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INFLUENCE OF GAMMA RADIATION ON EPDM COMPOUNDS PROPERTIES FOR USE IN NUCLEAR PLANTS

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Abstract. *Various types of EPDM rubbers are used in radiation areas such as coating materials for wire and electrical cables, due to their higher resistance to environmental effects when compared to other types of rubbers. Properties set for EPDM rubbers that include degradation and good chemical resistance, besides excellent electrical properties have been stimulating the application of this elastomer for low and medium voltage (up to 35 kV). EPDM rubber is classified as radiation-resistant, because EPDM structure includes in its principal chain totally saturated bonds, and consequently is able to absorb more energy without cracking polymeric chain. The purpose of this work was studying radiation influence on rubbers compounds used in wires and electrical cables installed in Nuclear Plants. There were prepared EPDM compounds samples, further subjected to gamma radiation at doses: 25 kGy, 50 kGy, 75 kGy, 100 kGy and 200 kGy. Mechanicals properties and swelling properties were assessed in non-irradiated and irradiated samples at different doses. It was observed a reduction in tensile at break values, proportional to the dose applied and pointing toward a raise in material fragility. This reduction is more severe for doses higher than 100 kGy, indicating the predominance of chain-scission with further polymer degradation.*

INTRODUCTION

EPDM – ethylene-propylene diene – it is a rubber very used at present and belongs to ethylene-propylene (EPM) rubbers group that includes copolymers and thermopolymers.

Ethylene-propylene (EPM) and Ethylene-propylene diene (EPDM) rubbers appeared in market from 1962 in United States [1]. Generally copolymers refers to "EPM" rubbers, where "E" and "P" letters mean respectively, ethylene and propylene and "M" letter means that the rubber has a saturated chain poli-methylene type (-(CH2)x-) [2].

Thermopolymers usually refers to "EPDM" rubber, where "E", "P" and "M" have the same meaning above explained, being "D" letter the third monomer, a diene capable to insert unsaturation in chain; consequently, EPDMs and EPMs are unsaturated [1][3][4].

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Ethylene-propylene polymers have a principal molecular structure, hydrocarbon origin, with completely saturated chains, i.e. without none double bond that imparts an excellent resistance to ozone, weathering, heat, oxidation and polar fluids. In Fig. 1 it is shown basic molecular structure for Ethylene Propylene copolymers [5].

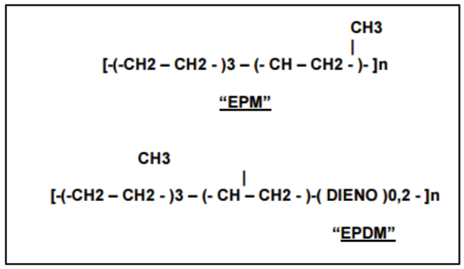

FIGURE 1. Structural schema for EPM and EPDM [5].

Structural properties of Ethylene-Propylene polymer, such as: Mooney Viscosity, Molecular Weight Distribution, Crystallinity, monomers units distribution (blocks) and possible branching influence directly vulcanized artifacts characteristics as well compounding processability.

Polymers exposure to ionizing radiations changes molecular structure and their properties [6, 7]. It occurs build-up of crossing bonds among chains, in parallel to atoms scission. Crosslinking promotes a raise in molecular weight that generally enhances properties improvement as long as chain-scission reduces weight presenting as final result properties deterioration. Table 1 shows a few gamma-radiation effects on polymeric materials properties [8, 9].

TABLE 1. Gamma-radiation effects on polymers properties

Properties	Croslinking	Chain Scission
Molar Mass	Increase	Decrease
Mechanical resistence	Increase	Decrease
Hardness	Increase	Decrease
Elongation	Decrease	Increase
Elasticity	Decrease	Decrease
Fragility	Occurs	Occurs
Solubility	Decrease	Decrease

Ionizing radiation application in EPDM rubber is highly relevant due to possibility of use in nuclear area, such as, nuclear plants, spatial aircrafts, irradiators, particles accelerators, among others. Polymeric materials in cables and accessories for nuclear engineering should resist to extreme environmental conditions. EPDM is one of polymers indicated for this purpose. One of the most important effects is the oxidative degradation process that depends on various factors as absorbed dose, dose rate, exposure environment, material chemical structure, among others [10, 11].

