

Synthesis and Characterization of Poly(vinyl alcohol)-Based Membranes for Direct Methanol Fuel Cell

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ABSTRACT: Membranes made of poly(vinyl alcohol) (PVA) and its ionic blends with sodium alginate (SA) and chitosan were synthesized and characterized for their ion-exchange capacity (IEC) and swelling index values to investigate their applicability in direct methanol fuel cells (DMFCs). These membranes were assessed for their intermolecular interactions, thermal stabilities, and mechanical strengths with Fourier transform infrared spectroscopy, X-ray diffraction methods, differential scanning calorimetry, thermogravimetric analysis, and tensile testing, respectively. Methanol permeability and proton conductivity were also estimated and compared to that of Nafion 117. In addition to being effective methanol barriers, the membranes had a

considerably high IEC and thermal and mechanical stabilities. The addition of small amounts of anionic polymer was particularly instrumental in the significant reduction of methanol permeability from $8.1 \times 10^{-8} \text{ cm}^2/\text{s}$ for PVA to $6.9 \times 10^{-8} \text{ cm}^2/\text{s}$ for the PVA-SA blend, which rendered the blend more suitable for a DMFC. Low methanol permeability, excellent physicochemical properties, and above all, cost effectiveness could make the use of these blends in DMFCs quite attractive. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1154–1163, 2005

Key words: membranes; blends; cross-linking; biomaterials

INTRODUCTION

Fuel Cells have strongly emerged as a viable option for electrical power because of their high energy efficiency and their environmental cleanliness.^{1,2} Among the various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) has been well established for over 5 decades and has been successfully commercialized as a source of electrical power in spacecrafts and submarines.³ The direct methanol fuel cell (DMFC), a variation of the PEMFC, also uses a polymer membrane as the electrolyte, wherein the fuel, methanol, gets oxidized catalytically at the anode, producing protons.⁴ These protons migrate through the membranes and react catalytically with oxygen to produce water at the cathode. A DMFC operates at 50–100°C and is frequently used for tiny to mid-sized applications. A major problem generally encountered with DMFCs is the permeation of methanol fuel from the anode to the cathode.⁵

A successful fuel cell membrane must allow the easy transportation of protons. This requirement has

led to many investigations focused on cation-exchange membranes⁶ with fixed anionic charges, which facilitate proton transport. Currently, the most commonly used polymer is a perfluorinated sulfonic acid membrane best known by its trade name Nafion. The widely accepted attributes of this polymer are chemical stability and a hydrophobic matrix filled with hydrophilic sulfonic acid clusters connected by pores.⁷

An effective DMFC membrane must not only conduct protons but must also prevent methanol transport across the membrane, which results in its consumption without the production of electricity. This situation not only lowers the efficiency of fuel utilization but also adversely affects the cathode performance.⁸ The ion-exchange membranes used for fuel cells generally have good proton conductivity but can be poor methanol barriers. Fuel cells that use Nafion membranes can have up to 40% of their methanol unaccountable, despite operation at low methanol concentrations.⁹ Hence, the primary criteria for choosing a DMFC membrane is not only high proton conductivity but also its efficiency as a good methanol barrier, which allows it to effectively operate with methanol fuel. Poly(vinyl alcohol) (PVA) membranes are used in the pervaporation-based dehydration of alcohols because they preferentially permeate water and retain alcohol.¹⁰

In this study, we explored the potential of PVA membranes and their blends with ionic polymers for

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DMFCs. The selected ionomers, namely, the anionic ionomer, sodium alginate (SA), and the cationic ionomer, chitosan (CS), have high affinity for water and, when combined with pervaporation membranes such as PVA, are known to improve the rejection of alcohol without causing a decrease in flux.¹¹ As a result of their high water permeability, these membranes can bring about high proton conductivity when they are equilibrated with acids. In this study, we attempted to synthesize such membranes and evaluate their thermal, transport, and mechanical properties and their ion-exchange capacities (IECs) and methanol permeabilities.

EXPERIMENTAL

Materials

PVA with a molecular weight of 50,000 g/mol was purchased from Loba Chemie (Mumbai, India). The degree of polymerization of PVA was 1570 ± 50 , and the saponification degree was 99%. SA and CS used for blending with PVA were obtained from Loba Chemie and Sigma Co. Methanol, isopropyl alcohol (IPA), HCl, and glutaraldehyde were purchased from s. d. Fine Chemicals (Mumbai, India).

