Preparation and Characterization of an Eco-Friendly Polymer Electrolyte Membrane (PEM) Based in a Blend of Sulphonated Poly(Vinyl Alcohol)/ Chitosan Mechanically Stabilised by Nylon 6,6

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Membranes for fuel cell applications were prepared using two polymer blends: poly(vinyl alcohol) (PVAL) and chitosan (CS), 80/20 (w/w) and 60/40 (w/w) with and without nylon. Sulfosuccinic acid (SSA) was used both as a crosslinking and a sulfonating agent. An increasing in the SSA content raised ionic exchange capacity and consequently proton conductivity in the membranes. The addition of nylon has improved membrane mechanical properties by decreasing stiffness. Membranes presented good proton conductivity (around 10^{-2} S cm^{-1}) and lower H_2 and methanol permeability rather than the standard membrane Nafion® 115. Membranes which showed to be stable under fuel cell operation were tested using hydrogen and methanol fuels. Membrane PVAL:CS, 80/20 (w/w), containing SSA crosslinker, (PVAL+CS)/SSA, of 4/1 (mol/mol), has shown the best performance under fuel cell environment. However, results have shown that an improvement is required in the adhesion between the membrane and the electrodes.

Keywords: *Fuel cell, Poly(vinyl alcohol), Chitosan, Nylon, Polymer electrolyte membrane (PEM)*

1. Introduction

Polymer electrolyte membrane (PEM) is an important component in many electrochemical devices. In PEM fuel cells, polymer electrolyte membrane allows the permeation of protons from the anode to the cathode, preventing also anode/cathode electronic direct contact. The most commonly used membrane in PEM fuel cells is a perfluorinated membrane, Nafion®, developed by DuPont.[1] However, this membrane presents some limitations, such as low ionic conductivity at low humidity, susceptibility to degrade at high temperatures and high cost.[2]

Several polymers used to produce PEM have been researched as alternatives to replace Nafion; among them, cost-effective and environmental-friendly polymer electrolytes can become promising substitutes. Therefore, natural polymer chitosan (CS) and synthetic polymer poly(vinyl alcohol) (PVAL) have drawn considerable attention.[3-6] CS is the second most abundant natural biopolymer obtained by chitin alkaline deacetylation. Due to its low cost production, natural abundance and eco-compatibility, CS is the preferred bio-material membrane for ultra-filtration, reverse-osmosis and pervaporation.[3,7,8] PVAL is also an attractive material for membrane electrolyte development as it is a cheap polymer holding high density functional –OH groups with potential for chemical crosslinking.[9-11] These polymers show good film forming properties, chemical resistance and the hydrophilic group high density allows chemical modifications of the polymer chain by crosslinking and grafting.[11,12]

Literature sustains that PVAL, CS and PVAL/CS blends in membrane forms have been reported by several researchers and used for some applications, e.g. in selective membranes and in ion exchange membranes.[13,14] Mobarak et al.[15] synthesized carboxymethyl chitosan membranes, by a solution-casting technique, for polymer electrolyte applications. Modified chitosan membranes presented amorphous properties and an ionic conductivity two orders of magnitude higher when compared to a pure chitosan membrane. Polymer electrolyte membranes for fuel cell applications were prepared using sulfonated PVAL synthesized from 4-formylbenzene-1,3-disulfonic acid and subsequently cross-linked with 1,3-bis(3-glycidyloxypropyl) tetramethyldisiloxane and 4,4'-oxydiphthalic anhydride. Such membranes presented good proton conductivity (0.218 S cm^{-1} at 70 °C) and low methanol permeability (at around 1.25×10^{-6} cm^2 s^{-1}), thus, suggesting that the membranes can be used in a direct methanol fuel cell (DMFC).[16] Ceramic-supported PVAL-CS composite membranes were also prepared for pervaporation dehydration purposes. Authors observed that the surface hydrophilicity decreased with chitosan content.[17] Zang et al.[18] prepared composite membranes comprising Nafion, chitosan and poly(vinyl alcohol) for DMFC. PVAL/CS membranes were used as a substrate while Nafion was used as a filling polymer. The electrostatic interaction between Nafion (polyanion) and CS (polycation) improved proton conductivity by 17 times when compared with PVAL/CS membrane.

Nylon presents characteristic amide groups in the backbone chain, being also called polyamide. Polar amide groups are able to form hydrogen bonds with other polymers and the polymer backbone itself, thus increasing polymer crystallinity. These characteristics can improve composite

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properties when blending nylon with other polymers, as described by Lu et al.[19] Chitosan/nylon 6,6 blends crosslinked with sulphuric acid were studied by Smitha et al.[20], who have evaluated physical-mechanical properties and their efficiency in a dioxane-water mixture dehydration. These blends presented good mechanical properties with improved stability in aqueous solutions; blends have also showed good selectivity to dioxane/water mixture.[20] In the present work, nylon 6,6 was used to reduce the excessive swelling of the prepared polymer electrolyte membranes, consequently improving their mechanical properties.

