

EFFECT OF GAMMA IRRADIATION ON SULFUR-CURED CHLOROBUTYL RUBBER

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ABSTRACT

Chlorobutyl rubber (CIIR) is similarly manufactured to butyl rubber (IIR). The insertion of chlorine atom in isoprene group represents an improvement in its properties, such as: high vulcanizing speed, low permanent stress and compatibility with other types of rubber. The presence of reactive chlorine in butyl chlorate allows a variety of vulcanizing techniques, being the cure via sulfur, the most conventional. In these compounds carbon-halogen bonds are weaker than carbon-carbon and carbon-hydrogen bonds, and the main effect of radiation is to break the carbon-halogen bond to give an organic free radical. Irradiations of certain alkyl chlorides can bring about isomerism in which the location of the halogen atom is changed, the carbon skeleton of molecule remaining unaltered. Irradiation of n-butyl chlorides gives high yields of tertiary carbon. The major effect of high energy photon, such as gamma rays, in organic polymers is the generation of free radicals, along changes in mechanical properties. This work aims to the study of irradiation effect on mechanical properties of a sulfur cured chlorobutyl rubber compound, gamma irradiated within 25, 50, 100, 150 e 200 kGy doses range. The techniques used in their characterization were: strength – stress analysis and elasticity modulus. Results obtained were investigated, demonstrated and discussed.

Key-Words: Chlorobutyl rubber, mechanical properties, gamma radiation, sulfur-cured.

1. INTRODUCTION

Chlorobutyl rubber (CIIR) is manufactured similarly to Butyl rubber (IIR) (isobutylene and isoprene copolymer) and is obtained from its chlorination, by varying chlorine contents within 1.1% to 1.3% range [1], by inserting chlorine in isoprene group. Rubber properties show various advantages, such as: high vulcanization speed, low permanent deformation and compatibility with other rubbers [2], making feasible the combination between an excellent ozone resistance and permeability to gases besides a good thermal stability and elevated resistance under oxygen action. It has been used in a lot of applications such as tires spare-parts (air chambers, tires internal coatings, etc.) and various artifacts (lids, gaskets, etc.) [3].

Elemental sulfur and organic accelerators are widely used to cross-link butyl rubber for many applications. The vulcanization proceeds at the isoprene site with the polysulfidic crosslinks attached at allylic positions, displacing the allylic hydrogen. The number of sulfur atoms per cross-link is more than one to four [4].

Compounds used to manufacture rubber products should be provided with high elasticity and good mechanical properties and in order to comply with these requirements rubbers are

vulcanized into different conditions. Physical properties exhibited by rubber compounds are influenced by the acceleration system used to perform their crosslinking. Usually, rubbers are crosslinked with sulfur or peroxide systems, at high temperatures, within 150-180°C [5]. Sulfur vulcanization reactivity and physical properties are affected by elastomers chemical structure and molecular weight [6]. Figure 1 illustrates the main effects of vulcanization on use-related properties [7].

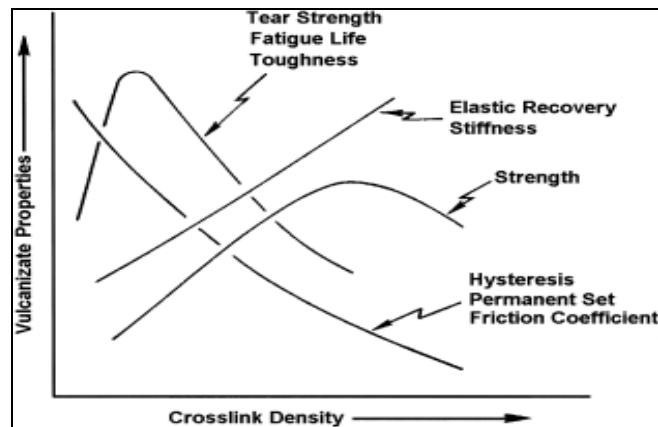


Figure 1. Properties versus crosslinks

Sulfur vulcanization with unsaturated rubbers takes place through complicated radical substitution in forms of mono, di, or polysulfide bridges (Fig. 2) and sulfur containing intracyclization with polymer molecules. Crosslink density and distribution affect their physical properties and the stability under aging process are dependent on accelerator type, ratio of accelerator to sulfur, reaction temperature and time [8].