Preparation of the membranes

We prepared the homogeneous, nonporous membranes by casting the respective polymer solutions, followed by drying at room temperature for a period of 24 h and crosslinking in solution for different periods (20, 40, 60, and 120 min) to make them insoluble in water and to control swelling. The polymer solutions used were solutions of PVA (10 wt %), PVA-SA (90/10 wt %), and PVA-CS (90/10 wt %) containing 5 vol % of glutaraldehyde as a crosslinking agent. The solution used for crosslinking the dry polymer films at room temperature was an IPA-water (90/10 vol %) mixture containing 1 vol % of hydrochloric acid as a catalyst. After crosslinking for 30 min, the membranes were stored in distilled water for 24 h to remove traces of unreacted glutaraldehyde remaining in the membrane, if any, and to prevent further crosslinking.¹²

Membrane characterization

Fourier transform infrared spectroscopy (FTIR) studies

The FTIR spectra of PVA, crosslinked poly(vinyl alcohol) (XPVA), and its blends were scanned with a Nicolet-740 PerkinElmer-283B (Boston, MA) FTIR spectrometer. These spectra are shown in Figure 1.

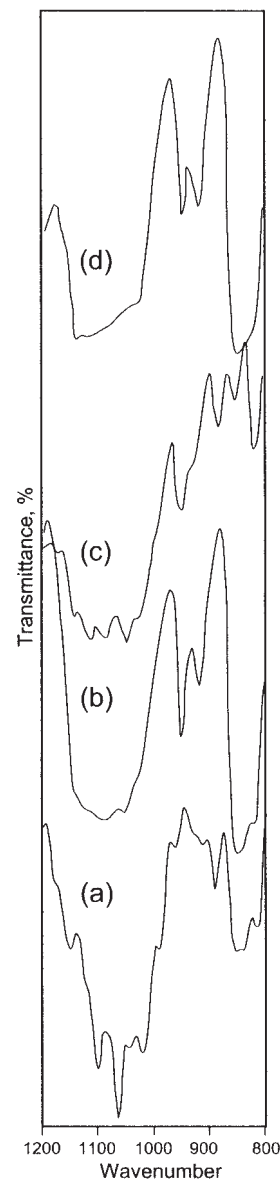


Figure 1 FTIR spectra for (a) PVA, (b) glutaraldehyde crosslinked poly(vinyl alcohol) (GPVA), (c) PVA-SA, and (d) PVA-CS.

X-ray diffraction (XRD) analysis

A Siemens D 5000 powder X-ray diffractometer was used to study the solid state morphology of XPVA in powdered form. X-rays with a wavelength of 1.5406 \AA were generated by a Cu K source. The X-ray diffractograms of the PVA membranes, crosslinked in a dry state for different time intervals, are shown in Figure 2. The angle of diffraction was varied from 0 to 65° to identify the changes in the crystal structure and intermolecular distances between the intersegmental chains after crosslinking.

Thermal analysis

Differential scanning calorimetry (DSC). The DSC spectra of the XPVA and PVA blend membranes were

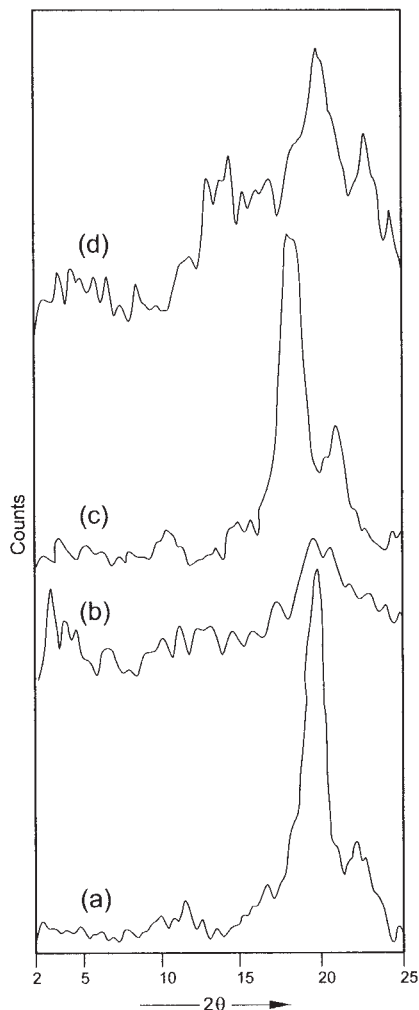


Figure 2 XRD of PVA membranes in a dry state crosslinked for different periods of time: (a) 20, (b) 40, (c) 60, and (d) 120 min.

obtained on a PerkinElmer DSC model 7. Measurements were performed over the temperature range 30–200°C at a heating rate of 5°C/min in hermetically sealed aluminum pans. Membrane samples were allowed to attain a steady state with the solvents and the sample pan conditioned in the instrument before the experiment was run. The results are shown in Figure 3. **Thermogravimetric analysis (TGA)** The thermal stability of the polymer films was examined with a Seiko 220TG/DTA analyzer from 25 to 700°C, heated at 10°C/min and flushed with nitrogen at 200 mL/min. The samples were subjected to TGA both before and after sulfonation to determine the thermal stability and decomposition characteristics. The results are shown in Figure 4.

