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Sustainable recycling of butyl rubbers: an insight into the radiation processing

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Abstract

This investigation presents a deep examination on the behavior of radiation effects on pristine (IIR) and halogenated butyl (IIR-Cl, IIR-Br) rubbers. The retrieving these materials is appropriately achieved by the radiolysis fragmentation of main chains that initiates the structural modifications based on the radiation susceptibilities of studied rubbers. The γ-irradiation process causes oxidation under air atmosphere and the effects are revealed by chemiluminescence and FTIR characterizations. The radiolysis on butyl rubbers is conducted onto a specific fragmentation, which allows the two antagonistic processes: oxidation and recombination. During the γ-radiolysis in rubbers is revealed the influence of the electronegativity possesed by the halogen atoms presented in polymer structures, determining the values of activation energy for their oxidative degradation. The γ-processing suggests an ecological procedure for an appropriate preparation of blends or for the recycling as composite products. The calculated activation energies place the polymers in the following stability order of IIR<IIR-Cl<IIR-Br.

Keywords: *halogenated butyl rubber, irradiation, chemiluminescence, FTIR.*

Data Availability: All data supporting the findings of this study are available from the corresponding author upon request.

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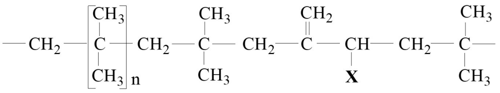
1. Introduction

The radiation processing is a pertinent procedure through which various classes of polymers may be converted into useful industrial products with foreseen characteristics[1]. The large interest in the remaking rubbers as the flexible and resistant items is motivated by the stability degree of material, which concerns the foreseen aplications of materials under specific operation conditions. The main-chain degradation promoted by exposure to the high energy radiation as an accelerated protocol has functional characteristic that depicts the warranty level addressed to special usage[2,3]. Accordingly, the special attention of any customer is directed onto the class of rubbers, whose extensive application ranges cover the areas of material engineering, commodity, transport, medicine wear or food packaging. Their versatility is based on the presence of weaker bonds in the polymer backbones, which allows the effortless breaking and the formation of free radicals which can be capable to promote crosslinking[4]. The butyl rubbers, including the halogenated versions are susceptible to scission, because their molecules contain unsaturated units, highly substituted carbon atoms and in some types polarizing atoms like chlorine or bromine atoms. The Figure 1 illustrates the molecular structure of raw rubber materials, which were studied in this work.

The modifications developed by the radiolysis of butyl rubbers were previously investigated[5-7] revealing the susceptivity to initiate the availability for their processing, but the energetic parameter were not quantified. The stability effects of weaker spots (quaternary carbon atoms, double bonds and halogenous substituents) are illustrated by the evaluation of degradation rates, the free volume and the accumulation of gel fraction.



$$-\mathrm{CH_2}-\left[\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{C}}}\right]_n-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_2}}{\overset{\|}{\mathrm{C}}}-\underset{\mathbf{X}}{\mathrm{CH}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$$

Figure 1. Molecular structure of halogenated butyl rubber. X = H (IIR); Cl (IIR-Cl); Br (IIR-Br).

The progress of oxidation is obtained after the attaining certain threashold dose (100 kGy), when the degradation hinders crosslinking. The achieved properties of the radiolysed butyl rubbers are comparable with the sulfur cured materials at low doses, when the free radicals are decayed preferentially by recombination to each other. This behavior is the solution for the compatibilization of rubber with other polymers like polyethylene[8] and ethylene-propylene elastomer[9]. It was reported the successful radiation grafting of butyl acrylate and methyl methacrylate on the macromolecules of butyl rubber[10]. The decomposition of butyl rubber occurred during its exposure to the action of high energy radiation and to the addition of small organic on its skeleton[11] was envisaged, when the target of study was the explanation of the product behavior. However, this kind of energetic treatment is appropriate over low dose range, when the examination of morphology shows a local curing of polymer.

Nowadays, the conversion of used polymers into valuable products by radiation recycling can be achieved[12]. The polymer blends consisting of one component that provides a large amount of radicals feeding the material processing and the second component that becomes a schceleton on which the crosslinking is occurred are the best systems, where the transformations take efficiently place[13]. As this paper demonstrates, butyl rubbers are appropriate materials that are able to promote recycling[14] due to their susceptibility to the fragmentation under γ-irradiation followed by the building up of new crosslinked phase[15,16]. .Accordingly, the association of butyl rubbers with other more stable polymer affords the initiation of recycling based on the despeached property of the modeling into new structured materials.

