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GAMMA-RADIATION EFFECT ON THERMAL AGEING OF BUTYL RUBBER COMPOUNDS

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ABSTRACT

Butyl rubber has a comprehensive use in sealing systems, especially in tires inner tubes, due to their low permeability to gases. So, it is required that butyl rubber compounds show a better performance, more and more. Butyl rubber is provided with excellent mechanical properties and oxidation resistance. Besides showing these properties, radiation exposures impart modifications in physical-chemical and morphological properties on butyl rubber materials. When exposed to gamma-radiation, rubbers suffer changes in their mechanical and physical properties, caused by material degradation. The major radiation effect in butyl rubbers is chain-scission; besides, ageing promotes too the same effect with further build-up of free radicals. This work aims to the study of gamma-radiation in physical-chemical properties of butyl rubber subjected to thermal ageing. Doses used herein were: 25 kGy, 50 kGy, 100 kGy, 150 kGy and 200 KGy. Samples were evaluated before and after ageing according to traditional essays, such as: hardness, tensile strength and elongation at break. From accomplished assessments it is possible to affirm that at doses higher than 50 kGy it was observed a sharp decreasing in butyl rubber physical-chemical properties, before and after exposure to ageing.

1. INTRODUCTION

Ageing effect study in rubber artifacts is relevant especially due to cost and quality, making the material resistant or not to exposure under more severe environmental conditions. Ageing degree depends on various factors as polymer type, formulation, product geometry and environmental conditions [1].

Accelerated ageing essays aim to reproduce within a relatively shorter time interval ageing effects due to air action, radiation and temperature from larger exposures. For this, an adequate combination is accomplished between exposure periods and temperatures. Thermal ageing in rubber compounds present their physical and mechanical properties changed in function of modifications in structure or in morphology.

Ageing expression for rubber compositions is related to molecular scission that provokes the appearing of smaller chains and a higher number of chain terminals and/or crosslinking favoring a network structure strongly connected [2].

Both two basic reactions yield to elastomer chemical structure alterations and are able to be exemplified according to mechanism shown in Fig. 1, for simplified radical [3].

Free radicals can be built up by decomposition of small amounts of hydro-peroxides, present in rubber after the processing. Depending on rubber type, these reactions lead either to a chain-scission or to a raise in crossing bonds [4].

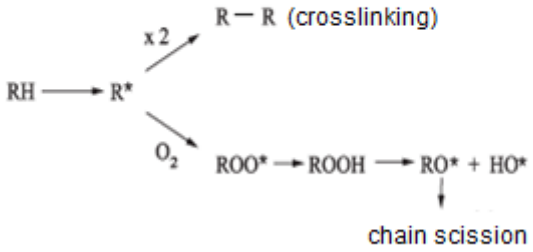

Figure 1: **Elastomers reaction mechanism after ageing**

It should be considered that chain-scission provokes a decreasing in viscosity; in case of crosslinking, the material becomes more rigid. Combination between scission and crosslinking results in creation of micro-cracks; the presence of oxygenated products was detected even before the occurrence of chain-scission [3].

Butyl rubber has in its composition: isobutylene copolymer (98%) and isoprene (2%). In hydrocarbon chain unsaturation level is very low, contributing with an excellent resistance to ageing [5, 6].

Butyl rubber when subjected to ionizing radiation exhibits two chemical effects: crosslinking and chain-scission with further degradation; nevertheless, chain-scission is predominant. Various authors concluded that the major and practically unique effect due to ionizing radiations in butyl rubber is chain-scission with a significant reduction in molar mass, prejudicing rubber physical and mechanical properties [7, 8].

Rubber ageing is a structural chemical phenomenon that affects directly material mechanical properties. Thermo-oxidative ageing and radiation modify compound molecular structure imparting changes in rubber properties. According to Farmer [9] and collaborators, oxidation in polymers occurs with settlement of molecular oxygen in double bond to yield oxidized peroxide.