Determination of the IEC

IEC indicates the number of milli-equivalents of ions in 1 g of the dry polymer. To determine the IEC,

specimens of similar weight were soaked in 50 mL of 0.01N sodium hydroxide solution for 12 h at ambient temperature. Then, 10 mL of each sample was titrated with 0.01N sulfuric acid.¹³ The sample was regenerated with 1M hydrochloric acid, washed free of acid with water, and dried to a constant weight. The IEC was calculated according to the following equation:

$$\text{IEC} = \frac{B - P \times 0.01 \times 5}{m}$$

where IEC is the ion-exchange capacity, B is the amount of sulfuric acid used to neutralize the blank sample, P is the amount of sulfuric acid used to neutralize the pervaporation membranes used in the study, 0.01 is the normality of the sulfuric acid, 5 is a factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration, and m is the sample mass (g).

Sorption characteristics

To determine their interaction, weighed samples of circular pieces of the polymer films (3 cm in diameter) were soaked in deionized water. The films were taken out after different soaking periods and quickly weighed after excess water/methanol was carefully

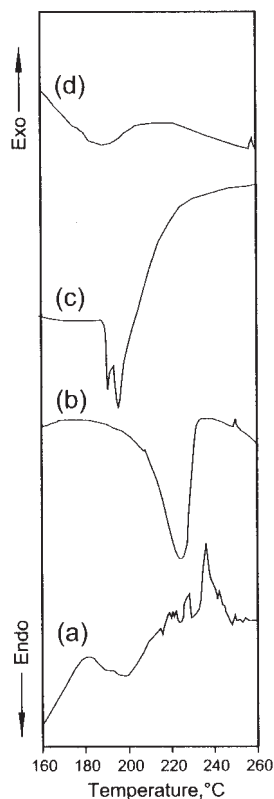


Figure 3 DSC thermograms of (a) PVA, (b) GPVA, (c) PVA-SA, and (d) PVA-CS.

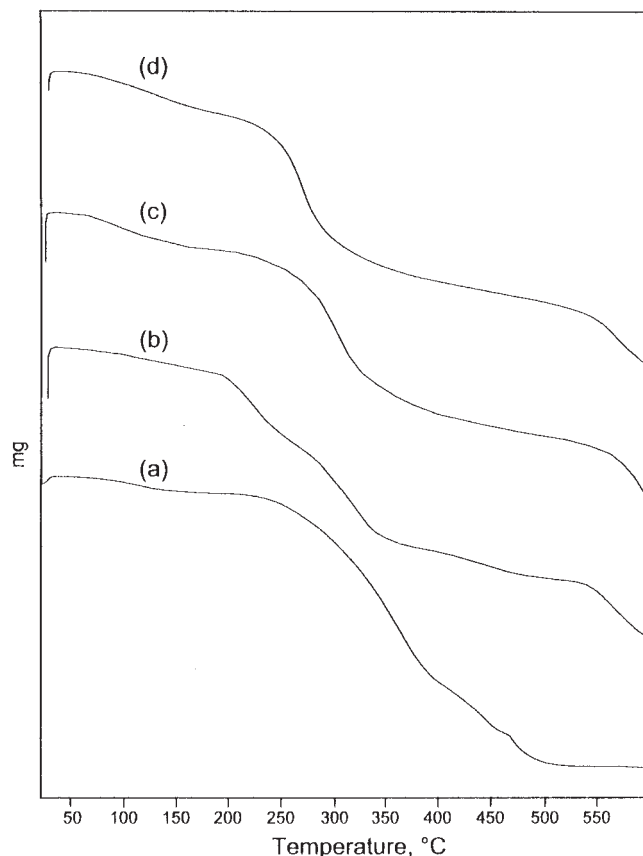


Figure 4 TGA curves of (a) PVA, (b) PVA-SA, (c) PVA-CS, and (d) CS.

wiped out to estimate the amount absorbed at a particular time. The film was then quickly placed back in the solvent. The process was repeated until the films attained steady state as indicated by a constant weight after a certain period of soaking time. The percentage sorption was calculated from the following equation:

$$\text{Sorption (\%)} = \frac{M_s - M_d}{M_d} \times 100$$

where M_s is the mass of the swollen polymer (g) and M_d is the mass of the dry polymer (g).

