# Synthesis and characterization of proton exchange membranes from blend of unsaturated polyester resin and natural rubber

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***Abstract*— In the present work proton exchange membranes were synthesized from the blend between unsaturated polyester resin and natural rubber. This polymer blend was vulcanized and loaded with titanium dioxide. The membranes prepared were characterized by evaluating water uptake, ion exchange capacity and tensile strength. Both, vulcanization and introduction of charge increase the water uptake and ion exchange capacity of polymeric membrane, however, vulcanized membranes show better water uptake (15.96%) and ion exchange (0.1210 meq/g) than charged with titanium and unmodified membranes. The blend prepared was proved to be suitable for fuel cells, since it exhibits Young's modulus and maximum strain higher than Nafion® commercial membranes. The results obtained suggest high potential for the application as proton exchange membrane for fuel cells.**

***Keywords*— Proton exchange membrane, unsaturated polyester, natural rubber, vulcanization, titanium dioxide.**

## 1. INTRODUCTION

A fuel cell is an electrochemical device that continuously converts chemical energy from a fuel and an oxidant into electrical energy, using an electrolyte (membrane). Among the various types of fuel cells, the proton exchange membrane fuel cells (PEMFC) are highlighted because they are efficient and there is no emission of polluting gaseous oxides [1], contributing to reduce the serious global warming problems that the current society has to face.

Most of the membranes currently used in PEMFC are polymeric, but these are expensive and their lifetime is low [2], this shows the need to develop alternative polymeric membranes presenting higher mechanical properties and proton conductivity, while presenting a better cost-benefit relation than that exhibited from commercially available membranes.

The present research project is focused on the synthesis and evaluation of a new hybrid proton exchange membrane from the blend of unsaturated polyester resin and natural rubber. This blend was subjected to the processes of vulcanization and introduction of titanium dioxide ($TiO_2$) as the inorganic load. Subsequently, the water uptake and ion exchange capacity were quantified for the membranes prepared, which are key parameters to determine the proton exchange since they are associated to the proton migration mechanisms presented in this type of membranes. Additionally, a tensile test was performed to verify that the blend prepared have acceptable mechanical properties for the operation in fuel cells.

## 2. EXPERIMENTAL

### 2.1. Materials

The unsaturated polyester resin used for the development of this research is distributed by the company BASF under the name Palatal® COP4. The natural latex was obtained from the company AV Guantes Industriales (AV Industrial Gloves). Distilled water, sulfur, rutile titanium dioxide, styrene, hydrochloric acid, sodium chloride, sodium hydroxide and phenolphthalein, were used as reactive for the preparation and characterization of the membranes.

### 2.2. Experimental design

In this paper, the blend between polyester and natural rubber was modified by the processes of introduction of $TiO_2$ as inorganic load and dynamic vulcanization. Two factors were studied: $TiO_2$ content (A) and vulcanization degree (B). The levels used are listed in Table I.

TABLE I
EXPERIMENTAL DESIGN: FACTORS AND LEVELS

| Levels | Factor A | Factor B |
|---|---|---|
| **1** | 0% $TiO_2$ content | Not vulcanized |
| **2** | 2% $TiO_2$ content | Vulcanized |

The dependent variables for this paper were water uptake and ion exchange capacity. The results were analyzed separately for each factor by one-way ANOVA analysis, carried out in Microsoft Excel 2010.

*2.3. Polymer blend modification and membrane preparation*

In order to make the polymer blend, two solutions were made. First, 5 g of natural rubber were dissolved in 200 ml of styrene at 75°C for two hours. In parallel, 5 g of polyester were dissolved in 40 ml of styrene at room temperature. Subsequently, the blend between both solutions is performed and then it was stirred for 2 hours to ensure proper dispersion of the components.

The blend prepared was modified through the vulcanization reaction and inorganic load introduction process. The blend was loaded by adding 0.204 g of rutile titanium dioxide, and mixing the components vigorously at 75°C for three hours. To produce the vulcanization reaction, 0.48 g of sulphur were added to the blend and reacted for 5 hours at 140°C [3].

