



Radiochemical ageing of butyl rubbers for space applications

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ABSTRACT

The effect of ⁶⁰Co gamma irradiation in inert atmosphere at 25 °C and 70 °C on a butyl elastomer filled with carbon blacks has been investigated by SEM, ¹³C NMR, swelling measurements and mechanical tests.

An increase of the tensile strength of the material was observed during ageing. This increase of the mechanical properties is due to a modification of the rubber network structure. This hypothesis was confirmed by swelling measurements done before and after ageing at various irradiation doses associated with an estimation of the crosslink density by the Flory–Rehner equation. Crosslinking and chains scission reactions occurred under irradiation and the contribution of both processes was estimated thanks to the Charlesby–Pinner equation. The high level of carbon blacks in the butyl rubber formulation plays also an important role in the degradation process. Correlations between mechanical properties and crosslink density are also presented. The modification of the rubber mechanical properties underlines that the degradation mechanism is strongly influenced by the temperature especially at high irradiation doses. At 25 °C, the chain crosslinking process predominates over the chain scission reactions whereas the two phenomena are in competition at the ageing temperature of 70 °C.

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1. Introduction

Over the years, synthetic rubbers have been used in a variety of technical applications and so in different conditions which widely vary and are often complex due to the number of potential stresses. Butyl rubber is a copolymer of isobutene and isoprene which is well known for its strong capability of energy dissipating combined with a good chemical stability and a good moisture ozone resistance [1,2]. Butyl rubbers and particularly their halogenated derivatives have recently received increasing interests thanks to their remarkable damping properties. Halogenated butyl rubbers could also be used for anti-vibrational systems in satellite applications. Therefore, these rubbers should fulfill the space technology requirements during all the satellite lifetime, which varies between 5 and 10 years. The space environment is especially harsh towards elastomers [3–6]. In most cases, radiations can be considered as the most important factor leading to the degradation of the rubber

properties. Damaging effects can obviously be aggravated by the other environmental factors (temperature, vacuum...). The use of rubbers in so severe conditions requires to have a reliable experimental method to obtain detailed data concerning the evolution of the material properties arising from this environment and so insure the durability of the satellites components. This necessitates accelerated degradation tests at laboratory scale in order to predict the material properties changes in service conditions.

In oxidative atmosphere, radiation effects on butyl rubbers have been studied by various authors [7–11], but only a limited number of works has been reported on the irradiation of butyl rubbers in inert atmosphere [9].

When polymers are subjected to gamma radiations, many chemical reactions may occur affecting the physical and mechanical properties of the material [10,12,13]. The primary event which occurs when a molecule interacts with ionizing radiation involves the ejection of an electron to form a radical which could lead to macromolecular chain scissions, crosslinkings, changes in stereochemistry or formation of grafts through complex chemical reactions processes. The role of the temperature on the degradation process is crucial for exposed materials [12] and should be considered carefully. The simultaneous action of high temperature and radiations on rubber materials could lead to dramatic modifications of the material properties since the heat treatment alone leads to thermal degradation in many cases [14]. Concerning the

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extent of degradation, it is difficult to make predictions since all the reactions which occur at room temperature, benefic as well as detrimental, may occur at elevated temperatures with higher rates. Hence, there is no general rule to predict the behavior of a specific rubber submits simultaneously to radiation and temperature and each case must be studied independently. Many techniques are used in order to investigate the resulting changes of the material and particularly the molecular structure (FTIR) [15,16], the thermal stability and the glass transition behavior (DSC, TGA) [17,18] or the mechanical properties (Dynamic Mechanical Analyses (DMA), tensile tests...) [19–21].

The chain scission process usually leads to a reduction of the tensile strength whereas the crosslinking process results in an increased tensile strength and a reduced elongation at break [22]. The predominance of one phenomenon above the other depends on several factors among them macromolecular structure, material composition, irradiation conditions (absorbed dose, dose rate and exposure environment), temperature, atmosphere ...

Butyl rubber is a copolymer composed of isobutylene units with a small percentage (1%) of isoprene units. It is known that polyisobutylene undergoes predominantly scission under irradiation [14,23,24]. In butyl rubber, crosslinking would be expected through the isolated isoprene units but Hill al. pointed out that scissions of the isobutylene sequences predominate [23]. Chandra et al. [25] observed the same effect of ionizing radiations and reported the evolution of the molar mass, tensile strengths and density of butyl rubbers submit to gamma irradiation at 25 °C. However, the mechanism of radiation-induced scission of this polymer is not completely understood. FTIR spectroscopic studies carried out by Turner and Higgins indicated the formation of vinylidene double bonds, ethyl groups and tri-substituted double bonds, accompanied by a drop in the substituent methyl groups content, indicating a methyl abstraction. They proposed a mechanism for the chain scission which implies that one vinyl group is formed for each scission [26]. This mechanism was confirmed by Bremer [24] who carried out Quantitative NMR analyses to determine the radiation yield of scission and assumed that every main chain scission results ultimately in both an unsaturated and a saturated chain end. However, it restrains this conclusion to relatively low radiation dose.

