an amino compound having at least two secondary amino groups with a multifunctional reagent that reacts with the secondary amino groups and the hydroxyl groups of PVA, and (iii) an inner layer of water-insoluble PVA that is present between the porous substrate and the ultrathin film. This procedure, developed by Nitto Electric Industrial Co. in Japan, has been described extensively in the patent literature.⁵⁷⁻⁵⁹

Typically, a porous polysulfone support is coated

with an aqueous solution of PVA, piperazine, and NaOH as acid acceptor, then dipped into a hexane solution of trimesoyl chloride, dried, and heat-treated at 110°C. In a slight variation of this procedure, aromatic diamines, e.g., *m*-phenylene diamine, are used instead of cycloaliphatic secondary diamines.⁶⁰ A similar approach has been followed by researchers at Sumitomo Chemical Co.,⁶¹ but they used poly(ethylene glycols) and other polyhydroxy compounds instead of PVA.

The RO performance of Nitto's NTR-7250 chlorine-resistant membranes in brackish water desalination applications has been discussed by Kamiyama et al.⁶² These thin-film composite PVA-based membranes exhibited high MgSO₄ retentions, but low NaCl retentions. After the NTR-7250, Nitto developed the NTR-729 and NTR-739 HF (high-flux) series membranes.^{63,64} These are thin-film composites made from modified PVA. They exhibit excellent chlorine resistance, high water flux, and high NaCl retention in brackish water desalination, even at low pressures of 1 MPa.

Scope of the Present Study

Our long-term research objective is to develop thin-film composite PVA-based RO membranes for desalination of brackish water and industrial wastewater. For this purpose, the final composite membrane must have high water permeability and adequate salt-retention capability at low operating pressures of ≤ 2 MPa. It must also exhibit good chemical resistance (particularly chlorine resistance), thermal stability up to 70°C, and hydrolytic stability. When membranes are formed directly on a porous substrate by interfacial polymerization of multifunctional monomers, it is difficult to completely cover fine pores on the substrate surface and defects are easily caused. Researchers at Nitto⁵⁷ showed that problems with low water permeability and reproducibility of membrane performance can be overcome if an inner layer of water-insoluble PVA is present between the porous substrate and the ultrathin polyamide skin layer.

We have decided to follow an approach similar to that of Nitto, but instead of a simultaneous cross-linking and polymerization of PVA and amino compounds, we have chosen to prepare the intermediate PVA gel layer and the ultrathin salt-retention barrier in two separate steps. The initial phase of our research focuses on the controlled *in situ* insolubilization of the intermediate PVA layer using heat-activated chemical reactions in solution-applied coatings. The primary objective is to prepare mechanically stable high-flux gel sublayers for RO

membranes. However, the potential use of these insolubilized PVA membranes in RO applications has been investigated by monitoring the effect of fabrication variables on salt-retention capability.

Insolubilization of PVA membranes by heat treatment in the presence of dialdehydes, as well as complex formation with Cu²⁺ ions, have been studied in our laboratory. The RO performances of the resulting membranes were disappointing, since extremely low water permeabilities were often recorded at 2 MPa and, in addition, the membranes lacked hydrolytic stability. We have previously reported the cross-linking of PVA gel-layer membranes with peroxydisulfate, as well as the performance of these membranes in RO tests on real industrial effluents.^{65,66} This article reports on the insolubilization of PVA by means of acid-catalyzed dehydration.

Thermal Degradation of PVA

The thermal stability of PVA has been investigated by numerous workers. Some of the most detailed works are those of Kaesche-Krischer and Heinrich,^{67,68} Duncalf and Dunn,⁶⁹ Tsuchiya and Sumi,⁷⁰ and Varma and Sadhir.⁷¹ The thermal degradation of PVA in the absence of oxygen occurs in two stages⁷⁰: The first stage begins at about 200°C and is mainly dehydration, accompanied by the formation of volatile products. The residue is predominantly macromolecules having polyene structures. In the presence of oxygen, oxidation of the unsaturated polymeric residue from the dehydration reaction introduces ketone groups in the polymer chain. These groups promote the dehydration of neighboring vinyl alcohol units, producing conjugated unsaturated ketone structures.⁷² In the second-stage decomposition, further heating of the polyene residue to 400–500°C yields carbon and hydrocarbons.⁷⁰

The physical properties of PVA are to a large extent dependent on the polymerization conditions of the parent PVAc and the hydrolysis conditions, which determine the composition of the final product.⁷³ Commercially available grades of PVA must, in fact, be regarded as copolymers of vinyl alcohol (VA) and vinyl acetate (VAc), since they usually correspond to a hydrolysis degree of 70–99%. Therefore, the thermal degradation behavior of PVA will depend on sample characteristics (e.g., molecular weight and degree of hydrolysis, as well as method of hydrolysis). Experimental conditions, such as heating rate, the surrounding atmosphere, and heating method (i.e., isothermal or dynamic) will also influence the degradation behavior. Comparative studies of the effect of degree of hydrolysis,

molecular weight, and heating rate on the thermooxidative degradation of various VA/VAc block copolymers (obtained by alkaline hydrolysis of PVAc) and statistical copolymers (obtained by acid-catalyzed hydrolysis of PVAc) have been conducted by Popa et al.⁷⁴ and Vasile et al.⁷⁵⁻⁷⁸

Drechsel and Görlich⁷⁹ studied the thermal degradation of PVA and found that pretreatment with sulfuric acid, hydrochloric acid, and perchloric acid promoted dehydration on drying at temperatures between 80 and 120°C. Sequences of double bonds were produced, and the higher the drying temperature, the longer these sequences. It was found that weak acids, such as phosphoric, was ineffective in catalyzing the dehydration reaction. Matsubara and Imoto⁸⁰ studied the thermal degradation of low molecular weight PVA and reported that infrared spectroscopy of the residue showed an increase in absorption at 1640 cm⁻¹ (—C=C—) and a decrease at 2900 cm⁻¹ (—CH₂—) as the degradation proceeded.

Perepelkin and Borodina⁸¹ confirmed that discoloration of PVA films that were heated in air at temperatures between 120 and 220°C was attributable to dehydration, resulting in conjugated unsaturation. Activation energies for the formation of conjugated unsaturated ketone structures —(CH=CH)_nCO— were measured from the rate of increase of UV absorbance at the appropriate wavelengths. Smirnov et al.⁸²⁻⁸⁵ investigated the UV spectra of PVA that had been heat-treated at temperatures between 70 and 190°C in relation to the methods of preparation of the specimens (i.e., whether they were produced by acid or alkaline hydrolysis)^{83,84} and as a result of acid-catalyzed dehydration.⁸⁵ Sequences of between four and 15 double bonds were obtained. They associated polyene sequences with certain UV absorption maxima,⁸⁶ but did not take into consideration the probability that the double bonds were conjugated to carbonyl groups, since their specimens were heated in air.

EXPERIMENTAL

Materials

Poly(arylether sulfone) (Victrex 4800G, a product of ICI, England) was used for the formation of asymmetric substrate membranes. Partially hydrolyzed PVA (degree of hydrolysis 86–89%; \bar{M}_w 72,000) was purchased from Saarchem. Concentrated sulfuric acid (98%) was used as the dehydration catalyst. Salt-retention capabilities of dehydrated PVA gel layers were determined using NaCl

(CP grade) and hydrated MgSO₄ (CP grade) feed solutions.

Membrane Fabrication

Tubular (13 mm diameter) and flat-sheet substrate membranes were manufactured in-house by the phase-inversion deposition of poly(arylether sulfone) (PES) on a poly(ethylene terephthalate) nonwoven fabric (Viledon™: Carl-Freudenberg, Germany). A discussion of PES casting solution compositions and fabrication conditions used in the manufacture of asymmetric substrate membranes falls beyond the scope of this article. Substrate membrane materials and optimization of membrane fabrication variables have been discussed in detail by Jacobs.⁸⁷ PES substrates were stored in distilled water to prevent drying and cracking.

