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DEVELOPMENT AND CHARACTERIZATION OF POLY (OXY-1,4-PHENYLENESULFONYL-1,4- PHENYLENE) FOR PROTON EXCHANGE MEMBRANES

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Key words: fuel cell, membrane sulfonation, polyethersulfone membrane, proton exchange membrane, nanoclay

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DEVELOPMENT AND CHARACTERIZATION OF POLY(OXY-1,4-PHENYLENESULFONYL-1,4-PHENYLENE) FOR PROTON EXCHANGE MEMBRANES

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Proton Exchange Membranes (PEMs) were synthesized from Poly (oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES), sulfonated for 1 and 2 h, and modified with 0, 5, and 10 wt% nanoclays. The membranes were characterized by evaluating their physicochemical properties, such as ion exchange capacity, oxidative stability, porosity and water uptake. PEMs were modified with the sulfonation time and nanoclays addition to favor the mechanical properties and proton conductivity, which were evaluated. The sulfonation time and the concentration of nanoclays directly favored properties such as contact angle, water absorption, porosity, and mechanical properties. However, a higher concentration of nanoclays (e.g., 10 wt%) damaged the mechanical properties of PES membranes specifically. The membrane with 5 wt% of nanoclay and a sulfonation time of 2 h achieved the best performance.

Key words: fuel cell, membrane sulfonation, polyethersulfone membrane, proton exchange membrane, nanoclay

INTRODUCTION

Natural processes and human activities emit greenhouse gasses (GHGs), and they have a far-ranging environmental and health effects. Human-driven activities release GHGs that alter the natural balance in the atmosphere and are highly likely to be the driving force of the observed warming since the mid-20th century [1].

The rush to reduce GHG emissions and decrease the use of fossil fuels has driven the search for alternative energy requirements in today's global society. Renewable energy technologies are one of these potential options. However, these still are involved in studies to improve their design, infrastructure, efficiency, and costs. The forecasts that place them between 30 - 50% of participation in the energy market by 2050 depend on these findings [2].

Proton exchange membrane fuel cell (PEMFC) has been receiving much attention as a new energy technology because of its excellent thermal and mechanical stability. Fuel cells have three main applications: portable uses, transportation and stationary installations. Generation of silent and clean electricity are among the advantages of this technology. In terms of productivity, fuel cells are more efficient in energy production than combustion turbines, as their thermodynamic efficiency derives from the chemical energy of a fuel (hydrogen) and an oxidant (oxygen), obtaining water as a secondary product [3]. Nafion, produced by Dow-DuPont, is the most common and commercial polymer film used in fuel cells. However, this material presents low conductivity at lower humidity, poor mechanical properties at higher temperatures, and the platinum required to build the electrodes in the fuel cells limits its development and implementation [4 - 6].

Numerous efforts have been made to develop membranes with higher performance in comparison to the Nafion ones. Hence, latex membranes have become a potential candidate, as they have shown an improved execution when they are modified with vanadium oxide (V_2O_5) [7], Acrylic Ester and Styrene [8], styrene-ethylene-butylene-styrene (SEBS) modified with titanium oxide (TiO_2) [9], or natural rubber [10]. In this study, the physicochemical and mechanical properties of sulfonated proton exchange membranes (PEMs) synthesized from phenylene) ofr proton exchange membrane-spoly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES) and modified with nanoclays were evaluated. Characterization analysis showed promising results for PEM membranes, offering a viable alternative for commercial use. These results contribute to the future design of PES-based membranes for sulfonated PEM fuel cells and their functionalization with nanoclays, setting the ground for optimizing and developing more energy-efficient and lower-cost fuel cells.

MATERIALS AND METHODS

Materials

Poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)(Sigma-Aldrich®) was used in the membrane's synthesis. Nanoclays used in this project were prepared by modifying the sodium montmorillonite clay with the surfactant Arquad HTL8-MS (kindly donated by AkzoNobel). Acetic anhydride, sulfuric acid, dichloromethane, and toluene used in the sulfonation process were purchased from PanReac AppliChem.

