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ORIGINAL ARTICLE

Study of mechanical properties of inner tubes exposed to gamma radiation§

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Abstract

Due to the technical evolution of tires, currently most automotive tires do not have an inner tube. However, truck, motorcycle and bicycle tires still use tires with inner tubes, mostly made of synthetic elastomeric material, which guarantees good potential for air restriction or longer periods for tire pressure failure. This work aims to study changes in the mechanical properties of a truck inner tire, after its exposure to gamma rays, to promote the subsequent recycling of the material. The choice of ionizing radiation is due to its ability to modify the structure and properties of materials, in addition to its applicability in recycling/recovering rubber. For the characterization of the samples, doses of 5, 10, 15, 20, 25 and 30 kGy were applied, and after irradiation as a sample, they were tested using the following characterization methods: traction and elongation at break, hardness, thermal aging and elemental analysis. Observed that is a decrease in the values of the mechanical properties of the samples after irradiation, mainly at doses greater than 10 kGy.

Keywords: *gamma rays, inner tubes, mechanical properties, rubber.*

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1. Introduction

Tires are currently constituted of various components, besides synthetic rubber. Being a product that aims at a long service life, considering that it is designed and manufactured to last under extreme physical, chemical and thermal conditions [1], it presents a complex structure to provide the required characteristics to its performance and safety, built to be indestructible [2]. Diagonal or conventional tires are used in buses and trucks which employ air chambers. Radial tires are used in cars, buses, trucks, off-road vehicles and no longer use air chambers. Conventional tires that still employ air chambers are easier to be crushed and, consequently, recycled.

There are about 450 tire plants all over the world. Tire production start with bulk raw- materials, such as synthetic rubber (60% - 70%)[3][4], carbon black and chemical products to produce different specialized components, which are assembled and cured. The different parts of a tire include lateral wall, rubber made; body canvas, produced from a rubber elastic mixture, polyester, nylon and polyamide; stabilizing canvas manufactured with small plaques of steel wires; undercarriage with three types of rubber of different compositions; stubs that are steel hoops wrapped by a rubber layer; and pond, composed of various rubber layers – all of them provided with an intrinsic function to impart firmness, safety, sealing, etc. Each tire part is manufactured separately and, to join all the parts, the companies use presses and mills [5]. Figure 1 shows the components of a car tire.

In 2019, the USA manufactured about 170 million tires [7]. More than 2.5 billion tires are fabricated yearly, making the tire industry a great natural rubber consumer. It is estimated that by the late 2019, 3 billion tires were sold worldwide each year [8].

Top Tire Manufacturers Ranking 2017,Bridgestone Corp. maintained the No. 1 position for the ninth year in a row with sales of $22.1 billion, easily ahead of the Michelin Group's $21.1 billion and Goodyear's $13.5 billion, according to the Tire Business survey [9,10].

1.1 The innerliner

A specific rubber compound is used as an air seal inside the tire. This inner liner layer has no cord reinforcement and is similar to an inner tube [11].

The air chamber inside the tires is composed of butyl rubber, a synthetic material having as major characteristics elasticity and the capacity to impede air leakage. It is a polymerized compound in isobutylene solution in a small isoprene percentage. A vulcanization process fixes the valve, which allows pressure control inside the air chamber. Depending on the additives used in chamber manufacturing, the rubber acquires more or less elasticity. A few manufacturers use this manufacturing technique to achieve a compound capable of reaching different tire sizes [12].

Figure 1. Typical passenger car tire and components of a run flat tire [6].

The air chamber is located inside the tire that does not have any extra sealing on the wheel to stand compressed air. The valve that allows filling is connected directly to the chamber, increasing the risk of injuries caused by negligent maintenance. The chambers consist entirely of a synthetic material that ensures a good potential of air restriction or higher periods for tire pressure control.

The advantage in using chamber in radial tires is that when the tire suffers any type of attack, such as drilling or infiltration due to improper repairs, it can have its service life extended with the use of an air chamber [13].

However, this recycling of solid residues has too high an energy cost and uses only car tires during the process. Some byproducts are disregarded, such as chambers still used in bicycle, motorcycle and truck tires. This work thus aims to study the changes in mechanical properties of tire chambers used in trucks after their exposure to gamma-rays for promoting further material recycling [14].

2. Materials and Methods

2.1 Materials

For the purposes of this study, samples from the production of truck tire chambers were extracted. The material was provided by manufacturers that required anonimity. The tire chambers received were used without any previous treatment and were characterized regarding their physico-chemical and mechanical properties.

