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Effect of the Sulfonation on Membranes Synthetized from SEBS and Natural Latex

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Abstract

In the present work, proton exchange membranes from the SEBS copolymer and latex were synthesized and modified with the addition of vanadium pentoxide and sulfonation to evaluate its application in a fuel cell. Through the FTIR analysis the modifications of the polymer were evidenced. The results show that the increase of the sulfonation time increased the water uptake, the ion exchange capacity and the mechanical properties of the membrane due to the hydrophilic character of the sulfonic groups added to the polymer. In the loaded and sulfonated membranes, the results favored to a greater extent the membrane loaded 0.5% and sulfonated 2 hours due to the good interaction between the load and the sulfonic groups, but it is necessary to increase the ion exchange capacity for its use in fuel cells.

Keywords: SEBS, latex, sulfonation, fuel cell, vanadium pentoxide

1. Introduction

Electrical energy has become a basic necessity for modern society, which is essential for most activities carried out in the day to day, being petroleum, natural gas and coal the most used sources for its generation which has caused the increase of greenhouse gases in the atmosphere such as CO_2, CH_4, N_2O, among others [1]. To minimize this problem related to climate change, fuel cells have been developed, these are electrochemical devices that take advantage of the chemical and calorific

energy of hydrogen to produce electrical energy through oxidation-reduction reactions. There is a wide variety of fuel cells, highlighting the type PEM or proton exchange membrane, which have certain advantages such as noiseless operation, efficient, compact and environmentally friendly, its main disadvantage is the high cost contributed by the polymeric membrane and the platinum catalysts [2]. Therefore, it is necessary to study new polymeric materials that can be used in these devices. It has been reported that the application of sulfonation reaction tends to improve the physicochemical and mechanical characteristics of the polymer [3, 4].

In the present investigation, proton exchange membranes are synthesized from SEBS copolymer and latex, modified with sulfonation reaction and addition of inorganic load of vanadium pentoxide to evaluate its possible application in fuel cells.

2. Materials and Methodology

2.1 Materials

Styrene-Ethylene-Butylene-Styrene (SEBS), latex, toluene, dichloromethane, vanadium pentoxide (V_2O_5), latekoll, acetic anhydride 98%, sulfuric acid 95-97%, methanol, hydrochloric acid, sodium chloride and sodium hydroxide were used for the preparation and characterization of the membranes.

2.2 Methodology

The unmodified membrane was prepared by diluting 0.66 mL of latex in 40 mL of toluene at 80 °C for 2 hours with continuous stirring, after this time 2 grams of SEBS were added progressively in a time of 3 hours. The solution was allowed to evaporate until reaching a level of 25 mL to be dosed in a Petri dish, it was left to rest for 5 days to complete its drying. Sulfonated membranes at 1 and 2 hours were prepared, following the procedure detailed to continuation. A similar procedure to the one previously described was performed, but toluene was replaced by dichloromethane and was made at room temperature. Once the SEBS was dissolved, this solution was placed in a flat bottomed flask to initiate the sulfonation reaction when mixed with the sulfonating agent [3]. A reduction of 60% was necessary in the reagents used for the preparation of the sulfonating agent, because under the proportions used of SEBS-latex when mixed with the traditional amounts of sulfonating agent, the immediate polymerization of the copolymer occurred, stopping the sulfonation in a few seconds after starting. The reaction was stopped 60 minutes later by adding 40 mL of methanol. The precipitated polymer was filtered and washed with distilled water until a neutral pH was obtained. This polymer was dried in an oven at 60 °C for 24 hours and then dissolved in 40 ml of toluene at 80 °C with continuous stirring. The solution was allowed to evaporate until reaching a level of 25 mL to be dosed in a Petri dish, it was left to rest for 5 days to complete its drying and obtain the membrane sulfonated 1 hour.

For the membrane sulfonated 2 hours, a similar procedure was performed but allowing the reaction inside the flat bottomed flask for 120 minutes.