Literature presents scarce studies on membranes prepared from the blend of sulphonated PVAL/CS acting as a methanol-barrier. Hence, this study proposes the application of PVAL/CS membranes containing sulphonic acid groups with and without nylon 6,6 in a fuel cell, using hydrogen and methanol. Therefore, the prepared membranes were characterized by infrared spectroscopy, thermal gravimetric analysis (TGA), dynamical mechanical (DMA), water uptake and proton conductivity tests, followed by PEMFC and DMFC tests.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVAL) (99% hydrolysed with a molecular weight of 89,000 to 98,000 g mol^{-1}), chitosan flakes with high molecular weight, Nylon 6,6 and sulfosuccinic acid (SSA, 70% aqueous solution) were supplied by Sigma Aldrich Chemical Co. The solvent formic acid was purchased from Fisher Scientific. Polymers and acid structures used are shown in Figure 1.
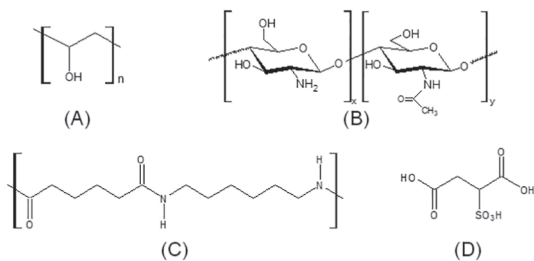

Figure 1: Monomeric unit of polymers and acid structures: (A) PVAL, (B) CS, (C) nylon 6,6 and (D) SSA.

2.2. Membrane preparation

10$_{wt}$% PVAL and 1$_{wt}$% CS aqueous solutions were prepared by dissolving the dry polymers in aqueous formic acid solution (50/50, w/w). Two polymer blends of PVAL/CS, 60/40 and 80/20 (w/w) were prepared. The blends were stirred for 2 h and SSA was added according to 16/1, 8/1 and 4/1 molar ratios, corresponding to the polymeric unit in the blend/SSA molar ratio. Final solutions were stirred for at least 24 h at room temperature, casted on a polystyrene plate and homogeneous membranes were obtained after solvent evaporation, at room temperature. Membranes were maintained at 100 °C for 1.5 h to

promote the crosslinking reaction in a vacuum oven. Nylon 6,6 addition to the blends was performed by preparing a 1wt% nylon solution in pure formic acid dropped to the PVAL/CS/SSA mixture two hours before completing the 24 h stirring time as described above. The amount of Nylon solution added corresponded to a 1 % mass fraction in relation to the polymer blend PVAL/CS. Membranes were further prepared as described above. Membrane chemical composition and their code are showed in Table 1.

Table 1: Chemical composition and molar ratio between monomeric unit and SSA.

Membrane code	PVAL/CS (w/w)	Blend/SSA (mol/mol)[a]	Nylon (wt%)
80_16/1	80/20	16/1	-
80_16/1 Nylon	80/20	16/1	1
80_8/1	80/20	8/1	-
80_8/1 Nylon	80/20	8/1	1
80_4/1	80/20	4/1	-
80_4/1 Nylon	80/20	4/1	1
60_16/1	60/40	16/1	-
60_16/1 Nylon	60/40	16/1	1
60_8/1	60/40	8/1	-
60_8/1 Nylon	60/40	8/1	1
60_4/1	60/40	4/1	-
60_4/1 Nylon	60/40	4/1	1

2.3. Characterization

Attenuated total reflection Fourier infrared (ATR-FTIR) spectra were recorded on a Nicolet IS 10 MX infrared spectrophotometer equipped cooled mercury-cadmium telluride detector (MCT). The internal reflection element was a germanium crystal and 16 scans were averaged for each spectrum at a resolution of 4 cm^{-1}.

Membrane thermal stability was evaluated using a thermogravimetric analyser (TGA) (TG209 F1 Netzch). A constant temperature ramp rate of 10 °C min^{-1} from room temperature up to 700 °C, under inert gas flow was applied. Before the analysis, membranes were maintained under vacuum for 24 h at 30 °C to remove absorbed water.

2.4. Water Uptake

Membrane sorption capacity was measured by immersing membrane samples into water at room temperature. First, samples were dried in a vacuum oven at room temperature until a constant weight, immersed into water for 24 h and wiped with a cleansing paper, and weighed quickly. This procedure was repeated until obtaining a satisfactory reproducibility. The swelling degree, Q, was calculated as follows (Equation 1):

$$Q = \left(\frac{m - m_0}{m_0} \right) \times 100 \qquad (1)$$

where m is the mass of the swollen sample and m_0 is the original mass.

2.5. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed using a DMA Q800-TA. Initially, membranes of PVAL/CS_SSA with and without nylon, 0.53 mm wide, were equilibrated at 100% relative humidity for 24 h. On the tensile deformation tests, samples were kept at 50 °C for 2 min and then submitted to 0.01 N s^{-1} rate strength, in which the maximum force applied was 18 N. The Young's modulus and the elastic strain were computed based on the strain and stress values obtained from average of three determinations for each membrane formulation.

