



Effect of gamma radiation on chlorobutyl rubber vulcanized by three different crosslinking systems

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ABSTRACT

The development of halogenated butyl rubber (chlorobutyl) in the 1950s and 1960s greatly extended the usefulness of butyl. Their properties allowed the development of more durable tubeless tires with the air retaining innerliner, chemically bonded to the body of the tire. Tire innerliners are by far the largest application for halobutyl. When polymers are subjected to high energy radiation, a number of chemical reactions may occur following the initial ionization and excitation events. These reactions lead to changes in the molecular weight of the polymer through scission (S) and crosslinking (X) of the molecules and affect the physical and mechanical properties. In the halobutyl rubbers the chain scission may predominate. This work aims to show effects of gamma radiation in properties of chlorobutyl rubbers vulcanized with sulfur, sulfur donor and phenolic resin. The butyl rubber has been already studied by us previously. The samples were characterized before and after irradiation. Gamma radiation doses used were: 25 kGy, 50 kGy, 100 kGy, 150 kGy and 200 kGy, in order to identify which cure system is the most stable under irradiation. In this study we observed that the properties of all samples were affected irrespective of the vulcanization system.

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1. Introduction

Chlorobutyl rubber (CIIR) is manufactured similarly to butyl rubber (IIR), from its chlorination. Chlorine content varies from 1.1 to 1.3% (Khairi, 1987). Chlorobutyl rubber shows advantages over butyl rubber as, for example, higher vulcanization speed, lower compression set and compatibility with other types of rubber (Morton, 1989). Besides conventional vulcanization with sulfur and accelerators it is possible to use other vulcanization techniques for CIIR, which are inadequate for butyl rubber (Exxon, 2006) such as vulcanizations with zinc oxide, resin, sulfur, sulfur donors and sulfur at low temperature (Morton, 1989). Through the use of sulfur vulcanization, the most used, it is possible to build various types of crosslinkings, mono- (C–S–C), di- (C–S–S–C) and polysulfide (C–S–S_n–C) structures (Sombatsompop, 1998).

The crosslinking structure for sulfur donors vulcanization is generally monosulfidic (C–S–C), i.e., shorter and less flexible than polysulfides. The level and the rate of crosslinking achieved by phenolic resin can be increased through the presence of halogen (Chough and Chang, 1996). In most cases, properties resulting from vulcanization depend on the number and the type of crosslinkings (Krambeer, 1991) as well as the stabilizer system (Spenadel, 1979).

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Charlesby (1960) studied the radiation processing of butyl rubber and showed a chain scission trend. Chapiro (1962) had already studied the radiation chemistry of butyl rubber and showed that its main chain scission tendency was caused by the presence of a tertiary carbon atom. Irradiation induces the isomerization of halo butane which is attributed to radical-free chain reactions (Martin and Williams, 1970). Irradiation of polymers by using ionizing radiation from industrial sources (gamma rays, accelerated electrons) promotes the creation of very reactive intermediates (ions and excited states), that can follow several reaction paths resulting in free radicals and consequently in disproportion, hydrogen abstraction, arrangements and/or the formation of new bonds. The degree of these modifications depends mainly on the structure of the polymer and the irradiation source (Lugao et al., 2007; Chmielewski et al., 2005). The major effect of ionizing radiation on butyl rubbers is chain scission accompanied by a significant reduction in molar mass (Chandra et al., 1982; Hill et al., 1995). According to Zaharescu et al. (2001), the energy transfer from radiation to matter is not selective, the lower the bond energy the faster is the bond scission.

Recycling of butyl rubber from inner tubes, using irradiation of cryogenically ground rubber crumbs, has been developed commercially in China, where a pilot scale plant is operating at 2,000 tons per year (Binglin et al., 1993; Yang, 1998; Yang and Liu, 2000). Despite the mentioned technology being a successful one,

the effects of the different vulcanization systems (sulfur, sulfur donor and resin) of the industrial waste on the recycling processes have not yet been studied. The aim of this work is to evaluate the changes in mechanical and thermal properties of CIIR vulcanized under the three mentioned systems at different radiation doses used in the recycling process, as well as to evaluate the radiation induced effects, by using mechanical and thermal analysis.

2. Materials and methods

2.1. Materials

Chlorobutyl rubber used in this study was chlorobutyl HT 1066 from Exxon Mobil Chemical, a resin *p*-octilfenol-formaldehyde (SP 1045), donated by Schenectady Brasil Ltda, having as a reference commonly used formulations in tires and automotive spare-parts industry. Admixtures were prepared in an open roll mill (*Copê*), 40 kg capacity, according to ASTM D-3182. Chlorobutyl rubber samples used three different types of cure (see Table 1). Optimum cure times were determined by a rheometer Monsanto R-100.

2.2. Methods

Samples were cured by thermal heating in a hydraulic press at 5 MPa and 170° for 12 minutes, supplied by HIDRAUL-MAQ.

