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SYNTHESIS OF PROTON EXCHANGE MEMBRANE BY POLY VINYL ALCOHOL - STYREN ACRILIC ESTER COPOLYMERS LOADED WITH NANOCLAYS

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ABSTRACT

Proton exchange membranes were synthesized by using Polyvinyl Alcohol (PVA) and Styrene Acrylic Ester (SAE) copolymers, and modified with addition of nanoclays as loaded in order to improve the physicochemical and mechanical properties and to implement as electrolyte in a fuel cell and to produce energy. Proton exchange membranes were characterized by water uptake, ionic exchange capacity, oxidative stability and FTIR spectra. Maximum effort, deformation and Young´s Modulus were determinate by the tensile tests. It is observed that the membranes loaded with 2% had the highest values of water uptake 129%, due to the high hydrophobicity of PVA, this is reflected in the mechanicals properties since this membrane presented the lowest value of maximum effort, while for ion exchange capacity, loaded 3% membrane present the highest value 1,429 meq/g.

Keywords: proton exchange membranes, polyvinyl Alcohol, Styrene Acrylic, nanoclays.

INTRODUCTION

Fuel cells are devices used to generate clean energy, since hydrogen is used as fuel that generates electricity, water and heat. This fuel cell does not generate pollution and these devices are a possible alternative for solving energy problems, the proton exchange membrane is the main part of the fuel cell. Currently, the perfluorinated Nafion membrane is the most widely used; however, it has low efficiency at high temperature and high production cost [1]. Many investigations have been carried out using different polymers such as vinyl acetate - acrylic ester, unsatured polyester, natural latex, acrylic ester - vinyl acetate copolymer, SEBS among others, these membranes were modified with different loads such as titanium dioxide, vanadium pentoxide and silica gel. Furthermore, these polymers were modified by the sulfonation technique to improve their physicochemical properties, and were characterized to analyze its implementation in a fuel cell. [2-5].

In this research, proton exchange membranes were synthetized by using PVA and styrene acrylic ester copolymer modified with nanoclays at different concentrations. Membrane characterizations such as water uptake, ion Exchange capacity, stability oxidative and FTIR spectrum were carried out to determine its use in fuel cells.

MATERIALS AND METHODS

Poly Vinyl alcohol and Styrene Acrylic Ester (SAE) is used to prepare the membranes. Initially, formaldehyde and potassium hydroxide were used for crosslinking of PVA and nanoclays were used to load membranes. Chemical substances used in characterizations were: chloride acid, sodium chloride, sodium hydroxide and hydrogen peroxide.

For the preparation of the membrane, the PVA was first diluted in distilled water by stirring for 24 hours, then the crosslinking process with formaldehyde and potassium hydroxide was carried out for 24 h to decrease the hydrophilicity of the PVA. SAE was added to the solution and stirred for 1 hour to obtain a homogeneous solution. For the addition of charge, nanoclays were added at different concentrations (1, 2, 3 and 4%) to the solution and stirred for 2 hours; each solution was served in a Petri dish to form laminated membranes.

Water Uptake characterization was carried out by immersion in distilled water of the membranes during 24 hours previously dried in a hoven, then membranes were weighed [3]. For calculated the water uptake it used the next equation:

$$\frac{(W_w - W_d)}{W_d} x100 \quad (1)$$

Where *Ww* is wet weight and *Wd* is dry Weight.

Ion exchange capacity was carried out by titration, first membranes were weight and immersed in chloride acid during 24 hours, then membranes were also submerged in sodium chloride during 24 hours and tittered with sodium hydroxide [5]. IEC is calculated by next equation

$$\mathrm{IEC} = \frac{V[\mathrm{NaOH}]}{m} \quad (2)$$

where *V* is volume of NaOH, and *m* is the mass of membranes.

Oxidative stability characterization was carried out by immersion of the membranes in hydrogen peroxide, for 7 days, membranes were weighed every 24 hours to determine the weight loss [6]. FTIR spectra were determined in Nicolet spectrometer. Mechanicals properties were carried out in universal machine at 250mm/s.

RESUSLTS

Figure-1 shows five type of membranes prepared: 0%, 1%, 2%, 3% and 4% loaded with nanoclays.

