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Electron Beam Irradiation Effect on the Mechanical, Thermal and Surface Properties of Fluoroelastomer

Claudia Giovedi [a], Eddy Segura Pino [b], Marcelo Rabelo Rossi [a], Luci Diva Brocardo Machado [b,*]

[a] *Centro Tecnológico da Marinha em São Paulo, Av. Prof. Lineu Prestes, 2468, Cidade Universitária, 05508-000, São Paulo, SP- Brazil.*

[b] *Instituto de Pesquisas Energéticas e Nucleares – IPEN/CNEN-SP, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-000, São Paulo, SP – Brazil.*

Abstract

Fluoroelastomer is a polymer used as a sealing material due to some excellent properties, such as resistance to high temperatures and to aggressive chemical substances, comparing to other elastomers. The aim of this work was to evaluate the effect of the ionizing radiation of electron beam (EB) on the mechanical, thermal and surface properties of a commercial fluoroelastomer containing carbon black and other inorganic fillers. The material was irradiated with overall doses between 10 and 250 kGy. The evaluated mechanical properties were tensile strength (stress and strain at break), hardness (Shore A) and compression set. Thermal behavior was evaluated by thermogravimetric analysis and differential scanning calorimetry. Surface modifications were verified using optical and electronic microscopy. Experimental results showed that EB irradiation promotes significant changes in the fluoroelastomer mechanical properties, increases the glass transition temperature and induces a better adhesion between elastomer and fillers.

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***Corresponding author**.

FAX: +55 11 38169186

E-mail addresses: lmachado@ipen.br and giovedi@ctmsp.mar.mil.br

1. Introduction

Elastomers are specified in a variety of industrial, automotive and aerospace applications where large volumes of high quality seals, tubes and hoses are needed to contain or transport a variety of gases and liquids [1]. Commercial fluoroelastomers were introduced in 1957 to meet the needs for high-performance sealing materials. Since then, the use of fluoroelastomers has spread out to many other applications, mainly due to its excellent properties such as, resistance to high temperatures, resistance to chemical substances, including oils, fuels and mineral acids, and low permeability to many substances.

A typical recipe of fluorelastomers includes, besides the polymer, a curing system, metal oxides, fillers, processing aids and other additives. These additives are incorporated in order to assure good processing characteristics and specific properties [2].

As in many other polymeric materials, ionizing radiation has a variety of effects on fluoropolymers. It may cross-link them, cause chain scission or modify their surface structure [3]. These effects occur simultaneously, and the final result will depend on the material chemical structure, type of radiation, dose and dose rate. In general, compounds from fluoroelastomers irradiated at optimum conditions attain better mechanical properties and thermal stability than non-irradiated chemical cured systems [4]. The influence of polyfunctional monomers on the structural changes of fluoroelastomers induced by electron beam (EB) has been also verified [5].

The aim of this work was to evaluate the effect of the ionizing radiation of EB on the mechanical, thermal and surface properties of a fluoroelastomer sealing material obtained by a conventional curing process.

2. Experimental

2.1 Samples

The fluoroelastomer samples were a commercial product obtained from two monomers, vinylidene and hexafluoropropylene, containing also specified percentages of fluoroelastomer, carbon black and inorganic fillers (magnesium oxide and calcium hydroxide), and obtained by a conventional chemical curing process. Mechanical and thermal measurements were carried out with samples obtained from molded plates. Surface studies were carried out using o-ring samples.

2.2 EB irradiation conditions

Samples were irradiated with high-energy electron at the IPEN-CTR facilities using a 1.5 MeV and 37.5 W Dynamitron Electron Accelerator model JOB-188. The irradiation were carried out at

a dose rate of 11.20 kGy s^{-1} and the overall applied doses were 10, 25, 50, 75, 100, 125, 150, 175, 200 and 250 kGy.

2.3 Solubility tests

The solubility in acetone of non-irradiated and irradiated samples was evaluated. The samples were dried and weighted before and after immersion in the solvent for a period of 24 hours.

2.4 Thermal analysis

TG/DTG curves were obtained with a TGA7 (PerkinElmer) Thermogravimetric Analyzer at heating rate of 10°C·min^{-1}. The experimental data were collected under a dynamic nitrogen atmosphere in the temperature range from 50ºC to 650°C, and in a synthetic air atmosphere from 650°C to 900°C, using sample of about 5 mg. The amount of fluoroelastomer polymer, carbon black and fillers were determined according to ASTM D6370-99 [6]. DSC curves were carried out using a DSC-50 (Shimadzu) Differential Scanning Calorimeter in the temperature range from -40°C to 80°C at heating rate of 10°C·min^{-1}, in a dynamic nitrogen atmosphere using sample of about 20 mg.

