Solvent effect on post-irradiation grafting of styrene onto poly(ethylene-alt-tetrafluoroethylene) (ETFE) films

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ABSTRACT

Radiation-induced grafting of styrene onto ETFE films in different solvent was investigated after simultaneous irradiation (in post-irradiation condition) using a ^{60}Co source. Grafting of styrene followed by sulfonation onto poly(ethylene-alt-tetrafluoroethylene) (ETFE) are currently studied for synthesis of ion exchange membranes. The ETFE films were immersed in styrene/toluene, styrene/methanol and styrene/isopropyl alcohol and irradiated at 20 and 100 kGy doses at room temperature. The post-irradiation time was established at 14 day and the grafting degree was evaluated. The grafted films were sulfonated using chlorosulfonic acid and 1,2-dichloroethane 20:80 (v/v) at room temperature for 5 h. The degree of grafting (DOG) was determined gravimetrically and physical or chemical changes were evaluated by differential scanning calorimeter analysis (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The ion exchange capacity (IEC) values showed the best performance of sulfonation for ETFE membranes grafted in toluene solvent. Surface images of the grafted films by SEM technique have presented a strong effect of the solvents on the films morphology.

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1. Introduction

One of the most important issues to level up the fuel cell technology is the reduction of the costs of the base materials. The proton exchange membranes are still an expensive component in the fuel cell system. Acting as a separator to prevent mixing of the reactant gases, as an electrolyte, performs protons transporting from the anode to the cathode. Nafion® by Dupont is the most frequently used PEM material owing to its chemical stability and commercial availability. However, in face of costs, efforts have been focused on the development of lower cost membrane materials. For high performance of the PEMFCs the membrane needs certain requirements such as: high proton conductivity, low water permeability, adequate mechanical strength, thermal stability, impermeability to gases, non-electronically conducting and moderate price (Nasef and Hegazy, 2004; Souzy and Ameduri, 2005).

In terms of polymer modification, ionizing radiation-induced polymerization has been applied to the manufacturing of polymeric nanocomposites and grafted polymers. Radiation grafting, in particular, is a versatile method for polymer modification, as in

the case of fluoropolymers, it can be useful to optimize their performance.

In general, two main reactions are involved in the grafting process: radical initiation of the polymeric backbone and growing of polymer chain from the polymeric backbone in both grafting techniques of simultaneous grafting or pre-irradiation grafting (Nasef and Hegazy, 2004; Souzy and Ameduri, 2005; Geraldes et al., 2007).

The method of radiation grafting offers a unique opportunity of polymer modification which already has a final physical shape (e.g. films, tubes). This method was earlier recognized as a convenient way for manufacturing different types of membranes for various applications. The most significant applications are for separation processes, electrochemical devices including fuel cells, batteries and sensors in addition to biological and biomedical uses (Nasef and Hegazy, 2004; Souzy and Ameduri, 2005). Example is the styrene graft onto a perfluorinated, partially fluorinated or non-fluorinated backbone via radiation and subsequently sulfonation, through which, proton conductivity is provided by the sulfonic groups performing good mechanical properties (Geraldes et al., 2007; Gubler et al., 2005; Gubler et al., 2006; Nasef et al., 2000a,b; Cardona et al., 2002; Walsby et al., 2000; Gupta and Scherer, 1994).

In this sense, grafting conditions play an important role when determining the degree of grafting and the structure built up inside the polymer. Usually, radiation grafting is performed in

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systems where monomers are diluted with a suitable solvent. Dilution of the monomer increases the accessibility to the grafting sites and the graft level. On the other hand, solvents are used during grafting to bring about swelling polymer, favoring the bulk reactions. The solvents usually applied include toluene, methanol, and isopropyl alcohol or mixed with solvents or water (Geraldes et al., 2007; Gubler et al., 2005; Gubler et al., 2006).

