2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-04-5

Radiation Induced Grafting of Tetrafluoroethylene on Nafion® Films for Ion Exchange Membrane Application

Adriana Napoleão Geraldes, Dionisio Furtunato da Silva, Helio Fernando Rodrigues Ferreto, Camila Pinheiro Souza, Duclerc Fernandes Parra, and Ademar Benévolo Lugão.

Instituto de Pesquisas Energéticas e Nucleares (IPEN), Av Professor Lineu Prestes, 2242, 05508-900, São Paulo, Brazil.
E-mail address of main author: drinager@ig.com.br

ABSTRACT

Grafting of TFE nanocomposites onto Nafion® was studied for synthesis of ion exchange membranes. Radiation-induced grafting of TFE gas onto Nafion® films was investigated after simultaneous irradiation using a ^{60}Co source. The thermal degradation of polytetrafluoroethylene (PTFE) waste has been used for production of TFE. Nafion films were irradiated at 15 kGy dose at room temperature and chemical changes were monitored after contact with TFE gas for grafting. The modified films were evaluated by differential scanning calorimetry analysis (DSC), thermogravimetric analysis (TG), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Characterization by XRD suggests crystallinity changes after TFE grafting. The ion exchange capacity (IEC) of membranes was determined by acid-base titration and the values for modified films were achieved similar to Nafion® pristine films. DSC measurements revealed a displacement in the endothermic peaks and it was probably associated with the TFE graft. The graft forces the Nafion® polymer chains to re-organize themselves and form a more cross-linked structure within the clusters.

1. INTRODUCTION

Fuel cells are clean and efficient electrochemical energy conversion reactors. The polymer electrolyte fuel cell (PEMFC) is particularly attractive for applications with variable load profile and intermittent operation (portable electronics, remote power sources, vehicle propulsion). The proton exchange membrane (PEM) is a central and often performance limiting component of all solid H_2/O_2 fuel cells.

Nafion, the most widely used PEM material, is a perfluorinated polymer that stands out for its high selective permeability to water and small cations, in particular protons [1]. The ionomers are generated by copolymerization of a perfluorinated vinyl ether comonomer with tetrafluoroethylene (TFE). However, Nafion have attracted enormous research interest for proton exchange membranes fuel cell and water electrolysers. Moreover, Nafion has high methanol permeation and is thermally and mechanically fragile in fuel cell environment. Considerable research effort was applied by the academia and industry to overcome this fragility, by trying to crosslink films and preparing Nafion mixture to form interpenetrating networks [2-6]. In our laboratory we have studied the radiation-induced graft of styrene onto fluoropolymers [7,8] and recently Nafion modification.

The relatively low mechanical strength of a hydrated PEM, and the fact that the membrane absorbs water, leading to residual stress in the membrane confined in the fuel cell hardware, is one of the major deficiencies. Therefore, reinforced membranes should be argument of study and development.

In addition, grafting of TFE nanocomposites onto Nafion was studied for synthesis of ion exchange membranes. Radiation-induced grafting of TFE gas onto Nafion films was investigated after simultaneous irradiation using a ^{60}Co source. The thermal degradation of polytetrafluoroethylene (PTFE) waste has been used for production of TFE gas. Nafion films were irradiated at 15 kGy dose at room temperature and chemical changes were monitored after contact with TFE gas for grafting. The modified films were evaluated by differential scanning calorimetry analysis (DSC), thermogravimetric analysis (TG), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The ion exchange capacity (IEC) of membranes was determined by acid-base titration.

2. EXPERIMENTAL

2.1 Membrane preparation

Nafion 117 film, PTFE waste has been used for production of TFE gas. Nafion 117 films purchased from DuPont were used in this study. Samples with 18 cm^2 were used to prepare material for chemical characterization. The films were put into a glass tube and TFE gas was added. The tube was sealed and submitted to gamma radiation at 15 kGy dose at 5 kGy h^{-1}. Gamma irradiation technique was performed in Gamma cell IPEN/CNEN-SP using a ^{60}Co source at 15 kGy dose.

2.2. Characterization

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

X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu Kα radiation source (l = 0.15406 nm). The diffractograms were recorded from2θ = 20° to 90° with a step size of 0.05° and a scan time of 2 s per step.