Mechanical properties

A universal testing machine (model AGS-10 kNG, Shimadzu) with an operating head load of 5 kN was used to carry out the tests. The cross-sectional area of a sample of known width and thickness was calculated. The films were then placed between the grips of the testing machine. The grip length was 5 cm, and the speed of testing was set at the rate of 12.5 mm/min. The tensile strength was calculated with the following equation:

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{Cross sectional area}} \text{ (N/mm}^2\text{)}$$

Permeability

The methanol permeability of the films was determined and calculated by the method described by Pivovar et al.¹⁴ Before testing, membranes were hydrated in deionized water for at least 24 h. The concentration of methanol in the samples was determined with gas chromatography. Samples were analyzed with a Shimadzu GC-15A gas chromatograph fitted with a diethylene glycol sebacate (DEGS)-packed column. A view of the cell used for methanol permeability determinations is shown in Figure 5.

Proton conductivity

The proton conductivity in water-equilibrated membranes was determined by a four-electrode electrochemical impedance spectroscopy method^{15,16} with a PGSTAT20 frequency analyzer by EcoChemie B. V. Spectra (The Netherlands), and spectra were recorded between 1 MHz and 0.1 Hz with 10 points per decade at a maximum perturbation amplitude of 10 mV. The

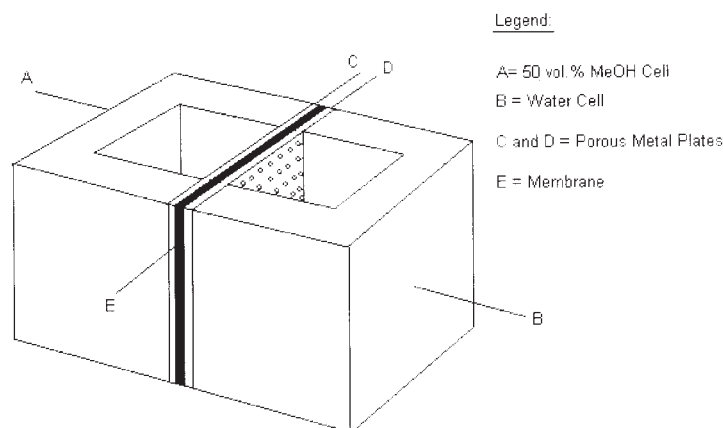


Figure 5 Methanol permeability cell.

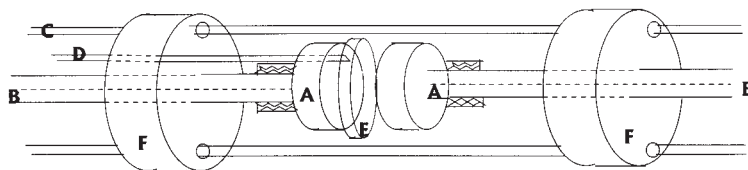


Figure 6 Schematic view of a conductivity cell. A represents the gold-plated electrodes, B represents the platinum wire, C represents the adjustable Hylam screws, D is the thermocouple, E is the membrane, and F represents the polytetrafluoroethylene (PTFE) disks.

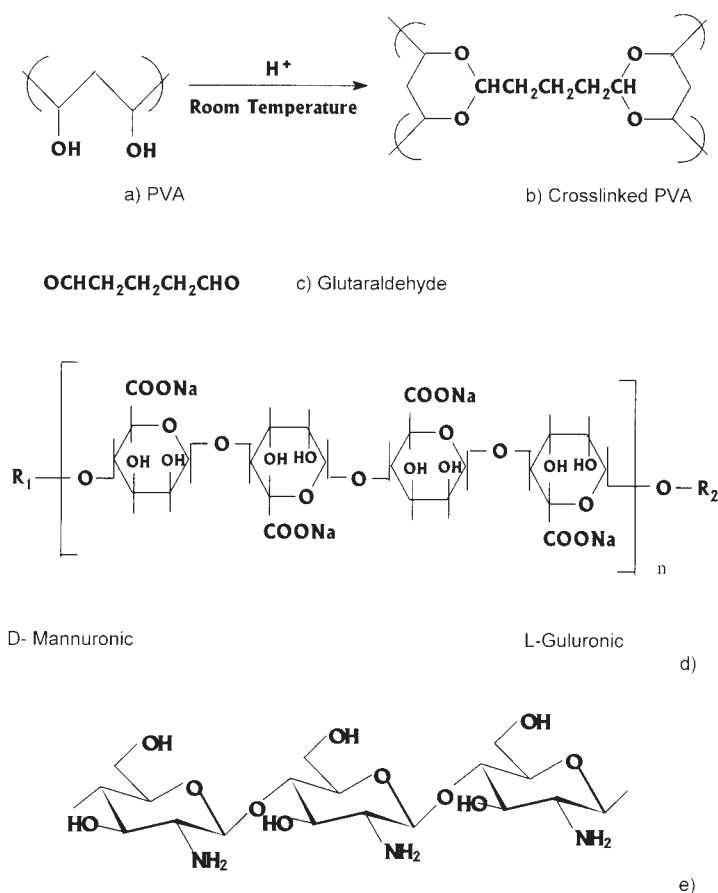
impedance spectra were fitted on the basis of the equivalent circuit shown by Haufe and Fleming.¹⁷ Zview 2.1b software by Scribner Associates, Inc. (Southern Pines, NC), was used for the curve-fitting procedure. To measure the temperature dependence of the conductivity, the cell was placed in a sealed, tempered, double-walled vessel, and the temperature was recorded in close proximity to the membrane with a K-type thermocouple. To avoid changes in the humidification levels during the measurements, a Teflon bowl filled with water was placed at the bottom of the vessel. Measurements were carried out in a conductivity cell at temperatures ranging from 30 to 150°C.