Cured sheets of 11.5 × 11.5 × 0.1 cm³ dimension and 250 g total weight were cut in pieces of about 1 mm, and used a ⁶⁰Co industrial gamma source, supplied by EMBRARAD and irradiated at a 5 kGy/h rate in air. Samples were irradiated at 25, 50, 100, 150 and 200 kGy doses and were reprocessed in a two roll mill to improve the uniformity of the mixtures after irradiation.

2.2.1. Mechanical properties

The characterization of the samples, tensile strength, elongation at break and elastic modulus were assessed and evaluated by using an EMIC dynamometer, model DL 300, 300 kN maximum capacity according to ASTM D 412.

2.2.2. Thermogravimetric analysis (TGA)

TGA was performed by using a Mettler-Toledo SDTA/851° apparatus, at a 10 °C min⁻¹ heating rate, from 25 °C to 700 °C, under O₂ atmosphere. The analysis accomplished under O₂ atmosphere reveals decomposition by oxidation effect.

3. Results and discussions

Figs. 1 and 2 show the mechanical properties of tensile strength and elongation at break as a function of dose and the

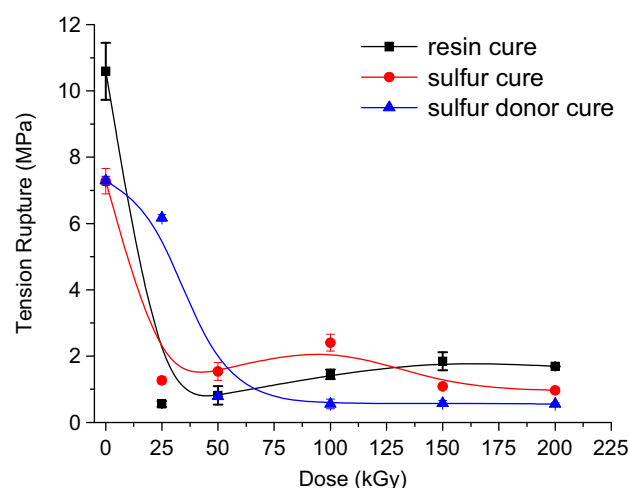


Fig. 1. Tension strength for chlorobutyl rubber cured with sulfur, resin and sulfur donor.

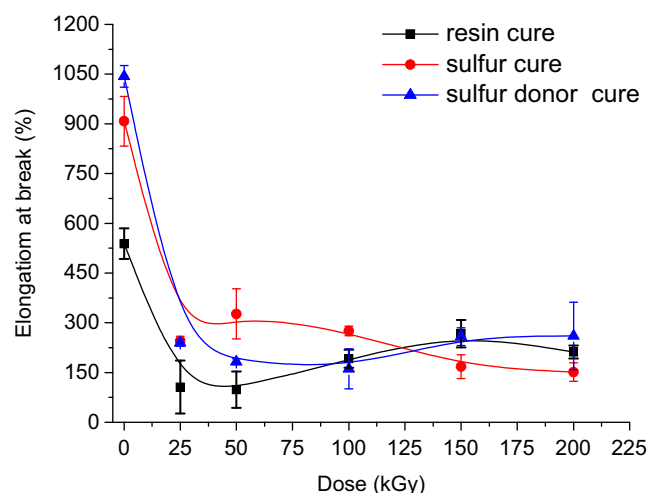


Fig. 2. Elongation at break for chlorobutyl rubber cured with sulfur, resin and sulfur donor.

curing system. It was observed that before irradiation the sample vulcanized with resin has a higher value of stress rupture and lower elongation compared to the values observed by the mixtures vulcanized with sulfur and sulfur donor. These results can be attributed to the higher level of cure of this compound, as the level of cure is directly related to the stress rupture (Ciesielski, 1999). After irradiation and roll mill processing, regardless of the vulcanization system, all samples have loss properties. i.e. the values of stress rupture and elongation suffer a marked decrease even at low doses (25 kGy). This loss property may be caused by shearing of the samples after irradiation, because even at increasing dose values the tensile strength and elongation did not suffer significant changes. The only explanation for this marked loss is the shearing in roll mill, because radiation causes losses which are proportional to the dose (Chandra et al., 1982; Hill et al., 1995; Dubey et al., 1995; Zaharescu et al., 2001).

The elastic modulus of the samples, resin, sulfur and sulfur donor, is shown in Fig. 3. The resin vulcanized sample presented the highest values, indicating a higher crosslink density. It was verified that the sample's elastic modulus decreases with radiation dose much smoother than tensile strength.

So we can understand that, after irradiation, the roll mill processing has caused, in a predominant way, a molecular chain scission without affecting the crosslink as strongly. Based on previous studies

Table 1

Formulation of chlorobutyl rubber.

Ingredients	Resin cure (phr)	Sulfur cure (phr)	Sulfur donor cure (phr)
Chlorobutyl Rubber	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	0,5	1	1
Magnesium Oxide	–	0,5	0,3
Plasticizer oil	5	28	15
Carbon Black	60	75	50
Phenol Resin	10	–	–
Sulfur	–	0,5	–
ZBEC	–	2	–
ZBDC	–	–	2

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