

Crosslinked Chitosan/Poly(Vinyl Alcohol) Blends with Proton Conductivity Characteristic

M. A. Witt,^a G. M. O. Barra,^b J. R. Bertolino^a and A. T. N. Pires^{*,a}

^aDepartamento de Química and ^bDepartamento de Engenharia Mecânica,
Universidade Federal de Santa Catarina, 88040-900 Florianópolis-SC, Brazil

A quitosana é um polissacarídeo natural obtido a partir da reação de desacetilação da quitina, sendo o polímero natural mais abundante, que apresenta propriedades químicas e físicas atrativas, como por exemplo, as requeridas para obtenção de membranas poliméricas. Neste trabalho a quitosana em solução de ácido clorídrico foi quimicamente modificada com ácido sulfosuccínico (SSA), o qual reticula as cadeias poliméricas de quitosana e atua como doador de prótons. O meio ácido induz a reação de ligação cruzada através da protonação do grupo carboxílico livre. A membrana polimérica foi obtida a partir da evaporação do solvente de uma solução aquosa de poli(vinil álcool) (PVAL) e quitosana-SSA. A influência da concentração de SSA no grau de reticulação das cadeias de quitosana foi avaliada por espectroscopia de infravermelho. A capacidade de troca iônica (IEC) e valores de absorção de água foram avaliados em relação à concentração de SSA presente no meio. As características físico-químicas, tais como condutividade protônica e condutividade elétrica, indicam a viabilidade da utilização desses materiais como membranas poliméricas em células a combustível.

Chitosan is a polymer which is easily obtained from the deacetylation of chitin, the second most abundant natural polymer. It offers attractive chemical and physical properties, including those required to obtain membranes. In this study, chitosan in chloridric acid solution was chemically modified with sulfosuccinic acid (SSA), which acts as a crosslinking agent and proton donor. The chloridric acid medium promotes the crosslinking reaction through inducing the protonation of free carboxyl groups. The membrane was obtained through casting of poly (vinyl alcohol) (PVAL) and chitosan-SSA solution. The influence of the SSA content on the crosslinking degree of the chitosan was evaluated through FTIR analysis. The ion exchange capacity (IEC) and water absorption values were also related to the SSA content in the systems. The physicochemical characteristics, such as the proton and electrical conductivity values, indicated the viability of the utilization of these materials as polymer electrolyte membranes (PEM) in fuel cells.

Keywords: crosslinked chitosan, sulfosuccinic acid, poly(vinyl alcohol), proton conductivity

Introduction

In recent decades, climate change has played a crucial role in the lives of human beings, and it will determine our way of life in the future. This change is the result of years of neglect by society regarding waste, fossil fuel use and greenhouse gas emissions. With the aim of minimizing this effect, a great effort has been made by researchers in different areas. When possible, the substitution of synthetic products (requiring processes that generate pollution) with biodegradable ones, is a preferable option.

Chitosan is a biopolymer obtained from the deacetylation reaction of chitin, the second most abundant natural polymer, generally found in the shells of crustaceans and insects. Structurally, both chitosan and chitin are linear polymers composed of 2-amino-2-deoxy-(1,4)- β -D-glucopyranose with different degrees of *N*-acetylation, which differentiates them. This polymer has attractive physicochemical and biochemical properties, being biodegradable, biocompatible, non-toxic and of low cost. A great variety of studies have used this polymer in different applications, including cell adhesion,¹ ion adsorption,^{2,3} as a precursor to obtain functional molecules,⁴ in the food industry^{5,6} and, more recently, to obtain proton exchange membranes for use in fuel cells, PEMFC (polymer

*e-mail: pires@qmc.ufsc.br

exchange membrane fuel cells).^{7,8} Some studies have shown that the chitosan interactions with sulfuric acid (crosslinking),⁹ phosphoric acid (acid-base electrolytes)¹⁰ and methanediphosphonic acid¹¹ guarantee a suitable chemical and physical stability of the materials in the presence of water, besides leading to proton conductivity. The most widely used PEMs was developed by DuPont Inc. (USA) is sulfonated tetrafluoroethylene, commercially known as Nafion[®], which strong acid groups [SO₃H].¹²

The addition of a thermoplastic such as poly(vinyl alcohol) (PVAL) favors the preparation of films with mechanical properties suited to obtaining MEA (membrane electrode assembly) devices. This polymer easily forms flexible and resistant films and its use includes a variety of applications.¹³⁻¹⁵ PVAL itself is a poor proton donor/conductor, due to the absence of charge in backbone chain. The addition of sulfosuccinic acid (SSA) which has strong proton conductor properties, depending on the medium, could be used to modify the PVAL profile. Rhim *et al.*¹⁶ have shown the attainment of PVAL membranes with different sulfosuccinic acid (SSA) content which achieved acceptable values for proton transport.