This work aims to the study of accelerated ageing in vulcanized compositions of butyl rubber before and after gamma-radiation, within 0 to 200 kGy. Behavior of studied materials for different doses applied was assessed for mechanical properties.

2. MATERIALS AND METHODS

2.1. Materials

The elastomer used in this study was butyl rubber manufactured by EXXON MOBIL CHEMICAL, named Butyl 268 as commercial name, zinc oxide, stearic acid, sulfur, 2,2-

dithiocarbaptobenzotiazol (MBTS) and tetrametiltiuram disulfide (TMTD), all of them commercial grade and used as such.

Prepared composition had as reference a formulation normally used in tires and auto-parts industry. Referred composition was irradiated and further subjected to accelerated ageing process.

2.2. Mixture and vulcanization process

Samples were prepared in an open cylinder (Copê), with two rolls, 40 kg capacity, according To ASTM D-3182 [10], at approximately 60º C. Just after, the compound was vulcanized in a HIDRAUL-MAQ hydraulic press, 5 MPa pressure and prepared according to ASTM D-3182 [10], at 180ºC, for 4 minutes; specimens were further packed in plastic bags and sent to irradiation.

2.3. Ageing

Butyl rubber composition investigated after irradiation was subjected to accelerated ageing in an air-forced oven, at 70ºC, for 72 hours, in accordance with ASTM D 573[11]. Aged mixtures were assessed for tensile strength, elongation at break and hardness. Specimens thickness used in ageing essays were: 0.6 cm for hardness and 0.2 cm for other tests.

2.4. Irradiation

Samples were irradiated in CBE/EMBRARD and subjected to gamma radiation, oxygen environment, at 25, 50, 100, 150 and 200 kGy doses, in Nordion Canadian Irradiator, Cobalt 60 source, Model JS 7500, 5 kGy h^{-1} dose ratio.

2.5. Compounding characterizations

Analyses were accomplished according with ASTM rules, in triplicate, for obtaining results average. Specimens were cut in accordance with specified methods for each essay. There were performed following tests:

2.5.1. Hardness

Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values, derived from ASTM D 2240 [12]. Hardness is one of the properties the most evaluated in rubbers, 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.

2.5.2 Tensile strength and elongation at break

Tensile strength and elongation at break values were determined according to ASTM D-412 [13], by using a model C specimen, in an universal essay machine (EMIC), model DL 300, 300 kN maximum capacity and 500 mm/min grips speed, at room temperature.

3. RESULTS AND DISCUSSION

In Figure 2 are shown results for Tensile Strength and in Figure 3 results for Elongation at Break, both accomplished in butyl rubber irradiated and non-irradiated, before and after thermal ageing.

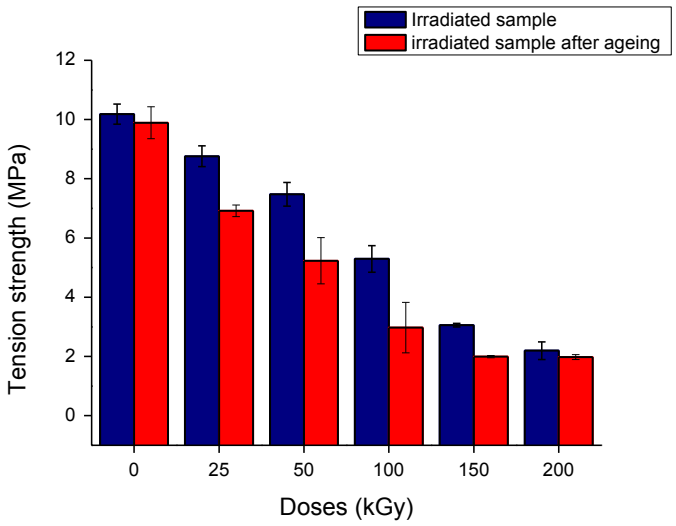

Figure 2:- Ageing effect in tensile strength in butyl rubber compounds, irradiated and non-irradiated, subjected to ageing.