Figure 6 gives the schematic view of the conductivity cell.

RESULTS AND DISCUSSION

Membrane characterization

Scheme 1 represents the structures of the polymers used in the study and also the structure of XPVA. Scheme 1(c) reveals the formation of acetal linkages when PVA was crosslinked with glutaraldehyde. Glutaraldehyde acted as a crosslinking agent for all three polymers, and the aldehyde groups present in it re-



Scheme 1 Schematic representation of (a–c) the crosslinking action of PVA with glutaraldehyde in the IPA–water mixture, (d) the structure of SA, and (e) the structure of CS.

TABLE I
Percentage Sorption of the PVA, PVA-SA,
and PVA-CS Membranes

Reaction time (min)	Sorption in water (%)		
	PVA	PVA-SA ^a	PVA-CS ^b
20	74	90	86
40	50	71	63
60	47	68	52
120	—	67	49

^a The composition of PVA-SA was 90/10 wt %.

^b The composition of PVA-CS was 90/10 wt %.

acted with the hydroxyl groups of PVA, SA, and CS. This was also confirmed by FTIR spectroscopy. On blending, the —OH groups of SA and the —OH and —NH₂ groups of CS formed a hydrogen bond with the hydroxyl groups of PVA. Both the homopolymer solution and the blend solutions of PVA-SA and PVA-CS were clear to the naked eye. Neither separation into two layers nor any precipitation was noticed when the blends were allowed to stand for 1 month at room temperature.

FTIR spectroscopy

Figure 1 represents the FTIR spectra of the PVA, XPVA, XPVA-SA, and XPVA-CS membranes. The formation of acetal linkages were confirmed from both the crosslinking reaction and by the strong C—O—C stretching peak at 1110 cm⁻¹ in the FTIR spectrum. It was evident that the crosslinking reaction between PVA and glutaraldehyde occurred only after the diffusion of the HCl catalyst into the membrane in the presence of water from the crosslinking solution because the reaction of the hydroxyl groups of the PVA with the aldehyde groups of the glutaraldehyde can take place only with the aid of protons (H⁺). In other words, adjusting the soaking time in the crosslinking solution helped to control the degree of crosslinking of PVA and the blend membranes.

For pure CS, the most intensive band appeared at 1091 cm⁻¹, indicating the hydroxyl groups, as in Figure 1. The disappearance of this peak in the blend suggested that an intermolecular interaction between PVA and CS disturbed the crystallization of CS in the blend state.¹² However, in the blends, the characteris-

tic crystallization-sensitive band of PVA at 1140 cm⁻¹ remained as such without undergoing a significant change.

Sorption characteristics

For the study on the relative degree of crosslinking, the percentage sorption of membranes subjected to various crosslinking reaction periods was obtained and is shown in Table I. The sorption decreased with increasing crosslinking reaction time, indicating that the degree of crosslinking increased with increasing reaction time. As shown in Table I, the reaction rate of crosslinking depended on the membrane composition, especially on the content of ionomers. Also, the percentage sorption of the PVA-SA and PVA-CS blend membranes, in which the ionomer content was only 10 wt %, decreased with increasing reaction time. This slow crosslinking reaction of the blend membranes might have been due to the competition between the swelling process and the crosslinking reaction occurring simultaneously in the IPA-water mixture. As a result, the sorption of the blend membranes crosslinked for the same reaction time were larger than that of the uncrosslinked PVA membrane. We considered the ideal crosslinking to be 40 min, keeping in view both the sorption and the mechanical strength of the membrane.