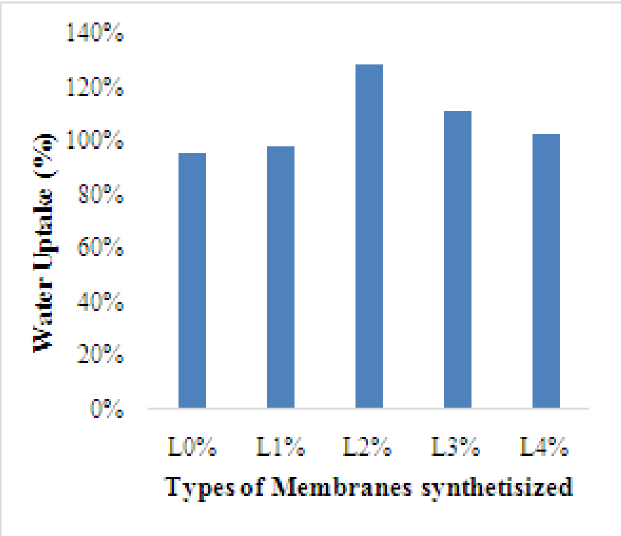

Figure-1. Proton exchange membranes loaded with nanoclay: a. 0%, b. 1%, c. 2%, d. 3%, d. 4%.

Water Uptake

The water absorption performance for each prepared membrane is shown in Figure-2.

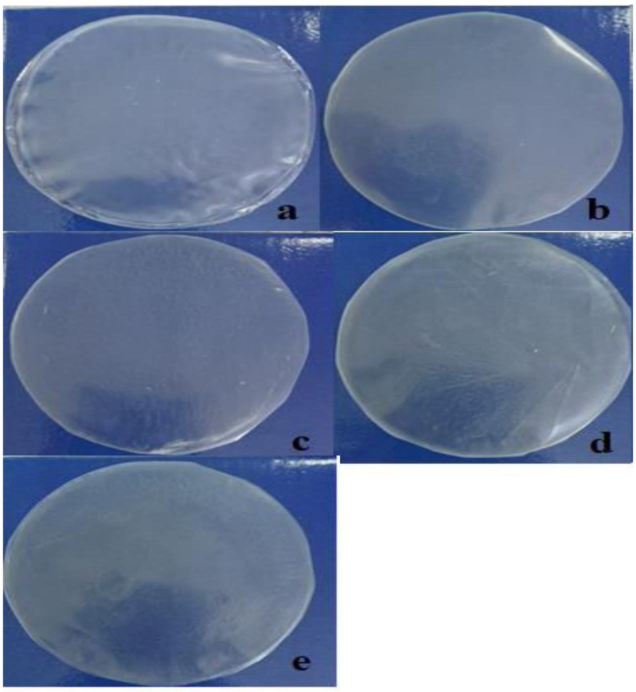

Figure-2. Water uptake for each prepared membrane.

Since 129% is the highest water absorption value corresponding to the loaded membrane of 2%? It is observed that all membranes have high water uptake values, due to the PVA is highly hydrophilic because of the hydroxyl groups that allow a hydrogen bonding to be formed in the water [7], and that is why crosslinking is implemented to reduce hydrophilicity in the polymer [8]; On the other hand, SAE is used as a waterproofing in construction, which also helps decrease water absorption [9].

While, the addition of Nanoclay until 2% increases the water uptake, however, high concentration of nanoclay particles significantly reduced the water absorption in composites due to the property of adhesion with the polymer matrix [10], that's why is establishing a maximum water uptake.

Ion Exchange Capacity

Ion exchange capacity of proton exchange membrane is directly proportional to the ion exchangeable groups in the membrane matrix [11]. IEC was calculated using eq 2 and its representation is observed in figure 3, it can see that the IEC values range from 0,755 to 1,429 meq/g. The membrane loaded 3% has highest value, the addition of nanoclays increase de IEC to maximum point, due to the nanoclays are easily dispersed only in hydrophilic polymers (vinyl alcohol, ethylene oxide) [12]; furthermore, it improves the IEC since the water uptake increases the ionic conductivity according to Grothus mechanism [13].

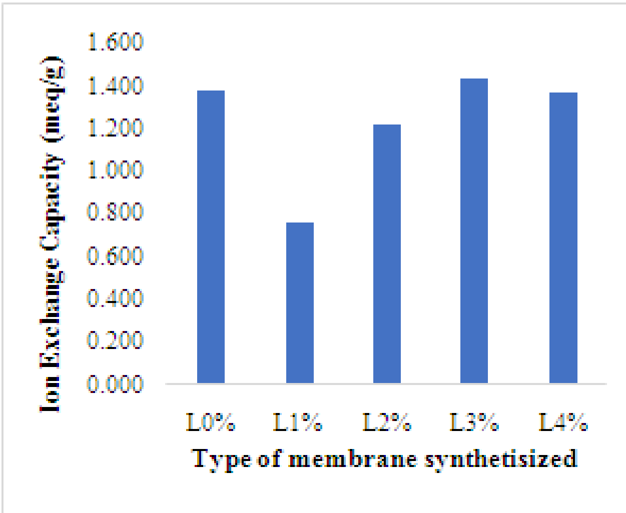

Figure-3. Ion Exchange Capacity for each prepared membrane.

