

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

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Abstract: Alternative copolymers to the well-known Nafion membranes are the styrene/acrylic acid PS/AA) copolymers, which have advantages in cost and availability of raw materials. Previous attempts to improve their mechanical properties involved crosslinking with divinyl benzene, but in this case the use of the tri-functional monomer TMPTMA (trimethylol propane trimethacrylate) is examined. Copolymers with a PS/AA molar ratio of 94/6 were prepared by a free radical polymerization reaction, including TMPTMA at 0.1, 0.01 and 0.001 % mol concentrations. Reactions were followed by percentage yield (gravimetry), Infrared spectroscopy (FTIR) and extent of crosslinking by gel percentage evaluation (soxhlet extraction) with three different solvents (water, tetrahydrofuran and dichloromethane). Thermal transitions were followed by calorimetry (DSC), stability by thermogravimetry (TGA) and mechanical properties by dynamic mechanical analysis (DMA). FTIR spectra show typical bands from the copolymer while the corresponding bands associated with crosslinking are overlapped; however, gel percentage evaluations show a higher level of crosslinking for the 0.1% TMPTMA copolymer and lack of solubility in water. DSC thermograms indicate an increment in the glass transition (T_g) and TGA exhibits a small increment in thermal stability for the crosslinked copolymers. Elastic moduli suggests a rubbery material for TMPTMA crosslinked copolymers while loss modulus confirms a T_g enhancement as observed by DSC. A 0.1 % TMPTMA copolymer does not form a membrane due to its insolubility and infusibility.

Keywords: Copolymers, TMPTMA, Fuel cell

1. INTRODUCTION

Recent restrictions in environmental pollution from human activities have initiated the search for modern alternatives to energy generation. Although, fuel cell technology is not considered a new option for such a purpose, optimization of their cost is quite recent. The most important item utilized in a polymeric fuel cell is the polyelectrolyte membrane (PEM). To date the well-known Nafion has been used for sometime for mobile applications [1], although sulphonated polystyrene membranes were the first low temperature commercial options offered from the General Electric Company since 1960 [2].

Alternative materials to improve Nafion membranes may include 3 possible groups: modified perfluorosulphonic acid poly-

mers, complex acid-base membranes and sulphonated hydrocarbon alternated polymers. The latter include a range of diverse materials and have low cost, absorb water in a wide temperature interval and can be recycled [3]. Sulphonation is the most common method to incorporate ionic groups into the backbone consisting of an aromatic electrophilic substitution reaction in the case of styrene polymers. It has also been mentioned that an aromatic ring hydrogen is removed by a sulphonation [3, 4].

Liu et al [4] studied ion conductivity and mechanical-dimensional behavior of sulphonated poly(aryletherketone) biphenilate prepared at different sulphonation grades. They found enhanced mechanical performance and high dimensional stability and ion conductivity, when compared with the Nafion. Deb and Mathew [5] 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

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pH sensors. Sherazi et al [6] 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 [7]. Recently Paula et al [8] reported the preparation of styrene-acrylic acid copolymers by further sulphonation with sulphuric acid as well, with possibilities of pH and humidity sensor applications. In this paper we report results on the reaction of styrene-acrylic acid copolymers crosslinked with a multifunctional agent (trimethylol propane trimethacrylate-TMPTMA) in order to enhance mechanical properties for use as membranes in fuel cells.

2. EXPERIMENTAL

2.1. 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 while keeping the reaction temperature at 100 °C, under nitrogen atmosphere and with 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 storage in a vacuum oven. The percent of copolymerization yield was calculated by gravimetric measurements.

2.2. 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 using a Nicolet Avatar 330 instrument utilising 64 scans and a resolution of 4 cm⁻¹.

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, dichloromethane 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 with 10 °C/min thermal ramp. A nitrogen atmosphere was always maintained during the analysis.

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 a nitrogen atmosphere. Mass loss was recorded along with 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. Static mechanical evaluations give less information than dynamic ones since the modulus value is not enough to understand the material behavior under stress; DMA allows one to follow the individual properties throughout our experiments, namely elastic and storage moduli. The combination of both properties at a specific temperature provides a complete view of the actual behavior of the membranes.

