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Study of Recycling Feasibility of Bromobutyl Rubber to Gamma Radiation

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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. Bromobutyl rubber has excellent mechanical properties and oxidation resistance, 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. The objective of this work is to develop controlled degradation processes (devulcanization) of Bromobutyl rubber and in order to characterize their availability to change and change its properties, such as strength, elongation, hardness, and rheological properties, etc. The experimental results obtained showed that the bromobutyl rubber irradiated to 25 kGy and subsequently sheared can be used as starting point for blending with virgin rubber.

1. Introduction

Polymeric materials (plastics and rubber) attain a comprehensive and rising continuous proportion of litter and industrial wastes discarded in landfills. The implementation of new technologies for 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 re-use [1].

Rubbers have a very low natural decomposition [2], due to their chemical structure weathering conditions and to enzymatic and microorganisms degradation resistant. Rubber recovering is made difficult by its insolubility due to its cross-linked structures [3]. In addition, this tridimensional structure causes various problems related to recovering and reprocessing of these materials [4].

So, as previously mentioned the most of rubber wastes, especially tires, are discarded and disposed in landfills. In other situations, they are used as combustible and incinerated to produce power; in addition, costs for these operations are very high. Other ways of re-use of rubbers include: asphalts, shoe soles manufacturing, rubber gaskets, rainwater pipelines, floor paints on sport courts, industrial floors, besides carpets for

autos. Consequently, recycling and recovering are the best options for management of these residues [1, 5].

Gamma ionizing radiation is capable to change structure and properties of polymeric materials and can be applied in almost every type of polymers [6]; irradiation is an expectation for management problem-solving of rubber residues that can be used as raw-materials or chemical additives.

Bromobutyl rubber, subject to high-energy radiation, there may be a variety of chemical reactions following the initial ionization and excitation events. These reactions alter the molecular weight of the rubbers by means of division or crosslinking and affect physical and mechanical properties [7].

Smith [8] e colaboradores, em 2013 estudaram o efeito da radiação gama usando uma fonte de ^{60}Co em atmosfera inerte a 25°C e 70°C em um elastômero de borracha butílica, carregado com negro de fumo. Confirmaram que sob irradiação ocorreram reações de reticulação e cisão de cadeia; a contribuição de ambos os processos foi dada pela equação de Charlesby-Pinner. Indicando que a modificação das propriedades mecânicas da borracha está associada ao mecanismo de degradação que é altamente influenciado pela temperatura, especialmente para doses elevadas de irradiação.

Rubbers products recovering can be accomplished by means of following processes:

- Chemical processes: they are carried especially in high pressure reactors with specific solvents at high temperatures in order to increase reactions output [1, 9]. This process presents the advantage of make viable the selective rupture of polysulfide crosslinking, without significant rupture of main chain [10].
- Biological processes: they are selective processes, in which chemical bonding of vulcanized rubbers are broken and sulfur is removed by bacteria biotreatment. Some of them have been using in NR, SBR and BR de-vulcanization, as *Nocardia*, *Thiobacillus* e *Mycolata*, without causing significant degradation of polymeric hydrocarbon. In Literature, these methods are cited as of de-vulcanizing low output, because they attack just samples surface and are not viable to be applied at industrial-scale [11, 12] and
- Physical processes that comprise processes:
 - I. Mechanical (rubber is sheared in open-mixers) [1],
 - II. Thermo-mechanical (rubber is inserted in a proper solvent to be swelled and further transferred to a roll-mill) [1];
 - III. Cryo-mechanical (rubber is dipped in liquid nitrogen and further micronized in balls or hammer mills)¹;
 - IV. Ultra-sound (within 16 KHz to 1 MHz, de-vulcanization is accomplished via combination between extrusion and ultrasound energy) [13, 14] and
 - V. Micro-waves (frequencies within 300 MHz to 300 GHz, effective for accomplishing recycling of polar

rubbers cross-linked, imparts destabilization of tridimensional net) [15, 16].

In shown physical processes, most of them generate rubber in powder, prone to be used as inert filler. Consequently, it is desirable a physical system that makes possible obtaining recycled rubbers that act as active filler.

This study intended for rubbers recovering and/or recycling employed processing with gamma-rays and further shear in an open roll-mill. As a major purpose it was studied the obtaining devulcanized rubbers that allow a new crosslinking (or vulcanization).

2. Experimental Section

2.1. Materials

Butyl rubber used in this study was bromobutyl grade 2222 from Exxon Mobil Chemical. It was studied an elastomeric composition, having as reference a formulation used in tires and auto-parts industry. Referred composition was irradiated and further sheared, aiming to a further use by re-vulcanization. Formulation used in this study is described in Table 1 and ingredients amounts are in phr or in parts by weight of material by one hundred parts of rubber.

