

ChemTech

2015

Vol.8. No.3. pp 1319-1326.

International Journal of ChemTech Research CODEN (USA): IJCRGG ISSN: 0974-4290

Synthesis of a Proton Exchange Membrane from Vinyl Acetate - Acrylic Ester Copolymer for Fuel Cells

Alvaro Realpe*, Karoll Romero, Anny Santodomingo

Department of Chemical Engineering, Research Group of Particles and Processes Modeling, Engineering Faculty, Universidad de Cartagena, Colombia

Abstract: In this work the proton exchange membranes were synthesized from a vinyl acetate and acrylic ester copolymer for its use in fuel cells. This copolymer was subjected to the introduction of titanium dioxide as the inorganic load and to the sulfonation reaction to modify the copolymers properties. Physical properties of the membranes prepared were characterized; from the results obtained the sulfonated membranes were selected to evaluate their proton conductivity, through the study of dry electrochemical impedance spectroscopy. These membranes exhibited an increase of 55.21% in water retention and 165.35% in ion exchange capacity, compared to unmodified membranes, due to the presence of sulfonic acid groups in the polymer chain which facilitate the proton transport mechanisms in the membrane. The proton conductivity of the membrane was 5.4×10^{-9} S/cm, which is similar to the results of the dry impedance spectroscopy performed, reported in other investigations. The proton conductivity obtained can be improved if the membrane is hydrated prior to impedance analysis, therefore, and taking into account the properties that the membrane exhibits, it is considered that the sulfonated polymer has a potential in the field of proton exchange membrane fuel cells. **Keywords:** Proton exchange membrane, copolymer, proton conductivity, fuel cell.

1. Introduction

The intensive use of fossil fuels has originated environmental problems that have accelerated global warming, due to greenhouse gas emissions to the atmosphere at an alarming rate. Out of these gasses, the most known and concerning is the CO_2 . To counter this environmental negative impact, clean energy sources were proposed, such as hydrogen fuel cells, which produces only heat and water¹.

One of the most important part in the fuel cell is the polymeric electrolytic membrane. Currently, commercial membranes are very expensive and its life time is short². This puts on evidence the need to develop alternative polymeric membranes with better physical, thermic, and conductivity properties, at the time that they present a better cost-benefit ratio. Results obtained in recent investigations have stimulated the research into the production of hybrid membranes from functionalizing hydrocarbon polymers and addition of inorganic solid proton conductors.

Most common functionalization is sulfonation polymers in which sulfonic acid groups (-SO₃H) that increase the ion exchange and water retention are introduced³⁻⁵, but they decrease the thermal stability⁶, and oxidative stability⁷. By other hand, the introduction of inorganic solids improves the thermal and chemical resistance of the membrane⁸; however, it originates frailty, associated with the load percentage⁹. This demonstrates the suitability of the hybrid membranes for its use in fuel cells. Moreover, there are other modifications for proton exchange membranes, such as, dynamic vulcanization which is highlighted by the

improvement brought not only in the mechanical properties, but also in the water retention capacity and in the ion exchange product phase separation $^{4-5}$.

In this article, a proton exchange membrane was synthesized from the modification of the vinyl acetate and acrylic ester copolymer. This copolymer is accessible from the economic viewpoint and it's widely available in the country. Furthermore, it is used as a surface coating as it has waterproof properties, and prevents materials from aging¹⁰. For the above reasons, this material is emerging as an electrolyte with good mechanical properties and with a proton exchange capacity that is potentially comparable to commercial membranes.

2. Experimental

2.1. Materials

The copolymer of copolymer Vinyl Acetate and Acrylic Ester was used. It is commercialized under the name of PVA Vinil Acrílico Recol \mathbb{R} . The used solvent was distilled water; the reactants utilized for the sulfonation reaction were acetic anhydride at 98%, supplied by Carlo Erba, and sulfuric acid at 95 – 97%, supplied by MERK. Titanium dioxide (rutile grade) was used to enhance the copolymer's conductivity. Hydrochloric acid at 37%, sodium chloride, and sodium hydroxide at 99% supplied by MERK were used for the determination of the membrane's properties.

2.2. Experimental Design

Four types of proton exchange membranes were synthesized, using a 2^2 factorial design. The levels and factors of the experimental design are shown on the Table 1.