2.1.2 Irradiation

The samples were subjected to gamma radiation at 5 kGy, 10 kGy, 15 kGy, 20 kGy, 25 kGy and 30 kGy doses. These low doses were selected to promote a controlled degradation of the material.

Charlesby (1953)[15] studied the processing of butyl rubbers by radiation and showed that the presence of a tertiary carbon in the polymer chain facilitates chain scission . Irradiation of polymers by ionizing radiation from industrial sources promotes the creation of very reactive intermediaries (ions and excited states), which can follow different paths resulting in: free radical reaction and hydrogen abstraction, arrangements and/or formation of new bonds.[16] acording Figure 2.

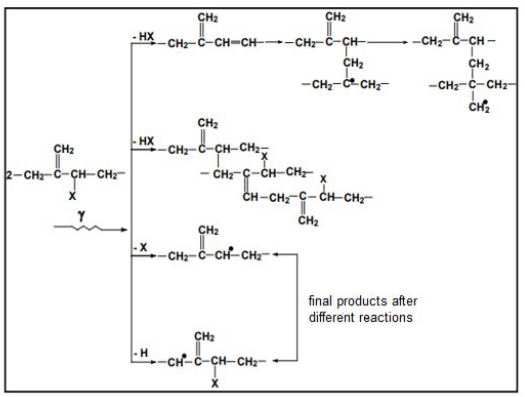

Figure 2. Isoprene irradiation unit reactions [17].

Radiation, when interacting with polymeric materials, transfers energy to the atoms of the polymeric chain, causing changes in its molecular structure. Such modifications can result in the reticulation or degradation (scission) of the polymeric chains, simultaneous and concurrent processes, whose preponderance of one or the other depends mainly on the molecular structure of the polymer and the dose of radiation with which the material was treated. Crosslinking is intermolecular bond formation of polymer chains. The degree of cross linking is proportional to the radiation dose. Cross linking during irradiation does not require unsaturated or other more reactive groupings. The mechanism of cross linking generally varies with the polymers concerned. The hydrogen atom is followed by the abstraction of a second hydrogen atom from a neighboring chain to produce molecular hydrogen. Next, two adjacent polymeric radicals combine to form a crosslink. Fission is the opposite process of crosslinking in which the breakage of C-C bonds occurs.

The final changes in polymer during irradiation are rather complex. There have always been competing reactions of cross linking and main chain scission simultaneously. The net effects of radiation depend on these competing reactions. Responses of different elastomers to the ionizing radiation are summarized in Table 1[18].

Samples were irradiated at IPEN (Instituto de Pesquisas Energéticas e Nucleares/ Nuclear and Energy Research Institute), in a Multipurpose Irradiator, installed in the CTR building, by ionizing radiation from ^{60}Co sources, at O_2 atmosphere, at a dose ratio of about 5 kGy.h^{-1}.

2.2. Methods

For characterizing the tire chambers, irradiated and non-irradiated samples underwent the following tests in triplicate.

- CHN Elementary Analysis – based on the Pregl-Dumas method
- Tensile and Elongation at Break - ASTM D 412
- Hardness - ASTM D 2240.
- Crosslink density by Flory Rhenner equation.

3. Results and Discussions

3.1 Elementary analyses

The results for the elementary analyses are shown in Table 2. The calculation for the minima formula indicates lower ratio in non-decimal numbers for element atoms that build a substance. For calculating the mass percentage of each element, it was divided by its corresponding molar mass. The analyzes were performed at the Analytical Center at the USP Chemistry Institute.

For all the irradiated truck chamber samples, a slight or almost no modification was observed at the carbon, hydrogen and nitrogen levels; variations occur due to the formulation used in the elastomer acquisition process. Therefore, no change was observed in the amount of carbon in the samples after irradiation.

3.2 Tensile and elongation at break

Tensile strength and elongation at break values were determined according to ASTM D-412 by using a model C specimen, in a universal essay machine (EMIC), model DL 300, 300 kN maximum capacity and 500 mm/min grips speed, at room temperature.

The results for tensile and elongation at break analyses of irradiated and non-irradiated truck chamber samples are shown in Figure 3 for Tensile and in Figure 4 for Elongation.

Values for tensile at break are observed to show a sharper decrease in values for doses higher than 10 kGy, pointing to a raise in chain-scission caused by irradiation. For doses higher than 10 kGy, there is an equity in values, suggesting a competition between scission and crosslinking. Due to the high molecular weight of polymers, relatively low doses of radiation can lead to a significant change in their physical properties on account of progressing radiation-induced reactions.

Table 1. Classification of elastomers according to their response to ionizing radiation[18].