Previous studies in our research group have been modified poly(ether ether ketone) in suspension by nitration, reduction to the amino group, and subsequent sulfonation, to obtain polymer with proton conductivity characteristic.^{17,18} The aim of this study is to obtain an electrolyte material by blending chitosan chemically modified with SSA and PVAL. This system was characterized and its physicochemical properties were analyzed, with the main focus being on proton conductivity.

Experimental

Materials

Chitosan (CS) and sulfosuccinic acid (SSA) (aqueous solution at 70%, m/m) were supplied by Sigma-Aldrich, and poly(vinyl alcohol) (PVAL), chloridric acid, acetic acid and sodium acetate by Merck. All reagents were used without further purification. Figure 1 shows the chemical structures of the monomeric unit of chitosan (where q and p denote the acetylated and deacetylated units, respectively), the poly(vinyl alcohol) monomer unit and sulfosuccinic acid.

Chitosan characterization: molecular weight and deacetylation degree

The chitosan average molecular weight determined through a viscosimeter method was 114,000, using the Mark-Houwink equation, where the parameters a and K

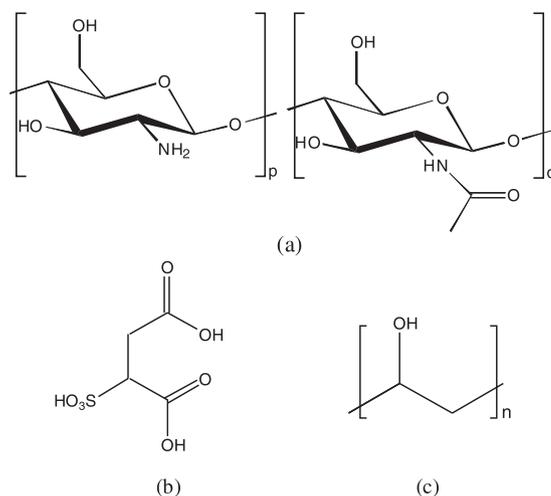


Figure 1. Chemical structures of (a) chitosan monomeric units, (b) sulfosuccinic acid, and (c) poly(vinyl alcohol).

are 0.93 and $1.81 \times 10^{-3} \text{ mL g}^{-1}$, respectively.¹⁸ The solution was 0.2 mol L⁻¹ sodium chloride in a 1% (m/v) acetic acid aqueous solution at 25 °C. The chitosan deacetylation degree (DD) more than 75% (according to the supplier) was determined through potentiometric analysis using a conductivimeter, model CG220 (Gehaka), at 25 °C. Initially, the chitosan was dissolved in a 0.09 mol L⁻¹ HCl aqueous solution, maintained under stirring for 24 h and the conductivity was evaluated with the addition of 0.01 mol L⁻¹ sodium hydroxide. From the conductivity *versus* base volume curve the chitosan deacetylation was calculated as 63%. Experiments were carried out at least in triplicate.

Blend preparation

Initially, to different flasks containing aqueous solutions of chitosan (0.8 g in 0.1%, m/v chloridric acid) sulfosuccinic acid was added to obtain a final composition range of 8 to 80% in relation to the amino group content in the chitosan side group, and maintained under stirring for 24 h. The chloridric acid was also used to induce the protonation of the free carboxyl group of the SSA, which can favor the crosslinking reaction. The chitosan/sulfosuccinic acid solutions were mixed with a PVAL aqueous solution to obtain a crosslinked chitosan-SSA/PVAL blend. All mixtures were stirred for 24 h and cast on glass plates at room temperature. The dense homogeneous membrane was obtained after complete solvent evaporation.

Water absorption in membranes

Membrane specimens of 2 cm × 2 cm were dried for 24 h under vacuum until constant weight, and then maintained under a relative humidity of 57% (sodium

bromide in saturated aqueous solution) or 100% at room temperature and the weight gain was monitored after different time periods.

