2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-05-2

DEGRADING RADIATION EFFECTS ON PROPERTIES OF BROMOBUTYL RUBBER COMPOUNDS

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ABSTRACT

The understanding of chemistry involved in degradation induced radiation is becoming more and more relevant in the re-use of polymeric materials, as well in beneficial radiation uses. Degrading radiation effects have been considered from viewpoint of controlled degradation for isoprene/isobutene in rubbers for recycling purposes. Bromobutyl rubber (BIIR) is an isobutylene/isoprene copolymer comprising 1.9 to 2.1% bromine and has a lot of applications including in tires air-chambers. In this work there were evaluated gamma-irradiation effects for re-use or recycling objectives in elastomeric bromobutyl compositions irradiated at 5, 15, 25, 50, 100, 150 and 200 kGy. Mechanical properties, hardness and swelling were assessed in non-vulcanized and vulcanized rubber, non-irradiated and irradiated at different doses. The major gamma radiation effect in butyl rubber is the generation of free radicals along changes in mechanical properties. Irradiation effects in bromobutyl rubber compounds were comprehensively investigated, demonstrated and discussed.

Keywords: degradation, bromobutyl rubber, radiation, properties

1. INTRODUCTION

Bromobutyl rubber (BIIR) is an isobutene/isoprene copolymer containing 1.9 to 2.1% bromine [1]. Due to the high saturation in Bromobutyl rubber main chain, the cure can be more complex when compared to general use rubbers, such as natural or polybutene elastomers. They have much more applications besides in air-chambers tires, such as tire side walls, automotive motors assembling, for special purposes, belt conveyor coatings and pharmaceutical uses [2].

Gamma-rays have been extensively used in last 50 years in polymers irradiation processes [3]. According IAEA (International Atomic Energy Agency) [4] there are 160 gamma-rays processing units worldwide, 30% for polymers processing aiming to an optimization of materials properties [5].

When Bromobutyl rubbers are subjected to high energy radiation can occur a great variety of chemical reactions and excitation events following initial ionizations.
These reactions change rubbers molecular mass via scission or crosslinking and interfere in physical and mechanical properties [6]. Main and prevalent exposure effect due to high energy radiation on butyl rubber is chain scission. Nevertheless, halogenated butyl rubbers

answer differently to high energy radiation effects [7]. C – Br bond energy is lower than C – H bond energy; so, butyl rubber halogenation used to build Bromobutyl rubber improves crosslinking efficiency under radiation [8], according shown in Figure 1. Butyl rubber via bromine is more effective for increasing crosslinking via ionizing radiation.

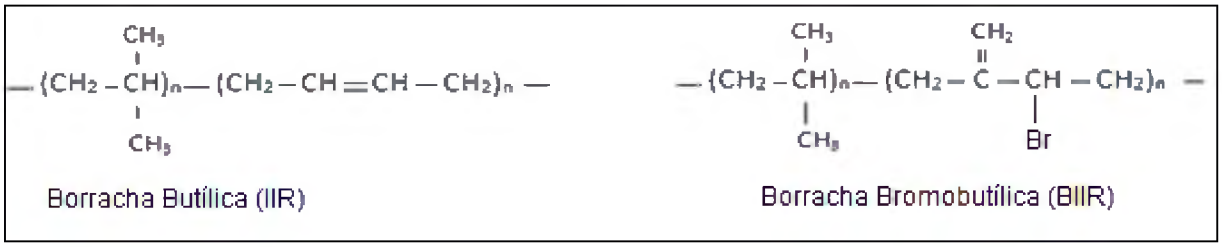

Figure 1: IIR bromine effect in efficiency of radiation crosslinking.

Besides Bromobutyl rubber vulcanizates have a lot of ingredients such as: fillers, carbon Black, activators and vulcanizing agents, chemical behavior under radiation is determined by rubbers chemical structure; so, degradation degree depends on fillers nature and vulcanization system used [9].

This work aims to show effects of gamma radiation in mechanical properties of bromo-rubbers. Compounds were subjected to 5, 15, 25, 50, 100, 150 and 200 kGy radiation doses. Irradiation effects in mechanical properties of rubber compounds were investigated.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Bromobutyl rubber used in this study was bromobutyl X-2 from Exxon Mobil Chemical, having as reference commonly formulations in tires and automotive spare-parts industry (Table 1). Admixtures were prepared in an open roll-mill (*Copê*), 40 kg capacity, according to ASTM D-3182 [10].

