

## Research Article

# Butyl Rubber Recycling Via Gamma Radiation Followed by Mechanical Shear

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## Abstract

Polymeric materials (plastics and rubber) have been contributing in a continuously and raising way for the generation of litter and industrial wastes discarded in landfills. The implementation of new technologies for the reduction of polymeric materials, acceptable from the environmental viewpoint and at an effective cost, proved to be a great problem, due to complexities inherent for the re-use, especially of rubbers. Gamma ionizing radiation has capacity for changing structure and properties of polymeric materials and can be applied to almost all types of polymers; irradiation is an expectation for problem-solving of rubber wastes management that can be utilized as raw-materials or chemical additives. The relatively low degree of unsaturation presented by butyl rubber (IIR) is responsible for the great resistance of butyl rubber to oxygen, ozone and heat, as well as low gas and water vapor permeability. At the initial stage of irradiation, the degradation of bromobutyl rubber occurs predominantly via random chain-scission and chain-crosslinking may occur caused from the isoprene copolymerized units. This work aims to the introduction of a new recovery technique for bromobutyl rubber, by using processing via gamma rays followed by shear. Rubber was irradiated at 0 kGy, 5 kGy, 15 kGy, 25 kGy, 50 kGy, 100 kGy, 150 kGy and 200 kGy doses, in order to study the feasibility of bromobutyl rubber for recycling. 25 kGy doses, applied to butyl rubber further sheared, pointed toward a less degraded material, indicating that this type of elastomer is able to be incorporated to a new rubber compound and replacing some parts of pristine rubber in formulations without imparting great losses in physical-chemical properties.

**Keywords:** Recycling, Gamma Rays, Butyl Rubber, Irradiation.

## Introduction

Polymeric materials (plastics and rubbers) cover a raising continuous proportion of urban and industrial residues disposed in landfills. Implementation of new technologies toward reduction of polymeric residues, acceptable under environmental viewpoint and at an effective cost proved to be a great problem, due to inherent complexities for polymers reuse [1].

Rubbers exhibit a very low natural decomposition [2] because of their chemical structure resistant to environmental conditions and to enzymatic degradation and microorganisms. Rubber recovery is hindered by rubber insolubility due to their crosslinked structures [3]. In addition, this tridimensional structure causes various problems for recovering and reprocessing of these materials [4].

Consequently, most of rubber scraps, especially tires, are discarded and disposed in landfills. These rubber scraps are used too as combustible and incinerated for electricity generation, considering that costs involved in these operations are very high. Other ways of rubbers reuse comprise use in asphalt, manufacturing of shoes soles, gaskets, pluvial ducts, pavements for sportive courts, industrial pavements, besides carpets for cars. So, recycling and recovering are considered the best options for management of these residues [1, 5].

Gamma ionizing radiation has capacity for changing structure and properties of polymeric materials and can be applied to almost all types of polymers [6]; irradiation is an expectation for management problem solving of rubber residues that can be used as raw materials or chemical additives.

Recovery of rubbers products can be accomplished by following processes:

- Chemical processes: they are used especially in high-pressure reactors with specific solvents and at high temperatures, for ameliorating reaction yield [1,7]. These processes have the advantage of causing

selective breakage of polysulfide cross linkages without a significant rupture of main chain [8].

- Biological processes: they are selective processes where chemical bonds of vulcanized rubbers are broken and sulfur is removed by means of bio-treatment with bacteria. Some of them have been used in NR, SBR and BR devulcanization as *Nocardia*, *Thiobacillus* and *Mycolata*, without causing a significant degradation of polymeric hydrocarbon. In literature, these methods are quoted as of de-vulcanization low throughput because they are effective just in samples surface and are not viable to be used in industrial scale [9,10] and

- Physical processes that comprise:

- Mechanicals (rubber is sheared by means of open mixers [1];
- Thermomechanical (rubber is immersed in an appropriate solvent to be swollen and further transferred to a cylinder [1];
- Crio-mechanicals (rubber is dipped in liquid nitrogen and micronized in ball or hammer mills [1];
- Ultrasound (within 16 KHz to 1 MHz, de-vulcanization is performed through combination between extrusion and application of ultrasound energy [11, 12] and
- Micro-waves (with frequencies within 300 MHz to a 300 GHz range, effective for accomplishing recycling of polar rubber crosslinks causes

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destabilization of tridimensional network [13,14].

In physical processes shown, the most part of them generates rubber powder form that can be used as inert load. Therefore, it is advisable a physical system that enables the attainment of recycled rubbers that act as active loads.

