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HIGH ENERGY RADIATION EFFECTS ON MECHANICAL PROPERTIES OF BUTYL RUBBER COMPOUNDS

Cristina A. Pozenato[1], Sandra R. Scagliusi[1], Elisabeth C. L. Cardoso[1]andAdemar B. Lugão[1]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
cangioletto@gmail.com

ABSTRACT

The high energy radiation on butyl rubber compounds causes a number of chemical reactions that occur after initial ionization and excitation events. These reactions lead to changes in molecular mass of the polymer through scission and crosslinking of the molecules, being able to affect the physical and mechanical properties. Butyl rubber has excellent mechanical properties and oxidation resistance as well as low gas and water vapor permeability. Due to all these properties butyl rubber is widely used industrially and particularly in tires manufacturing. In accordance with various authors, the major effect of high energy, such as gamma rays in butyl rubber, is the yielding of free-radicals along with changes in mechanical properties. There were evaluated effects imparted from high energy radiation on mechanical properties of butyl rubber compounds, non-irradiated and irradiated with 25 kGy, 50 kGy, 150 kGy and 200 kGy. It was also observed a sharp reducing in stress rupture and elongation at break for doses higher than 50 kGy, pointing toward changes in polymerical chain along build-up of free radicals and consequent degradation.

1. INTRODUCTION

Butyl rubber (IIR) is a copolymer of isobutene (98%) and isoprene (2%) [1]. Its chain has a very low unsaturation level that imparts excellent ageing resistance, low gases permeability, good thermal stability, high resistance to oxygen, ozone, solar radiation, humidity and chemical substances attack [2,3].

Currently, butyl rubbers with unsaturation degree within 0.8% to 2.2% range are produced; higher the degree, higher vulcanization speed and heat resistance.Butyl rubber has been used in applications such as tires (air-chambers, tires inner coating, etc..), lids, gaskets, etc….[4].

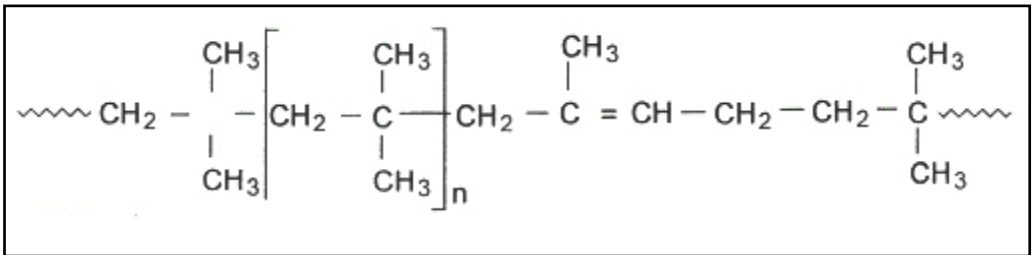

Figure 1: Butyl rubber structure.

Due to the low insaturation degree in polymeric structure of butyl rubbers, the use of faster cure agents such as MBTS, TMTD, etc, in order to obtain compounds with more effective vulcanization is required. Chemical crosslinking promoted by vulcanization inserts covalent bonds along molecular chain.Cure systems are specified according to product final application and how will be its behavior plays a crucial role on compound processing [5].

Gamma rays are comprehensively used in last 50 years in polymers irradiation processes [6] aiming to the modification of their properties. For butyl rubbers the main effect caused by high ionizing energy is chain scission [7].This characteristic is explained by the presence of quaternary carbon atom in isobutene present in butyl rubber macromolecules. Chain scission occurred in polymeric chains is accompanied by a significant reduction in molar mass [8,9].

The objective of this work is showing gamma radiation effects in mechanical properties of butyl rubber irradiated at 25 kGy, 50 kGy, 150 kGy and 200 kGy. This study,so far, is purely scientific, and will be used in subsequent studies.

2. MATERIALS AND METHODS

2.1. Materials

Elastomer used as matrix was butyl rubber Butil 268, from EXXON MOBIL CHEMICAL, kindly supplied by Pirelli; zinc oxide, stearic acid, sulfur, 2,2-dithiocarbaptobenzothiazol (MBTS) and disulfide of tetramethyltiuram (TMTD), all of them commercial grade and used as received.

