

Thermal analysis of sulfonated polymers tested as polymer electrolyte membrane for PEM fuel cells

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Abstract An aromatic polymer, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was sulfonate with different sulfonation degrees (30, 50, and 75 % theoretical degree) to obtain an electrolytic polymer suitable as proton exchange membrane for fuel cells. Thermal behaviors of sulfonated PPO were tested by differential scanning calorimetry and thermogravimetry. The sulfonation degrees were correlated with glass transitions temperatures (T_g) and the percent of weight loss. One notices a good fitting between sulfonation degree and the percent of weight loss thanks splitting of sulfonic moieties but it is not the same for glass transition temperatures that have a random variation.

Keywords Polymer electrolyte membrane · Polyphenylene oxide · Sulfonation degree · Thermal behavior

Introduction

Polymer electrolyte fuel cells (PEMFCs) are electrochemical devices able to convert chemical energy of hydrogen and other small compounds (methanol) to electrical energy. The capacity to produce a high power density operating at low temperature (below 200 °C) makes them suitable as power sources for mobile and automotive applications.

The main chemical reactions that occurring in a fuel cell are: catalytic oxidation of fuel (hydrogen and methanol) to anode, and catalytic oxygen reduction to cathode.

Oxidation of fuel release electrons and protons. The electrons pass to the cathode through an external circuit yielding electric current. The protons are transported through polymer electrolyte membrane to the cathode and react with oxygen forming water (Fig. 1). It is known that the platinum catalyst from electrodes is susceptible to be poisoned with carbon monoxide (CO) at temperatures below 100 °C. The poisoning effect of CO decrease when temperature increased, and this is a reason to prefer fuel cells working above 100 °C. The PEM Fuel Cells that operating at high temperatures (100–200 °C) requires materials that properly work at these temperatures.

There are several approaches to develop high temperature polymer exchange membranes for fuel cells: (1) from modified perfluorosulphonic acid (PFSA) polymers; (2) from partially fluorinated and aromatic hydrocarbon polymers; (3) using inorganic–organic composites; (4) membranes based on acid–base polymers [1].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an engineering plastic, thermally and chemically stable, that could be modified by polymer analogous reactions, particularly through sulfonation. Furthermore, thermal properties of these modified polymers do not change more comparing with pristine PPO [2].

The basic structure of PPO contains an aromatic ring, two methyl groups and a hydroxyl (phenol) ending group (Fig. 2). These groups make possible the participations of PPO to many polymer-analogous reactions. Sulfonation is a conventional electrophilic substitution reaction [3] used to prepare the sPPO with variable charge density. As sulfonating agent may be used: concentrated sulfuric acid, chlorosulfonic acid, pur or complex sulfur trioxide, or acetylsulfate. sPPO has one or two sulfonic groups bonded to the aromatic ring (Fig. 2). The sulfonation can be controlled by adjusting time, temperature, concentration, and solvent.

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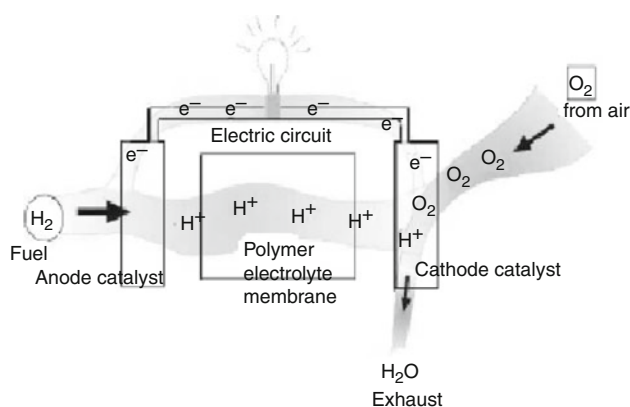