This study intended for rubber recovering and /or recycling used the processing via gamma rays followed by shearing in open cylinder. It was studied, specifically, the acquisition of de-vulcanized rubbers that allow a new crosslinking (or vulcanization).

## Materials and Methods

### Obtainment of formulations

Butyl rubber used in this study was butyl rubber grade 268 from Exxon Mobil Chemical. It was studied an elastomeric composition having as reference a formulation used in tires and auto-parts industry. Above-mentioned composition was irradiated and further sheared aiming to utilization via re-vulcanization. Formulation used in this study is described in Table 1 and components amounts are in phr or in parts in weight of material by one hundred parts of rubber.

Admixtures were prepared in an open roll-mill, each roll with a 40kg capacity. The samples were cured in an electrically heated HIDRAUL-MAQ, at 5 MPa pressure. They were vulcanized at 180 °C for 10 minutes, according to ASTM 3182-08.

### Irradiation Process

Specimen of butyl rubber compound was irradiated at 0 kGy, 5 kGy, 15 kGy, 25 kGy, 50 kGy, 100 KGy, 150 kGy and 200 KGy, in a Cobalt-60 source, 5 kGyh<sup>-1</sup> dose rate.

After irradiation, samples were mechanically sheared in a roll mill.

### Compositions characterization, before and after irradiation and shearing

**Mooney Viscosity:** Mooney viscosity tests were performed in an Alpha Technologies model MV 2000 viscosimeter. Mooney viscosimeter measures viscosity of pure elastomer and/or from non-vulcanized composition, in function of resistance to shearing [15].

**Rheometrical Parameters:** Compounds characterization before and after irradiations was accomplished by mechanical analyses and rheometrical parameters: ML, minimum torque, MH, maximum torque and T90, optimum cure time were obtained in accordance with ASTM D 3084-08 norm, in an oscillating disk rheometer (ODR), Monsanto model MDR 2000.

**Tension and elongation at break:** Tension and elongation at break were performed at 25 ± 5 °C, in an universal testing machine, EMIC model DL 300, 20 KN load cell, in accordance with ASTM D 412-08 norm.

**Hardness:** Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values, derived from ASTM D 2240, being the Shore A, Instrutemp, portable digital model Dp-100

Table 1: Formulation of butyl rubbers.

Ingredients	Quantities (phr)
Butyl rubber	100
Zinc Oxide	5
Steric Acid	1
Naphtenic Oil	25
Carbon Black	70
Sulfur	2
TMTD	1
MBT	0,5

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.

**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 test, specimens were weighed and dried at room temperature, for 24 hours. These analyses were performed according to ASTM D-3616. Swelling degree was calculated in accordance with Equation 1:  $Q = [(M - M_0)/M_0] * 100$  (1)

Where:  $M_0$  is sample initial mass (g) and  $M$ , the final sample mass (g) [16].

**Scanning Electronic Microscopy (SEM):** Characterization of butyl rubbers compositions morphology were performed in an HITACHI, model TM 3000 electronic microscope, allocated in Centro de Ciência e Tecnologia de Materiais (CCTM), IPEN-CNEN/SP. Samples were investigated at specimen rupture point subjected to tensile and elongation test and enlarged 200 to 250 times.

## Results

Results irradiation for Mooney viscosity in butyl rubbers (non-vulcanized) are shown in Figure 1. Viscosity was measured after 1 minute of pre-heating followed by 4 minutes under shearing at 100 °C temperature.

Butyl rubber shows a viscosity sharp decline up to 100 kGy dose, but even at 5 kGy the decline is intense, indicating the total preponderance of chain-scission. It is observed that within 100 to 200 kGy doses occurs a balance of values suggesting a simultaneous scission and crosslinking or generalized oxidation creating crosslinking and hydrogen bridge that partially counterbalance radiation-induced scissions.

Maximum torque ( $M_H$ ) results obtained for butyl rubbers, irradiated, irradiated, and sheared are shown in Figure 2 (a) e (b). Maximum torque is related to a raise in rigidity of elastomeric

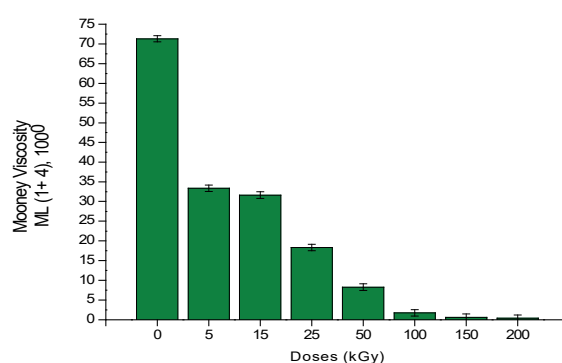


Figure 1: Mooney viscosity for non-vulcanized butyl rubber.