2.6. Ion exchange capacity (IEC)

Membrane ion exchange capacity was determined through acid–base titration. The acidic dry membrane was immersed into 20 mL of saturated sodium chloride aqueous solution for 24 h in order to exchange protons for sodium ions. The released acid was subsequently titrated using a 0.01 mol L^{-1} sodium hydroxide standardized solution and the indicator phenolphthalein. IEC (mmol g^{-1}) was calculated using equation 2:

$$IEC = \frac{M \times V}{W_{dry}} \quad (2)$$

where M is the concentration of the titrant (mmol mL^{-1}), V is the added volume of titrant at the equivalent point (mL) and W_{dry} is the sample dry mass (g).

2.7. Fuel cell tests

PVAL/CS membranes with different sulfonation degrees were sandwiched between Toray carbon papers loaded with a catalyst considering the effective area of 4.84 cm^2, using a Pt loading of 0.5 mg$_{Pt}$ cm^{-2} ((10 wt.% Pt)/Vulcan®, ElectroChem SA) at the anode and the cathode. PEMFC was operated at 50 °C with a feed flow rate of 200 mL min^{-1} of hydrogen at 1 bar and 400 mL min^{-1} of air at 1 bar; the relative humidity used during the tests was 75%, 90% and 100%. Membranes were characterized by electrochemical impedance spectroscopy (EIS) and polarization curves. Each polarization curve was obtained in potentiostatic mode, starting at OCV and decreasing the potential. AC impedance spectroscopy was obtained in the frequency range from 100 kHz to 100 mHz with a 5 mV perturbation amplitude using a Zahner IM6e electrochemical workstation coupled with a potentiostat PP-241. The proton conductivity (s) was obtained using the following equation 3:

$$\sigma = \frac{l}{R \cdot S} \quad (3)$$

where s is the proton conductivity (S cm^{-1}), l is the distance between the electrodes (membrane thickness , cm), R is membrane resistance (W), and S is the surface area required for a proton penetrating the membrane (electrode area) (cm^2). Membranes with the best mechanical properties and proton conductivity were further tested in a direct methanol fuel cell. Thus, membranes were sandwiched between Toray carbon papers loaded with catalyst considering the effective area of 4.84 cm^2. Pt was used as a catalyst on the cathode (0.5mg$_{Pt}$ cm^{-2} (10 wt. % Pt)/Vulcan®, SA) and Pt:Ru on the anode (1.0 mg$_{Pt:Ru}$ cm^{-2} (20 wt. % PtRu(1:1 Pt:Ru)/Vulcan®, ElectroChem, SA). DMFC tests were performed at 50 °C with a 2 mL min^{-1} feed flow rate of methanol solution (2 mol L^{-1}) on the anode and 300 mL min^{-1} of oxygen on the cathode at 100 % of relative humidity. Fuel cell characterization was performed as described above.

Linear sweep voltammetry (LSV, scan rate of 5 mV min^{-1}) was employed to evaluate hydrogen and methanol crossover. Therefore, hydrogen or 2 M methanol solution were fed into the cathode compartment of the electrolytic cell and the cathode served as a reference/counter electrode. In this configuration, hydrogen evolves at the cathode which is being used as a dynamic hydrogen reference electrode (DHE); the same process occurs when methanol is used. On the other hand, nitrogen (2 L$_N$ min^{-1}, atmospheric pressure) was fed into the anode compartment of the electrolytic cell, serving as a working electrode.

3. Results and Discussion

3.1. Infrared

Figure 2 shows membrane PVAL/CS_SSA infrared spectra crosslinked at 100 ºC for 1.5 h in the region 3700-600 cm^{-1}, being (A) the membrane spectra with 80/20 PVAL/CS and (B) the membrane spectra with 60/40 PVAL/CS, both with different SSA amounts. The absorption bands that characterize polymers PVAL and CS are described in Table 2 and can be seen in Figures 2 (A), (B). However, the absorption band intensities are not the same in all spectra since the blends were formed from different polymer quantities. Absorption bands that characterize chitosan in the region 1650-1300 cm^{-1} can be observed pre-eminently in the membrane spectra formed from the blend 60/40 (PVAL/CS) (Figure 2 (B)).