Table 1. Formulation of Bromobutyl rubber.

Ingredients	Amounts (phr)
Bromo-butyl rubber	100
Zinc Oxide	3
Acid Stearic	1
Plasticizer	25
Carbon Black	70
Sulfur	0.5
MBTS	0.5
ZMDC	0.1

Used additives such as: zinc oxide, sulfur and stearic acid were supplied by Basile Química; MBTS e ZMDC by Enro Industrial Ltda; Carbon black, from Cabot Brasil. All materials were used as received.

Samples were cured in an electrically heated HIDRAUL-MAQ at 5 MPa pressure and 180°C temperature to their optimum cure times (determined from a rheometer Monsanto R-100).

2.2. Methods

Cure sheets in 11.5 x 11.5 x 0.1 cm^3 dimension, 250g total weight, were irradiated in Embrarad/CBE, gamma rays Cobalt 60 (^{60}Co) in air, at 5 kGy/h rate, within a 5, 15, 25, 50, 100, 150 and 200 kGy doses range.

2.2.1 Tensile Strength and Elongation at Break

Tensile Strength and Elongation at Break were analyzed according to ASTM D-412 [11], by using a C model specimen, in an essay universal machine (EMIC), model DL 300, 300 kN maximum capacity, 500 mm/min grips speed, at room temperature (Figure 2).

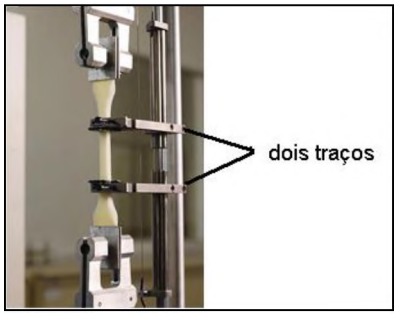

Figure 2: Picture of tensile strength and elongation at break specimen.

2.2.2 Hardness

Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values, derived from ASTM D 2240 [12]. Hardness is one of the properties the most evaluated in rubbers, being the Shore A, *Instrutemp,* portable digital model Dp-100 the durometer used herein. This instrument is provided with a conical needle emerging from the apparatus, kept at zero level by means of a spring.

2.2.3 Determination of rubber swelling index

Previously weighed 1.5 x 1.5 cm specimens were immersed in toluene up to weight stabilization (approximately Five days). At the end of essay, specimens were weighed and dried at room temperature, for 24 hours. These analyses were performed according ASTM D-3616 [13]. Swelling degree was calculated in accordance with Equation 1:

$$Q = [(M - M_o)/M_o] * 100 \qquad (1)$$

Where: M_0 is sample initial mass (g) and M, the final mass of sample (g) [14]

3. RESULTS

In Figure 3 are shown results for Tensile Strength and in Figure 4 are shown Elongation at Break accomplished in Bromobutyl rubber, irradiated and non-irradiated.

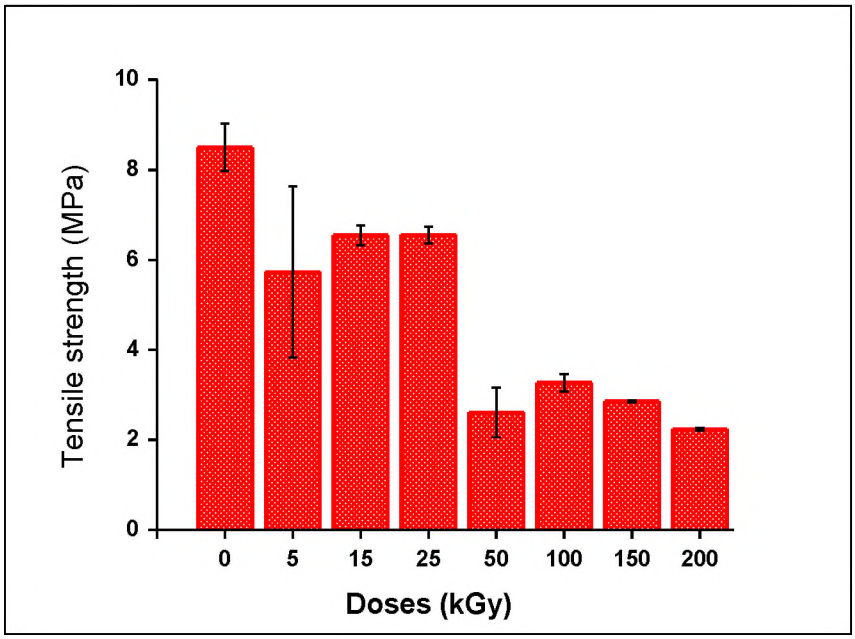

Figure 3: Tensile strength for irradiated and non-irradiated Bromobutyl rubber.