Synthesis and modification of membranes

Preparation of nanoclays: Nanoclays were prepared by following Durán and coworkers' protocol [11]. Initially, a solution was prepared by adding 15 g sodium montmorillonite clay to 1200 ml of water/ethanol mix (4:1 v/v) and stirred for 2 h at 60°C. Another solution was prepared by adding 5g Arquad HTM8-MS to 100 ml of distilled water and mixed until homogenized. Both solutions were mixed in an ultrasonic processor for 1 h and then stirred for 12 h at 60°C. The sample was washed with a water/ethanol mix (1:1 v/v), dried in an oven for 8 h at 60°C and stored for future use.

Preparation of sulfonated and loaded membranes: The sulfonation process was conducted according to the procedure described by Mokrini & Acosta [12]. Two solutions were prepared separately. For the first solution, 25 ml of cold dichloromethane was mixed with 1.2 ml of acetic anhydride. Then, 0.65 ml of 96% sulfuric acid was added. This reaction was kept at 0° C in an ice bath until it was added to the reaction medium. The poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) polymer was dissolved in 25 ml dichloromethane. The nanoclay was then added at two different percentages (5% or 10% w/w) and mixed in an ultrasonic processor. Consequently, both solutions were mixed and stirred for about 2 h (sulfonation time). Finally, the mix was poured into a Petri plate and labeled accordingly.

Characterization

Water uptake capacity was evaluated by weighing the membrane before and after immersing it in distilled water for 24 h. The percentage of water uptake was calculated with the following expression:

$$\% \text{ Water uptake} = \left(\frac{W_w - W_d}{W_d} \right) * 100 \quad (1)$$

Where W_w and W_d represent the weights of the hydrated and dried membranes, respectively [13].

Membrane porosity was measured by weighing the membranes after being immersed in distilled water for 1 h and after being dried at 60 ° C for 24 h. The following equation was used to determine the porosity of the membrane:

$$P(\%) = \left(\frac{Q_0 - Q_1}{\frac{\rho_{\text{water}}}{A * h}} \right) * 100 \quad (2)$$

Where Q_0 is the weight of the wet membrane, Q_1 is the weight of the dry membrane, ρ_{water} is the density of water, A is the surface area of the membrane, and h is the thickness of the membrane [14].

The sessile drop technique was used to measure the contact angle that a liquid drop makes with the membrane surface. A drop of water was placed on the membranes' dry surface, and the angle was recorded using a goniometer.

The membrane's ion exchange capacity (IEC) was determined by the titration method. Membranes were washed and immersed for 24 h in 1 M HCl and 1 M NaCl. Subsequently, the H^+ protons solution was titrated with a 0.01 M NaOH solution using a phenolphthalein indicator [8]. The IEC was calculated according to the following equation:

$$IEC = \frac{V * M}{W} \quad (3)$$

Where V was the titration solution volume when the equilibrium was reached, M is the titration solution's concentration, and W is the weight when the sample was dry.

The oxidative stability in the membranes was tested by immersing them in a solution of (50 wt%) for three days, weighing every day. The membranes' tolerance to the exposure of was established by the following expression:

$$\text{Tolerance to } H_2O_2 = \left(\frac{W_w - W_d}{W_d} \right) \quad (4)$$

Where W_w and W_d are the weights of the hydrated and dry membranes, respectively.

Mechanical properties, like tensile strength and break elongation were determined in the membranes, following the ASTM D882 procedure, and using a SANTAM model STM-20 universal testing machine.

The proton conductivity test was carried out using the electrochemical impedance spectroscopy technique. For the test, samples of sulfonated membranes with dimensions of 0.5 x 0.5 cm were used.