The recycling of butyl rubbers can be accomplished by the radiation processing due to the free radicals generates by γ-exposure, when their mixture is able to be associated by grafting on other polymer backbones[17]. The electron beam processing at 70-100 kGy proves to be a valid method for the achieving optimal mechanical properties, when the regeneration of rubber wastes is under consideration[18]. While the early breaking of molecular chains is followed by the disproportion of intermediate radicals, this process generates unsaturation which becomes a new source of radicals[19]. This mechanism was previously reported for halogenated butyl rubber[5], when the ongoing effects of radiation are certain modifications involving the crosslinking by the formation of several intermolecular bridges. At higher dose, excceding 100 kGy, the peroxidation of molecules on the α-position in respect with the initial double bond is followed by scission and, consequently, alcohols and aldehydes are formed[20]. A significant application of butyl rubber is its usage in the manufacture of products destined to the cosmic space[21]. The Charlesby-Pinner representation discloses the main outcome of post-irradiation heating on the irradiated samples as a positive result, because it promotes the recombination of radicals instead of their oxidation. This treatment indicates the possibility to decelerate oxidative degradation and the increase of durability of irradiated polymer materials[22].

The decrease of degradation rates of irradiated rubbers can be reached by the addition of stable fillers in their producer formulations, like graphene oxide[23,24], which acts as an efficient scavenger hindering the progress of material deterioration[25]. The radiation protection can be achieved, when the degrading polymer follows a radical mechanism. It demonstrates that the scavenging action during the migration of intermediates radials into the free space of carbon layers promotes the progress of stability[26].

The technological support of radiation processing concerns the intimate compatibilization of components[27], crosslinking[28], grafting[29], copolymerization[30]. The basic concept is the generation of radicals, which are able to participate at the reconstruction of a new polymer structure. This recombination step defines the availability of raw material for the increase of stability. Simultaneously, the oxidation must be hindered. The radiation treatment ensures the fragmentation of initial macromolecules without other simultaneous processes that decrease the efficiency of reassambling.

The present paper presents the behavior of butyl rubber samples as raw halogenated structures. The presented results can be used for the preparation and characterization of various formulations for sealing materials, food packaging and medical wear applications. The degradation experiments perfomed in this study provided a comparative evaluation of material strengths, when they are subjected to an intensive exposure to an accidental event or these materials are inserted in some formulations destined to radiation recycling.

2. Materials and Methods

2.1 Materials

The pristine materials were purchased by Exxon Mobile Chemicals, Machelen (Belgium) as the following grades: butyl rubber (IIR) – Butyl 268, chlorobutyl rubber (IIR-Cl) – chlorobutyl HT 1066 and bromobutyl rubber (IIR-Br) – bromobutyl 2222. These raw products were used as received, because the obtained results are addressesed to the interested industrial manufacturers.

2.2 Methods

The preparation of samples was carried separately out by the dissolution of rubbers in chloroform. Each series of samples containing one of the three specific solutions was poured into round aluminum caps. The dry and thin films with the weights around 3 μg are finaly obtained. These specimens were submitted to γ-processing in an irradiation machinery provides with ^{60}Co source by the greatful aid of IPEN (Sao Paulo, Brazil); the exposures at 25, 50 and 100 kGy were achieved. The FTIR and CL investigations were carried on the non-irradiated; the irradiated samples show the existent differences between the polymers with similar structures.

The stability characterization of material was carried out by chemiluminescence (CL) using LUMIPOL 3 spectrometer (Slovak Academy of Sciences, Bratislava, Slovakia). The both investigation methods, isothermal and nonisothermal CL measurements were applied. While the nonisothermal determintions were done at a heating rate of 5 °C min^{-1}, the isothermal measurements were carried out at 160, 170 and 180 °C. The rate evidences between the recorded intensities emited by oxidized fragments and hydroperoxide content at any measurement stage is the key of the result interpretation from CL spectra. Figure 2 shows the basic reaction that illustrate the photon release from the reaction intermediates.

The complementary procedure of this study, infrared spectroscopy (FTIR), was also preferred for the evaluation of oxidation degrees. The device, JASCO 4200 (Japan), allowed to record the transmission spectra for the characterization of the accumulation of carbonyl compounds by the absorbance at 1720 cm^{-1}.

