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Electron beam irradiation effects on the mechanical, thermal and surface properties of a fluoroelastomer

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Abstract

Fluoroelastomer can be used as a sealing material for different purposes. The aim of this work is the evaluation of the effects of the ionizing radiation of an electron beam (EB) on the mechanical, thermal and surface properties of a commercial fluoroelastomer containing carbon black and inorganic fillers. The material was irradiated with overall doses between 10 and 250 kGy. Tensile strength (stress and strain at break), hardness (Shore A) and compression set were evaluated. Thermal behavior was evaluated by thermogravimetric analysis and differential scanning calorimetry. Surface modifications were inspected using scanning electron microscopy (SEM) and optical microscopy. The experiments have shown that EB irradiation promotes beneficial changes in the fluoroelastomer tensile strength behavior while compression set remain constant and the glass transition temperature increases. The SEM micrographs have shown compactness in the irradiated samples, although optical observations showed no surface morphology changes.

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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 for many other applications, mainly due to their excellent properties such as resistance to high temperatures, resistance to the attack of chemical substances including oils, fuels and mineral acids, and low permeability to many substances [2].

A typical composition of fluoroelastomers includes, besides the polymer, a curing or cross-linking agent, metal oxides, fillers, processing aids and other additives. These additives are incorporated in order to assure good processing characteristics and specific properties [3].

As in case of 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 [4]. Quite often, these effects occur simultaneously, and the final result will depend on the material chemical structure, type of radiation, dose rate and total absorbed dose. In general, compounds from fluoroelastomers irradiated at optimum conditions attain better mechanical properties and thermal stability than non-irradiated

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chemical cured systems [5]. There are also studies showing the influence of polyfunctional monomers on the structural changes of fluoroelastomers induced by electron beam (EB) [6].

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, which was previously obtained by a conventional curing process.

2. Experimental

2.1. Samples

The fluoroelastomer studied in this work was a commercial product obtained from two monomers, vinylidene and hexafluoropropylene, containing also specified percentages of polymeric material, carbon black and inorganic fillers such as magnesium oxide and calcium hydroxide. Mechanical and thermal experiments were carried out with specific samples obtained from molded plates (150 mm × 150 mm). Surface investigations were carried out on the O-ring samples (internal diameter of 18.4 mm; cross-section area of 5.3 mm^2).

2.2. EB irradiation conditions

Samples were irradiated with high-energy electron beam at the IPEN-CTR facilities using a model JOB-188 Industrial Dynamitron Electron Beam Accelerator of 37.5 kW (1.5 MeV–25 mA). The irradiation processes were carried out at a dose rate of 11.2 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 weighed before and after remaining 24 h immersed in the solvent. Before each weighing step, the samples were adequately dried.

2.4. Thermal analysis

TG/DTG curves were obtained using a Thermogravimetric Analyzer TGA7 (Perkin Elmer, Inc.) in the temperature range from 50 °C to 900 °C with a heating rate of 10 °C min^{-1}, under a dynamic nitrogen atmosphere in the temperature range from 50 °C to 650 °C, and under synthetic air atmosphere from 650 °C to 900 °C, using samples of about 5 mg weight. The amounts of fluoroelastomer, carbon black and fillers were determined according to ASTM D6370-99. DSC curves were carried out using a DSC-50 differential scanning calorimeter (Shimadzu Corp. Japan) in the temperature range from −40 °C to 80 °C at a heating rate of 10 °C min^{-1}, under dynamic nitrogen atmosphere using samples of about 20 mg weight.

2.5. Mechanical tests

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

2.6. Scanning electron microscopy (SEM) and optical microscopy

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

3. Results and discussion

The results obtained in the solubility tests are shown in Fig. 1. The data indicate that there is a progressive decrease in the solubility as a function of the applied radiation dose. This is in agreement with the fact that higher radiation doses increase the cross-linking degree of polymeric materials 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 Fig. 2. The TG experimental data allow verification that the irradiation process, in the range of applied doses, does not affect the composition of the samples. Therefore, the amount of fluoroelastomer and carbon