Analyses results showed that after irradiation occurs a reduction in tensile strength values, even for low doses such as 5 kGy, indicating the prevalence of chain scission with consequent mass molar reduction, because smaller polymeric chains break easier. For doses from 5 to 25 kGy it can be observed scission and crosslinking simultaneous events. Build-up of cross linked structures can be attributed to free-radicals and strong bonds from hydrogen bonds between halogens and hydrogen. Hydrogen bridges are stronger intermolecular forces and a special type of permanent dipole; they occur when a hydrogen atom is connected to a very electronegative element as fluorine, chlorine, bromine, oxygen or nitrogen, constructing a very strong dipole [15]. For doses above 50 kGy it is observed the prevalence of chain scission and further polymeric chain degradation.

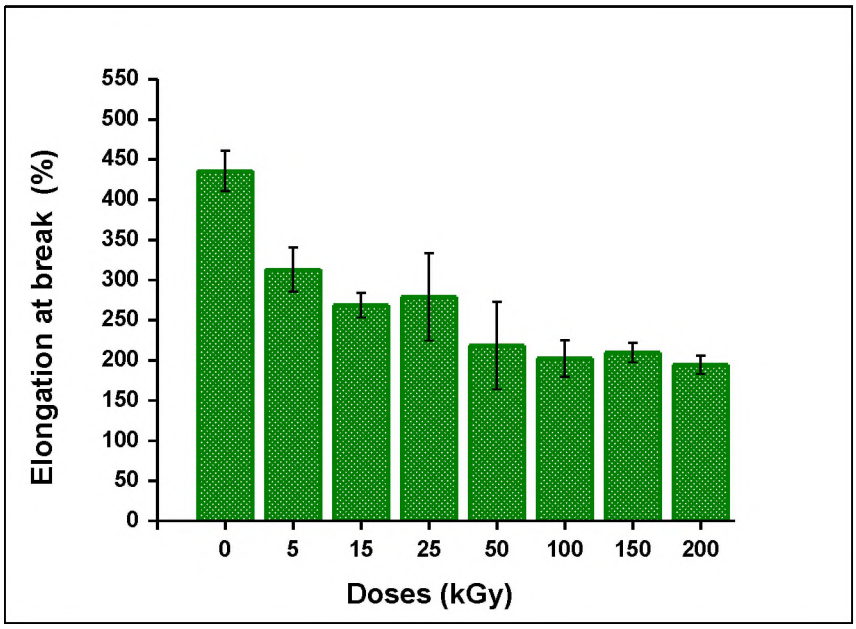

Figure 4: Elongation at break for irradiated and non-irradiated Bromobutyl rubber.

Figure 4 showed that elongation at break for Bromobutyl rubber compound presented values reduction after irradiation pointing toward predominance of chain scission. Nevertheless, for all applied doses within 5 to 200 kGy it is observed an apparent similarity for elongation at break values. A more probable explanation for the phenomena is that hydrogen bridges make viable intermolecular interaction in spite of intense chain scission.

Hardness results for Bromobutyl rubber compounds before and after irradiation are shown in Figure 5.