RESULTS AND DISCUSSIONS

Water uptake and porosity

The sulfonated PES membranes have hydrophilic regions formed by ionic groups, primarily responsible for water absorption [15]. Therefore, it can be assumed that the longer the sulfonation time, the higher the water uptake capacity. On the other hand, nanoclays have on their surface remaining ions, such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} obtained during the ion exchange before its synthesis, which makes them polar molecules and affinity to water due to their electronegativity difference (Figure 1).

Increasing the percentage of nanoclay and the sulfonation time during the membrane synthesis resulted in an

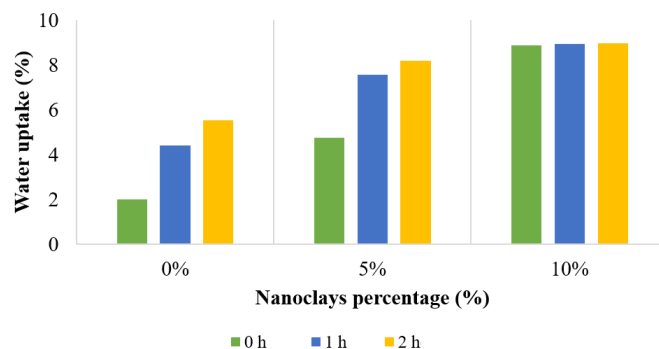


Figure 1: Quantification of water uptake percentage for each type of membrane

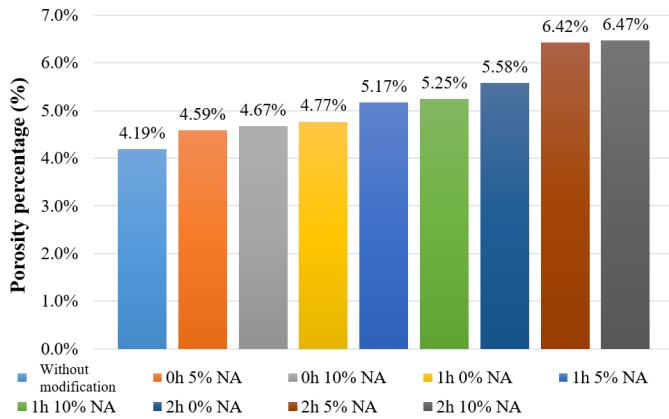


Figure 2: Evaluation of porosity percentage of each type of membrane

increment in the membrane porosity rate (Figure 2).

This raise in pore content resulted from the nanocomposites agglomeration along the membrane's surface, thus affecting the contact area at specific points of the polymer matrix [16].

Hydrophobicity

The hydrophobicity results obtained in this study agree with previous findings [17, 18]. These data suggest an inverse correlation between the contact angle and the nanoclay concentration, attributed to the high hydrophilic montmorillonite present in the clay [16]. Also, the high content of sulfonic acid groups was observed as the sulfonation time proceeded. This phenomenon is attributed to the strong hydrophilicity of the sulphonated group.

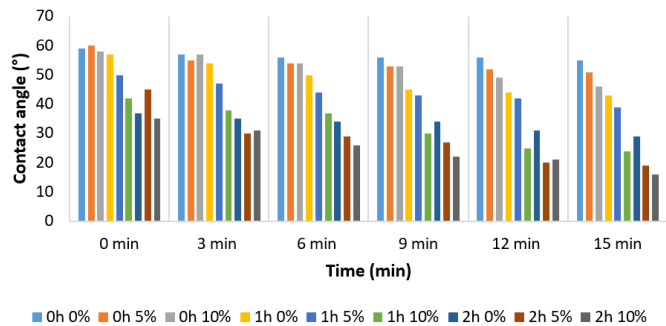


Figure 3: Contact angle of each type of membrane over 15 minutes

Ion Exchange Capacity

The fuel cell's performance depends on the ability of the electrolyte transportation capacity of ions from the anode to the cathode [19]. This test was performed by the titration technique. Figure 4 shows the values for each membrane assessed.

The sulfonation process favored the membranes' ion-exchange capacity (IEC), as it was registered at 1 and 2 hours. These findings were attributed to the hydrophilic sulfonic acid groups present in the polymer matrix [20].