The ion exchange (IEC) capacity was determined after acid-base titration according to the equation (1):

$$IEC = (C_{NaOH} \times V_{NaOHi})/W_f \qquad (1)$$

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

3. RESULTS AND DISCUSSION

Characterization by XRD suggests crystallinity changes after TFE grafting and this result is shown in Fig. 1. The shift of the diffraction peak observed was attributed to the structural changes related to the TFE graft that contributes to the crystalline phase.

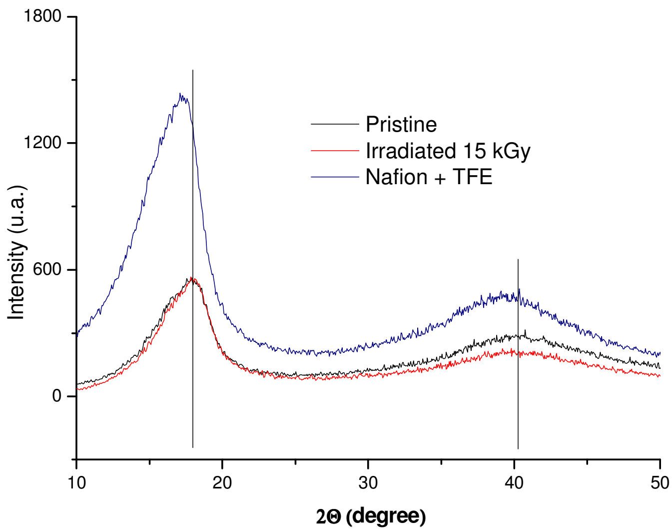


Figure 1: X-ray diffraction of Nafion pristine and modified films.

The thermal stability of the films was determined by TG, Fig 2. The results of irradiated and grafted films were similar to that of pristine film. There are three decomposition steps: the first one between 30 and 150 °C is attributed to residual water evaporation and beginning of the loss of sulfonic groups, the second between 240 - 350 °C loss of sulfonic groups and above 400 °C polymer chain decomposition [9].

The results of DSC analysis reveal information about the state of water in Nafion membrane as well as the sulfonic cluster transition. According to Tan *et al*. there are three different states of water in Nafion ionomer: 1) unbound freezable water, 2) bound freezable water, and 3) unfreezable water [10]. The unbound freezable water behaves much like bulk water and is not interacting with the polymer; the bound freezable water is the water found inside the pores or clusters of the polymer but not strongly associated with the polymer contrarily to unfreezable water, which would be strongly associated with the polymer and for which it is not possible to observe the crystallization and melting transition. DSC curves are shown in Fig. 3. The endothermic peaks (T_m) located between 100 and 150 °C in the films irradiated and grafted with TFE were shifted to higher temperatures. The values were 120 °C for the pristine film, 128 °C for the film irradiated at 15 kGy and 134 °C for the grafted film. DSC measurements revealed a displacement in endothermic peaks (14 °C) and it was probably associated with the TFE graft. The TFE graft forces the Nafion polymer chains to re-organize themselves and form a more cross-linked structure within the clusters which increase the cluster transition temperature.

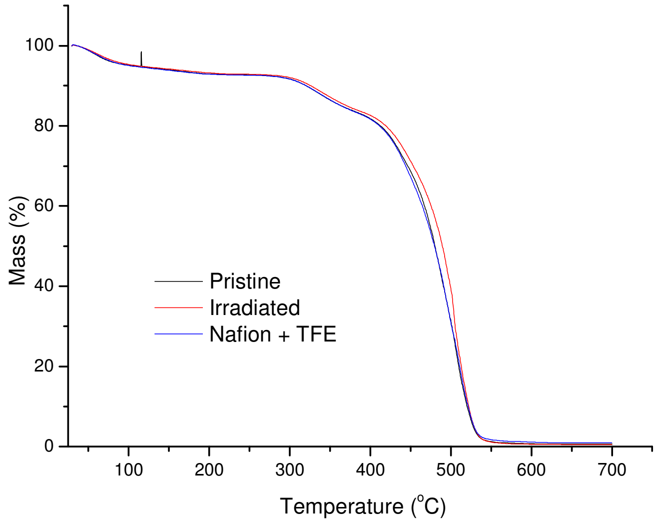


Figure 2: TG curves of Nafion pristine irradiated at 15 kGy and grafted with TFE.