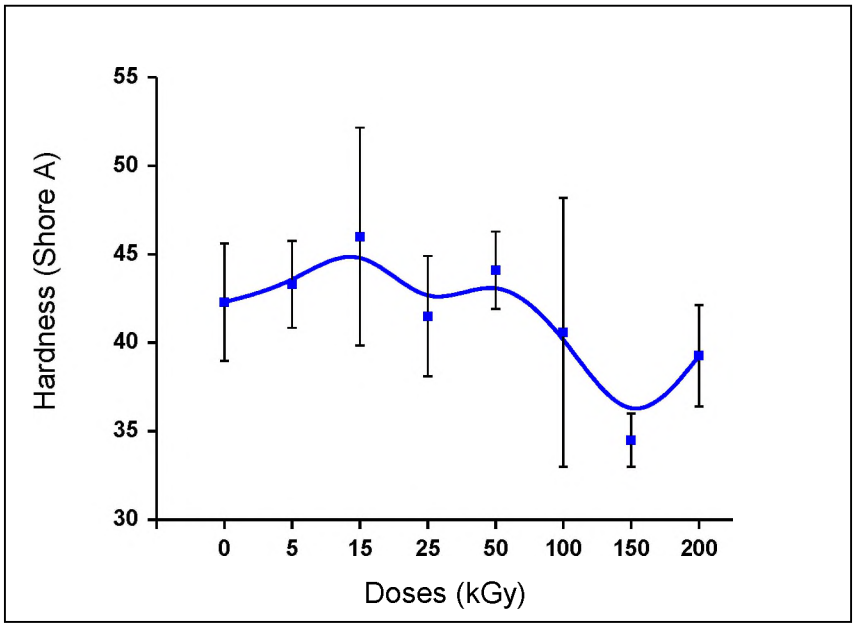

Figure 5: Hardness for irradiated and non-irradiated Bromobutyl rubber.

When analyzing hardness it was verified that after irradiation practically occurs values stability up to 15 kGy pointing toward simultaneous occurrence of scission and crosslinking; and at 25 kGy it was observed very low values indicating high chain scission and reduction of molar mass and crosslinking density. At doses higher than 25 kGy, in spite of intense chain scission – due to higher free radicals build-up, some crosslinking points can recombine and originate new crosslinking reactions.

Vulcanizates rubbers are insoluble in solvents due to crosslinking bonds among chains, that have capacity of absorbing liquids and this causes a volume raise, known as swelling phenomena in solvents. Swelling index of irradiated and non-irradiated of Bromobutyl rubber samples were determined by comparing initial mass (g) with final mass (g), variations in %. specimens mass variation was daily accomplished and results are shown in Table 2, where are exhibited values from average of 3 measurements individually for each time.

Table 2: Swelling results for Bromobutyl rubber, non-irradiated and irradiated at 5, 15, 25, 50, 100, 150 and 200 kGy

Doses (kGy)	24 hs	48 hs	72 hs	96 hs	120 hs
0	152.48	152.15	152.82	152.42	151.55
5	152.20	150.92	150.43	150.57	150.11
15	152.20	150.92	150.43	150.57	150.11
25	155.77	155.88	156.19	155.22	153.36
50	160.80	157.91	158.70	157.67	155.69
100	164.49	158.53	158.85	165.96	164.87
150	165.80	163.56	160.33	158.93	155.15
200	150.63	141.59	137.28	136.08	137.01

It was observed for samples from 0 to 50 kGy the occurrence of mass stability after 24 hours, suggesting the existence of empty spaces in polymeric net due to chain scission and the presence of some crosslinking points: if the polymer is provided with crosslinking among chains, it just swells up to an equilibrium swelling [16]. When increasing the dose (from 100 kGy to 200 kGy) occurs mass variation reduction after 48 hours immersion solvent pointing toward lesser crosslinking bonds due to intense chain scission: when penetrating inside a polymer with low density of crosslinking bonds the solvent has a plasticizer action on it, forming a gel swelling layer that makes the polymer susceptible to break and without empty spaces impeding solvent penetration [17].

3. CONCLUSIONS

When Bromobutyl rubber is exposed to high ionizing radiation, as gamma rays, occur simultaneously chain scission and crosslinking. For low doses it was kept the scission and crosslinking and at high doses, degradation.

It can be concluded that radiation can change the mechanical properties of rubber by destroying the cross-links that maintain united rubber molecules. By affecting this cross-

linkage, radiation can change the tensile strength, elongation at break and the hardness of the rubber.

Swelling test showed that irradiated Bromobutyl rubber can be reclaimed due to radiation instability at low doses. The radiation processing of Bromobutyl rubber in doses higher than 100 kGy creates a medium plasticized material.

ACKNOWLEDGMENTS

The authors thank Embrarad/CBE for irradiation process, Pirelli for elastomers, and Basile Chemistry for raw materials, IPEN/CNEN-SP and CNPQ Process n ° 140175/2010 agencies for financial support.

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