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**

STUDY OF RADIATION-INDUCED MODIFICATION OF FEP IN NITROGEN AND AIR ATMOSPHERES

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ABSTRACT

Fluoropolymers are a class of polymer with specific characteristics like chemical inertia and stability under aggressive chemical environmental. These properties are a consequence of the chemical structure, C-F bonds. Poli (tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) is inserting in these class of polymer. FEP has good chemical and physical resistance, its working in temperature of 200°C and has a surface extremely smooth. This polymer is used as component in films, coatings, tapes, wires and cables in a variety of industries including telecommunications, semiconductor, chemical, food processing and packaging. In this study was used film with 100mm of thickness that were submitted to gamma radiation under nitrogen and air atmospheres in order to observe the effect of atmosphere in the polymer matrix. The irradiated doses were: 5, 10, 20, 40 and 80kGy at room temperature. The characterization was made by thermogravimetric analysis (TG), scanning electron microscope (SEM) and infrared spectroscopy using attenuate reflectance (ATR-IR). The TG analysis shown two degradation steps and for the samples irradiated under air the initial degradation began 10 degrees earlier than the samples irradiated under nitrogen. After the analysis, the results obtained were expected: the degradation reactions occurred in the samples irradiated under air atmosphere and the film has no changes in the structure when was irradiated under nitrogen atmosphere.

1. INTRODUCTION

Poli(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) contains 80-90% of tetrafluoroethylene and 10-20% of hexafluoropropylene units in its backbone chain [1]. These polymers are chemical inert, stable in different kinds of environment and have excellent chemical resistance, even at high temperature. These properties are a consequence of the chemical structure, the C-F bonds presented in the chain. Besides that, the fluor atoms have a bigger size when compared to the carbon atom which possibility them to protect the chain polymer [1]. Although the C-F bonds leads to good and important chemical properties, these bonds also contributed to scission reactions when FEP is submitted to ionizing radiation.

Because of these excellent properties of fluoropolymers, it is very hard to modify the surface of them. For modification the surface is necessary chemically treatment like etching or using high energy radiation, like gamma radiation [2, 3].

When the polymer is submitted to radiation process the crosslinking and scission reactions occur at the same time in the backbone, which will predominate depend on the molecular structure, polymer morphology and experimental irradiation conditions. For the fluoropolymers, like , PTFE – polytetrafluorothelyne and PFA – poly(tetrafluorethylene-*co*-perfluoro-(propyl vinyl ether)) is common to be predominant the degradation upon radiation [4].

Crosslinking is the intermolecular bond formation of polymer chains and the degree of crosslinking is proportional to the radiation dose because the molecular mass of the polymer steadily increases with radiation dose, forming a three-dimensional polymer network. Scission reaction is the opposite process of crosslinking in which the rupturing of bonds occurs, reducing the average molecular weight. In this case when the polymer is subjected to high-energy radiation in the presence of air or air, occurs the formation of hydroperoxides or diperoxides depending on the nature of the polymeric backbone and the irradiation conditions.

In this work was investigated the effect of different atmospheres during radiation process: the inert atmosphere (nitrogen gas) and the oxidizing atmosphere (air).

2. EXPERIMENTAL

2.1 Materials

Poly (tetraflororoetileno-*co*-hexafluoropropylene) (FEP) film with 100 mm of thickness was purchased by Goodfellow Ltda . FEP films were placed into nylon bags under nitrogen and air and subjected to gamma radiation, at doses of 5, 10, 20, 40, and 80kGy, in order to evaluate the dose effect of the polymer chain.

2.2 Characterization

The spectra of the pristine and irradiated FEP films were measured by a Thermo Nicolet Nexus 670 FTIR spectrophotometer at ambient conditions in transmittance mode. The spectra were detected by an attenuated total reflectance (ATR) accessory, in the range of 400 – 4000 cm^{-1}.

Thermal gravimetric analysis (TG) was performed on pristine and irradiated FEP films. TG runs were carried out with a sample weight of 5±1 mg using Mettler-Toledo TG/SDTA 851

at range of 25 to 750ºC. All the analyses were made at a constant heating rate of 10°C min^{-1}, in nitrogen atmosphere.

Scanning electron microscope images were obtained in a Phillips XL 30 microscope, amplified at 1,000X. The samples were covered with gold in a Sputter Coater BAL-TEC SCD 050.

