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EVALUATION OF ELECTRON BEAM IRRADIATION UNDER HEATING PROCESS ON VULCANIZED EPDM

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ABSTRACT

The Global consumption of rubber is estimated around 30.5 million tons in 2015, when it is expected an increase of 4.3% of this volume in the coming of years. This demand is mainly attributed to the production of elastomeric accessories for the automotive sector. However, the generation of this type of waste also reaches major proportions at the end of its useful life, when it is necessary to dispose the environmental liability. Rubber reprocessing is an alternative where it can be used as filler in other polymer matrices or in other types of materials. The devulcanization process is another alternative and it includes the study of methods that allow economic viability and waste reduction. Therefore, this study aims to recycle vulcanized EPDM rubber with the use of ionizing radiation. In this work we are using the electron beam irradiation process with simultaneous heating at absorbed doses from 150 kGy to 800 kGy, under high dose rate of 22.3 kGy/s on vulcanized EPDM powder and on samples about 4 mm thick. Their characterization, before and after the irradiation process, have been realized by thermal analysis and their changes have been discussed.

1. INTRODUCTION

Elastomeric materials have specific properties that allow the development and use of a variety of products [1]. The application of elastomeric compounds in the automotive industry has increased considerably; due this, high volume of parts are disposal and among these, thermosetting materials, that are not easily recyclable [1]. Thus, the environmental impact is evident, thereby promoting essential damage.

The existence of the cross-linked structure in the elastomer makes it impossible to recycle with conventional methods [1]. The rubber waste recovery is a wide theme that needs more research once each kind of rubber requires specific kinds of treatment.

Tang [2], in 2003 developed a process for recovering rubber cured with sulfur, such as natural rubber (NR), polybutadiene (BR), styrene-butadiene (SBR), ethylene-propylene diene (EPDM) polymer, neoprene (CR), and nitrile rubber (NBR). The process uses a combination with small amounts of non-toxic chemicals and a twin screw extruder, used to retrieve especially vulcanized rubber scrap [2]. The chemicals added to the vulcanized rubber, in combination with the extrusion process, contribute to suitably shear and devulcanize natural and synthetic rubber cured with Sulfur [2]. The recycled rubber produced by this process can be revulcanized as a new product without the addition of any binder and still retain most of the physical properties of the compound rubber stock; or the properties of the recycled rubber can be improved by the addition of virgin rubber [2].

In summary, all devulcanized tire can be milled and combined with conventional additives and cured for 10 minutes at 160 °C to obtain a product with physical properties of about 700 psi tensile strength, 180% elongation, and 71 N/mm in tear strength. In addition, the reused rubber can be mixed with virgin rubber at various proportions to produce new compounds. The properties of the resulting revulcanized material depend on the characteristics of the original compound and the raw material. For example, industrial rubber scrap provides better physical properties than scrap of post-consumption [2].

Hirayama and Sharon [3], in 2012 studied the milling process of styrene-butadiene rubber (SBR) and evaluated for subsequent devulcanization parameters of devulcanization processes by microwaves. The results showed that an effective reduction of the rubber particle size was not possible with the cryogenic grinding and the devulcanization by batch was more efficiently obtained compared to the method developed in continuous mode [3]. The improvement of elastomer devulcanization techniques by microwave shows promising prospects for mechanical recycling of thermoset elastomers [3].

Zeid and collaborators [4,6], studied in 2008 the mixture of composite rubber of ethylene-propylene diene rubber (EPDM), high density polyethylene (HDPE) and tire rubber powder (GTR) that were mixed in different proportions and subjected of gamma irradiation at various doses up to 250 kGy. The physical, mechanical and thermal properties were investigated as a function of irradiation dose and composition of the mixture. The gamma irradiation led to a significant improvement in the properties of all mixture compositions [4,6]. The results indicated improvements in properties are inversely proportional to the ratio of the replaced GTR. This improvement is attributed to the development of interfacial adhesion between GTR and the components of the mixture. The results were confirmed by analysis of the fracture surfaces by scanning electron microscopy [4,6].

