

## STUDY OF RADIATION-INDUCED MODIFICATION IN NITROGEN AND AIR ATMOSPHERES OF PFA

**Heloísa A. Zen, Camila P. de Souza and Ademar B. Lugão**

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)  
Av. Professor Lineu Prestes 2242  
05508-000 São Paulo, SP  
[helozen@ipen.br](mailto:helozen@ipen.br)

### ABSTRACT

Fluorinated polymer films such as polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluoro-(propyl vinyl ether)) (PFA), poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) and poly(vinylidene fluoride) (PVDF) have been extensively used as substrates to be submitted to radiation process. Those polymers are insoluble in the major common solvents so, the radiation process is a large used technique to promote modification in their structures to apply them in different areas and is well known for its merits and potential in modifying the chemical and the physical properties of polymeric materials without cause drastic changes in their inherent properties, depend on the dose irradiated. In this study was used PFA film with 100mm of thickness that having excellent thermal, chemical and mechanical properties. This film was submitted to gamma radiation under nitrogen and oxygen 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), infrared spectroscopy using attenuate reflectance (ATR-IR) and X-ray diffraction. The TG analysis shown only one degradation step and for the samples irradiated under oxygen the initial degradation began 30 degrees earlier than the samples irradiated under nitrogen. The results demonstrated which was expected, the degradation reactions were observed for the samples irradiated under oxygen atmosphere and in nitrogen the film has no changes in the structure.

### 1. INTRODUCTION

When polymers are irradiated both crosslinking and degradation reactions occur simultaneously, one of them being predominant. The structure of fluorinated carbon polymers changes in two different ways when submitted to radiation. Perfluorinated polymers, for example, polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluoro-(propyl vinyl ether)) (PFA), poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) and and perfluoroalkylvinyl ethers, have more tendency to degradation process. In the order hand, hydrogen containing fluorocarbon polymers, for example copolymers of vinylfluoride, poly(vinylidene fluoride) (PVDF), have more tendency to crosslinking and to form a network.

Perfluoroalkoxy resins (PFA) are a class polymer in which perfluoroalkyl side-chains are connected to the carbon-fluorine (tetrafluoroethylene) backbone of the polymer through a flexible oxygen linkage. The radiation stability of polytetrafluoroethylene (PTFE) in air is two orders lower than that of polyethylene [1] and the mechanism of PTFE radiolysis leading to destruction has not been established. This is a consequence of the competition between

radical formation and a reaction of the radical sites with O<sub>2</sub> (oxygen gas) which leads to oxidative degradation.

During the irradiation under oxygen atmosphere the oxygen products are useful indices of polymer degradation. The extent of that can affect mechanical, electrical and chemical properties. These effects depend on the irradiation conditions, such as: pressure, dose, temperature and polymer.

This work presents the results of PFA irradiated under oxygen (air) and nitrogen atmosphere in order to determine the degradation effect on the polymer chain.

## **2. EXPERIMENTAL**

### **2.1. Materials**

The commercial poly(tetrafluorethylene-*co*-perfluoro-(propyl vinyl ether)) (PFA) films with 100µm were supplied by Goodfellow Cambridge Limited. The films were submitted to gamma radiation at 5, 10, 20, 40 and 80 kGy at dose rate of 10 kGy h<sup>-1</sup> under oxygen and nitrogen atmospheres in order to evaluate the influence of these atmospheres in the polymer chain.

### **2.2. Characterization**

The infrared spectroscopy was performed on Nexus 670 Thermo Nicolet equipment using attenuated total reflectance (ATR) measurements with crystal to probe the surface of the pristine and modified films. The wavenumber range used in this study was 400 – 4000 cm<sup>-1</sup> to detect the functional groups of the films.

Thermogravimetric (TG) was recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance in dynamic atmosphere from 25 to 700°C at a heating rate of 10°C min<sup>-1</sup> under inert atmosphere.

The X-ray diffraction (XRD) analysis were conducted at ambient temperature using a Rigaku MiniflexII X-ray diffractometer ( $\lambda$  (CuK $\alpha$ ) = 1.54Å) in configuration theta/theta on slabs of materials. XRD spectra were recorded in the 0.5°– 80° 2 $\theta$  range with a step of 0.05° and step time of 1s.