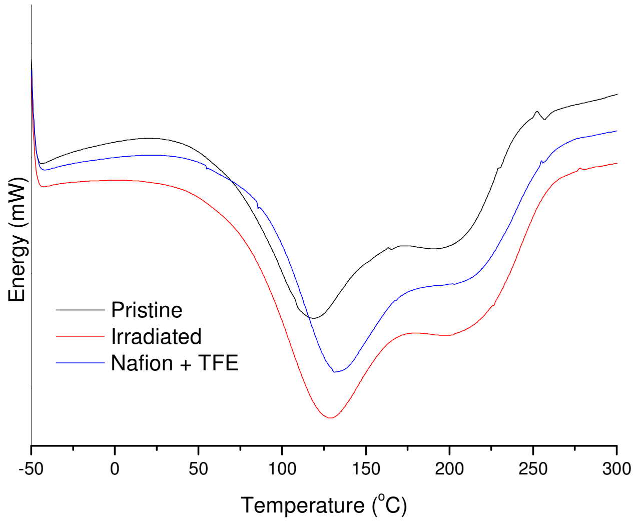
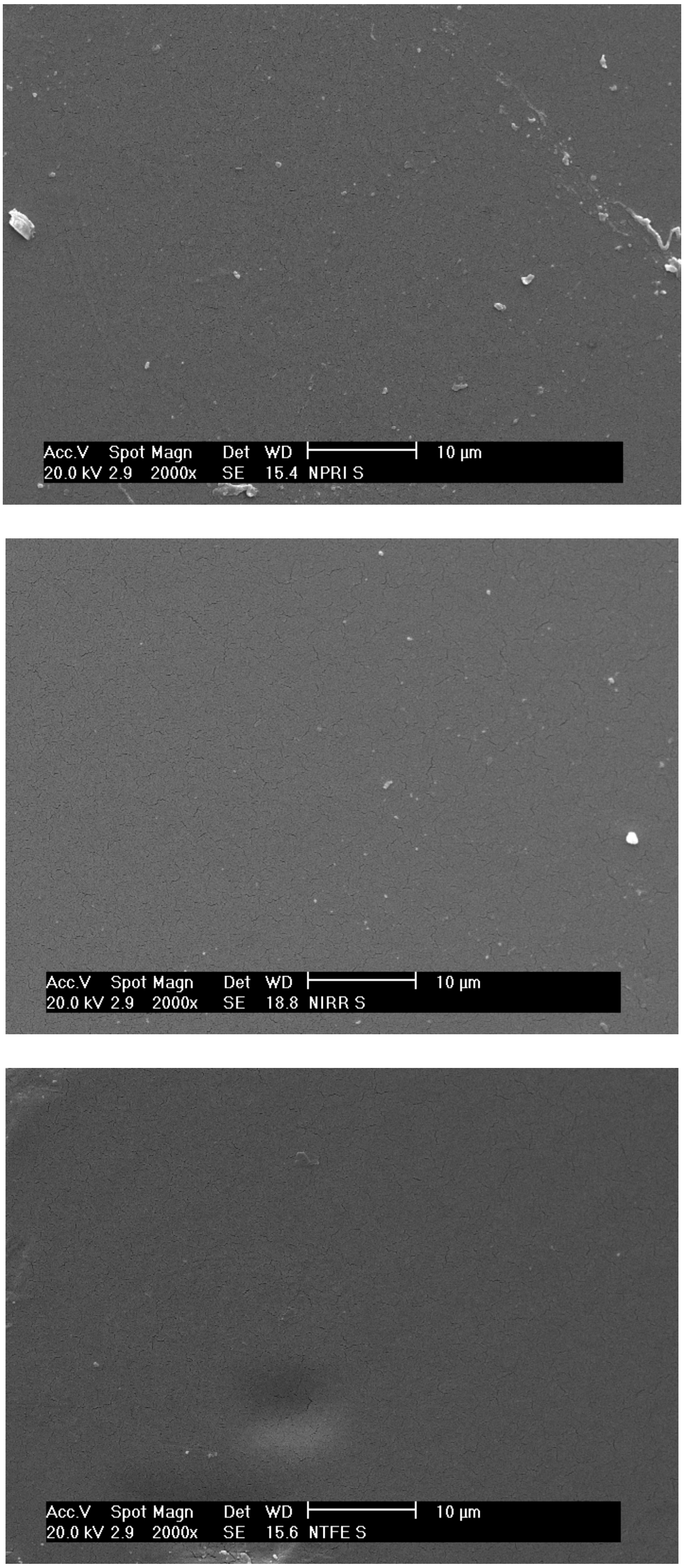


Figure 3: DSC curves of Nafion pristine, irradiated at 15 kGy and grafted with TFE.

