

STUDY OF MECHANICAL AND CHEMICAL PROPERTIES STABILITY OF INNER TUBES EXPOSED TO GAMMA RADIATION

Sandra R. Scagliusi¹, Elizabeth L.C. Cardoso¹, Fernando Caviquioli¹, Ricardo M. Sales¹ and Ademar B. Lugão¹

¹ Centro de Química e Meio Ambiente - Instituto de Pesquisas Energéticas e Nuclearaes- (IPEN / CNEN - SP) Av. Professor Lineu Prestes 2242 05508-000 São Paulo, SP, Brazil srscagliusi@ipen.br

ABSTRACT

Nowadays, car tires are not provided with inner air or tubeless, pointing toward a technical evolution. Nevertheless, trucks tires even use at present inner tires, composed almost fully by a synthetic material, which ensures either a good potential for air constraint or longer periods for inspection of tires pressure. Inner tire is located inside the tire which does not have any extra sealing in the wheel to withstand compressed air. It is designed to resist to expansion of these elements, inside common tires. This rubbery and vulcanized coating has chemical and physical characteristics which enable it to bear a very high air pressurization, avoiding leakages while protects tire outer frame. Inner tires models are exposed to higher temperatures and pressures that contribute to accelerate abrasion. This work aims to the study of mechanical properties changes of an inner tire used in trucks, after gamma rays exposure, in order to promote further material recycling. Ionizing radiation choice was due to its capacity to modify structure and properties besides its applicability materials for rubbers recycling/recovery. For samples characterization, non-irradiated and irradiated at 5, 10, 15, 20, 25 and 30 kGy, there were accomplished following tests: tensile and elongation at break, hardness, thermal ageing and CHN elementary analysis. It was observed a decrease in mechanical properties for irradiated samples at doses higher than 20 kGy,.

1. INTRODUCTION

Currently, tires are constituted by various components, besides synthetic rubber; being a product that aims to a long time of utile life, considering that they are designed and manufactured to last under extreme physical, chemical and thermal conditions [1], it presents a complex structure with the purpose to assign required characteristics to its performance and safety, built to be indestructible [2]. Diagonal or conventional tires are used in bus and truck which employ air chambers. Radial tires are used in cars, bus, trucks, off-road vehicles and do not use anymore air chamber. Conventional tires that still employ air chamber are easier to be crushed and consequently recycled.

There are about 450 tires plants all over the world. Tires production start with bulk rawmaterials, as synthetic rubber (60% - 70%) [3] [4], carbon black and chemical products and produces various specialized components which are assembled and cured. Different parts of a tire include lateral wall, rubber made; body canvas, produced from a rubber elastic mixture, polyester and nylon; stabilizing canvas manufactured with small plaques of steel wires; undercarriage constituted by three types of rubber with different compositions; stubs that are steel hoops wrapped by a rubber layer; and pond composed by various rubber layers – all of them provided by an intrinsic function to impart firmness, safety, sealing, etc...This shows the great variety of raw-material used in tires fabrication. Each tire part is manufactured in separate and to joint all parts the companies use presses and mills [5]. In Fig. 1 it is shown the components of a car tire.



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

In 2015, EUA manufactured almost 170 million of tires [7]. More of 2.5 billion of tires are yearly fabricated, making tires industry a great natural rubber consumer. It is estimated that up to the end of 2019, 3 billion of tires will be worldwide sold each year [8].

From 2011, three major tires manufacturing companies were Bridgestone (190 million of tires), Michelin (184 million), Goodyear (181 million); and, in order, Continental and Pirelli [9] [10].

1.1 The Innerliner

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

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

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

The advantage in using chamber in radial tires is explained by the following: when the tire suffers any type of attack as drilling or infiltration due to improper repairs, it can have its long service life with the use of air chamber. It is a very effective solution, considering that majority of storing tires does not have equipment capable to fulfill the needs of a repair in radial tires [13].

However, this recycling of solid residues has too a high energetic cost and during the process uses just cars tires. Some sub-products are put aside as chambers still used in tires in bikes, motorcycles and trucks. So, this work aims to the study of changes in mechanical properties of tire chamber used in trucks after gamma-rays exposure, for promoting further material recycling.

2. MATERIALS AND METHODS

2.1. Materials

For study purpose, there were removed samples from production of tires chambers for trucks, given by manufacturers of this material, whose name was not authorized to divulge. Tires chambers received were used without any previous treatment and were characterized regarding their physico-chemical and mechanical properties.