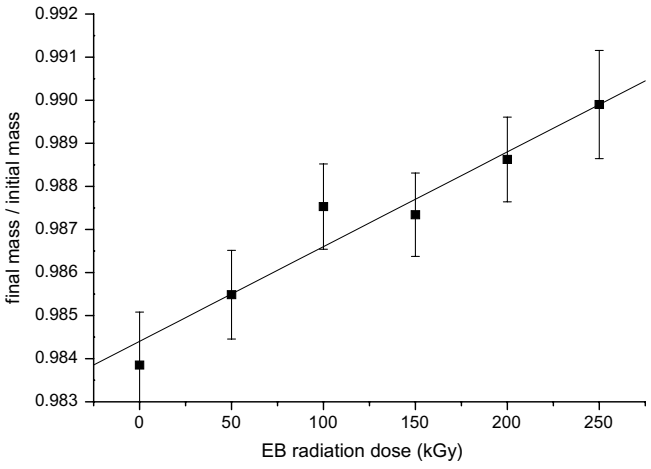

Fig. 1. Final and initial mass ratio from the solubility test as a function of the applied dose.

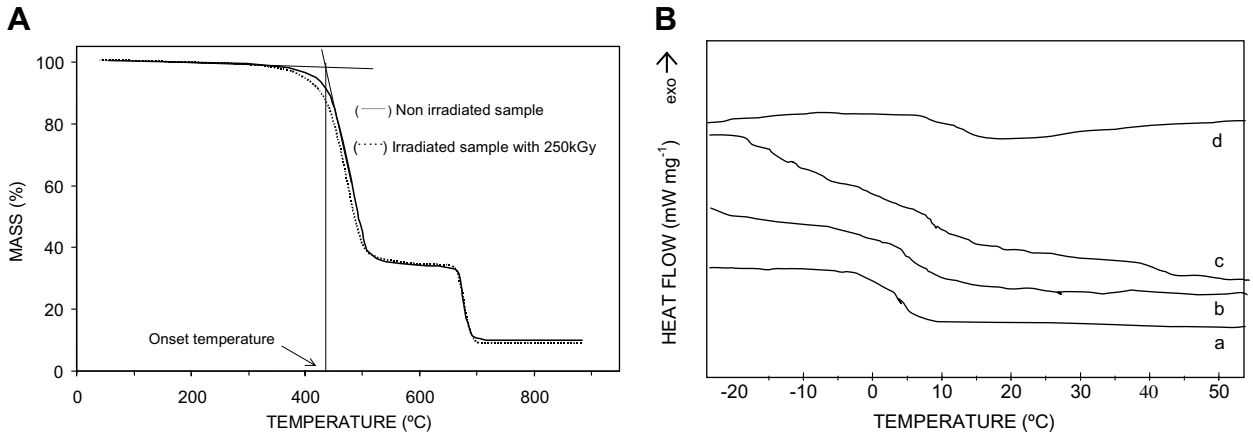

Fig. 2. (A) TG curves from non-irradiated sample (—) and from sample irradiated with 250 kGy (---); (B) DSC curves from: (a) non-irradiated sample, and samples after EB irradiation processing with different doses of (b) 75 kGy, (c) 150 kGy and (d) 250 kGy.

black, corresponding to the first and second mass loss steps, remain constant at 66% and 25%, respectively, and the content of fillers at 9%, corresponding to the thermally stable residual component observed in the temperature range of 690–900 °C. Moreover, the thermal stability estimated by onset temperature, represented in Fig. 2(A) for the beginning of the thermal decomposition, is similar for non-irradiated samples and for samples irradiated with doses up to 50 kGy. For these samples the estimated thermal decomposition onset temperature is about 445 °C. In addition, samples irradiated with doses in the range from 75 kGy up to 250 kGy present thermal stability slightly lower, with onset temperature at about 435 °C. Nevertheless, taking into consideration the experimental errors, the variation was not considerable. This fact means that, under the studied conditions, there was not significant chain scission induced by irradiation process.

Furthermore, DSC curves showed a progressive increase of the glass transition temperature as a function of absorbed radiation dose, as shown in Fig. 2(B). The values changed from 3.3 °C for non-irradiated samples to 12.9 °C for samples irradiated with 250 kGy, showing that the increasing of radiation doses, in the studied range, gradually increase the cross-linking degree of the samples.

The mechanical test results are shown in Table 1. The obtained data show that the stress at peak load increases about 25% within the range of radiation dose applied.