2.5 Mechanical tests

Tensile strength measurements were carried out in an Instron Universal testing machine model 5565 in accordance to ASTM D1414-78 [7]. Hardness was evaluated using a Type A durometer Woltest model SD300 according to ASMT D 2240-86 [8]. Compression set measurements were carried out in a appropriate device for compression set test under constant pressure according to Method B, ASTM D 395-85 [9].

2.6 Scanning Electron Microscopy (SEM) and Optical Microscopy

SEM micrographs of the surfaces from fractured samples were obtained using a scanning electron microscope model JXA-6400 (JEOL). Optical imagines of non-irradiated and irradiated o-rings were obtained using a microscope model Polyvar MET (Reichert-Jung) attached to a CCD Color Camera model KC-512NTX (KODO).

3. Results and Discussion

The obtained results of the solubility tests are shown in Figure 1. The data indicate that there is a progressive decrease in the solubility as a function of the applied dose. This is in agreement with the fact that at higher radiation doses the cross-linking degree increases and, consequently, the sample solubility decreases.

Representative curves of thermal behavior of non-irradiated and irradiated samples evaluated by means of TG and DSC are shown in Figure 2. The TG experimental data allow to verify that the

composition of the samples, in the range of studied doses, is not affected by the irradiation process. Therefore, the amount of fluoroelastomer and carbon black corresponding, respectively, to the first and second mass loss steps remain constant at 66% and 25%. Additionally, the content of fillers corresponds to the residual component of 9%, obtained at about 690ºC.

Moreover, the thermal stability estimated by onset temperature, represented in Figure 2A, for the first mass loss step is similar for non-irradiated samples and for samples irradiated with doses up to 50 kGy. For these samples the estimated temperature for the beginning of the thermal decomposition is about 445^{o}C. In addition, irradiated samples with doses in the range from 75 to 250 kGy present slightly lower thermal stability, at about 435^{o}C. Therefore, considering the experimental errors, the variation was not considerable. This fact means that, under the studied conditions, there was not significant chain scission induced.

On the other hand, DSC curves showed a progressive increase of the glass transition temperature in the range of radiation dose studied, as shown in Figure 2B. The values changed from 3,3^{o}C for non-irradiated sample to 12,9^{o}C for sample irradiated with 250 kGy, denoting that radiation doses increase the cross-linking degree.

The results obtained from mechanical tests are shown in Table 1.

The data show that the stress at peak load increases 34% within the range of radiation dose applied. On the other hand, the strain decreases considerably, from 347% for non-irradiated samples to 109% for the highest applied dose (250 kGy). The values of Shore A hardness present an increase of 15% within the range of applied doses and compression set measurements showed that the values remain practically stable independent of the radiation dose applied.

The investigation of the fracture behavior by SEM showed that the micrographs obtained for non-irradiated samples present several voids between the filler particles and the matrix (elastomer) with very heterogeneous surface. However, with the increase of the radiation dose applied the amount of voids decreases and the fracture surface is more homogeneous than the one for non-irradiated sample. The micrograph obtained for the sample irradiated with the highest applied dose (250 kGy) presents a homogeneous surface, as shown in Figure 3.

The effect of EB radiation on o-rings defects from their obtainment process was also evaluated. An example of the results obtained is shown in Figure 4. The micrographs show that there are no considerable changes in the o-ring defects induced by the EB irradiation processing.

4. Conclusion

The tests showed that the sample solubility decreases as a function of radiation doses, denoting an increase in the cross-linking degree. This is also confirmed by glass transition temperatures, which present a considerable increase as a function of the radiation dose applied. On the other hand, thermogravimetric data showed that no considerable chain scission was induced by EB radiation under the studied conditions.

The results showed that EB radiation, in the studied conditions, promotes significance changes in the fluoroelastomer mechanical properties resulting in an increase of hardness, tensile strength and stiffness. On the other hand, compression set data is not affected by the EB processing. These mechanical results are important parameters to be considered for the end use of fluoroelastomers under EB radiation exposition.

