Contemporary Engineering Sciences, Vol. 10, 2017, no. 36, 1747 - 1755
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/ces.2017.712202

Effects of Sulfonation of Natural Rubber and Vinyl Acetate-Ester Acrylic on the Physico-Chemical Properties of Proton Exchange Membranes

Realpe Jiménez Alvaro, Pino Bello Yina and Acevedo Morantes María

Department of Chemical Engineering, Research Group of Modeling of Particles and Processes, University of Cartagena, Av. Consulado, Cartagena, Colombia

Abstract

Proton exchange membranes were prepared by natural latex and vinyl acetate-ester acrylic for determining its use in a fuel cell. The time of sulfonation reaction of two and three hours were used, and the vanadium pentoxide was also used as load. Sulfonated and loaded membranes have highest values of water uptake and ionic exchange capacity, while membranes without load are more stables than loaded membranes. FTIR spectra analysis was carried out for determining the characteristic functional groups of the each membrane. Sulfonated membranes during three hours have the highest mechanical properties such as tensile stretch, and elongation.

Keywords: Proton exchange membrane, sulfonation, fuel cell, vanadium pentoxide

1 Introduction

80% of the world's energy is generated by fossil fuels, however, it is known that they are finite resources, in addition their combustion is harmful to the environment due to greenhouse gases and the constant emissions that contribute to the problem of global warming [1]. This problematic has generate the development of new energy sources, in actuality, many alternative energy sources are studied such as, solar energy, wind energy, among others, the evolution of these depend on economic and environmental factor, and the capacity of supply the whole world. Fuel cell is also an attractive alternative for energy generation, due to its advantages

of clean and efficient conversion systems. Furthermore, this devices have high potential at temperature range of 60 to 100 C° [2]. Fuel cells produce energy converting chemical energy into electrical energy using hydrogen making them more friendly with the environment, because do not produce CO_2 emissions. In its structure it has a polymer electrolyte between two electrodes (anode and cathode) [3]. Currently, many researches about fuel cell and proton exchange membrane have been developed with the final purpose that obtain a new proton exchange membrane for used in fuel cell. The commercial electrolyte as Nafion® 117 by Dupont [4] shows chemical stability and strong thermal resistance [5], but it has a high cost [6]. By other side, another type of polymers as Vinyl Acetate – Acrylic Ester, insatured polyester and rubber natural, acrilic ester – styreneme, and SEBS (styrene – ethylene- butadiene – styrene) are studied to syntheze membranes [7-13] employing sulfonation method and differents type of load.

In this research was performed the synthesis and characterization of the proton exchange membrane by rubber Natural and Vinyl Acetate–Acrilic Ester. Furthermore, membranes were sulfonated and loaded with V_2O_5, to determine the water Uptake, ionic exchange capacity, mechanicals properties, and oxidative stability and to define the potential for using in a fuel cell.

2 Materials and Methods

2.1 Materials

The materials used for preparation of membrane were natural rubber and vinyl acetate- ester acrylic. Pentoxide vanadium was used for loading membranes. Sulfuric acid and anhydride acetic were used for preparing sulfonant agent and methanol to stop the reaction of sulfonation. Chlorohydrin acid, sodium chloride, sodium hydroxide, and oxygen peroxide were used for characterization.

2.2 Membrane preparation

For preparing sulfonated membranes, first 10 g of polymers (5gr of natural Rubber and 5 gr of ester acrylic – Vinyl acetate) are solved in 100 ml of distilled water, by other side sulfonant agent is prepared in dichloromethane 4.76 ml, then, anhydride acetic is added in an ice bath for 10 minutes, after 2.63 ml of sulfuric acid is added it is cool for 10 minutes, subsequently sulfonate agent is added slowly in polymer solution in a ball and is mixed for two or three hours according. The reaction is stopped by adding 100 ml of methanol to precipitate the polymer and finally is filtered and wash to neutralize. For preparing the membranes the polymer is dissolved in a solution of toluene 10% W/V, in agitation for 6 hours. Then, the solution is poured into a Petri dish and the solvent is expected to evaporate. For membranes loaded, after the shake of the polymer sulfonated the load is added and shake for 16 hours to dissolve the load.

2.3 Characterization methods

Water uptake for membranes was determinate by the immersion of the samples with area 10 x 10 mm in distilled water at room temperature for 24 hours, then liquid in the surface of the membrane was removed and weighed (wet weight), previously to this, samples are dried in the oven for 1 hour and weighed (dry weight) [14]. By other side, ionic exchange capacity was measured by titration, samples previously weighed and in its protonated form were submerged in 1M HCl solution for its sodium form during 24 hours to exchange the H+ ions with Na^+ ions, then the H^+ exchanged within solution were titrated with 0.01M NaOH solution [15].