As nanoclays were loaded on the membrane, its IEC was favored by more than 200%. However, when the

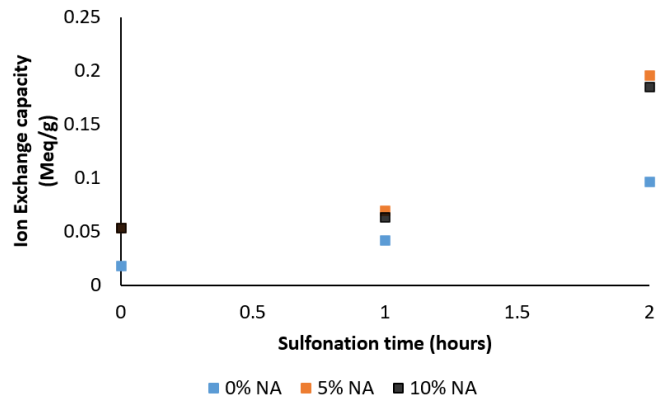


Figure 4: Ion Exchange Capacity (IEC) for each type of membrane

nanocomposite loading charge was at 10 wt%, probably a decrease in the number of millimoles H^+ ions that could be exchanged through the membrane, per unit of dry membrane mass, might occur [21] (Figure 4).

Oxidative Stability

The membranes' oxidative stability was evaluated by immersing them in 50 wt% hydrogen peroxide (H_2O_2) for three days. Daily, a membrane was taken out of the H_2O_2 solution, the remaining water on its surface was removed, and the membrane was weighted. This procedure was carried out in three technical replicates for each type of membrane. The results were averaged and plotted. Figure 5 shows the tolerance of the polymer membranes against H_2O_2 as a function of immersion time.

These results showed a stable behavior throughout the immersion time for most of the membranes, i.e., the hydrogen peroxide tolerance did not present a high variation during the three days of incubation time assessed. However, during the immersion time, the membranes did not show any degradation, so their consistency remained immutable. These findings indicate high oxidative stability. This analysis is consistent with previous reports, as it is well documented that PES membranes have excellent oxidative stability due to its rigid molecular structure [22].

The influence of nanoclays on the chemical stability of the membranes was evaluated by H_2O_2 immersion.

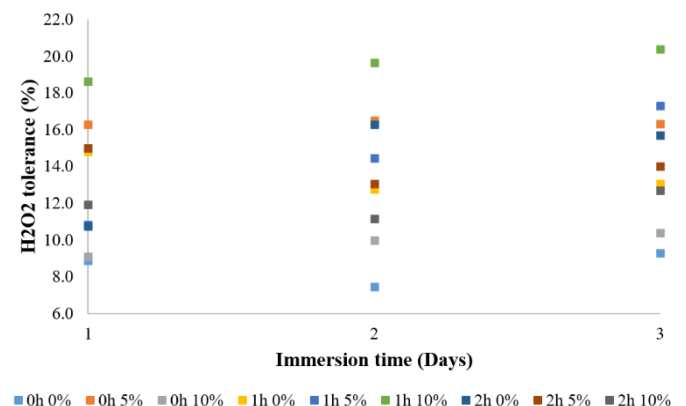


Figure 5: Evaluation of membranes' oxidative stability by H_2O_2 at 50 wt%

Increasing the nanoclay percentage load to the membranes leads to a rise in the membrane tolerance to H₂O₂ due to the increase in their porosity, which facilitates high liquid adhesion.

Mechanical Properties

As the sulfonation time increased, the membrane tensile stretch decreased due to an increment in its porosity (Figure 6). Consequently, the membrane became more brittle, altering its toughness [20]. As a result, there is a decrease in the total deformation energy that the membrane can absorb before reaching the rupture under stress conditions. Similar results were obtained when the elongation percentage was evaluated on the membranes when subjected to stress conditions. Similarly, elongation properties were also affected. As the sulfonation time increased, the membranes became more rigid and brittle, and consequently, the membrane elongates less (Figure 7).

