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Effect of Vulcanization Process on The Polymeric Membranes Prepared Using Rubber For Application In a Fuel Cell

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Abstract

Polymeric membranes for application in fuel cell were prepared from vulcanization of natural rubber. In order to compare synthesis methods, membranes were modified by addition of titanium dioxide as inorganic load. Physicochemical properties were investigated by water uptake, ion exchange capacity, stress–strain tests and FTIR spectra. Furthermore, the FTIR spectra of the membranes indicate the presence of sulfur in the prepared membranes. Water uptake and ion exchange capacity of vulcanized membranes and loaded with titanium dioxide (TiO_2) were found to be lower than that of the pure latex membrane.

Keywords: Fuel cell, Rubber vulcanization, Titanium dioxide.

Introduction

The fuel cell is considered one of the most promising sources of energy. Fuel cells are characterized by higher efficiency than conventional power plants, but they are also environmentally clean, have extremely low emission of sulfur and have very low noise. For the near future, hydrogen is one of the most promising energy carriers, because it can be used without emissions in almost every application where fossil fuels are used today [1, 2]. Fuel cell with a polymeric proton exchange membrane (PEM) utilizes hydrogen and oxygen to generate electricity, water and heat, have high power density, and have long life [3]. The critical operating parameters are the regulation of flow of oxygen and hydrogen feeds, heat and management of water.

Polymeric membrane is the core of the fuel cells that allows the transport of water and protons, and separates the reactants H_2 and O_2, which converts the chemical energy into electrical energy [4]. These membranes must have high ion conductivity, good proton conductivity, chemical stability in the presence of oxygen and hydrogen, impermeability to gases, such as hydrogen and oxygen, good tensile strength and flexibility [5, 6]. The development of improved membrane materials has been the focus of research for decades, and success in this regard would represent a key step forward in low-temperature fuel cell technology and low cost [7-9]. A several of sulfonated polymers have been investigated as membranes for application in a fuel cell, including polystyrene copolymers [10,11], poly(ether sulfone), and polyimides [12,13]. Although these membrane display good proton conductivity under certain conditions, their application in fuel cell membranes is hampered by their instability toward hydrolysis and heat. Introducing flexible linkages, separating the sulfonic acid group from the diamine parts, and using aliphatic diamines could improve the stability of these materials, but research on more stable membranes would remain highly desirable [14].

During the last three decades, perfluorosulfonic acid polymers like Nafion® have been used in fuel cell [15]. The perfluorinated structure provides good thermal and chemical stability and high proton conductivity. Nevertheless, inherent drawbacks such as difficult synthesis, high cost, and moderate operating temperature. Thus, the development of low-cost, high-performance PEMs, and easy recycling to avoid environmental damage [15, 17] has been the focus of considerable research throughout the past decade [9–11]; thus, several projects related to the production and treatment of hydrogen by economically viable and environmentally has been developed [18, 19], as renewable energy project to produce hydrogen [20]. The objective of this work is to study the effect of vulcanization of natural rubber on the physicochemical properties of membranes such as water uptake, ion exchange capacity, stress and strain, and functional groups. Furthermore, the effect of TiO_2 on the vulcanized membrane properties was examined.

Experimental

Materials

The natural latex was obtained from the company AV Guantes Industriales (Colombia Company). Titanium dioxide, toluene, and hydrochloric acid are reactive of analytic grade used for the preparation of the membranes modified by vulcanization and addition of titanium dioxide as inorganic load.

Membrane synthesis

Unmodified and Vulcanized Membranes

The unmodified membranes (UM) were prepared by dissolving natural rubber in distilled water for 20 min for preparing a 15% m/v solution, then the solution was casted into a Petri dish and dried at room temperature for 4 days to get the films as detail in [17, 19]. The vulcanized membrane was prepared by dissolving the natural rubber in toluene with continuous stirring at 75 °C to form a 3.64%m/v solution. Then, 0.32 g of sulfur was added and the solution was heated at 140°C for 5 hours to develop the vulcanization reaction [21]. The resulting solution was cast onto a Petri dish until solvent was evaporated

Vulcanized Membranes and loaded with TiO_2

The natural rubber was dissolved in toluene, then, TiO_2 was added to it with continuous stirring during 3 hours to form a homogeneous solution. After, it was carried out the vulcanization process as explained above. Finally, the product obtained was poured into a petri dish for laminating the membrane.

Membrane Characterization

Water Uptake

The dry samples were weighed and then immersed for 24 hours in a container with distilled water at room temperature. Then the samples were taken from the containers and surface water was removed with absorbent paper, to obtain the wet weight. The percentage of water retention is calculated by the following equation [22].

$$\text{Water uptake (\%)}=\frac{W_{wet}-W_{dry}}{W_{dry}}\times 100 \tag{1}$$

where, W_{wet} and W_{dry} are the wet and dried membrane weights, respectively.