PVA was dissolved in distilled water by continuous stirring for a period of 24 h. All solutions were filtered before use to remove undissolved particles. Flat-sheet composite membranes were prepared by depositing aqueous PVA/H₂SO₄ solutions on PES substrates, using a technique that will be referred to as dip-coating. Typically, the substrate membrane was first drained of excess water for 2 min, then immersed in an aqueous PVA/H₂SO₄ solution for 5 min, removed, and drained of excess PVA solution for 5 min. The membrane coatings were then heat-treated in an oven at 100–125°C for 10–30 min to effect insolubilization. Four membranes were prepared from each coating solution. Variables that were studied in an attempt to optimize the reverse osmosis performance of the composite membranes included PVA concentration, H₂SO₄ concentration, wetting, draining, and curing times, as well as curing temperature. The compositions and fabrication conditions of flat-sheet composite membranes are given in Table I.

PVA/H₂SO₄ coatings were also deposited on 13 mm tubular PES substrate membranes. The compositions of the coating solutions and the membrane fabrication conditions are summarized in Table II. These membranes were cured in a vertical updraft oven, which permitted an even distribution of heat and, consequently, much better control over the extent of dehydration. The effects of PVA concentration, H₂SO₄ concentration, and curing temperature on RO properties of tubular membranes were investigated.

Evaluation of Membrane Performance

A schematic representation of the membrane evaluation equipment is shown in Figure 1. Testing con-

Table I Compositions of Coating Solutions and Membrane Fabrication Conditions: Flat-sheet PVA/H₂SO₄ Membranes

Membrane No.	PVA Concentration (Mass %)	H ₂ SO ₄ Concentration (Mass %)	Wetting Time (min)	Draining Time (min)	Curing Time (min)	Curing Temp. (°C)
A.1-A.4	0.5	0.2	5	5	20	120
A.5-A.8	1.0	0.2	5	5	20	120
A.9-A.12	2.0	0.2	5	5	20	120
B.1-B.4	2.0	0.1	5	5	20	125
B.5-B.8	2.0	0.2	5	5	20	125
B.9-B.12	2.0	0.5	5	5	20	125
C.1-C.4	2.0	0.5	5	5	10	125
C.5-C.8	2.0	0.5	5	5	20	125
C.9-C.12	2.0	0.5	5	5	30	125
D.1-D.4	2.0	0.5	5	5	20	100
D.5-D.8	2.0	0.5	5	5	20	110
D.9-D.12	2.0	0.5	5	5	20	125
E.1-E.4	2.0	0.1	5	5	20	125

ditions for the individual experiments are indicated in the tables and figures in the Results and Discussion section. Typically, flat-sheet membranes were tested at 2 MPa, pH 6.5, and 25°C on either a 2000 mg/L NaCl or a 500 mg/L MgSO₄ feed solution. Tubular membranes were tested at 2 MPa, pH 6.0, and 20°C on a 2000 mg/L NaCl feed solution, unless stated otherwise. The salt-retention and permeate flux values are defined as follows:

Retention = 1

$$- \frac{\text{Conductivity of permeate}}{\text{Conductivity of feed}} \times 100 (\%)$$

$$\text{Flux} = \frac{\text{Volume of permeate recovered}}{\text{Membrane area} \times \text{Time}}$$

(Lmd: liters per square meter per day)

In all experiments, reverse osmosis tests were con-

ducted within 2 h after membrane manufacture. To allow the salt-retention and flux values to stabilize, a period of between 22 and 24 h elapsed between the start-up time and the time at which the first permeability measurements were taken.

Chlorine Treatment

The effect of chlorine treatment on the RO performance of both flat-sheet and tubular membranes was investigated by using sodium hypochlorite (NaOCl) as the source of active chlorine. Flat-sheet composite membranes (prepared by dip-coating a PES support with an aqueous solution of 2% PVA and 0.5% H₂SO₄ and heating the membranes at 120°C for 20 min) were immersed in an aqueous solution of 350 mg/L NaOCl at pH 6.0 and 25°C. After an exposure time of 6 h, the membranes were removed and evaluated in RO experiments.

Table II Compositions of Coating Solutions and Membrane Fabrication Conditions: Tubular PVA/H₂SO₄ Membranes

Membrane Code	LP-1	LP-2	LP-3	LP-4	LP-5	LP-6	LP-7	LP-8
PVA (mass %)	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
H ₂ SO ₄ (mass %)	0.4	0.4	0.8	0.8	0.4	0.4	0.8	0.8
Substrate predraining time (min)	5	5	5	5	5	5	5	5
Wetting time (min)	5	5	5	5	5	5	5	5
Draining time (min)	5	5	5	5	5	5	5	5
Curing time (min)	20	20	20	20	20	20	20	20
Curing temp (°C)	110	110	110	110	130	130	130	130

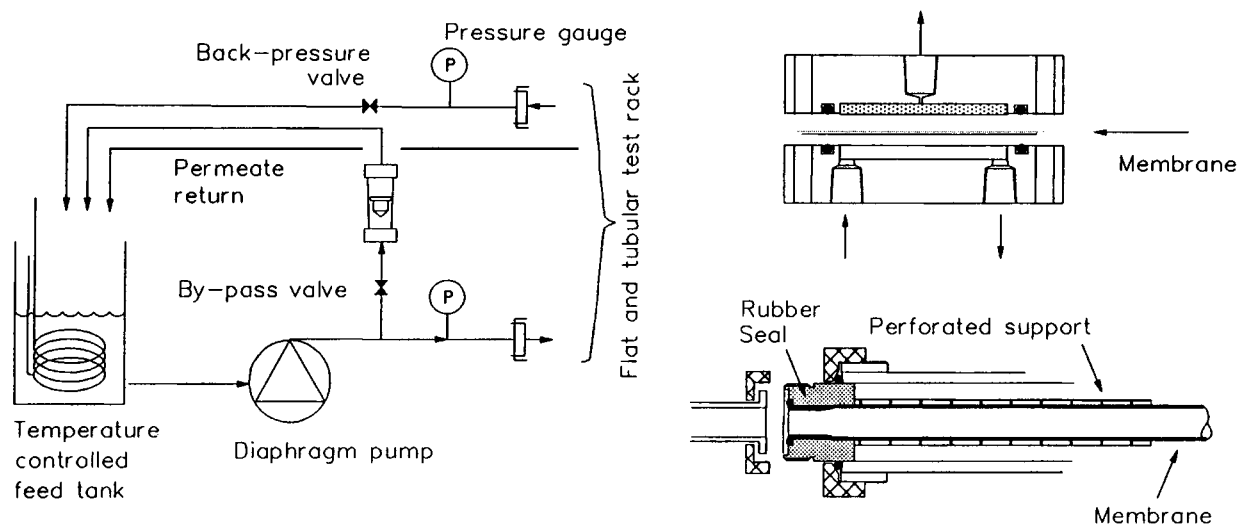


Figure 1 Schematic diagram of membrane evaluation equipment.

In the case of tubular PES-PVA composites, membranes LP-1 to LP-8 (shown in Table II) were first evaluated in RO experiments on a NaCl feed solution. After 75 h of operation, the feed tank was rinsed and filled with distilled water. The temperature of the water was adjusted to 20°C, the pH was adjusted to a value of 6.0, and the membranes were shock-treated with chlorine by adding 350 mg/L NaOCl to the feedwater. After running the membranes on NaOCl solution for 6 h, NaCl (2000 mg/L) was again added to the feedwater. The salt-retention and flux values were measured at regular intervals over a period of 120 h to monitor changes in membrane performance. The chlorine shock treatment was repeated after a total operating time of 200 h.