Infrared spectroscopy

Infrared spectroscopy (FTIR) spectra of chitosan/PVAL blends with or without sulfosuccinic acid were obtained on a 16 PC Perkin Elmer spectrophotometer, performing 32 scans at a resolution of 4 cm⁻¹ and using sample films prepared on Si plates.

Thermal analysis

Thermal analysis was carried out using a TGA 50 Shimadzu thermogravimetric analyzer. A non-isothermal experiment was performed at 20 °C min⁻¹ from 25 to 600 °C. The nitrogen flow was maintained at 50 cm³ min⁻¹. Before the analysis, the samples were dried under vacuum until constant weight.

Ion-exchange capacity (IEC)

The IEC of the membranes was determined by a classical titration method using sodium chloride as the exchange agent. Membrane specimens previously stored under vacuum were stirred for 24 h in a saturated NaCl aqueous solution in order to promote the exchange of H⁺ ions with Na⁺. The amount of H⁺ released from the membrane was determined through titration with 0.01 mol L⁻¹ NaOH aqueous solution, using phenolphthalein as an indicator. The ion-exchange capacity was determined using equation 1.

$$IEC = \frac{\text{concentration}_{\text{NaOH}} \times \text{volume}_{\text{NaOH}}}{\text{weight}_{\text{membrane}}} \quad (1)$$

Conductivity measurements

The proton conductivity was measured using a glass cell as described by Slade *et al.*²⁵ Two platinum gauze electrodes immersed in aqueous sulfuric acid (1 mol L⁻¹) solution were connected to a Keithley, Model 6220, current source where currents of 0.1 to 100 mA were applied. This applied current induces water electrolysis, producing hydrogen and oxygen at the cathode and anode, respectively. The two reference saturated calomel electrodes (SCEs), placed at a fixed distance from the membrane using Luggin capillaries, were connected to a Keithley, Model 6517, electrometer to measure the potential difference between the SCEs. Plots of the potential difference *versus* the applied current

obeyed Ohm's law, which allows the measurement of the cell resistance. The blend film resistance is the difference between the cell and the electrolyte resistance, measured in the absence of the blend film. The resistance area can be calculated through the product of cell area and film resistance, and the conductivity through the ratio of film thickness to resistance area. Different pre-treatments were used for the sample measurements, in order to achieve better conditions to promote the proton transfer through the membrane. The samples were submitted to two conditions: saturated aqueous vapor (for 48 h) or 0.1 mol L⁻¹ sulfuric acid aqueous solution (for 24 h). The influence of the electrolyte medium on the proton conductivity was also evaluated, using ethanol or aqueous acid solution. The electrical conductivity of the blend films (with thickness less than 0.1 mm) was measured using the ASTM D-257 standard two-probe method, using a Keithley 6517 electrometer/high resistance meter and a Keithley resistivity fixture Model 8009.

Results and Discussion

All of the crosslinked chitosan-SSA/PVAL blends with different sulfosuccinic acid content were maintained at a constant ratio of 1:1 (mol/mol) monomeric unit of chitosan and PVAL. The sulfosuccinic acid content in the blend composition was expressed as the chitosan amino groups content (mol/mol) considering the deacetylation degree as 63%, and its influence in the system was evaluated through infrared spectroscopy, as shown in Figure 2. In the range of 1500 to 1750 cm⁻¹, the spectrum of the polymer blend with 8% of sulfosuccinic acid content is comparable to the spectrum of the blend without acid, with a characteristic

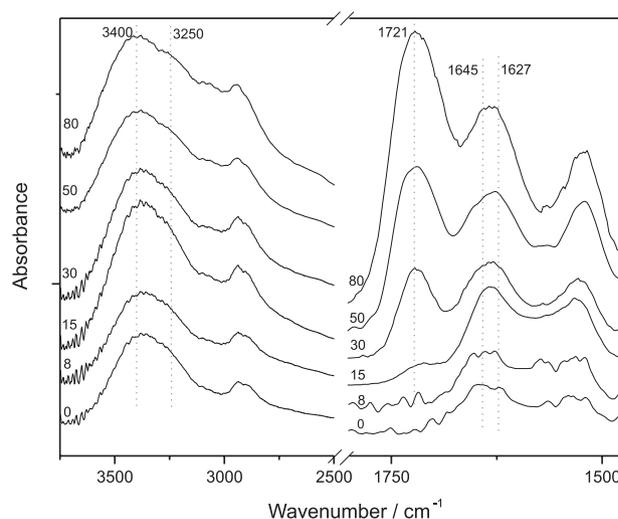


Figure 2. FTIR spectra of the chitosan-SSA/PVAL blends with different acid contents (8 - 80%).

absorption band at 1645 cm^{-1} due to the amide I group from the acetylated units of chitosan. Increasing the percentage of sulfosuccinic acid, the absorption band at 1627 cm^{-1} becomes evident (overlapping with that of amide I), suggesting that the reaction between the amino and carbonyl groups occurred.

