



High ionic exchange capacity polyphenylsulfone (SPPSU) and polyethersulfone (SPES) cross-linked by annealing treatment: Thermal stability, hydration level and mechanical properties

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ABSTRACT

Thermal stability, hydration and mechanical properties of thermally cross-linked sulfonated aromatic polymers (SAP) with high ionic exchange capacity (IEC) were measured and compared to untreated samples. The formation of cross-linking greatly stabilizes sulfonated polyphenylsulfone (SPPSU) in terms of thermal, mechanical, and hydrolytic degradation: it can resist in water even at a temperature of 145 °C with improved mechanical properties, while TGA experiments demonstrate that SPPSU membranes are stable well above 200 °C. Sulfonated polyethersulfone (SPES) membranes show, instead, a hydrolytic instability.

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1. Introduction

Polyphenylsulfone (PPSU) and polyethersulfone (PES) are fully aromatic high performance polymers known to be amorphous thermoplastic materials. Among the other amorphous thermoplastic polymers, especially PPSU presents superior properties like an excellent thermal stability, a high chemical resistance, exceptional toughness and impact resistance ideal for aerospace, automotive and medical applications. Furthermore, PPSU and PES are not expensive and readily available [1]. The aromatic structure can be functionalized and when ionomeric groups, like sulfonic acid, are inserted in the polymeric backbone, the macromolecule can be used as a polymer electrolyte membrane. Sulfonated polyphenylsulfone (SPPSU) and polyethersulfone (SPES) belong to the family of sulfonated aromatic polymers (SAP), well known compounds in the community of polymer electrolyte membrane fuel cells (PEMFCs) [2–8]. Famous exponents of this class are sulfonated polyetheretherketone (SPEEK), sulfonated polyetherketoneketone (SPEKK), and sulfonated polysulfone (SPSU).

Although in the past, they were regarded as possible alternative to perfluorinated membranes, like Nafion, both in direct methanol and hydrogen fuel cells, today there is a large scepticism regarding their utilization especially in H₂ PEMFCs working at intermediate

temperature. The problems that affect this class of polymers seem, in fact, difficult to solve. The main drawback is that in SAPs the water-filled channels are narrow and tortuous with a low separation between hydrophilic and hydrophobic domains. The distance between adjacent sulfonic groups is consequently large and for this reason SAPs necessitate a higher IEC compared to perfluorinated membranes to attain the required conductivity [9–11]. Unfortunately, high IEC leads also to morphological instability and large swelling [9,12]. In our laboratory, we have followed two different approaches to obtain stable and long-life membranes: the synthesis of hybrid organic–inorganic networks [13–16] and the formation of covalent cross-linking bonds between the macromolecules [17,18].

The formation of cross-links is a well-established technique to improve the performances of polymers, used in a variety of applications [19–21]. The main drawbacks of this technique are the presence of cross-linker molecules that are in general sensible to the severe conditions in a fuel cell and the elaborate or expensive procedures that make the entire process little competitive from an industrial point of view. A direct cross-linking reaction performed in situ during the casting procedure can be instead an interesting and promising methodology to obtain stable and long-life membranes.

In a previous paper, we have illustrated the possibility to perform cross-linking reactions through sulfonic groups directly by thermal treatment of SPEEK membranes [22]. This reaction can be applied to the whole family of SAP and in this work we present the first data obtained for SPPSU and SPES.

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Contrary to the better-known polysulfones, SPPSU and SPES have not received much attention and not many papers exist in the literature regarding their utilization in PEMFCs [23–31]. Polyphenylsulfone presents some peculiarities with respect to the other members of the SAP family. The direct linkage between aromatic moieties makes the structure more rigid, but at the same time it leads to the presence of two activated phenyl rings for the electrophilic aromatic substitution reaction. Consequently, it is easily possible to introduce two sulfonic acid groups per repeat unit, which leads to a high ionic exchange capacity (IEC = 3.57 meq/g) [32]. A part of sulfonic acid groups can be sacrificed to perform further functionalization, such as cross-linking, without a sensible loss in electrochemical performances. An elevated IEC is in fact an essential requisite for SAPs to obtain suitable proton conductivity for PEM fuel cells [33].

Instead, PES is difficult to sulfonate due to the electron withdrawing effect of the sulfone linkages that deactivate the adjacent aromatic rings for electrophilic substitution and its sulfonation required stronger reagents or/and longer time [34,35]; under these conditions, up to two sulfonic groups can however be inserted per repeat unit. SPES is more hydrophilic than other SAP membranes due to its short and polar repeat unit. Its low molecular weight (312 g/mol) leads to high IEC values even for a relatively low degree of sulfonation (DS = 1 corresponds to 3.2 meq/g) and it reaches conductivity values similar to highly sulfonated SPEEK. However, SPES membranes with suitable DS dissolve easily in water.

In this contribution, we examine if the formation of covalent bonds among macromolecular chains can stabilize the polymer microstructure and can make them suitable for further investigations. We present experiments on thermal stability, hydration and mechanical properties of thermally cross-linked SPPSU and SPES membranes, which are compared to untreated samples.