3. RESULTS AND DISCUSSION

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

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

Polystyrene shows the C-H stretching bands over and below 3000 cm⁻¹, aromatic ring overtones below 2000 cm, and the corresponding ring vibrations at 1600, 1492 and 1450 cm⁻¹, and finally the C-H bendings from the backbone polymer 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 shows 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. The formation of the C=O carbonyl stretching band at 1704 cm⁻¹ and the small C-O stretching band at 1240 cm⁻¹, both coming from the presence of acrylic acid in the copolymer were also observed. The C-O-H bending vibration is overlapped with the bands from the aromatic ring at 1430 cm⁻¹ [9].

An indication of the incorporation of TMPTMA into the copolymer is seen as the 1732 cm⁻¹ shoulder originating from the 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 this band with an unchanged band from the backbone (758 cm⁻¹). Such a shoulder is also observed in the PS/AA copolymer and can be a signal due to some oxidized species formed during the copolymerization reaction. The latter is basically the reason for measuring the signal increment through TMPTMA

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

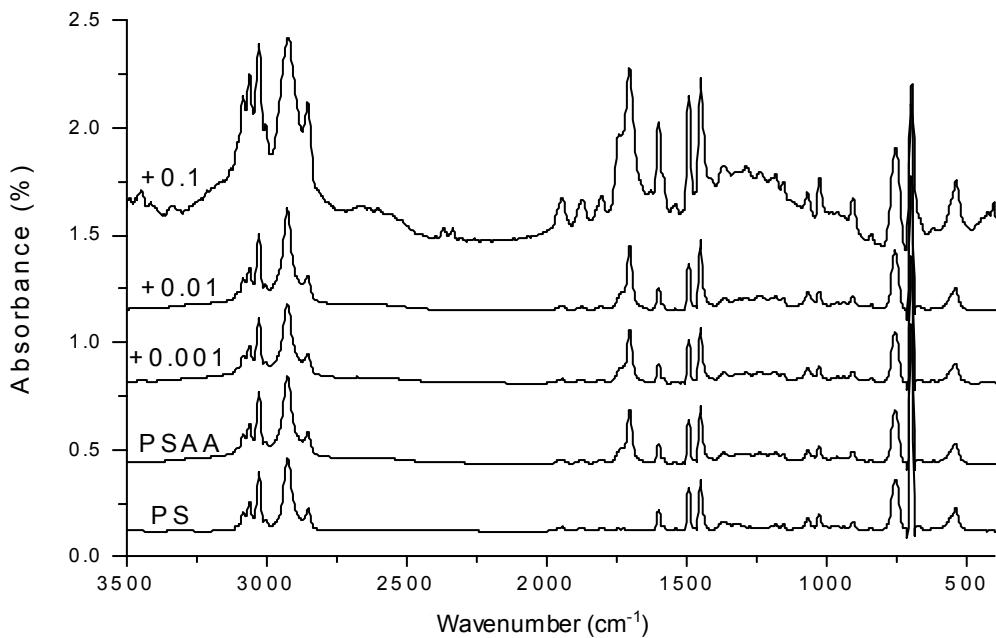


Figure 1. FTIR spectra of polystyrene (PS), the copolymer with acrylic acid (PSAA) and the copolymer prepared including different levels of TMPTMA.

addition (Table 2).

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

It is clear 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 required 8 hours. None of the solvents dissolved the most crosslinked material with the higher level of TMPTMA (0.1%), as seen by other reports[10].

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

Polystyrene shows its Tg transition at 102°C as it is well known, but the copolymer with 6 % mol of acrylic acid enhances the transi-

tion up to 117°C due to interactions between acrylic acid functionality. The crosslinked materials with low amount of TMPTMA (0.001 and 0.01 %) does not produce any changes to the copolymer transition, perhaps due to difficulties considering the low crosslinking level [11]; however, the 0.1 % TMPTMA material reduced the transition considerably as well as extending the thermal interval. Such an effect has been associated with the consequence of the rubbery status acquired for the higher amount of agent [12].

In order to evaluate changes in thermal stability for the prepared materials, TGA thermograms were obtained. All membranes loose weight at the usual temperature of the polystyrene homopolymer [13] (409°C), with a small increment when crosslinked, as can be seen in their traces depicted in Figure 4 and in their DTG maxima values in Table 3. The most crosslinked material (0.1 % TMPTMA) has the higher thermal stability and the copolymer is more sensitive to degradation compared with the polystyrene homopolymer.