Gamma radiation can induce free radicals on material during the exposure. These generated free radicals will be able to combine in a competitive way among them or with molecular oxygen. It is known that diffusion of gaseous oxygen in polymeric materials can be minimized by immersions in water or in aqueous solutions, in order that oxidant agent is not fed with enough amount to promote polymer ageing [12]. In this case radicals recombination enlarges molecular network because its rate exceeds oxidation ratio. This means that the most part of free radicals is consumed and just a small amount of reactive units will be available for oxidation [13].

This work aims to the study of influence of gamma radiation on EPDM rubber compounds used in wire and cables for electricity conduction in a Nuclear Plant.

MATERIALS AND METHODS

Materials

In this work it was used: EPDM rubber supplied by LANXESS – Keltan 5470, 4.6 % diene, Mooney viscosity (ML 1 + 4@ 100 ºC) 55; other materials that compound rubber formulation, as activators (stearin and zinc oxide); and accelerators (sulfur, MBTS and TMTD) supplied by Basile Química Ltda.

Samples preparation

Mixture homogenizing was accomplished in an open roll mill at 45º C, for 40 minutes. Vulcanizing process characteristics were determined from parameters obtained from vulcanizing curve. It was used Monsanto Rheometer, model R 100, assembled to a graph recorder. Measurements were performed in accordance with ASTM D-2084 [14].EPDM mixtures were vulcanized at 175ºC, for 4 minutes, in a hydraulic press, 5Kg/cm^2 pressure. After vulcanizing process samples were characterized.

Tensile and Elongation at Break Characteristics

Elastomers can present electrical failures due to material tearing, a special type of mechanical rupture, typical for rubbers. Elongation at break and tensile are generally used for characterizing performance of these materials in operational conditions. In case of EPDM application in cables and electrical insulators these characteristics play a fundamental relevancy because these electrical devices are exposed to mechanical exertion of high intensity.

Tensile and elongation at break essays were accomplished in a Instron machine model 1127, by using standardized specimens under specified conditions of temperature and tensile speed. It was used ASTM D 412-8 [15] for tensile strength and elongation at break.

Determination of rubber swelling index

There were cut specimens in approximate dimensions 1.5 x 1.5 cm, previously weighed and immersed in toluene up to weight stabilization (around five days). When finished the essay, specimens were weighed and dried at room temperature for 24 hours. For these analyses it was used ASTM D-3616-5 [16].

Swelling degree was calculated in accordance with equation 1:

$$Q = \frac{\mathrm{M} - \mathrm{Mo}}{\mathrm{Mo}} \qquad (1)$$

Where:
M_o is initial mass for sample (g) and
M is final mass for sample (g) [17].

Samples Irradiation

Samples were irradiated in CBE/EMBRARAD and specimens in blankets were subjected gamma radiation, air environment, within 25 kGy, 50 kGy, 75 kGy, 100 kGy and 200 kGy doses, in a gamma irradiator, Cobalt-60 (^{60}Co), Nordion model JS 7500, dose ratio about 0.5 kGy h^{-1}.

Results and Discussions

The rubbers have the ability to absorb liquids, which causes an increase in volume, the phenomenon known as swelling in solvents. The equilibrium swelling of the organic solvent is one of the simplest methods to characterize the structure of crosslinking elastomers.

The change in mass of the samples expressed in percentage when immersed in toluene was accompanied daily and the results are shown in fig. 2, where they are shown the results for the average of three measures each time.