For the loaded and sulfonated membranes, a solution similar to that used for the sulfonated membrane 1 hour was prepared. Once the sulfonated polymer was dissolved in 80 mL of toluene, 0.5 mL of latekoll was added to the solution for 2 hours with continuous stirring [5], then 0.01 g of V_2O_5 corresponding to the 0.5% load was added and 4 hours later the solution was allowed to reach a level of 25 mL to start the drying stage in a Petri dish and obtain the membrane loaded 0.5% and sulfonated 1 hour. A similar procedure was repeated substituting the load amount for 0.02 g of V_2O_5 to obtain the membrane loaded 1.0% and sulfonated for 1 hour. In the same way it was done to obtain the membrane loaded 0.5% and sulfonated 2 hours, and the membrane loaded 1.0% and sulfonated 2 hours.

2.3 Characterization of the membranes

The water uptake was obtained by immersing samples of each membrane in distilled water for 24 hours, the samples were weighed before (W_s) and after immersing (W_h), they were superficially dried with absorbent paper and then the percentage of water absorption calculated through weight variation [5]. The ion exchange capacity was calculated by applying the titration method, in which the samples were immersed in a 1 M HCl solution for 24 hours, then placed in a 1 M NaCl solution for a further 24 hours, finally the samples were extracted and a titration was carried out with 0.01 NaOH [4]. A mechanical tests were carried out, including maximum effort, maximum deformation and Young's modulus, through the EZ-S Shimadzu equipment at a constant speed of 250 mm/min. Finally, an infrared spectroscopy analysis was done to identify the functional groups present in the membrane through a Nicolet 6700 reference Fourier transform spectrophotometer.

3. Results and discussion

Fig. 1 shows the seven types of membranes synthesized, each characterized by water absorption, ion exchange capacity, mechanical tests and FTIR analysis.

3.1 Water uptake

Figure 2a shows the sulfonated membranes 1 and 2 hours reaching values of 5.9% and 10.8% respectively, exceeding the unmodified membrane which has 3.91%, this occurs since the sulfonation reaction increases the hydrophilic character of the polymer by introducing sulfonic groups (SO_3H^-) which facilitate the retention of water through the formation of hydrogen bonds with water molecules [6]. In the loaded and sulfonated membranes are observed that all exceed the water absorption capacity of the unmodified membrane, being the membrane L 0.5% - S 2h the one with the highest increase with a value of 18.2% which shows the good interaction

between the sulfonic groups and the vanadium pentoxide load, which due to its oxidative power contributes to the swelling of the membrane creating spaces available for the introduction of water molecules [7]. It is also observed that when increasing the load to 1.0%, the membranes decreased their water retention due to the fact that the saturation level of the optimum load was exceeded, hindering the addition of new sulphonic groups [8].