The absorption band of esters (-COO-) is at 1725 cm^{-1} and can be observed in Figure 2A, denoting that the crosslinking reaction involving the hydroxyl group from PVAL or CS and SSA has occurred. This absorption band intensity increases with SSA concentration in the molar range of 16/1, 8/1 and 4/1 (polymer monomeric unit /SSA). The absorption band at 1235 cm^{-1} is related to C-O ester group stretching mode and also increases with the polymer monomeric unit/SSA ratio (Figure 2A). However, a small absorption band dislocation was observed, 1718 cm^{-1} and 1220 cm^{-1}, respectively, when the membranes formed from the 60/40 (PVAL/CS) blends and SSA were analysed (Figure 2B). This is probably related to the higher amount of CS in the blend and consequently to an increased amino group content. These amino groups react with SSA, forming the amide group, causing a band shift to lower wavenumbers. It is possible to identify the absorption bands that indicate the reaction between SSA and the amino groups: at 1640 cm^{-1} in the 80/20 blend (Figure 2A) and at a higher intensity, 1630 cm^{-1}, for the 60/40 blend. When increasing SSA content, absorption bands in the region 3500-3200 cm^{-1} show lower intensities, since the reaction between the hydroxyl and the amino groups with SSA reduces these free groups in
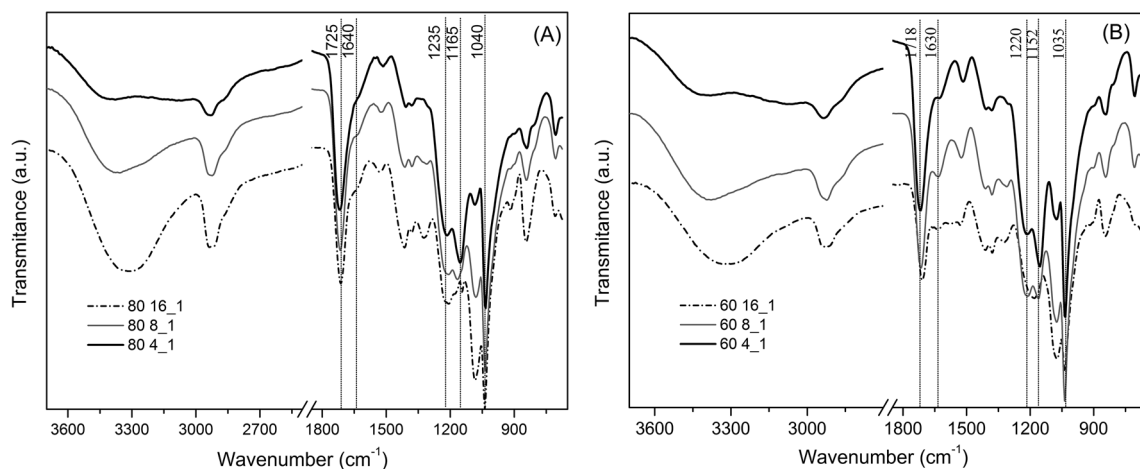
Figure 2: Infrared spectra of blends PVAL/CS, 80/20 (A) and 60/40 (B), with SSA in the indicated ratio, in the region of 3700-650 cm^{-1}.

Table 2: IR bands of polymers PVAL[11], CS[21] and Nylon 66[22] and compound SSA[23]:

Sample	IR band (cm^{-1})	Description*
PVAL	3300	ν(-OH)
	2940	ν(-CH$_2$)
	1433	ν_{as}(C-H)
	1140	ν(C-O) and ν(C-C) (crystallinity degree)
	1096	ν(C-O)
CS	3750-3000	ν(O-H) overlapped to the ν_s(N-H)
	2920 and 2875	ν_{as}(C-H) and ν_s(C-H)
	1660	ν(C=O) secondary amide
	1553	ν(-NH$_3^+$) protonated amine
	1420,1376	ν(C-H)
	1313	ν_s(-CH$_3$) tertiary amide
	1260	ν(C-O-H)
	1156,1065, 1026	ν_{as}(C-O-C) and ν_s(C-O-C)
	890	ν(C-H)
	3300	ν(N-H)
	3080	ν_s(N-H)
Nylon 66	1640	ν(C=O) amide I
	1540	ν(C-N) and ν_{as}(CO-N-H)
	940	ν(C-CO)
SSA	3200-3600	ν(O-H) from -SO$_3$H, COOH and free water
	2800-2900	ν_{as}(C-H) and ν_s(C-H)
	1724	ν(COCH)
	1632	ν (-OH)
	1300-1500	ν (C-H)
	1167	ν_{as}(O=S-O)
	1041	ν_s (S-O)
	860	ν(C-H)

the polymer. The absorption band around 1040 cm^{-1} results from symmetric S-O stretching and can be observed in the spectra of both blends and is due to SSA in the membranes.

The addition of nylon has not promoted any visible changes in the membrane infrared spectra, probably, due to the low quantity of nylon used. Moreover, nylon presents absorption bands that overlap CS absorption bands, as observed in Table 2.

3.2. Thermal properties

Thermal stability of PVAL/CS_SSA and PVAL/CS_SSA/Nylon membranes was studied by TGA (Figures 3, 4). Thermograms of PVAL/CS/SSA blends show several decomposition steps, better appreciated in the derivative thermogravimetry (DTG) plots inserted into the TG plots. The main degradation stages occur due to dehydration, degradation and decomposition of polymeric backbone and blend.[4,6,24] Thermal degradation starts at 140 °C for lower CS content membranes (Figure 3 (A)). DTG (Figure 3 (A)) shows that SSA crosslink interferes directly with membrane degradation process. Membranes with a larger concentration of CS (Figure 3 (B)) present best stability and polymer degradation only starts after 190 °C, with the exception of membrane 60_4/1. This exception occurred, probably, due to the high SSA content in the membrane, which can induce membrane degradation at lower temperatures.[6]

Figure 4 (A) shows that the nylon in 80/20 (PVAL/CS) blends improved thermal stability of all the membranes tested. For 60/40 (PVAL/CS) blends, thermal stability of all membranes was not affected by nylon (Figure 4 (B)). In the DTG graphics inserted in Figure 4 (A), (B) the initial temperature for membrane degradation can be accurately observed.