2.2. Processing

Samples were prepared in an open mill (Copê), with two rolls, 40 kg capacity, according ASTM D-3182 [10], within 50^{o} to 60^{o}C temperature range,

Compound prepared was immediately vulcanized in a HIDRAUL-MAQ hydraulic press under 5 MPa pressure, according ASTM D-3182 [10], at 180^{o} C, for 4 minutes; afterwards, wrapped in plastic bags and sent to irradiation, in air, in CBE, via Nordion Canadian irradiator, Cobalt 60 source, model JS 7500, .5 kGy h^{-1} rate, γ rays, at 25, 50, 150 and 200 kGy.

2.3. Characterizations

Analyses were accomplished in accordance with ASTM norms, in triplicate, for providing results average, Specimens were cut in accordance with specified method for each essay. There were performed following tests:

Hardness: values were determine according to ASTM D- 2240 [11], via Shore Durometer, A, Instrutemp, portable digitalmodel Dp-100.

Tensile Strength and Elongation at Break: Tensile strength and Elongation at Break analyses were accomplished according ASTM D-412 [12], by using a model C specimen, in an essay universal machine (EMIC), model DL 300, 300 kN maximum capacity, 500 mm/min, 500 mm/min grips speed, at room temperature.

Scanning Electronic Microscopy (SEM): Compounding morphology characterization was performed in an electronic microscope HITACHI, model TM 3000, located in CCTM – IPEN/CNEN/SP. Samples were accomplished just at the rupture point in specimens subjected to tensile-elongation essays, 200 times enlargement.

3. RESULTS AND DISCUSSIONS

Tensile strength and elongation at break are shown in Figure 2:

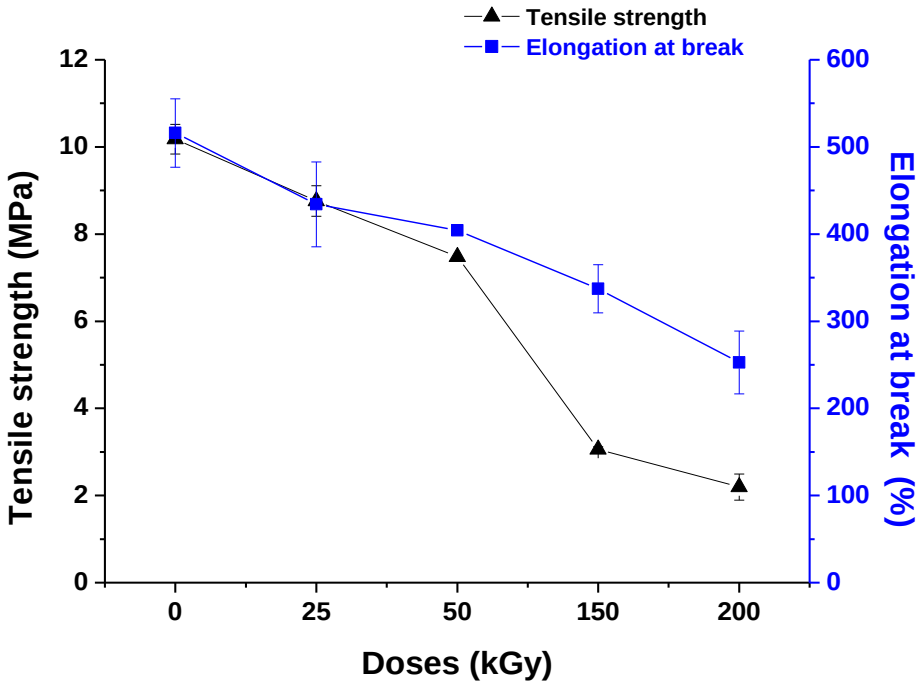

Figure 2: Ionizing radiation effect in tensile strength and elongation at break

Butyl rubber compounds showed a reduction in tensile strength proportional to doses, indicating that up to 25 kGy there was the simultaneously occurrence for scission and crosslinking; for doses higher than 50 kGy, just an intense chain scission. Such effect can be justified by a reduction in molar mass, because smaller polymeric chains are provided with a lower molecular mobility and, consequently, a lower tensile at break [8].

For elongation at break after radiation it was observed a significant reduction in values proportional to radiation doses. This is an indicative of chain scission and further molar mass reduction. The intense chain scission is responsible by changes in compound properties [13].