Mechanical properties were evaluated by means of DMA and the results of elastic and viscous moduli for the materials are shown in Figure 5. The 0.1 % TMPTMA crosslinked material is not included since it was impossible to obtain films for the evaluations.

The elastic modulus is considerably higher 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. Moreover, the viscous traces have a lower modulus value and peak broadening dependent on the level of crosslinking. It is known that such peaks tend to disappear when the crosslinking is high [12].

Table 2. Esther formation in copolymers with addition of TMPTMA

Polymer	Band ratio (1732/758 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

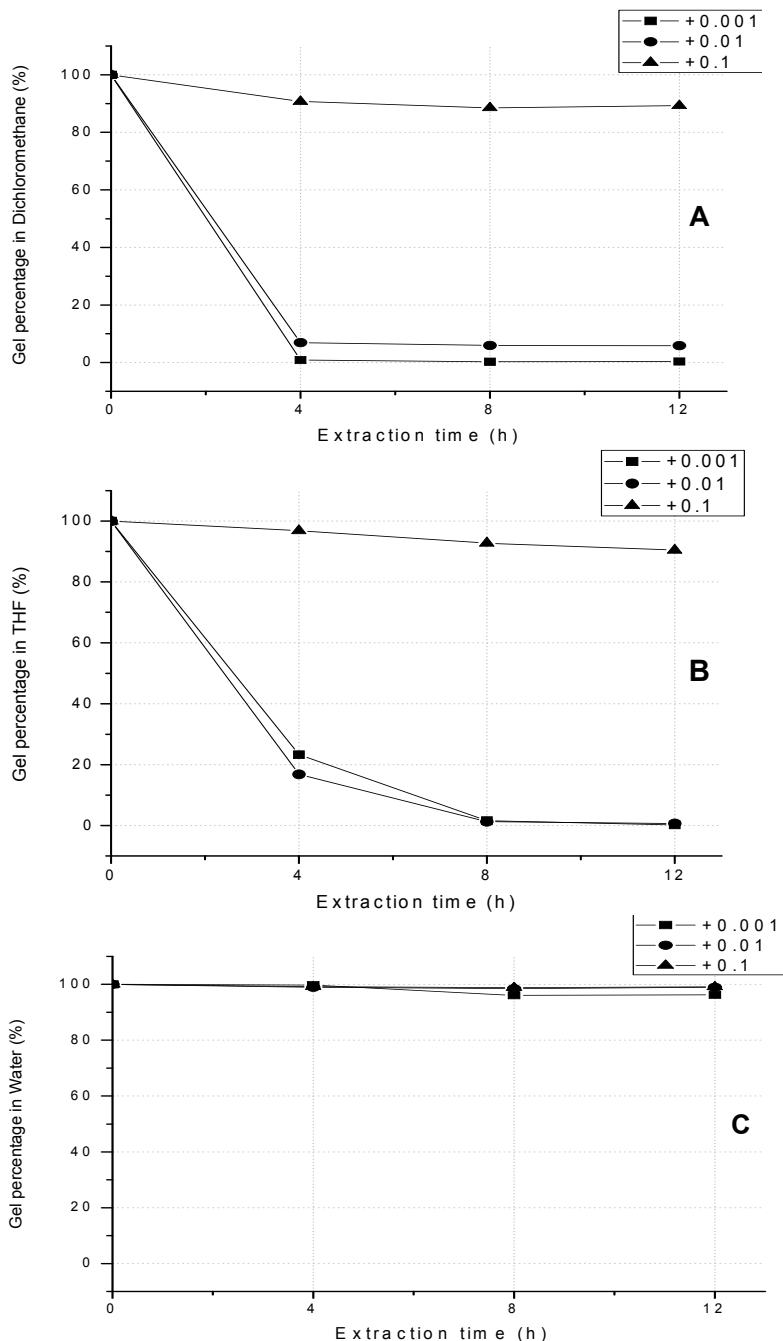


Figure 2. Percentage of gel obtained for the materials at different times using Dichloromethane (A), Tetrahydrofuran (B) and Water (C).