The resulting solution from each process was poured in 3 Petri dishes and allowed to stand on a level surface, so that the solvent evaporated and consequently the proton exchange membranes were formed as thin films, for further characterization.

*2.4. Membrane characterization*

For the water uptake measurement, a sample of the dry membrane prepared is weighed and immersed in distilled water for 24 hours, then excess water is removed with absorbent paper and the wet sample is weighed [4]. The water uptake was calculated according to the following equation:

$$\%\ \text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100$$

Where $W_w$ is the wet sample weight and $W_d$ is the dry sample weight.

The ion exchange capacity is measured by a classic titration method. Initially, the membranes must be converted to its proton form by soaking them in 1 M HCl solution for 24 hours [5]. Subsequently, the membranes were washed with distilled water and immersed in a 1M solution of NaCl for 24 h, to perform the exchange of $H^+$ protons for $Na^+$ ions. Then the solution with $H^+$ protons was titrated with a 0.01 M NaOH solution, using phenolphthalein indicator [6]. The ion exchange capacity was calculated according to the following equation:

$$\text{IEC (mEq/g dry sample)} = \frac{V \times M}{W}$$

Where V is the titrant solution volume when equilibrium point is reached, M is the concentration of titrant solution and W is the dry sample weight.

Finally, a tensile strength test was performed to measure mechanical properties of the unmodified membrane, such as maximum stress, maximum strain and Young's modulus. This test was performed in the universal testing machine EZ-S Shimadzu (short type).

## 3. RESULTS AND DISCUSSION

Figure 1 shows prepared membranes. The one loaded with $TiO_2$ exhibits grey colour, meanwhile, in the vulcanized membrane, ramifications can be seen from the crosslinks between polymer chains that takes place in the vulcanization reaction.

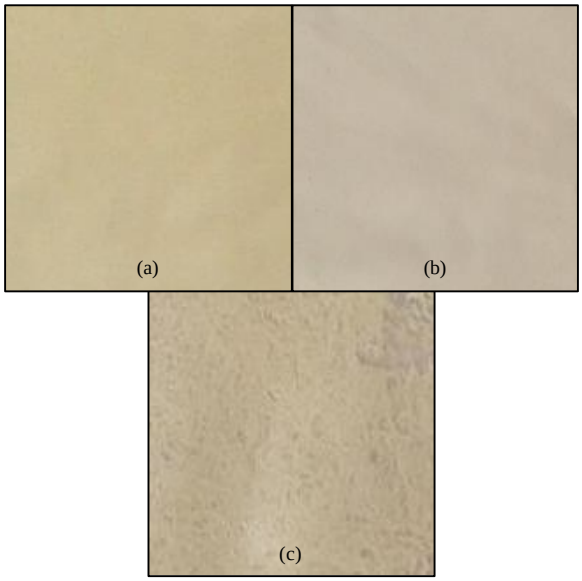


Fig. 1 (a) Unmodified membrane, without $TiO_2$ and not vulcanized. (b) Membrane with $TiO_2$. (c) Vulcanized membrane.

*3.1. Water uptake*

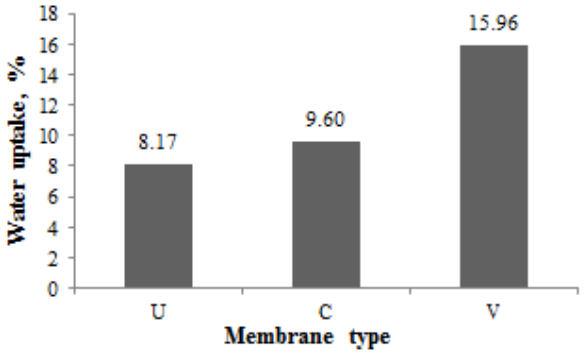


Fig. 2 Water uptake of membranes prepared. U: unmodified, without $TiO_2$ and not vulcanized, C: charged with 2% $TiO_2$, V: vulcanized and without $TiO_2$.