Thermogravimetric Analysis (TGA)

The thermal degradation of PVA under dynamic thermogravimetric conditions was studied using a DuPont 9900 computer/thermal analyzer coupled with a DuPont Model 951 thermogravimetric analyzer. Samples were heated in air (flow rate 50 mL min⁻¹) at heating rates of 5 and 10°C min⁻¹. The sample weight was restricted to the 20 ± 2 mg range. Dynamic TGA scans were recorded in the temperature range 25–450°C. Most of the analyses were conducted using 86–89% hydrolyzed PVA of M_w 72,000 (Saarchem), since this polymer was used for the preparation of insolubilized PVA membranes. To compare the degradation behavior of partially hydrolyzed PVA with that of the fully hydrolyzed polymer, a sample of 100% hydrolyzed PVA (M_w

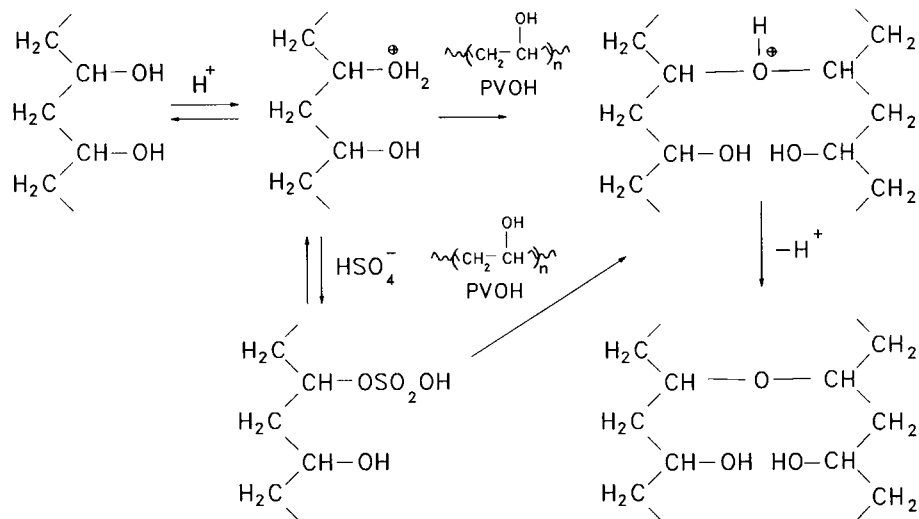
115,000, Aldrich Chemical Co.) was also analyzed by TGA.

RESULTS AND DISCUSSION

Mechanism of Insolubilization of PVA

Insolubilization of PVA/H₂SO₄ membranes occurs by means of acid-catalyzed dehydration. Dehydration of alcohols with H₂SO₄ can result in different products. Apparently, the most important reactions are ether-bond formation and double-bond formation. In the dehydration of alcohols to form ethers by aliphatic nucleophilic substitution, the species from which the leaving group departs is ROH₂⁺ or ROSO₂OH. The former is obtained directly on treatment of alcohols with H₂SO₄ and may go (by an S_{N1} or S_{N2} route) directly to the ether if attacked by another molecule of alcohol. On the other hand, it may (again by either an S_{N1} or S_{N2} route) be attacked by the nucleophile HSO₄⁻, in which case it is converted to ROSO₂OH, which, in turn, may be attacked by an alcohol molecule to give ROR.⁸⁸ These processes are summarized in Scheme 4 for R = PVA chain.

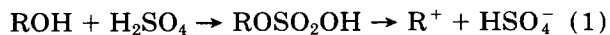
In the reaction shown in Scheme 4, elimination is always a side reaction. Therefore, dehydration of PVA in the presence of H₂SO₄ also results in the formation of double bonds by β-elimination (Scheme 5). The ease of elimination increases with branching, and tertiary alcohols are dehydrated very easily. When proton acids catalyze alcohol dehydration, the mechanism is E1.^{89,90} The principal process involves conversion of ROH to ROH₂⁺ and cleavage of the



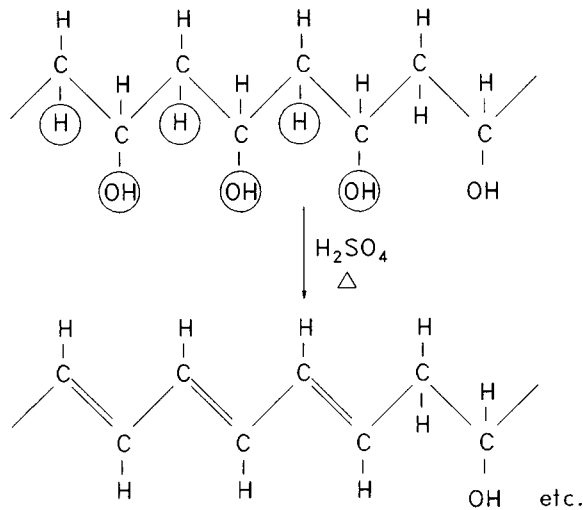
FORMATION OF ETHER CROSSLINKS
BY NUCLEOPHILIC SUBSTITUTION

Scheme 4

latter to R^+ and H_2O , though with some acids (e.g., H_2SO_4), a secondary process probably involves conversion of the alcohol to an inorganic ester and ionization of this ester:



If there is a double bond already in the molecule that can be in conjugation with the new double bond, then the conjugated product usually predominates.



FORMATION OF CONJUGATED OLEFINIC BONDS
BY β -ELIMINATION (POLYACETYLENE STRUCTURE)

Scheme 5

Elimination is favored over substitution by increasing temperature, therefore, higher temperatures favor the formation of double bonds over the formation of ether linkages.

In view of the discussions above, it is clear that dehydration of PVA by H_2SO_4 can result in crosslinking through formation of ether linkages (Scheme 4), double-bond formation through β -elimination (Scheme 5), or a combination of both processes. It is difficult to predict which process will predominate. However, during preparation of PVA/ H_2SO_4 membranes, heat treatment resulted in discoloration of the membranes. As the H_2SO_4 concentration, curing temperature, and curing time were increased, the color of the membranes changed from a very light brown to almost black. This would indicate that double-bond formation definitely predominated. It is also known that the formation of one double bond increases by many times the probability of the formation of another adjacent double bond. It is therefore suggested that dehydration of PVA resulted in the formation of sequences of conjugated double bonds (i.e., polyenes) and that the conjugated unsaturation was responsible for color development. On the other hand, the possibility that some ether crosslinks were also formed in the process cannot be completely excluded. Another factor that has to be considered is that ketone groups may form during subsequent oxidation of the dehydrated polymer, although oxidation appears to be only of importance during prolonged heat treatment at temperatures above $180^\circ C$.

Thermooxidative Degradation of PVA

A TGA thermogram of partially hydrolyzed PVA (\overline{M}_w 72,000; degree of hydrolysis 86–89%) is shown in Figure 2. For this particular grade of PVA, which is the one used for membrane preparations, weight loss due to degradation became significant at temperatures above 275°C. Below this temperature, weight loss could be attributed mainly to the loss of absorbed water in the sample and some intramolecular dehydration. The severe discoloration of PVA membranes that were heated at 120°C for 20 min in the presence of H₂SO₄ catalyst suggested that long sequences of conjugated double bonds were formed by intramolecular dehydration. Figure 2 shows that, in the absence of H₂SO₄ catalyst, degradation due to water elimination is not significant at this low temperature. In the temperature range 100–125°C (used for membrane preparations), a weight loss of only about 2% occurred. It can therefore be concluded that the role of H₂SO₄ is to shift the onset of degradation to lower temperatures and to accelerate the rate of water elimination at low temperatures.

In Figures 3 and 4, the degradation behavior of partially hydrolyzed and fully hydrolyzed PVA samples are compared. Even below 200°C, where the percentage weight loss is small, a difference between these two grades of PVA can be detected (Fig. 3). In the temperature range 200–400°C, it is clear that the degradation of 100% hydrolyzed PVA starts at

a lower temperature and proceeds more rapidly than is the case for partially hydrolyzed PVA (Fig. 4). Table III shows the effect of heating rate and hydrolysis degree on weight loss at temperature intervals of 50°C. The heating rate did not have a significant effect on the degradation of partially hydrolyzed PVA. This was probably because the difference between heating rates of 5 and 10°C min⁻¹ was too small.