Different interactions between hydroxyl, sulfonated group and amine group of sulfosuccinic acid and chitosan, can be taking place as shown in Figure 3. The blends with an acid content of up to 15% showed a strong absorption band at 1721 cm^{-1} which may be related to the carbonyl groups from the acid, indicating the presence of an excess of acid and a limit of SSA amount in terms of the crosslinking reaction, and the absorption band at 1627 cm^{-1} is related to the acetyl group obtained from SSA/chitosan reaction. The effective crosslinking will be occurring with the two covalent links (Figure 3b). However, the competitive formation of only one covalent linking (Figure 3c) and hydrogen bonding (Figure 3a) reduce the crosslinking degree, but maintain the sulfonated sulfosuccinic acid in the blend system. The higher wavenumber region in the infrared spectra shows broad prominent absorption bands related to the -OH stretching vibration, with the characteristics of a self-associating (lower wavenumber at 3250 cm^{-1}) and non-hydrogen-bonded (higher wavenumber at 3400 cm^{-1}) system. In fact, Radic *et al.*²⁰ reported that chitosan/PVAL (80:20, m/m corresponding to 1:1, mol/mol monomeric unit) blend miscibility is favored due to the interaction

between the hydroxyl groups of the macromolecular polymer chain content in the mixture.

As reported in the literature, SSA may act as a crosslinking agent and proton donor. Rhim *et al.*¹⁶ prepared membranes of PVAL/SSA and studied, after thermal treatment, their behavior as proton exchange membranes. The order in which the components are added was also considered since the SSA molecules could potentially react with the hydroxyl groups of the PVA under thermal treatment instead of the amino group of chitosan.

Figure 4A shows the thermogravimetric curves for the blends with different acid content. The derivative of the thermogravimetric curves (DTG) for the blend with no acid content showed a single decomposition stage, with a maximum decomposition rate temperature at $280\text{ }^{\circ}\text{C}$, as shown in Figure 4B. This temperature decreased by $30\text{ }^{\circ}\text{C}$ when SSA was added to the system, the curve profile being unaltered under the same experimental conditions. For the blends with acid content of up to 15% two peaks at higher temperatures appeared, due to the presence of SSA in excess. The decrease in the thermal stability of the blends containing acid could be related to the formation of amide linkages during the crosslinking reaction, which influences the degradation kinetics and its stability at higher temperatures.

The IEC of the blends quantifies the groups distributed in a random manner in the polymeric chain capable of ion exchange. This method of analysis was previously