3.3. Water Uptake, Mechanical Properties and Ion Exchange Capacity (IEC)

PVAL has a large density of hydrophilic groups –OH in the polymeric chain that can absorb water. Therefore,
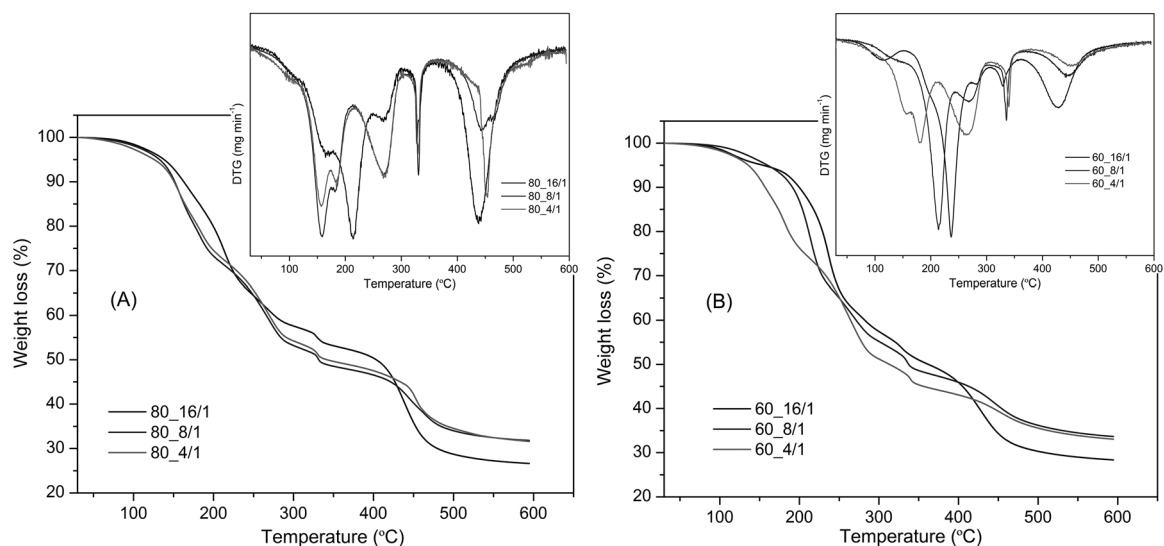
Figure 3: TG thermograms for the blends PVAL/CS, 80/20 (A) and 60/40 (B), respectively, with SSA in the proportion indicated inside the plots.
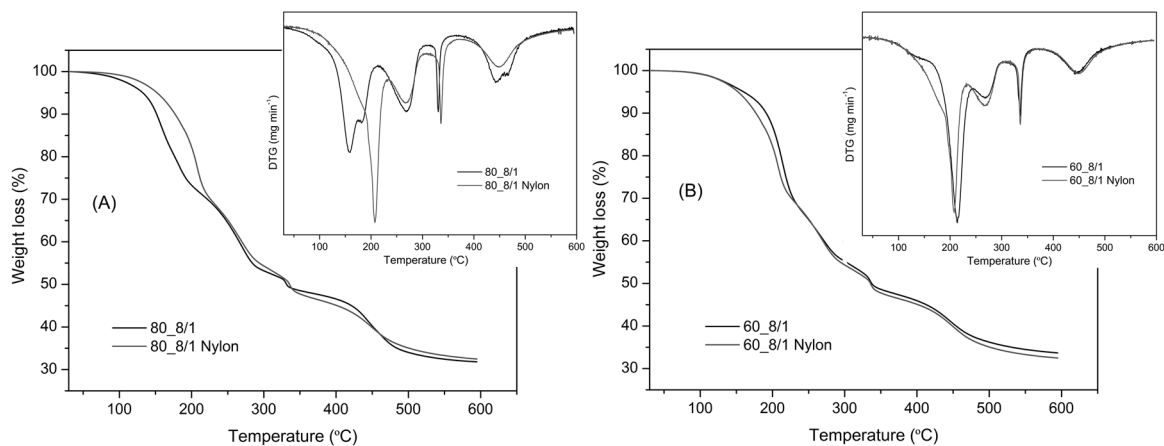

Figure 4: Comparison between TG thermograms for the blends PVAL/CS, 80/20 (A) and 60/40 (B), respectively, with the proportion of 8/1 of SSA and with or without nylon addition.

membranes with a higher content of PVAL, absorbed more water (80/20 blends) than the lower PVAL content blends (60/40) (Figure 5). CS has two hydrophilic groups in its chain (-OH and -NH3) but the most part of its chain presents hydrophobic properties. Therefore, increasing SSA content in the blends increases the hydrophilic groups. On the other hand, the rise of crosslinking degree occurs. Moreover, 80/20 blends (80_16/1 and 80_8/1) water uptake decreases as SSA concentration increases, probably due to the rise of crosslinking degree, which consumes free –OH groups. Contrarily, membrane 80_4/1, with the highest SSA content, presents a water uptake similar to membrane 80_8/1. In this case, the crosslinking reaction effect is probably compensated by the presence of SSA hydrophilic groups. Concerning 60/40 blends, it can be suggested that CS interacts by hydrogen bonding with PVAL, decreasing the free volume of the polymeric membranes. This causes a more rigid structure and decreases water uptake. Results have also shown that the addition of SSA to 60/40 blends may interfere with the

PVAL/CS interaction, and as SSA has hydrophilic groups the membranes absorb more water. However, with the presence of higher SSA contents the crosslinking density increases and the free volume in the polymeric structure reduces, this resulting in a decrease of water molecule mobility and consequently less water is uptaken.