Mechanical properties

The PVA, PVA-SA, and PVA-CS membranes exhibited tensile strengths of 51.31, 42.78, and 60.66 N/mm², respectively. As shown in Table II, an enhancement in the mechanical strength was observed for the PVA-CS blend membrane compared to that of the XPVA membrane. The PVA-CS blend membrane exhibited the highest mechanical strength of 60.66 N/mm², followed by the XPVA membrane (51.31 N/mm²) and the PVA-SA membrane (42.78 N/mm²). This effect could be explained from the fact that the blending of CS with PVA led to an intermolecular interaction between the two; that is, the —OH and —NH₂ groups in CS formed a hydrogen bond with the —OH group of PVA, and this interaction prevented CS from crystallization but did not significantly destroy the crystalline component of PVA.¹²

TABLE II
Tensile Strength and Percentage Elongation of the PVA, PVA-SA, and PVA-CS

Reaction time (min)	Tensile strength (N/mm ²)			Elongation at break (%)		
	PVA	PVA-SA	PVA-CS	PVA	PVA-SA	PVA-CS
40	51.31	42.78	60.66	7.5	6.8	12.0
60	39.18	29.62	46.36	6.9	6.2	11.1

TABLE III
IEC Values of Polymers Prepared for this Study

Polymer	IEC
PVA	0.499
PVA-CS	0.6217
PVA-SA	0.7976

The lower mechanical strength of the PVA-SA blend could be attributed to the rigidity induced into the polymer matrix on the introduction of SA, which was a highly rigid polymer. We also observed that the tensile strength and percentage elongation at break of PVA and its blend decreased with increasing crosslinking time.

XRD

The microstructures of the PVA membranes crosslinked under different conditions were studied with XRD. In this study, dried samples 20 μm thick were used. Figure 2 presents the XRD patterns of the crosslinked, dried PVA membranes. All of the dried PVA membranes, including those of the blends, showed very similar XRD patterns and appeared to be semicrystalline, despite the different degrees of crosslinking. All of the XRD analyses showed broad peaks around 10° on the contact angle (2θ), indicating the average intermolecular distance of the amorphous part and relatively sharp semicrystalline peaks centered around 20° of 2θ .¹⁸ From this result, we inferred that despite the different degrees of crosslinking, the average intermolecular distances in PVA and its blends were almost the same.

Thermal properties

DSC The thermal properties of the blends were examined with DSC. It was of particular interest to us to estimate how the thermal transition of PVA blends varied with blending because the SA and CS homopolymers used in this work did not show any significant transition in the temperature range of the DSC scan.

The results of the measurements are shown in Figure 3. The homogeneous PVA, represented by Figure 3(a), gave a relatively large and sharp melting endotherm with a peak [melting temperature (T_m)] around 201–208°C. On blending, a decrease in the endothermic peak was observed. That the T_m of the blend was somewhat lower than that of PVA implied that a comparable but attenuated relative crystallinity occurred because of blending. This was also confirmed by FTIR analysis.

TGA The thermal degradation behavior of PVA and its blends was examined with TGA, as shown in Fig-

ure 4. PVA exhibited two weight loss stages at 250–360 and 430–460°C followed by a final decomposition of the polymer that began around 460°C. The weight loss in the first and second stages could be attributed to the decomposition of the acetal linkage formed during crosslinking and the splitting of the main chain before the final decomposition of the polymer.

The crosslinked blend of PVA and SA also exhibited three weight loss stages ranging from 200–270, 290–340, and 540–570°C, followed by a final decomposition at 540°C. The blend appeared to be stable up to 340°C, beyond which the splitting of the chain was likely. The blend thus exhibited an increase in thermal stability compared to PVA or SA individually. However, the final decomposition of the blend was likely to occur around 570°C.

Unlike the XPVA/SA blend, the XPVA-CS blend exhibited two weight loss stages at 270–330 and 520–570°C, followed by the final decomposition of the polymer chain. An increase in the thermal stability of this blend was also evident. The second degradation of the blend occurred at 540°C, which was more exothermic than that of either PVA or CS polymers.

For pure CS, two weight loss stages at 240–280 and 530–560°C, followed by a final decomposition, was noted. The thermal degradation of CS took place in two steps, the first one at 275°C, followed by a second stage at 530°C. The causes for weight losses were similar to the ones stated previously.

IEC

IEC provides an indication of the content of ionic groups present in a polymer matrix,¹³ which are responsible for the conduction of protons, and thus is an indirect approximation of the proton conductivity. The results are based on the sample calculations reported in the Appendix.¹³ The IEC values of all of the polymers used for this study are tabulated in Table III. The IEC values for the PVA-SA (0.798) and PVA-CS (0.62) blends were higher than that of XPVA (0.499).