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

On the other hand, the strain at peak load decreases about 68% from non-irradiated samples to the samples, which received the highest applied dose (250 kGy). The values of Shore A hardness presented an increase of 15% within the range of applied doses and compression set measurements showed that, in the experimental errors of this kind of test, the values remain 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 sur-

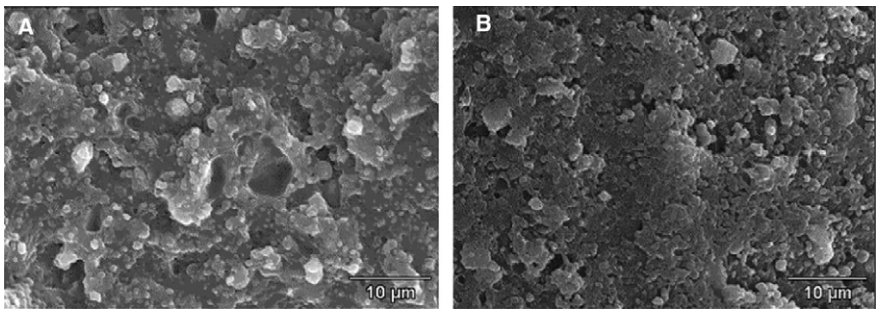

Fig. 3. SEM micrographs of fractured surfaces from: (A) non-irradiated sample and (B) sample after EB irradiation processing up to 250 kGy.

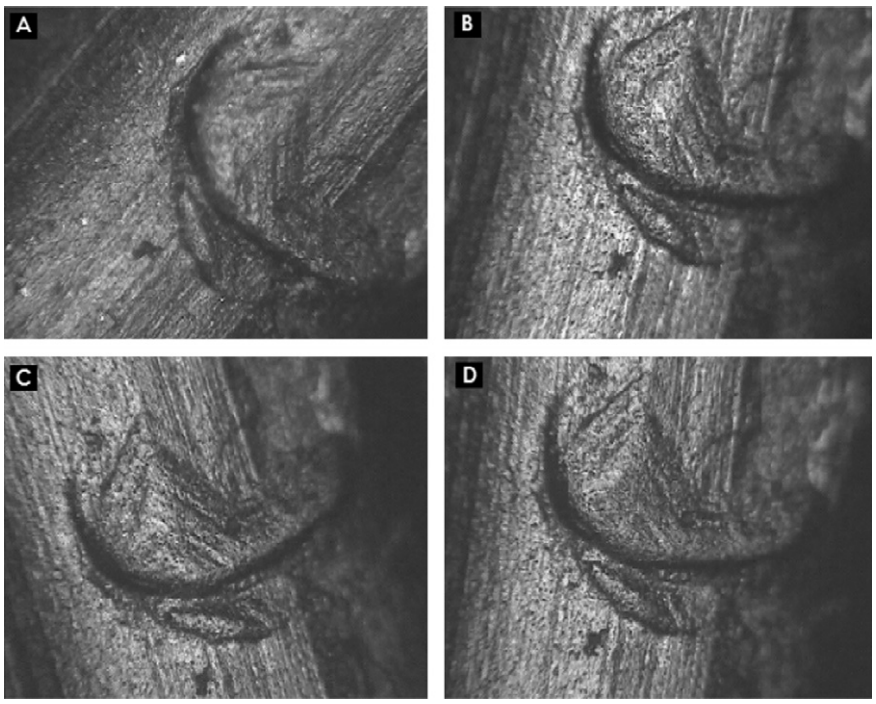

Fig. 4. Optical micrographs of the same O-ring surface defect: (A) non-irradiated sample and the same sample after irradiation processing up to doses of (B) 50 kGy, (C) 250 kGy and (D) 500 kGy.

face. However, with the increase of the applied radiation dose the amount of voids decreases, and the fracture surface is more homogeneous than that from non-irradiated samples. The micrograph obtained for the sample irradiated with the highest applied dose (250 kGy) presents a homogeneous surface, as shown in Fig. 3(B).

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

4. Conclusion

The sample solubility decreases as a function of rising radiation doses, denoting an increase in the cross-linking degree, which is confirmed by a considerable increase in the glass transition temperature of the samples. Moreover, thermogravimetric data showed that no considerable chain scission was induced by EB radiation under the studied conditions.

The experimental results showed that EB radiation, in the studied conditions, promotes beneficial changes in the fluoroelastomer tensile strength mechanical properties and also an increase in hardness and stiffness. On the other hand, compression set test data are 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. Despite the changes induced by EB irradiation processing, in the studied doses range, the surface defects produced during the O-ring manufacturing process remain unharmed.

To summarize, the evaluated properties of irradiated fluoroelastomer samples show that this polymeric material can be applied in devices working in high level ionizing radiation without losing their sealing characteristics but with an increase of their mechanical properties.

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