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Use of a Try-functional Crosslinking Agent in Styrene/Acrylic Acid Copolymers to Enhance Mechanical Properties for their use as Membranes in Fuel Cells

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ABSTRACT

Polymer electrolyte membranes used in hydrogen fuel cells need some mechanical resistance in order to stand for the humid environment observed into a cell in operation. Alternative copolymers to the well-known Nafion membranes are the styrene/acrylic acid copolymers; with advantages in cost and availability of raw materials to prepare them. Previous attempts to improve mechanical properties of such materials involved crosslinking with divinyl benzene, but in this work we are reporting the use of the tryfunctional monomer TMPTMA (trimethylol propane trimethacrylate) for such purpose. Copolymers with a PS/AA ratio of 94/6 were prepared by radical polymerization reaction, including TMPTMA at 0.1, 0.01 and 0.001 %mol concentrations. Reactions were followed by percentage yield (gravimetry), FTIR and crosslinking level by gel percentage evaluation (soxhlet extraction) with three different solvents (water, THF and dicloromethane). Thermal transitions were followed by DSC, stability by TGA and mechanical properties by DMA. FTIR spectra show typical bands from the copolymer while the corresponding bands to crosslinking are overlapped; however, gel percentage evaluations show higher level of crosslinking for the 0.1% TMPTMA copolymer and lack of solubility in water. DSC thermograms indicate increment of Tg and TGA a small increment in thermal stability for crosslinked copolymers. Elastic moduli suggests a rubbery material for TMPTMA crosslinked copolymers while loss modulus confirm Tg enhancement as observed by DSC. 0.1 % TMPTMA copolymer does not even form a membrane due to insolubility and infusibility.

1. Introduction

Recent restrictions in environmental pollution from mankind activities have initiated the search for modern alternatives to energy generation. Although, fuel cells technology is not considered a new option for such purpose, optimization of their cost is quite recent. The most important item into a polymeric fuel cell is the polyelectrolyte membrane (PEM) and the well-known Nafion has been used for decades for mobile applications [12], although sulphonated polystyrene membranes were the first low temperature commercial options offered from General Electric Company since 1960 [8].



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Alternative materials to improve Nafion's membranes include 3 groups: modified perfluorosulphonic acid polymers, complex acid-base membranes and sulphonated hydrocarbon alternated polymers. The latter include diverse materials, have low cost, absorb water in a wide temperature interval and can be recycled [15]. Sulphonation is the most common method to cleave ionic groups into the backbone consisting of an aromatic electrophilic substitution reaction in the case of styrenic polymers, where a hydrogen from the aromatic ring is changed by a sulphonic group [15, 16].

Liu et al [16] studied ion conductivity and mechanical-dimensional behaviour of sulphonated poly(arilethercetone) bifenilate prepared at different sulphonation grades. They found enhanced mechanical performance and high dimensional stability and ion conductivity, comparing with Nafion. Deb and Mathew [19] studied the synthesis of sulphonated styrene-acrylic acid copolymers with a styrene molar rate of 47-55 %; they also reported their ion exchange properties and suggested their use as pH sensors. Sherazi et al [17] crosslinked ultra high molecular weight polyethylene with styrene and obtained membranes by hot press molding to finally sulphonate with chlorosulphonic acid, obtaining membranes with superior proton conductivity and low permeability to methanol when comparing with Nafion.

A practical way to obtain membranes is the preparation of the crosslinked styrene-divinyl benzene copolymers in one step and their further sulphonation with concentrated sulphuric acid [18]. Recently Paula et al [20] reported the preparation of styrene-acrylic acid copolymers with further sulphonation with sulphuric acid as well, with possibilities of pH and humidity sensors applications. In this report we are showing results when styrene-acrylic acid copolymers are crosslinked with an agent (trimethylol propane trimethacrylate-TMPTMA) to enhance mechanical properties to be able to use them as membranes in fuel cells.