Polymers predominantly crosslinking	Polymers predominantly degrading
Copolymer of styrene and butadiene (SBR)	Isobutylene-isoprene rubber or butyl rubber (IIR)
Chlorinated polyethilene (CM)	Chorobutyl rubber (CIIR)
Chlorosulfolnated polyethylene (CSM)	Bromobutyl rubber (BIIR)
Polybutadiene (BR ou PB)	
Natural rubber (NR)	
Polychloroprene (CR)	
Copolymer of acrylonitrile and butadiene (NBR)	
Hydrogenated NBR (HNBR)	
Ethylene-propilene rubber (*EPM)*	
Ethylene-propilene-diene rubber (EPDM)	
Polyurethanes (PUR)	
Polydimethyl silicone (MQ)	
Polydimethylpenylsylicone (PMQ)	
Fluorocarbon elastomers, based on vynilidene floride (FKM)	
Isobutylene rubber (IR)	

Table 2. Elementary analysis results for irradiated and non-irradiated truck chambers.

Dose (kGy)	Carbon (%)	Hidrogen (%)	Nitrogen (%)
0	86.415	8.370	0.305
5	86.310	8.450	0.330
10	85.450	8.355	0.345
15	85.900	8.420	0.395
20	86.205	8.505	0.305
25	86.210	8.490	0.545
30	86.235	8.300	0.200

If these reactions lead to break of the valence base, a decrease in the molecular weight and destruction of the polymer is observed. If additional molecular cross links are formed, the molecular weight of the polymer increases, which leads to radiation polymerization [19]

For the results of elongation at break, a rise is observed in values for doses up to 10 kGy, suggesting the occurrence of crosslinking; for doses higher than 15 kGy, there is a decrease in values, indicating a rise in chain-scission, because lower chains present lower elongation. These results are in agreement with the study carried out by Hong-Bing Chen and collaborators (2017) who showed the effects of gamma irradiation on butyl rubber (BRP)-based material and concluded that the absorbed dose seems to be extremely important for the properties of butyl rubber compounds. As the dose increases, the tensile strength decreases, inversely proportional to the results of elongation at break, which shows a slight increase in values [20]

3.3 Hardness

Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values derived from ASTM D 2240 . Hardness is one of the most evaluated properties in rubbers, being 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.

The results for hardness are characteristic of the rigidity presented by a rubber compound. Hardness results for irradiated and non-irradiated truck chamber samples are shown in Figure 5.

After irradiation, samples showed a lower decrease in values; nevertheless, with a rise in dose, an equity of values was verified for all doses. As expected, hardness is reduced after mechanical shearing; this is explained by the degradation mechanism that leads to a de-polymerization, i.e., the weakening of the elastomer matrix imparted by chain-scission and/or a rise in cross links.

3.4 Cross linking density

The density of crosslinks was calculated by the equation developed by Flory – Rehner (Equation 1) , based on the equilibrium swelling in organic solvents[21]. The crosslink density was calculated by using from the equilibrium swelling.

$$\nu = \frac{-(\ln(1-V_B)+V_B+\chi.(V_B{}^2))}{(\rho_B).(V_0).\left(V_B^{\frac{1}{3}}-\frac{V_B}{2}\right)} \quad (1)$$

Where, : η: cross-link density (mol/cm^3), χ the interaction parameter polymer-solvent or Flory-Huggins parameter (0.5)[22], ρ_B the rubber density, V_0 the molar volume of the solvent (106.4 cm^3 mol^{-1}) and V_B is the volume fraction of rubber from swollen form, determined from weight gain by swelling.

The samples were weighed daily until there was no further weight change, which took 24 hours. The samples were then dried in a vacuum oven at 60°C for 4 hours. The specimens used had dimensions of 2.0 x 2.0 x 0.2 cm , with the result of the arithmetic mean of three determinations. Figure 6 shows the crosslink density results of the irradiated and non-irradiated.

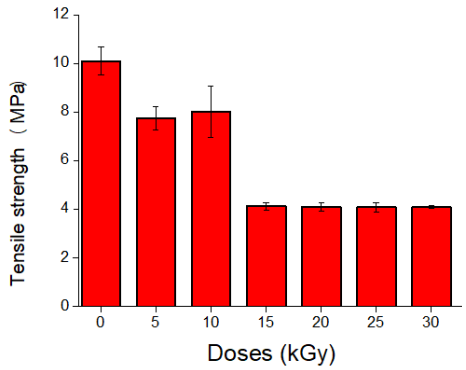

Figure 3. Tensile Strength for irradiated and non-irradiated truck chambers.