While butyl rubber is known to undergo predominantly chain scission during exposure to high energy radiation, a drastically different response towards high energy radiation has been found for bromobutyl rubbers [23]. In bromobutyl rubber, carbon–halogen bonds are weaker than carbon–carbon and carbon–hydrogen bonds, and the main effect of radiation is the carbon–halogen bond break, giving an organic free radical. Carswell-Pomerantz et al. [27] who studied the degradation of bromobutyl rubbers irradiated with high energy radiation through Electron Spin resonance characterizations pointed out that most of the radicals are generated on the halogenated isoprene units, due to the labile C–Br bond and they observed that crosslinking predominates over chain scission up to a limiting dose of 50–100 kGy.

The studies concerning the degradation of bromobutyl rubber under radiation found in the literature reported complex phenomena with radicals formation which could lead to chain scissions, crosslinking or other reactions [27]. These reactions occur simultaneously and make difficult to visualize a distinct trend as many parameters are implied in the predominance of one reaction above the others: environment, dose, additives, temperature, curing agents and curing conditions (number of sulfur per bridge). Moreover, the materials properties as tensile strength for example are a complex function of crosslink chemical density and crosslink nature, both chemical and physical interactions involved.

The aim of this paper is to evaluate the behavior of a halogenated butyl rubber submit to gamma radiations and temperature

ageing. The morphological, chemical and mechanical properties modifications are studied using classic tensile tests, Dynamic Mechanical Analysis (DMA), Scanning Electron Microscopy (SEM) and Nuclear Magnetic Resonance (NMR) investigations. A better comprehension of the physico-chemical mechanisms involved during ageing under simultaneous action of ionizing radiation and temperature is targeted.

2. Experimental

2.1. Material

A butyl rubber (Lanxess®) was mixed with 66 phr of reinforcing carbon blacks (Cabot®). Two carbon blacks were used: 60 phr of Medium Thermal (MT) and 6 phr of Semi Reinforcing Furnace (SRF) with an average particle radius of 201–500 nm and 61–100 nm respectively. Chemical processing additives were added to the compound and the mixture was then cured with sulfur as vulcanizing agent.

The glass transition temperature of vulcanized rubber was $-64 \text{ °C} \pm 0.5 \text{ °C}$, measured by Differential Scanning Calorimetry (DSC).

The sheets were compression molded in an electrically heated press at a temperature of 170 °C for 14 min.

2.2. Irradiation of the sample

A series of gamma irradiation experiments were performed using a ^{60}Co source at the SCK. CEN. Center (Belgium). Five different doses (5, 10, 50 and 100 kGy) were applied under argon atmosphere at room temperature and at 70 °C. The dose rate was fixed at 500 Gy/h for all selected doses. These conditions were chosen in order to extrapolate the effects of irradiations to which the material will be subjected during its service life.

2.3. Scanning Electron Microscopy (SEM)

The dispersion of the carbon black fillers and other additives before and after irradiation ageing was studied by Scanning Electron Microscopy.

Samples were freeze-fractured before analysis and coated with gold to increase the conductivity. They were examined using a Zeiss Supra 40 VP Field Emission Scanning Electron Microscope with a low acceleration voltage (1–5 keV) in order to minimize the degradation caused by the electron beam on the rubber.

2.4. Mechanical and dynamic mechanical properties

The tensile properties of unaged and irradiated rubbers were carried out on an MTS DY35 testing machine at $25 \pm 2 \text{ °C}$ according to the NF T46-002 specifications. The crosshead speed was fixed to 500 mm min^{-1} and five separate measurements were recorded and averaged to assure the reliability of the results and to obtain mean values of the tensile strengths at 50 and 100% of elongation and of the stresses and strains at break.

Dynamic mechanical analysis was performed on a TA Instruments DMA 2980 analyzer. A single cantilever tool was used at a frequency of 10 Hz with oscillation amplitude of 6 μm . The temperature range was from -100 to 40 °C with a 3 °C min^{-1} heating rate. The sample dimensions were approximately 4–5 mm thick, 17.5 mm long and 15 mm wide. The evolutions of $\tan \delta$ and storage modulus G' versus temperature were recorded.

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