3. RESULTS AND DISCUSSION

By infrared spectroscopy (Fig. 1 and Fig 2) was possible to verify no drastic structural changes in the polymer chain. The appearance of characteristics peaks at 1143 and 1200 cm^{-1} related to the difluorinated compounds (CF_2) involving the CF_2 out-of-phase stretch are presented in all spectra for all samples. The peaks at 500 and 550 cm^{-1} are attributed to the C-F stretch vibration [5, 6].

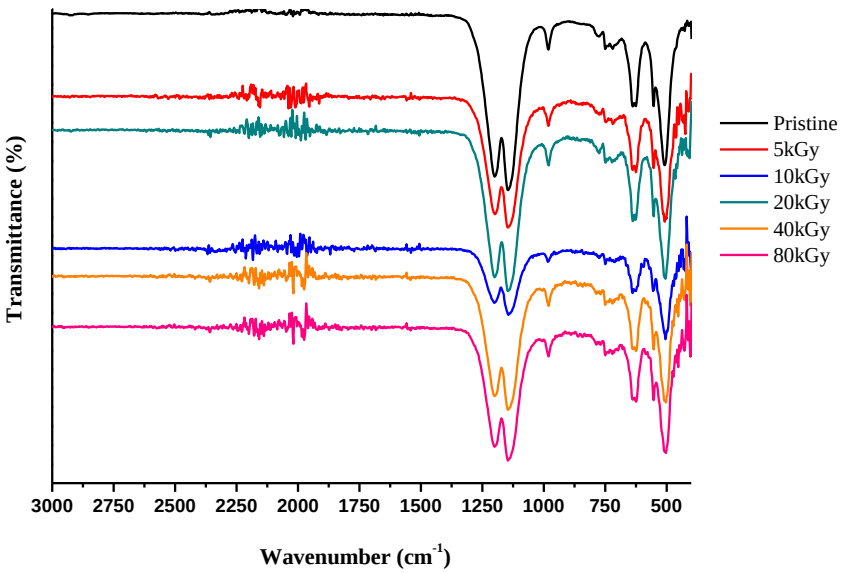


Figure 1. Infrared spectra for pure and irradiated samples under nitrogen atmosphere

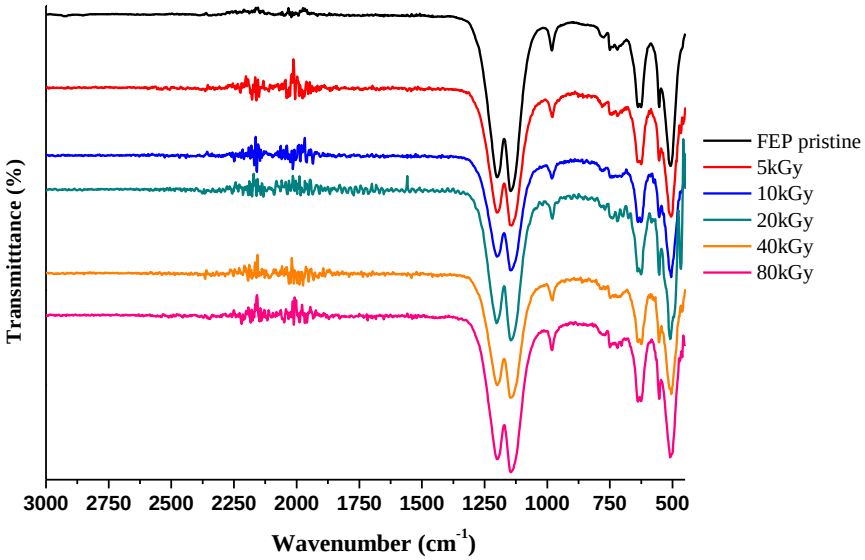
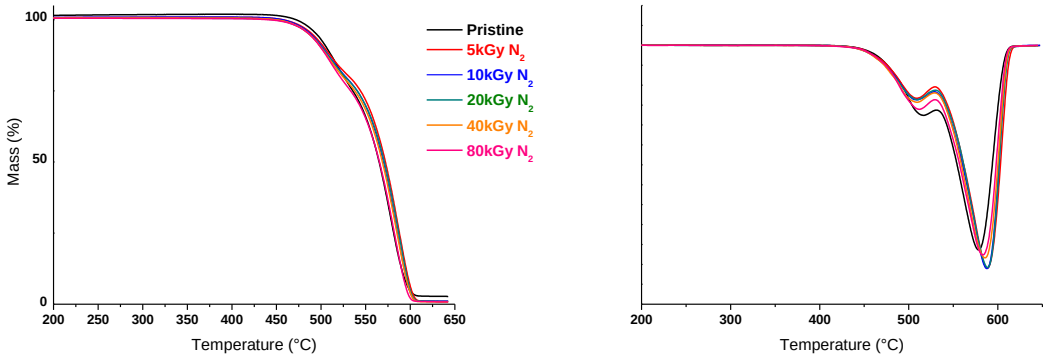