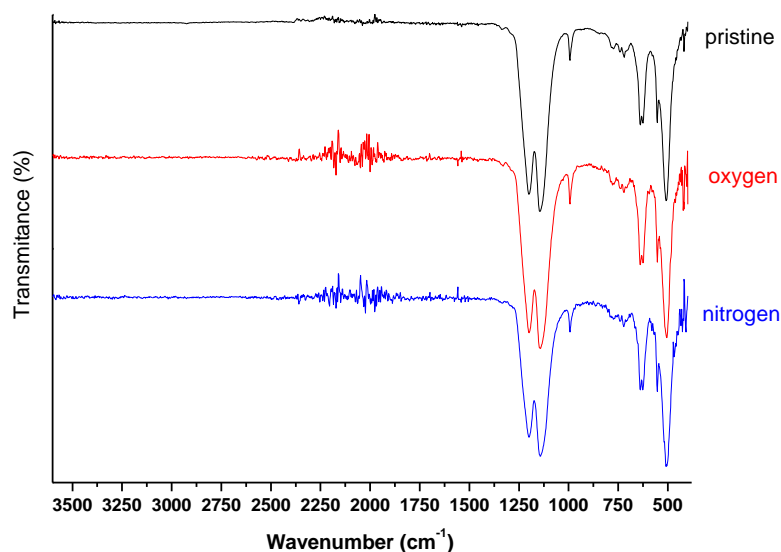
The scanning electron microscope images were obtained in a Phillips XL 30 Microscope and were amplified at 1,000x. The samples were covered with gold in a Sputter Coater BAL-TEC SCD 050.

## **3. RESULTS AND DISCUSSION**

All characterization was carried out in pristine and irradiated films at 5, 10, 20 and 40kGy. After the samples had been irradiated at 80kGy under nitrogen and oxygen atmospheres, it

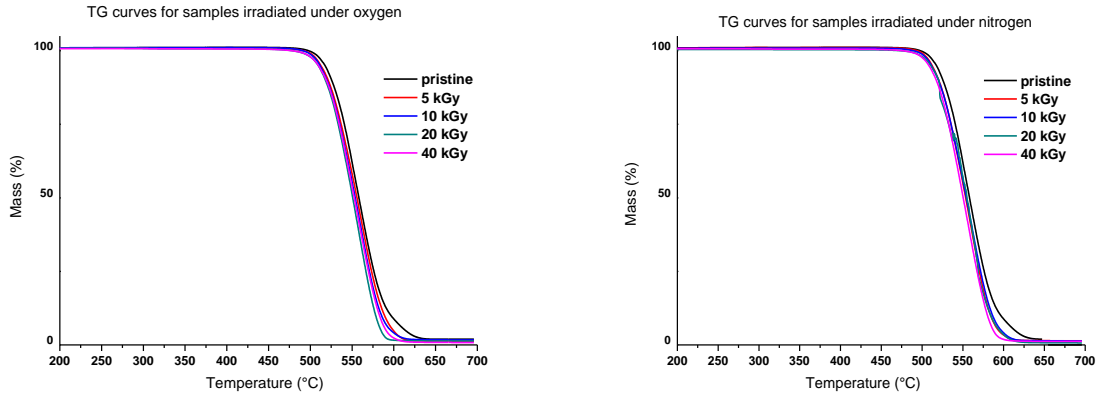
was not possible to characterize them due to the high level of degradation even the manipulation was hard it.

By IR-ATR (Fig. 1) was not possible to verify changes in the polymer structure. In both atmospheres the spectra were identical to the pristine sample. The spectrum of the unmodified samples shows the strong band at 1150 and 1250  $\text{cm}^{-1}$ , which represent the  $\text{CF}_2$  out-of-phase stretching vibration present in the original PFA film. These peaks appear in the spectra of irradiated films [2, 3].



**Figure 1. Infrared spectra of the PFA films pristine and modified**

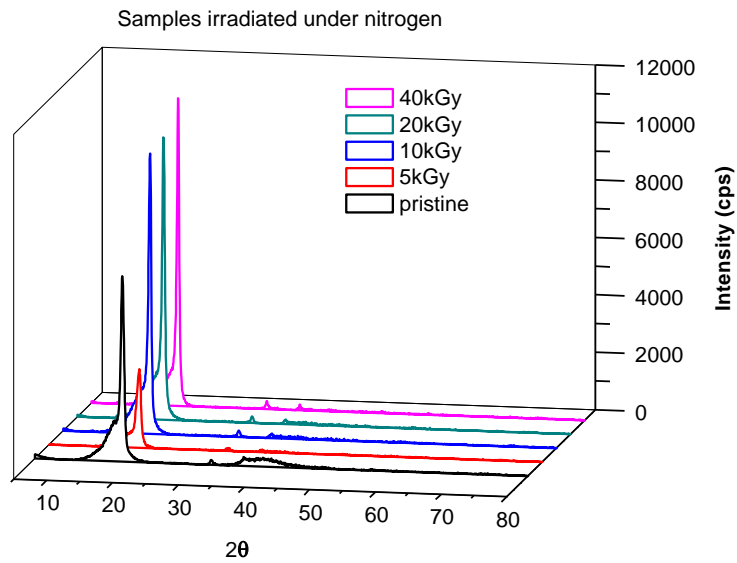
The thermal stability (Fig. 2a and 2b) of the samples was not affected as revealed by the thermogravimetric analysis. For all samples the initial and final degradation temperature ( $T_{\text{onset}}$  and  $T_{\text{endset}}$ , respectively) didn't have any drastic change, independent of the atmosphere. The pristine sample have high stability to degradation [1], that begun at 524°C and for the modified samples (both atmospheres) was decreased about one degree with the increase irradiated dose in both atmospheres.