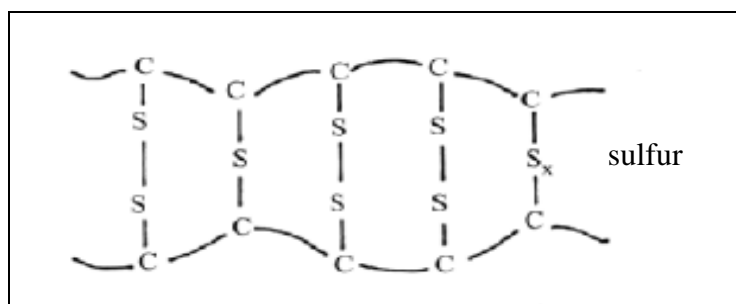


Figure 2. Schematic representation showing forms of mono, di and polysulphidic linkages (predominantly polysulphidic $x > 3$).

The irradiation causes effects in vulcanized butyl rubber properties, especially shown in mechanical analyses [9]. The major effect of ionizing radiations on butyl rubber is chain scission accompanied with a significant reduction in molar mass [10]. The energy transfer

from the radiation to the matter does not take place selectively, but the lower the bond energy, the faster the bond scission [11]. Radiation chemical behaviors are determined by the presence of tertiary butyl chlorides [12] [13]. The isomerizations are attributed to free radical chain reactions [14].

This work aims to show effects of gamma radiation in properties of chlorobutyl rubbers vulcanized with sulfur. Compounds were subjected to 25, 50, 100, 150 and 200 kGy radiation doses. Irradiation effects in properties of rubber compounds were investigated.

2. MATERIALS AND METHODS

2.1. Sample Preparation

Chlorobutyl rubber used in this study was chlorobutyl Ht 1066 from Exxon Mobil Chemical, having as reference commonly formulations in tires and automotive spare-parts industry (Table 1). Admixtures were prepared in an open roll-mill (*Copê*), 40 kg capacity, according to ASTM D-3182 [15].

Table 1. Formulation of chlorobutyl rubber.

Ingredients	Sample (phr)
Chlorobutyl Rubber	100
Zinc Oxide	5
Stearic Acid	1
Magnesium Oxide	0,5
Naphthenic oil	28
Carbon Black GPF 660	75
Sulfur	0,5
ZBEC	2

Samples were cured in an electrically heated HIDRAUL-MAQ at 5 MPa pressure and 165°C temperature to their optimum cure times (determined from a rheometer Monsanto R-100).

2.2. Methods

Cure sheets in 11,5 x 11,5 x 0,1 cm³ dimension, 250g total weight, were irradiated in Embrarad/CBE, gamma rays Cobalt 60 (⁶⁰Co) in air, at 5 kGy/h rate, within a 25, 50, 100, 150 and 200 kGy doses range.

For the characterization of triplicate samples, there were assessed following properties, before and after radiations:

2.2.1 Rupture tensile

It is defined as the applied force by initial area unit of a specimen, at the rupture point (ASTM D 412) [16]. Tests were accomplished in an *EMIC* dynamometer; model DL 300, 300 kN maximum capacity.

2.2.2 Elongation or elastic stress

Generally it is expressed as the percentage between two marks in uniform cross section. Ultimate elongation is the elongation at which rupture occurs in the application of continued tensile stress (ASTM D 412) [16].

Tests were accomplished in an *EMIC* dynamometer, model DL 300, 300 kN maximum capacity.

2.2.3 Modulus of elasticity

Modulus of elasticity is a measure of how a material or structure will deform and strain when placed under stress. This property is often determined in a laboratory, using an experimental technique known as *tensile testing*, which is usually conducted on a sample with specific shape and dimensions.

Tests were accomplished in an *EMIC* dynamometer; model DL 300, 300 kN maximum capacity.

2.2.4 Hardness

Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values, derived from ASTM D 2240 [17]. 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.