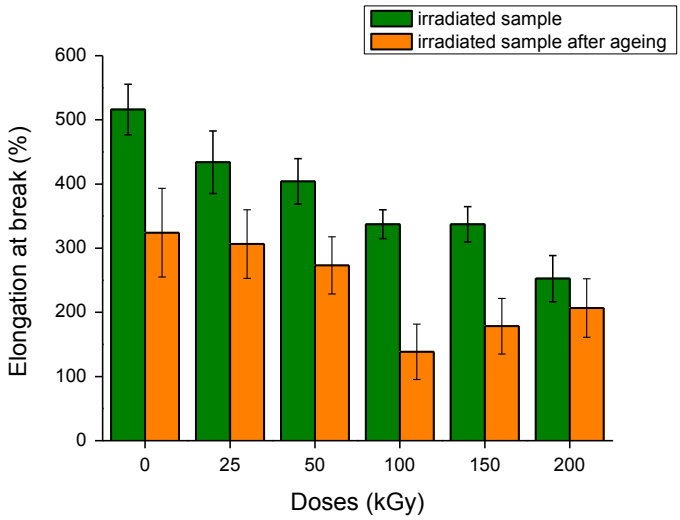

Figure 3: - Ageing effect in elongation at break of butyl rubber compounds, irradiated and non-irradiated subjected to ageing.

Tensile strength and elongation at break results for butyl rubber samples showed that for low doses up to 25 kGy there is equivalence among tensile and elongation values after ageing, indicating that degradative effects were not enough to change these properties. For doses within 25 kGy and 50 kGy it is observed a decreasing in tensile and a balance in elongation results; this is probably due to a competition between scission and crosslinking, with number of crosslinking compensating chain scission. For doses within 100 kGy and 200 kGy it was observed a predominance of chain scission: smaller molecular chains have weaker intermolecular forces that do not resist to tensile strength.

Hardness is directly associated to rubber crosslinking degree: the more vulcanized the higher compound hardness. In Figure 4 are shown results for accelerated ageing of irradiated butyl rubber samples.

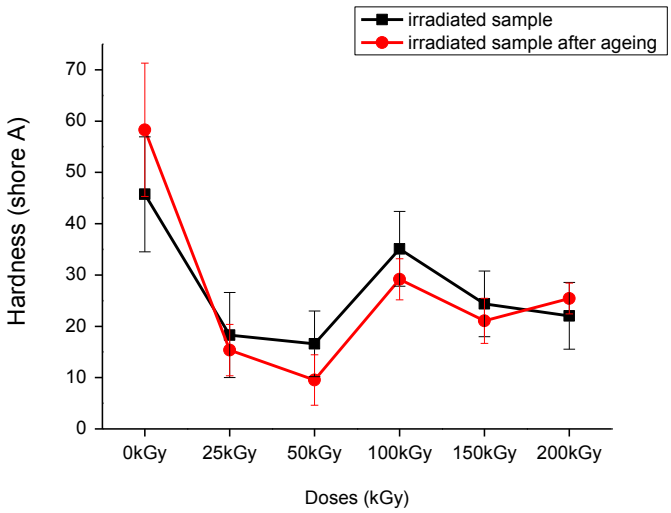

Figure 4: - Effect of ageing in hardness of butyl rubber compounds, irradiated and non-irradiated subjected to ageing.

According previously explained, hardness increases in function of a raise in crossing bonds [14]. Results showed that for non-irradiated sample (0 kGy) occurs an increase in hardness after ageing pointing toward a raise in build-up of crossing bonds: this will impart a higher stability to the compound. After irradiation and thermal ageing the hardness diminishes with further reduction in density of crossing bonds. For higher doses (above 50 kGy) occurs a slight raise non proportional to applied dose, probably due to oxidative degradation of polymeric chain.

