

EFFECT OF RADIATION-INDUCED MODIFICATION IN FLUROELASTOMER

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Note: fluoropolymer, radiation, characterization

ABSTRACT

Polymers exposed to ionizing irradiation, even at low doses, often undergo structural changes accompanied by molecular crosslinking and chain scission (degradation) reactions. The general effect of the radiation on polymers is determined by the ratio of crosslinking to chain scission events. This ratio depends on parameters such as chemical structure, physical state, radicals stability and mobility, irradiation rate and irradiation atmosphere. 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 fluoroelastomer with 70% - fluor that having excellent thermal, chemical and mechanical properties. Vulcanized and non-vulcanized samples of this material were submitted to gamma radiation under air atmosphere in order to observe the effect of atmosphere in the polymer matrix. The irradiated doses were 5, 10 and 20kGy, at room temperature. The characterization was made by scanning electron microscope (SEM), infrared spectroscopy using attenuate reflectance (ATR-IR) and X-ray diffraction. The results demonstrated which was expected, the degradation reactions were observed.

1. INTRODUCTION

The fluoroelastomer is a polymer with excellent thermal, chemical and mechanical properties resistance to high temperatures, resistance to the attack of chemical substances including oils, fuels and mineral acids, and low permeability to many substances, which has been used in different areas that there are necessary the resistance to aggressive chemicals and thermal environments. Some of these areas are automotive and aerospace industrials. With this class of polymer is possible to assemble high quality of o-ring, gaskets, seals and tubes which are used to transport a variety of gases and liquids [1-3].

Because of the chemical inertia, especially due to the C-F bonds, it is difficult to modify the surface and the bulk of the polymer with fluor content. The use of radiation process is a well-known technique used to modify a large number of fluor subtracts, including polymer. Fluoropolymers, fluorinated (PTFE, FEP and PFA) or partially fluorinated (PVDF and ETFE) polymers are well known to be sensitive to ionizing radiation [4]. Both chain scission and crosslinking reactions occur simultaneously during the radiation process and the final result will depend on the material chemical structure, type of radiation, dose rate and total absorbed dose. In the case of PTPE, FEP and PFA undergo predominant degradation reactions in this process.

In this work was carried out two different processes to compare the effect of gamma radiation in elastomer. The first process was submitted samples without vulcanization under 5, 10 and 20 kGy doses. In the second process, the samples were vulcanized in a hydraulic press with electrical temperature at 195°C and after that the material were submitted at the same doses of the first process. Both materials with and without vulcanization was carried out in air atmosphere.

2. EXPERIMENTAL

2.1. Materials

The commercial fluoropolymer compound was supplied by Croslin Compostos de Borracha Ltda. This compound is a terpolymer vinylidene fluoride (VDF), hexafluoropropylene, and tetrafluoroethylenewith fluorine content of 70%, Mooney viscosity 60 ML (1 + 10) at 121°C. The fluoroelastomer was submitted to gamma radiation at 5, 10 and 20 kGy at dose rate of 10 kGy h⁻¹ under air atmosphere in order to evaluate the influence of this process 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⁻¹ to detect the functional groups of the samples.

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

The scanning electron microscope images were obtained in a tabletop microscope Hitachi TM 3000, amplified at 1,000x with Energy Dispersive X-ray Spectrometry (EDS) coupled. The samples were analyzed without covered of gold or carbon.