Van Duin and collaborators [5,6] in 2009 described an invention concerning a method for devulcanizing EPDM rubber cured with sulfur. The devulcanization occurs under heating (275 °C +/-) of the rubber in the presence of a devulcanizing agent. The devulcanizing agent is an amine compound selected from the group constituted by octylamine, hexadecylamine, dioctylamine, trioctylamine, benzylamine and 4-piperidinopiperidine. A disadvantage of this method is only sulfur crosslinks the rubber main chain and it causes the broken chain [5,6], besides, this method also causes the split of the main chain. Additionally, other undesirable side reactions can occur, such as forming cyclic compounds [5,6]. The devulcanization of sulfur-cured rubber was carried out for 2 hours in high-pressure press at 267 °C and pressure of 7.6 MPa in a nitrogen atmosphere without devulcanizing agent. The method has been proved particularly suitable for the devulcanization of sulfur cured rubbers and polymers with few unsaturated carbon-carbon bonds in the main chain [5,6].

In this context, the present study explore the irradiation process by electron beam under simultaneous heating and its effects on vulcanized EPDM .

2. MATERIALS AND METHODS

2.1. Feedstock

The supplied material is vulcanized EPDM in powder and in slices. This material was supplied by EDRAECOSISTEMAS, where its characteristics are presented in table 1 and probable composition is in table 2.

Table 1: Charcateristics of vulcanized EPDM.

Parameter	Characteristic value*
Hardness Shore "A"	70
Stress Rupture (MPa)	10 MPa 11.5 min.
Break elongation (%)	350 560 min

* The tests were performed according to the ASTM D 2000 standard for rubber classification [7].

Table 2: Formulation of the elastomer in the process f vulcanization [8].

Keltan 5508	**100**
N 660	200
Parafine Oil	155,00
Zinc Oxide	5,0
Vulcallux BD	2,0
Polyethylene wax	3,0
MBTS	1,5
TMTD	0,5
ZBDG	2,0
Sulfur	1,5
Total	470,5

2.2. Preparation of vulcanized EPDM Samples and irradiation process

Powder and slices of 4 mm thickness samples were distributed in petri dishes to undergo radiation under heating process .

Powder and slices of material was placed in a heating chamber at 160 °C (temperature recommended by ASTM D 1349-14 [9]).

The irradiation process using the thermal chamber was performed in a Job 188 Dynamitron® Electron Beam Accelerator with 1.5 MeV of energy. The intensity of the beam was 25 mA and the beam power was 37.5 kW; the scan range was 50 to 120 cm. Absorbed doses of 150 kGy, 200 kGy, 400 kGy, 600 kGy, and 800 kGy and dose rates of 22.3 kGy/s.

2.3. Characterization of Compounds

2.3.1. Hardness

The hardness was determined according to ASTM D 2240 [10] in triplicate with a hardness tester model Digital S1 from Instron brand.

2.3.2. Thermogravimetric analysis (TGA)

The evaluation of thermal decomposition of materials was performed in a TGA model SETARAM - Labsys type, under synthetic air atmosphere (50 ml/min), in a range from 25 to 800 ° C and heating rate of 10 °C/min.

2.3.3 Determination of the swelling index of the rubber

The determination of the swelling index comprises the variation of initial and final mass of the sample after swelling in a suitable solvent. The result indicates if sample composition sufered changes. The tested samples were previously weighed and immersed in toluene according ASTM D 3616 [11], being analyzed untill weight stabilization in a period between 24 to 120 hours.

Degree of Swelling was calculated by:

$$Q = (M - Mo) / Mo \times 100$$

Where:

Mo = is the initial mass of sample (g), and
M = is the mass end of the sample (g).