Table 1. Formulation of Bromobutyl Rubber.

Ingredients	Quantities (phr)
Bromobutyl rubber	100
Zinc oxide	5
Stearic acid	1
Naphthenic oil	25
Carbon black N 330	70
Sulfur	2
TMTD	1
MBTS	0.5

Admixtures were prepared in an open roll-mill, each roll with a 40kg capacity, as per ASTM D 3182-08 [17]. Samples were cured in an electrically heated HIDRAUL-MAQ, at 5 MPa pressure and further vulcanized at 180°C , for 10 minutes.

Irradiation Process

Specimen of bromobutyl rubber sample was irradiated at 5 kGy, 15 kGy, 25 kGy, 50 kGy, 100 kGy, 150 kGy and 200 kGy doses, in a Cobalt-60 source with kGy, 5 kGyh^{-1} dose rate. After irradiation, samples were mechanically sheared in a roll-mill.

2.2. Characterization of Compounding Before and After Irradiation and Shear

2.2.1. Rheometric Parameters

Characterization of compounds before and after irradiations was accomplished by means of mechanical analyses and rheometric parameters: minimum torque (M_L), maximum torque (M_H) and optimum cure time (T_{90}), in accordance with ASTM D 2084-08 [18], in an oscillating disk rheometer (ODR) Monsanto model MDR 2000.

2.2.2. Tension and Elongation at Rupture

Tensile and elongation at rupture mechanical tests were accomplished at $25 \pm 5^\circ\text{C}$, in an EMIC model DL 300 universal essay machine, load cell 20 kN, in accordance with ASTM D 412-08 [19].

2.2.3. Hardness

Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values, derived from ASTM D 2240 [20], 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.

2.2.4. 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 to ASTM D-3616. Swelling degree was calculated in accordance with Equation 1:

$$Q = [(M - M_0)/M_0] * 100 \quad (1)$$

Where: M_0 is sample initial mass (g) and M , the sample final mass (g) [21].

To calculate the variation of dry matter (P) mass ratio shown in Equation 2 was used:

$$P = [M_0 - M_s/M_0] * 10 \quad (2)$$

where: M_0 is the weight of sample (g) and before swelling

M_s is the weight of the dry sample (g) after the swelling test.

3. Results and Discussion

3.1. Reometric Properties of Irradiated and Non-irradiated BIIR

Maximum torque (M_H) and minimum torque (M_L) results obtained for bromobutyl rubber compounds are shown in Figure 1 and Figure 2 respectively.

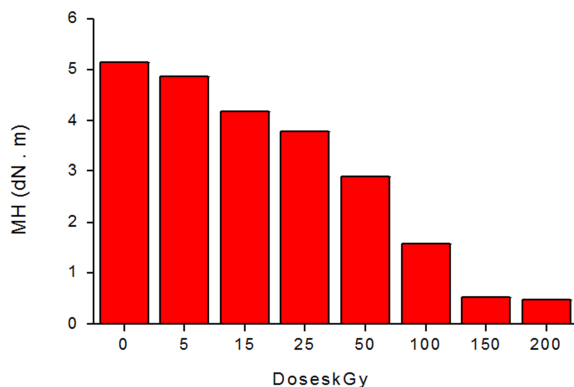


Fig. 1. Irradiation dose effect with further shear for maximum torque for bromobutyl rubber compounds.

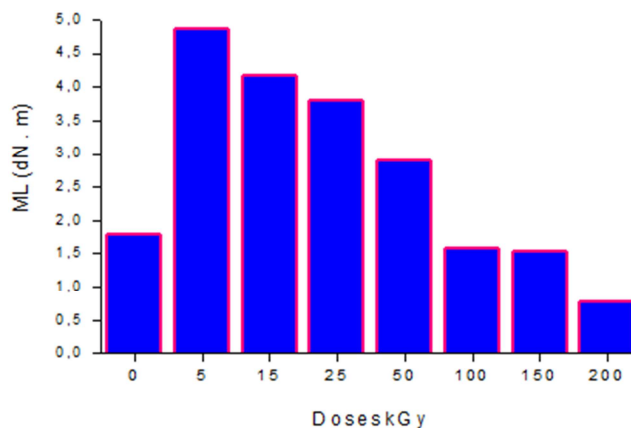


Fig. 2. Irradiation dose effect with further shear for minimum torque for bromobutyl rubber compounds.

It is verified a balance in maximum torque values (M_H) for doses up to 50 kGy, pointing toward a simultaneous scission and crosslinking occurrence. For doses higher than 100 kGy, it was observed a torque decreasing, due probably to high polymer degradation. In addition, this decreasing can be caused by mechanical mastication and crosslinking bonding rupture polysulfide type, considered weaker than monosulfide and disulfide bonding.