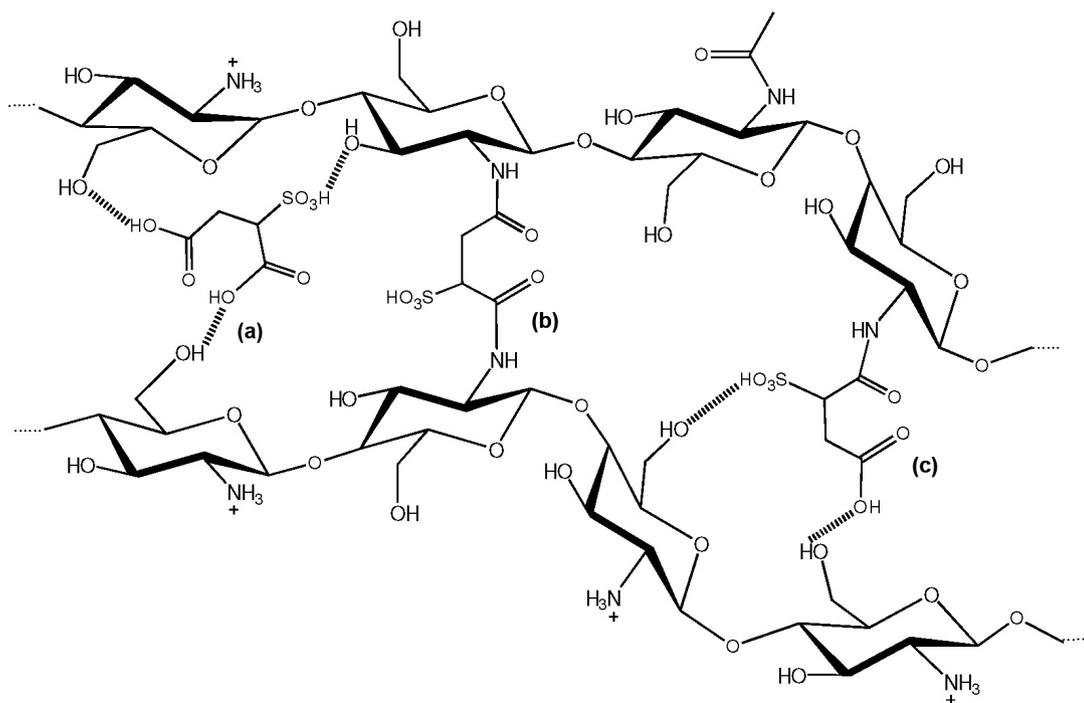


Figure 3. Structural scheme proposed for the different chitosan-SSA interaction.

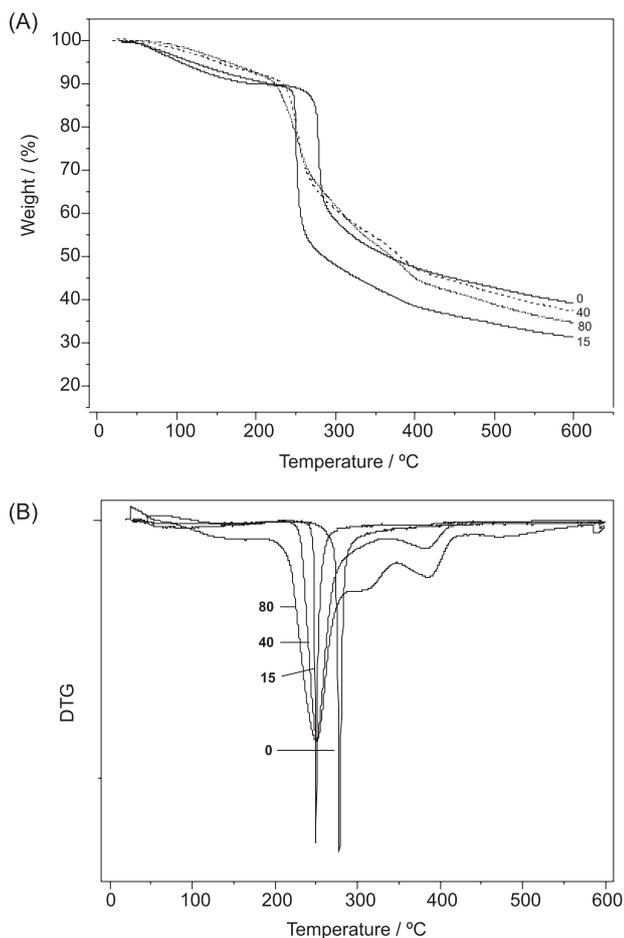


Figure 4. (A) Thermogravimetric curves and (B) derivative of thermogravimetric curves of the blends.

used in our research group to evaluate the ion exchange capacity of a sulfonate poly (ether ether ketone)/polyaniline (SPEEK/PANI) system where values in the range of 0.12 to 1.16 mequiv. g⁻¹ were observed.²¹ In this study, increasing the SSA content in the blend increased the IEC values from 0.0336 mequiv. g⁻¹ to 3.12 mequiv. g⁻¹ for the blends without and with 80% of SSA, respectively, as shown in Table 1. These values could be related to an increase in the content of -SO₃H and -COOH groups in the medium, which are