Fig. 1 Basic fuel cell operation

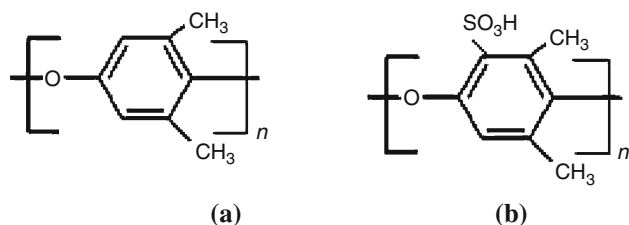


Fig. 2 Chemical structures of unsulfonated (a) and sulfonated (b) PPO

This article aims to demonstrate the good potential usage of these membranes in medium temperature fuel cells and the properties that make them potential candidate for PEM fuel cells working above 100 °C. This study offers an analysis of thermal characteristic of sulfonated polyphenylene oxide reported to sulfonation degree. High glass transition temperatures of sulfonated polyphenylene oxide and high value obtained for ion exchange capacity (IEC) are the reasons to proceed the improving this materials.

Experimental

Materials

PPO from Aldrich, ($T_g = 210$), chloroform for synthesis, $c = 99.5\%$, from Merck, chlorosulfonic acid for synthesis, $c = 97\%$, from Merck, sodium bicarbonate, 99.7%, ACS reagent from Aldrich, sulfuric acid and methanol from Aldrich.

Sulfonation of polymer

Sulfonation was carried out in chloroform at ambient conditions using chlorosulfonic acid as sulfonating agent. First, 10 g of PPO was dissolved in 100 ml of neutralized chloroform, in a three-necks round bottom reaction flask. The mixture was stirred for about 30 min under the ambient conditions to form a 7 wt% solution. The

sulfonating agent, solutions with concentration between 0.2 and 0.6 mol/l chlorosulfonic acid in chloroform (corresponding to the request sulfonation degree) was first kept on the ice bath and then slowly added, with a dropping funnel to the PPO chloroform solution at 25 °C with vigorous mechanical stirring [4, 5]. Sulfonation degree was controlled by concentration of chlorosulfonic acid in chloroform. If there were precipitated materials in the flask, the precipitated polymer was separated, and the liquid was discarded. If not, the reaction solution was stirred at 25 °C for another 3–4 h; then, the reaction was stopped, with 25 ml of methanol, and the liquid mixture was precipitated into deionized water. The precipitated product, substituted PPO with chlorosulfonate groups was then boiled with 100 ml saturated solution of NaHCO_3 for about 5 h and the sulfonated product was precipitated with 6 M sulfuric acid solution. The precipitated polymer sPPO was washed with deionized water repeatedly and dried in atmosphere for 24 h at ambient temperature followed by vacuum drying at 60 °C for about 48 h.

Membrane casting

The membrane was carried out by recasting from solution. A 40 % weight to volume sPPO was dissolved in methanol and stirred with magnetic stirrer. The homogeneous solution was laminated with a COATMASTER film applicator device and the solvent was evaporated in time at normal pressure and 60 °C. There were obtained membranes with thickness between 20 and 40 microns.

Fourier transform infrared (FTIR) spectrometer

FTIR spectra of the PPO and sPPO samples were obtained with a spectrometer Bruker Vertex 70 using the attenuated total reflectance (ATR) method.

Determination of IEC and sulfonation degree

IEC represents the milliequivalents of sulfonic acid groups per gram of dried polymer and the sulfonation degree (SD) is the number of sulfonic acid groups for a monomer units. IEC and SD were determined by titration method.

First, the membrane samples were swollen in 0.1 mol/l HCl solution to bring all the sulfonic groups to acid form. After 24 h the samples were rinsed with deionized water and dried at 50 °C under vacuum atmosphere for about 8 h. Then samples were weighted obtaining the dry sample masses (m_s). The membrane samples were swollen in 0.1 mol/l NaCl solution for 24 h to exchange the H^+ ions from the sulfonic groups with Na^+ . Finally, the acidity of NaCl solution was titrated with a 0.01 mol/l NaOH solution in the presence of phenolphthalein as indicator. On

noted the volume of NaOH solution V_t used for titration. The IEC was calculated with the formula:

$$\text{IEC} = \frac{V_t \cdot C_{\text{NaOH}}}{m_s} \quad (1)$$

Sulfonation degree was calculated from the value of IEC [6] with relation:

$$\text{SD} = \frac{120 \cdot \text{IEC}}{1000 - 80 \cdot \text{IEC}} \cdot 100 \quad (2)$$

where 120 is the value of molar weight of monomer unit and 80 is the molar weight of sulfonic group (SO_3).