Table 3. Degradation temperatures obtained by derivative TGA

Polymer	Maxima at DTG curves (°C)
PS	409 ± 1.5
PS/AA	405.5 ± 1.5
PS/AA + 0.001 TMPTMA	407.5 ± 1.5
PS/AA + 0.01 TMPTMA	407.5 ± 1.5
PS/AA + 0.1 TMPTMA	411 ± 1.5
TMPTMA	344, 463, 613 (± 1.5)

4. CONCLUSION

The polystyrene-acrylic acid copolymer was prepared and was confirmed structurally by FTIR and the TMPTMA effectively behaved as an crosslinking agent. Water does not extract the polymeric material during % gel evaluations but organic solvents evaluated (THF and DCM) were convenient in order to dissolve and prepare the membranes. Glass transition was effectively enhanced when TMPTMA was added, as observed by DSC evaluations and confirmed by DMA. A rubbery status was obtained, especially for the 0.01 % TMPTMA material, according to viscous and elastic

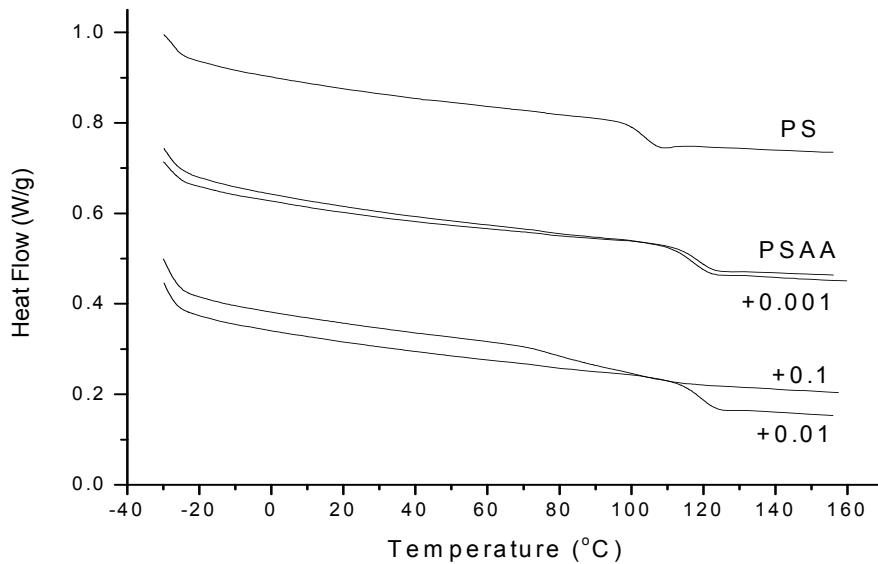


Figure 3 DSC thermograms for PS, PS+AA and the copolymer added with different levels of TMPTMA