For 100% hydrolyzed PVA, the highest percentage weight loss was recorded in the temperature range 225–325°C, whereas 86–89% hydrolyzed PVA exhibited the highest percentage weight loss at 275–375°C. The yield of residue increased with decreasing degree of hydrolysis. At 400°C, the yield of residue was 47% for 86–89% hydrolyzed PVA and only 27% for the 100% hydrolyzed polymer. The difference in degradation behavior between these two grades of PVA can be explained in terms of the difference in polymer composition, since one sample is a homopolymer of PVA while the other one is, in fact, a vinyl alcohol/vinyl acetate copolymer. The 86–89% hydrolyzed PVA was obtained by alkaline hydrolysis of PVAc, which results in copolymers with a block structure. The results of this preliminary TGA study suggest that these residual vinyl acetate blocks interrupt the dehydration reaction, especially at temperatures below 300°C. Further thermoanalytical studies are being conducted to attempt to quantify the effect of H₂SO₄ pretreatment on both the rate and the extent of dehydration at

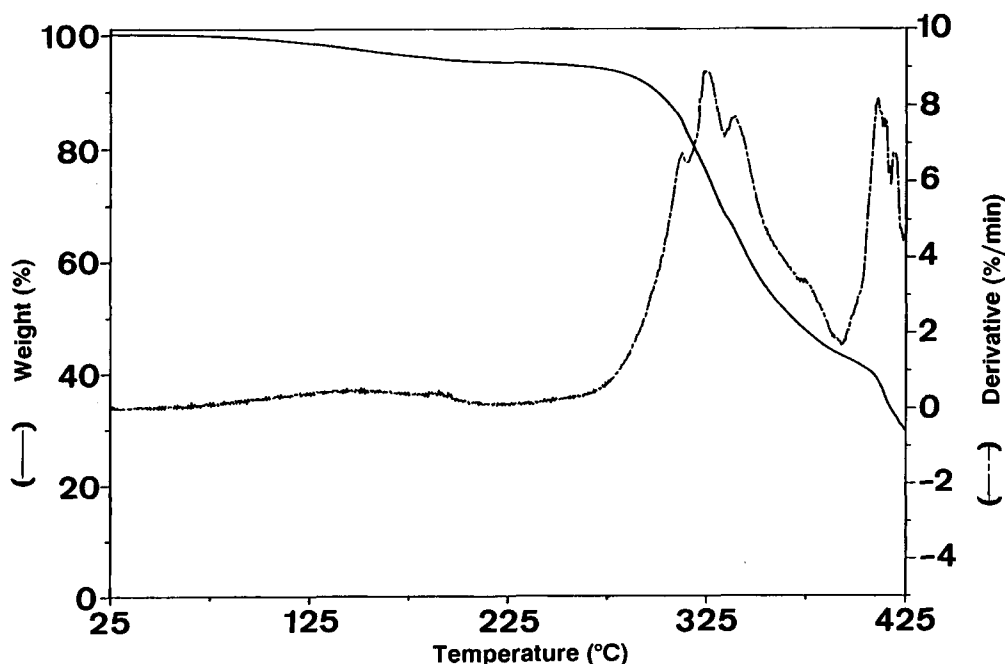


Figure 2 Dynamic TGA scan of 86–89% hydrolyzed PVA of \overline{M}_w 72,000.

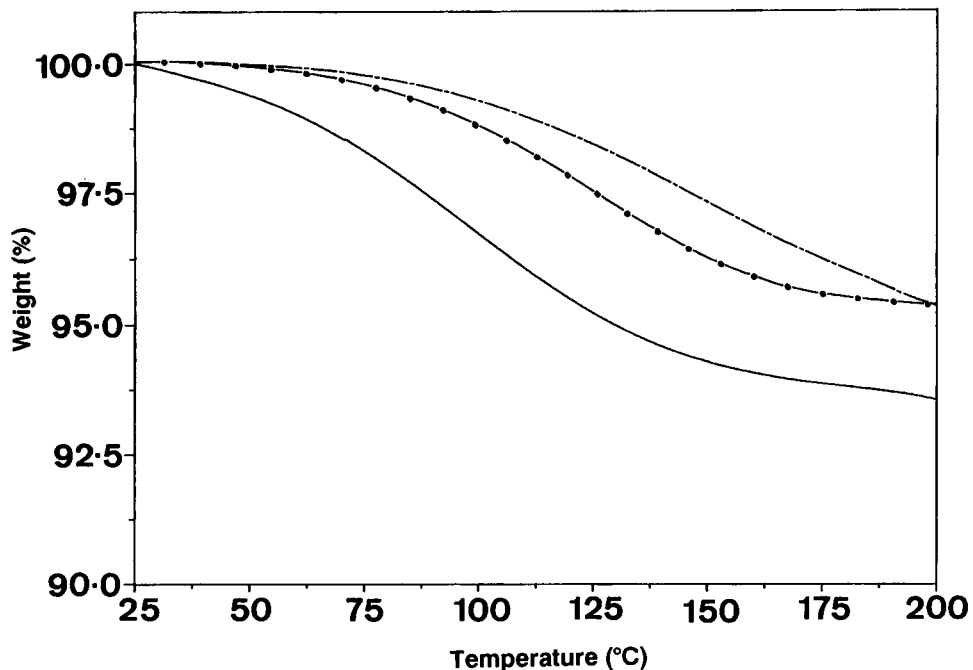


Figure 3 Comparison of the degradation behavior of partially hydrolyzed and fully hydrolyzed PVA samples in the temperature range 25–200°C: (—●—) PVA \overline{M}_w 72,000, degree of hydrolysis 86–89%, heating rate 5°C/min; (---) PVA \overline{M}_w 72,000, degree of hydrolysis 86–89%, heating rate 10°C/min; (—) PVA \overline{M}_w 115,000, degree of hydrolysis 100%, heating rate 5°C/min.

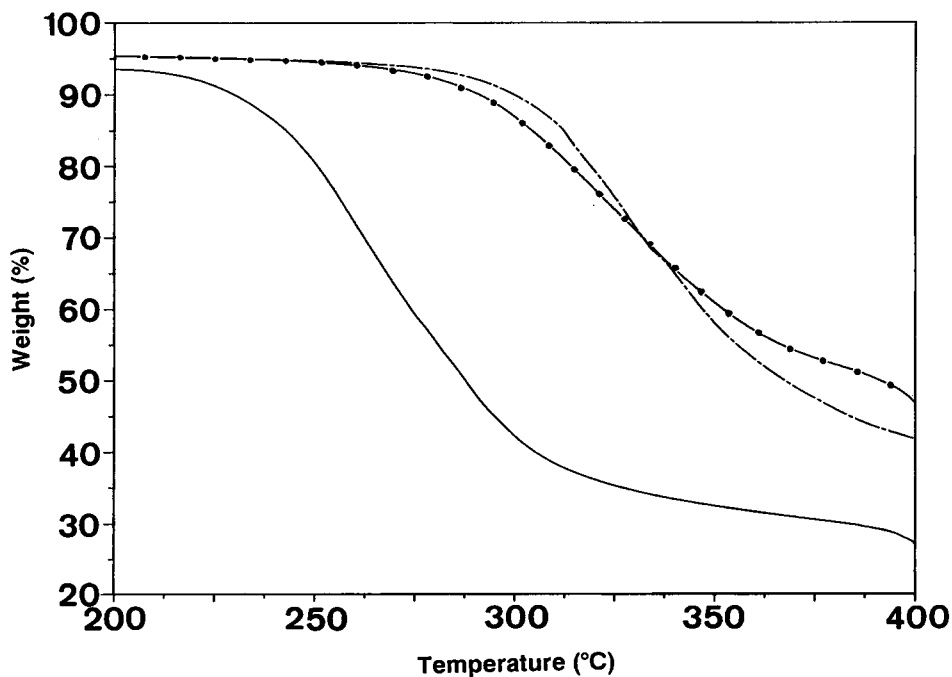


Figure 4 Comparison of the degradation behavior of partially hydrolyzed and fully hydrolyzed PVA samples in the temperature range 200–400°C: (—●—) PVA \overline{M}_w 72,000, degree of hydrolysis 86–89%, heating rate 5°C/min; (---) PVA \overline{M}_w 72,000, degree of hydrolysis 86–89%, heating rate 10°C/min; (—) PVA \overline{M}_w 115,000, degree of hydrolysis 100%, heating rate 5°C/min.