Table 1. Levels and Factors of the Experimental Design

Levels	Factors		
	Α	В	
-	Without sulfonation	Without titanium dioxide	
+	With sulfonación	7.5% titanium dioxide	

2.3. Modification of the Copolymer and Membrane preparation

100ml of solution of Vinyl Acetate –Acrylic Ester (PVAc-EA) copolymer with 10% concentration in water, with no modifications, was prepared. In addition, 100ml of a titanium dioxide (TiO₂) solution at 7.5% was prepared and 10 g of the PVAc-EA copolymer were added to it. Later, both solutions were cast onto a petri dish, allowing the complete evaporation of the solvent. As a result, there were obtained membranes without modifications and loaded membranes.

A heterogenous sulfonation method was applied, in which the synthetized membranes in the shape of films were soaked in the sulfonating agent (acetyl sulfate) for 3 hours. This gave as result sulfonated membranes and sulfonated-loaded membranes. Before the reaction took place, the membranes were immersed in distilled water for 24 hours so that they would swell and that channels were opened inside the polymeric network. This would allow a larger mobility of the sulfonating agent and would guarantee the inclusion of the SO₃H⁻ groups⁶. Acetyl sulfate was obtained from the reaction of acetic anhydride with sulfuric acid in a [15:1] molar ratio. 37.84ml of acetic anhydride were added to 800ml of distilled water, and after 10 minutes, 24.12ml of sulfuric acid were also added to the solution. The previous reaction was carried out in an ice bath, to prevent the mixture decomposition.

2.4. Membrane Characterization

The water uptake capacity of the synthetized membranes was measured using the following method: a dry sample from the synthetized membrane was taken; it was weighted and immersed in distilled water for 24 hours. Then, the excess water was removed with the aid of paper towels and the wet sample was weighted¹¹. The water uptake capacity was calculated with the following equation:

% Water uptake
$$-\frac{W_{h}-W_{s}}{W_{s}}x100$$
 (1)

where W_h is the weight of the wet sample, and W_s is the weight of the dry sample.

To measure the ion exchange capacity, the membranes were converted to their protonic form by immersion in a 1M HCl solution during 24 hours¹². Then, the samples were immersed in a 1M NaCl solution during 24 hours to exchange the H^+ protons for Na⁺ ions. Finally, the remaining solution was titrated with a 0.01M NaOH solution using phenolphthalein as indicator¹³. The proton exchange capacity was calculated according to the following formula:

$$IEC \left(\frac{m \ equiv}{g \ dry \ sample} \right) = \frac{VxM}{W}$$
(2)

where V is the volume of the titrant solution added until the equilibrium point was reached, M is the concentration of the titrant solution and W is the weight of the dry sample.

The mechanical properties of the membranes, such as maximum stress, maximum strain, and Young modulus, were determined according to the NTC 942 test method, which is identical to the ASTM D882 test method. This test was performed in the universal test equipment EZ-S by Shimadzu.

FTIR analysis was performed on the samples using a Fourier transform spectrophotometer Nicolet 6700 reference, obtaining the infrared spectrum in the range of wavelengths between 400 y 4000 cm⁻¹.

2.5. Determination of proton conductivity

The type of membrane that presented the best properties, according to the results of the characterization tests to determine their proton conductivity, was chosen. A HIOKI 3532-50 reference equipment to measure reference impedance was used. The impedance measurement was performed in the AC mode; the frequency range was 50 Hz to 5 MHz at 50 $^{\circ}$ C, on dry basis. The proton conductivity was calculated by the following equation¹⁴:

$$\delta = \frac{1}{R_b} \left(\frac{d}{s} \right) \tag{3}$$

where δ is the proton conductivity, *d* is the thickness of the film, *S* is the area of the electrodes in contact with the proton exchange membrane, and R_b is the resistance of the membrane, which was estimated from the Nyquist diagram, obtained from the electrochemical impedance test.

3. Results and Discussion

The synthesized membranes are shown in Fig. 1. As seen, the loaded membranes (b) and the sulfonateddoped ones (d) exhibit a characteristic white color due to the titanium dioxide.



Fig. 1. Synthesized membranes. (a)Unmodified membrane, (b)loaded membrane, (c)sulfonated membrane, (d) sulfonated-loaded membrane.