2. Experimental

2.1. Synthesis

2.1.1. SPPSU: sulfonation of PPSU

Polyphenylsulfone (Solvay, PPSU, MW = 46173 g/mol, 20 g, 50 meq) was dissolved in H₂SO₄ (Carlo Erba 96%, 1 L) and stirred at 50 °C for 5 days. The solution was poured in a large excess of ice-cold water under continuous stirring, obtaining a white precipitate. After standing overnight, the precipitate was filtered and washed several times with cold water to neutral pH. The sulfonated polymer (SPPSU) was then dried under vacuum for 4–6 h at room temperature. The degree of sulfonation (DS) was evaluated both by elemental analysis and by titration. Both methods gave according results, indicating a DS = 2 corresponding to an IEC of 3.57 meq/g.

2.1.2. SPES: sulfonation of PES

Polyethersulfone (Victrex, PES, MW = 67080 g/mol, 10 g, 32 meq) was dissolved at room temperature with chlorosulfonic acid (Sigma Aldrich 99%, 50 ml) and stirred at RT for 20 h. The solution was then poured in 150 ml of sulfuric acid (Carlo Erba 96%) and kept under stirring at RT for 2 h. It was then precipitated with ice-cold water while stirring. After standing overnight, the precipitate was washed with ice-cold water until pH value of 5–6 and dried at 80 °C for 20 h under vacuum [36]. The degree of sulfonation, evaluated by titration and NMR, was DS = 0.83 corresponding to an IEC of 2.78 meq/g.

2.2. Preparation of membranes

The procedure for membrane preparation using dimethylsulfoxide (DMSO) as solvent casting was previously described [21]. In a

typical experiment ~250 mg sample was dissolved in 30 mL of solvent. The resulting mixture was stirred for 4 h, evaporated to 5 mL, cast onto a Petri dish, and heated to dryness for 16 h at 120 °C. After being allowed to cool to room temperature, the resulting membranes were peeled off and heated under dynamic vacuum for 24 h at 80 °C for solvent removal (called “untreated samples” in the following discussion). However, a small amount of DMSO remained in the membranes after this step [21].

In the case of highly sulfonated PES, the membrane casting was more difficult, because the samples were very hydrophilic and did not separate easily from the Petri dish. The Petri dish was treated with silicon oil to reduce the membrane adhesion.

Subsequent thermal treatments of SPPSU membranes were performed at 170 °C for 24, 48 or 64 h (IEC 2.35, degree of cross-linking per repeat unit was 0.8) and for SPES at 160 or 170 °C for 64 h (called “treated samples” in the following discussion).

2.3. Measurements

2.3.1. Structural characterization

FT-IR spectra of membrane samples heated to different temperatures were collected in transmission mode in the range of 4000–400 cm⁻¹ (32 scans, 2 cm⁻¹ resolution) with a Bruker Equinox 55. The membrane thickness was ca. 60 μm in all cases. A background spectrum was run and sample spectra were normalized against the background spectrum.

¹H nuclear magnetic resonance spectra were recorded in d₆-DMSO with a Bruker Avance 400 spectrometer operating at 400.13 MHz. Chemical shifts (ppm) are referenced to tetramethylsilane (TMS).

The morphology and the roughness of the membranes were monitored by atomic force microscopy (AFM) with a PARK AUTO-PROB Cp. The AFM images were obtained with scans of 80, 20 and 5 μm using MPP31 probes (Silicon Cantilever).

2.3.2. Mechanical properties

Stress–strain tests. The mechanical properties of SPPSU were investigated using an ADAMEL Lhomargy DY30 test machine at room temperature at a constant crosshead speed of 5 mm/min with aluminium sample holders as described in Ref. [37]. Prior to the measurements, the polymer samples were stabilized at ambient temperature and humidity, which was (50 ± 10)% RH. The measurement time was below 5 min.

2.3.3. Thermal behaviour

The thermal degradation of polymer membranes was investigated by high resolution thermogravimetric analysis (TGA Q500, TA Instruments), performed between 25 and 600 °C with a maximum heating rate of 5 K min⁻¹ under air flux in platinum sample holders.

2.3.4. Water uptake measurements

Water uptake was measured by two complementary experiments. (i) By full immersion in deionized water at temperatures between 25 and 145 °C: polymer samples were weighed before and after immersion times between 1 h and 6 days (hydrothermal treatments above 100 °C were performed in hermetically closed Teflon vessels) [38]; (ii) by equilibration with water vapour at 25 °C under 0–95% RH [37]. The water sorption isotherms were recorded using a TA5000 thermogravimetric analyzer. RH was modified in 5 or 10% steps and the water uptake recorded at each step for 2 h at 25 and 50 °C. Prior to all experiments, the membranes were first dried in situ for 3 h at 80 °C under 0% RH.