Table III The Effect of Degree of Hydrolysis and Heating Rate on the Degradation Behavior of PVA Samples under Dynamic Thermogravimetric Conditions

Temperature Range (°C)	Weight Loss (%)		
	PVA-I ^a	PVA-II ^b	PVA-III ^c
25–75	0.42	0.24	1.69
75–125	2.07	1.35	3.09
125–175	1.96	2.19	1.37
175–225	0.46	1.22	2.65
225–275	2.17	1.26	31.85
275–325	19.02	18.08	24.05
325–375	20.72	28.19	4.72
375–425	19.36	17.85	22.33

^a PVA: \overline{M}_w 72,000 and degree of hydrolysis 86–89%; heating rate 5°C min⁻¹.

^b PVA: \overline{M}_w 72,000 and degree of hydrolysis 86–89%; heating rate 10°C min⁻¹.

^c PVA: \overline{M}_w 115,000 and degree of hydrolysis 100%; heating rate 5°C min⁻¹.

temperatures below 200°C. Analytical investigations are also in progress to determine the chemical composition, as well as the thermal stability, oxidation stability, and hydrolytic stability, of membranes obtained by acid-catalyzed dehydration of various grades of PVA (different molecular weights; different degrees of hydrolysis). These studies will be reported in a forthcoming paper.

Reverse Osmosis Performance of Flat-Sheet Composite Membranes

Effect of PVA Concentration

Table IV shows the salt retention and permeate flux as a function of PVA concentration. Moderate increases in salt-retention capability were observed when the concentration was increased from 0.5 to 2%. The flux values obtained for membranes consisting of 2% PVA were considerably lower than

those obtained for membranes prepared from a 0.5% polymer solution. An increase in the polymer concentration results in an increase in membrane thickness, with a corresponding decrease in the rate of water transport.

Effect of Sulfuric Acid Concentration

The effect of H₂SO₄ concentration on reverse osmosis performance is shown in Table V. As the H₂SO₄ concentration increased, the salt retention of the membranes increased, while the flux values decreased correspondingly. Commercial grades of PVA are usually produced by alkaline hydrolysis and therefore contain some residual sodium acetate. It is known that sodium acetate also promotes dehydration of PVA on heating, resulting in discoloration of films.⁸⁵ Apparently, the addition of an equivalent amount of H₂SO₄ greatly reduces the rate of discol-

Table IV The Effect of PVA Concentration on RO Properties^a of Flat-sheet Membranes

	PVA Concentration (Mass %)											
	0.5				1.0				2.0			
	Membrane No. ^b											
	A.1	A.2	A.3	A.4	A.5	A.6	A.7	A.8	A.9	A.10	A.11	A.12
Retention (%)	49.4	46.6	44.5	47.1	56.8	53.4	55.4	59.2	60.4	61.8	63.4	62.0
Permeate flux (Lmd)	1598	1621	1628	1611	1541	1570	1566	1519	1091	1085	1025	1081

^a Membranes tested at 25°C, pH 6.5, and 2 MPa on 2000 mg/L NaCl feed.

^b See Table I for fabrication conditions.

Table V The Effect of H₂SO₄ Concentration on RO Properties^a of Flat-sheet Membranes

	H ₂ SO ₄ Concentration (Mass %)											
	0.1				0.2				0.5			
	Membrane No. ^b											
	B.1	B.2	B.3	B.4	B.5	B.6	B.7	B.8	B.9	B.10	B.11	B.12
Retention (%)	55.1	54.0	51.3	52.2	60.8	65.8	59.7	62.4	77.1	81.6	75.4	78.1
Permeate flux (Lmd)	1518	1560	1588	1526	997	978	1017	1015	817	761	825	802

^a Membranes tested at 25°C, pH 6.5, and 2 MPa on 2000 mg/L NaCl feed.

^b See Table I for fabrication conditions.

oration, but any excess promotes acid-catalyzed dehydration. Since sulfuric acid presumably acted only as a catalyst, and not as a reactant, concentration was not expected to play such a significant role. The increase in salt retention with increasing concentration of H₂SO₄ seems to indicate that a higher acid concentration increases the rate of dehydration at a specific temperature. Therefore, it is possible that similar levels of salt retention could be achieved if membranes with lower acid contents are heated for much longer periods of time.

Effect of Curing Time

Table VI shows the effect of curing time on reverse osmosis properties of flat-sheet composite membranes. It is evident that excessive curing times (longer than 20 min at 125°C) resulted in considerable decreases in water flux, without a significant increase in salt retention.

Effect of Curing Temperature

The effect of curing temperature on salt retention and permeate flux is shown in Table VII. The rate

of water elimination is expected to be strongly dependent on heat-treatment temperature. Temperatures in excess of 130°C were considered to be undesirable, because of the detrimental effect that prolonged heat treatment at high temperatures could have on the asymmetric pore structure of the PES substrate membranes. In the temperature range studied (100–125°C), it appears as though a curing temperature of around 125°C gave the tightest membrane with the highest salt retention and the lowest flux. However, flux values of about 800 Lmd for membranes cured at 125°C were regarded as quite promising.

Tables IV to VII show clearly that a simple manipulation of one or two variables could lead to PVA gel-layer membranes with widely differing salt retention and water permeability characteristics.

Effect of Operating Pressure

The effect of operating pressure on salt retention and permeate flux is shown in Table VIII. In this experiment, the H₂SO₄ content was only 0.1% and, therefore, salt retentions at 2 MPa were relatively

Table VI The Effect of Curing Time on RO Properties^a of Flat-sheet Membranes

	Curing Time (min)											
	10				20				30			
	Membrane No. ^b											
	C.1	C.2	C.3	C.4	C.5	C.6	C.7	C.8	C.9	C.10	C.11	C.12
Retention (%)	53.4	47.2	51.0	48.4	76.1	79.3	80.1	76.2	83.7	81.6	83.2	81.0
Permeate flux (Lmd)	1266	1332	1298	1321	822	797	774	835	254	311	271	345

^a Membranes tested at 25°C, pH 6.5, and 2 MPa on 2000 mg/L NaCl feed.

^b See Table I for fabrication conditions.

Table VII The Effect of Curing Temperature on RO Properties^a of Flat-sheet Membranes

	Curing Temp (°C)											
	100				110				125			
	Membrane No. ^b											
	D.1	D.2	D.3	D.4	D.5	D.6	D.7	D.8	D.9	D.10	D.11	D.12
Retention (%)	61.5	59.1	60.2	58.0	67.2	68.1	68.5	72.8	77.0	81.1	74.1	79.7
Permeate flux (Lmd)	1098	1218	1185	1234	963	941	952	851	821	774	833	789

^a Membranes tested at 25°C, pH 6.5, and 2 MPa on 2000 mg/L NaCl feed.

^b See Table I for fabrication conditions.

low. As expected, permeate flux varied linearly with operating pressure. The flux values obtained at 2 MPa for this particular coating formulation were very promising, whereas the fluxes at 1 MPa were still useful.

Effect of Pretreatment

The RO performances of dehydrated PVA membranes that were subjected to various pretreatments are summarized in Table IX. Membranes 1 and 2 were immersed in a solution of sodium hypochlorite before evaluation of RO performance. After an operating time of 70 h at 2 MPa, the NaCl retention capability of these membranes remained unchanged, while the permeate flux increased. In the case of the dry-stored membrane (no. 3), the salt retention increased by about 10% after 70 h of operation, while the permeate flux remained unchanged. The NaCl retention of the wet-stored membrane (no. 4) remained unchanged, while the flux increased markedly.

Membranes 3 and 4 exhibited similar salt retentions after 70 h of operation, but the flux of the wet-

stored membrane was considerably higher than that of the dry-stored membrane. Although membranes subjected to chlorine pretreatment exhibited lower salt retentions, the fluxes were twice as high as those of untreated membranes. These results are not yet conclusive and further investigations of the effect of storage conditions and chlorine pretreatment will be conducted.