Thermal analysis: differential scanning calorimetry (DSC) and thermal gravimetric (TG) analysis

There were used two devices to study the thermal behaviors of sulfonated and unsulfonated polymers: DSC 131 from Setaram to obtain the DSC curves and a thermal-gravimetric analyzer SDT Q600 from TA that record the thermal decomposition of samples with increasing the temperature (TG curves). Both devices used a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ over a temperature range of $50\text{--}550 \text{ }^\circ\text{C}$ in nitrogen inert atmosphere.

Results and discussion

FTIR spectra of sulfonated polymers

The FTIR spectra of unsulfonated and sPPO were recorded on the bulk polymer samples, by ATR method. On notice the characteristic absorption bands for the presence of the $-\text{SO}_3\text{H}$ substitute to aromatic rings (Fig. 3):

- A broadband between $3,600$ and $3,200 \text{ cm}^{-1}$ characteristic for hydrogen interaction between $-\text{OH}$ groups from $-\text{SO}_3\text{H}$;
- a peak corresponding to the symmetric stretching of SO_2 at $1,060 \text{ cm}^{-1}$;
- an absorption peak at 673 cm^{-1} due to C–S stretching vibration;

it is clear that the sulfonate groups have been introduced successfully into the polymer backbone.

IEC and sulfonation degree

The amount of chlorosulfonic acid was stoichiometric calculated to obtain different sulfonation degrees (Table 1). The theoretical values (SD_t) are higher than the experimental values of SD calculated (relation 2) by using the IEC values determined by titration (Table 1).

Theoretical values of SD are not the same with the obtained value, because the efficiency of sulfonation process is not 100 %, which means not all the molecules of sulfonating agent will react with polymer replacing hydrogen atoms from aromatic ring. Another reason could be precipitation of sulfonated polymer when sulfonation degree exceeds a certain value. Polymer chains are more

Table 1 The theoretical values of sulfonation degree and the value of IEC and SD obtained by titration

Sample	$\text{SD}_t/\%$	Chlorosulfonic acid/ml	IEC/meq/g	SD/%
S ₁	30	1.7	1.4	19
S ₂	50	2.8	2.5	37.5
S ₃	75	4.2	2.9	45

Fig. 3 Comparison between FTIR spectra of unsulfonated and sulfonated PPO

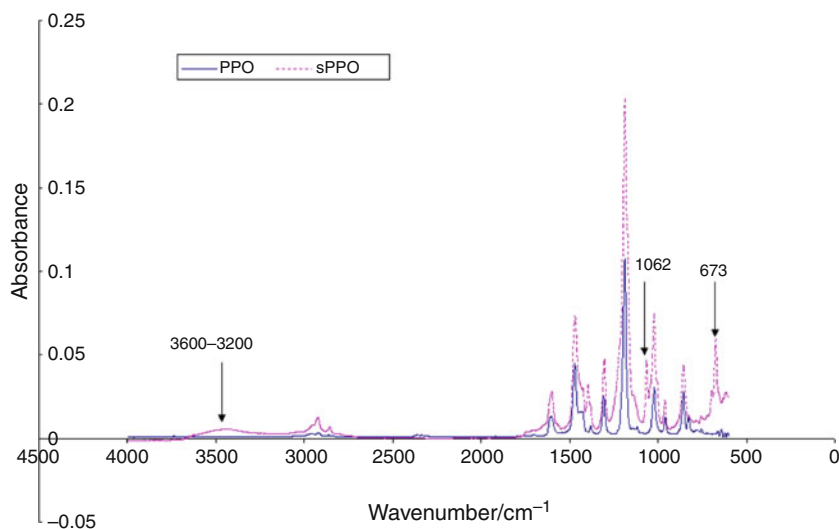
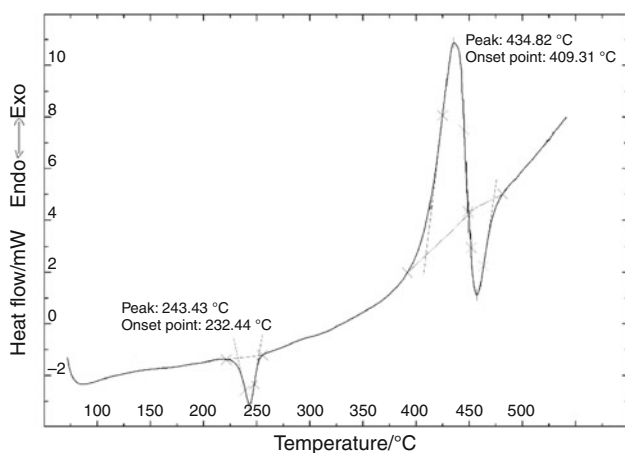