2. Experimental

Synthesis of crosslinked copolymers

A 100 ml glass reactor was loaded with styrene and acrylic acid in a 94:6 molar ratio, TMPTMA crosslinking agent (trimethylol propane trimethacrylate) was also added at three different concentrations: 0.001, 0.01 and 0.1 % mol. Radical copolymerization was carried out using benzoyl peroxide (0.05 % mol) as initiator and keeping reactor temperature at 100 °C, under nitrogen atmosphere and mechanical stirring (250 rpm) during 2 hours. The copolymer was dissolved with acetone and the solution precipitated with methanol; the latter procedure was repeated twice in order to eliminate low molecular weight material and the solid dried overnight and then into a vacuum oven. The percent of copolymerization yield was calculated by gravimetric measurements.

Characterization of copolymers

An aliquot of each copolymer (0.02 g) was dissolved with THF (1 ml) and the solution deposited in a flat confined glass plate in order to have films of approximately 0.03 mm thickness after solvent evaporation (casting). FTIR spectra of the films were recorded in a Nicolet Avatar 330 instrument. 64 scans and a resolution of 4 cm⁻¹ were used.



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Gel formation was also evaluated in order to obtain the crosslinking level for each copolymer; as it is an indirect evaluation, three solvents were used: water, dicloromethane and THF. Aliquots of 0.5 g were placed into cellulose thimbles and then into soxhlet extraction systems. The copolymers were extracted with the different solvents during various extraction times: 4, 8 and 12 h. Gel percentage was calculated gravimetrically.

DSC thermograms were obtained from a TA Instruments 2920 MDSC apparatus, a first thermal scan was carried out to eliminate thermal history and the second scan recorded to observe transitions in the -30 to 150 °C temperature interval at 10 °C/min thermal ramp. A nitrogen atmosphere was always kept during evaluations.

TGA thermograms were carried out in a Q500 TA Instruments apparatus. Approximately 20 mg of sample was placed into the thermobalance and evaluated from ambient up to 700 °C, with a 10 °C/min thermal ramp under nitrogen atmosphere. Mass loss was recorded along temperature and the first derivative calculated for each run.

Dynamic mechanical properties were evaluated by means of a DMA TA Instruments Q800. A tension accessory was used for deformation, with an amplitude of 20 microns and a frequency of 1 Hz in the temperature range of ambient to 130 °C with a ramp of 5 °C/min.

3. Results and discussion

Copolymerization reactions were carried out and the yield percentages obtained gravimetrically are relatively low, as shown in the Table 1, particularly for the homopolymer (polystyrene). The highest value was obtained for the copolymer including 0.1% of crosslinking agent, suggesting is due to the reactive media involving the tryfunctional monomer. The latter was an insoluble material due to the high level of crosslinking, unable to use it for making films (membranes) by casting.

Table 1. Yield percentages obtained for reactions

Polymer	Yield (%)
PS	30.5
PS/AA	40.5
PS/AA + 0.001 TMPTMA	37.1
PS/AA + 0.01 TMPTMA	37.6
PS/AA + 0.1 TMPTMA	56

The films obtained from the casting of copolymers synthesized were evaluated by FTIR; except the one prepared with 0.1 % TMPTMA, as mentioned before. FTIR show expected differences, as can be seen in Figure 1.