The use of a poor solvent is most likely to lead to surface grafting due to the reduction in monomer diffusibility, thus low degrees of grafting are obtained. However, the use of good solvent results in homogeneous grafting in the bulk. Increasing the swelling, enhances the diffusion of monomer into the internal layers of the polymer substrate, and thus the interactions between the internal active sites and the monomer molecules increase, leading to higher degrees of grafting. Some works have reported the effect of solvents in the grafting styrene onto fluorinated polymer (Geraldes et al., 2007; Gubler et al., 2005; Gubler et al., 2006; Nasef et al., 2000a,b; Cardona et al., 2002; Walsby et al., 2000; Gupta and Scherer, 1994). Cardona et al. and Nasef observed an increase of styrene graft for PFA in benzene or dichloromethane when compared to methanol (Walsby et al., 2000; Gupta and Scherer, 1994).

In our previous study polystyrene grafted and sulfonated onto PVDF and PTFE membranes were prepared by simultaneous radiation-induced grafting at room temperature. The membranes were characterized by evaluation of their thermal stability and surface structural properties. The grafting yield and surface morphology were found to be dependent mainly on the radiation dose and solvent (Geraldes et al., 2007).

The viscosity of the substrates controls the diffusion of the monomer to the grafting sites. The solvent, on its turn, was useful to induce swelling of the grafted layers, enhancing the monomer accessibility to grafting sites (Cardona et al., 2002).

The present work reports the study on radiation grafted and sulfonated membranes based on ETFE film by a simultaneous radiation. After the radiation process the sealed samples were kept at room temperature, for 14 day in order to evaluate the grafting yielding in this period of the post-irradiation simultaneous process. The graft and ungraft samples were characterized by TG, DSC, SEM and gravimetric analysis was employed for degree of grafting (DOG) determination. The ion exchange capacity (IEC) was also determined and the effects of solvents on grafting yield and surface morphology were accessed by diluting styrene in toluene, methanol or isopropyl alcohol during simultaneous irradiation and post-irradiation.

2. Experimental

2.1. Membrane preparation

ETFE films with 125 μm thickness were purchased from Goodfellow Ltda. The graft solution used was styrene monomer mixed with toluene, methanol or isopropyl alcohol in a proportion of 1:1 (v/v), without purification. Samples with 18 cm^2 were used to prepare material for chemical characterization. The films and graft solution were put into a glass tube and nitrogen was bubbled to guarantee inert atmosphere. The tube was sealed and submitted to gamma radiation at 20 and 100 kGy doses at 5 kGy h^{-1}. After simultaneous irradiation process the samples were kept in the tube at room temperature for periods of 14 day in inert atmosphere to avoid undesirable reactions of free radicals with oxygen.

Grafting of styrene was performed in three different solvents: toluene, methanol and isopropyl alcohol. The influence of solvent type was observed on the graft level, after grafting time of 14 day

and using radiation dose of 20 and 100 kGy both at room temperature.

In the sequence, thermal treatment of the irradiated samples was made in vacuum oven for 4 h at 70 °C.

Extraction procedure of the samples was carried out after thermal treatment in Soxhlet system by using hot toluene as solvent. The extraction to remove the remaining homopolymer was effective in 8 h. The films were dried in vacuum oven to eliminate residual solvents, up to constant mass, at the temperature of 70 °C.

The sulfonation reaction was carried out with the grafted polymer immerse in a solution of chlorosulfonic acid and 1,2-dichloroethane for 5 h at room temperature. The sulfonated membranes were washed with water up to pH 7 and then were immersed in 3 mol L^{-1} NaCl for 15 h, at room temperature. The H$^+$ ions released in this solution was titrated with 0,05 mol L^{-1} NaOH. The NaOH volume consumed in the titration was used to calculate the IEC per mass unity (mmol g^{-1}) of the grafted membrane.

2.2. Characterization

The degree of grafting (DOG) was calculated as the following Eq. (1):

$$\text{DOG (\%)} = [(W_f - W_i)/W_i] \times 100 \tag{1}$$

where W_i and W_f are the masses of the ETFE samples before and after grafting, respectively.

Thermogravimetric measurement (TG) was recorded with a Mettler–Toledo TGA/SDTA 851 thermobalance in nitrogen atmosphere, from 25 up to 700 °C at a heating rate of 10 °C min^{-1}.

