

The Structural Changes in Butyl and Halogenated Butyl Elastomers During Gamma Irradiation

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SYNOPSIS

Ionizing radiation induces various changes in the molecular structure of elastomers; consequently, the macroscopic properties of the irradiated elastomers will be modified. The newly formed products and the alteration of the initial chemical structure are the result of free-radical reactions which provide the crosslinking and/or the depolymerization of the tested materials and destructive simultaneous processes involving diffused aggressive agents. This paper describes the behavior of butyl and chlorinated and brominated butyl elastomers under the action of gamma radiation for total doses up to 0.5 MGy. The experimental data provided by several procedures emphasize a complex chemistry circumstance consisting of the simultaneous crosslinking and scission of the macromolecular chains and consecutive processes involving free radicals. Evaluation of the studied changes was via gel content, oxidation level, unsaturation, and halogen distribution as dependent on the total radiation dose. The mechanism of the degradation and a relationship between the crosslinking/scission ratio and the absorbed dose are discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In almost all cases of elastomers and their vulcanizates the chemical structure, and indeed the physical properties, are profoundly altered by high-energy radiation action, either in an inert atmosphere or an oxygen environment. 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. Thus, the probability of the generation of any certain radical depends on the strength of the interatomic bonds. The ongoing effects of the radiation-induced aging are found as the chemical changes: intermolecular bridges, the macromolecule scission, and unsaturated structure formation and/or consumption. These processes bring out the significant consequences of several physical characteristics. The large-scale use of the elastomers and their vulcanizates motivates extensive evaluation of radiation-induced degradation.¹⁻⁴

Butyl elastomer, and especially its halogenated derivatives, have not yet been extensively studied because of their high radiation resistance. Unlike the majority of the elastomers with high levels of unsaturation, butyl rubber exhibits significant degradation damage by ionizing radiation action. The molecular scission generates allyl radicals, which were detected with the ESR technique by Ranby and Rabek.⁵

The high-energy photons, such as gamma rays, act on any material by three physical mechanisms: photoelectric effect, Compton scattering, and pair formation; the main events in organic polymers are the generation of free radicals, accompanied by changes in electrical, optical, and mechanical properties.^{6,7} Practical support for this study is provided by operation of this kind of material⁶ in nuclear power plants, high-energy particle accelerators, and industrial and research irradiation facilities. An estimation of environmental factors—total absorbed dose and dose rate, operating temperature, external pressure, mechanical stress, and chemical environment, on the one side, and the consequences on the material's chemical nature on the other—must be well known.

As previously stated by Clough,⁴ gamma rays induce a large destructive effect on butyl rubber vulcanizates;

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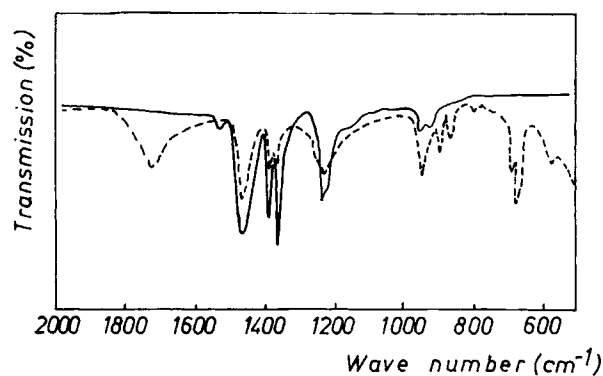


Figure 1 Characteristic IR spectra for the butyl rubber samples: (—) unirradiated; (---) after receiving 0.5 MGy gamma dose.

this was particularly demonstrated by the sudden reduction of the relaxation effort.^{8,9} The butyl vulcanizate irradiation experiments were carried out by Drozdovskii and Mikhailova^{10,11} in their reclaim work.

This paper presents the behavior of butyl and chlorinated and brominated butyl rubbers under gamma irradiation up to 0.5 MGy.

EXPERIMENTAL

This investigation was carried out on three different uncompounded rubbers: butyl rubber (BK-1645, Russia), chlorinated rubber (10-66, ESSO, Canada), and brominated butyl rubber (2030, Polystar, Canada); their chemical structures have been extensively studied by Vukov.^{12,13} Both halogenated rubbers present the same halogen content (2%). The irradiation was performed in air inside a ⁶⁰Co facility to measured absorbed doses of 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 MGy at room temperature, the dose rate being 0.6 kGy/h. The changes in the rubber properties were studied by several procedures to provide a quantitative view of the ongoing processes in relation to the gamma absorbed dose. These tests delivered the following information:

- the extractible fractions obtained by means of cyclohexane and characterized by the IR spectra, especially for the halogen atom distribution;
- the organic fraction identification and evaluation in the irradiated samples by IR spectroscopy; and
- the gel content by solvent extraction and the molecular mass distribution by chromatography.