The SEM micrographs showed that the enhancement of mechanical performance is associated to a better adhesion between elastomer and fillers as well as to the increasing of cross-linking degree as a function of radiation doses. This fact assures better performance of irradiated sealing materials. Despite of the changes induced by EB irradiation processing, in the studied doses range no modification on the o-ring defects from the obtainment process was observed.

Acknowledgments

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Table 1

Fluoroelastomer data of stress at peak load, strain at peak load, hardness and compression set as a function of applied doses.

Dose (kGy)	**Stress at Peak Load (kg cm^{-2})**	**Strain at Peak Load (%)**	**Hardness (Shore A)**	**Compression Set (%)**
0	113	347	81	---
10	114	341	83	4.0
25	116	285	85	3.5
50	119	239	87	3.5
75	123	210	88	3.0
100	127	187	89	2.8
125	131	168	89	2.5
150	135	149	90	3.5
200	142	125	92	4.0
250	151	109	93	3.0

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Captions of figures:

Figure 1: Final and initial mass relation as a function of the applied dose for the solubility test.

Figure 2: A) TG curves for non-irradiated and irradiated with 250 kGy samples and B) DSC curves of: a) non-irradiated sample, and irradiated with different doses: b) 75 kGy, c) 150 kGy and d) 250 kGy.

Figure 3: SEM micrographs of fractured surfaces for different samples: A) non-irradiated and B) irradiated with 250 kGy.

Figure 4: Optical micrographs of surface o-ring defect for sample: A) non-irradiated and irradiated with B) 50 kGy, C) 250 kGy and D) 500 kGy.

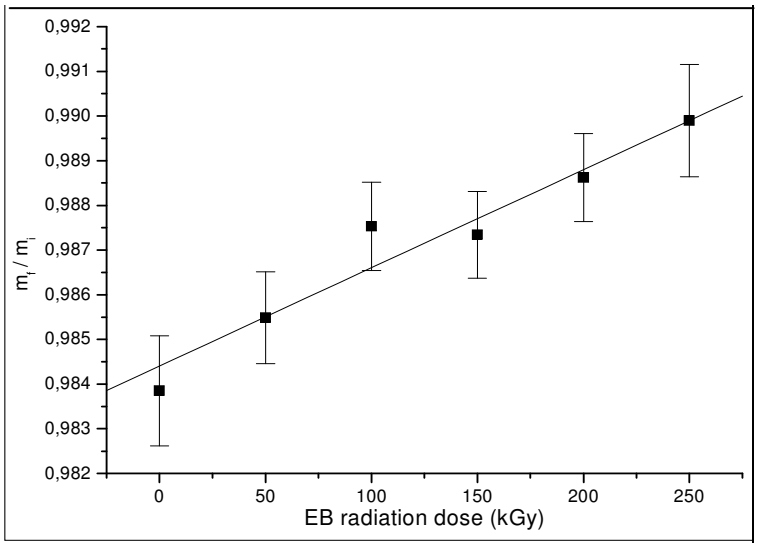


Figure 1: Final and initial mass relation as a function of the applied radiation dose on the solubility test.