MgSO₄ Retention

The retention of divalent ions by the membranes shown in Table IX was also investigated. For this purpose, the 2000 mg/L NaCl feed solution was replaced with a 500 mg/L MgSO₄ solution. The RO properties at 2 MPa are given in Table X. MgSO₄ retentions of up to 92% were obtained. Membranes pretreated with chlorine exhibited much higher fluxes than those of the untreated membranes. In another experiment conducted with MgSO₄ as the feed solution, the membranes were not subjected to any pretreatments, but were tested immediately after manufacture. The results are shown in Table XI. The concentration of H₂SO₄ used in this experiment

Table VIII The Effect of Operating Pressure on RO Properties^a of Flat-sheet Membranes

	Pressure (MPa)											
	0.5				1.0				2.0			
	Membrane No. ^b											
	E.1	E.2	E.3	E.4	E.1	E.2	E.3	E.4	E.1	E.2	E.3	E.4
Retention (%)	41.2	34.5	35.3	38.4	48.6	40.7	42.1	46.2	57.2	49.3	51.3	54.0
Permeate flux (Lmd)	341	425	386	374	699	816	789	777	1488	1770	1588	1576

^a Membranes tested at 25°C and pH 6.5 on 2000 mg/L NaCl feed.

^b See Table I for fabrication conditions.

Table IX Reverse Osmosis Performance^a of PVA/H₂SO₄ Flat-sheet Membranes^b after Various Pretreatments

	Membrane No.			
	1 ^c	2 ^c	3 ^d	4 ^d
Retention (%)	68.7	63.7	70.5	83.6
Flux (Lmd) at 2 MPa	1655	1688	768	827
Retention (%)	60.9	56.6	67.5	74.9
Flux (Lmd) at 1 MPa	817	916	323	373
Retention (%)	49.8	44.9	67.2	71.8
Flux (Lmd) at 0.5 MPa	483	543	180	215
Retention (%) after 70 h	68.0	62.7	81.6	82.9
Flux (Lmd) at 2 MPa after 70 h	1742	1848	761	924

^a Membranes tested at 25°C and pH 6.5 on a 2000 mg/L NaCl feed solution.

^b PVA (\bar{M}_w 72,000): 2%; H₂SO₄: 0.5%; membranes wetted for 5 min, drained for 5 min, and cured for 20 min at 125°C.

^c Membranes 1 and 2 pretreated with chlorine before evaluation of RO performance.

^d Membranes 3 and 4 not treated with chlorine. Membrane 3 was dry-stored for a few days at room temperature; membrane 4 was stored in distilled water for 24 h before being tested.

was 0.1%, compared with 0.5% for membranes shown in Table X. The lower salt retentions can therefore be explained in terms of a lower extent of dehydration.

Reverse Osmosis Performance of Tubular Composite Membranes

The salt retentions and fluxes of tubular membranes, tested at different operating pressures before and after shock treatment of the membranes with chlorine, are given in Table XII.

Effect of Fabrication Variables

There were no significant differences between the RO properties of membranes LP-1 to LP-8. However, if LP-1 and LP-2 are compared with LP-7 and LP-8, it is evident that high H₂SO₄ concentrations and high curing temperatures resulted in lower

fluxes and higher salt retentions. Membranes LP-3 and LP-4 (0.8% H₂SO₄; cured at 110°C) exhibited lower NaCl retentions and slightly higher fluxes than those of LP-7 and LP-8 (0.8% H₂SO₄; cured at 130°C), which shows that temperature plays a significant role in the dehydration reaction.

The fluxes obtained with tubular membranes were markedly lower than those obtained with flat-sheet membranes. This phenomenon can probably be attributed, at least in part, to the fact that casting-solution compositions and fabrication conditions used for the preparation of flat-sheet PES substrate membranes differed considerably from those used in the manufacture of tubular substrates. For example, the PES concentration and casting-solution viscosity were considerably higher in the case of tubular membranes. This usually results in membranes with more dense asymmetric structures, which, in turn, could affect water permeability.

Table X MgSO₄ Retention^a of PVA/H₂SO₄ Flat-sheet Membranes^b at 2 MPa after Various Pretreatments^c

Membrane No.	Retention (%)		Flux (Lmd)	
	6 h	18 h	6 h	18 h
1	83.0	83.3	1375	1330
2	78.4	78.6	1548	1498
3	90.1	91.2	541	525
4	91.3	91.7	620	600

^a Membranes tested at 25°C and pH 6.5 on a 500 mg/L MgSO₄ feed solution.

^b See Table IX.

^c Pretreatments summarized in Table IX.

Table XI MgSO₄ Retention^a of PVA/H₂SO₄ Flat-sheet Membranes^b at 2 MPa

Membrane No.	Retention (%)	Flux (Lmd)	Retention (%)	Flux (Lmd)
	6 h	6 h	18 h	18 h
1	73.5	868	74.1	844
2	69.8	924	70.2	891
3	76.1	822	77.0	796
4	70.8	902	71.4	870

^a Membranes tested at 25°C and pH 6.5 on a 500 mg/L MgSO₄ feed solution.

^b PVA (\overline{M}_w 72,000): 2%; H₂SO₄: 0.1%; membranes wetted for 5 min, drained for 5 min, and cured for 20 min at 125°C.

The random selection of substrate membrane recipes in this study does not, in fact, permit a comparison of the two membrane systems. Therefore,

the RO characteristics of flat-sheet PES-PVA composite membranes cannot be extrapolated to the tubular membrane system. It is obvious that any at-

Table XII Reverse Osmosis Performance^a of Tubular PVA/H₂SO₄ Membranes at Different Operating Pressures

Hours		Membrane Code							
		LP-1	LP-2	LP-3	LP-4	LP-5	LP-6	LP-7	LP-8
<u>Before chlorine treatment</u>									
66	Flux (Lmd) at 2 MPa	410	537	293	339	360	365	285	291
	Retention (%)	54.3	50.9	58.4	57.7	56.4	56.4	65.9	64.3
69	Flux (Lmd) at 1.5 MPa	293	377	163	230	291	250	194	199
	Retention (%)	46.8	41.6	50.0	49.5	49.1	47.9	56.0	55.2
71	Flux (Lmd) at 0.5 MPa	79	107	50	63	70	69	53	55
	Retention (%)	19.5	18.9	24.8	24.1	23.0	22.0	28.2	27.5
<u>After first chlorine treatment</u>									
81	Flux (Lmd) at 2 MPa	438	606	348	357	428	386	300	306
	Retention (%)	61.1	59.0	62.5	62.5	61.7	61.2	68.6	67.6
146	Flux (Lmd) at 1.5 MPa	410	543	357	355	421	373	293	303
	Retention (%)	55.2	51.7	56.8	56.3	55.8	55.8	63.3	60.1
173	Flux (Lmd) at 2 MPa	492	620	435	438	516	466	339	360
	Retention (%)	56.7	53.8	58.7	58.0	57.7	57.7	65.0	62.1
176	Flux (Lmd) at 1.5 MPa	373	465	314	318	350	339	248	283
	Retention (%)	50.5	47.4	52.0	51.5	51.5	51.5	58.7	55.9
194	Flux (Lmd) at 1 MPa	243	301	199	204	227	205	159	170
	Retention (%)	38.8	35.3	40.5	40.3	40.0	40.0	46.5	44.3
196	Flux (Lmd) at 0.5 MPa	100	127	81	84	96	85	67	71
	Retention (%)	20.7	18.1	22.9	21.4	20.9	21.2	24.9	23.9
<u>After second chlorine treatment</u>									
241	Flux (Lmd) at 0.5 MPa	123	145	106	106	114	110	79	84
	Retention (%)	22.7	22.5	24.0	24.0	22.7	23.3	27.3	24.9
313	Flux (Lmd) at 0.5 MPa	145	160	130	130	134	120	91	95
	Retention (%)	19.7	19.7	22.4	22.1	20.8	20.8	24.7	22.6

^a Membranes tested at 20°C and pH 6.0 on a 2000 mg/L NaCl feed solution.

tempt to optimize the reverse osmosis properties of the PVA gel layer will have to include a simultaneous optimization of the PES substrate properties.