In relation to minimum torque (M_L) irradiated samples showed higher values pointing toward crosslinking, up to 50 kGy, suggesting that mechanical mastication promoted new points for crosslinking, probably by the presence of residual sulfur. For doses higher than 100 kGy it was observed a reduction in minimum torque, confirming the predominance of polymer scission and oxidative degradation.

Table 2 shows obtained values for ΔM for bromobutyl rubber samples, non-irradiated and irradiated and sheared. $\Delta M = (M_H - M_L)$ values give a qualitative clue for cross-linked bonding density, considering that an increase in difference between torques points toward a raise in crosslinking degree. It is observed that all samples showed an abrupt decreasing of ΔM values after irradiation and shear due to a high degree of chain-scission and oxidative degradation.

Table 2. ΔM (dN.m) for Bromobutyl Rubber Samples, Non-Irradiated and Irradiated and Sheared.

Doses	ΔM (dN.m)
0 kGy	3.37
5 kGy	0.21
15 kGy	-
25 kGy	-
50 kGy	-
100 kGy	-
150 kGy	-
200 kGy	-

3.2. Mechanical Properties of Irradiated and Non-irradiated BIIR

Tensile and elongation at rupture results for bromobutyl rubber samples non-irradiated and irradiated and sheared are shown in Figure. 3 and Figure. 4, respectively.

Results showed a sharp decreasing in tensile and elongation at rupture even at 5 kGy dose, indicating scission increasing in consequence of shear, suggesting that mechanical mastication provided enough energy to break bonding. The sharp decrease of tensile and elongation at break, after irradiation and shear indicated further deterioration of rubber radiated as a function of shear.

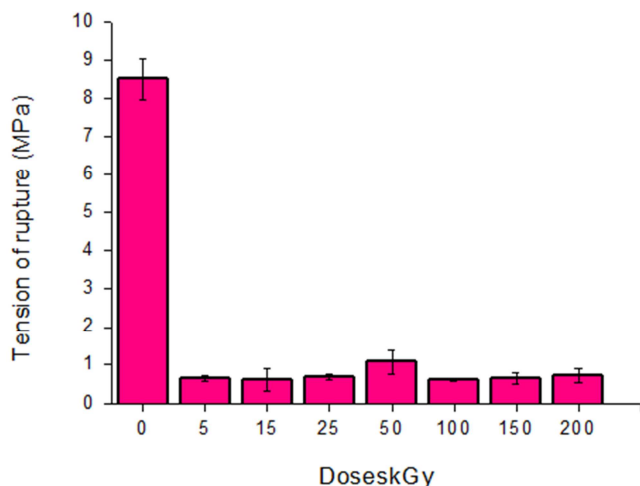


Fig. 3. Irradiation dose and shear effect in tensile of rupture for bromobutyl rubber compounds.

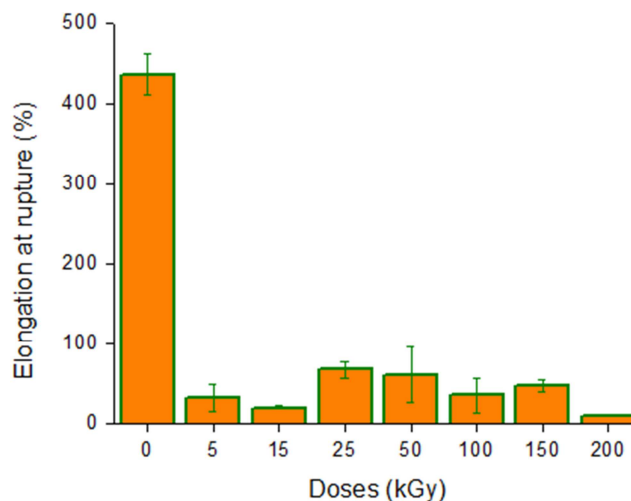


Fig. 4. Irradiation dose and shear effect in elongation at rupture for bromobutyl rubber compounds.

3.3. Hardness of Irradiated and Non-irradiated BIIR

The hardness results for all samples shown (Figure 5) for doses ranging from 5 kGy to 100 kGy, equivalent hardness values, again demonstrating the competition between scission and crosslinking. Doses of between 150 kGy and 200 kGy increase in hardness, indicating a surface oxidized by radiation.

