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Research Article

Radiation Effects on Crosslinking of Butyl Rubber Compounds

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Abstract

When butyl rubbers are subjected to high energy radiation, they form easy free radicals that initiate various chemical reactions. These reactions alter the molecular distribution of irradiated rubbers by crosslinking or scission affect their physical and mechanical properties. This work aims to the analysis of effect induced by γ-exposure on the crosslinking density in butyl rubbers by swelling measurements accomplished before and after irradiation at 25, 50, 100 and 200 kGy, with further evaluation of crosslinking density accomplished by Flory-Rehner equation; this is a proper procedure for the qualification of radiation resistance. It can be noticed that changes in material structure was due to build-up of new three-dimensional network in studied rubbers. Changes in crosslinking density of butyl rubber compounds emphasize that degradation mechanism is strongly influenced by gamma-radiation doses higher than 50 kGy, since chain scission process predominates over crosslinking reaction.

Keywords: Butyl Rubbers; Crosslinking; Degradation; Chain Scission; Gamma Rays

Introduction

Butyl rubber is a synthetic rubber, a copolymer of isobutylene with isoprene. Butyl rubber is produced by polymerization of about 98% of isobutylene with about 2% of isoprene. Structurally, polyisobutylene resembles polypropylene, having two methyl groups substituted on every other carbon atom [1]. In its hydrocarbonated chain (Figure 1), unsaturation level is very low and this imparts an excellent resistance to ageing, low permeability to gases, good thermal stability, high resistance to oxygen, ozone and solar radiation action and excellent resistance to humidity and to chemical substances attack [2,3].

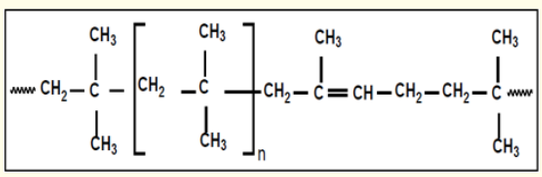

Figure 1: Butyl rubber structure illustration.

Butyl rubber compound acquires mechanical properties due to build-up of crosslinks among polymer macromolecules. These bonds aim to unite elastomer macromolecules, hindering that they flow on each other. This molecular arrangement grants to the elastomer the capacity to support stresses associated to elastic deformations imparting to the material the capacity to recover its original form [4].

The formed intermolecular elastically effective crosslinks are usually classified as carbon-carbon (C–C) crosslinks and sulfidic crosslinks. The C–C crosslinks are created directly between the polymer chains. In contrast, the sulfidic crosslinks are made of a variable number of sulfur atoms. Depending on this number, sulfidic crosslinks are further subdivided into monosulfidic (C–S–C); disulfidic (C–S2–C); and polysulfidic (C–Sx–C, x ≥ 3) crosslinks. All of these crosslinks show varying structure and length, resulting in various characteristics. As a result, they provide different properties to the material. Therefore, it is generally assumed that after the crosslink density, the crosslink structure is the second most important parameter influencing the elastomer properties [5,6].

Due to vulcanization rubber acquires mechanical resistance contributing for a raise in elasticity modulus and mechanical prop-

erties [7]. Elastomers crosslink density determines comprehensively elastomers mechanical properties. In order to improve the performance of these systems it is fundamental to understand relationship among vulcanization process, resulting network structure and their physical properties. Structural characterization of elastomeric networks is generally performed by mechanical essays [5].

Characterization of the network introduced into elastomers by vulcanization has been a fascinating problem since a quite long past. Flory (1943) has developed an equation connecting the equilibrium swelling volume with the degree of cross-links [8].

When polymer is subjected to gamma radiations, many chemicals reactions may occur affecting physical and mechanical properties of material [9-11]. The primary event occurs when a molecule interacts with ionizing radiation, involving the injection of an electron to form a radical, which could lead to macromolecular chain scissions, crosslinking, changes in stereochemistry or formation of grafts through complex chemical reaction process [12].

The major effect of ionizing radiation in butyl rubber is chain scission with a significant reduction of molar mass [13]. Transference of radiation energy to butyl rubber does not occur selectively but the low unsaturation degree of these rubbers favors a quicker scission [14].