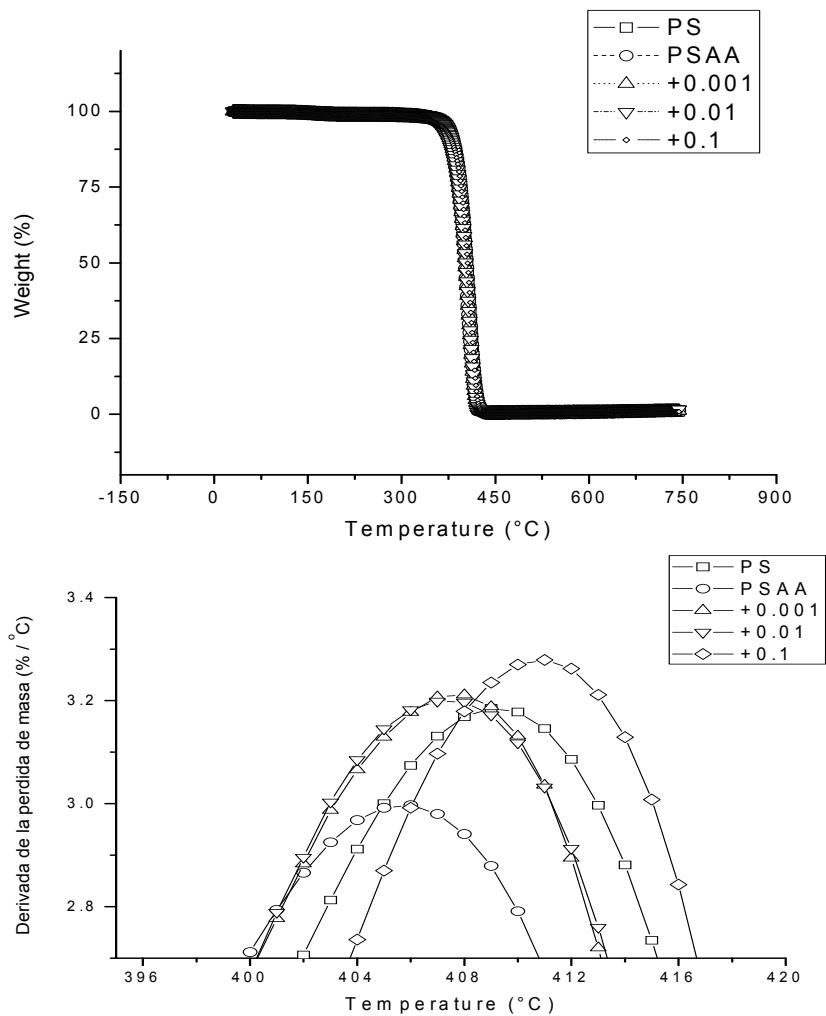


Figure 4. TGA and DTG thermograms for PS, PS+AA and the copolymer added with different levels of TMPTMA

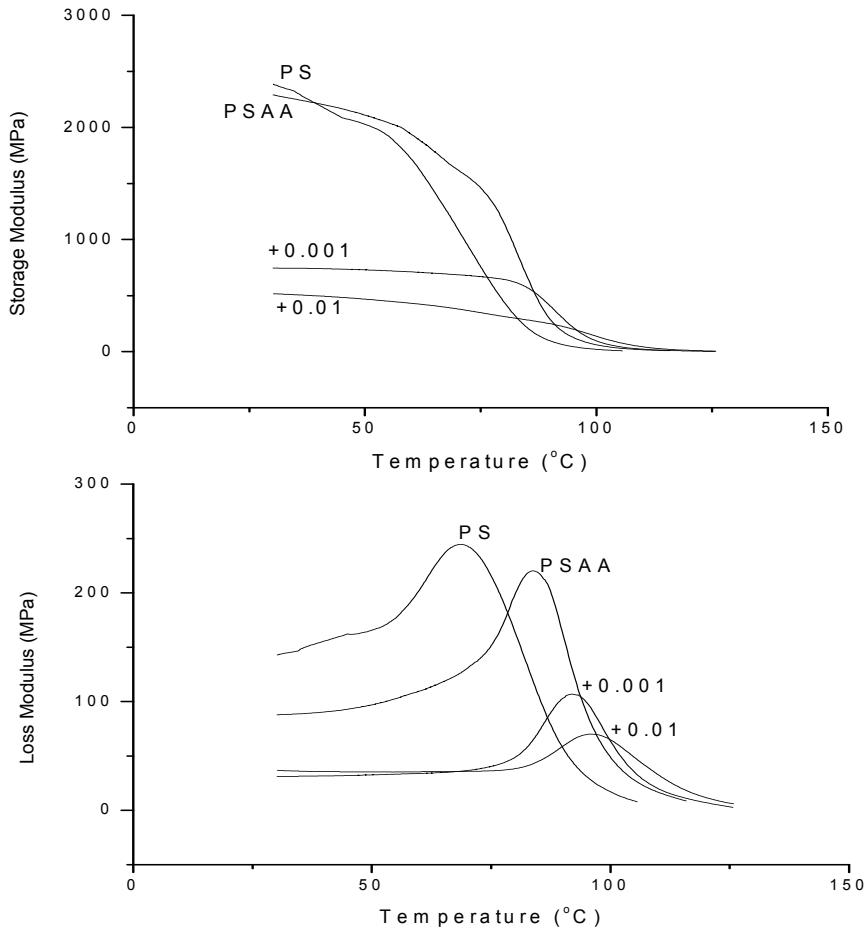


Figure 5. DMA traces (storage and loss modulus) for materials added with different levels of TMPTMA

traces obtained by DMA. A rubbery behavior is highly desired for fuel cell membranes since they will be in use under hot and humid conditions. Thermal stability was slightly enhanced for the crosslinked copolymers. In future studies these materials will be tested for practical use into a fuel cell and the results published in the near future.

5. ACKNOWLEDGEMENTS

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