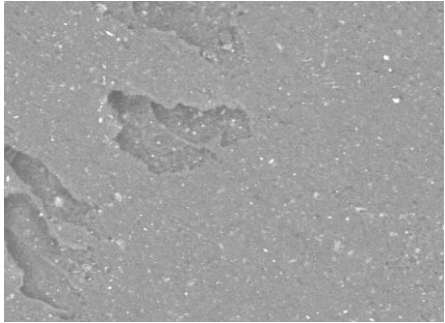
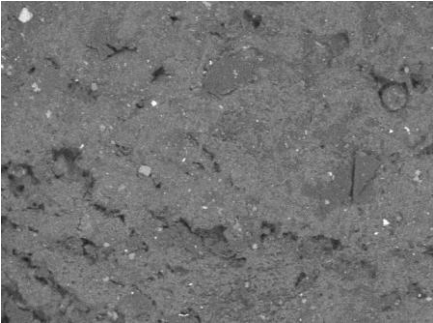
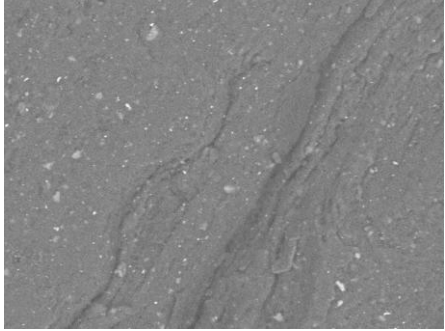
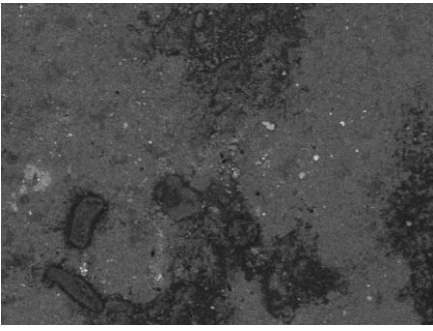
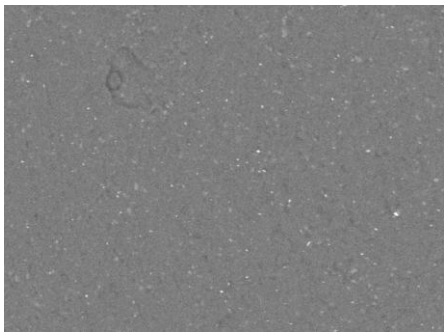
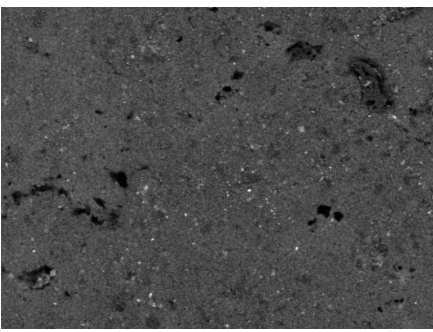
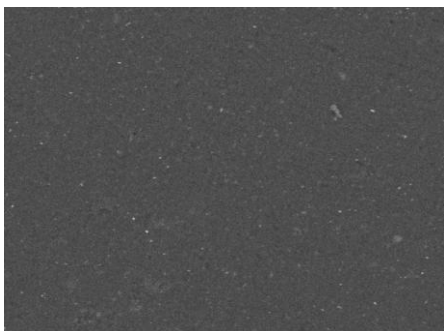
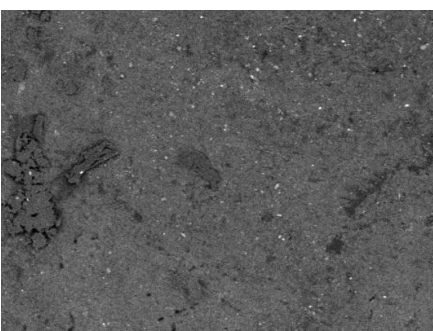
3. RESULTS

The images (Table 1) obtained with SEM technique revealed what was expected, the vulcanized materials are smooth and homogeneous aspect while the unvulcanized samples presented roughness and heterogeneous surface.

The EDS experiment was carried out in the surface of the images obtained by SEM. The results of the quantity of chemical element in all samples (vulcanized and unvulcanized) were very similar and are describes in Fig. 1. The amount of Fluor and Carbon represent almost

98% of the samples, which is in according to the polymer chain that has C-F bonds as the major components of the matrix.