For determining the oxidative stability, samples was submerged in H_2O_2 36% during 7 days and weighed every 24 hours. Also, FTIR was carried out in spectrophotometer to identify functional groups. By other side, mechanicals properties is carried out to in the universal testing machine EZ-S Shimazu.

3 Results and Discussions

3.1 Membranes Prepared

Figure 1 shows six type of membranes synthetized, sulfonated 2 hours (S2H), sulfonated 3 hours (S3H), sulfonated 2 hours and loaded 2% (S2HL2%), sulfonated 2 hours and loaded 4% (S2HL4%), sulfonated 3 hours loaded 2% (S3HL2%) and sulfonated 3 hours loaded 4% (S3HL4%). Membranes sulfonated 2 and 3 hours are white and translucent; while membranes sulfonated and loaded have an orange color, characteristic of the vanadium pentoxide.

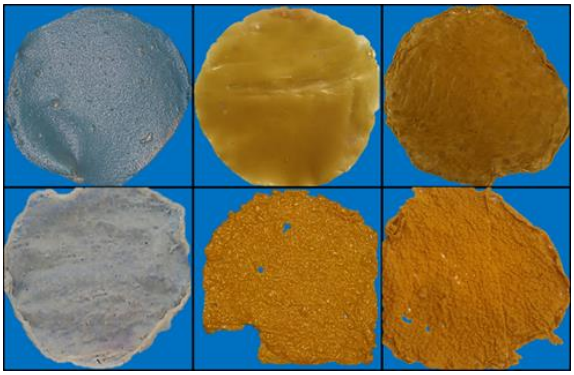

Figure 1. Membranes Prepared, (a) S2H, (b) S2HL2% (c) S2HL4% (d) S3H (e) S3HL2% (f) S3HL4%

3.2 Water uptake

Figure 2 shows the water uptake for each membrane prepared, it is observed that the water uptake increases with increasing the sulfonation time and with the

vanadium pentoxide addition. This same behavior it observed in [16] where the sulfonation time is modified. Sulfonation reaction adds SO_3H+ groups in the polymer chain, which have hydrophilic characteristic that permits the formation of hydrogen bonds with the water molecules [17]. Furthermore, the values reported in this research are near to Nafion 117 reported by [18] that present 21% water uptake values.

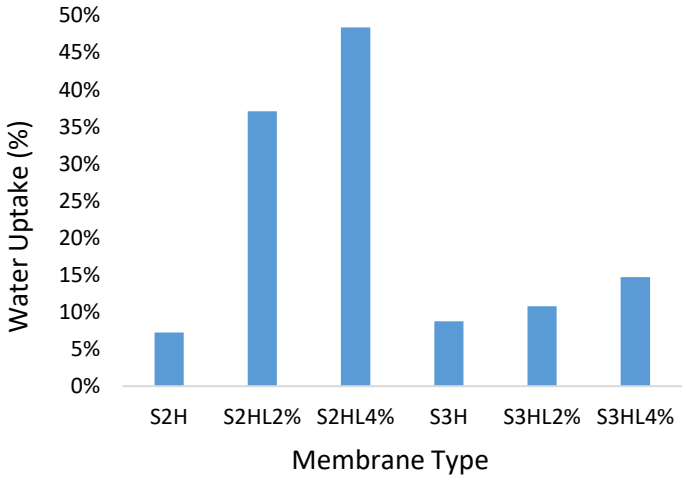

Figure 2. Water Uptake

3.3 Ionic Exchange Capacity

Figure 3 shows ionic exchange capacity for each membrane, it is observed that the time of sulfonation and the loaded addition increase the ionic exchange capacity for membranes due to the formation of the actives sites that permit the transference of the protons [12], by the Grotthus mechanism where the sulfonic groups have the transference agent that is to say they are H+ donors, in addition, the acid functionalities, such as sulfonics acid groups contribute to the proton conduction in a membrane which is proportionately linked to IEC [19]. Sulfonated and loaded membranes presented highest values due to the higher density of ionic positions in the polymeric matrix that generate a greater number of functional groups for the exchange [20]. By other side, it is observed that the IEC present same behavior that the water uptake respect with the addition of the load.

3.4 Oxidative Stability

Figure 4 shows the oxidative stability where it is indicated the variation of weight of polymer immerse in H_2O_2. Sulfonated membranes are more stables than loaded membranes, due to the oxidative properties of the vanadium pentoxide. Loaded molecules tend to be added to the hydrogen peroxide forming V-OH links, doing the weight of the samples change. To prevent that the H_2O be absorbed by the membranes, the samples were dried in an oven vacuum before weighing them.