Stability Oxidative

Oxidative stability was carried out to determinate the membrane durability in oxidizing environment, the weight variation with respect to time it is observed in Figure-4. Initially membrane lost a significant weight, this is attributed to the hydrophilicity of PVA which allows that samples to absorb the water present in the H_2O_2 due to the polymer chains are attacked by the H_2O_2 and degrading the samples quickly; while the low Hydrophilicity activity of nanoclays helps maintain a stable weight for the remaining days.

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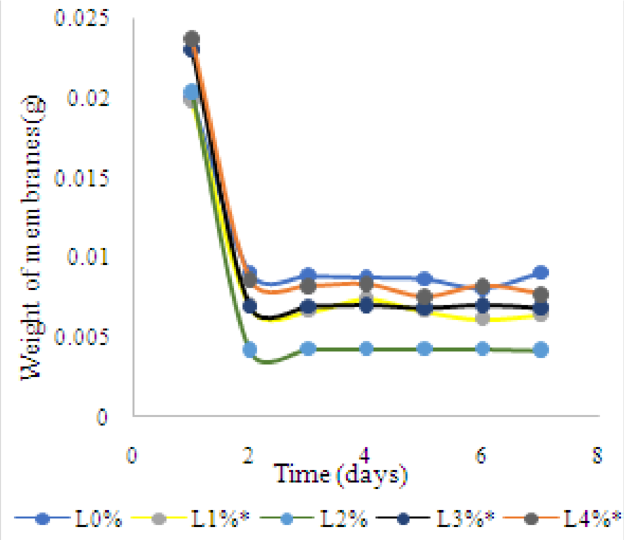

Figure-4. Oxidative stability for each prepared membrane.

FTIR Spectrum Analysis

Figure-5 shows the spectra of unmodified and loaded membranes, a wide peak is observed in the range of 3000 to 3400 cm^{-1} corresponding to the hydroxyl group of PVA, [17]; by other side, a peak observed in 1733 cm^{-1} is attributed to carbonyl group C=O present in SAE, in the range of 1507cm^{-1} and 1558cm^{-1} is found peaks corresponding to the vibrations of the C=C bond of the aromatic ring, there also is a band in 1457cm^{-1} related to the C-H bond of the CH_2 group. Finally, it is observed the band corresponding to the benzene ring of styrene which are 759 cm^{-1} and 699 cm^{-1} [14]. For loaded membranes with nanoclays is observed a characteristic 525cm^{-1} peak of inorganic material O-SI-O in the spectrum [15].

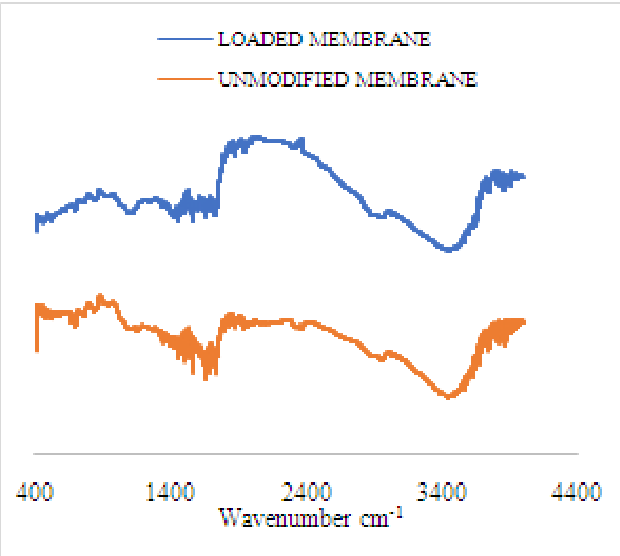

Figure-5. FTIR spectra for unmodified and loaded membranes.

Mechanical Properties

Maximum effort, deformation and Young's Modulus were determinate for each membranes as indicated in Table-1. It is observed that L2% loaded membranes presented the lowest value of maximum effort. This membrane has the highest water absorption value that causes deterioration of the polymeric matrix, and therefore reduces the mechanical resistance [16-17], this maximum effort value is higher than Nafion 117 (43, 5 N) [18].

Table-1. Mechanicals properties of membranes.

Sample	Maximun Effort (Kpa)	Deformation (%)	Young´s modulus (Kpa)
L0%	120,9	157,49	0,44
L1%	63,675	36,13	0,23
L2%	52,62	30,51	0,41
L3%	60,325	73,70	0,41
L4%	78,1	105,53	0,42

CONCLUSIONS

In the present research, proton exchange membranes were synthesized using the PVA and SAE polymers, it was found that the addition of nanoclays increases water absorption to a maximum point, and then decreases as more nanoclays is added; the same behavior happens with the ion exchange. The maximum effort decreases with increasing the water content. The membrane synthetized has characteristics for application in fuel cells.

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