Table 2 The glass transition temperatures T_g and melting point T_m for sulfonated polymers and unsulfonated PPO

Sample	S ₁	S ₂	S ₃	Commercial PPO
$T_g/^\circ\text{C}$	188	174	207	–
$T_m/^\circ\text{C}$	261	257	254	243.5

**Fig. 4** DSC curve for unsulfonated PPO

entangled in bulk than in solution so the reaction sites of polymer are better exposed when polymer is in solution.

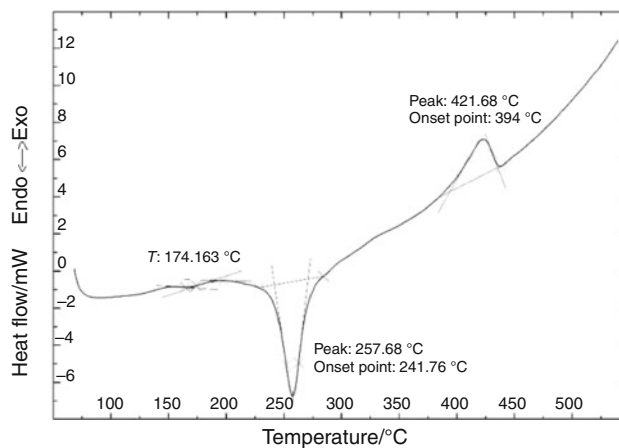
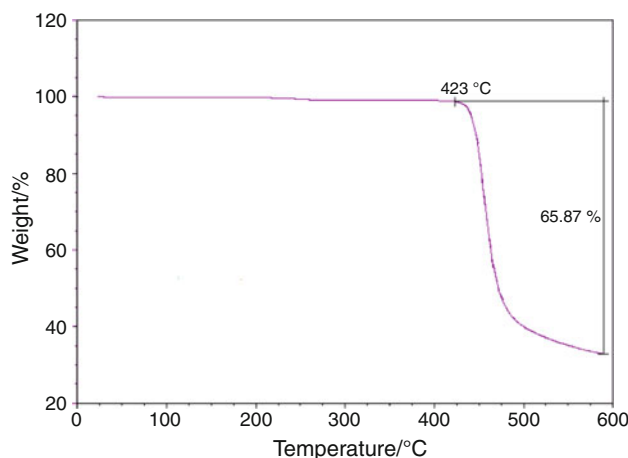
Thermal behavior of unsulfonated and sulfonated polymers

The thermal transitions and characteristic temperatures: glass transition (T_g), crystallization (T_c), or melting temperature (T_m) are obviously on the DSC spectra. The glass transition temperatures for sulfonated polymers (Table 2) show a random variation but all sPPO samples have a high T_g above 170 °C. The melting temperatures of sulfonated samples are higher values than the unsulfonated one.

From DSC spectra of the unsulfonated PPO (Fig. 4), we notice two thermal effects: first is an endothermic effect [7] characteristic for melting, with the melting point at 243.5 °C and the second is an exothermic effect [7] due to polymer chain degradation, beginning at 409 °C. The specific glass transition temperature (T_g) could not be highlighted here. The melting temperature (T_m) is increased with sulfonation degree and the onset temperature of degradation peak slowly decreases.