The chain scission process usually leads to a reduction of mechanical properties whereas the crosslinking process results in an increase in mechanical properties. Moreover, the materials properties as mechanical for example are a complex function of crosslink chemical density and crosslink nature, both chemical and physical interactions involved [15].

The aim of this paper is the analysis of effect induced by gamma-exposure on the crosslinking density in butyl rubbers by swelling measurements accomplished before and after irradiation.

Experimental

Materials

Elastomeric compounds were prepared using Butyl grade 268, from Exxon Mobil Chemical. Samples were prepared with formulation based on standards commonly used in tires according to automotive industry (Table 1). Parts per hundred rubber (phr) is a measurement unit used in formulation of rubber compounds and refers to the amount of a particular compound in relation to the total amount of rubber used per 100 parts of rubber.

Ingredients	Amounts (phr)
Butyl rubber	100
Zinc Oxide	5
Stearic Acid	1
Parafinic Oil	25
Carbon Black	70
Sulfur	2
MBTS	0.5
TMTD	1

Table 1: Formulation of butyl rubber.

Preparation of mixtures

Admixtures were manufacturer of the equipment, open roll-mill (Copê), 40 kg capacity according to ASTM D-3182-9 [16]. Samples were cured in an electrically heated HIDRAUL-MAQ at 5 MPa pressure and 180°C temperature to their optimum cure times (determined from a rheometer Monsanto R-100).

Irradiation

Cure sheets in 11.5 x 11.5 x 0.1 cm dimension, 250 g total weight, were irradiated in Embrarad/CBE, gamma rays Cobalt 60 (^{60}Co) in air, at 5 kGy/h rate, within a, 25, 50, 100 and 200 kGy doses range.

Characterization

Characterizations were accomplished before and after irradiation according to following:

- Determination of the swelling rubber

The specimens wirh approximate dimensions 1.5 x 1.5 cm were exposed at room temperature (25°C), previously weighed and immersed in toluene up to weight stabilization (about five days). Each value was obtained from five samples average, at various time periods. The specimens were removed, gently wiped and paper dried to remove solvent excess in sample surface and reweighted after 30 s. Upon completion of test samples were weighed and then dried at room temperature for 24 hours. These analyses were performed in accordance with ASTM D 3616-9 [17].

Degree of swelling was calculated according to Equation 1.

$$Q = \frac{M - Mo}{Mo} \times 100 \qquad (1)$$

Where

M_0 is the initial weight of sample (g) and

M is the final weight of sample (g)

- Crosslink density

Crosslink density was calculated by equation developed by Flory and Rehner (Equation 2), based on the equilibrium swelling in organic solvents [18]. Crosslink density [υ] was calculated from the equilibrium swelling.

$$v = -\frac{1}{V}\left[\frac{\ln(1 - VR) + VR + \mu VR^2}{VR^{1/3} - \frac{VR}{2}}\right] \quad (2)$$

Where

- Vr is the volume fraction of swollen rubber;
- μ is the parameter Rubber - solvent interaction (IIR toluene - 0,5) [18];
- V is the molar ratio of the solvent volume in cm3. mol^{-1} (toluene =105.91 $cm^3.mol^{-1}$) [18,19].

Samples were weighed daily at that extent no more weight change was verified within 24 hours. Then, samples were dried in a vacuum oven at 60° C for 4 hours. Specimens dimensions used were 2.0 x 2.0 x 0.2 cm and the representative one was the result arithmetic mean of five determinations.

Results and Discussions

Applications of radiation processing for the manufacture of new products or for polymeric recycling are based on the instant bonds breakage.

The penetration of solvent molecules depends on many factors, such as free space between molecules, size of molecules and crosslinking degree, all of them of relevant significance. The exposure to ɣ-radiation causes a reduction in molecular characteristics: molecular weight, size and distribution; the nature of bonds existing in irradiated materials defines the amplitude of modifications.