Effect of Operating Pressure

Figure 5(a) and (b) show the effect of operating pressure on the RO properties of some tubular membranes. It is evident that the NaCl retention increased asymptotically to an equilibrium value, although this value was not yet reached at 2 MPa. Permeate flux increased linearly with increasing

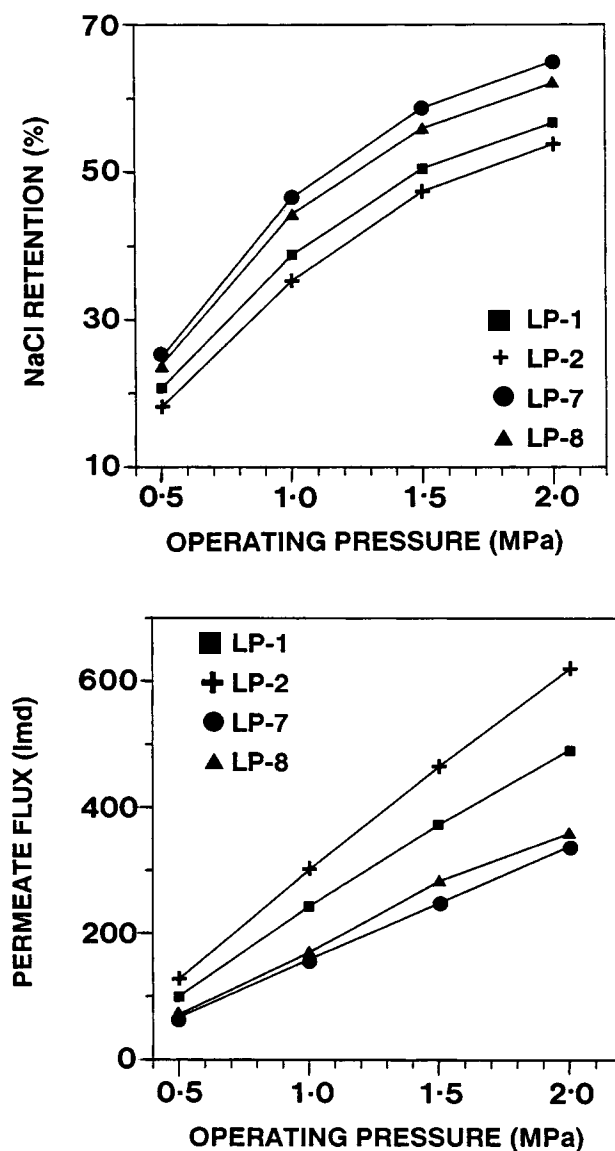


Figure 5 Effect of operating pressure on (a) NaCl retention and (b) permeate flux of dehydrated PVA tubular membranes. Testing conditions: 20°C; pH 6.0; 2000 mg/L NaCl feed.

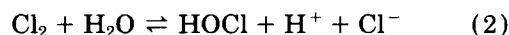
operating pressure. At pressures below 2 MPa, the fluxes were too low to be of practical use.

Effect of Chlorine Shock Treatment

Chlorine is commonly used as a disinfectant in water treatment. In RO systems, chlorine may be added to feedwater for control of microorganisms and, in addition, to prevent membrane fouling by microbiological growth. Hence, the resistance of membrane-forming polymers to chlorine attack is always an important consideration in the development of RO membranes. It is common practice to study the interaction of chlorine and other halogen compounds with RO membranes by monitoring the decay in membrane performance.

Chemical attack of chlorine on RO membranes is in some cases revealed by an increase in permeate flux, accompanied by increasing salt permeability. This is evidently related to the breaking of chemical bonds within the polymer. Other membranes respond to chlorine attack by decreased permeate flux, which can probably be attributed to halogen addition to these polymers, resulting in increased hydrophobicity.

In an aqueous solution, the reaction of NaOCl with acid results in the liberation of chlorine. The latter reacts with water to produce several chemical species, as shown in eqs. (2) and (3):



The distribution of the chlorine species in aqueous solution depends on pH and equilibrium constants for the above reactions. In acidic solution, Cl_2 and HOCl are the most chemically active species.

The RO properties of tubular membranes before and after chlorine shock treatment are shown in Figure 6(a) and (b). The NaCl retentions at 2 MPa increased slightly after addition of chlorine, but no significant changes in salt retention were observed over a period of 100 h (i.e., retentions after 175 h of operation were similar to those measured before chlorine shock treatment). Moderate flux increases occurred after chlorine shock treatment during the same period [Fig. 6(b)].

The RO performances of membranes tested at 0.5 MPa before and after chlorine treatments are shown in Figure 7(a) and (b). After two chlorine shock treatments, the retentions measured after about 310 h of operation did not differ much from the values obtained before chlorine treatment [Fig. 7(a)]. However, the permeate fluxes increased

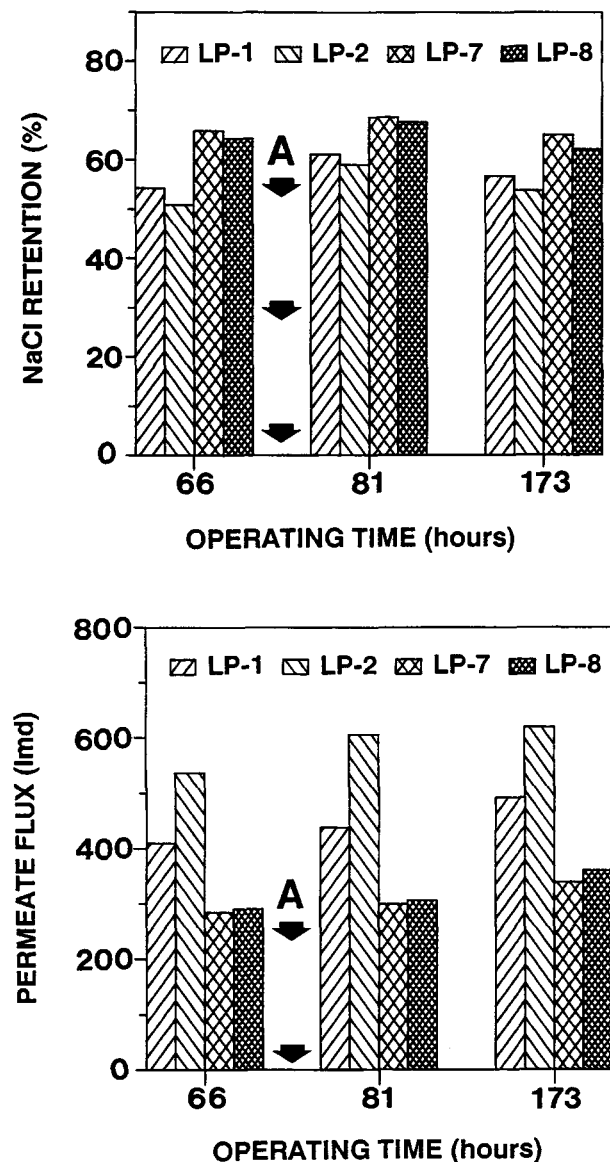


Figure 6 Effect of operating time on (a) NaCl retention and (b) permeate flux of dehydrated PVA tubular membranes tested at 2 MPa before and after chlorine shock treatment. Testing conditions: 20°C; pH 6.0; 2000 mg/L NaCl feed. (A) Chlorine treatment after 75 h.

markedly over the same period [Fig. 7(b)]. The RO performances of these tubular membranes were not promising enough to justify the effort of monitoring the concentration of available chlorine in the feed solution as a function of time.

Since the dehydrated PVA contains sequences of conjugated double bonds, and possibly also some isolated double bonds, the carbon-carbon double bond is the functional group in this polymer. Dehydrated PVA will therefore undergo reactions typ-

ical of alkenes and dienes, namely, electrophilic and free-radical additions. In the present study, chlorine treatment of membranes was carried out at low temperature in aqueous solution and in the absence of a free-radical source. Therefore, only electrophilic additions of Cl_2 and HOCl (the most chemically active species) to carbon-carbon double bonds need to be considered.