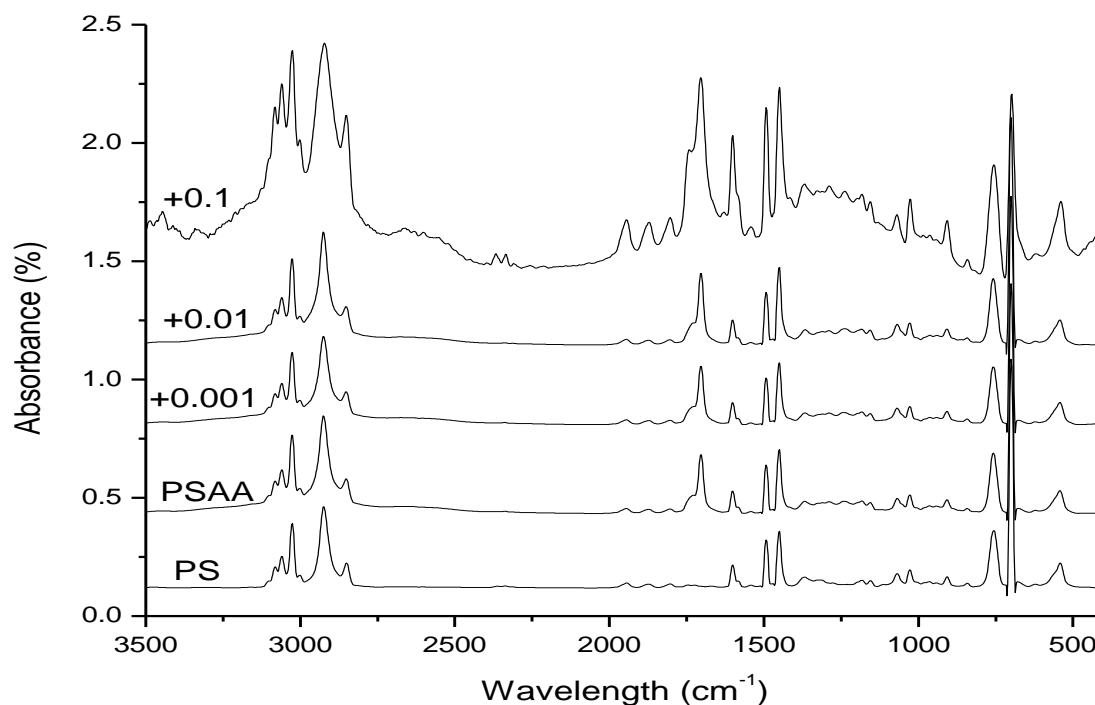


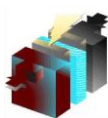
Figure 1.- FTIR spectra of polystyrene (PS), the copolymer with acrylic acid (PSAA) and the copolymer prepared including different levels of TMPTMA.

Polystyrene shows the C-H stretching bands over and below 3000 cm^{-1} , aromatic ring overtones below 2000 cm^{-1} , and the corresponding ring vibrations at 1600 , 1492 and 1450 cm^{-1} , and finally the C-H bendings from backbone at 758 and 700 cm^{-1} , as well as the one from the ring at 541 cm^{-1} . Once the copolymer was prepared (PSAA), the FTIR spectra show a slight broadening for the C-H aromatic and aliphatic bands around 3000 cm^{-1} , as a consequence of the OH group from the acrylic acid. It is also clear the formation of the C=O carbonile stretching band at 1704 cm^{-1} and the C-O stretching band at 1240 cm^{-1} , both coming from the presence of acrylic acid in the copolymer. The C-O-H bending vibration is overlapped with the bands from the aromatic ring at 1430 cm^{-1} .

Indication of TMPTMA into the copolymer is seen as the 1732 cm^{-1} shoulder coming from an ester functionality. The latter is higher for the 0.1% mol TMPTMA addition to the reaction mixture, as seen in the sequence (Table 2) obtained when correlating such band with an unchanged band from the backbone (758 cm^{-1})

Table 2. Esther formation in copolymers with addition of TMPTMA

Polymer	Band ratio ($1732/758\text{ cm}^{-1}$)
PS/AA	0.3704
PS/AA + 0.001 TMPTMA	0.3929
PS/AA + 0.01 TMPTMA	0.4091
PS/AA + 0.1 TMPTMA	1.1262



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The extraction properties of materials in water are very important, considering they do have to support humid environments during operation. Extraction in organic solvents are useful to understand the real level of crosslinking during addition of TMPTMA and needed to prepare the membranes. Figure 2 show the results of extraction at different time intervals for the crosslinked materials when using 3 solvents.