In Figure 2 swelling degrees corresponding to longer immersion times (72, 96 and 120 h) for irradiated and non-irradiated butyl rubber. At 200 kGy evaluation was prejudiced because samples were completely dissolved.

The radiation stability of butyl rubber allows the easy diffusion of foreign molecules when irradiation dose becomes considerable. At very low dose, 25 kGy, butyl rubber does not change dimensional features according to negligible increase of swelling degree. The presence of double bond in the backbone of butyl rubber determines similar values of swelling degree for low irradiation doses For exposures exceeding 50 kGy it is noticed an advanced level of degradation.

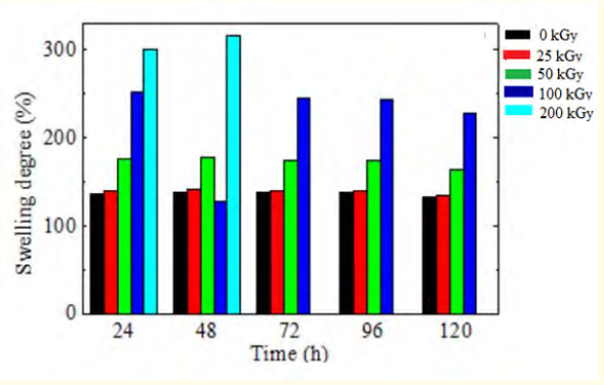

Figure 2: Swelling degree of butyl rubber after and before gamma radiation.

In Figure 3 the values of free volumes describe similar tendencies of degradation, according to swelling determinations. The decrease of free volumes from fragmentation occurred during radiolysis can be explained by the advanced swelling when more incorporated solvent enlarges the size of entangled zones.

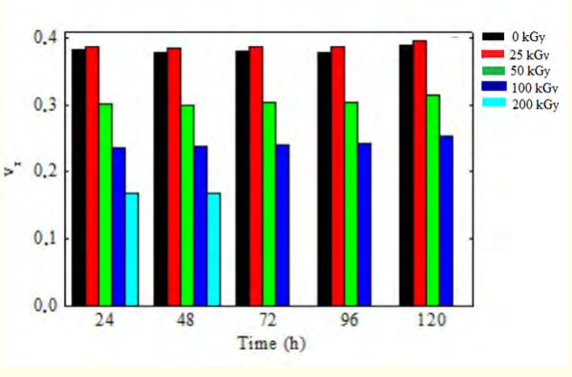

Figure 3: Modification in the free volumes of butyl rubber irradiated and non-irradiated.

The action of gamma radiation concerns not only the fragmentation of molecules, but also the cleavage of intermolecular bridges that joint macromolecules in gel islands. Figure 4 illustrates the reaction of butyl rubber to the damaging action of energy transferred into radiation processed butyl elastomers.

The strike diminution of crosslinking density in ɣ-irradiated butyl rubber is the effect of the presence of high insoluble frac-

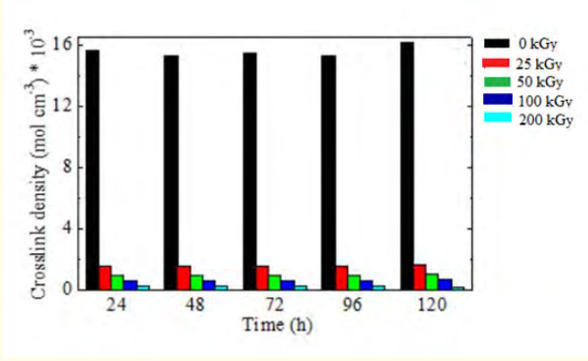

Figure 4: Modification in crosslinking density of butyl rubbers irradiated and non-irradiated.

Conclusions

Swelling of butyl rubber showed a comprehensive predominance of chain-scission with molar mass reduction. Another relevant phenomenon is a higher fragility of butyl rubber to ionizing radiation with a complete solubilisation after 48 h for irradiated rubber at 200 kGy.

The availability of butyl rubbers to the diffusion of foreign entities, either molecules or free radicals is demonstrated by the adequate swelling properties, which can be considered as the basic information for their radiation processing for other applications including the reclaiming polymer wastes.

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