2.2.5 Scanning electron microscopy (SEM)

This analysis aimed to study rubber morphology at different enlargements. It was used a PHILIPS XR-30 scanning electron microscope, located in Centro de Ciência e Tecnologia de Materiais (CCTM), IPEN-CNEN/SP. All samples were investigated by using enlargements of 1,000 times.

3. RESULTS

Chorobutyl rubber shows a significant degradation under ionizing radiation. The major and practically single effect of ionizing radiation on this type of rubber is the chain scission with a significant reduction in molar mass. The presence of halogens in butyl rubber induces a diminishing in material resistance to radiation action, due to different dissociation energies.

Results for tensile, ultimate elongation (elongation at break) and hardness at different radiation doses are presented in Fig. 3 and Fig. 4, respectively.

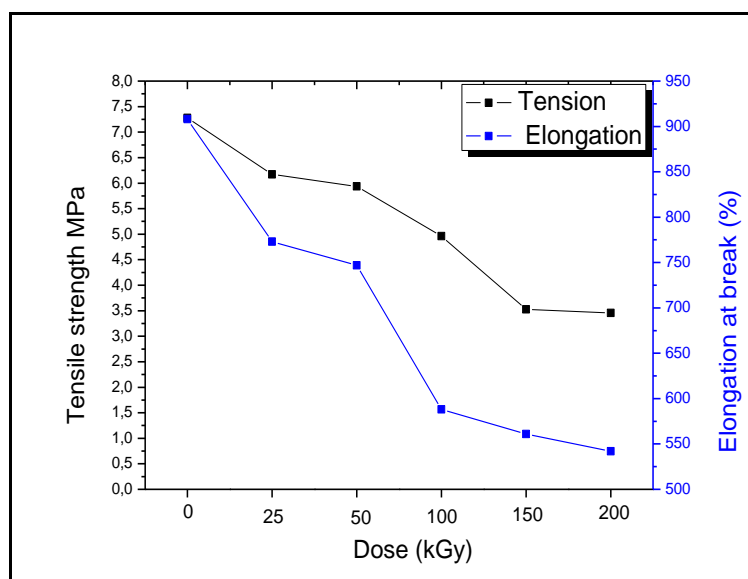


Figure 3. Tensile strength and Elongation at break values for irradiated and non-irradiated rubber.

According to Figure 3 it can be concluded that a raise in irradiation dose imparts a significant loss in properties of vulcanized compounds; a loss in rupture tensile is proportional to a reduction in elongation, indicating a less elastic and more rigid material, once the lower the elongation the higher the rigidity. A sharp decline even at low doses, some of them proportional to the applied dose, points at a relatively high flexibility of tridimensional network structure, due to the presence of polysulfides ($C-S-S_n-C$), being “n” value higher than one [18].

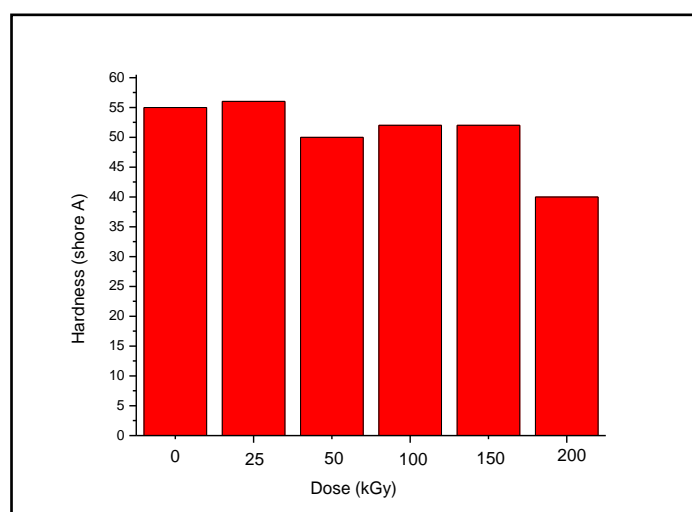


Figure 4. Effects of radiation doses on hardness of chorobutyl rubber.

Figure 4 shows hardness variation in function of radiation dose, with no significant changes in compound hardness when raising radiation dose. It was verified that for doses higher than 150 kGy takes place a softening in rubber, probably caused by polymeric chain flexibility, due to the presence of poli-sulfide bonds.