Permeability

The values of methanol permeability for the test membranes are shown in Table IV. The notable feature is the permeability of Nafion 117 ($27.6 \times 10^{-8} \text{ cm}^2/\text{s}$),

TABLE IV
Methanol Permeability of the Test Membranes

Membrane	Methanol permeability ($10^{-8} \text{ cm}^2/\text{s}$)
PVA	8.1
PVA-SA	6.9
PVA-CS	9.45
Nafion 117	27.6

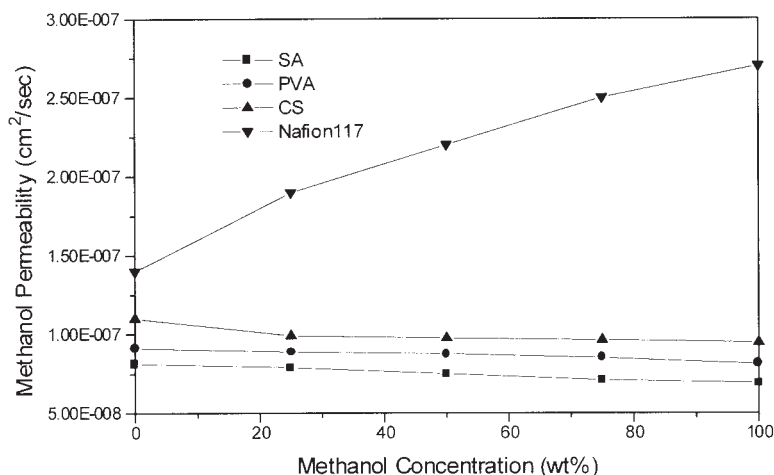


Figure 7 Methanol permeability versus concentration.

which is orders of magnitude higher than that observed in this study. This showed that a significant reduction in methanol crossover was achieved with the membranes, which were much less permeable to methanol. It is known that the methanol permeability in Nafion increases with increasing methanol concentration,¹⁴ but for PVA and its blends used in this study, the trend was entirely reversed. As shown in Figure 7, the methanol permeability in Nafion increased with the increasing concentration of methanol. Thus, at higher methanol concentrations, Nafion acted as a poor barrier, whereas the PVA and PVA blend membranes exhibited good barrier properties.

Among the polymers used in this study, the blend of PVA with the anionic ionomer SA displayed a relatively lower permeability of $6.9 \times 10^{-8} \text{ cm}^2/\text{s}$ compared with the XPVA membrane having a methanol permeability of $8.1 \times 10^{-8} \text{ cm}^2/\text{s}$. This result could be explained on the basis of the lack of significant chemical interaction between methanol and the ionic clusters introduced in the membrane on doping with SA. Although the methanol permeability for the PVA-CS blend ($9.45 \times 10^{-8} \text{ cm}^2/\text{s}$) was marginally greater than that of the PVA membrane, it still remained a good methanol barrier membrane because its permeability was only about one-third of the value reported for pure Nafion 117.

The permeability values obtained by crosslinking PVA membranes in the IPA-water solution without heating were much higher than those obtained with the thermally XPVA membranes ($1.4 \times 10^{-7} \text{ cm}^2/\text{s}$), as reported by Pivovar et al.¹⁴ The higher permeability values could be attributed to the different crosslinking method. Crosslinking the membranes in a solution at room temperature prevented the membrane from getting crystallized and dehydrated, which gave higher permeabilities than the thermally XPVA membranes.

Proton conductivity testing

The measurement of conductivity is important for the assessment of the contribution of various ionic groups in the blends. The conductivity of PVA was compared to its blend membranes as a function of temperature in the range 30–140°C in Figure 8. As shown in the graph, the blend of PVA and SA (0.01) showed better conductivity performance, followed by the PVA-CS blend (0.0099) and PVA itself (0.009). The proton conductivity of the membranes used in the study was much lower when compared to Nafion 117 (0.1 S/cm). However, the PVA-based membranes in a way compensated for the lower proton conductivity by exhibiting better barrier properties to methanol in comparison with Nafion, thereby limiting fuel losses. Moreover, these membranes allow a sizable reduction in the fabrication costs. There also exists the possibility of attaining conductivities close to Nafion by the doping of these membranes with acids.¹⁹

The Arrhenius plot in Figure 9 is an indication of the mechanism of proton transport. As shown in the plot,

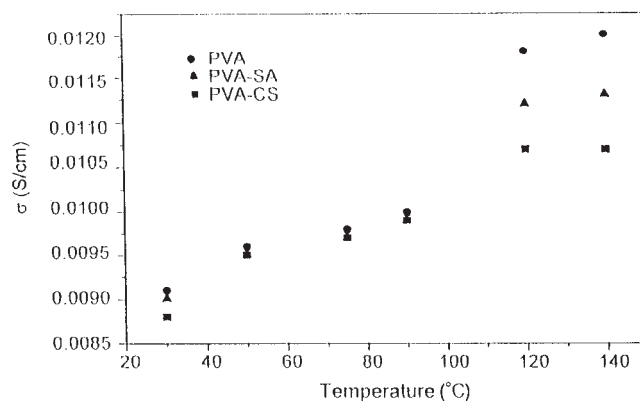


Figure 8 Proton conductivity versus temperature at 100% relative humidity. σ represents the proton conductivity.