3. RESULTS AND DISCUSSION

As it is observed in Fig. 1, Shore A hardness presents a deep reduction on sample irradiated at 400 kGy (about 30 A units), where it characterizes a modification in this material structure. In other verified irradiation doses, samples had a small reduction (lesser than 8 A units) compared to reference sample.

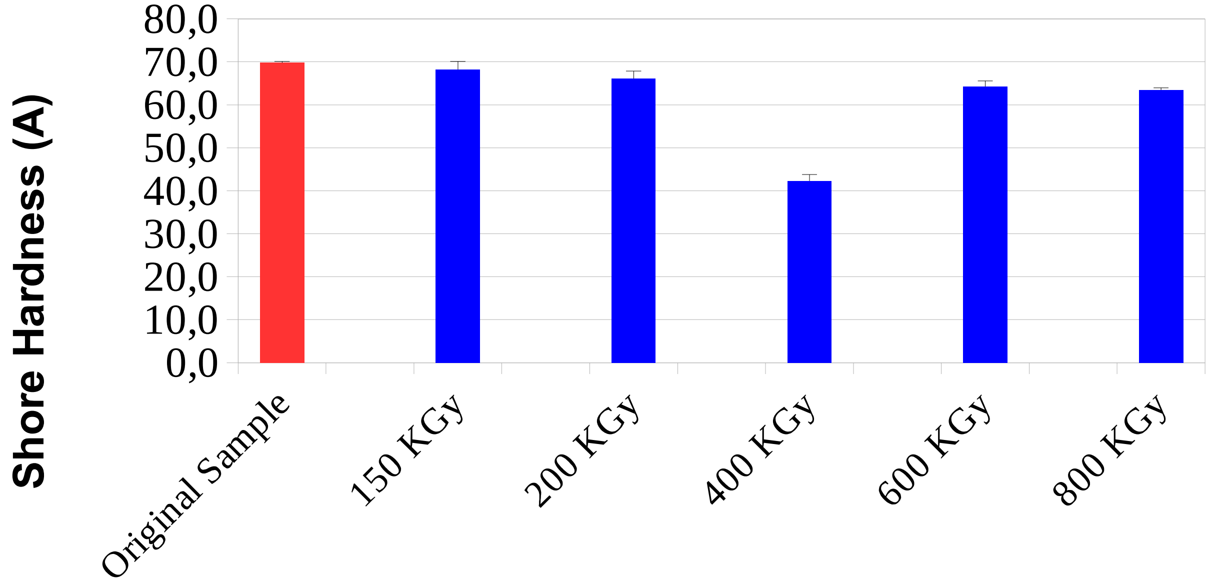

Figure 1: Shore hardness of original and irradiated EPDM samples.

Fig. 2 shows thermal analysis of pure Keltan EPDM 5508, where is observed a weight loss between 440-500 °C in a single event.

However, vulcanized EPDM samples subjected to the process of ionizing radiation of electron beam (Fig. 3), show a mass loss between 250 - 400 °C concerning the dilution oil. According to Bhowmick, et al [12,13], the use of these oils favors processing ensuring a good surface finish, and promotes the vulcanization process. Another degradation track is located approximately at 450 °C and is relative to the organic material referent to the fraction of EPDM elastomer used in the composition [13]. In addition to the mass losses related the oil and EPDM. Another phenomenon that can be observed is the degradation related to the combustion of carbon black (NC).

Irradiated vulcanized EPDM samples shows a decrease of the region corresponding to the fraction of volatile additives (oil and parafin) and of EPDM elastomer and an increase in the proportion of final degradation products, that suggests the irradiation process under simultaneous heating promotes bond sicission. It seems samples irradiated at 400 kGy have higher proportion of EPDM elastomer than that samples irradiated at 150 kGy and 800 kGy. This last suggests 400 kGy is the ideal absorbed dose to broke the cross-link responsible for vulcanized material without a great elastomer degradation.