Differential scanning calorimeter (DSC) was carried out in an 822 Mettler–Toledo under nitrogen atmosphere at a heating rate of 10 °C min^{-1}, in the temperature range of 30 to 350 °C.

The ion exchange (IEC) capacity was determined after acid–base titration according to the Eq. (2):

$$\text{IEC} = (C_{NaOH} \times V_{NaOH})/W_f \tag{2}$$

where C_{NaOH} is the NaOH concentration and V_{NaOH} is the volume consumed in the titration.

The SEM images were obtained in a Phillips XL 30 Microscope in magnitude of 5,000× using samples covered with gold in a Sputter Coater BAL-TEC SCD 050.

3. Results and discussion

Graft levels in function of dose were plotted for different solvents in illustration of Fig. 1.

Grafting in the toluene solvent yielded the highest graft levels, mainly at 100 kGy dose. Considering that toluene allows higher concentration of styrene in the inner solid phase of the film, an increase of the dose causes an increase of the radicals available for grafting and in consequence at 20 kGy the graft level is lower.

The graft levels at methanol or isopropyl alcohol were lower than values determined for toluene. In fact, the chain transfer for styrene in alcohol systems is stronger than in the case of toluene system, which results in faster chain termination. The use of a poor solvent (methanol or isopropyl alcohol) is most likely to lead to surface grafting due to reduction in monomer diffusibility and thus, low degrees of grafting were obtained. Fortunately, the use of good solvent (toluene) results in homogeneous grafting in the bulk. Increasing the swelling, the diffusion of monomer enhances into the internal layers of the polymer substrate (see also SEM images), and thus the interactions between the internal active
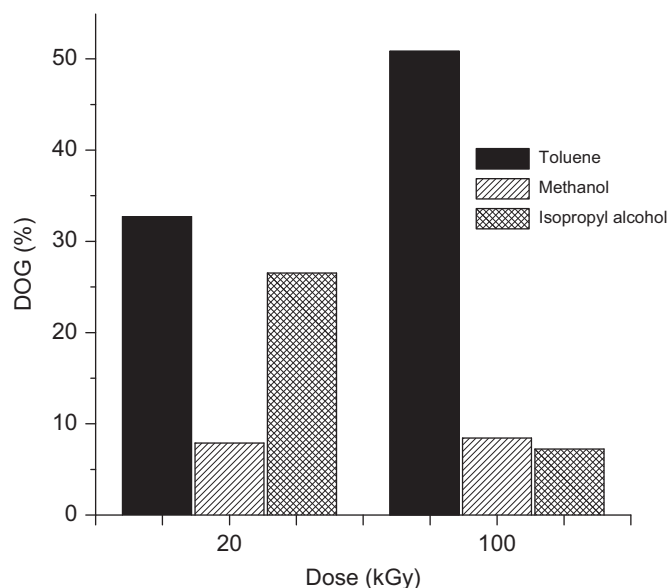
Fig. 1. Degree of grafting (DOG) in ETFE films at toluene, methanol and isopropyl alcohol.

Fig. 2. TG curves, in N_2 atmosphere, at a heating rate of $10\,°C\,min^{-1}$ for original and grafted ETFE films at 20 and 100 kGy doses, in toluene, methanol and isopropyl alcohol.

Table 1
DSC data of original and grafted ETFE films.

Film	Dose (kGy)	T_m (°C)
Pristine	–	264
Toluene	20	261
	100	261
Methanol	20	261
	100	263
Isopropyl alcohol	20	261
	100	263

T_m (°C) = Melting temperature.

sites and the monomer molecules increase, leading to higher degrees of grafting.

Another observation concerns to the viscosity. Viscosity is a parameter evolved during polymerization in solution, which influences dynamically the growth rate. In solution or bulk polymerization, the viscosity changes with the conversion or with the polymer growth, respectively. The viscosity of the system styrene/toluene that remains unchanged throughout the period of grafting while arrangements styrene/methanol and styrene/isopropyl alcohol show a large increase in viscosity during the reaction. Each polymer chain influences its neighbors and therefore changes the surrounding viscosity for the remaining initiators and the growing chains. The viscosity increases by the homopolymerization of styrene monomer, insoluble in methanol and isopropyl alcohol. In a system toluene/styrene, due to low conversion in the bulk solution, the viscosity is assumed to be constant during the grafting reaction at the value determined by the composition of the grafting solution. The radiation promotes the production of polymer radicals in a solvent cage, which can recombine or separate by diffusion. The polymer radicals react then with the monomer to form more polymer chains (Farquet et al., 2007).