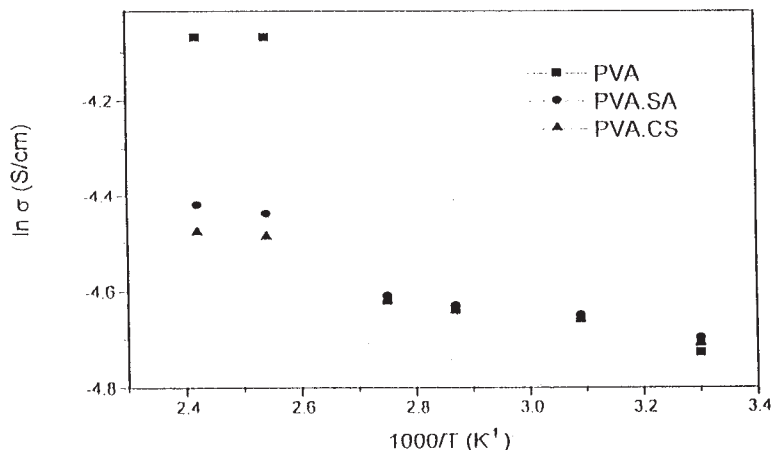


Figure 9 Arrhenius plot of conductivity versus temperature (T).

the proton transport might have occurred by two mechanisms. The first of these, a Grotthuss or jump mechanism, can be idealized as the proton being passed down the chain of water molecules. The second transport mechanism, called a *vehicle mechanism*, assumes a proton combines with the solvent molecules, yielding a complex like H_3O^+ or CH_3OH_2^+ . This complex then diffuses intact. In Nafion, both the mechanisms are believed to exist.²⁰ In this study, the vehicle mechanism was the most likely one because CH_3OH_2^+ or some similar methanol containing complex was responsible for the transportation of protons. When glutaraldehyde was used for the partial crosslinking of PVA and its blends, a fraction of the hydroxyl groups were chemically bonded, whereas a majority of them were still available for proton exchange.

CONCLUSIONS

The study revealed the possibility of the preparation of low cost PVA-based membranes with IEC values comparable to that of Nafion but with relatively lower methanol permeabilities. This result implies that an improvement in fuel utilization efficiency could be realized with proton-exchange membranes that control the magnitude of fuel bypass. To strike a balance between methanol permeability and IEC, the doping of the ionic polymers was restricted to 10 wt % in PVA. The crosslinking of PVA and its blends in IPA-water baths containing HCl catalyst appeared to be more effective than thermally induced crosslinking (in terms of attaining better methanol barrier properties), despite the retention of glutaraldehyde as the crosslinking agent in both cases.

Characterization revealed adequate thermal and mechanical stability in the membranes, which is essential for fuel cell applications. FTIR spectroscopy clearly indicated an interaction between PVA and the ionic polymers and the crosslinking agent. Not much

reduction in crystallinity was observed after crosslinking by the XRD patterns. Although these membranes offer no significant advantages over Nafion, so far as proton conductivity is considered, suitable modifications may yield more desirable results. Despite the achievement of only a marginal improvement in the proton conductivity of the blends relative to pure PVA, the possibility of enhancing the proton conductivity by improving the doping concentrations cannot be overlooked. The membranes made from PVA and ionic polymers appeared to be tailor-made for DMFCs because of their low methanol permeability and relatively good water sorption.

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APPENDIX

Calculations of IEC¹³

Consider the case of XPVA. The initial conditions were as follows:

Mass of dry XPVA = 0.01429 g.
 Normality of H_2SO_4 = 0.01N (N_1).
 Normality of NaOH = 0.01N (N_2).

After 12 h, the blank titration was 7.0 mL, the sample titration was 6.86 mL, and the volume of neutralized NaOH was 10 mL.

IEC of the membrane was calculated as follows:

IEC

$$= \frac{(\text{Blank titration} - \text{Sample titration}) \times \text{Normality} \times 5}{\text{Membrane weight}}$$

$$= 0.4895$$

IEC values for PVA-SA and PVA-CS were calculated on the same lines.

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