The spectral measurements were performed with two different instruments: a Perkin Elmer 577 (USA) for the IR region and a Spekord UV-VIS Jena (Germany) for the UV interval.

The gel content was determined by extraction in boiling cyclohexane for 24 h using a Soxhlet extractor.

RESULTS

Changes in the Main Peaks of the Butyl Rubber IR Spectra

IR spectra of all three studied rubbers show changes in their chemical structures. Figure 1 shows two

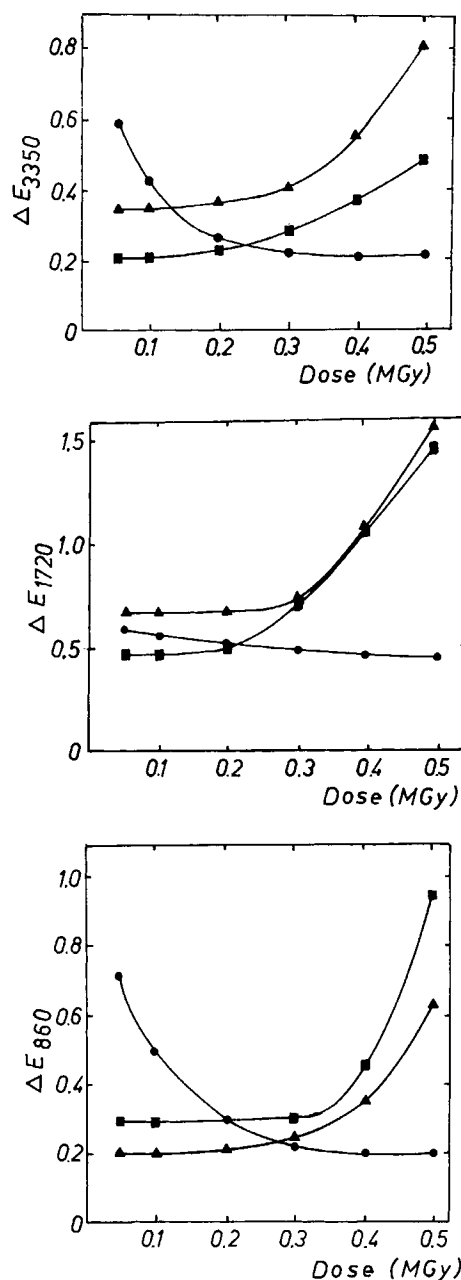


Figure 2 Development of some main vibration bands versus the absorbed dose: (a) 3350 cm^{-1} ; (b) 1720 cm^{-1} ; (c) 860 cm^{-1} : (●) butyl rubber; (▲) chlorinated rubber; (■) brominated rubber.

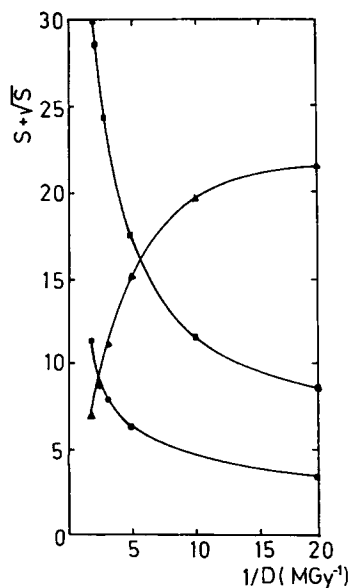


Figure 3 Charlesby-Pinner representation for the tested rubbers: (●) butyl rubber; (▲) chlorinated rubber; (■) brominated rubber.

spectra of the halogenated butyl rubber (the halogen nature had no importance) before its irradiation and after receiving a 0.5-MGy total absorbed dose. One may note the presence of some important bands: 3,500–3,200 cm^{-1} , ascribed to the OH stretching vibration of the associated hydroxyl units of the hydroperoxy and acidic configuration; 1,720 cm^{-1} , the carbonyl band of the COOH/ $>\text{C}=\text{O}$ structures, accompanied by the different lower intensity shoulders (1,780, 1,740, and 1,680 cm^{-1}) of the carbonyl/carboxyl vibrations closely placed near vinyl groups^{14,15}; 1,260 cm^{-1} , the maximum provided by the $-\text{CO}-\text{CX}-$ units; 905 and 860 cm^{-1} for vi-