2.1.1 Irradiation

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 in order to promote a controlled degradation of the material.

Samples were irradiated in IPEN (Instituto de Pesquisas Energéticas e Nucleares), in a Multipurpose Irradiator, installed in CTR building, by using ionizing radiation from 60 Co sources, at O₂ atmosphere, at a dose ratio about 5 kGy.h⁻¹.

2.2 Methods

Characterization

For the characterization of tires chambers and bycicle chambers samples there were accomplished following tests:

- CHN Elementary Analysis based in Pregl-Dumas method
- Tensile and Elongation at Break ASTM D 412
- Thermal Ageing ASTM D 573
- Hardness ASTM D 2240.

2.2.1 CHN Elementary Analysis

CHN Elementary Analyses were accomplished by Central Analitica located in Instituto de Química da Universidade de São Paulo (USP), in a Perkin-Elmer – CHN 2400 equipment, capable to accurately investigate Carbon, Hydrogen and Nitrogen contents.

2.2.2 Tensile and Elongation at Break

Tensile and Elongation at Break essays is an important instrument to evaluate properties loss and the evolution of elastomer degrading process.

The test was accomplished in an essay universal machine (EMIC), model DL 300 with 300 kN of maximum capacity and separation speed between claws equal to 500 mm/min, at room temperature (FIG. 2)



Figure 2: Photo of specimen designed for tensile and elongation at break, marked with two dashes.

2.2.3 Thermal ageing

Thermal ageing is a complex chemical process that ocurs under influence of heat, light, oxygen, mechanical tensile, etc...It results in changes in physical and chemical properties, which are time dependent. Ageing caused by heat action is the most studied.

"Ageing" term in rubber compounds is related to molecular scission, resulting from smaller chains and in the build-up of free radicals and /or crosslinking.

All samples were subjected to an accelerated ageing, in an air-forced oven, at 70 $^{\circ}$ C, for 96 hours. Aged mixtures were further evaluated with respect to tensile and elongation at break. Specimens thicknesses were 6 mm for hardness and 2 mm for remaining tests.

2.2.4 Hardness

A Shore A durometer, Instrutemp, Dp-100 portable digital model, was used for evaluations. This property is related to crosslinks density.

3 RESULTS AND DISCUSSION

3.1 Elementary analysis

There were obtained following results, for elementary analyses, according it is shown in table 1. The calculation for minima formula indicates lower ratio, in non decimal numbers, for elements atoms which build a substance. Calculation was accomplished by dividing mass percentage of each element, by corresponding molar mass. Found values are divided by lower number obtained, for completing compounds minima formula.

Dose (kGy)			
	Carbon _{1(%)}	Hydrogen (%)	Nitrogen (%)
0	86,415	8,37	0,305
5	86,31	8,45	0,33
10	85,45	8,355	0,245
15	85,9	8,42	0,395
20	86,205	8,505	0,305
25	86,21	8,49	0,545
30	86,235	8,3	0,2

Table 1 Elementary analysis results for irradiated truck chambers

It was observed for all irradiated truck chambers samples a slight or almost none modification in carbon, hydrogen and nitrogen levels; variations observed occur due to formulation used in elastomer acquisition process.

3.2 Tensile and Elongation at break

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



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



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

It is observed that values for tensile at break show a more sharp decrease in values for doses higher than 15 kGy, pointing to a raise in chain-scission caused by irradiation. For doses higher than 15 kGy, there is an equity in values suggesting a competition between scission and crosslinking.

For elongation at break results it is noted a raise 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 raise in chain-scission, because lower chains present lower elongation.

3.3 Thermal ageing

For comparison purpose, all properties after thermal accelerated ageing were identical to those ones exhibited for original materials, whose tensile and elongation at break results were previously discussed.

Figs 5 and 6 present obtained results for tensile and elongation at break, respectively, for truck chamber samples, after exposed to thermal ageing.



Figura 5. Tensile Strength for irradiated truck chamber before and after ageing.



Figura 6. Elongation at break for irradiated truck chamber before and after ageing

It was observed a slight increase in values for elongation at break for irradiated and aged truck chambers, indicating a competition between scission and crosslinking, due to the exposute to essay temperature. Tensile at break for irradiated and aged samples presented a decrease in values proportional to applied dose suggesting that chain scission prevailed on crosslinking.