3.1. Water uptake capacity

Fig. 2 shows that the sulfonated membranes have increased water uptake, presenting a 55.21% increase compared to unmodified membranes. This is due to the sulfonation reaction, which introduces sulfonic groups into the polymer chains, allowing the formation of hydrogen bonds with water molecules. The -SO₃H groups

tend to assemble to form ionic clusters, which constitute a large percentage of the hydrophilic region⁷. This increase is consistent with the reports in other research¹⁵, who sulfonated poly(ether-ether-ketone) and found that the water retention capacity in the sulfonated membranes varies linearly up to a 65% increase compared to the non-sulfonated copolymer.



Fig. 2. Water uptake of synthesized membranes, UM: unmodified, L: loaded S: sulfonated, S-L: sulfonated-loaded.

Additionally, it should be noted that the presence of polyvinyl acetate, which is highly hydrophilic, causes the polymer chain to have a marked tendency towards water adsorption, which is confirmed with the high retention percentage that the unmodified membranes present (68.57%). On the other hand, the TiO_2 particles addition drastically decreases the polymer water uptake capacity. According to the reports by¹⁶, this happens when the size of the inorganic particles doesn't match the pore size of the membrane, since they don't fit into the polymer chain, the TiO_2 becomes a ceramic filler that reduces the free volume of the membrane and decreases its swelling capacity¹⁷. When the particle size is adequate, significant increases sre observed in water uptake, such as in⁵, by introducing 2% titanium dioxide rutile grade into the membrane, achieved a 15% increase in said property.

In the case of the sulfonated-loaded membranes, the decrease in water retention suggests that the interaction between the TiO_2 and the sulfonic groups is not the most appropriate. The optimum percentage of TiO_2 in a membrane varies with the polymeric material that is being used. After certain saturation level of the membrane, its performance diminishes. As a result of this saturation, sulfonic groups are blocked by the ceramic material, so that the hydrophilic region decreases and as a consequence, the water retention capacity also decreases¹⁸. This, in addition to the incompatibility of the particle size, would be the main causes for the decrease in water uptake on this kind of membranes.

3.2. Ion exchange capacity

Fig. 3 indicates that the sulfonated membranes have highest ion exchange capacities with a value of 0.2006 meq/g, which is a 165.4% higher than unmodified membrane. This is due to the increase of available sites for proton conduction which also indicates the presence of sulfonic groups¹⁹, which is consistent with the reports by¹⁹. According to them, the ion exchange capacity of the sulfonated membranes can increase up to 200 % compared to non-sulfonated membranes.



Fig. 3. Ion exchange capacity for prepared membranes. UM: unmodified, L: loaded S: sulfonated, S-L: sulfonated-loaded.

In addition, the ion exchange capacity is deeply tied to the water uptake capacity, due to the proton migration mechanisms that are present in proton exchange membranes: the Grotthuss mechanism in which protons "jump" from a H^+ donor site to any water molecule receiving that is in the vicinity, forming the H_3O^+ complex and the vehicular movement, in which protons are transferred through hydronium ions¹⁸. So, according to this, the sulfonated membrane has the highest exchange capacity because it has the Grottuss mechanism transfer agent (sulfonic groups) and also has the best water retention capacity, allowing vehicular mechanism to be present.

The unmodified membrane shows a low exchange capacity, despite having a high water retention capacity, which demonstrates the importance of sulfonic acid groups for proton transfer. Meanwhile, the loaded membranes don't show a reduction of exchange capacity proportional to the reduction in water retention capacity; because the proton transfer occurs mainly through the mechanism of Grotthuss, not by the vehicular one, so that a lower hydration in the membrane does not significantly affect its exchange capacity.

In the case of the sulfonated-loaded membranes present a decrease in the proton exchange with respect to the sulfonated membrane; this happens due to the agglomeration of TiO₂ which interrupts the conduction of protons through the Grotthuss mechanism by blocking the effect of the sulfonic groups¹⁸. Besides, the presence of ceramic filler particles causes restrictions in the vehicular mechanism, because they remain embedded in the channels that connect the clusters of sulfonic groups¹⁸. This occurs due to the incompatibility of the particle size with respect to the pores of the polymer network. In circumstances of compatibility, TiO₂ particles are effective ion-exchange sites, as reported by⁵, who obtained an increase of 33.33 % by introducing 2 % of TiO₂ in the synthesized membranes. Finally, the difference between the ion exchange capacities of sulfonated membranes and sulfonated-loaded membranes indicates that blockade of TiO₂ on the sulfonic groups clusters is partial.