On the other hand, as the concentration of nanoclay increased in the membrane content, it improves its resilience under mechanical stress (Figure 6). This increment was observed when the nanoclay percentage increased from 0% to 5%, regarding the sulphonated incubation time, reaching a maximum ability to bend and not break at the highest percentage. However, as the nanoclay content increased in the membranes, it caused them to

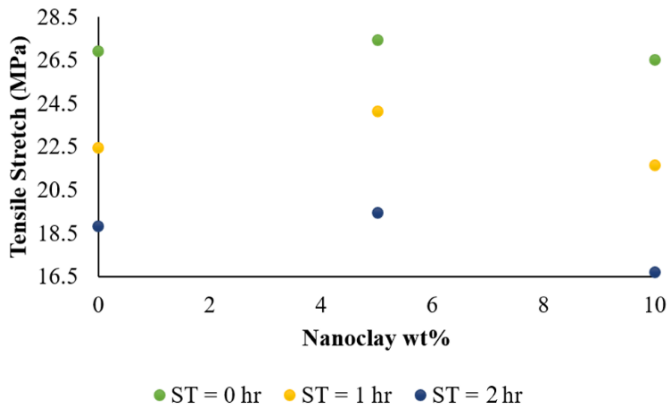


Figure 6: Membrane tensile stretch vs. Load of nanoclay in the membrane

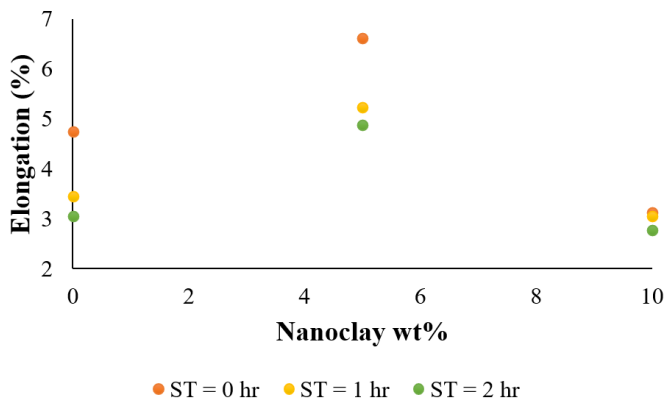


Figure 7: Membrane elongation vs. Load of nanoclay in the membrane

lose stiffness, leading to break even when exposed to low mechanical stress [16].

In addition, tensile elongation as a function of the sulfonation time showed similar performance in comparison to the tensile stretch as a function of the percentage of nanoclay present in the membrane (Figure 7). Moreover, the effects on the percentage of elongation due to an increase in the nanoclay content in the membrane were higher than those due to an increase in the sulfonation time.

Proton conductivity

Proton conductivity was obtained by impedance spectroscopy. The sample exposed to 2 h sulfonation and with 5 wt% nanoclay content was selected, as it displayed the best performance during the physicochemical and mechanical evaluation. The membrane material in the fuel cells, impose a restriction in the temperature permissible to its performance. For example, commercial fuel cells, like Nafion by Dow-DuPont, that works below 100°C [19, 23]. Hence, we use 60°C for this test, that is the closest temperature at which the commercial fuel cells work. Figure 8 shows the Z impedance spectra, using the Nyquist representation in function of Z' and Z'', where Z' is the real part and Z'' is the imaginary part [24]. Analysis of the impedance spectra was done in the Zview software.