Since this effect occurs in this type of membranes, by the hydrophilicity of the sulfonics groups and vanadium pentoxide [17].

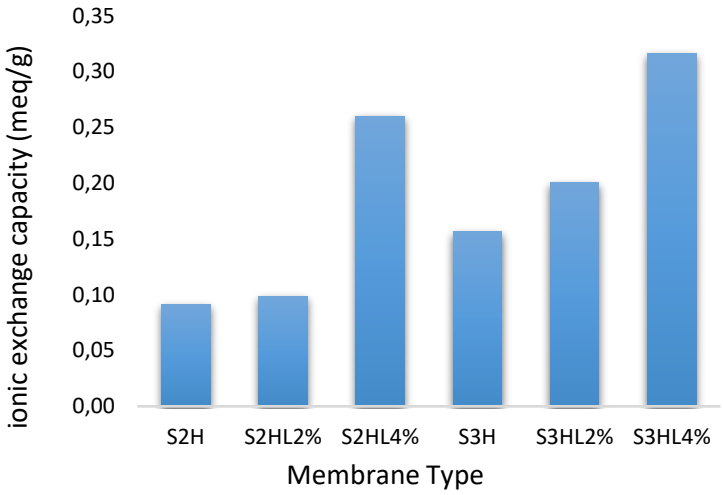

Figure 3. Ionic Exchange Capacity

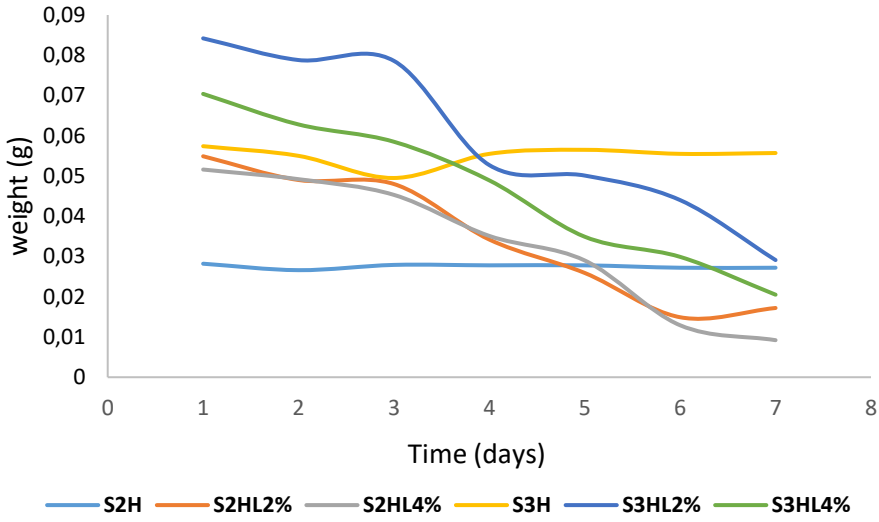

Figure 1. Stability Oxidative

3.5 FTIR

Figure 5 shows the functional groups for each membranes carried out by FTIR spectrum. For each spectra, peaks nearly 837 cm^{-1} corresponding to stretching of C=O bond of the isoprene present in natural latex, the peak in region 2929-2962 cm^{-1} can be attributed to C-H bond by Vinyl ester, [21]. 1730-1750 range has charac-

teristic peak of high density vibration of C=O by the carbonyl group. The peak in the region 1150-1300 corresponding to low density vibrations of C-O bond, this groups are present in the esters [21]. By the addition of V_2O_5, the characteristic peak for V=O is found at 1024 cm^{-1}, however this values is overlapped by the interaction of the sulfonic groups that present a peak in 1022 cm^{-1} corresponding to symmetrical stretching vibration of O=S=O bond [14]. Furthermore, it is observed a peak more intensity in S3H membrane than S2H membrane.