Unlike the DSC curve of unsulfonated sample, on the DSC curves for sPPO samples on notice that the endothermic effect of melting transition increase and the exothermic effect of chain degradation decrease with increasing the sulfonation degree (Fig. 5).

The TG analysis determines changes of the sample mass in relation to change in temperature.

**Fig. 5** DSC curve for sulfonated PPO, S₂**Fig. 6** TG curve for unsulfonated PPO

The unsulfonated PPO has just a single step of mass loss until the 500 °C. The decomposition begins at 423 °C and to 500 °C the mass loss was around 60 %. Above this temperature the rate of mass losses decreases (Fig. 6).

The TG curves for the sPPO samples (Fig. 7) show three stages of mass losses, corresponding to following processes:

- the first stage, when the polymer loses the water and solvents absorbed in its matrix;
- the second stage (230–340 °C) [4] represents the splitting of the sulfonic groups;
- the third stage is the polymer chain degradation.

We notice that the ratio between the percents of mass loss in the second step and the sulfonation degrees are the same (2/3) for PPO with $SD_t = 50$ and 75 %.

For a better comparison of the unsulfonated and sulfonated samples, the temperature values corresponding of 5, 10, and 25 % mass losses was summarised in Table 3, and

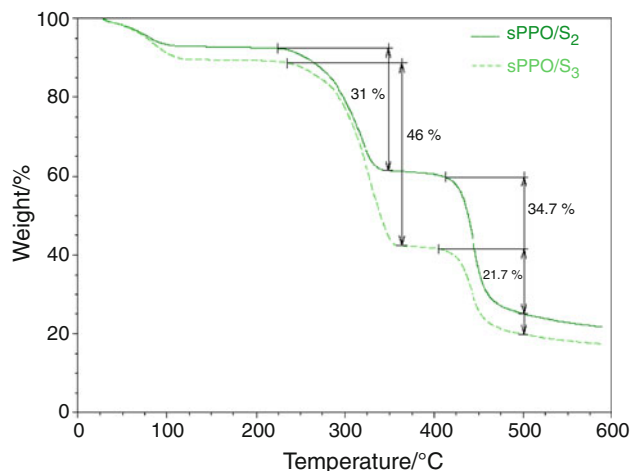


Fig. 7 TG curves for thermal decomposition of sPPO with different sulfonation degrees, S_2 , S_3

Table 3 Temperatures corresponding to 5, 10, and 25 % mass loss and the residue at 500 °C for the unsulfonated and sPPO samples

Sample parameter	PPO	S_1	S_2	S_3
$T_{5\%}/^{\circ}\text{C}$	440	64	77	80
$T_{10\%}/^{\circ}\text{C}$	448	75	130	112.5
$T_{25\%}/^{\circ}\text{C}$	454	177	204	210
Residue at 500 °C/%	38	32	37	38

also the residue remained after the samples reach the temperature of 500 °C.

The mass loss begins at low temperature (under 100 °C) for sulfonated polymers but the value is not relevant. At 25 % mass loss, the sulfonated polymers already loss a part of the sulfonic moieties. Residue at 500 °C has almost the same values for all the samples.

Conclusions

Sulfonation of polyphenylene oxide was proved by FTIR analysis. The IEC of sulfonated polymers has high values

between 1.4 and 2.9 that make the polymers a good proton conductor.

The polyphenylene oxide kept good thermal characteristics after sulfonation: high values for T_g , above 170 °C and also for losing the sulfonic acid groups (between 200 and 300 °C—second stage). In terms of thermal behavior sulfonated polyphenylene oxide is a suitable material for medium temperature PEM fuel cells.

The future purposes of our work are to choose the optimum sulfonation degree and to find a method to retain water into membrane at high temperature. Including the inorganic hygroscopic particles into the polymer lattice could be an approach to improve water retention into membrane, at temperature above 100 °C.

The benefits of sulfonated polyphenylene oxide membranes are the low cost of pristine polymer (polyphenylene oxide), the good control of sulfonation degree and the facile processability.

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