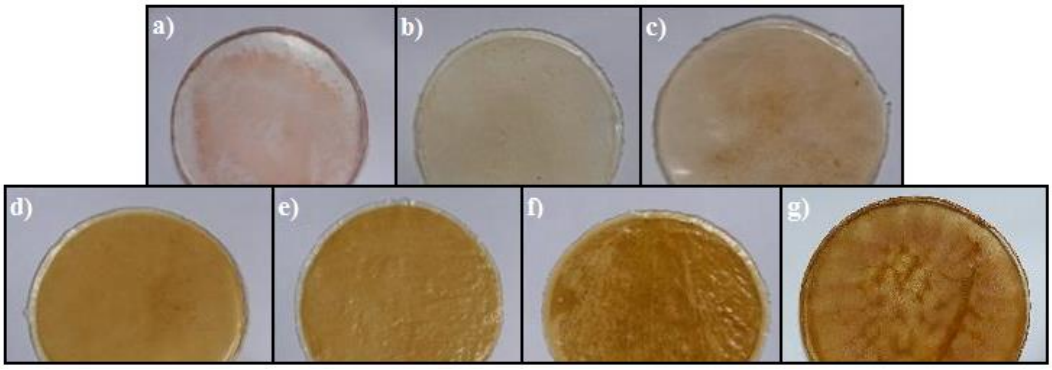

Fig. 1: Prepared membranes: a) Unmodified (UM), b) Sulfonated 1 hour (S 1h), c) Sulfonated 2 hours (S 2h), d) Loaded 0.5% - Sulfonated 1 hour (L 0.5% - S 1h), e) Loaded 0.5% - Sulfonated 2 hours (L 0.5% - S 2h), f) Loaded 1.0% - Sulfonated 1 hour (L 1.0% - S 1h), g) Loaded 1.0% - Sulfonated 2 hours (L 1.0% - S 2h)

3.2 Ion exchange capacity

In Fig. 2b is observed that the results present similar tendencies to the values obtained in the water retention test since water provides the means for proton transport, through "jumps", known as the Grotthuss mechanism and by diffusion, known as vehicular transport [9]. By realizing the sulfonation reaction for 1 and 2 hours, the ion exchange capacity of the unmodified membrane was increased 52.6% and 66.7% respectively, since the added sulfonic groups increase the number of active sites for the transfer of protons [3].

The loaded membrane 0.5% and sulfonated 2 hours had the highest ion exchange capacity, this being 0.21 meq/g given by the good interaction between the load amount and the sulfonic groups, however, in the loaded 1.0% and sulfonated membranes a decrease in the ion exchange capacity is observed. This behavior is attributed to a blockage in the internal channels of the membrane caused by the excess of load, which reduces the protonic transport [10].

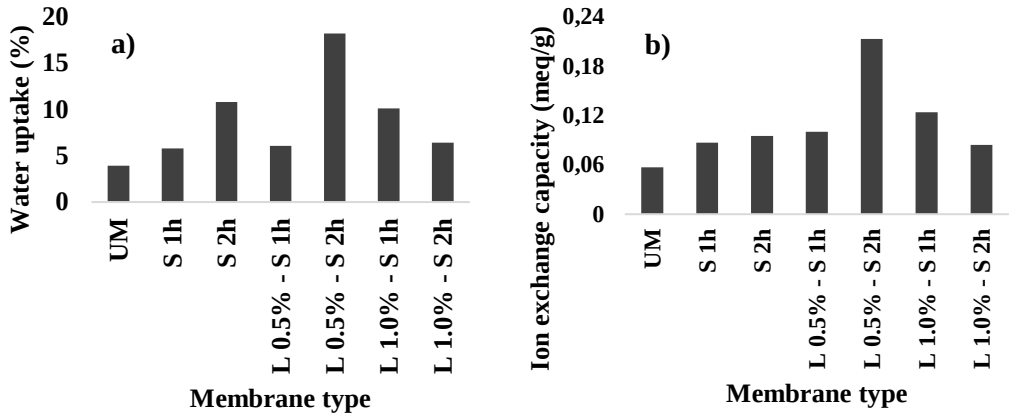

Fig. 2: a) Water uptake for each membrane. b) Ion exchange capacity for each membrane.

3.3 Mechanical tests

Table 1 shows that the unmodified membrane has the highest percentage of deformation with a value of 315.2%, this is due to the elasticity contributed by the latex in the SEBS-latex mixture, and for this have been reported values of maximum deformation of up to 952.3% [11]. The sulfonated membranes have higher values than the unmodified membrane, highlighting the sulfonated membrane 2 hours, which has the largest Young's modulus of all the synthesized membranes, it has the best resistance to stretching, that is attributed to the sulfonation increases the polarity of the polymer and improves the mechanical properties through the hydrogen bond between the chains of the polymer [12].

Table 1: Mechanical properties of each membrane

Membrana type	Maximum effort (MPa)	Maximum deformation (%)	Young's modulus (MPa)
UM	16	315,2	36,1
S 1h	3,8	135,2	37,5
S 2h	16,1	214,7	100,0
L 0.5% - S 1h	4,5	117,8	47,7
L 0.5% - S 2h	2,4	85,6	13,1
L 1.0% - S 1h	3,7	122,0	32,3
L 1.0% - S 2h	3,1	97,4	22,4

The loaded and sulfonated membranes have the lowest values compared to the unmodified membrane and the sulfonated membranes, attributed to the fact that the presence of excess inorganic load can cause a non-uniform dispersion in the polymer matrix, leading to a poor response of the membrane when this is subjected to the action of external forces [5].