Radiation doses effects on butyl rubber hardness is shown in Figure 3.

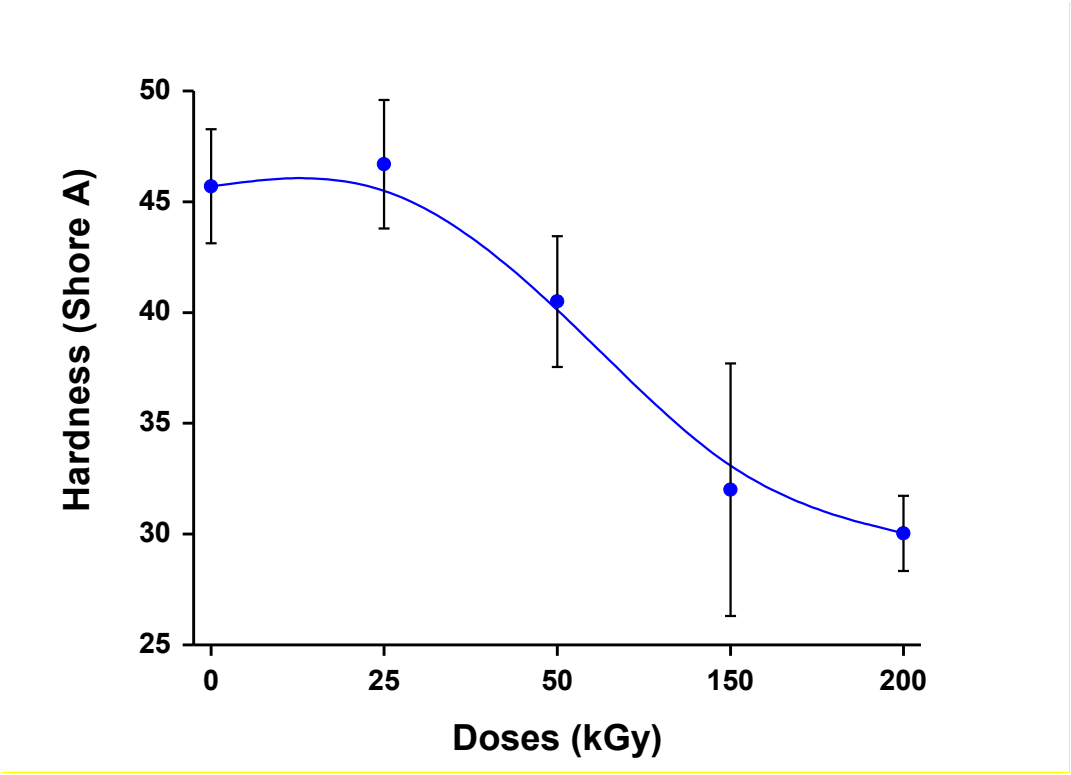

Figure 3: Ionizing radiation effect on Shore A hardness for butyl rubber compound sulfur cured.

This property is related to cross linked bond build-up [14]. For doses lower than 25 kGy it was observed a similarity in hardness values pointing toward the occurrence of scission and crosslinking. For doses higher than 50 kGy occurred predominantly chain scission, probably due to the intense build-up of free radicals that react with peroxide radicals formed in irradiation under O_2 atmosphere and cause compound degradation [15]. The presence of crackles and holes in compound shown in SEM analyses could be one of explanations for sharp reduction in hardness values.

SEM pictures for butyl rubbers are shown in Figure 4.