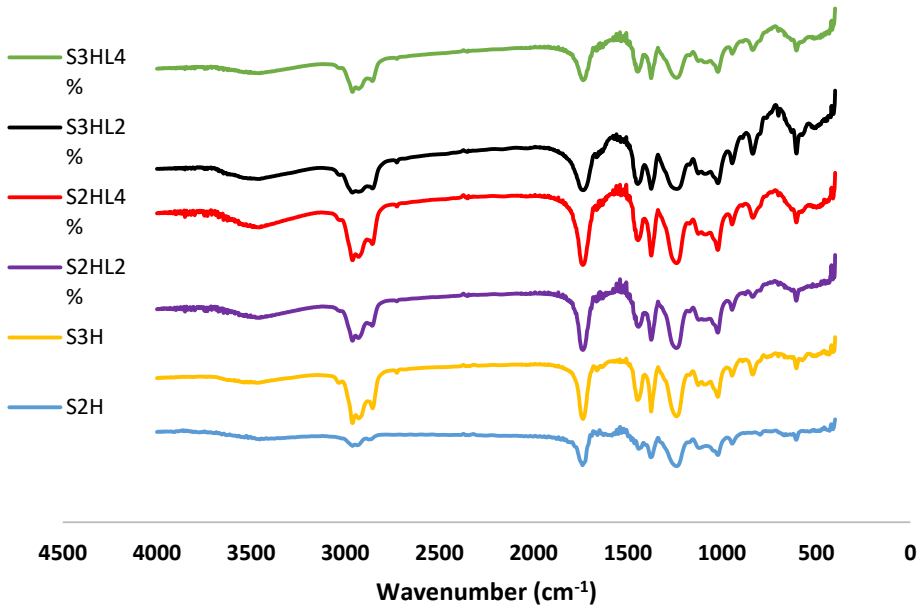

Figure 5. FTIR Spectrum

3.6 Mechanicals Properties

Table 1 shows mechanical properties for each membranes, is observed that S3H membrane presents the highest of tensile stretch, displacement and break values; these characteristics confirmed that the addition of sulfonic groups to membrane get better the mechanical properties. In addition, this property is related with the water uptake, since these membranes present the values lowest, due to the water uptake is an important characteristic but decrease the mechanical resistance in the membrane [9]. Loaded membranes present lowest values, however it is observed that a greater amount of load improvement these values, due to the thickness of the membranes increases with the addition.

Table 1. Mechanicals Properties

Sample	Tensile Stretch (N/mm^2)	Displacement (mm)	Break (N)
S2H1	7,2	64,1	5,0
S2HL2%	5,0	38,9	3,5
S2HL4%	8,2	3,3	4,4
S3H	15,3	83,8	9,9
S3HL2%	3.3	7,5	1,2
S3HL4%	4.2	4,6	1,8

4 Conclusions

Proton exchange membranes were prepared in this research, modifying the sulfonation time and the vanadium pentoxide percentage. The sulfonated membrane at three hours presents highest water uptake and ionic exchange capacity, being these the more important characteristics of proton exchange membranes for fuel cell, although mechanicals properties have low values in comparison with commercial membranes of Nafion 117, this not determinate its use in a fuel cell.

Acknowledgments. Authors of this paper would like to express their gratitude to Administrative Department of Science, Technology and Innovation (COLCIENCIAS, Colombia) and University of Cartagena for providing the funding recourses and the space to perform this project.

References

[1] E. Allegrini, A. Micangeli, E. Michelangeli and M. Ricci, Heat Transfer Simulation of Evacuated Tube Collectors (ETC): An Application to a Prototype, *Contemporary Engineering Sciences*, **9** (2016), 1125–1136. https://doi.org/10.12988/ces.2016.6429

[2] C. Yang, P. Costamagna, S. Srinivasan, J. Benziger and A.B. Bocarsly, Approaches and technical challenges to high temperature operation of proton exchange membrane fuel cells, *Journal of Power Sources*, **103** (2001), 1–9. https://doi.org/10.1016/s0378-7753(01)00812-6

[3] P. Sapkota and H. Kim, Zinc–air fuel cell, a potential candidate for alternative energy, *Journal of Industrial and Engineering Chemistry*, **15** (2009), 445–450. https://doi.org/10.1016/j.jiec.2009.01.002

[4] Y.S. Li, T.S. Zhao and W.W. Yang, Measurements of water uptake and transport properties in anion-exchange membranes, *International Journal of Hydrogen Energy*, **35** (2010), 5656–5665.

https://doi.org/10.1016/j.ijhydene.2010.03.026

[5] K. Suzuki, Y. Iizuka, M. Tanaka and H. Kawakami, Phosphoric acid-doped sulfonated polyimide and polybenzimidazole blend membranes: high proton transport at wide temperatures under low humidity conditions due to new proton transport pathways, *Journal of Materials Chemistry*, **22** (2012), 23767–23772. https://doi.org/10.1039/c2jm34529c

[6] D. Sangeetha, Conductivity and solvent uptake of proton exchange membrane based on polystyrene(ethylene–butylene) polystyrene triblock polymer, *European Polymer Journal*, **41** (2005), 2644–2652. https://doi.org/10.1016/j.eurpolymj.2005.03.018

[7] A. Realpe, K. Romero and A. Santodomingo, Synthesis of a Proton Exchange Membrane from Vinyl Acetate - Acrylic Ester Copolymer for Fuel Cells, *International Journal of ChemTech Research*, **8** (2015), 1319–1326.