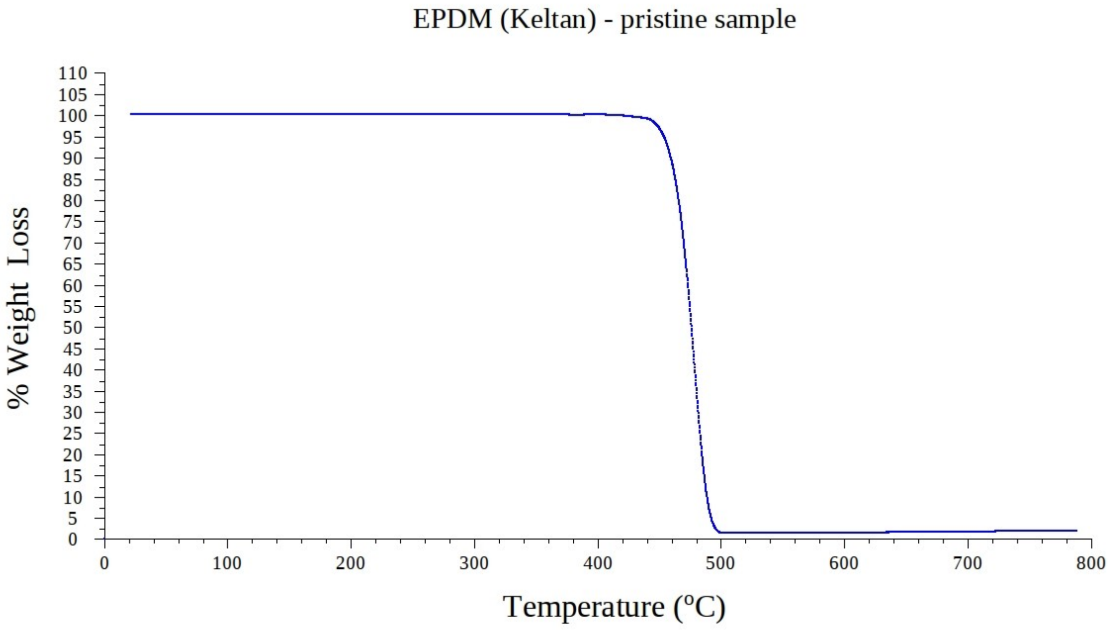

Figure 2: Thermogravimetric Analysis of pure Sample of EPDM 5508.