Figure 2 shows water uptake for diverse membrane type. As noted, the water uptake of unmodified membranes is low (8.17%), this is due to the strong hydrophobic character of the polymers present in the membrane, meanwhile, $TiO_2$ increases the water uptake, due to the formation of Ti-OH bonds on the surface of the inorganic load that promotes the water retention; theses bonds are formed because of the strong oxidation potential of $TiO_2$ that oxidizes the water molecules around the inorganic particles [7].

On the other hand, the vulcanization process increases twice the capacity of water uptake, in comparison with the

unmodified membranes. In previous investigations, it was found that the water uptake is reduced in the vulcanized membranes [8], but it should be noted that in this research the dynamic vulcanization process was used, which produces a dispersion of crosslinked polymeric material within the uncrosslinked polymer material [3]. In this case, the polyester used is an unsaturated resin composed of phthalic acid and standard glycols [9]. These glycols have alcohol and hydroxyl type functionalities in their structure. It is likely that in the vulcanization process the phthalic acid insaturations had reacted with sulphur, crosslinking with the natural rubber chains, and that the uncrosslinked polymeric material is constituted only by the polyester resin hydroxyl and alcohol functionalities, which facilitate the formation of hydrogen bonds with water molecules, resulting in the increased retention of this component into the membrane.

In the unmodified membranes, the proximity of the hydroxyl and alcohol functionalities with phthalic acid (with strong hydrophobic character) might have restricted the formation of hydrogen bonds, but when the insaturations of the phtalic acid reacted in the vulcanization a phase separation may had occurred which freed alcohol and hydroxyl groups from the hydrophobic effect of the acid, allowing the water uptake.

The results were submitted to an ANOVA analysis; the results are shown in Table II.

TABLE II
ANOVA RESULTS FOR WATER UPTAKE

| ANOVA Parameters | Factor | |
|---|---|---|
| | $TiO_2$ content | Vulcanization degree |
| Fcrit | 7.7086 | 7.7086 |
| F | 1.4651 | 61.6153 |
| P | 0.2928 | 0.0014 |

As noted, in the case of $TiO_2$ content, the value of P is higher than 0.05 and F is lower than Fcrit, so it is concluded that the introduction of 2% of $TiO_2$ does not have a statistically significant effect on the water uptake capacity of the membranes. On the other hand, the parameter P of the vulcanization degree factor is less than 0.05 and also the F parameter is greater than Fcrit, indicating that the vulcanization of the membranes has a significant impact on the studied property; this is confirmed by the increase of the property (95.35%).

*3.2. Ion exchange capacity.*

The results of ion exchange capacity are shown in Figure 3. As seen, the modifications made to the polyester and natural rubber membrane originate increases in ion exchange capacity.

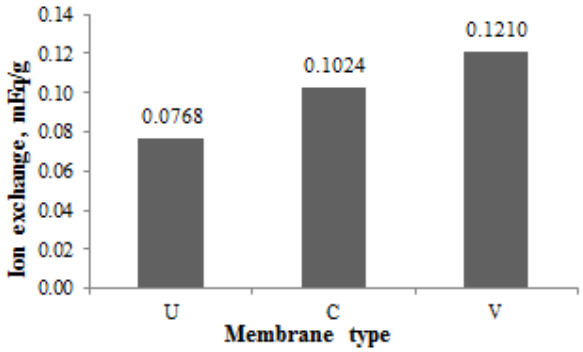


Fig. 3 Ion exchange capacity of membranes prepared. U: unmodified, without $TiO_2$ and not vulcanized, C: charged with 2% $TiO_2$, V: vulcanized and with $TiO_2$

The ion exchange capacity is deeply linked with the water uptake capacity of the membrane, due to migration methods presented in proton exchange membranes which are mainly Grotthuss and vehicular mechanisms. In the Grotthuss mechanism, protons "jump" from an $H^+$ donor site to any receiving water molecule in the vicinity, forming an $H_3O^+$ complex, while in the vehicular mechanism, protons are transferred through said hydronium ions. It can be noted that the presence of water is necessary for proton conduction in both mechanisms [10].