In addition to conjugated double bonds, the electrophilic reagent may attach itself not only to a pair

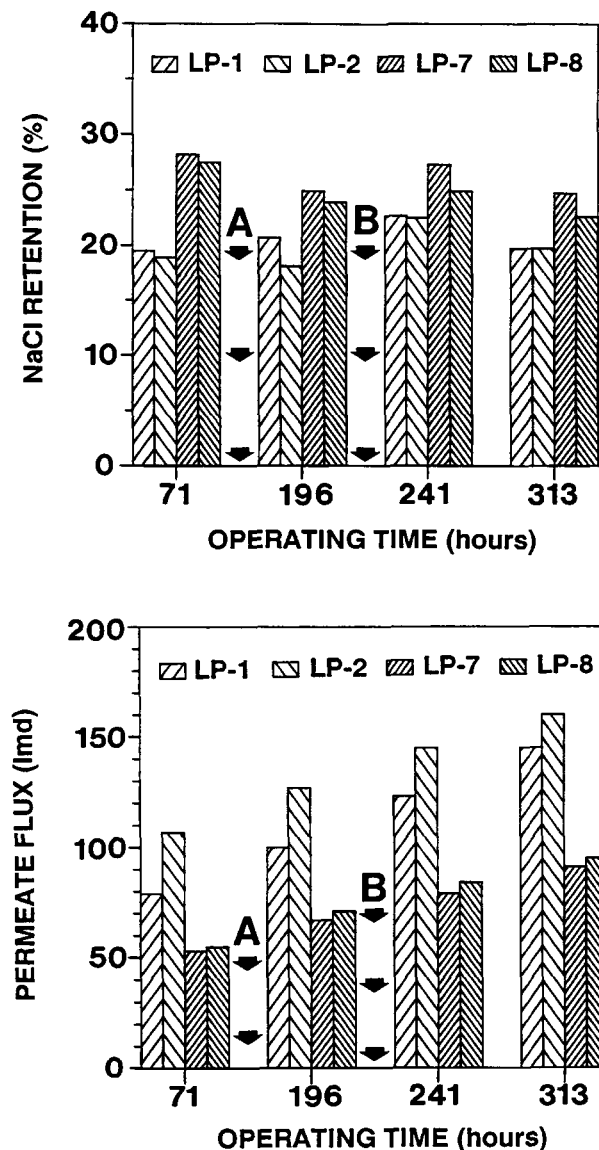
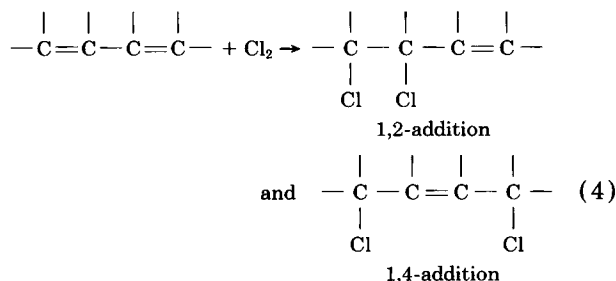


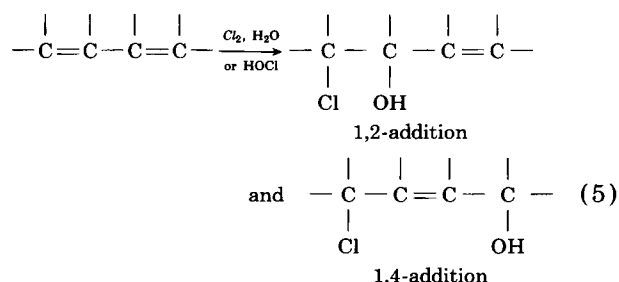
Figure 7 Effect of operating time on (a) NaCl retention and (b) permeate flux of dehydrated PVA tubular membranes tested at 0.5 MPa before and after chlorine shock treatments. Testing conditions: 20°C; pH 6.0; 2000 mg/L NaCl feed. (A) First chlorine treatment after 75 h; (B) second chlorine treatment after 200 h.

of adjacent carbons (1,2-addition), but also to the carbons at the two ends of the conjugated system (e.g., 1,4-addition in the case of conjugated dienes). This is shown in eq. (4) for the addition of Cl_2 to a conjugated diene:



Since addition of chlorine to double bonds is expected to increase the hydrophobic character of the membranes, chlorination of the dehydrated PVA does not explain the significant increases in water flux that occurred after chlorine shock treatment of membranes LP-1 to LP-8. Furthermore, chlorination of double bonds is usually carried out in an inert solvent such as carbon tetrachloride.

In aqueous solution, the reaction between Cl_2 and H_2O results in the *in situ* formation of hypochlorous acid, HOCl [eq. (2)]. Therefore, in the present study, it seems more likely that the addition of Cl_2 in the presence of H_2O will involve the addition of the elements of hypochlorous acid, namely, HO — and $-\text{Cl}$.⁹¹ If 1,2-addition occurs, as shown in eq. (5) for a conjugated diene, this reaction yields compounds containing chlorine and hydroxyl groups on adjacent carbons, i.e., chlorohydrins. Obviously, an increase in the length of the conjugated double-bond sequences will also increase the number of possible addition products:



The addition of both chlorine and hydroxyl groups to the double bonds of dehydrated PVA seems to offer the best explanation for the fact that the increase in permeate flux after chlorine treatment was not accompanied by a significant decrease in salt retention. However, the mechanism of interaction of hypochlorous acid with dehydrated PVA needs to

be investigated in considerably more detail before any definite conclusions can be reached. Other reactions, such as hydration (addition of H_2O to double bond) and hydroxylation (addition of two hydroxyl groups to double bond), could also result in an increase in water permeability, but this will certainly be accompanied by a loss of salt-retention capability.

CONCLUSIONS

- Both flat-sheet and tubular composite membranes could be prepared by depositing aqueous PVA solutions on asymmetric porous PES substrate membranes. The PVA coatings were insolubilized by dehydration during heat treatment in the presence of H_2SO_4 as catalyst. Elimination of water during heat treatment resulted in discoloration of the membranes due to formation of conjugated unsaturation.
- The influence of several variables on the RO performance of PES-PVA composite membranes was investigated. It was found that heat-treatment temperature and H_2SO_4 concentration played the most significant role in determining the extent of dehydration and, consequently, flux and salt-retention properties. The results of this investigation showed that a simple manipulation of one or two variables could lead to gel-layer membranes with widely differing salt-retention and water-permeability characteristics.
- Although shock treatment of the membranes with chlorine apparently had no detrimental effect on salt-retention capability, it resulted in a considerable increase in permeate flux. This could possibly be attributed to the interaction of hypochlorous acid with the double bonds of dehydrated PVA, resulting in addition of both chlorine and hydroxyl groups.
- For the flat-sheet PES-PVA gel-layer membrane system, NaCl retentions (tested on a 2000 mg/L NaCl feed) of 70–85% and permeate fluxes of 700–800 Lmd could be achieved at 2 MPa. Retention of divalent ions was even more promising and MgSO_4 retentions (tested on a 500 mg/L MgSO_4 feed) of > 90%, with accompanying fluxes of about 600 Lmd, could be obtained at 2 MPa.

- (e) The promising RO performances obtained at 2 MPa indicated that the PES-PVA gel-layer membrane system could function as medium-retention, medium-flux RO membranes at relatively low operating pressures, even in the absence of an interfacially formed salt-retention barrier. However, an optimization of salt-retention and water permeability characteristics by further chemical modification of partially dehydrated PVA will be desirable.
- (f) Double bonds introduced during acid-catalyzed dehydration provide convenient sites for chemical modification by, e.g., electrophilic addition, free-radical addition, and cycloaddition reactions. These possibilities are presently being investigated and will be reported on as results become available.
- (g) For desalination of brackish water and industrial wastewater, a thin salt-retention barrier will ultimately be formed on the PVA gel layer by interfacial polycondensation. In this case, the insolubilized PVA coating is not required to exhibit high salt-retention capabilities. Consequently, coating solution compositions and fabrication conditions can be adjusted to give low-retention, high-flux gel layers. For this purpose, the use of low catalyst concentrations and curing temperatures $\leq 100^{\circ}\text{C}$ will be advisable.

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