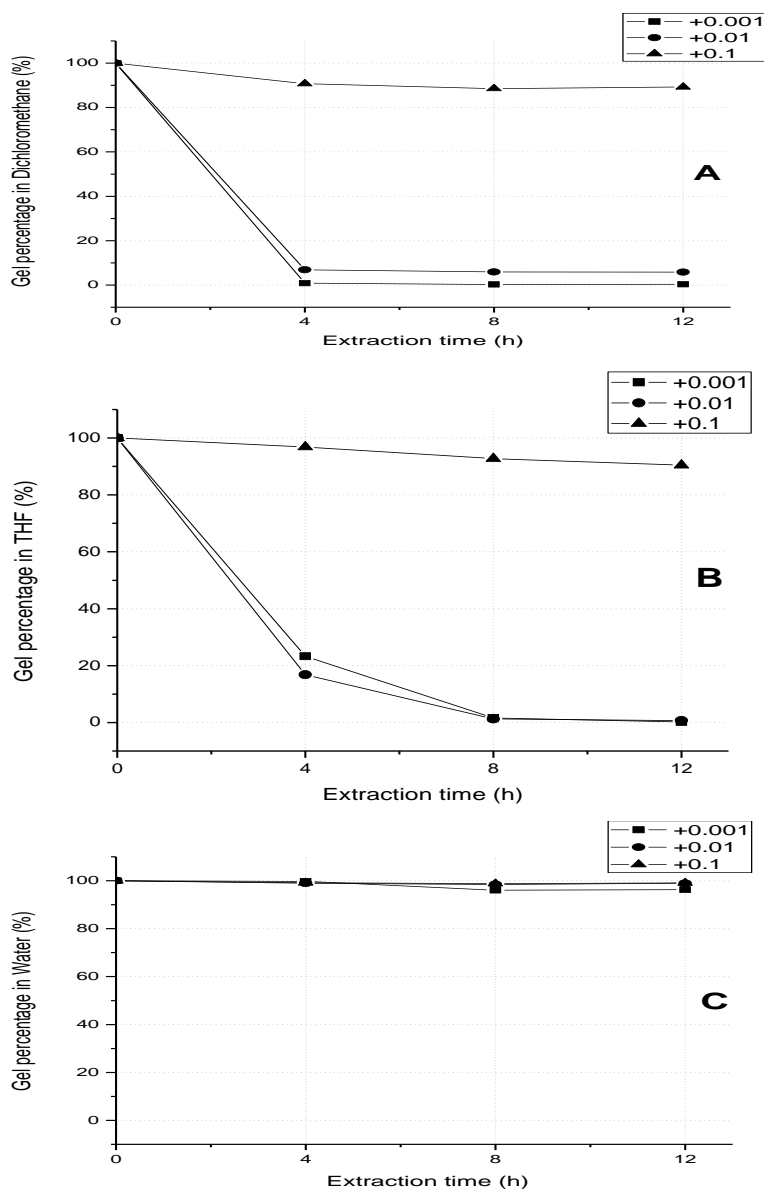


Figure 2.- Percentage of gel obtained for the materials at different times using. Dichloromethane (A), Tetrahydrofuran (B) and Water (C).

It is clear to observe that water does not dissolve any of the crosslinked materials (0.1, 0.01 and 0.001 %TMPTMA) and needs 8 hours to dissolve just the 4% for the 0.001 % material. Dichloromethane is the most effective solvent,

since only 4 hours are needed to dissolve almost all of the low crosslinked materials while THF need 8 hours to do so. None of the solvents dissolve the most crosslinked material with 0.1% TMPTMA.

Thermal transitions were evaluated by DSC in order to identify possible changes in T_g as a consequence of copolymerization and crosslinking reactions. Figure 3 shows DSC thermograms for the materials prepared.