Nylon induced two different effects in membrane water uptake (Figure 6); 60/40 blends with Nylon showed a slightly increase in water absorption, probably due to the changing operated by Nylon in the interaction between the PVAL and CS or/and between PVAL/CS and SSA. For 80/20 blends, nylon addition decreased water uptake, most likely to its easy interaction with the free –OH from PVAL, decreasing the number of –OH able to take up water in the membranes. The interaction among the polymers can also decrease membrane free volume, thus becoming more difficult for water diffusion.

Membrane mechanical properties were evaluated by tensile tests using DMA (Table 3). Membranes prepared
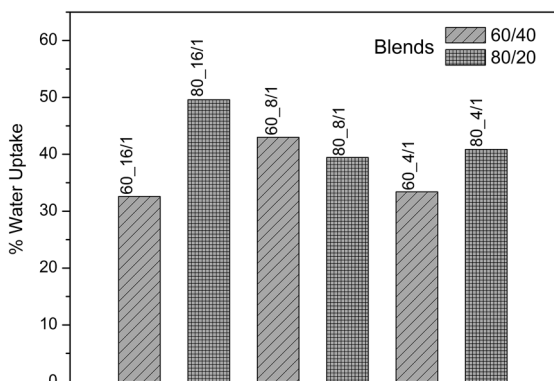
Figure 5: Water uptake percentage to blends 60/40 and 80/20 with different SSA ratios.

with PVAL/CS and SSA are in general stiff, as the crosslink promoted by SSA restricts chain segmental mobility. The addition of nylon caused a decrease in the Young's modulus (E) and an increase in the elastic strain (ε_e), possibly, related to nylon plasticizer behaviour, facilitating the movement among the chains. This plasticizer action was more pronounced on the 60/40 blends, where the Young's modulus decreased significantly with nylon addition. These results confirm the greater interaction between nylon and the 80/20 (PVAL/CS) blends, as explained above. The results of elastic strain (ε_e), showed in the Table 3, corroborate with the Young's modulus results and confirm the plasticizer action of Nylon in the membranes. Figure 7 shows a representative tensile test curves for each blend studied.

IEC indicates the density of ionisable hydrophilic groups in the polymer matrix which is responsible for membrane ionic conductivity. IEC increased with SSA content, from 1.1 to 3.92 mmol g^{-1} in the 60/40 (PVAL/CS) blend and from 1.56 to 3.99 mmol g^{-1} in the 80/20 blends. This is related to the sulfonic acid group in SSA (Table 3). All the blends presented an IEC value higher than the one obtained for Nafion® 115, 0.91mmol g^{-1}. On the other hand, blends prepared with nylon presented an IEC slightly higher than those without nylon, but this result is probably due to the residual solvent, pure formic acid, used to prepare the nylon solution,
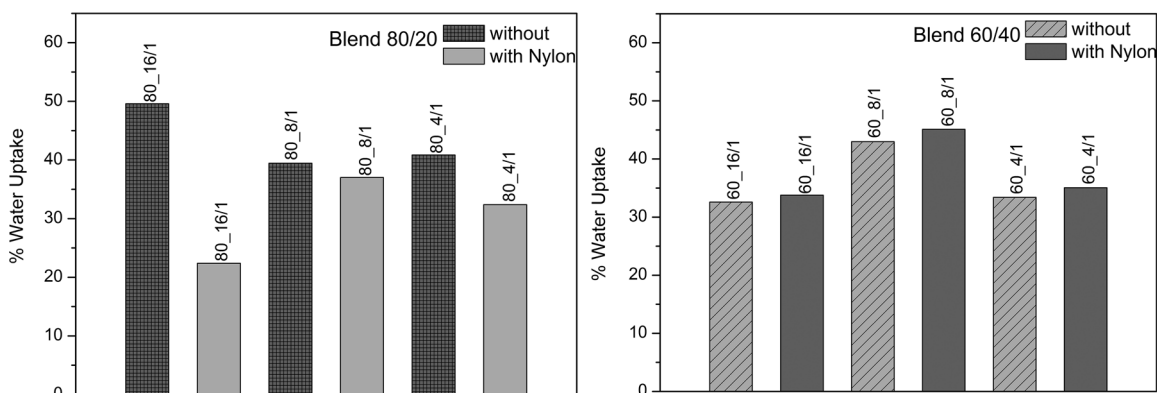
3.4. Fuel cell tests