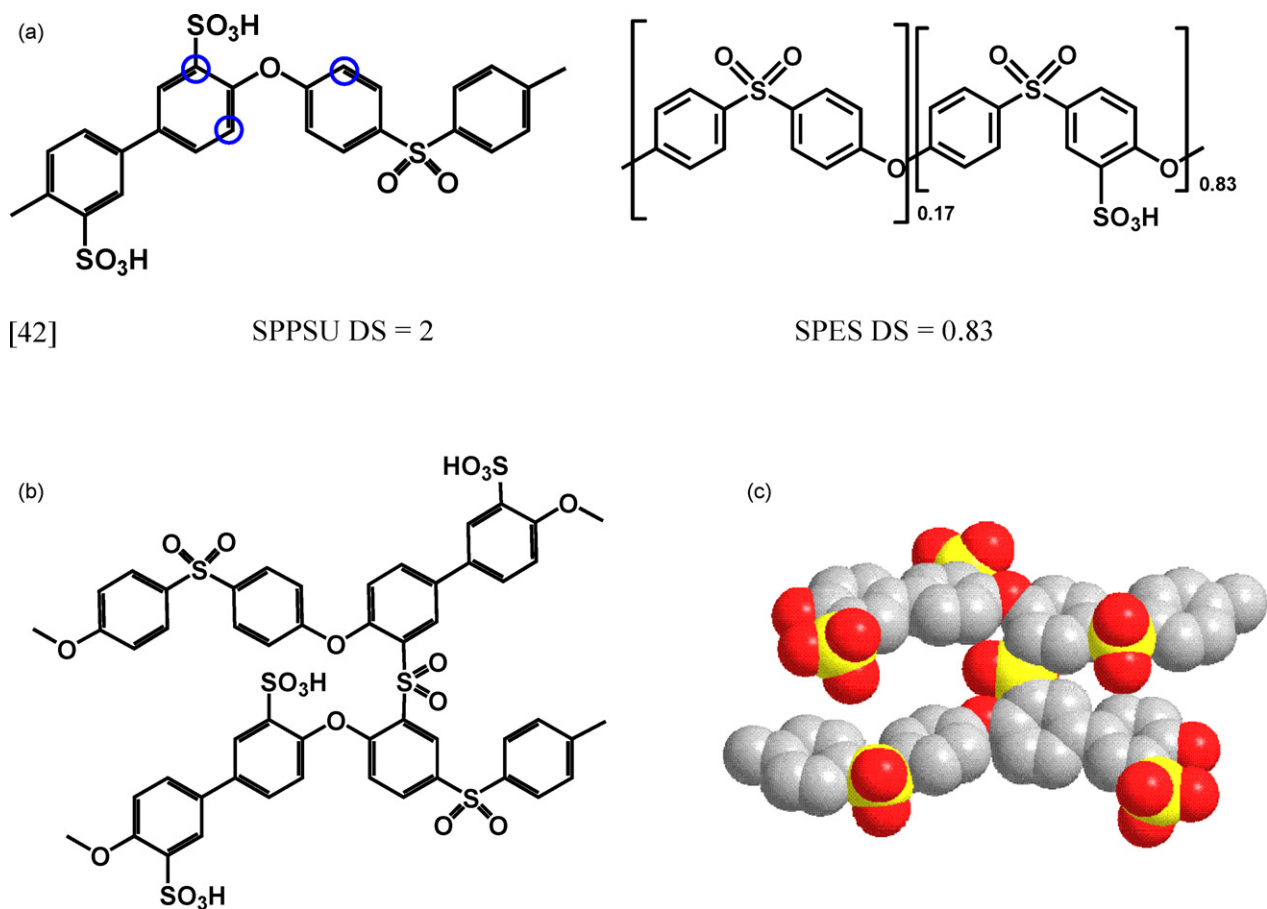


Fig. 1. (a) Repeat unit of SPPSU with DS = 2 and SPES with DS = 0.83. The blue circles represent the possible positions for the formation of sulfone bridges. (b) A possible repeat unit of cross-linked SPPSU. (c) Three-dimensional representation of cross-linked SPPSU showing the distance between the chains. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3. Results and discussion

3.1. Structure and microstructure

Fig. 1 shows the repeat units of SPPSU (before and after the cross-linking) and SPES. The reaction pathways for cross-linked SPEEK are discussed in Ref. [21]. They involve electrophilic aromatic substitution over SO_2^+ electrophilic intermediates generated during solvothermal treatment of casted membranes. The charge separation is facilitated by the presence of the high dielectric constant solvent DMSO in the membranes. The formation of cross-links between macromolecular chains during solvothermal treatment in presence of DMSO is common to many SAP.

Fig. 2 shows FT-IR analysis of an untreated SPPSU sample and a sample heated at 170 °C for 64 h. Both spectra are dominated by PPSU infrared bands, in particular it is possible to observe signals at 1320 and 1150 cm^{-1} due to S=O stretching (asymmetric and symmetric respectively) together with band at 1105 and 1084 cm^{-1} (ν C-S). The signal at 1170 cm^{-1} is due to two contributions: $-\text{SO}_3$ groups and ring modes of 1:2-substituted benzene, while the absorptions at 1020 cm^{-1} ($\nu_{\text{sym}}-\text{SO}_3\text{H}$), and 965 cm^{-1} ($\delta-\text{SO}_3\text{H}$) are due to aromatic sulfonic groups [18]. Considering that cross-linking leads to the formation of sulfone bonds, already present in the backbone of the polymer, no appreciable difference between the two spectra can be expected. However, subtraction of the normalized spectrum of untreated SPPSU from that of 170 °C treated SPPSU (Fig. 2c) reveals the presence of supplementary S–O stretching vibrations at 1155 cm^{-1} , due to PhSO_2Ph generated in the cross-linking reaction. Signals due to 1:2:4-substituted phenyl

rings are present at 1080 cm^{-1} . It is also possible to observe bands of aromatic sulfone moieties at 1210 cm^{-1} (shoulder) and 1065 cm^{-1} (tail) [39]. Intensity variation of signals due to aromatic sulfonic groups (1180 and 1020 cm^{-1}) is also observed indicating a reduced amount of acidic groups in the treated SPPSU.