Surface analysis by SEM technique of Nafion pristine, irradiated and grafted films have presented a homogeneous surface, Fig. 4.



Nafion pristine

Nafion irradiated

Nafion + TFE

Figure 4. SEM images of pristine, irradiated at 15 kGy and grafted.

The ion exchange capacity (IEC) of membranes was determined by acid-base titration according to Eq.1, and the values for modified films were achieved similar to Nafion pristine films according to Table 1.

Table 1: Ion exchange capacity (IEC) of films.

Sample	IEC (meq g^{-1})
Pristine	0.78
Nafion irradiated at 15 kGy	0.76
Nafion + TFE	0.78

4. CONCLUSIONS

Grafting of TFE onto Nafion films was investigated after irradiation at 15 kGy using a ^{60}Co source. We have examined the grafting by XDR, TG, DSC and SEM techniques. The XDR and DSC techniques showed evidences regarding the TFE grafting.

ACKNOWLEDGMENTS

This work was supported by CNPq - Conselho Nacional de Pesquisa e Desenvolvimento; IPEN - Instituto de Pesquisas Energéticas e Nucleares.

REFERENCES

1. K. S. Rohr, Q. Chen, "Parallel cylindrical water nanochannels in nafion fuel-cell membranes". *Nature Materials*, **7**, pp. 75-83 (2008).
2. M. H. Woo, O. Kwon, S. H Choi, M. Z. Hong, H. W. Ha, K. Kim, "Zirconium phosphate sulfonated poly (fluorinated arylene ether) composite membranes for PEMFCs at 100–140 °C", *Electrochimica Acta*, **51**, pp. 6051-6059 (2006).
3. E. Chalkova, M. V. Fedkin, D. J. Wesolowski, S. N Lovov, "Nafion/TiO_2 Proton Conductive Composite Membranes for PEMFCs Operating at Elevated Temperature and Reduced Relative Humidity", *Journal of Electrochemical Society*, **152**, pp. 1742-1747 (2005).
4. M. B. Satterfield, P. W. Majsztrik, H. Ota, J. B. Benziger, A. B. Bocarsly," Mechanical properties of Nafion and titania/Nafion composite membranes for polymer electrolyte membrane fuel cells", *Journal of Polymer Science B: Polymer Physics*, **44**, pp. 2327-2345 (2006).
5. E. I. Santiago, R. A. Isidoro, M. A. Dresch, B. R. Matos, M. Linardi, F. C. Fonseca, "Nafion–TiO_2 hybrid electrolytes for stable operation of PEM fuel cells at high temperature", *Electrochimica Acta*, **54**, pp. 4111–4117 (2009).
6. Y. Liu, Y. Baolian, S. Zhi-Gang, D. Xing, H. Zhang," Carbon Nanotubes Reinforced Nafion Composite Membrane for Fuel Cell Applications", *Electrochemical and Solid-State Letter*, **9**, pp. 356-359 (2006).

7. A. N. Geraldes, H. A. Zen, D. F. Parra, H. P. Ferreira, A. B. Lugão, "Effects of solvents on post-irradiation grafting of styrene onto fluoropolymer films", *e-Polymers*, **63**, pp. 1-12 (2007).
8. A. N. Geraldes, H. A. Zen, G. Ribeiro, H. P. Ferreira, C. P. Souza, D. F. Parra, E. I. Santiago, A. B. Lugão, "Post-irradiation time effects on the graft of poly (ethylene-alt-tetrafluoroethylene)(ETFE) films for ion exchange membrane application", *Rad. Phys. Chem.*, **79**, pp. 246–249 (2010).
9. U. Sen, A. Bozkurt, A. Ata, "Nafion/poly(1-vinyl-1,2,4-triazole) blends as proton conducting membranes for polymer electrolyte membrane fuel cells", *Journal of Power Sources*, **195**, pp. 7720-7726 (2010).
10. S. Tan, D. Belanger, "Characterization and transport properties of Nafion/polyaniline composite membranes", *Journal of Physical Chemistry B*, **109**, pp. 23480-23490 (2005).