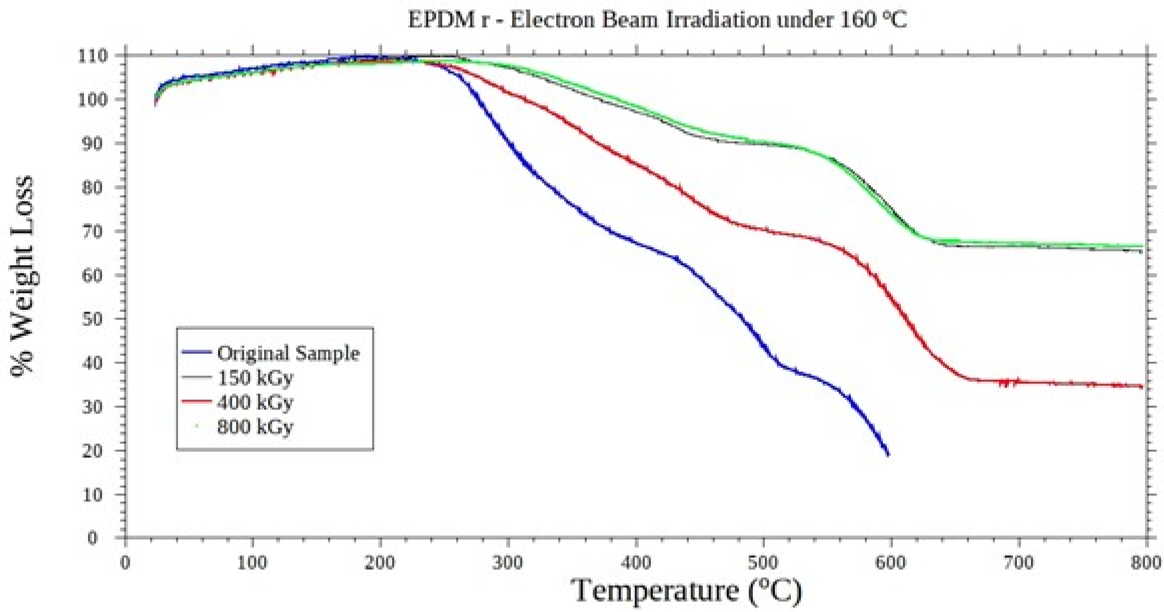

Figure 3: Thermogravimetric Analysis of the samples.

On rubbers, the phenomenon of swelling is inversely proportional to the density of cross-link bonds [14], that is, the bigger the swelling, the bigger the empty space between its molecule chains, what means that there are less density of bonds, which indicates a probable devulcanization.

In the swelling index test, the sample that showed the biggest swelling index was the sample with the dose of 400 kGy, in comparison with the other samples, as shown on the graphic of Fig. 4. This result indicates the ideal dose to cause bonds scission and a consequent sample devulcanization.

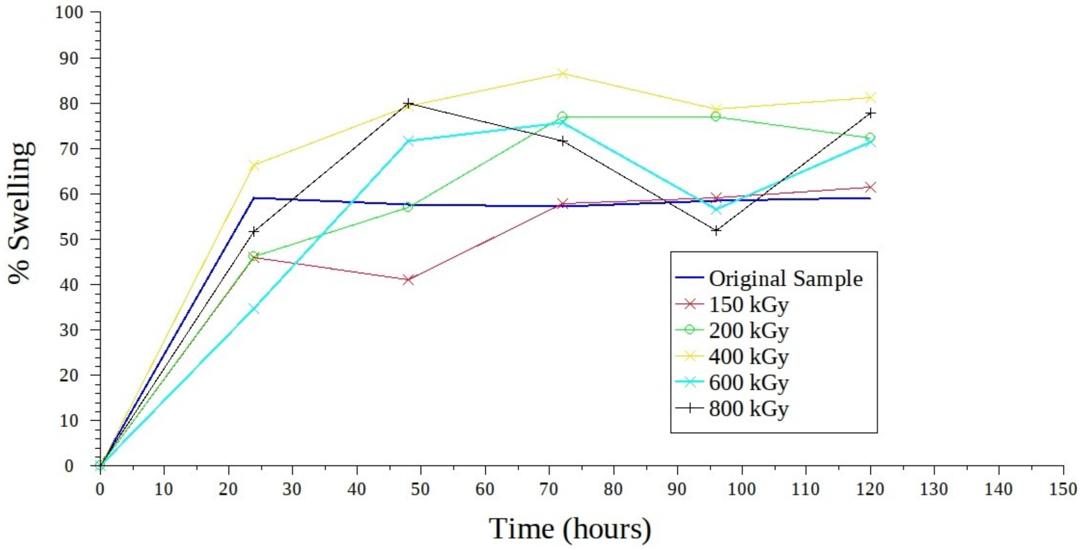

Figure 4: Results of Determination of the swelling index of the EPDM samples.

4. CONCLUSION

Electron beam irradiation with simultaneous heating can be a process highly relevant on rubber processing. In this work, the high temperature and a dose of 400 kGy allow the modification of vulcanized EPDM, resulting in a material with low hardness and with a large swelling characteristic. These results suggest the ideal thermal and irradiation dose are essential to allow bond scission. The high value of absorbed dose may be related to the high radiation resistance that is a characteristic of EPDM Keltan 5508 samples.

This preliminary results on effects of irradiation process under simultaneous heating pointing this non-hazardous process may used on the reprocessing and reuse of this material.

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