Figure 2. Infrared spectra for pure and irradiated samples under air atmosphere

The modification in thermal stability of irradiated FEP films compared to the original was studied by thermogravimetric analysis. The thermal degradation behavior of FEP film was studied in nitrogen atmospheres in comparison with air atmosphere.

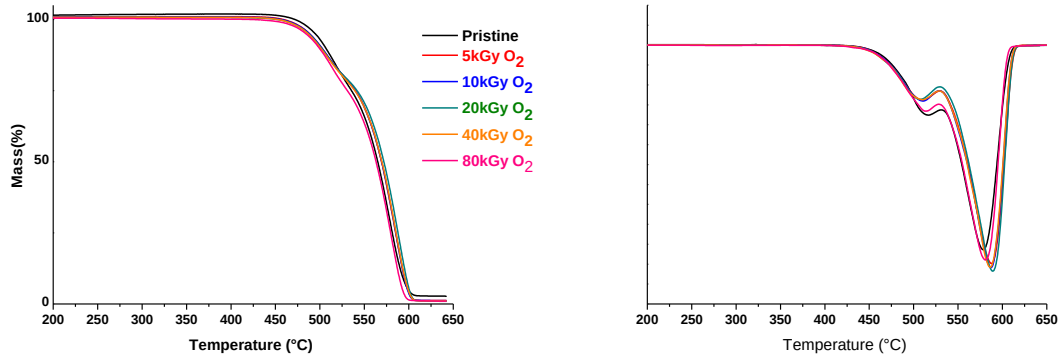
The original film was found to be thermally stable up to approximately 490°C for the hexafluoropropylene chain units and up to 560°C for the tetrafluoroethylene chain units [7]. According to the derivative analysis (Fig. 3b and 4b) the mass loss quantity of hexafluoropropylene is smaller (20%) than the quantity of tetrafluoroethylene (75%) which was expected.

All the irradiated samples even in nitrogen (Fig. 3) or air (Fig. 4) have the same curve profile of the pristine sample [8]. The initial degradation temperature for both chain units doesn't change according to the unmodified sample.



a) b)

Figure 3. a) TG and b) DTG curves for pure and irradiated samples under nitrogen atmosphere.



a) b)

Figure 4. a) TG and b) DTG curves for pure and irradiated samples under air atmosphere.

The SEM images are presented in Fig. 5 and 6. The images of pristine film are homogeneous and no cavities were verified. The samples irradiated at 5, 10 and 20kGy presented a heterogeneous surface with cavities and a roughs surface. The morphology of samples irradiated at high doses 40 and 80kGy was not altered by radiation dose.