[8] A. Realpe, K. A. Romero and M. T. Acevedo, Síntesis de Membranas de Intercambio Protónico a Partir de Mezcla de Poliéster Insaturado y Látex Natural, para su uso en Celdas de Combustible, *Información Tecnológica*, **26** (2015), 55–62. https://doi.org/10.4067/s0718-07642015000100006

[9] A. Realpe, N. Méndez, E. Toscano and M. T. Acevedo, Síntesis y Caracterización Fisicoquímica de una Membrana Cargada con TiO2 Preparada a Partir de la Sulfonación de un Copolímero de Éster Acrílico y Estireno, *Información Tecnológica*, **26** (2015), 97–104. https://doi.org/10.4067/s0718-07642015000500013

[10] A. Realpe, N. Mendez and M. Acevedo, Proton Exchange Membrane from the blend of Copolymers of Vinyl Acetate Acrylic Ester and Styrene-Acrylic Ester for power Generation Using Fuel Cell, *International Journal of Engineering and Technology*, **6** (2014), 2435–2440.

[11] K. A. Romero, A. Realpe and M. Acevedo, Synthesis and characterization of proton exchange membranes from blend of unsaturated polyester resin and natural rubber, *International Journal of Engineering Trends and Technology*, **4** (2013), 4005–4009.

[12] Y. Maza Puerta, A. Realpe Jimenez and M. Acevedo Morantes, Synthesis of Proton Exchange Membranes from Acrylic Ester and Styrene Resin, *International Journal of Engineering Trends and Technology*, **7** (2014), 1–4. https://doi.org/10.14445/22315381/ijett-v7p216

[13] A. Realpe, Y. Pino and M. T. Acevedo, Development of Sulfonated Latex Membranes and Modified with $Va_2O_5$for Application in PEM Fuel Cells,

International Journal of ChemTech Research, **9** (2016), 157–163.

[14] P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang and S. Kaliaguine, Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes, *Journal of Membrane Science*, **229** (2004), 95–106. https://doi.org/10.1016/j.memsci.2003.09.019

[15] M. Gil, X. Ji, X. Li, H. Na, J. E. Hampsey and Y. Lu, Direct synthesis of sulfonated aromatic poly(ether ether ketone) proton exchange membranes for fuel cell applications, *Journal of Membrane Science*, **234** (2004), 75–81. https://doi.org/10.1016/j.memsci.2003.12.021

[16] A. Basile, L. Paturzo, A. Iulianelli, I. Gatto and E. Passalacqua, Sulfonated PEEK-WC membranes for proton-exchange membrane fuel cell: Effect of the increasing level of sulfonation on electrochemical performances, *Journal of Membrane Science*, **281** (2006), 377–385. https://doi.org/10.1016/j.memsci.2006.04.006

[17] H. Dai, R. Guan, C. Li, J. Liu, Development and characterization of sulfonated poly(ether sulfone) for proton exchange membrane materials, *Solid State Ionics*, **178** (2007), 339–345. https://doi.org/10.1016/j.ssi.2006.09.013

[18] J. Schauer and L. Brozova, Heterogeneous ion-exchange membranes based on sulfonated poly(1,4-phenylene sulfide) and linear polyethylene: preparation, oxidation stability, methanol permeability and electrochemical properties, *Journal of Membrane Science*, **250** (2005), 151–157. https://doi.org/10.1016/j.memsci.2004.09.047

[19] T. Higashihara, K. Matsumoto and M. Ueda, Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells, *Polymer*, **50** (2009), 5341–5357. https://doi.org/10.1016/j.polymer.2009.09.001

[20] J. Mosa, A. Duran and M. Aparicio, Membranas Hibridas Basadas en Estireno-Metacrilato-Sílice y Acido Fosfowolframico Obtenidas por Sol-Gel Para Pilas de Combustible de Intercambio Protónico (PEMFC), *Boletín de la Sociedad Española de Cerámica y Vidrio*, **46** (2007), 267–272. https://doi.org/10.3989/cyv.2007.v46.i5.229

[21] S.J. Peighambardoust, S. Rowshanzamir and M. Amjadi, Review of the proton exchange membranes for fuel cell applications, *International Journal of Hydrogen Energy*, **35** (2010), 9349–9384. https://doi.org/10.1016/j.ijhydene.2010.05.017

Received: December 15, 2017; Published: December 28, 2017