Proton conductivity was obtained using the equation $\sigma = (d / (R+S))$, where conductivity (σ) is expressed in function of the inverse proportion of thickness (d) to the sample area that is in contact with the electrodes (S) plus the sample resistance (R). In this study, the analyzed sample had 0.22 cm thickness, 0.7854 cm² membrane area, and 13690 Ω extrapolated from the Nyquist plot, resulting in a proton conductivity of 9.3×10^{-5} S/cm. The low proton conductivity of this sample in comparison with Nafion 117 (0.035 S/cm at 60 °C and 70% relative humidity (RH) [25]), might be due to that the membrane was non saturated with water, at 30% RH, lowering their proton conductivity capacity [13]. Previous studies have demonstrated that PES sulfonated at high relative humidity (RH) displayed a higher conductivity, in comparison with Nafion [26]. On the contrary, at lower HR, PES sulfonated behaves as a dielectric. It should be noted that Nafion 117 was tested at a higher RH than the

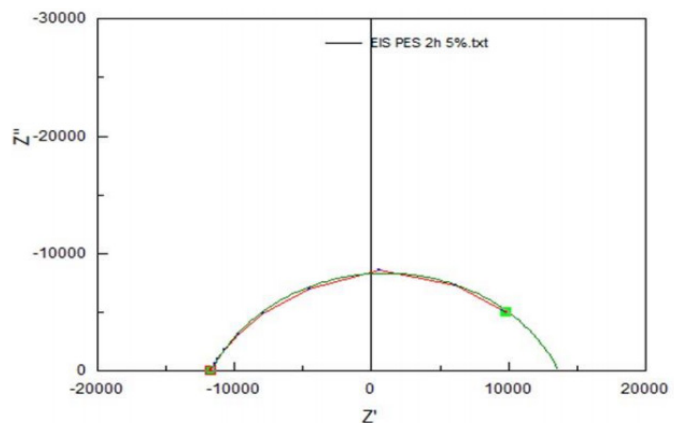


Figure 8: Nyquist plot for a PES sample

sulfonated PES membrane, and its proton conductivity results are favored by the amount of HSO_3 groups [27, 28] due to pretreatment applied with hydrogen peroxide (solution 3%), sulfuric acid (0.5 M) and distilled water (boiled) described by Yang et al. [29] and Kawamura et al. [30]. In addition, the proton conductivity found for the Nafion 117 membrane is approximately between 4 to 6×10^{-3} S/cm at 47.6 and 66°C, respectively, with 30% RH [31]. The proton conductivity of the chitosan membranes at room temperature was reported around 10-7 S/cm at low humidity [32]. Another proton conductivity value at room temperature was specified for the sulfonated membranes of interpenetrating polymer networks (SIPN-SO₃H) at 3.83×10^{-5} S/cm [33] which is close to the data obtained from the sulfonated PES membrane with 5 wt% nanoclay in this study. The sulfonic groups are not uniformly distributed in the membranes under dry conditions or low RH, so they create clusters, which are separated by microphases [15] that restrict the mobility of protons due to the absence of water.

CONCLUSIONS

The synthesis and characterization of proton exchange membranes from PES sulfonated and modified with nanoclays was performed successfully, among which the PES membrane with a sulfonation time of 2 hours and modified at 5 wt% nanoclay stands out for its properties. The findings showed a considerable increase in the performance of the membranes related directly to the raise in the concentration of organophilic nanoclays in the polymer matrix. The membrane's surface hydrophilicity improved as the organophilic nanoclays concentration in the polymer matrix increased. This phenomenon is due to sulfone groups ($\text{R-SO}_2\text{-R}'$) in the membranes, which allows the dispersion of the nanoclays favoring the affinity for water. The PES membranes properties, such as water uptake, porosity, and ion exchange capacity, increased also directly by the sulfonation time rising. These results agree with other published studies.

The mechanical properties of the membranes were not favored with a higher composition of nanoclays (10 wt%), nor with sulfonation, due to the increase in porosity and the conformation of clusters that lead to the disturbance of the cohesion between the components of the membrane.

The proton conductivity of the membrane at low relative humidity was similar to other studies. This result can be improved with the pretreatment of membranes with hydrogen peroxide, sulfuric acid, and distilled water. Finally, characterization results demonstrated that these membranes should be considered potential candidates for future commercialization, setting the ground to develop more efficient and affordable technologies.

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