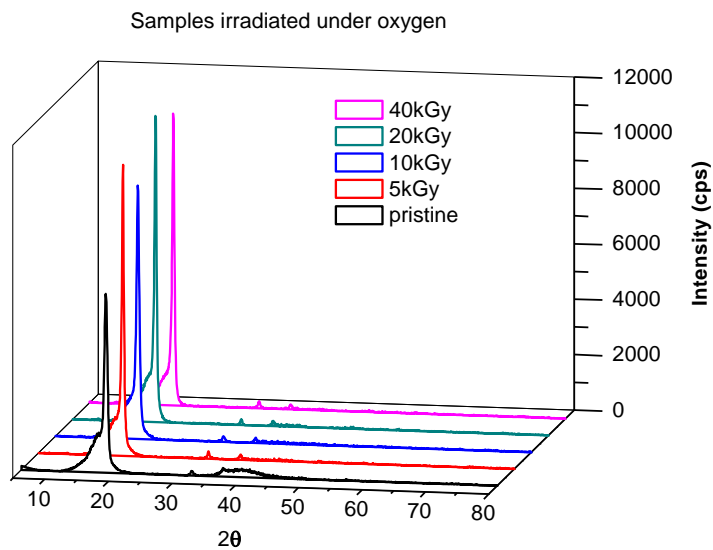
**Figure 2. Thermogravimetric curves of the PFA films pristine and modified under oxygen (a) and nitrogen (b) atmospheres**

By XRD analyses was verified that the Bragg's angle ( $2\theta$ ) showed almost no significant shift in all the irradiated films compared to pristine sample. The diffractograms in figures 3 and 4 presented almost the same pattern and profile, for all samples. It is also shown that the pattern is characterized by the appearance of one intense and sharp peak in the  $2\theta$  range from about 16.4 to 17.2 which can be a sign of that the crystalline phase is the dominant phase in the PFA polymer. These peaks are attributed to tetrafluoroethylene ( $C_2F_4$ ) units present in the polymer chain [4, 5].

According to X-ray diffractograms (Fig. 3 and 4) it is possible to observe an increase in the peak intensity with the dose irradiated. The sample irradiated under nitrogen atmosphere had a higher increase in the intensity than the samples irradiated under oxygen atmosphere. The exception in this observation was the sample irradiated at 5kGy under nitrogen atmosphere that had a decrease in its intensity.



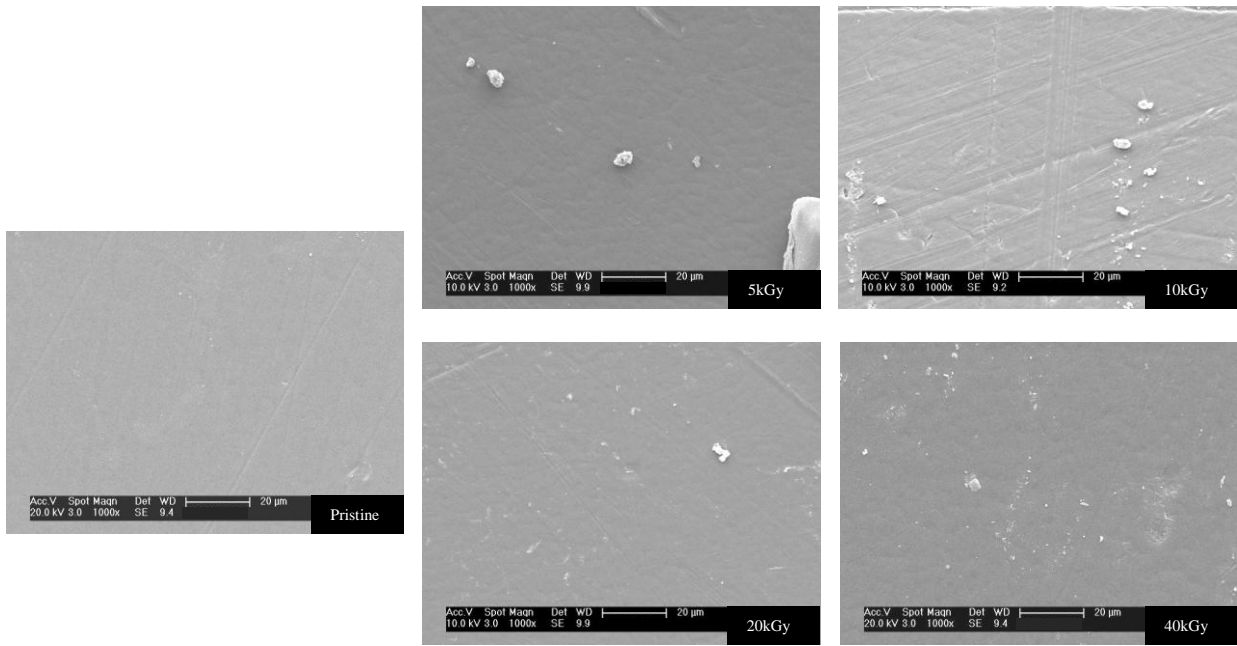
**Figure 3. XRD for samples irradiated under nitrogen atmosphere.**