Ion Exchange Capacity

The ion exchange capacity of the membranes was evaluated using a classical method of titration. The membranes were immersed in a 1 M HCl solution for 24 hours to bring them to protonic form, and then they were washed with large amounts of distilled water to remove excess acid. Subsequently the membranes were placed in a 0.1 M NaCl solution for 24 hours, and then the solution was titrated with 0.01M NaOH. The ion exchange capacity was calculated using the following relation [23, 24].

$$\text{IEC(mequiv/g dry membrane)}=\frac{C_{Na^+}\times V_{sol}}{W_d} \tag{2}$$

where C_{Na^+} is concentration of Na^+ in the solution, V_{sol} is the NaOH volume and W_d is the membrane weight.

Mechanical Properties

The mechanical properties of the membranes were measured using a Universal Tester EZ - S Shimadzu, at a crosshead speed of 250 mm/min. The samples were carefully cut into a size of 25 mm x 70 mm, with a thickness of 0.03 mm, which was needed for the calculation of tensile strength.

Results and Discussion

Figure 1 shows prepared membranes according to the procedure explained above, which have different appearances due to the modifications. The vulcanized membrane shows ramifications due to the crosslinks between polymer chains and sulfur that takes place in the vulcanization reaction.

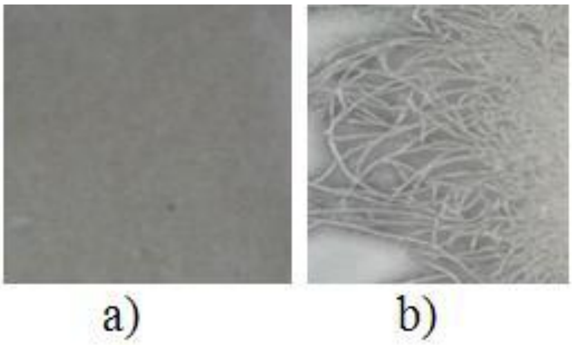

Figure 1: Membranes synthesized. a) Unmodified, b) Vulcanized.

Water Uptake

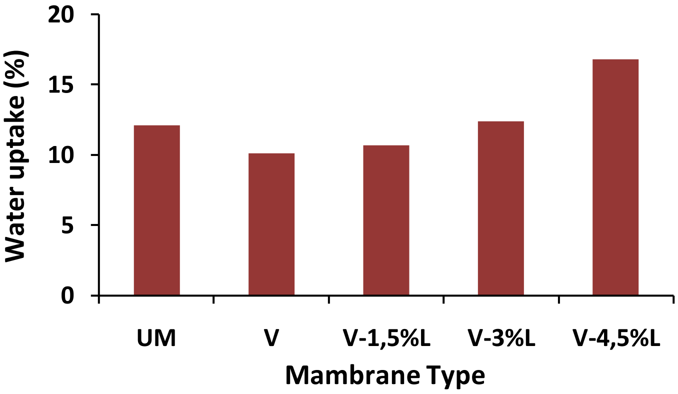

Figure 2: Water uptake of membranes synthesized, U: unmodified, V: vulcanized, V-#%L: Vulcanized and loaded with #% TiO_2.

Figure 2 shows the effect of vulcanization process on the water uptake. Vulcanized membranes showed a decrease in water uptake of 16.75% compared to unmodified membranes, this result provides an indication of the formation of crosslink density and better interaction between the sulfur and latex, due to the molecular structure of vulcanized polymer becomes stiffer and less penetrable by the water molecules [25]. However, the increase of TiO_2 content in vulcanized membranes from 1.5% and 4.5% increased the water uptake from 10.7 % to 16.8 %, respectively. This can be attributed to the presence of the hydrophilic inorganic TiO_2 particles reinforced in Latex matrix [17, 26].

Ion Exchange Capacity

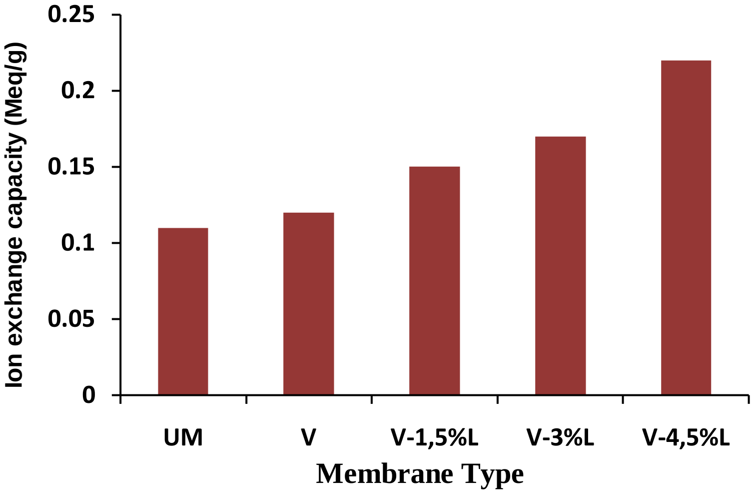

Figure 3: Ion exchange capacity of membranes synthesized, U: unmodified, V: vulcanized, V-#%L: Vulcanized and loaded with #% TiO_2