This increasing in viscosity observed can explain the low yield of grafting for most reactions in these alcohols. This fact is in agreement with the findings by Nasef (2001, 1999, 2000a,b).

As described in previous article (Geraldes et al., 2010), the thermal stability of the ETFE films were determined by TG, Fig. 2. The original ETFE (Fig. 2a) has only one event of mass loss that was ascribed to the decomposition of polymer main chain, at 420 °C. For the grafted ETFE there are two decomposition steps: the first one is attributed to grafted styrene decomposition and the second to the polymer chain decomposition (Fig. 2b,c,d,f,g).

The initial degradation temperature (T_{onset}) at higher temperatures in the solvents methanol (Fig. 2b and c) and isopropyl alcohol (Fig. 2d and e) suggests that the polymer matrix is protected by the grafts.

There are three events of thermal decomposition in the TG curve of the grafted film in toluene at 20 kGy (Fig. 2f): one at around 100 °C of mass loss suggests the presence of surface structures of polystyrene of very low molecular weight grafted onto the matrix. The second event of decomposition also starts at
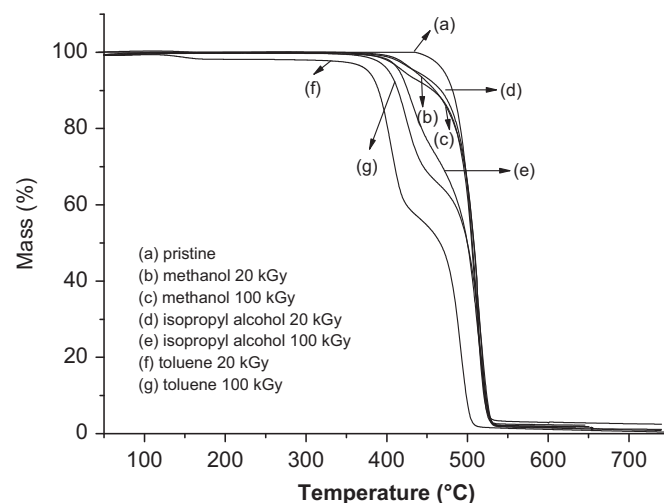
a lower temperature than the samples obtained at other doses, suggesting also that the grafts are superficial. The next stage of decomposition, attributed to decomposition of the polymer matrix occurs at temperature above the decomposition of pristine film. This observation suggests that in these conditions of polystyrene radiation and graft have increased the porosity of the matrix providing faster decomposition. The TG curves of ETFE grafted in methanol (Fig. 2b and c) can be explained by the formation of grafts penetrated more within the matrix.

DSC data of original and grafted ETFE films are presented at Table 1. As it can be observed, the original ETFE film presents a transition at 264 °C, which can be assigned to the melting temperature (T_m).

It was observed in all samples, a small variation in the melting temperature (T_m) (Table 1). The literature reports that the formation of polystyrene grafted onto the polymer matrix causes no variation in T_m (Li et al., 2005; Gubler et al., 2004) considering that the grafting reactions occur in the amorphous regions. Furthermore, the polystyrene grafts are not spread homogeneously.

The surface morphology of the grafted polystyrene in ETFE films was analyzed by SEM. In Fig. 3 images of films grafted and sulfonated in toluene, methanol and isopropyl alcohol at 20 and 100 kGy are observed. The surface of the ETFE films was differently covered by polystyrene layers showing that the morphology of the grafts is dependent on the solvent used.

In toluene, the film surface was rugged while spherical polystyrene clusters were observed in methanol or isopropyl alcohol graft conditions.