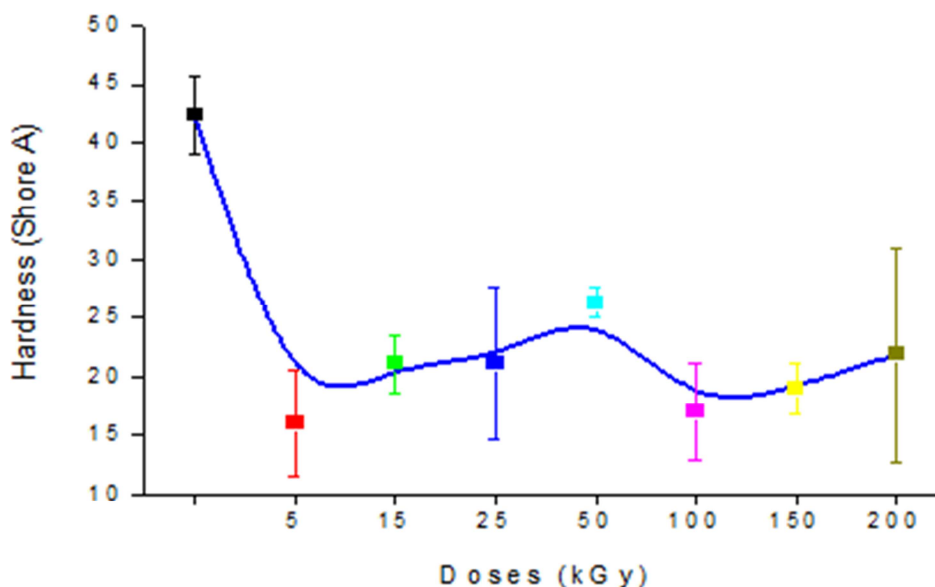


Fig. 5. Irradiation dose and shear effect in hardness for bromobutyl rubber compounds.

3.4. Swelling Index of Irradiated and Non-irradiated BIIR

The swelling index is determined by comparing the initial sample weight to the final mass shifts indicate changes in the polymerization system. In the rubber swelling phenomenon which is inversely proportional to the crosslink density occurs. The vulcanized rubbers are insoluble in solvents because the presence of crosslinking between the chains prevents the molecules to be separated with the solvent.

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

Swelling variation results in irradiated and sheared samples of bromobutyl rubber are shown in Figure 6. In Table 3 are shown dried mass variation in function of irradiation and shear obtained from swelling essay.

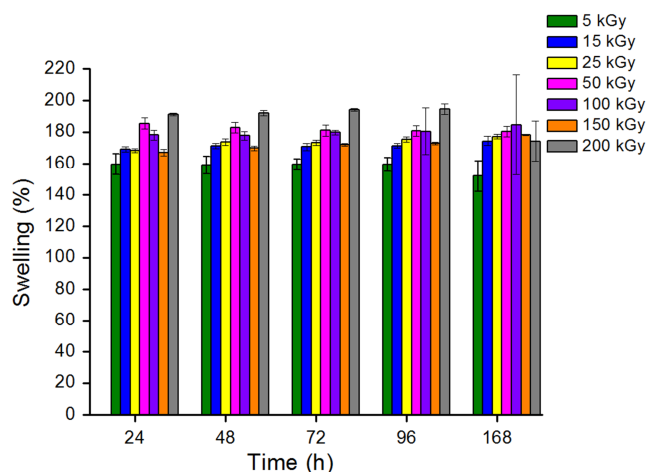


Fig. 6. Swelling for bromobutyl rubber compounds irradiated at 5, 15, 25, 50, 100, 150 e 200 kGy doses and sheared.

It was observed that the stability weight of all samples occurred after 24 hours immersion in toluene as the polymer swells to achieve a degree of swelling of equilibrium.

The results shown in Figure 6 show the values of equilibrium swelling after 24 hours immersion in toluene, indicating stabilization of crosslinking. It was observed a rise in swelling for doses up to 50 kGy associated to a considerable mass loss (Table 3), pointing toward the occurrence of intense scission. For higher doses it is noted a slight reduction in swelling, associated to a high mass loss of approximately 30%. Therefore, in spite of an evident and comprehensive chain-scission, simultaneous generation of radicals during irradiation makes viable the build-up of a dense cross-linked net.

Table 3. Dried Mass Variation for Bromobutyl Rubber Compounds Irradiated and Sheared.

Doses	Dry Mass
0 kGy	-3.71
25 kGy	-13.05
200 kGy	-31.51

4. Conclusions

Mechanical essays of tensile and elongation at rupture showed chain-scission for doses up to 25 kGy; for doses higher than 50 kGy, an intense degradation.

Swelling tests showed that BIIR rubber shows trend to chain-scission. Mechanical shear for irradiated BIIR rubber helped in reduction of values for maximum torque and minimum torque.

Processing with gamma rays followed by shear in bromobutyl rubber showed a great technical feasibility for application in industrial processes of recovering for this type of rubber, especially irradiated rubber at 25 kGy and sheared, that showed intense chain-scission without a high degradation.

Considering difficulties in recycling of vulcanized rubbers, especially related to their processing, it should be emphasized the relevance and efficiency in the incorporation of residues from these materials in their original process

without none additive addition.

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