^1H NMR spectra of PES and SPES in DMSO are shown in Fig. 3. The presence of a sulfonic acid group causes a significant down-field shift of the hydrogen located in *o*-position at the aromatic ring. From the spectrum, one can calculate the degree of sulfonation, according to Ref. [31] (DS = 0.83); furthermore, it is possible to exclude the degradation of the polymer during sulfonation.

Fig. 4 presents AFM images of sulfonated PPSU membranes before and after thermal treatment. The membrane surfaces are very smooth; the RMS value is about 2 nm and decreases slightly after thermal treatment.

3.2. Properties

The maximum working temperature of SAP membranes is currently limited to 80–90 °C, which is a strong limitation for use in PEMFC. Working temperatures in the range of 120–130 °C are highly desirable [40] and all the physical and chemical modifications able to increase thermal stability, durability, performance and cost are expected to have positive effects on the development of PEMFC systems. Furthermore, the behaviour of thinner membranes is less sensitive to temperature changes, which may be an important aspect for the working characteristics of the fuel cell. However, prerequisite for use of thin membranes is high performance mechanical properties of the ionomer. Analysis of the

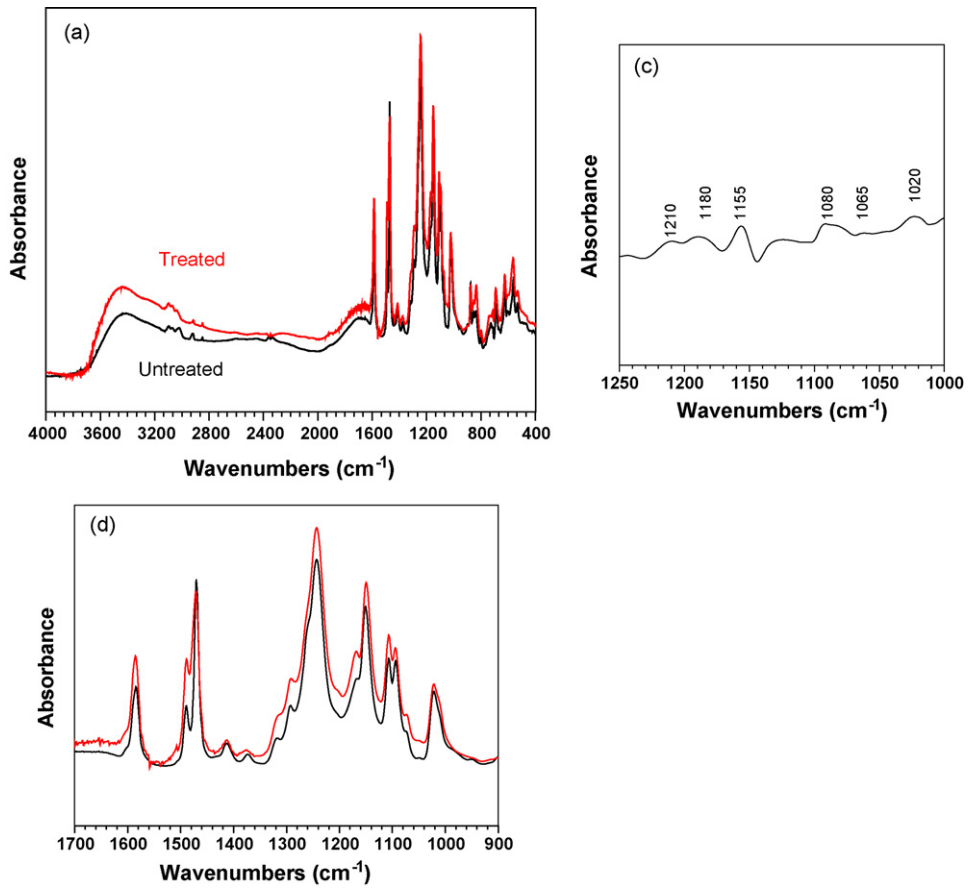


Fig. 2. (a) FT-IR spectra of SPPSU. Black: untreated membrane, red: membrane treated at 170 °C for 64 h; (b) zoom on region: 1700–900 cm^{-1} . (c) Difference spectrum [(black line) - 1(red line)].