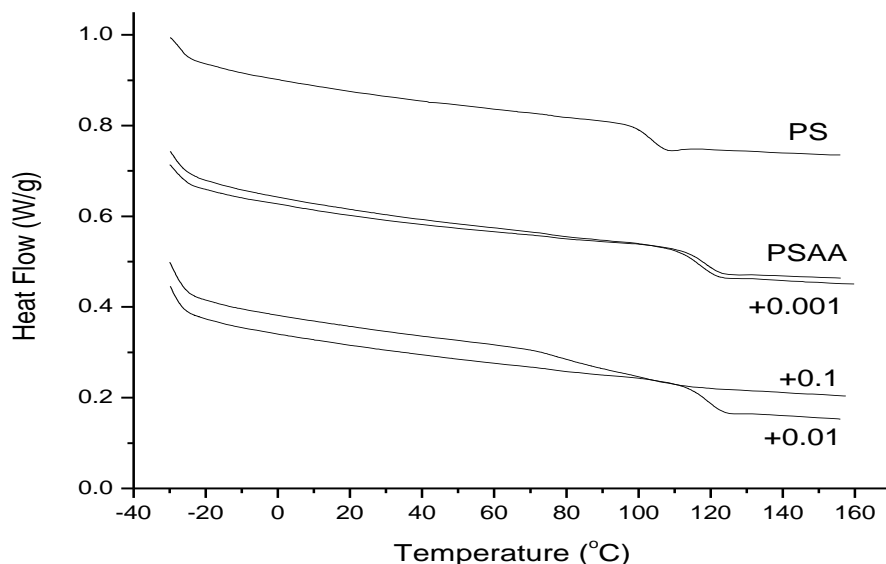


Figure 3.- DSC thermograms for PS, PS+AA and the copolymer added with different levels of TMPTMA

Polystyrene shows its T_g transition at 102°C as it is well known, but the copolymer with 6 % mol of acrylic acid enhances the transition up to 117°C due to interactions between acrylic acid functionality. The crosslinked materials with low amount of crosslinking agent (0.001 and 0.01 % of TMPTMA) does not produce any changes to the copolymer transition, however the 0.1 % TMPTMA material reduce the transition considerably as well as extends the thermal interval for it. Such effect has been mentioned to be the consequence of the rubbery status acquired for the higher amount of agent [9].

In order to evaluate changes in thermal stability for the materials prepared, TGA thermograms were obtained and the loss weight is happening at higher temperature as known for styrenic materials (350°C), and an increment for the crosslinked materials. Figure 4 show their traces and Table 3 the temperature values for the curve maxima from the DTG traces. The most crosslinked material (0.1 % TMPTMA) has the higher thermal stability and the copolymer is more sensible to degradation comparing with the polystyrene homopolymer.

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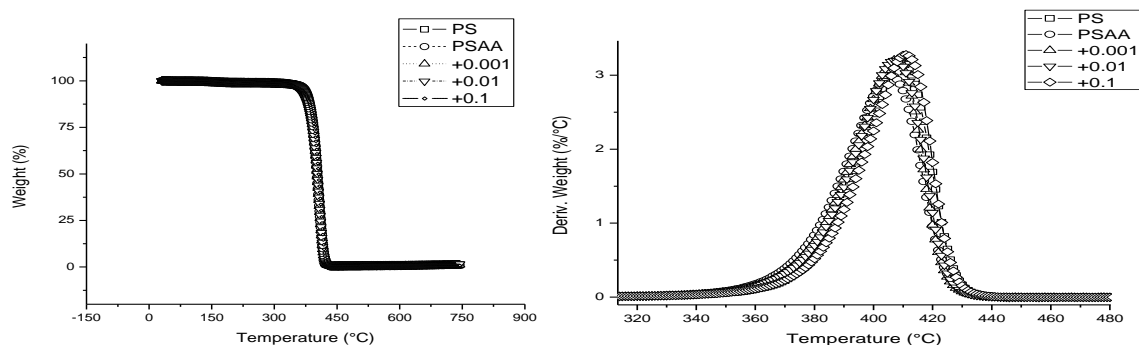
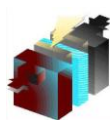
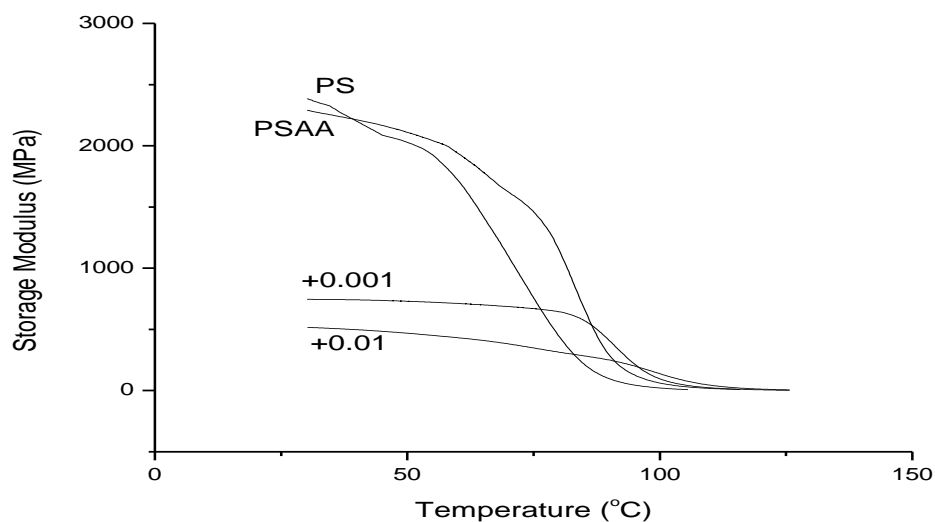