In this regard, ion exchange results obtained are consistent with the retention of water. The introduction of titanium dioxide and consequent formation of Ti-OH bonds increases the amount of water absorbed because of the formation of hydrogen bonds, and additionally increases number of exchange sites in the hybrid membranes [7]; this is confirmed by the 33.30% increase in the ion exchange capacity.

The vulcanized membranes have the highest exchange capacity, which is primarily due to the high water uptake they present, but also because of the phase separation between the crosslinked and uncrosslinked materials. The carboxyl groups from phthalic acid are weak proton exchangers [11], so their effect on the unmodified membranes is low, but when the phase separation between crosslinked and uncrosslinked material was made in the vulcanization, the carboxylic groups involved in the crosslinking reaction (because of the phthalic unsaturations) would end up to be closer, and consequently their effect of proton exchanger would be higher.

Analogous to the water uptake tests, the results of ion exchange capacity were submitted to an ANOVA analysis; the results are shown in Table III. For both factors it is observed that F is higher than Fcrit and P is lower than 0.05, so the null hypothesis is rejected and it is concluded that both factors have a significant effect on the ion exchange capacity of the prepared membranes, which supports the results shown in Figure 3.

TABLE III
ANOVA RESULTS FOR ION EXCHANGE CAPACITY

| ANOVA Parameters | Factor | |
|---|---|---|
| | $TiO_2$ content | Vulcanization degree |
| Fcrit | 7.7086 | 7.7086 |
| F | 26.8981 | 27.4780 |
| P | 0.0066 | 0.0063 |

### 3.3. *Mechanical properties*

The tensile strength test is shown in Figure 4, and the rupture stress (maximum stress), rupture strain (maximum deformation) and Young's modulus of the unmodified membrane of polyester and natural rubber can be seen in Table IV. Also the table shows the respective values for the commercial membrane Nafion ® 117 [12], for comparison purposes.

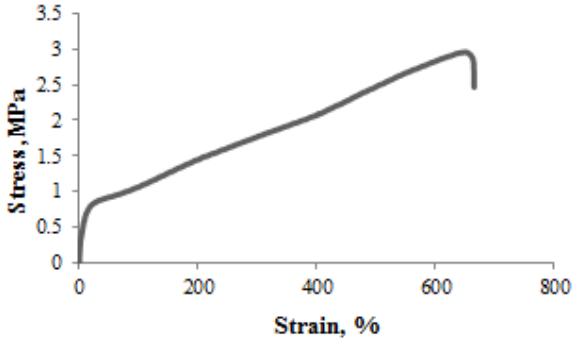


Fig. 4 Stress – strain curve for unmodified membrane.

TABLE IV
UNMODIFIED POLYESTER-NATURAL RUBBER AND NAFION 117® MECHANICAL PROPERTIES

| Property | Unmodified Polyester-natural rubber | Nafion® 117 |
|---|---|---|
| Maximum stress | 2.95 MPa | 43.5 MPa |
| Maximum strain | 648.2% | 225% |
| Young's modulus | 759.68 MPa | 249 MPa |

Maximum stress of the unmodified membranes is lower than that presented by Nafion ® 117 membrane; however, this does not preclude the membranes made in this investigation for its use in fuel cells because in previous researches membranes with much lower maximum stress values than Nafion® 117 have been synthesized yet have operated without problems in fuel cells [13, 14]. Additionally, it was found that maximum strain values and Young's modulus of unmodified membranes are superior to those exhibited by Nafion® 117, indicating that unmodified membranes are more rigid and stable against external stresses than commercial membranes.

## 4. CONCLUSIONS

In the present paper, proton exchange membranes were synthesized from the polyester and natural rubber blend. The blend was modified by the introduction of $TiO_2$ as inorganic load and by inducing crosslinking using dynamic vulcanization.