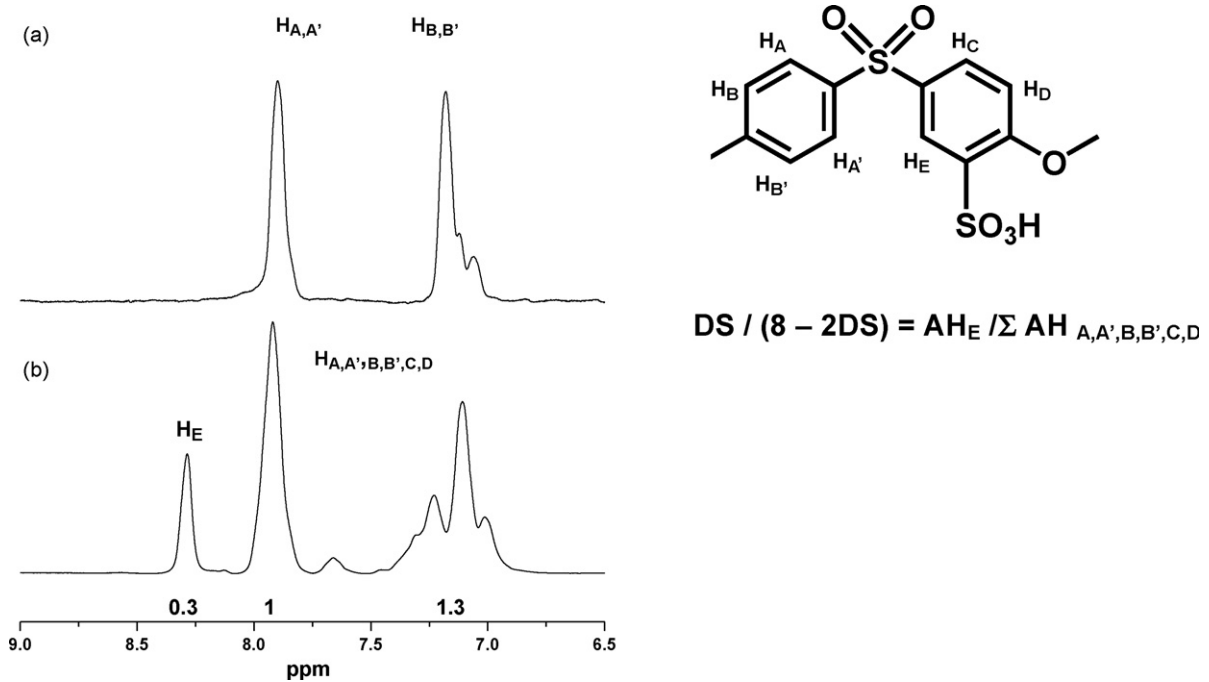


Fig. 3. ^1H NMR of (a) unsulfonated PES and (b) sulfonated PES in d_6 -DMSO.

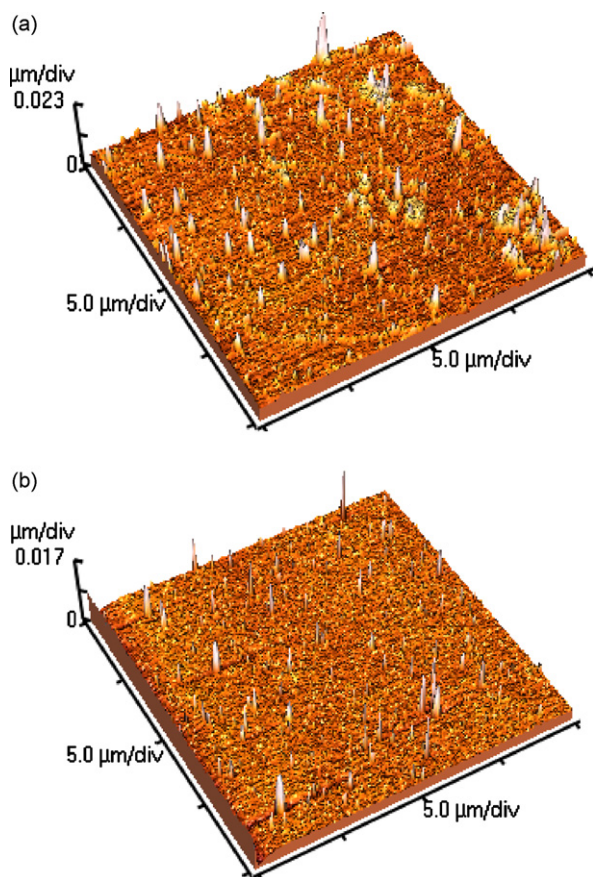


Fig. 4. AFM images of S-PPSU membranes (a) untreated and (b) after heat treatment at 170 °C for 64 h.

mechanical properties is thus an important element for membrane development.

The new cross-linked SAP membranes are very promising from a degradation point of view. In fact, among the causes that lead to the degradation of SAP membranes, we can individuate three important reasons: (a) thermal degradation; (b) mechanical degradation; (c) hydrolytic degradation. These factors will now be discussed, based on our results.

3.2.1. Thermal degradation

Fig. 5 shows the thermogravimetric analysis of untreated SPPSU and SPPSU annealed at 170 °C for 48 or 64 h. The first mass loss above 150 °C is observed only for untreated samples: it corresponds to loss of residual solvent DMSO. The mass loss above 200 °C is due to the removal of sulfonic acid groups; heat-treated samples present a distinctly lower mass loss, because a part of the sulfonic acid groups has reacted previously during thermal treatment to form sulfone cross-links. There is also a large difference between the two treated samples, showing that many more cross-links were formed after 64 h than after 48 h at 170 °C. This might indicate a time of latency for the cross-linking reaction. Furthermore, the removal of sulfonic acid groups due to cross-linking increases the temperature of pyrolysis of the polymer up to about 450 °C; however, there seems to be an optimum concentration of sulfonic acid groups above which the pyrolysis temperature decreases again.