Figure 4.- TGA and DTG thermograms for PS, PS+AA and the copolymer added with different levels of TMPTMA

Table 3. Degradation temperatures obtained by derivative TGA

Polymer	Maxima at DTG curves (°C)
PS	409
PS/AA	405.5
PS/AA + 0.001 TMPTMA	407.5
PS/AA + 0.01 TMPTMA	407.5
PS/AA + 0.1 TMPTMA	411
TMPTMA	344, 463, 613

Mechanical properties were evaluated by means of DMA and the results of elastic and viscous modulii for the materials are shown in Figure 5. The 0,1 % TMPTMA crosslinked material is not included since it was imposible to obtain films for the evaluations.



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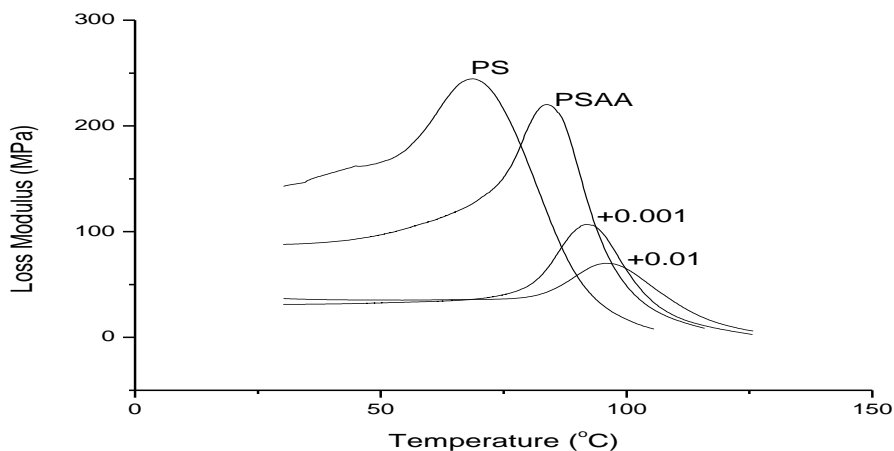


Figure 5.- DMA traces (storage and loss modulus) for materials added with different levels of TMPTMA

The elastic modulus is considerably high for the homopolymer and the copolymer but once the crosslinking agent is added the reduction of E' values confirm the rubbery behavior of the materials. The viscous or loss modulus traces also confirm the effect observed by DSC, where glass transition temperature is enhanced for the crosslinked materials, with temperature differences in the order of 30°C.

4. Conclusions

The polystyrene-acrylic acid copolymer was prepared as it is confirmed by FTIR and the addition of TMPTMA effectively worked as crosslinking agent. Water does not extract polymeric material during gel % evaluations but organic solvents evaluated (THF and DCM) are convenient to dissolve and prepare membranes. Glass transition is effectively enhanced when TMPTMA is added as observed by DSC and confirmed by DMA while a rubbery status is obtained specially for 0.01 % TMPTMA addition. Thermal stability is slightly enhanced for crosslinked copolymers.

5. Acknowledgements

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6. References

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