The vulcanized membranes showed the best results in terms of water uptake and ion exchange, because of the separation between crosslinked and uncrosslinked material from the vulcanization reaction and subsequent phase separation in hydrophobic and hydrophilic regions, allowing increased water uptake and promoting proton migration. Additionally, the carboxylic groups in the hydrophobic phase are closer thereby increasing the potential proton exchange capacity.

The load percentage affects more significantly the ion exchange than the water uptake, due to the Ti-OH bonds that are formed on the surface of the inorganic particles, which constitute new proton exchange sites.

Regarding mechanical properties, it was found that the behavior of the unmodified membrane is suitable for its application as the electrolyte in fuel cells.

The above results indicate that the blend between unsaturated polyester resin and natural rubber constitutes a material with high potential for further studies concerning their application as proton exchange membranes in fuel cells.

## 5. ACKNOWLEDGMENTS

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## REFERENCES

[1] N. Jalani, S. Mizar, P. Choi, C. Furlong and R. Datta, "Optomechanical characterization of proton-exchange membrane fuel cells", Proc. SPIE, vol. 5532, pp. 316–571, 2004.

[2] S.M.J. Zaidi and T. Matsura (Eds), Polymer membranes for fuel cells. Ed. New York, United States of America: Springer, 2009.

[3] J. Mark, B. Erman and M. Roland (Eds), Science and Technology of Rubber, 3rd ed., Ed. Waltham, United States of America: Elsevier Academic Press, 2013

[4] V. Shahi, "Highly charged proton-exchange membrane: Sulfonated poly(ether sulfone)- silica polyelectrolyte composite membranes for fuel cells", Solid State Ionics, vol. 177, pp. 3395–3404, 2007.

[5] J. Balster, O. Krupenko, I. Pünt, D. Stamatialis and M. Wessling, "Preparation and characterisation of monovalent ion selective cation exchange membranes based on sulphonated poly(ether ether ketone)", Journal of Membrane Science, vol. 263, pp. 137–145, 2005.

[6] L. Wang, Li. K., G. Zhu and J. Li, "Preparation and properties of highly branched sulfonated poly(ether ether ketone)s doped with antioxidant 1010 as proton exchange membranes", Journal of Membrane Science, vol. 379, pp. 440–448, 2011.

[7] L. Barbora, S. Acharya and A. Verma, "Synthesis and Ex-situ Characterization of Nafion/$TiO_2$ Composite Membranes for Direct Ethanol Fuel Cell", Macromolecular Symposia, vol. 277, pp. 177–189, 2009.

[8] S.J. Skinner and T.J. Drakeley, "Water Absorption by Rubber. Part II. Vulcanized Rubber", Rubber Chemistry and Technology, vol. 6, pp. 12-23, March 1933.

[9] (2013) The BASF Chemical Company, Chile. [Online]. Available: http://www.basf.cl/sac/web/chile/es_ES/palatal/ resina_poliester/

[10] M. Amjadi, S. Rowshanzamir, S. Peighambardoust, M. Hosseini and M. Eikani, "Investigation of physical properties and cell performance of

Nafion/$TiO_2$ nanocomposite membranes for high temperature PEM fuel cells", International Journal of Hydrogen Energy, vol. 35, 9252–9260, 2010.

[11] P. Martínez and E. Rus, Separation operations in chemical engineering, calculation methods [Operaciones de separación en ingeniería química, métodos de cálculo], Ed. Madrid, España: Pearson Educación S.A., 2004.

[12] "DuPont Nafion PFSA Membranes: N 115, N 117, N 1110 data sheet", DuPont, Wilmington, United States of America.

[13] F. Barroso-Bujans, R. Verdejo, A. Lozano, J. Fierro and M. Lopez-Manchado, "Sulfonation of vulcanized ethylene–propylene–diene terpolymer membranes", Acta Materialia, vol. 56, pp. 4780 – 4788, 2008.

[14] Z. Yang, D. Coutinho, D. Yang, K. Balkus and J. Ferraris, " Proton-conducting membranes based on HTFSI-doped PEI/SiO2 nanocomposites", Journal of Membrane Science, vol. 313, pp. 91–96, 2008.