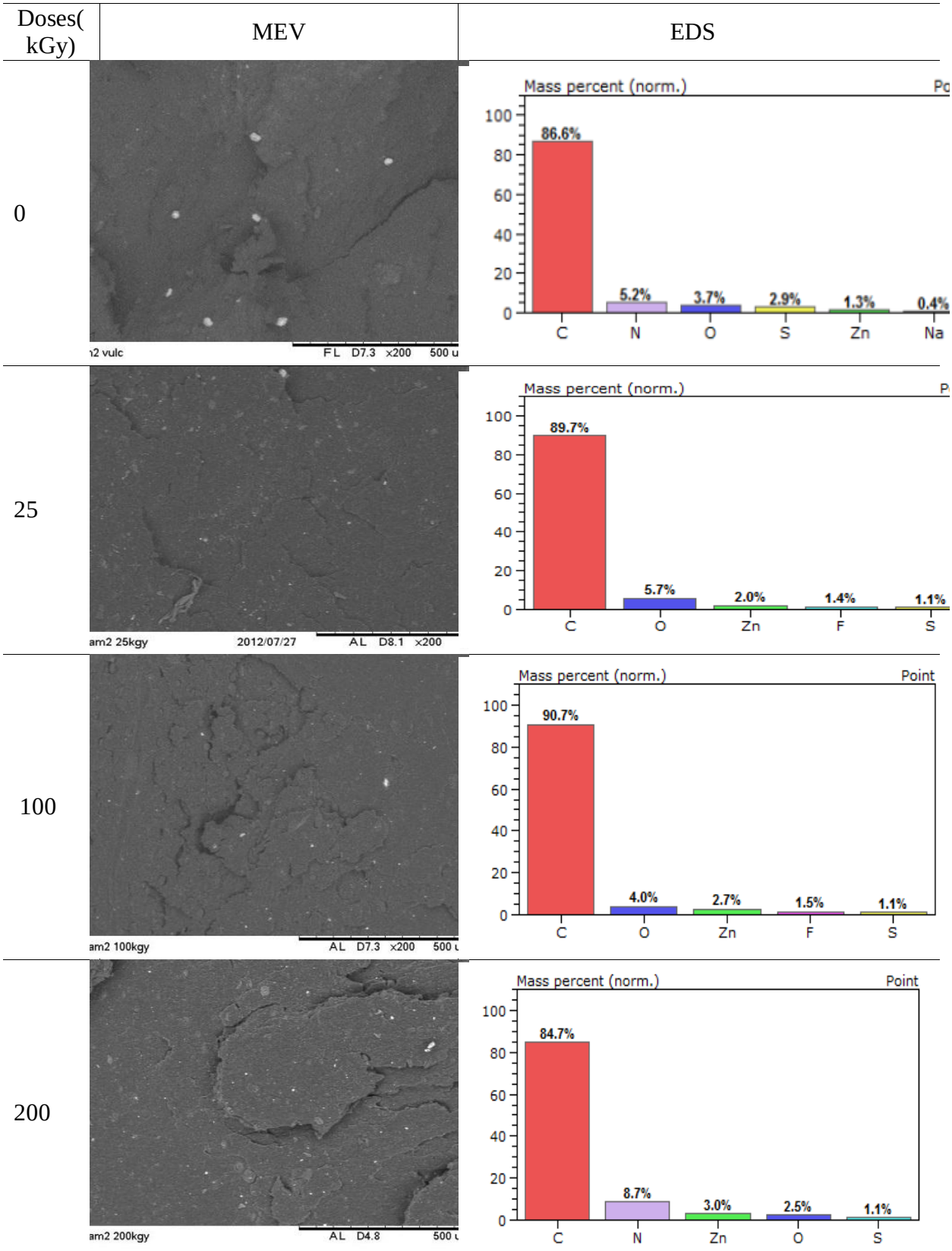

Figure 4: SEM pictures and EDS graphs for rupture surfaces in non-irradiated and irradiated rubber, at 25 kGy, 100 kGy and 200 kGy.

SEM pictures for rupture surface in butyl rubber 200 times enlarged showed that in non-irradiated sample there are a few disperse materials on the surface, ratified by EDS results, where it can be observed the amount of substances present in compound rupture surface, even nitrogen from the build-up of nitrosamines generated from the reaction of vulcanizing accelerators and from nitro-agents during rubber processing. For 25 kGy doses it was observed a reduction of disperse substances on rupture surface, as well EDS result showed a reduction in disperse sulfur indicating recombination of molecular chain due to low build-up of free radicals and formation of new crosslinking points. For higher doses (100 kGy and 200 kGy) it was observed a more porous and weak surface pointing toward the polymer degradation.

4. CONCLUSIONS

The use of high ionizing energy (gamma-rays) changed mechanical properties of butyl rubber. Elongation at break showed a reduction proportional to applied dose, while tensile at break diminishes abruptly for doses higher than 50 kGy. Hardness of these rubbers showed too a reduction proportional to dose.

The results show that the main effect of ionizing radiation in butyl rubber is chain scission and that this type of rubber exhibits a very high degradation degree for very high doses.

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