3. Results and Discussions

The radiation stability investigation of polymers involves the evaluation of the oxidation states characterized by the degradation level as well as the generation routes of final products[31,32]. The competition between the basic processes, scission and crosslinking[33] in the irradiated butyl rubbers configurates the material behavior determining the distribution of final products and the generation of certain structures in direct relation with the radiation resistance of processed substrate[3].

In this paper, two complementary methods of the stability investigation are used due to their availability to the detailed introspection, high sensitivities, reliability of evidences[34,35].Thus, the progress of oxidation is described accurately and the results are rightly evaluated.

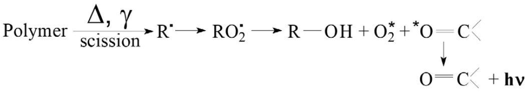
3.1 FTIR

The accumulation of oxygen-containing final products occurs by the reactions of free radicals that are consumed during radiolysis. Figure 3 presents the evolution of transmission peak characterized by the formation of carbonyl functions for the three investigated butyl rubbers.

By the distinct evolutions of this peak it is possible to understand either the differenes that exist between the radiation resistance of rubbers or the various contributions of the further consumption reactions as the steps of oxidation mechanism. The order of stability is demonstrated by the hights and widths of these peaks. The presence of small shoulders indicates the complexity of carbonyl type structures, which consists of aldehyde, ketones, peracids[36].The increase of peak hights is the consequence of the fragmentation of backbones either on various molecular positions and the attack of oxygen on the radical head or on the disproportion intermediates. The contributions of halogen atoms on the degradation progress are designed by the peak widths for IIR-Cl and IIR-Br irradiated at 25 kGy,which are larger in comparison with the similar characteristic peak of IIR. At the the dose of 100 kGy, the brominated rubber presents the most advanced level of degradation indicated by the highest amounts of carbonyl structures, whose the proportional contributions to the peak formation also determine the shape of the degradation curves.

3.2 Nonisotermal chemuluminescence

The accelerated oxidation induced by radiation exposure can be satisfactorily characterized by the photon emission counting, which are provided by the degrading polymer samples[37]. The formation of hydroperoxides according with the autooxidation scheme[38] takes place after the macromolecules scission and the deexcitation of triplet carbonyl allows their amount to be counted[39]. The increase of the degradation temperature of samples causes faster oxidation, which starts after the attaining the characteristic values of onset oxidation temperatures (OOT). The structural deterioration causes a deacrease on the OOT values, because the presence of the higher amount of radicals reacting with oxygen determines a higher number of emitted photon. Figure 4 presents the nonisothermal CL spectra recorded at all applied irradiation doses.



$$\text{Polymer} \xrightarrow[\text{scission}]{\Delta,\,\gamma} R^{\bullet} \longrightarrow RO_2^{\bullet} \longrightarrow R{-}OH + O_2^{*} + {}^{*}O{=}C\langle \;\downarrow\; O{=}C\langle + h\nu$$

Figure 2. The emission reaction.

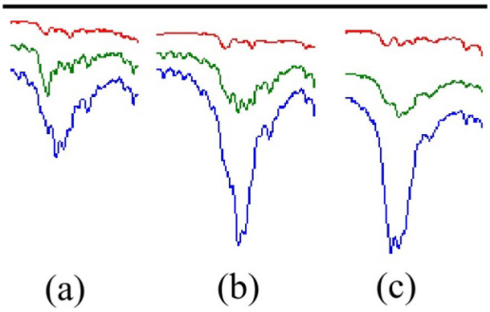


Figure 3. The transmission peaks at 1720 cm^{-1} for (a) IIR; (b) IIR-Cl; (c) IIR-Br. (upper line) 0 kGy; (middle line) 25 kGy; (lower line) 100 kGy.