Tabel 1 : Images of scanning electron microscope, amplified at 1,000X for all samples

Sample	Vulcanized	Unvulcanized
Pristine		
5kGy		
10kGy		
20kGy		

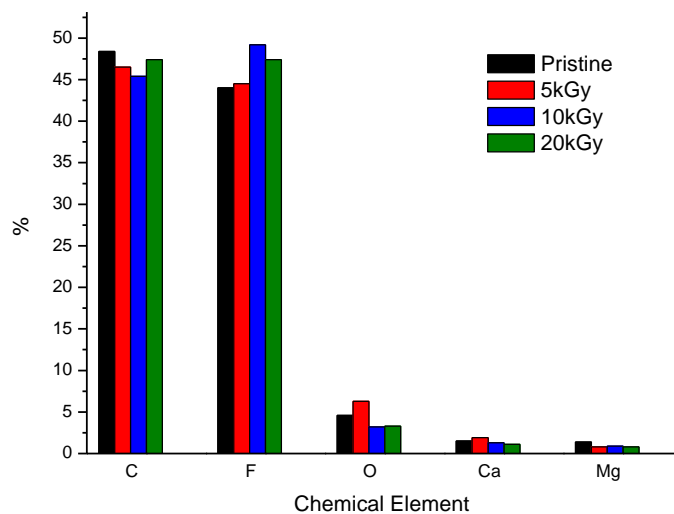


Figure 1: Results of chemical composition by EDS

In the X-ray diffraction for vulcanized samples was observed an increase in the intensity of the peak at $2\theta = 17$. One of the characteristic of elastomer is it has no cristalinity, which is confirmed in the black line of the pristine sample. The only crystalline product among the fluoroelastomer compound is a layered $Mg(OH)_2$.

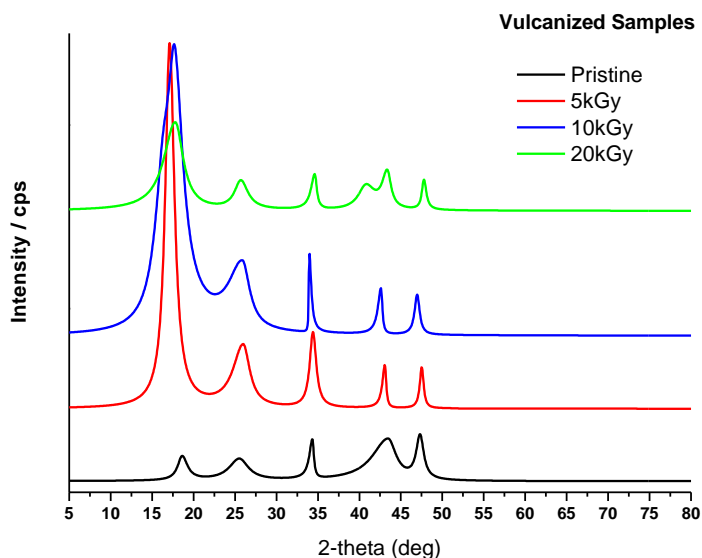


Figure 2: X-rays diffractograms for vulcanized samples

The diffractograms for unvulcanized (Fig. 3) samples revealed a dislocated peak at $2\theta = 17$ for minor values for irradiated samples when compared to the pristine. The samples irradiated

at 5kGy shown a different profile for this peak, which can be investigated for others technique.