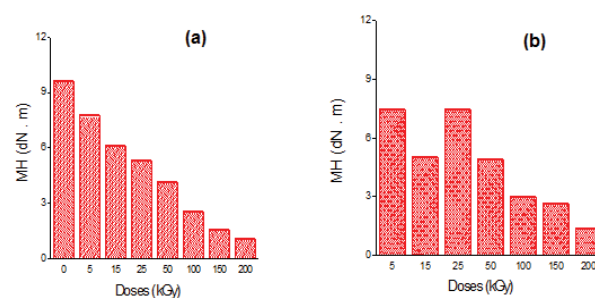


Figure 2: Maximum torque for butyl rubber compound, irradiated and non-irradiated (a) and in butyl rubber compound irradiated and sheared (b).

network when practically took place the entire crosslinking. This rigidity is associated to density of build-up crosslinked bonds.

It was observed that irradiated butyl rubber sample presents a similar behavior to butyl rubber (raw-material), that is, a sharp decline in torque values between 0 kGy and 100 kGy and a less sharp decrease between 150 and 200 kGy. For butyl rubbers compounds, irradiated and sheared (Fig. 2 (b)) it can be observed that at low doses, there is a simultaneous occurrence of scission and crosslinking. For doses higher than 50 kGy there is polymeric chain degradation due to intense mechanical breakage of rubber molecules.

ML minimum torque results for irradiated compounds, non-irradiated, irradiated, and sheared for butyl rubbers are shown in Figure 3 (a) and (b). Minimum torque is related to composition viscosity at essay temperature and consequently is a sign of processability [17].

In FIG. 3  $M_L$  results for butyl rubber compounds, irradiated and non-irradiated (a) and irradiated and sheared (b), indicate that there was a raise in torque after irradiation, pointing toward a raise in build-up of crosslinkings.

Butyl rubber compounds just irradiated showed a sharp increase in ML values, indicating a raise in viscosity up to 50 kGy dose suggesting the competition between scission and crosslinking. For irradiated and sheared samples there was too a balance in minimum torque values, up to 50 kGy dose, indicating the occurrence between scission and crosslinking. For doses within 100 kGy and 200 kGy it was observed a reduction in torque proportional to dose, suggesting a high degradation index and a probable destruction of molecular chain due to mechanical shear.

Tension and elongation at break for butyl rubber compounds, non-irradiated, irradiated, irradiated, and sheared are shown in Figure 4 (a) e (b) e, Figure 5 (a) e (b), respectively.

Figures 4 (a) and 5 (a) showed that for low doses up to 25 kGy there is an equivalency for tension and elongation at break values, showing that degradative effects were not enough for changing properties. For doses within 25 kGy and 50 kGy it is observed a decline in tension of rupture and a balance in elongation at rupture values, probably

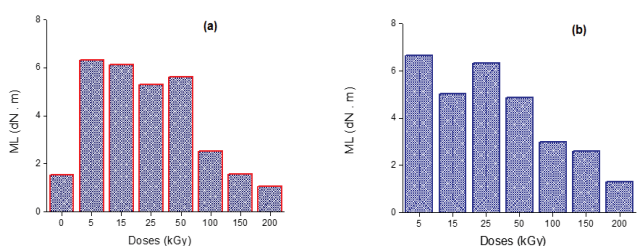


Figure 3: Minimum torque for irradiated and non-irradiated butyl rubber compound (a) and for irradiated and sheared butyl rubber compound (b).

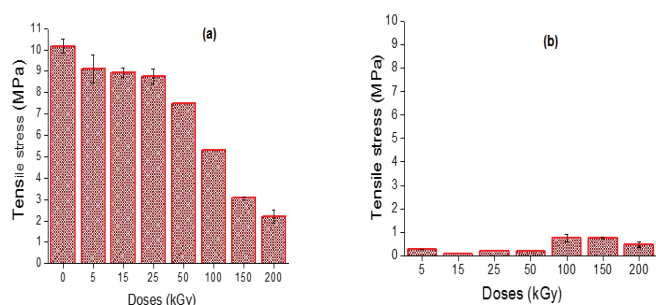


Figure 4: Radiation dose effect (a) and radiation and shearing (b) in tension at break for butyl rubber compounds