PVAL/CS_SSA and PVAL/CS_SSA/Nylon membranes were tested in a fuel cell using H_2/O_2. Proton conductivity, permeability and I/V curves were obtained and data are shown in Table 4. Results are presented only for membranes that have showed to be stable under fuel cell conditions. According to that, 60/40 (PVAL/CS) membranes showed low stability inside the fuel cell and only membranes 60_4/1 and 60_4/1 nylon were tested. Nylon decreased proton conductivity on the membranes with a 4/1 monomeric unit/SSA molar ratio. The standard membrane, Nafion® 115, under the same conditions (90 % relative humidity), presented a proton conductivity of 5.7x10^{-2} S cm^{-1},[6] 80/20 membranes showed an increasing in the proton conductivity with the rise of acid content and humidity level. These membranes have shown proton conductivity similar to some results found in the literature for membranes using PVAL or CS.[4,5,11,18] Proton conductivity results are in agreement with IEC values, both increased with SSA quantity.

Hydrogen permeability increased with nylon in both cases. This suggests that polar molecules had some difficulty passing through the membrane structure formed with PVAL, CS and nylon (eg. water, as mentioned above) and that the nonpolar molecules (H_2) passed easily through the same structure. Permeability to hydrogen is shown in Table 4. These values were lower than the corresponding ones for the Nafion® 115 membrane, 8.33x10^{-12} mol cm bar^{-1}s^{-1}cm^{-2}, under the same conditions.[6]

PEMFC performance employing PVAL/CS/SSA and PVAL/CS/SSA_Nylon membranes was studied (Table 5). Membrane 80_4/1 showed the best performance in the fuel cell environment, followed by 60_4/1 Nylon. Membranes formed from the 80/20 (PVAL/CS) blends presented better performance than the corresponding 60/40 (PVAL/CS) blends. Moreover, increasing relative humidity augmented peak power density for most of the membranes tested. In a previous study, membranes using PVAL/SSA loaded with boehmite nanoparticles had shown a PEMFC performance, on average, twice better than the membranes currently analysed.[6] This probably happened due to the presence of the hydrophobic CS and nylon, in the current work, decreasing proton transport.

Figure 6: Water uptake percentage to blends 80/20 and 60/40, without and with nylon, with different SSA ratios.

Table 3: Water uptake, Young's Modulus (E), elastic strain (ε_e) and ion exchange capacity (IEC) to analysed membranes.

Membrane code	Water uptake (%)	E (MPa)	ε_e (%)	IEC (mmol g^{-1})
60_16/1	32.60±1.03	2.589±0.04	2.35±0.10	1.10±0.11
60_16/1 Nylon	33.78±3.14	0.788±0.02	2.65±0.07	1.32±0.03
60_8/1	42.99±2.87	1.281±0.02	1.21±0.02	2.72±0.04
60_8/1 Nylon	45.12±1.33	0.642±0.05	2.00±0.10	2.83±0.03
60_4/1	33.40±2.62	2.339±0.04	1.11±0.06	3.74±0.15
60_4/1 Nylon	35.05±1.06	0.418±0.03	2.57±0.04	3.92±0.02
80_16/1	49.58±0.61	2.336±0.07	2.18±0.04	1.56±0.10
80_16/1 Nylon	22.39±1.86	2.268±0.05	3.08±0.08	1.92±0.03
80_8/1	39.43±3.34	1.960±0.02	1.76±0.05	2.26±0.07
80_8/1 Nylon	37.01±1.86	1.709±0.05	1.88±0.11	2.37±0.02
80_4/1	40.86±2.56	10.14±0.15	1.18±0.04	3.93±0.15
80_4/1 Nylon	32.38±1.75	3.413±0.11	1.95±0.06	3.99±0.04
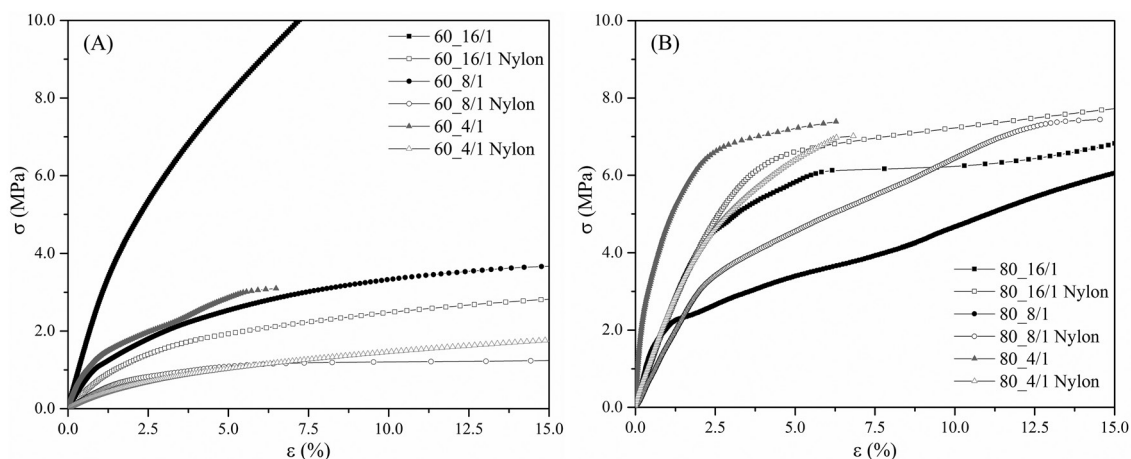
Figure 7: Representative tensile test curves for blends 80/20 and 60/40, without and with nylon, with different SSA ratios.