The nonisothermal determinatons of material stability provide the functional details on the capacity of substrate to preserve the oxidation state when the operation temperature is increasing. The thermal evolution is related to the safeguard capacity of material by which the product can be properly used. In the present cases, the shapes of nonisothermal curves indicate which temperature is suitably selected for the processing material, when they are associates with other structures for the development of new caterial construction. The analysis of these spectral highlights suggests some specific features:

- these rubbers start their oxidation at high temperature, around 217-220 °C, when they are not γ-irradiated. It means that their oxidation reactions are not influenced by the presence of halogen atoms;

- the pristine butyl rubber is the most stable structure of studied polymers under the action of γ-rays. It presents the most less prominant oxidation peak at 100 °C, when the scission of backbones takes simultaneously place on different positions of the molecules;

- the bromine rubber is somewhat resistant at low radiation doses in comparison with chlorinated form due to its lower electronegativity. However, at 100 kGy the brominated rubber is stronger oxidized than the other two studied configurations, because the bond energy of C – Br is 276 kJ.mol^{-1}, while the bonds C – Cl and C – H are characterized by the energies of 339 kJ.mol^{-1} and 413 kJ.mol^{-1}, respectively[34];

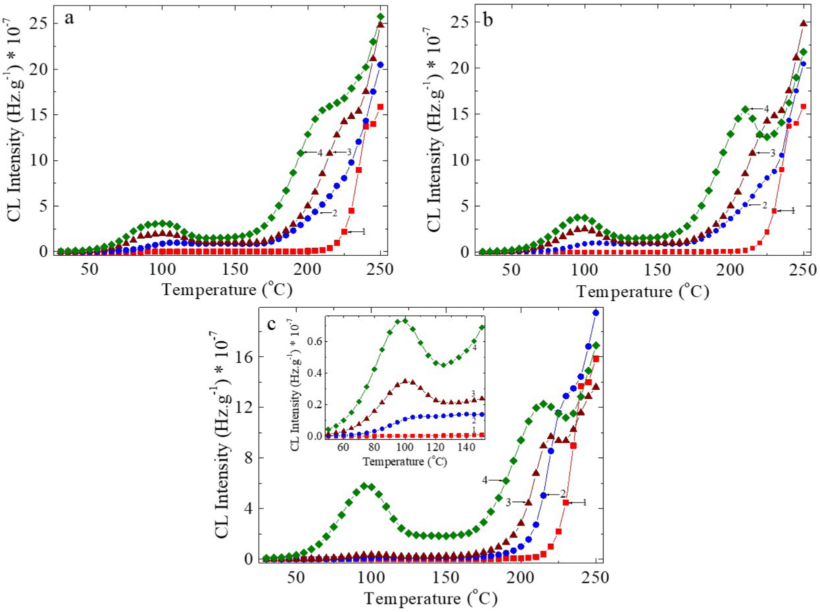


Figure 4. The nonisothermal CL spectrarecorded on (a) IIR samples; (b) IIR-Cl sampels; (c) IIR-Br sample. Heating rate: 5 °C.min^{-1}.

Dose: (1) 0 kGy, (2) 25 kGy, (3) 50 kGy, (4) 100 kGy.

- the general aspects of presented curves suggest that the initiation of degradation does not start by the breaking C – X bond. As it was reported earlyer[20], the tautomery of double bonds makes possible to promote scission, because its localization on the backbones facilitates the scission;

- the increase in the processing dose shifts the initial oxidation peaks towards lower temperatures indicating an advanced sensitization of double bond and the acceleration of degradation.

The nonisothermal CL measurements demonstrate that the butyl rubbers can be process at lower temperatures, when these materials are the raw components for the manufacture of new structures by their compatibilization with other polymers[40,41] or in the presence of appropriate fillers[15,42] by radiation processing.

3.3 Isotermal chemuluminescence

The isothermal CL curves allowed to identify the values of the oxidation induction time (OIT). These periods when the oxidation degree does not suffer any change are presented in Figure 5. The evolution of oxidation studied by isothermal CL measurements differs from one rubber to the other, the degradation rates being a basic criterium for comparison of polymer stabilities. The families of the isothermal CL spectra recorded on the three butyl rubber compounds are differently positioned, because these materials are unlikely oxidized. The butyl rubber samples (IIR) present certain OIT periods, that indicate their thermal stability even at medium exposure doses up to 50 kGy. The presence of halogen atoms drops down the radiation stability due to the contribution of breaking C – X bond.

The polymer instability at all processing doses is increased by the halogen atoms. In the case of IIR-Br irradiated at 50 kGy, an interesting aspect of the degradation may be emphasized. This sample presents a mimimum CL intensity after 22 min of degradation followed by an increase in the measured intensity. It may be ascribed to the further fragmentation of the free bromine intermediates. This feature is slightly emphasized by the irradiated IIR-Cl structures. It would be correct to assume that a part of halogenated molecules is not damaged and its contribution to the material degradation would appear later. The same behavior can be noticed in the case of IIR. In addition, the duration of degradation for irradiated IIR-Cl polymer is longer, because it progresses by the two scission ways: one route involves partially C – Cl bond breakand the other way is the decay of intermediates by the recombination and disproportionation[42]. The results of isothermal measurements confirm the sequence of stabilities establishes on the nonisothermal determination data.