3.3. Mechanical Properties

Table 2 indicates that the loaded membranes are rigid, harder and slightly more fragile than the unmodified membranes, because the TiO_{2} , and in generally all ceramic fillings, are grouped together and are embedded in the existing channels between the polymer chains restricting the mobility of the chains, resulting in an increased mechanical strength of the modified copolymer²⁰. By other hand, the sulfonation is a modification that compromises the mechanical properties of the copolymer, since the introduction of sulfonic acid groups in the polymer chains leads to an alteration in their cohesion, due to the high polarity of these groups, resulting in a lower tensile strength of the modified copolymer⁷.

The synthesized membranes exhibit maximum strain values and Young's modulus values lower than those exhibited by the commercial Nafion membrane (117), which are 43.5MPa and 249MPa, respectively (See Table 2). However, other investigation²¹ report that they fabricated membranes with a maximum stress of 5.2MPa which were still suitable for use in fuel cells. Considering the above, the sulfonated membranes were assembled into a fuel cell and subjected to hydrostatic pressure testing at normal operating conditions (approx. latm), and under high pressure (up to 3atm), with no evidence of structure damage. This confirms that the sulfonated PVAc -EA membranes, can be implemented in fuel cell applications.

Type of membrane	Maximum strain (MPa)	Maximum deformation (%)	Young modulus (MPa)		
UM: Unmodified	5.99	427.15	176.39		
L: Loaded	5.29	350.26	196.49		
S: Sulfonated	1.64	423.42	9.29		
S-L: Sulfonated-Loaded	1.58	354.35	64.16		

1 abic 2. Results obtained if one the deformation-strain tes	Ta	able	2.	Results	obtained	from	the	deforma	tion-	strain	test
--	----	------	----	---------	----------	------	-----	---------	-------	--------	------

3.4. Infrared Spectroscopy

The Fig. 4 shows the spectra obtained for each type of membrane. In the case of the TiO₂, the absorption should appear in the zone between 450 and 550 cm^{-1 22}. However, no matching peaks are observed in this range. This means that the TiO₂ is dispersed within the copolymer but there is no chemical bond to secure it to the polymeric material's structure²³. By other hand, the presence of the sulfonic group (bond O=S=O) is confirmed by peaks around the frequency of 1020 cm⁻¹²⁴, corresponding to the symmetric stretching vibration of said link. In the Fig. 4, it can be seen that all samples contain different peak intensities between 1018 and

1020 cm⁻¹ with the exception of the loaded sample. This means that there are links of type O=S=O even in the non-sulfonated copolymer. This is because in the copolymerization of PVAc –EA, dodecyl sulfonated is used as a stabilizing agent and ammonium persulfate is used as reaction initiator, both of them contain O=S=O.

The loaded membranes don't exhibit a strong peak at 1020 cm^{-1} , which means that TiO_2 has a blockage effect on the groups with O=S=O links. As explained by¹⁸, it occurs when the amount of TiO₂ within the polymer is very high. This blockage effect was also evident in the water uptake test and on the ion exchange capacity.



Fig. 4. Infrared spectra of the studied samples.

In the sulfonated membranes, the peak in the 1020 cm^{-1} frequency is evident, since the sample has a greater number of O=S=O links, corresponding to the -SO₃H groups. This is confirmed by the spectrum of the sulfonated-loaded sample, which also shows the peak at 1020 cm⁻¹, suggesting that given the bigger amount of sulfonic groups, the TiO₂ blockage is only partial since the amount of the introduced inorganic material is not enough to overshadow all present sulfonic groups.

3.5. Proton Conductivity

According to the results of the characterization tests, the sulfonated membrane was chosen to assess its performance in proton conductivity. From the Nyquist diagram of the electrochemical impedance test, it was found that the membrane resistance R_b is $10.32 \times 10^6 \Omega$. Applying the equation mentioned in previous sections, it was found that the sulfonated membrane has proton conductivity in dry medium of 5.4×10^{-9} S/cm.

The conductivity obtained from the dry impedance test is low because the sulfonic groups are not uniformly distributed into the membrane, but they form clusters, that separate themselves into microphases⁷. That is due to a substantial number of exchange sites as shown in the results of ion exchange capacity tests, the mobility of protons is limited in no hydrated environments since it does not have water molecules receiving protons that can make the transfer of these species from an organic cluster to another.