3.4 Hardness

Hardness results are characteristic of rigidity presented for a rubber compound. Hardness results for irradiated and non-irradiated truck chamber samples are shown in Fig. 7.



Figure 7. Hardness of non-irradiated and irradiated truck chambers.

After irradiation, samples showed a decrease in values; nevertheless, with a raise in dose, it was verified an equity of values for all doses. According to expected, hardness is reduced after mechanical shearing: this is explaned based in degradation mechanism that leads to a de-polimerization, i.e., the weakning of elastomerc matrix imparted by chain-scission and/or a raise in crosslinks.

3. CONCLUSIONS

Elementary analysis did not reveal significant changes in Carbon (C) and Hydrogen (H) levels, present in all irradiated and irradiated samples, indicating that even after shearing the amount of atoms from the polymeric chain was preserved and conserved.

Tensile and elongation at break mechanical tests showed for irradiated samples values decreasing in function of a raise in dose, suggesting the occurrence of chain-scission, because smaller chains present smaller elongation and suffer rupture easily.

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

So, analyses showed that it is possible to accomplish controlled degradation of truck tire chambers, considering that in doses higher than 15 kGy occurs chain-scission. In a future work, it will be considered a mixture of a recovered rubber via irradiation with a virgin rubber and afterwards to accomplish material recycling.

ACKNOWLEDGMENTS

The authors thank to IPEN by truck tire chambers irradiation and to FAPESP by financial support.

REFERENCES

- 1. L. S. N. Ramos, A logística Reversa de Pneus Inservíveis: O problema da Localização dos Pontos de Coleta. Dissertação de Mestrado. Universidade Federal de Santa Catarina, Programa de Pós- Graduação em Engenharia de Produção, Florianópolis.(2005)
- 2. E. Kamimura, Potencial dos resíduos de borracha de pneus pela indústria da construção civil. Dissertação de Mestrado em Engenharia Civil. Universidade Federal de Santa Catarina, Programa de Pós-Graduação em Engenharia Civil, Florianópolis(2004).
- 3. "Materials". Michelin The tire digest. Disponivel em <u>https://wangyutire.en.made-in-china.com/?gclid=CjwKCAjw36DpBRAYEiwAmVVDMLzi1tynmAomkI-F8IRmwzJ-aCqvz6BabEJWW1-6_4NxfJPNDWC4wBoCoLsQAvD_BwE</u>, Acesso em 05.07.2019.
- 4. D. S. T. Suárez, G. E. Motter, H. Ramlow, Borracha sintética e borracha natural. Universidade Regional de Blumenau, Centro de Ciências Tecnológicas, Departamento de Engenharia Química (2010).
- 5. "The world's largest tire manufacturers in Q1 and Q2 2016, based on tire-related sales", Statista, 2016.
- 6. K.C. Barnawal, ASTM Standards & Testing of Recycled Rubber, Akron Rubber Development Laboratory, Rubber Division, ACS Meeting, San Francisco, CA, (2003).
- 7. D. Bruce. "2015 was strong year for U.S. tire industry". Tire Business. Crain Communications. Retrieved 13 December 2016.
- 8. "World Tires". Freedonia. Freedonia Group. Retrieved 19 May 2017.
- 9. "Research Report on World's Top 50 Tire Enterprises, 2010-2011 Market Research Report", Companiesandmarkets.com, Vertical Edge Limited, December 2, 2010, archived from the original on January 20, 2011.
- 10. "The world's largest tire manufacturers in Q1 and Q2 2016, based on tire-related sales (in billion U.S. dollars)", Statista, 2016.
- 11. "An unknow object: the tire Materials". Michelin The tire digest. Retrieved 2017.

- 12. P. da S. Campos, Aproveitamento Industrial da Borracha Reciclada de Pneus Usados. Dissertação (mestrado). 2006. 157 f. Universidade do Minho – Pós-graduação em Gestão Ambiental.
- 13. E. M. Beretta; J. O. Aguiar, M. B. Lauzer, J. I. Picoli, S. M. K Troncoso, Reaproveitamento da Câmara do Pneu de Bicicletas: Parâmetros Para Corte E Gravação A Laser, dezembro 2014 vol. 1 num. 4 - 11º Congresso Brasileiro de Pesquisa e Desenvolvimento em Design.