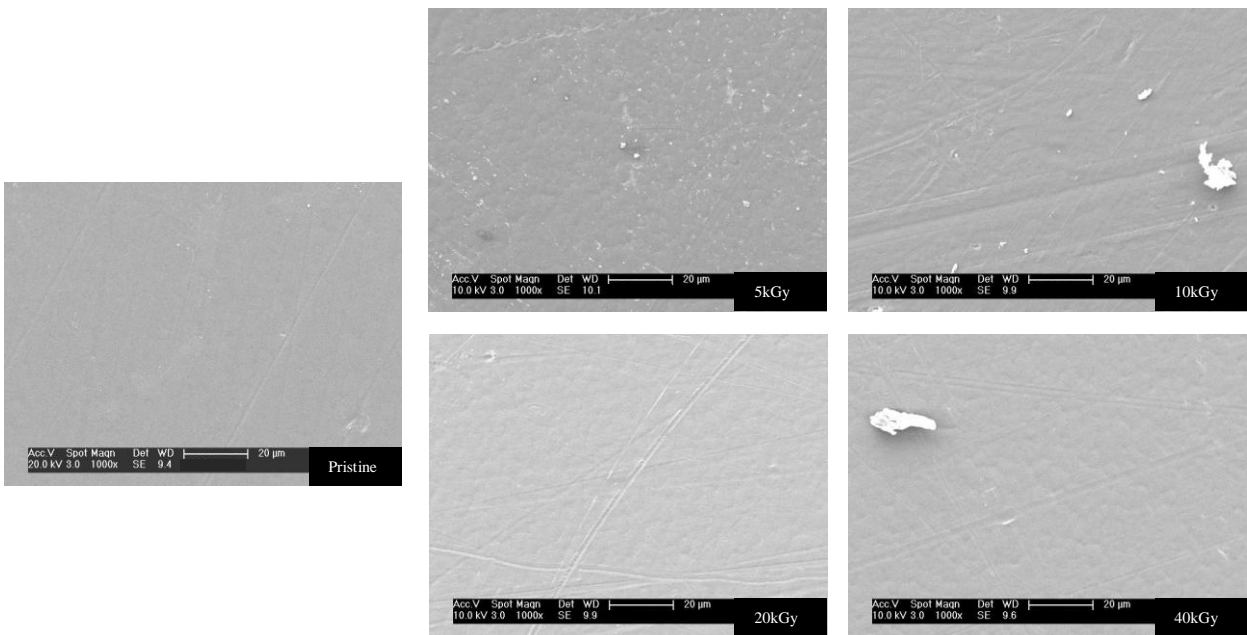
**Figure 4. XRD for samples irradiated under nitrogen atmosphere.**

The film surface was investigated using SEM. The micrographs obtained for different samples are shown in Figures 5 and 6. Observing the non irradiated sample is possible to identify a homogeneous surface.

The films irradiated under nitrogen atmosphere indicate small agglomerates appearing. The images for the irradiated samples under oxygen atmosphere (Fig. 5) revealed a roughness surface, which indicate degradation effect.



**Figure 5. SEM images for samples irradiated under nitrogen atmosphere.**



**Figure 6. SEM images for samples irradiated under nitrogen atmosphere.**

#### 4. CONCLUSIONS

The influence of the atmosphere during irradiation process was investigated in this work. The films irradiated under inert atmosphere (nitrogen) had their properties almost unaltered, which was expected. The polymer irradiated oxygen atmosphere demonstrates by SEM images the degradation effect in the material surface as result directly of the irradiation. The thermal properties of the irradiated PFA film had a little decrease compared to the original film.

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