Fig. 6 shows TGA of untreated SPPSU up to 300 °C (a: mass loss, b: derivative curve). The first mass loss above 150 °C corresponds to loss of DMSO, the second to loss of sulfonic acid groups, as discussed before. The second loss is clearly different for pretreated and untreated samples: for treated samples the derivative curve has a Gaussian shape, whereas for untreated ones the loss of sulfonic acid

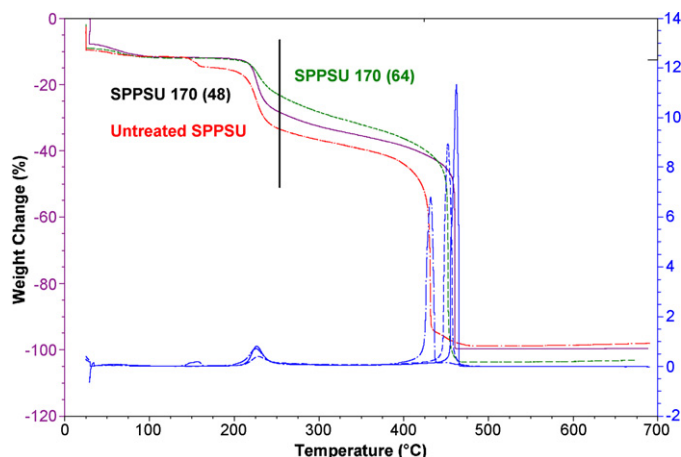


Fig. 5. Thermogravimetric analysis of untreated SPPSU (red line), SPPSU treated at 170 °C for 48 h (black line) and SPPSU treated at 170 °C for 64 h (green line). The blue curves represent the derivative signal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

groups starts earlier and the curve is asymmetrical, indicating “in situ” cross-linking.

Fig. 6c shows a more elaborate TGA experiment: curve 1 is the mass loss until 300 °C. The insert represents a zoom of the curve 1. After cooling the same sample to 50 °C, a second run (heating from 50 to 700 °C, curve 2) does not show a mass loss before 450 °C. All these measurements confirm that the cross-linking reaction leads to loss of sulfonic acid groups and this is fully consistent with the IR analysis and previous results reported in [21].

Fig. 7 presents TGA of SPES treated at 160 °C for 64 h. Features similar to SPPSU can be observed for SPES with a slightly higher temperature of loss of sulfonic acid groups, which might be due to hydrogen bonding between the near sulfonic acid moieties. The final pyrolysis temperature is slightly below that for SPPSU.

Altogether, TGA experiments demonstrate that SPPSU and SPES membranes are stable well above 200 °C. Usual SAP membranes stop working at high temperatures due to the low glass transition temperatures of the polymers. Dynamical mechanical analysis results on SPEEK and SPPSU showed that the thermal treatment increases the glass transition temperature well above 200 °C for SPPSU [41]. Although the long-time thermal stability of membranes cannot be assessed from TGA data alone, these results are still very encouraging for the future use of these membranes in intermediate temperature PEM fuel cells.

3.2.2. Mechanical degradation

Typical mechanical traction experiments (stress–strain curve) of SPPSU (Fig. 8) permit the calculation of elastic modulus E , tensile strength MPa and elongation at rupture. The very high elastic modulus, relatively high tensile strength and low elongation at rupture of SPPSU are consistent with a polymer well below its glass transition temperature ($t_g > 200$ °C). In the case of SPES it was impossible to obtain sufficiently large samples for the mechanical tests, because they were damaged on separation from the Petri dish.

During fuel cell operation, the dimensional changes due to membrane swelling in different humidification conditions and the exothermic combustion of the fuel cause perforations, fractures and pinholes. These defects further increase gas crossover and therefore a critical sequence of increasing gas crossover and pinhole formation is quickly established [42]. We observe here that when SAP are thermally treated in selected conditions the mechanical properties are greatly improved. This effect was previously observed for SPEEK and attributed in part to the presence of cross-linking and in part to irreversible changes of conformation [50]. Furthermore, treated