Table 1. Ion-exchange capacity (IEC) values of the chitosan-SSA/PVAL blends

| SSA content / (%) | [H ⁺] _{add} / (mmol) | IEC / (mequiv. g ⁻¹) |
|-------------------|---|----------------------------------|
| 0 | 0 | 0.0336 |
| 8 | 0.746 | 0.0794 |
| 15 | 1.53 | 0.752 |
| 20 | 2.28 | 1.07 |
| 30 | 3.01 | 1.45 |
| 40 | 3.81 | 1.84 |
| 50 | 4.52 | 2.13 |
| 80 | 7.50 | 3.12 |

capable of an exchange between the protons and Na⁺ ions. In agreement with the data of the FTIR spectra, evidence of the crosslinking reaction could be also observed from the difference between the number of moles of H⁺ added during the blend preparation and number remaining, evaluated through the titration method (also shown in Table 1). As can be seen in Table 2, the proportional increase in the IEC values for the membranes produced from similar blend systems with twice the thickness and the same mass also indicates that ion exchange occurs at the surface and inside the membrane. The influence of temperature on the polymer/SSA crosslinking reaction was evaluated through thermal treatment at 100 °C for 1 h. These conditions can favor the formation of amide linkages, since water molecules were formed as a by-product. However, no significant influence on the IEC values at different acid concentrations after thermal treatment was observed, as shown in Figure 5, suggesting no temperature effect on the crosslinking degree, and that the crosslinking reaction is effective during the solvent evaporation step.

An important parameter which renders these systems suitable for use as proton exchange membranes is the hydration capacity, given that in most proton conduction mechanisms the water molecules are considered crucial for the proton transport through the membrane.²²⁻²⁴ One of the factors related to the hydration capacity is the presence and distribution of hydrophilic groups in the polymeric chain.

Table 2. IEC values for two samples of each blend with same mass and different thickness

| Blend | Thickness / mm | IEC / (10 ⁴ equiv. g ⁻¹) |
|--------------------------------|----------------|---|
| Chitosan/PVAL | 0.032 | 0.97 |
| | 0.060 | 1.11 |
| Chitosan-SSA/PVAL (40% SSA) | 0.056 | 19.0 |
| | 0.104 | 20.0 |

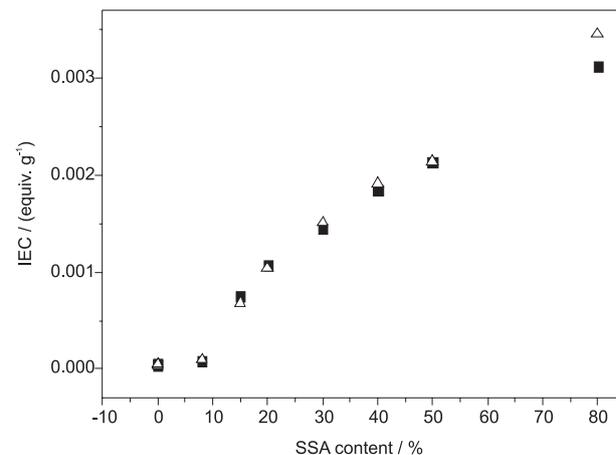
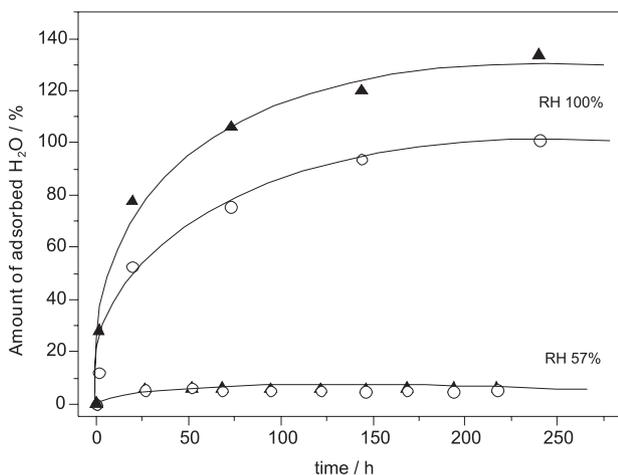


Figure 5. IEC values of the chitosan-SSA/PVAL blends with: (Δ) thermal treatment and (■) no thermal treatment.