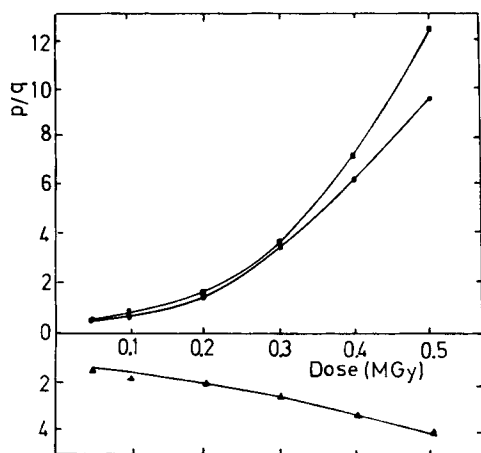


Figure 4 Crosslinking/scission ratio dependence on the absorbed dose: (●) butyl rubber; (▲) chlorinated rubber; (■) brominated rubber.

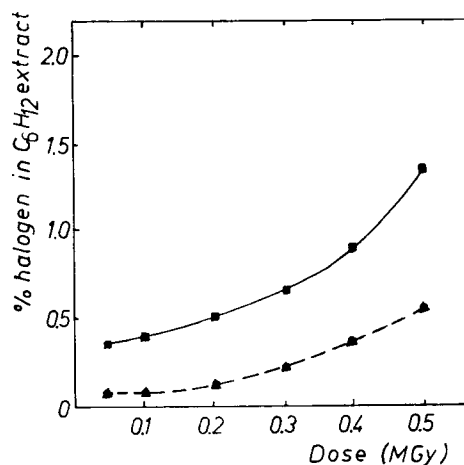


Figure 5 Halogen percentage in the cyclohexane phase versus the absorbed dose: (●) butyl rubber; (▲) chlorinated rubber; (■) brominated rubber.

nyl and trans $\text{C}=\text{C}$ configurations; and 730–720 cm^{-1} for $-(\text{CH}_2)-_{n>4}$ and ethyl groups. The changes in the main bands are presented in Figure 2. The oxygen-containing functions are generated after oxygen and ozone diffusion into the irradiated samples; this process is followed by the peroxy radical formation and, later, the final product accumulation. The UV measurements performed by Morand¹⁶ had revealed the development of conjugated polyene after the reaction of the singlet oxygen. The higher the radiation dose absorbed, the larger the discrepancy between the degradation product quantities for these three rubbers at the same total dose. The isobutyl-isoprene ratios are the same for the butyl and halogenated butyl rubbers: the presence of the halogen atoms induces a

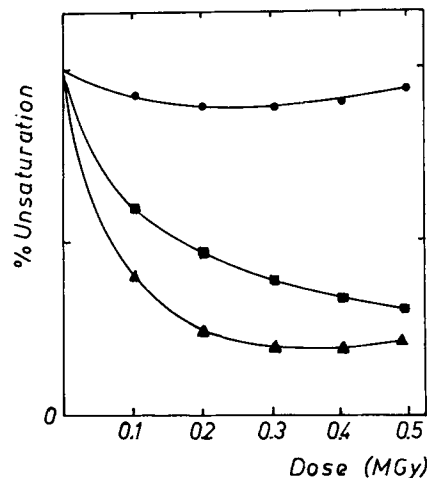


Figure 6 Unsaturation content change versus the absorbed dose: (●) butyl rubber; (▲) chlorinated rubber; (■) brominated rubber.

decrease of the material resistance to radiation action, its degradation level depending on the chemical nature of the halogen. This behavior is also supported by the different bond energies of the atom pairs. The carbon bonds present the lowest energy for C—Br (15.5 kJ/mol)¹⁷; the C—Cl bond (18.7 kJ/mol)¹⁷ is stronger than the former but at the same time weaker than C—C (20 kJ/mol).¹⁷ All rubbers studied in this paper contain the same halogen concentration, but the degradation rate of the brominated butyl rubber reaches a higher level (Fig. 2).

Changes in the Macromolecule Mass Distribution

Gamma rays act as a powerful degradation agent because the radiation energy penetrates the irradiated materials, bringing about the scission of the rubber molecules. Free radicals participate in the reactions according to their affinities, the local concentration of the various entities, and the diffusion characteristics for each kind of radical. The Charlesby-Pinner representation¹⁸ (Fig. 3) and the dependence of the crosslinking/scission ratio on the total dose (Fig. 4) demonstrate the contribution of the main simultaneous processes (crosslinking and scission) to the material changes.