The SEM image of the film grafted in methanol at 100 kGy also showed micro fibrils, at the right of the image. Moreover, cavities
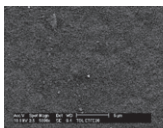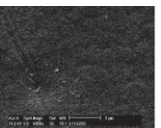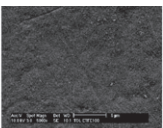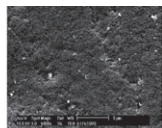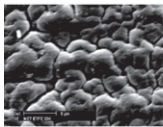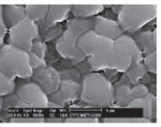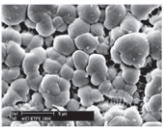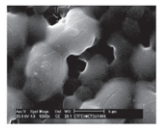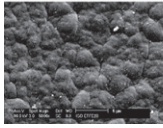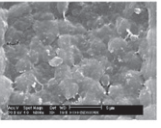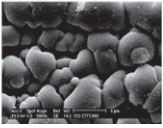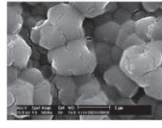
Fig. 3. SEM images of a surface in ETFE grafted in toluene, methanol and isopropyl alcohol. $5{,}000\times$ magnification.

Fig. 4. SEM images showing the holes and cracks of a surface in ETFE grafted in isopropyl alcohol. $5{,}000\times$ magnification.

were observed for both solvents (methanol and isopropyl alcohol). The films grafted in toluene, and sulphonated in the sequence have as a result a roughed surface. For instance, films graf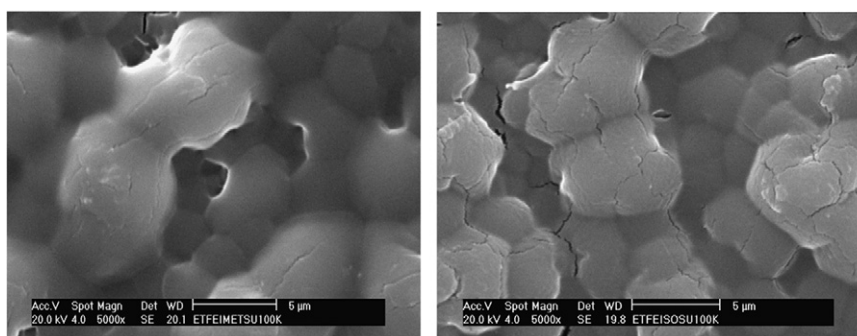ted in methanol or isopropyl alcohol and sulphonated presented holes and surface cracks (as seen in Fig. 4) indicating that the chlorosulphonic acid used to sulfonated the grafted may have weakened the layers of polystyrene.

Considering only the effect of irradiation dose, the morphology of samples was not altered by radiation dose. Therefore, the radiation dose has no influence in the morphology of the samples while the type of solvent used causes different morphological profiles on those surfaces. This fact is in agreement with reports in the literature (Geraldes et al., 2007; Walsby et al., 2000) where films grafted in methanol and isopropyl alcohol have large amount of homopolymer formed reporting images of clusters of grafts on the surface of polystyrene films.

The ion exchange capacity was calculated in the sulphonated films as to apply the grafted membranes in fuel cells. The ion exchange capacity (IEC) of grafted membranes is the measurement of the molar content of sulfonic acid groups per mass of the dry membrane; it is determined by titration of the proton content of the membrane, after exchanging it with a salt solution (NaCl solution). The IEC value is an important parameter for the proton carriers and mobility across the membrane thickness, which can be controlled by performing to sulfonation procedures and graft levels. Thus, a low graft level (films which are only surface grafted) induces a low IEC and consequently the conductivity value is very low, or even unmeasurable. In the results, the films grafted in toluene (Table 2) showed the best performance of sulfonation.