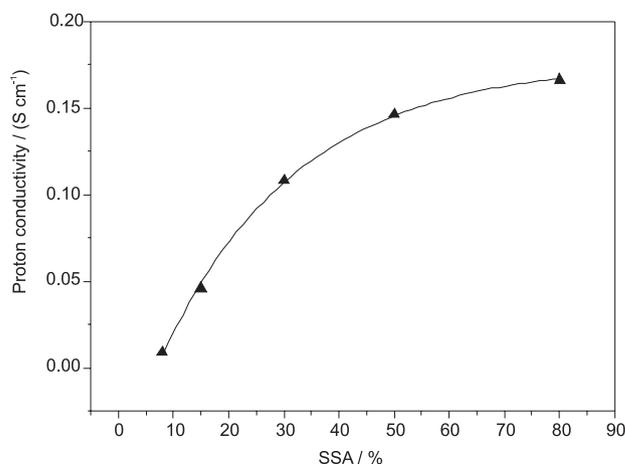
Table 3. Proton conductivity of chitosan-SSA/PVAL blends with different acid content

| SSA content / (%) | Proton conductivity $\times 10^3 / (\text{S cm}^{-1})$ | | |
|-------------------|--|-----------------------|--|
| | ethanol acid solution pre-treatment RH 100% | aqueous acid solution | |
| | | pre-treatment RH 100% | pre-treatment $[\text{H}_2\text{SO}_4] 0.1 \text{ mol L}^{-1}$ |
| 0 | 0.67 | 9.1 | - |
| 30 | 1.07 | 11.1 | 108 |
| 50 | 0.79 | 21.0 | 146 |

The percentage of adsorbed water in the blend without and with 80% SSA was 6% at a relative humidity of 57% for 220 h, as shown in Figure 6. However, at a relative humidity of 100% the percentage of adsorbed water for the blend with SSA was lower than that for the blend without acid, and for both blends these values were higher than those obtained at a relative humidity of 57%. The blend containing SSA absorbed less water, maybe due to the fact that some of the hydrophilic groups are involved in the crosslinking. The membrane maintained in a water-saturated atmosphere reached a hydration level suitable for the proton conductivity evaluation.

**Figure 6.** Amount of water adsorbed by (▲) blend without SSA and (○) blend with 80% of SSA as a function of exposure time at relative humidity (RH) of 57% or 100%.

The proton conductivity values of the blends were determined in ethanol/sulfuric acid and aqueous/sulfuric acid solutions after being maintained at a relative humidity (RH) of 100% for 24 h, as shown in Table 3. The proton conductivity values determined in ethanol acid solution were lower than the values measured in aqueous acid medium, due to the different ionic mobilities. The membranes pre-treated in H_2SO_4 $[0.1 \text{ mol L}^{-1}]$ aqueous solution showed proton conductivity values which increased with the SSA content in the blend, reaching 0.17 S cm^{-1} at 80% of acid content, as shown in Figure 7. This pre-treatment applied to the blend containing only 30% of SSA increased the value

**Figure 7.** Proton conductivity of the chitosan-SSA/PVAL blends pre-treated in H_2SO_4 mol L^{-1} .

for the proton conductivity ten-fold compared with same blend without previous treatment, as described in Table 3. The presence of SSA acid inhibits the blend solubility in acid medium, and enables membranes with proton conductivity similar to the values for the Nafion[®] membrane obtained in this study (0.29 S cm^{-1}) and by Slade *et al.*²⁵ (0.16 S cm^{-1}), using the same experimental conditions, which are promising electrolytes for fuel cell applications. The pre-treatment of the membranes has a considerable influence on the proton conductivity measurement,²⁵ and the crosslinking degree showed no influence on the proton conductivity behavior. As reported by Mukoma *et al.*⁹ the chitosan/sulfuric acid membranes showed crosslinking and proton conductivity characteristic due to the presence of acid in the medium. Membranes for fuel cells should prevent the electron flow produced during the fuel gas (H_2) oxidation. The electrical conductivity values for all blends were in the range of 2.0×10^{-9} to $50.0 \times 10^{-9} \text{ S m}^{-1}$, which is characteristic of insulating materials.

Conclusions

The crosslinked chitosan-SSA/PVAL blends with different acid contents showed a crosslinking limit at 15% of SSA, occurring *via* the chitosan amino groups. The evidence of the crosslinking reaction can be supported

through infrared spectra and the proton content remaining after the blend preparation. The thermal stability of the blends containing acid decreased due to the formation of amide linkages. The amount of water absorbed by the blend containing 80% of SSA indicates a suitable hydration level, which is an important characteristic in terms of the proton conductivity through the membrane. The blend pre-treated in H₂SO₄ aqueous solution showed the highest proton conductivity values, reaching 0.17 S cm⁻¹. These blend materials represent potential proton exchange membranes for application in fuel cells.

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