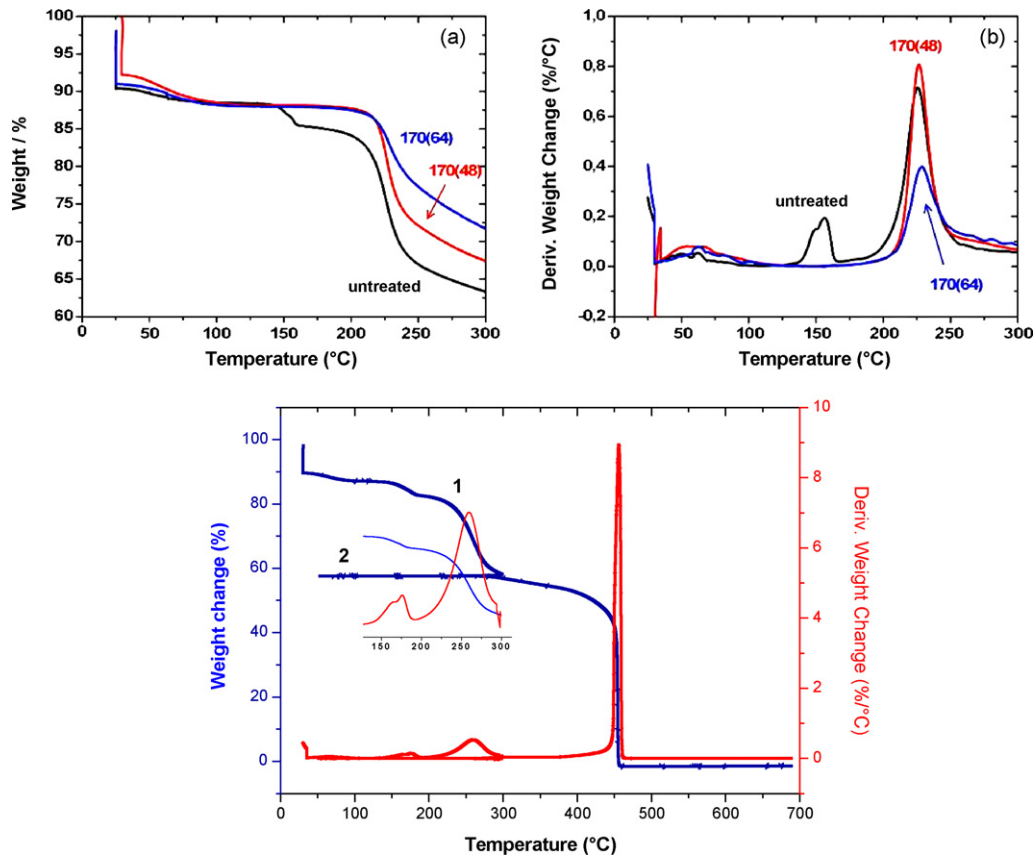


Fig. 6. Thermogravimetric analysis of untreated SPPSU (black line), SPPSU treated at 170 °C for 48 h (red line) and SPPSU treated at 170 °C for 64 h (blue line). (a) Weight change and (b) derivate weight change. (c) TGA of untreated SPPSU (1) up to 300 °C and (2) after heating up to 300 °C and cooling to 50 °C. The insert represents a zoom of the curve 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

membranes also show a minor pinhole distribution linked with the treatment performed. In fact, the AFM images made did not reveal any pinholes.

3.2.3. Hydrolytic degradation

The water uptake kinetics of SPPSU in liquid water at various temperatures is shown in Fig. 9. SPES, instead, dissolves in water at room temperature after 24 h due to the still very high hydrophilicity of the polymer. Attempts to improve the water uptake behaviour by formation of a hybrid organic–inorganic membrane are currently in progress.

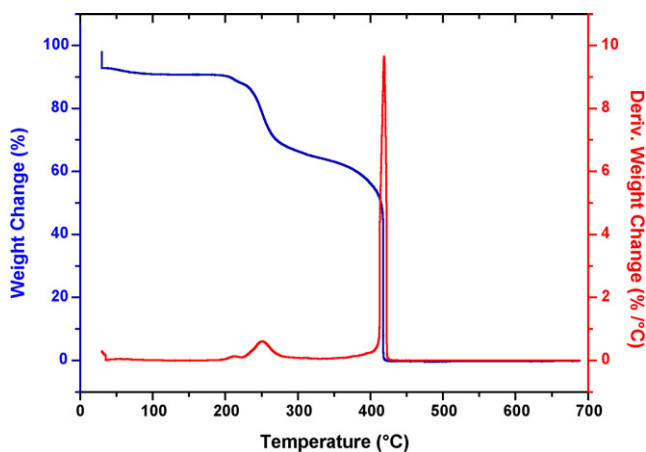
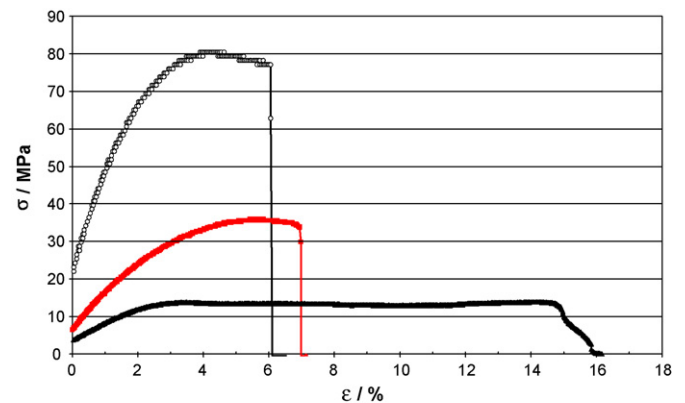


Fig. 7. Thermogravimetric analysis of SPES membrane treated at 160 °C for 64 h.