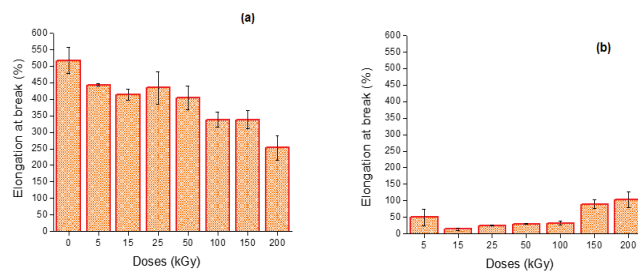


Figure 5: Radiation dose effect (a) and radiation and shearing (b) in elongation at break for butyl rubber compounds

due to a competition between scission and crosslinking, by number of crosslinkages compensating chain-scission. For doses within 100 kGy and 200 kGy it was observed the predominance of chain-scission, considering that lower molecular chains have weaker intermolecular forces that do not withstand tensile.

Figures 4 (b) and 5 (b), results showed a sharp decrease in tension and elongation at break values from 5 kGy dose indicating a raise in scission due to shearing suggesting that mechanical mastication supplied enough energy to break bonds

It was verified too for irradiated and sheared compounds, for doses up to 50 kGy, there was a sharp decline in property, suggesting prevail of chain-scission intensified by mechanical shearing. For doses within 100 kGy and 200 kGy it was observed a raise in tension and elongation at break values suggesting build-up of new points of crosslinks, probably as a result of residual sulfur in these compounds that create new crosslinks in function of a raise in temperature generated by shearing. It was observed that mechanical shearing fosters rubber degradation. Comprehensive degradation can be explained not just by radiation-induced scission but too by oxidative degradation reactions. Radiation effects in hardness of butyl rubber compounds, irradiated and non- irradiated and irradiated and sheared are shown in Figure 6 (a) and (b), respectively.

For samples just irradiated, Figure 6 (a), there is a balance in hardness for doses within 5 kGy and 25 kGy, suggesting competition between scission and crosslinking. For doses higher than 50 kGy it was noticed a slight reduction in values pointing toward a raise in chain-scission and probable oxidative degradation. Hardness results for butyl rubber compounds, irradiated and sheared, are shown in figure 6 (b). Hardness results showed for doses within 5 kGy and 50 kGy values presented a decline in hardness, indicating high chain-scission. For doses higher than 100 kGy it is observed equity in hardness values suggesting simultaneous occurrence of scission and crosslinking, predominating crosslinking.

Swelling index is determined by comparing sample initial mass with final mass; variations indicate changes in polymerization system. In rubbers occur swelling phenomena, inversely proportional to crosslinking bonds density [18]. Vulcanized rubbers are insoluble in solvents: the presence of crosslinks bonds hinders molecules segregation by solvent; but they have the capacity of absorbing liquids

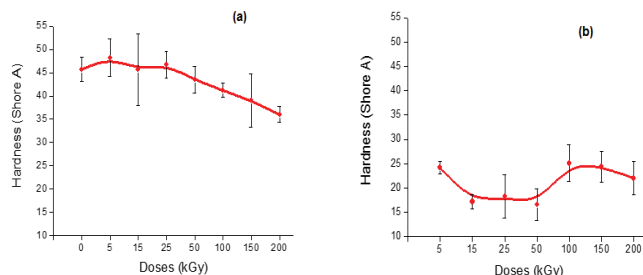


Figure 6: Effect of radiation (a) and radiation and shearing (b) effect in butyl rubber compounds

and that imparts a raise in volume, called as phenomena of swelling in solvents. Equilibrium swelling via organic solvent is one of more simple methods for characterizing crosslinked structure of elastomers.

Mass variation in specimens was daily checked and results are shown in Figure 7 (a) for irradiated rubbers and (b) for irradiated and sheared rubbers, where are exhibited results from three measurements in each time.

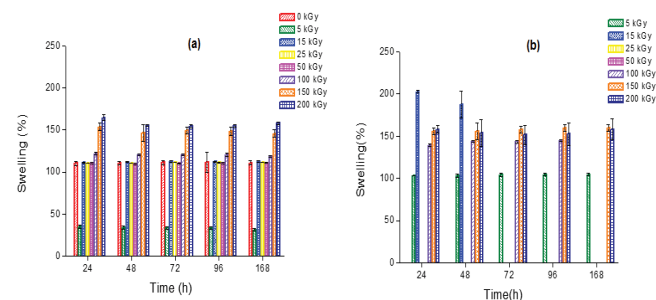
In Figure 7 (a), it was observed mass stability for all compounds, independent from applied dose, after 24 hours immersed in toluene: polymer swell up to reach an equilibrium swelling degree [19], indicating stabilization of crosslinks build-up. It was observed too an intense decrease in swelling at 5 kGy dose and a quick recovering of original values in doses up to 100 kGy. Apparently occurred an intense crosslinking imparting rigidity to the chain followed by fast degradation in function of irradiation. For doses higher than 100 kGy it was observed a significant increase in swelling due to a decrease in crosslinking density pointing toward an intense chain-scission, allowing an easy penetration of the solvent in the polymeric chain.