The behavior of the halogenated butyl rubbers during their gamma irradiation may also be described by the halogen distribution in the cyclohexane extraction phase (Fig. 5) and unsaturation percentage change for the irradiated materials (Fig. 6). All measured changes prove the radical reaction mechanism.¹⁹ The rubber radiolysis starts with dehalogenation and dehydrohalogenation with subsequent crosslinking promoted by vinyl and vinylidene structures (Scheme 1). This statement is supported by the polyene amount change during irradiation (Fig. 7).

The average molecular mass changes in the same manner as the gel content does. While the butyl

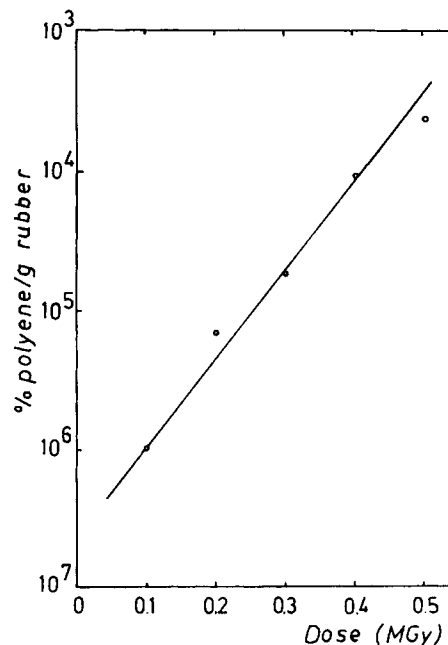
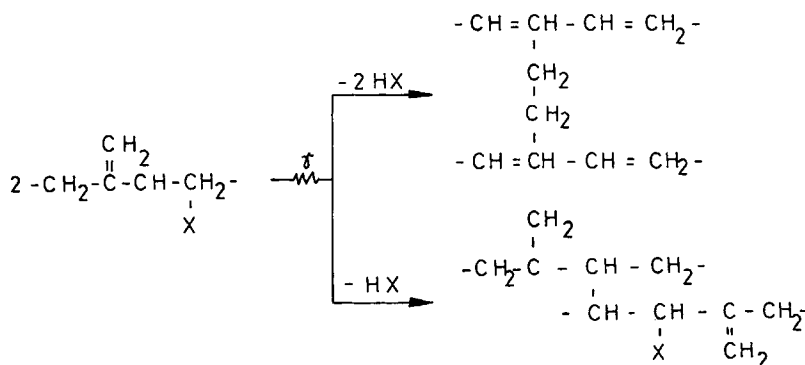


Figure 7 Change of the conjugated polyene content versus the absorbed dose: (●) butyl rubber; (▲) chlorinated rubber; (■) brominated rubber.

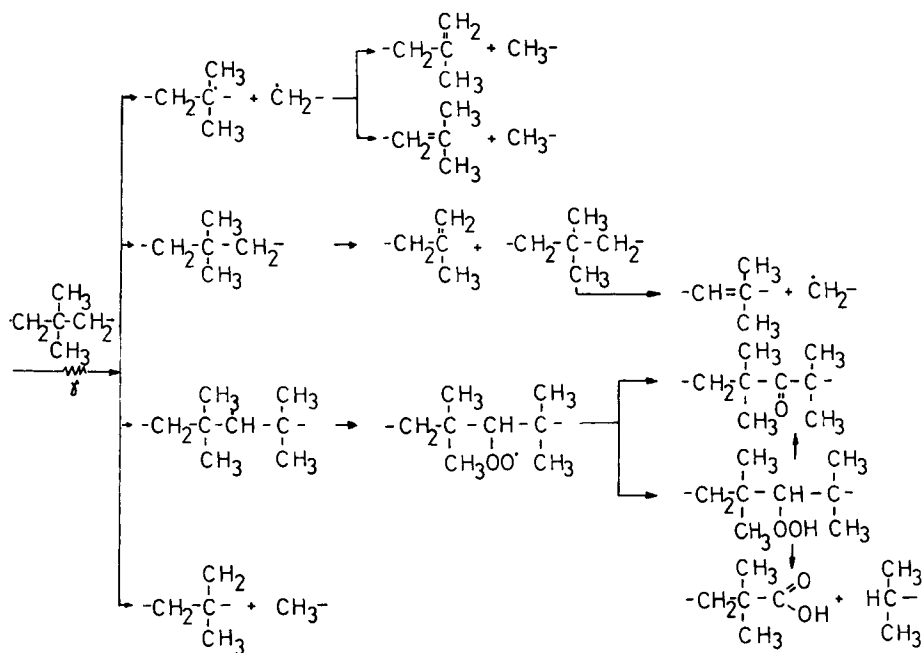
rubber tends to generate intermolecular links smoothly, the chlorinated and brominated elastomers predominantly promote scission with a higher rate for the latter polymer. This explains the pH value changes for the aqueous extraction phase, from 7.0 to 6.2 in the case of the low-dose range, and from 7.0 to 5.6 for the high doses. This means that halogenated acid is formed; and its amount, proportional to the total absorbed doses, provides an argument for the degradation paths.