Table 4: Proton conductivity (σ)and permeability (ρ) to fuel measurement in the fuel cell.

Membrane code	75 % RH		90 % RH		100 % RH	
	σ (10^{-2} S cm^{-1})	ρ (10^{-11} mol cm bar s^{-1} cm^{-2})	σ (10^{-2} S cm^{-1})	ρ (10^{-11} mol cm bar s^{-1} cm^{-2})	σ (10^{-2} S cm^{-1})	ρ (10^{-11} mol cm bar s^{-1} cm^{-2})
60_4/1	0.583	4.507	-	-	-	-
60_4/1 Nylon	0.235	10.77	0.575	7.754	1.028	6.476
80_16/1	0.003	3.257	0.017	3.970	0.186	20.47
80_8/1	0.119	3.433	-	-	-	-
80_4/1	0.382	4.959	0.108	4.687	1.191	5.483
80_4/1 Nylon	0.242	12.89	-	-	0.727	16.64

* Fuel cell operation temperature of for all the tests was 50 °C.

Membranes 80_4/1 Nylon and 60_4/1 Nylon were also tested in a DMFC environment (Figure 8); peak power density was 11.43 mW cm^{-2} and 8.83 mW cm^{-2}, respectively. Methanol permeability was very low, 9.92 x 10^{-11} mol cm bar s^{-1}cm^{-2} and 6.66 x 10^{-11} mol cm bar s^{-1}cm^{-2}, respectively. Brandão et al.[25] tested methanol permeability using the standard Nafion membrane 1135 (89 mm), under similar experimental conditions as those used in this study, and a value of 2.00 x 10^{-9} mol cm bar^{-1} cm^{-2} was observed, ca. 100 times higher.

Methanol is a polar molecule and as already mentioned before has difficulty to permeate the membrane. Despite the low methanol permeation obtained, further fuel cell tests are still required in order to optimize membrane electrode assembly fabrication, and accurately determine the performance of these membranes. In practice, membranes described may encounter large interfacial resistance due to the poor adhesion between membranes and catalyzed electrodes, resulting in a poor cell performance, using either H$_2$ or methanol as fuel.

Table 5: Maximum values to current density (*j*) and power density (*P*).

Membrane code	75 % RH		90 % RH		100 % RH	
	j (mA cm^{-2})	P (mW cm^{-2})	j (mA cm^{-2})	P (mW cm^{-2})	j (mA cm^{-2})	P (mW cm^{-2})
60_4/1	22.73	5.89	-	-	-	-
60_4/1 Nylon	67.47	17.77	118.4	30.27	177.2	54.08
80_16/1	9.067	2.203	15.89	3.590	61.67	15.28
80_8/1	45.47	10.38	-	-	-	-
80_4/1	274.1	58.86	251.1	69.48	-	-

* Fuel cell operation temperature of for all the tests was 50 °C.
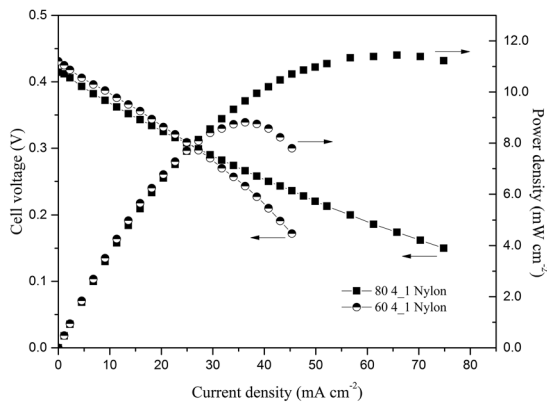

Figure 8: Polarization curves for the DMFC tests using the PVAL/CS/SSA membranes indicated 80_4/1 Nylon and 60_4/1 Nylon.

4. Conclusions

PVAL/CS based membranes were prepared and characterized for fuel cell applications. SSA was used as a crosslinking and a sulfonating agent, acting simultaneously as an inter-crosslinked structure and a sulfosuccinic acid functional group. SSA content increased proton dissociation due to the good connectivity between the ionic sites and the higher density of protogenic groups. Nylon was added to improve the mechanical properties and the results have shown that it had promoted a decreasing in the membrane stiffness. Moreover, as the nylon backbone is formed mostly by hydrophobic molecules, a decrease on methanol permeability in the membranes tested was observed. However, nylon induced a slightly decrease in proton conductivity. This happened probably due to an improvement on polymers interaction, thus narrowing the hydrophilic channel size and hindering proton diffusion. Membranes have showed a quite poor fuel cell performance using H_2 and methanol. This problem is probably due to a large interfacial resistance, deriving from a poor adhesion between the catalytic layer and the membranes, resulting in a poor cell performance.

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6. References

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