Figure 3 shows the effect of TiO_2 load of vulcanized membrane on the ion exchange capacity. The ion exchange capacity of vulcanized membrane increases with increasing of TiO_2 content due to that the vulcanizing process allows the interaction between polymer structure and sulfur which causes a membrane stiffer and less penetrable by the water molecules [25], this phenomenon decreases proton transfers. The methods of proton transfer presented inside the PEM are mainly the Grotthuss and the vehicular mechanisms. In the Grotthuss mechanism, the protons jump from one place to another through the membrane, while in the vehicular mechanism the hydrated proton (H_3O^+) diffuses through the aqueous medium in response to a difference electrochemical [27].

Analysis of FTIR Spectra For Unmodified and Vulcanized Membrane

Figure 4 indicates the specific peaks that can be used for analysis of spectra of the unmodified and vulcanized membranes in the range of 500-4000 cm^{-1}. In both spectra, the peaks between 2.939-2.912 cm^{-1} correspond to CH and CH_2 groups [16]. The peak at 1650 cm^{-1} is associated to the water absorption in the surface [17-19, 25]. On the other hand, the vulcanized membrane presents high intensity of peaks between 600 and 700 cm-1 with respect to unmodified membrane, due to the C-S bond attributed to addition of sulfur atom [28].

Mechanical Properties

The mechanical properties of unmodified and vulcanized membranes are shown in Table 1. In addition, the Nafion NRE 211-10 commercial membrane is presented in the same table by comparing with prepared membranes.

The maximum tensile strength and maximum elongation of vulcanized membranes increase with increasing the TiO2 load, because the incorporation of ceramic filler such as TiO_2 increases the mechanical stability of the polymer structure [29]. Meanwhile, the maximum stress and maximum strain of commercial Nafion® 211-10 membrane are 8.30 MPa and 102.5%, respectively [29]. By comparing these properties is observed that the maximum stress of the unmodified membrane is lower than commercial membrane. However, in other investigations, membranes with values of maximum tension lower than Nafion membrane values have been used in fuel cells [30, 31].

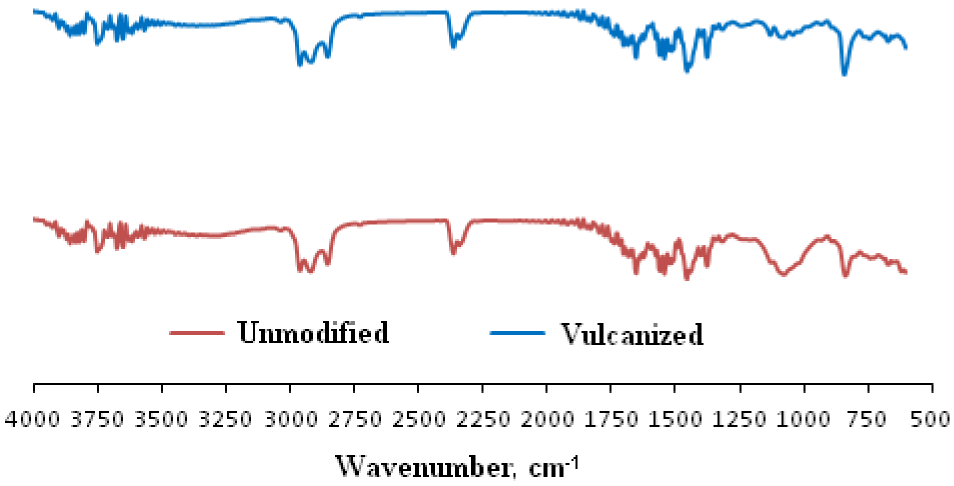

Figure 4: FTIR Spectra of Prepared Membranes

Table 1: Mechanical Properties of Prepared Membranes

Membrane Type	**Maximum tensile strength (Mpa)**	**Maximum elongation (%)**
Nafion NRE 211-10	8.30	102.5
Sin modificar	1.10	833.0
Vulcanizada	1.43	715.6
Vulcanizada cargada 1.5%	1.61	659.8
Vulcanizada cargada 3%	1.64	620.4
Vulcanizada cargada 4.5%	1.76	549.2

Conclusions

The effects of vulcanization and TiO_2 load on the proton exchange membranes prepared using vulcanization of natural rubber were studied. Water uptake of vulcanized membranes is lower than the unmodified membranes, this behavior is due to the formation of high crosslink that occur in the vulcanization, which transform the molecular structure of polymer in stiffer and less penetrable by the water molecules. However, maximum tensile strength and ion exchange capacity increase with increasing the TiO_2 load of vulcanized membrane. The results obtained suggest high potential for the application as proton exchange membrane for fuel cells.

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