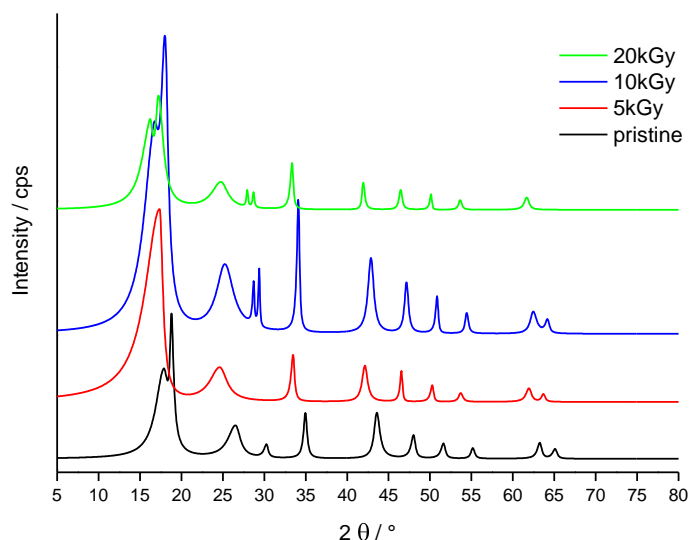


Figure 3: X-rays diffractograms for unvulcanized samples

The infrared analysis results are shown in Fig. 4 and Fig. 5 (vulcanized and unvulcanized samples, respectively). The spectra are almost identically in all samples studied. The band at 1397 cm^{-1} is ascribed to stretch $\nu(\text{CF})$ and remained unchanged even after the radiation exposure in both samples processed. The pristine sample for unvulcanized sample has no peak at 2925 cm^{-1} refers to asymmetric stretch $\nu(\text{CH}_2)$ and 2854 cm^{-1} to the symmetric stretch $\nu(\text{CH}_2)$, instead of appears for all the other samples as weak doublets in the region. This fact indicated the increase in the dominance of the CH bonds over the CF bonds in the elastomer matrix, due to the irradiation process which has as a consequence the degradation reactions. In spite of the vulcanized pristine sample was not submitted to radiation process, this degradation is related to the temperature that the material was submitted during the curing [5-7].

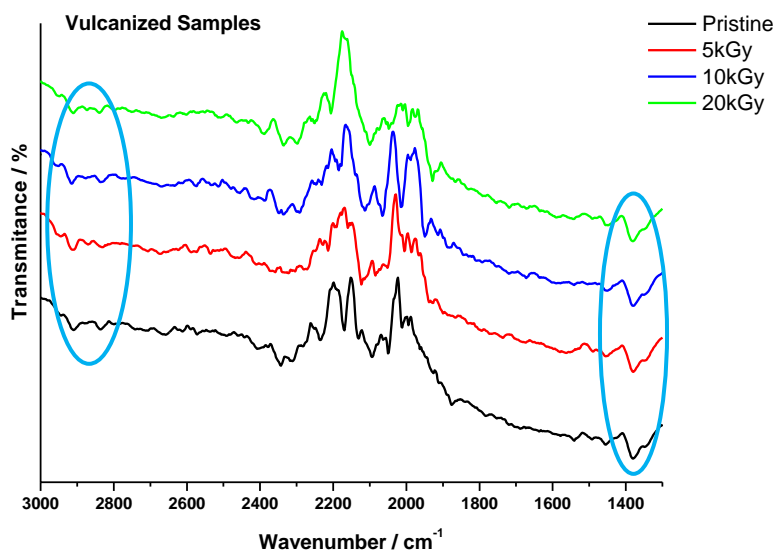


Figure 4: Infrared spectra for vulcanized samples

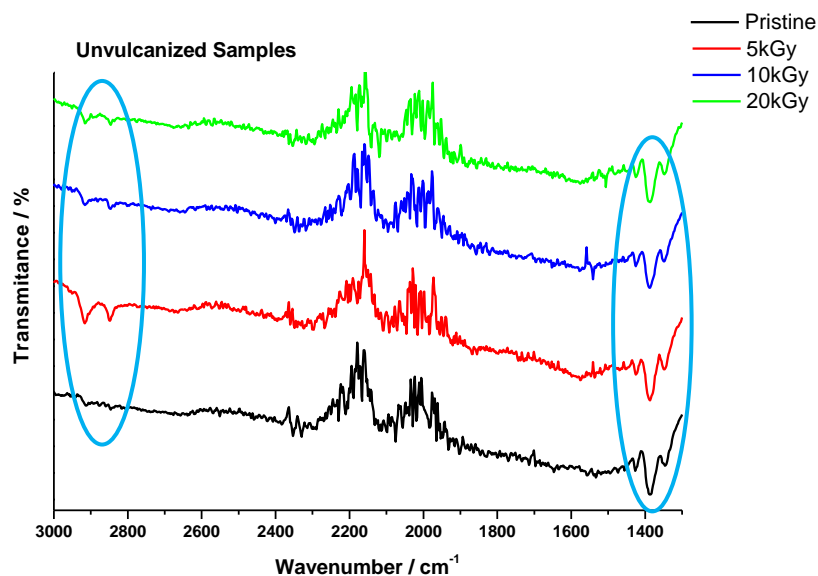


Figure 5: Infrared spectra for unvulcanized samples

4. CONCLUSIONS

The work was successfully carried out. The images of SEM revealed the samples' surface and any damage were evidenced.

The presented techniques demonstrated degradations reactions. Although, further experiments like mechanical and thermal analysis, are been studied to investigate the reactions that can occur when the elastomer is irradiated before or after vulcanization process.

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