3.4 FTIR analysis

In Fig. 3 is observed that the unmodified membrane presents signals in 2924 cm^{-1} and 2852 cm^{-1} corresponding to the C-H bond and CH_2 groups of SEBS [13]. The peak in 690 cm^{-1} represents the out of plane bending of C-H bonds in the aromatic ring, and the peak at 1450 cm^{-1} belongs to the asymmetric stretching of C-H bonds in the CH_3 groups of the ethylene–butylene blocks in the polymer [14]. The signal observed in 1660 cm^{-1} and 1544 cm^{-1} represents the vibration of the C=C double bond of poly(cis-1,4-isoprene) which is the main compound in the latex structure [15].

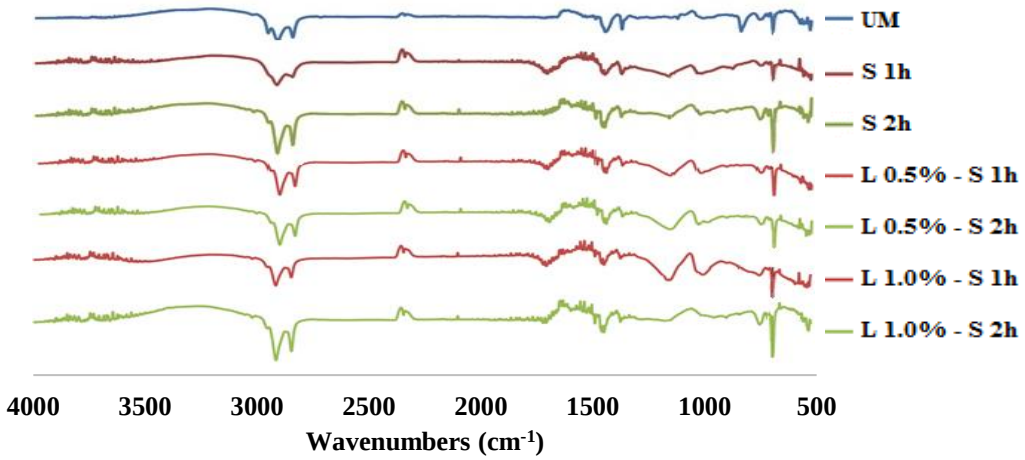

Fig. 3: Infrared spectra of each membrane.

The signals in 1124 cm^{-1} and 1164 cm^{-1} are appreciated in the sulfonated membranes, corresponding to vibrations of the sulfonic acid groups in the aromatic rings, while the wide absorbance peak in 3200-3600 cm^{-1} is attributed to the O-H bond vibrations [16]. Finally, the presence of vanadium pentoxide is evidenced by a peak near 1000 cm^{-1} corresponding to the vibration mode of terminal oxygen bond V=O and in 829 cm^{-1} with the vibration of the V-O-V bond [5].

4. Conclusions

Proton exchange membranes were obtained from the copolymer SEBS and latex, modified with sulfonation reaction and addition of inorganic filler. It was observed in the sulfonated membranes that the properties of the polymer were improved as the sulfonation time was increased, due to the hydrophilic character of the sulfonic groups added, which allowed greater water uptake through the formation of hydrogen bridges, favoring the proton transport and stretch resistance. In the loaded and sulfonated membranes it was evidenced that the action of the sulfonic groups was affected when increasing the load percentage, because the optimum level of saturation was exceeded. The modification of the polymer was evidenced through the FTIR analysis. The membrane loaded 0.5% and sulfonated 2 hours presented

the best characteristics, however it is necessary to improve its ion exchange capacity for its application as an electrolyte in a fuel cell.

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