This dependence between proton conductivity and hydration has been confirmed in other studies³, who synthesized chitosan membranes with high degree of crosslinking , which showed a proton conductivity in the range of 10^{-9} to 10^{-10} S/cm in dry impedance tests, but when hydrating certain type of membranes the proton conductivity increased to the order of 10^{-2} S/cm. In other hand, the proton conductivity provided by the commercial Nafion® 117 membrane at the same temperature and at 100% relative humidity was $6x10^{-2}$ S/cm and $4x10^{-3}$ S/cm at relatively low humidities $(30\%)^{25}$. This conductivity is greater than the membranes of the sulfonated copolymer PVAc -EA, however, it is estimated that they have potential in the field of fuel cells, due to the proton exchange ability they are exhibiting.

4. Conclusions

In this article the vinyl acetate and acrylic ester copolymer was modified to synthesize proton exchange membranes. The modifications made were: the introduction of sulfonic groups ($-SO_3H$) through sulfonation of the polymeric material and the addition of titanium dioxide (TiO_2) as the inorganic load. The copolymer sulfonation increased the polarity of the membrane, due to the presence of the $-SO_3H$ groups, increasing the water uptake capacity. The ion exchange capacity was also increased by 165.35 %, which demonstrates the importance of the presence of the $-SO_3H$ groups introduced within the membrane. Contrary to the above, the

mechanical properties exhibited a decline after the sulfonation treatment, because the high polarity of the sulfonic groups alters the cohesion of the polymer chains, resulting in a lower tensile strength.

The introduction of the TiO₂ decreased the water uptake capacity by 39.3 % and the ion exchange capacity by 4.1%, compared to unmodified membrane. This is attributed to that the TiO₂ became a ceramic filler because of its particle size. However, the mechanical properties of the membranes increased since the TiO₂ was grouped and it lodged in the channels of the polymer chains, thus reducing their mobility of and increasing their tensile strength. Considering the results of the ion exchange capacity and water retention capacity, the sulfonated membrane was chosen to evaluate its proton conductivity. The electrochemical impedance spectroscopy in dry medium showed a conductivity value of 5.4×10^{-9} S/cm at 50°C, which is similar to reported values of impedance analysis in dry medium, performed on previous research, which are in the order 10^{-9} and 10^{-10} S/cm. Because of the set of properties they exhibited, the sulfonated vinyl acetate and acrylic ester copolymer membranes have high potential in the field of proton exchange membranes for fuel cells.

Acknowledgments

We thank the University of Cartagena for their support in the physicochemical characterization of the membranes, the facilities, materials and reagents that were provided. We thank Dr. Henry Reyes, professor at the University of Quindio, for his contribution with the electrochemical impedance spectroscopy tests.