Results for accelerated ageing tests in butyl rubber compounds showed that these compositions, even after irradiation, keep a lesser crosslinking index.

3. CONCLUSIONS

Processing by using gamma rays in butyl rubbers proved a tendency toward chain scission with further free radicals build-up. Obtained results showed that gamma rays processing followed by thermal ageing caused a higher degradation in this type of rubber. Tensile strength tests showed gel build-up and consequently a more rigid and less elastic rubber.
Based in given results it can be concluded that aged butyl rubber compounds show a higher crosslinking density and exhibit a higher vulcanization degree when compared to non-irradiated compound; consequently, there will be achieved best properties. Gamma rays are a powerful degradation agent for rubbers; along thermal agent imparts to rubber a low crosslinking density even at low doses. By increasing the dose take place chain-scission with molar mass reduction followed by degradation and creation of crosslinking sites.

It can be concluded that ageing mechanisms in butyl rubber contribute as well for the weakening of elastomeric matrix due to a backbone chain-scission reducing analyzed properties.

Material ageing imparts modification in crossing bonds structure as well in its length, quantity and type.

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REFERENCES

1. H. F. Mark, *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, New Jersey- Nova York (2007).
2. M.Garbarczyk, W. Kuhn, J. Klinowski, S. Jurga, "Characterization of aged nitrile rubberelastomers by NMR spectroscopy and microimaging". *Polymer*, **43**, pp. 3169–3172 (2002).
3. P. Lucas, M. Baba, J. Lacoste, J. L. Gardette,"Crosslinking of dienic elastomers resulting from ageing: X-ray diffraction and refractometry measurement",7**6**,pp.449-453(2002).
4. A. E. Somers, T. J. Bastow, M. I. Burgar, M. Forsyth, A. J.Hill, "Quantifying rubber degradation using NMR", *Polymer Degradation and Stability*, **70**, pp.31 -37 (2000).
5. "Borracha Butílica: PoliisobitilenoIsopreno (IIR)", http://ctborracha.com/?page_id=4330, (2015).
6. M.Smith, S.Berlioz, J. F. Chailan, "Radiochemical Ageing of Butyl Rubbers For Space Applications", *Polymer Degradation and Stability*, **98**, pp. 682-690 (2013).
7. T. Zaharescu, C. Postolache, M. Giurginca, "The structural changes in butyl and halogenated butyl elastomers during gamma irradiation", *Journal of Applied Polymer Science*,**59**, pp. 969-974(1996).
8. S. R. Scagliusi, E. C.L. Cardoso, A. B. Lugão, "A Influência da Incorporação de Borracha Irradida em Compostos de Borracha Clorobutílica",*Revista Ibero-americana*, **16** (4),pp. 185-190 (2015)
9. E. H. Farmer, H. P. Koch, D. A. Sutton, "The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. VII. Rearrangement of Double Bonds During Autoxidation". *Journal of the Chemical Society*,**3**, pp. 541-547(1943).
10. Annual Book of Astm Standards. "Standard Practice for Rubber- Materials, Equipment, and Procedures for Mixing Standart Compounds and Preparing Standard Vulcanized Sheets" .**v. *09.01***, 2008 (ASTM D-3182).
11. Annual Book of Astm Standards. "Standard Test Method for Rubber – Deterioration in Air Oven", **v. 09.01**, 1996 (ASTM D-573).
12. Annual Book of Astm Standards. "Standard Test Method for Rubber Property – Durometer Hardness". **v. 09.01**, 2008 (ASTM D-2240).
13. Annual Book of AstmStandards."Standard Test Methods for Vulcanized Rubber and Thermoplastic Rubber and Thermoplastic Elastomers – Tension", **v. 09.01**, 2008 (ASTM D-412).
14. R. Joseph, K. E. George, D. J. Francis, "Studies on the Cure Characteristics and VulcanizateProperties of 50/50 NR/SBR Blend". *Journal of the Chemical Society,* **35,** pp**.** 1003–1017 (1988).