DISCUSSION

The experimental data reflect the differences between the irradiated butyl elastomers. Thus, the bu-



Scheme 1 Intramolecular reactions involved in the crosslinking process.

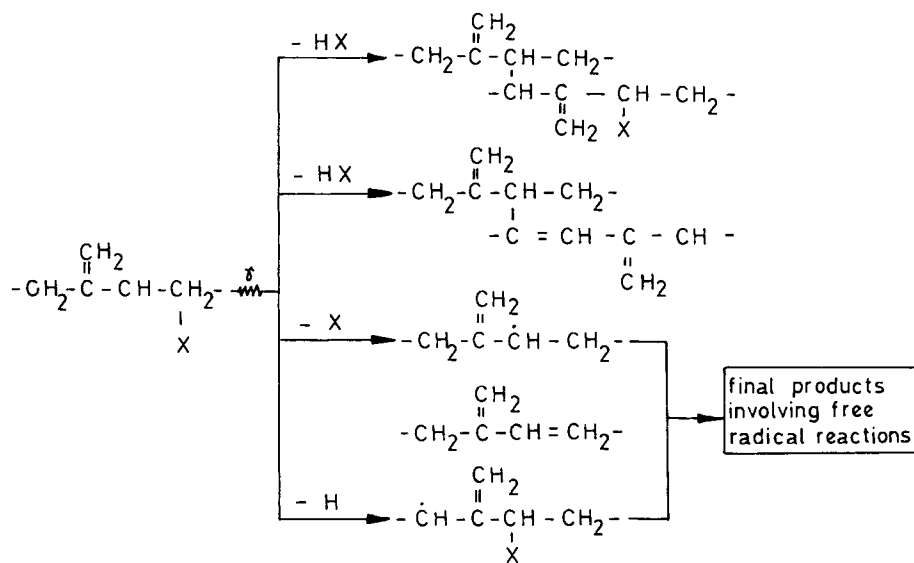


Scheme 2 Irradiated isobutylene unit reaction.

tyl and brominated butyl rubber undergo a depolymerization process, while the chlorinated rubber principally exhibits a crosslinking reaction. The larger volume of the bromine atom promotes a short free path; the probability of its reaction with any neighboring radical is greater than for chlorine atoms. On the other hand, the halogen affinity for hydrogen atoms (based on the bond energy values) facilitates the halogenated acid accumulation either by direct atomic interaction or after the abstraction

reaction from the rubber macromolecules by the free hydrogen and halogen atoms.

The reactions which take place on the isobutyl-enic units (in the case of the halogenated butyl rubbers—the isoprenic fragments) provide the principal reactions of the systems. The isobutylene units reach an activated state which generates stable molecules and free radicals by disproportionation; at the same time, they are also directed to the final unsaturation structures like vinyl and vinylidene (Scheme 2). The



Scheme 3 Irradiated isoprene unit reactions.

accumulation of the oxygenated products (aldehydes, ketones, peracids, diketones, etc.) is enhanced to a large extent via peroxy radicals after the reaction of the diffused oxygen with free radicals and double bonds.

The halogenated elastomer degradation follows Scheme 1, but occurs with additional reactions due to the isoprene units. Scheme 3 includes these specific reactions. After the subsequent rearrangements, these structures are stabilized either by crosslinking or by oxygen attack. Dever²⁰ has suggested a similar degradation mechanism in the oxygen atom attack.

According to the butyl rubber answer to the gamma-radiation attack, the relationship between the crosslinking/scission ratio, obtained from the Charlesby-Pinner equation¹⁸ and the absorbed doses is described by the following relationship:

$$p/q = k.D^\alpha$$

where p/q is the crosslinking/scission ratio, k is a constant, and α expresses a function of the experimental factors (the chemical structure of the polymer, the dose rate, the testing temperature—which influences the diffusion processes of oxygen into the sample—and halogen and hydrogen inside the bulk). This time-dependence expression answers the question of the overall view of the radiooxidation of these elastomers, i.e., the final result of the free-radical reaction competition.

CONCLUSION

The butyl and halogenated butyl rubbers exhibit a degradation process via halogen elimination which demonstrates their thermal degradation similarity. The free radicals promote useful reactions by halogen abstraction, but the tested materials are severely damaged after large absorbed doses.

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