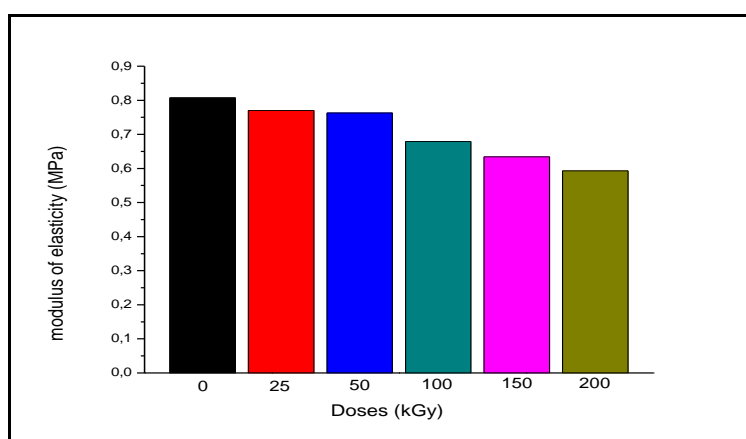


Figure 5. Radiation effects on elasticity modulus

Figure 5 shows that the variation in elasticity modulus is proportional to dose, that is, the higher the dose the lower the modulus.

It was observed too effects caused by irradiation in rubber morphology, from investigations performed by SEM (Scanning Electron Microscopy), within 1,000 times. Micrographies obtained are presented in Fig. 6.

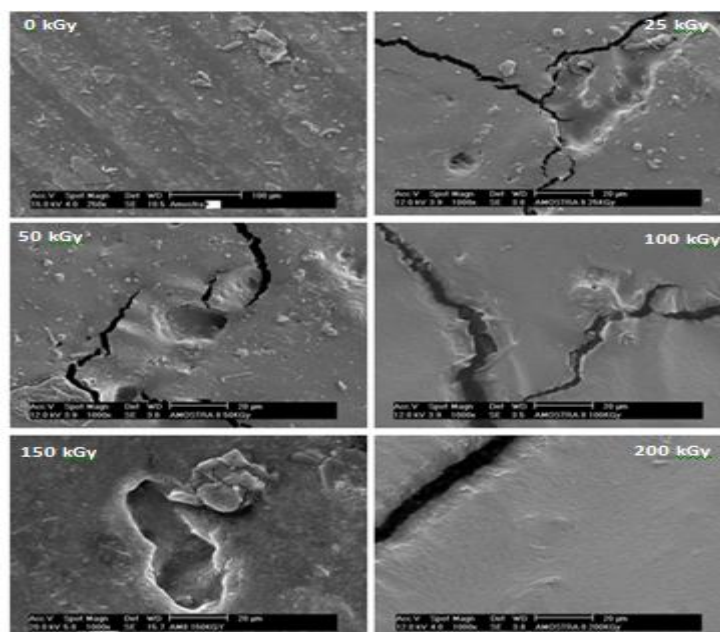


Figure 6. Micrographies for irradiated and non-irradiated samples (1000 times enlargement).

Fig. 6 indicates the occurrence of failures in surface of irradiated samples and a certain rugosity caused by irregular dispersion of fillers in mixtures. Fractures and wrinkles in material surface for high doses indicate that radiation can damage polymer surface. Fractures observed in micrographies give a clue of polymer degradation in function of gamma rays. Apparently the application of radiation does not produce morphological modifications in the material, but makes it fragile, causing wrinkles on the surface.

4. CONCLUSIONS

The highest degradation occurred in chlorobutyl rubber cured with sulfur. For low doses it was kept the crosslinking and at high doses occurred degradation. It was observed that for doses higher than 100 kGy there was a prejudice in assessed properties

It can be concluded that radiation can change the mechanical properties of rubber by destroying the cross-links that keep together rubber molecules. By affecting this cross-linkage, radiation can change the tensile strength and the hardness of the rubber.

Rubber cured with sulfur when exposed to higher doses of radiation showed a decreasing in tensile strength and elongation at break tests results, consequently reducing the distance that the rubber can stretch before breaking. Low doses of radiation can just impart a few changes in rubber structure.

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