References

- 1. Cano, U., Las celdas de combustible: Verdades sobre la generación de electricidad limpia y eficiente vía electroquímica. Boletín del Instituto de Investigaciones Eléctricas, 1999, 23(5), 208 215.
- Ahmad, M., Zaidi, S., and Rahman, S., Proton conductivity and characterization of novel composite membranes for medium-temperature fuel cells, Desalination, 2006, 193, 387 – 397.
- 3. Shin, K., Choi, E., and Hwang, T., Preparation and characterization of ion-exchange membrane using Sty/HEA/LMA terpolymer via post-sulfonation. Desalination, 2010, 263, 151 158.
- 4. Realpe, A., Mendez, N., and Acevedo, M., 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 Technology2014, 6(5), 2435-2440.
- Realpe, A., Romero, K., and Acevedo. M, 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, 2015, 26(1), 55-62.
- 6. Barroso-Bujans, F., Verdejo, R., Lozano, A., Fierro, J., and Lopez-Manchado, M., Sulfonation of vulcanized ethylene–propylene–diene terpolymer membranes, Acta Materialia, 2008, 56, 4780 4788.
- 7. Dai, H., Guan, R., Li, C., and Liu, J., Development and characterization of sulfonated poly(ether sulfone) for proton exchange membrane materials. Solid State Ionics, 2007, 178, 339–345.
- 8. Mosa, J., Membranas inorgánicas e híbridas orgánico inorgánicas para pilas de combustibles de intercambio de protones (PEMFC). Memoria para optar al grado de Doctor en Ciencias Químicas, Universidad Autónoma de Madrid, Madrid, España, 2008.
- 9. Namazi, H., and Ahmadi, H., Improving the proton conductivity and water uptake of polybenzimidazole-based proton exchange nanocomposite membranes with TiO₂ and SiO₂ nanoparticles chemically modified surfaces, Journal of Power Sources, 2011, 196, 2573 2583.
- 10. Recol SAS., PVA Vinilacrílico, 2012, recuperado el 11 de Febrero de 2012, de Fichas técnicas: http://www.recol.co/
- 11. Shahi, V., Highly charged proton-exchange membrane: Sulfonated poly(ether sulfone)- silica polyelectrolyte composite membranes for fuel cells, Solid State Ionics, 2007, 177, 3395–3404.
- 12. Blaster, J., Krupenko, O., Pünt, I., Stamatialis, D., and Wessling, M., Preparation and characterisation of monovalent ion selective cation exchange membranes based on sulphonated poly(ether ether ketone). Journal of Membrane Science, 2005, 263, 137–145.
- Wang, L., Li, K., Zhu, G., and Li, J., Preparation and properties of highly branched sulfonated poly(ether ether ketone)s doped with antioxidant 1010 as proton exchange membranes. Journal of Membrane Science, 2011, 379, 440 – 448.
- 14. Qian, X., Gu, N., Cheng, Z., Yang, X., Wang, E., and Dong, S., Methods to study the ionic conductivity of polymeric electrolytes using a.c. impedance spectroscopy, Solid State Electrochem, 2001, 6, 8 15.
- 15. Zaidi, J., Polymer sulfonation, a versatile route to prepare proton conducting membrane material for advanced technologies, The Arabian Journal for Science and Engineering, 2003, 28 (2B), 183 194.

- Jian-Hua, T., Peng-Fei, G., Zhi-Yuan, Z., Wen-Hui, L., and Zhong-Quiang, S., Preparation and performance evaluation of a Nafion-TiO2 composite membrane for PEMFCs, International Journal of Hydrogen Energy, 2008, 33, 5686 – 5690.
- 17. Devrim, Y., Erkan, S., Bac, N., and Eroglu, I., Preparation and characterization of sulfonated polysulfone/titanium dioxide composite membranes for proton exchange membrane fuel cells. International Journal of Hydrogen Energy, 2009, 34, 3467 3475.
- Amjadi, M., Rowshanzamir, S., Peighambardoust, S., Hosseini, M., and Eikani, M., Investigation of physical properties and cell performance of Nafion/TiO₂ nanocomposite membranes for high temperature PEM fuel cells. International Journal of Hydrogen Energy, 2010, 35, 9252 – 9260.
- Park, J., Koh, J., Roh, D., Shul, and Kim, J., Proton-conducting nanocomposite membranes based on P(VDF-co-CTFE)-g-PSSA graft copolymer and TiO₂–PSSA nanoparticles, International Journal of Hydrogen Energy, 2011, 36, 1820 - 1827.
- 20. Kumar, G., Kim, A., Nahm, K., y Elizabeth, R., Nafion membranes modified with silica sulfuric acid, International Journal of Hydrogen Energy, 2009, 34, 9788 9794.
- 21. Yang, Z., Coutinho, D., Yang, D., Balkus, K., y Ferraris, J., Proton-conducting membranes based on HTFSI-doped PEI/SiO₂ nanocomposites, Journal of Membrane Science, 2008, 313, 91–96.
- 22. Hernández, J., Serrano, L., Zeifert, B., García, R., Zermeño, B., and Del Angel, T., Síntesis y Caracterización de Nanopartículas de N-TiO2 Anatasa. Superficies y Vacío, 2008, 21(4), 1-5.
- Cabrera, J., Paredes, C., Urday, E., y Santiago, J. (2007). Preparación y caracterización de películas de alcohol polivinílco conteniendo nanopartículas de TiO2. Revista Iberoamericana de Polímeros, 8(4), 323 332.
- Xing, P., Robertson, G., Guiver, M., Mikhailenko, S., Wang, K., and Kaliaguine, S., Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. Journal of Membrane Science, 2004, 229, 95–106.
- 25. Mittal, K., Polyimides and other high temperature polymers: Synthesis, characterization and applications, 2003, Volume 2. Zeist: VSP BV.