For irradiated and sheared samples, figure 7 (b), it is verified for lower doses a significant raise in swelling associated to intense chain-scission. For intermediate doses, after 24 hours of immersion in solvent, it can be noted the complete sample dissolution.

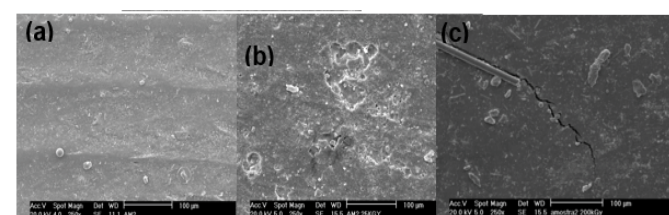
SEM tests with 250 times enlargement were accomplished in rupture surface for rubber samples irradiated within 25 kGy and 200 kGy doses; micrographies are shown in Figure 8.

It can be observed from micrographies 250 times enlargement taken in rupture surface of butyl rubbers a reduction in dispersed particles in function of a raise in dose suggesting a better compatibility of eventual particles or agglomerates. In various samples appear too fissures with dose denoting a more fragile and brittle material emphasizing the degradation (scission and crosslinking) for rubber and suggesting high oxidation. Accumulation of effects (fractures, porosity, cracks, etc.) and damages induced by radiation leads to a failure in rubber interior corresponding to transition from elastic behavior to fragile behavior [20]. Radiation can make flexible samples rigid and brittle specially when are applied elevated doses.

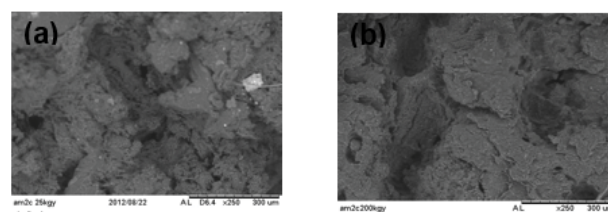
Micrographies in rupture surfaces for butyl rubber compounds, irradiated at 25 kGy and 200 kGy doses, are shown in Figure 9.



**Figure 7:** Effect of radiation (a) and radiation and shearing (b) dose in swelling for butyl rubber compounds.



**Figure 8:** Micrographies for butyl rubber non-irradiated (a) and irradiated within 25 kGy (b) and 200 kGy (c) doses.



**Figure 9:** Micrographies in rupture surface for butyl rubber irradiated in 25 kGy (a) and 200 kGy irradiated and sheared (b)

Figure 9 shows great rugosity in rupture surface for 25 kGy dose in consequence of a decline in mechanical properties of these irradiated and sheared compounds. It is observed that even after shearing compounds present high agglomerate contents, indicating heterogeneous gelation or crosslinking zones. At 200 kGy dose, it is observed a smoother and sticky surface, pointing toward rubber molecule scission.

## Conclusion

Butyl rubber compound presents a tendency toward chain-scission and crosslinking. Visual aspect of rubbers after irradiation confirmed that butyl rubber suffered intense degradation with raises in doses.

Mechanical tests for tensile and elongation at break showed chain-scission for doses up to 25 kGy and intense degradation for doses higher than 50 kGy. Micrographies for butyl rubber samples, after irradiation, showed for low doses a smooth rupture surface indicating chain-scission. For doses higher than 100 kGy, rupture surface presented crackles and failures attributed to regions extremely crosslinked and oxidized.

Butyl rubber samples, just irradiated, did not show acceptable values for controlled degradation, that is, a few compounds showed some crosslinking evidence, even at high doses (higher than 100 kGy). Processing via gamma-rays followed by shearing in butyl rubber showed a great technical viability for application in recovering industrial processes for this type of rubber, especially rubber irradiated at 25 kGy and sheared, presenting an intense chain-scission without intense degradation.

Considering difficulties in recycling vulcanized rubbers, especially referred to their reprocessing, it should be highlighted the relevance and efficiency in incorporation of residues from these materials in original process without addition of any additive.

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