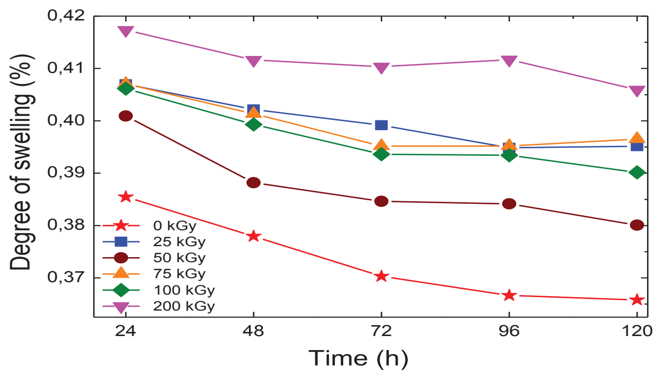

FIGURE 2. Results of the swelling of irradiated EPDM rubber compound at doses of 25, 50, 75, 100, and 200 kGy and not irradiated (0 kGy).

The results presented in Fig. 2 show that the swelling process progresses till the entangled molecules forming little balls are sutured by toluene after 72 hours. The decrease in the lithe amount of penetrated solvent is explained by the minimization of the free volume. After the attending a certain degree of swelling (the maximum amount of absorbed solvent), a pseudo equilibrated adsorption keeps solvent in the surrounding volume. The variation of so-called swelling, an adsorption in equilibrium is reached.

The fig. 3 and 4 show the results of tension and elongation at break, where can observe for doses until 50 kGy a little increase in values because the gel dose of EPDM is placed between 5 kGy and 10 kGy, the doses of 25 kGy and 50 kGy causes a slight crosslinking based on the scission of unsaturated fraction (component) the proof of crosslinking is the swelling of 50 kGy indicated samples, which exhibit lower swelling degree in comparison with 25 kGy sample.

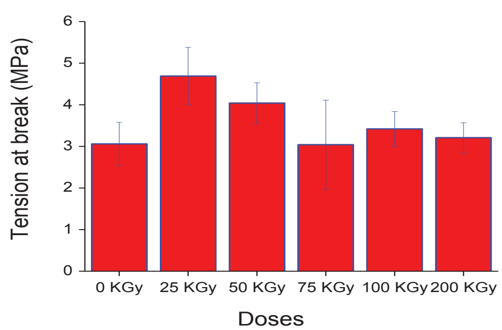

FIGURE 3. Results of tension at break of irradiated EPDM rubber compound at doses of 25, 50, 75, 100, 200 kGy and not irradiated (0 kGy).

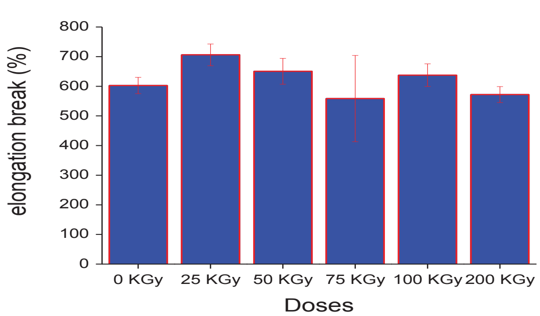

FIGURE 4. Results of elongation at break of irradiated EPDM rubber compound at doses of 25, 50, 75, 100, 200 kGy and not irradiated (0 kGy).

The increase of dose brings the real start of degradation. The package curves on 75 kGy and 100 kGy demonstrate that the degradation becomes significant, but not enough advanced.

At 200 kGy, where the scission is predominant process, the swelling is higher and the mechanical properties become decreased.

CONCLUSION

When subjected to gamma-radiation a few EPDM rubber compounds bonds are broken and new ones are built-up, being able to occur intermediary reactions, recombination or oxidations, and by them it is originated final products capable to build bonds between molecular chains. Results show that up to 25 kGy dose there is a slight crosslinking; after that the material is worsening because the degradation.

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