The sulfonated membranes (Fig. 5c,d) prepared in toluene and isopropyl alcohol at 20 kGy exhibit four different steps of thermal degradation: (1) around $100\,^{\circ}$C it is related to the desorption of water bonded to the sulfonic groups; (2) the second occurs between 240 and $350\,^{\circ}$C and is related to the sulfonic acid groups decomposition; (3) the step between 370 and $450\,^{\circ}$C also has to do with the styrene grafted degradation and (4) the last step on thermal degradation which starts at $480\,^{\circ}$C was assigned to the polymer main chain degradation. The initial degradation temperature for the original polymer is $420\,^{\circ}$C and for the polymer matrix in the sulfonated membrane prepared in toluene reaches $480\,^{\circ}$C. This increase indicates that the main chain of sulfonated ETFE has slightly higher thermal stability than the original ETFE and then it is speculated that the main chain structure of sulfonated, after-SO$_3$H groups were split off, is not identical to the original polymer. For instance for all samples, the amount of residues is different and it is speculated that sulfonation degree depends on the solvent. The higher amount of residue, the higher was the sulfonation degree achieved.

The films prepared in methanol exhibit small DOG value and the membranes were not able to be sulfonated satisfactorily. Probably these films are only surface grafted and induce a low IEC and consequently the conductivity value is very low.

Table 2
Ion exchange capacity of ETFE membranes.

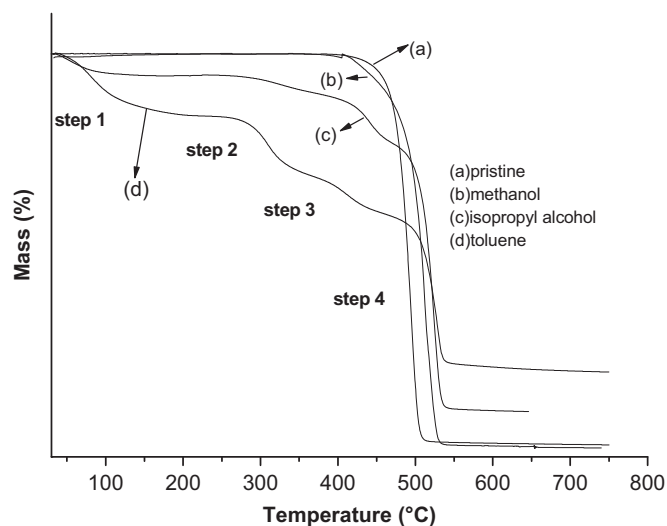| Solvent	Dose (kGy)	DOG (%)	IEC$_t$ (meq g^{-1})
Toluene	20	30.7 ± 2.1	1.8
	100	50.8 ± 3.0	2.6
Methanol	20	7.9 ± 0.4	0.64
	100	8.4 ± 0.1	0.68
Isopropyl alcohol	20	26.5 ± 1.7	1.7
	100	7.2 ± 0.4	0.59

Fig. 5. TG curves in N$_2$ atmosphere, at a heating rate of 10 °C min^{-1} for original sulfonated membranes of ETFE at 20 kGy doses, in toluene, methanol and isopropyl alcohol.

4. Conclusion

In this work, films of ETFE were modified in order to prepare membranes for low temperature fuel cells. The work was carried out in three different solvents, toluene, methanol and isopropyl alcohol. Polymer electrolyte membrane was prepared under controlled conditions by using the radiation-induced grafting of styrene onto ETFE in post-irradiation condition, followed by sulfonation of the simultaneous method. Dealing with the radiation grafting process, it is important to understand that every preparation step (irradiation, grafting and sulfonation) induces changes in the structure and properties of the grafted films and membranes.

The increase of the graft level in different solvents was apparently accompanied by morphological and structural changes, the dimensions of the polystyrene grafted increase with the change of solvent. Nonetheless, the dose of irradiation affects no significantly the morphology of polystyrene grafted, whereas the surface of films grafted in toluene has not been affected. Likewise, the T_m of the grafted films and membranes was significantly influenced by the change of solvent.

The influence of irradiation dose using different solvents showed that the toluene was a better choice to the grafting onto ETFE films. Therefore, the dose of radiation affects no significantly the grafting, in morphological viewpoint (SEM images). The yield of radio-induced grafting depends on the solvent (monomer plus diluent) affinity to the matrix and by the solvent affinity to the polystyrene branch.

When toluene is used, the films surface is homogeneous, but when methanol or isopropyl alcohols are used, their surfaces are heterogeneous and present cavities. Membranes synthesized in toluene exhibited superior DOG and IEC values.

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