Fig. 10 presents the water uptake kinetics of SPPSU. Fig. 11 shows the water uptake isotherm of SPPSU and SPES membranes in water vapour at 50 °C. The water uptake above 80% RH is impossible to determine for SPES, which swells and dissolves. It is evident that the heated SPPSU membranes have a distinctly lower water uptake, which is consistent with the data obtained with liquid water. The



SPPSU T (t)	Elastic modulus E (MPa)	Tensile strength σ_{max} (MPa)	Elongation at rupture ϵ_r (%)
Untreated	540±130	13±4	17±6
170 (48)	850±200	30±10	6±1
170 (64)	2950±300	80±3	7±3

Fig. 8. Typical nominal stress–strain curve for SPPSU membranes (a) untreated, (b) treated at 170 °C for 48 h and (c) treated at 170 °C for 64 h.

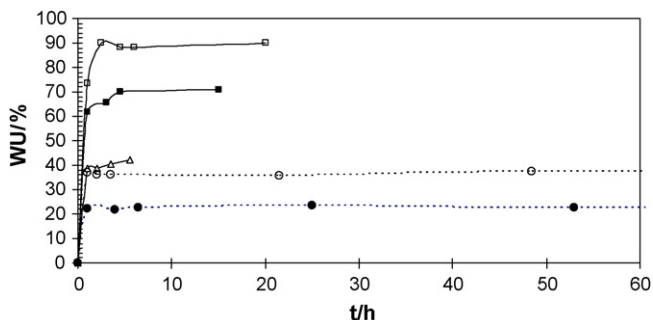


Fig. 9. Water uptake kinetics by immersion in liquid water of a SPPSU membrane heated at 170 °C for 64 h. (●) 25 °C, (○) 60 °C, (△) 100 °C, (■) 120 °C and (□) 145 °C.

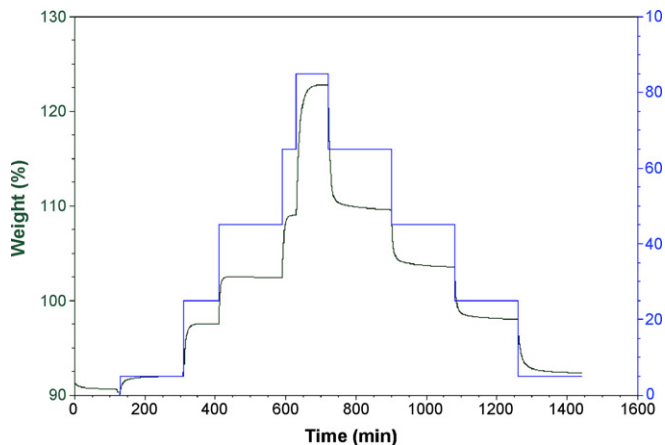


Fig. 10. Typical water uptake kinetics of untreated SPPSU membranes.

water uptake remains very reasonable even in liquid water at temperatures as high as 145 °C. Swelling phenomena are very reduced after heat treatment. The higher mechanical strength of thermally treated SPPSU membranes due to irreversible changes of conformation and covalent cross-linking between macromolecular chains increases the resistance against penetration of water. The cross-links are stable against hydrolysis, as can be deduced from the following experiment: very remarkably, once cross-linked membranes are immersed in water and water is removed by drying over P₂O₅, the water uptake remains identical after renewed immersion in water. The kinetic analysis (Fig. 9) shows that the sorption of water is a fast process. Alberti et al. [38] discussed the decrease of water uptake rate with the temperature in Nafion as result of two distinct processes, the first very fast and the second very slow. The fast process was attributed to the equilibration necessary for the water diffusion within the thin membrane, while the slow process was associated with a modification of the polymer conformation

with the temperature. Similar mechanisms seem to be applicable also to SAP.

4. Conclusion

The new method for introducing a certain degree of covalent bonds between adjacent polymeric chains by heat treatment of cast membranes is really economic, since the cross-linking reaction can be performed directly after membrane casting. Due to its simplicity, it is furthermore very suitable for industrial preparation of cross-linked membranes, because the procedure can be easily up-scaled. However, a delicate balance still exists between hydrophilic character of membranes and their properties. For example, highly sulfonated SPES membranes are difficult to separate from the casting substrate. All in all, cross-linking of highly sulfonated SAP by thermal treatment, especially for SPPSU, opens new horizons for use as PEM fuel cell membranes. In the case of SPES the formation of an organic–inorganic hybrid in the macromolecular chain seems very promising to reduce the hydrophilicity of the polymer.

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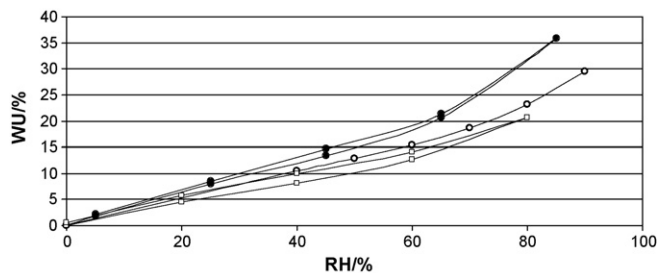


Fig. 11. Water sorption/desorption isotherms at 50 °C of SPPSU membranes (●) untreated, (○) heated 170 °C for 64 h and SPES membrane treated at 160 °C for 64 h (□).

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