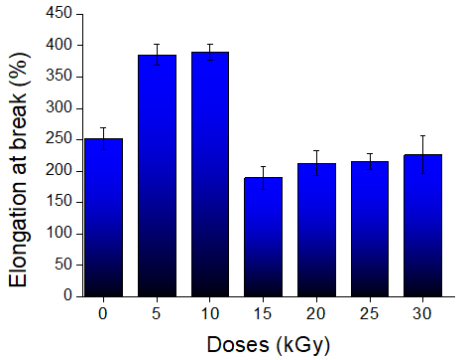

Figure 4. Elongation at break for irradiated and non-irradiated truck chamber.

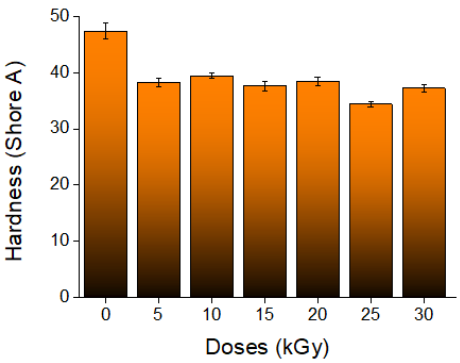

Figure 5. Hardness of non-irradiated and irradiated truck chambers.

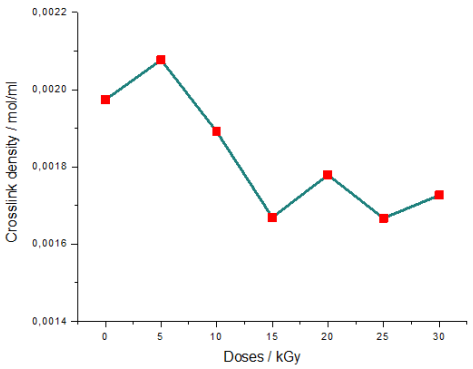

Figure 6. Crosslinking Density of non-irradiated and irradiated truck chambers.

The results shown in Figure 6, indicate that the cross-linking density for doses above 5 kGy decreases with increasing dose, denote that there is a decrease in cross-links, suggesting disruption of C-S bonds. Corroborating results of tensile strength of a polymer is a function of crosslink density and energy dissipation. The tensile strength increases with crosslinks and decreases with lower crosslink density. However, fission reactions at high radiation doses causing reduced tensile strength values cannot be ruled out. Decreased traction strength and elongation at break at higher radiation doses are reported for ethylenepropylene rubber[23]. The increase in irradiation can be attributed to changes in the the crosslink density.

4. Conclusions

Elementary analyses did not reveal significant changes in Carbon (C) and Hydrogen (H) levels, present in all irradiated and non-irradiated samples, and results were not conclusive.

Tensile and elongation at break mechanical tests showed that irradiated sample values decreased in function of a rise in dose, suggesting the occurrence of chain-scission, because smaller chains present smaller elongation and suffer rupture more easily.

The hardness result, which indicates material rigidity, presented lower values after irradiation; this is probably caused by the degradation mechanism that leads to a de-polymerization, i.e., weakening of the elastomeric matrix caused by chain-scission and / or a rise in crosslinking.

The decrease of cross-links with the increase of the dose proved that the decrease of values for the tensile strength with the increase of the dose is due to the increase of the chain scission.

The analyses showed that it is possible to accomplish controlled degradation of truck tire chambers, considering that doses higher than 10 kGy cause chain-scission. In a future work, the intention is to consider a mixture of recovered rubber via irradiation with virgin rubber and then conduct the material recycling.

5. Author's Contribution

- **Conceptualization** – Sandra Regina Scagliusi; Ademar Benevólo Lugão; Helio Wiebeck.
- **Data curation** – Sandra Regina Scagliusi.
- **Formal analysis** – Sandra Regina Scagliusi.
- **Funding acquisition** – Sandra Regina Scagliusi; Elizabeth Leite Carvalho Cardoso.
- **Investigation** – Sandra Regina Scagliusi.
- **Methodology** – Sandra Regina Scagliusi; Ademar Benevólo Lugão.
- **Project administration** - Sandra Regina Scagliusi.
- **Resources** - Sandra Regina Scagliusi; Elizabeth Leite Carvalho Cardoso; Fabio José Esper.
- **Software** – Sandra Regina Scagliusi; Elizabeth Leite Carvalho Cardoso.
- **Supervision** – Ademar Lugão.
- **Validation** – Helio Wiebeck.
- **Visualization** – Sandra Regina Scagliusi.
- **Writing – original draft** – Sandra Regina Scagliusi.
- **Writing – review & editing** – Sandra Regina Scagliusi; Elizabeth Leite Carvalho Cardoso; Helio Wiebeck.

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