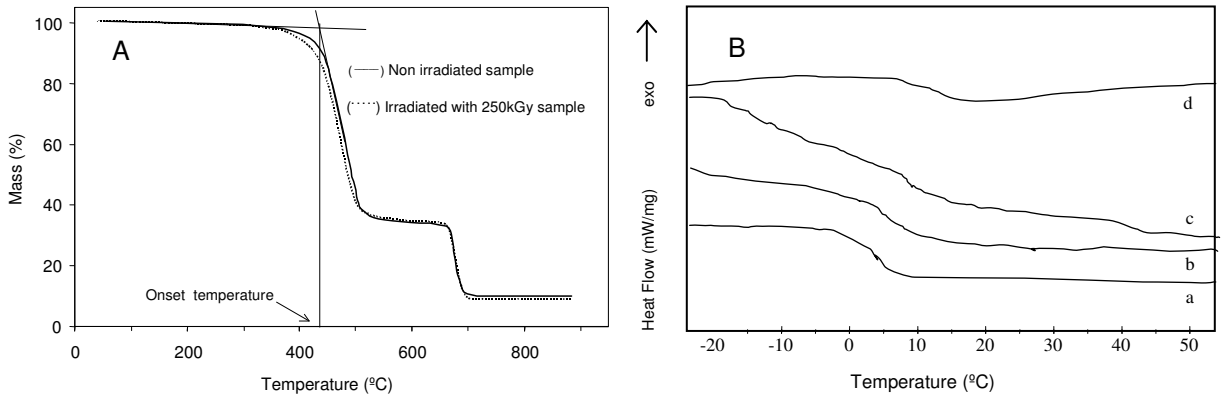
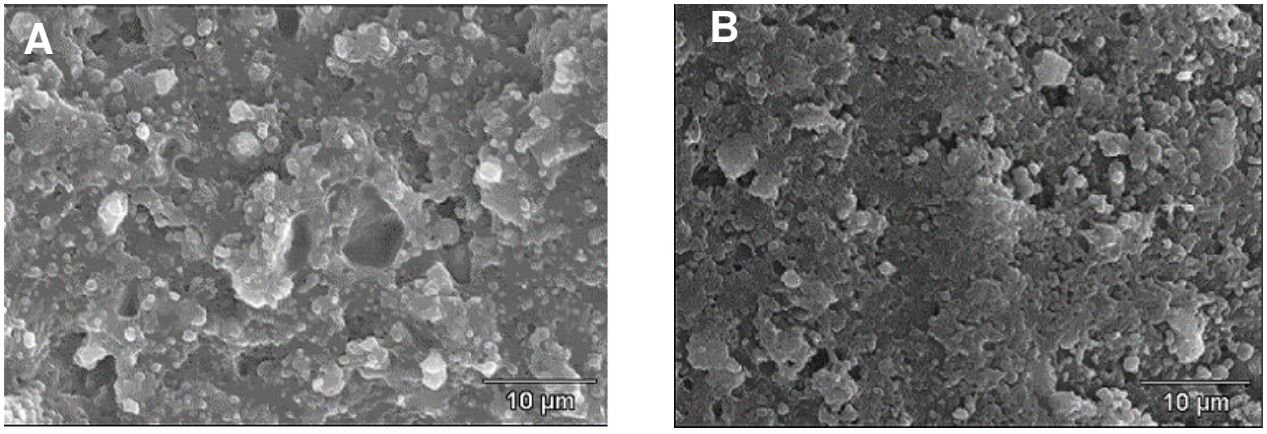


Figure 2: A) TG curves for non-irradiated and irradiated with 250 kGy samples and B) DSC curves of: a) non-irradiated sample, and irradiated with different doses: b) 75 kGy, c) 150 kGy and d) 250 kGy.



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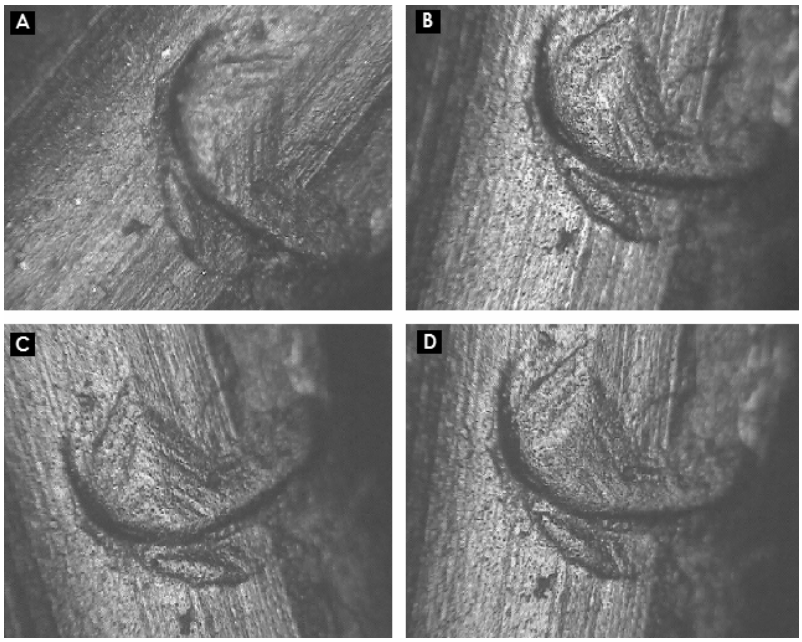

Figure 4: Optical micrographs of surface o-ring defect for sample: A) non-irradiated and irradiated with B) 50 kGy, C) 250 kGy and D) 500 kGy.