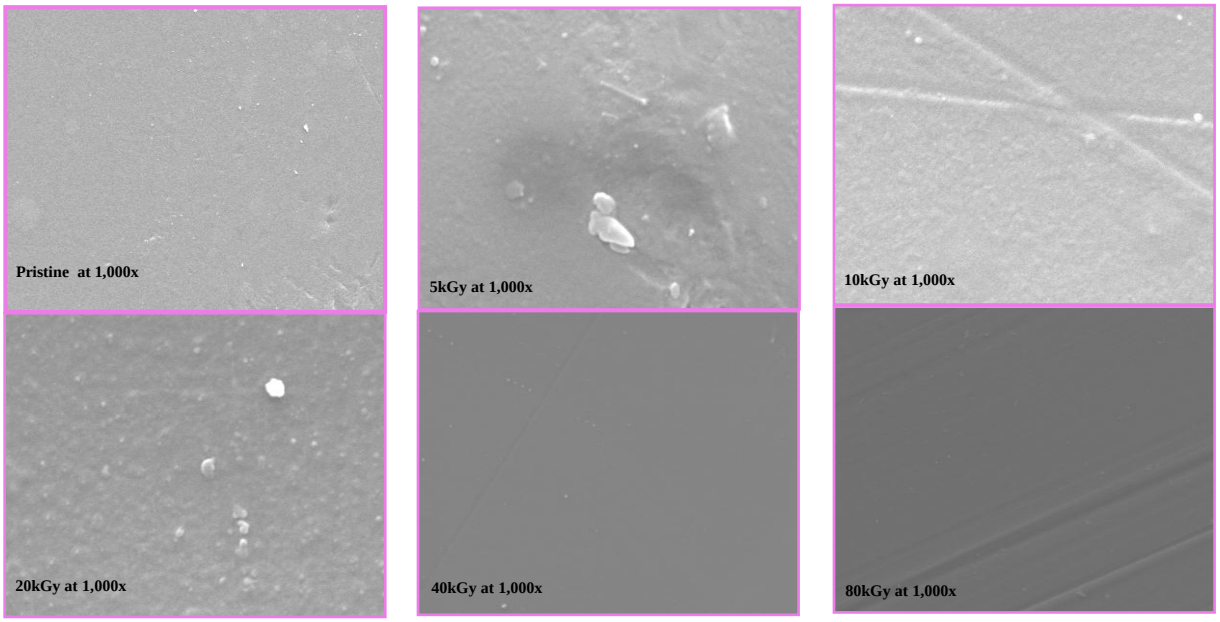


Figure 5. SEM images of pure and irradiated samples under nitrogen atmosphere

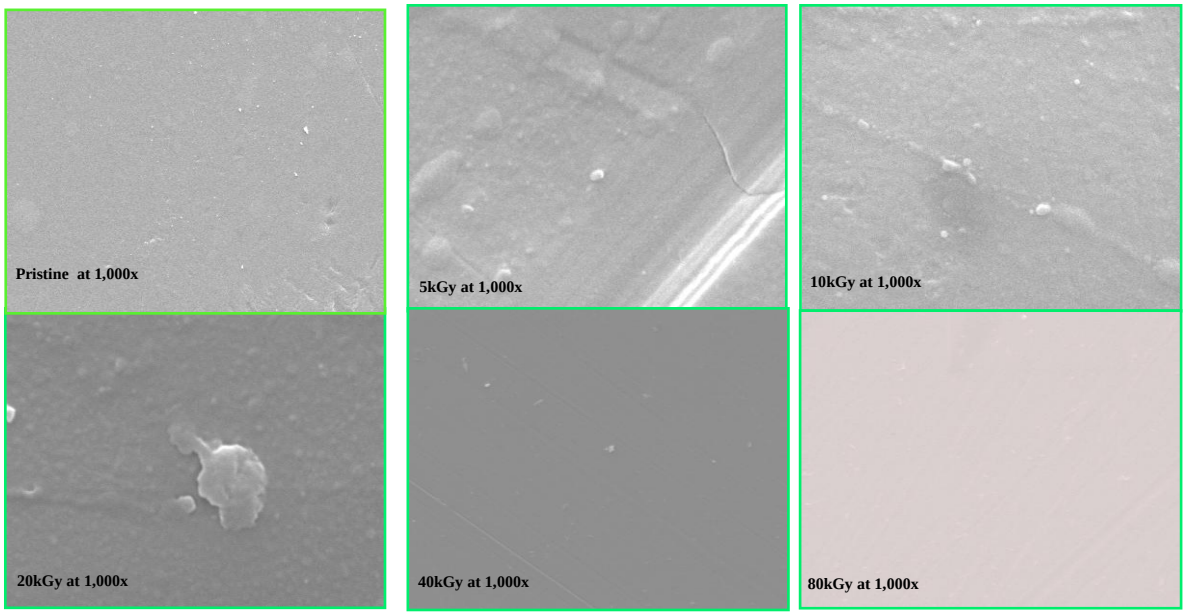


Figure 6. SEM images of pure and irradiated samples under air atmosphere

4. CONCLUSIONS

The main focus of this work was to understand the influence of atmosphere during the irradiation process. The characterization techniques showed that even when the polymer is submitted to gamma radiation under air atmosphere, the degradation effect was not evidenced. The thermal stability of the films is almost constant with the increase of irradiation dose.

ACKNOWLEDGMENTS

The authors thank to CNPq (Conselho Nacional de Pesquisa e Desenvolvimento) process number: 372540/2010-4, IPEN/CNEN-SP, EMBRARAD/CBE.

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