The isothermal CL determinations at three temperatures provide the value of oxidation induction time by the calculus of the activation energies (Ea) required for the thermal oxidation (Table 1). The Ea values are similar with the other reported results on polymers[43], whose degradation is propagated by the self-catalytic mechanism initiated by the diffused molecular oxygen[37]. The kinetic study carried out on IIR-Br[44] confirms the present results, which represent an evaluation of the ageing behavior during the radiation processing. These Ea values confirm the contribution of substituents to the structural stability, when the γ-exposure is applied for the material processing.

The preparation of butyl rubber blends and composites may be accomplished starting from the present stability information due to the inteactions between the minor components and polymer matrix[45]. The initiation of oxidation in hybrid compound based on the application of radiation processing is a convenient procedure to obtained new structures.

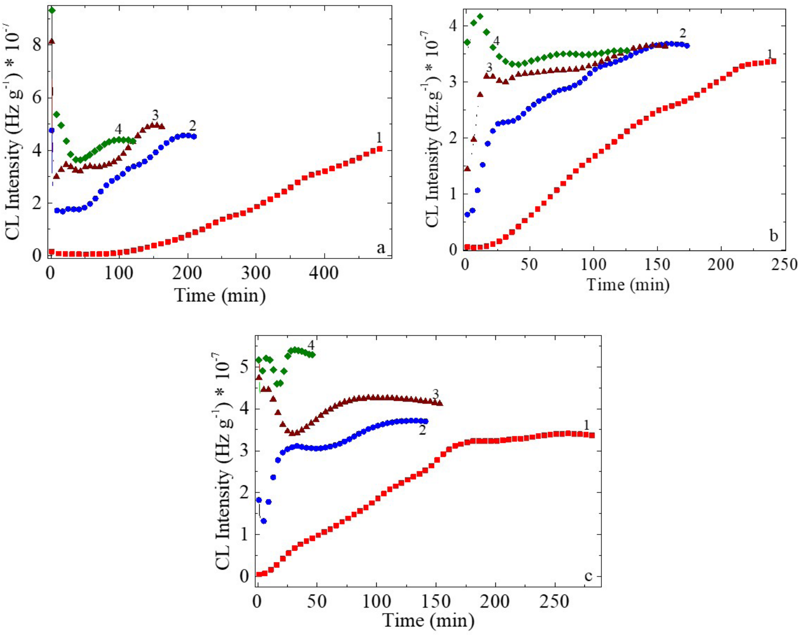


Figure 5. The isothermal CL spectra recorded on (a) IIR samples; (b) IIR-Cl sampels; (c) IIR-Br samples at 180°C. Irradiation doses: (1) 0 kGy; (2) 25 kGy; (3) 50 kGy; (4) 100 kGy.

Table 1. Activation energies for the degradation of the studies IIR structures.

Polymer	OIT (min)			Correlation factor	Activation energy (kJ mo1^{-1})
	160 ºC	170 ºC	180 ºC		
Irradiation dose: 0 kGy					
IIR	225	124	62	0.99840	105
IIR-Cl	104	58	36	0.99898	86
IIR - Br	68	38	25	0.99673	82
Irradiation dose: 100 kGy					
IIR	93	52	31	0.99979	89
IIR-Cl	50	33	20	0.99778	76
IIR-Br	38	21	15	0.98950	69

A certain long term stability can be reached by the appropriate fillers, like metallic oxides[46].

The radiation technologies applied to the butyl rubbers have received a special attention[7,11,16,47], because the application areas of these materials are extended on various technical articles, especially the manufacture of tires[47]. Due to several considerations less energetic consuming, the lack of wastes, the high processing volumes, the different versions of formulations, the easiness of manufacture by radiation exposure, the availabilities of various additive and fillers that ensure the high performances, the high energy irradiations by gamma and electron beams provide the desired quality of resulting materials with foreseen characteristics. After the irradiation of butyl and halobutyl rubbers may be successfully used in the compositions of other flexible rubber products due to the molecular fragmanation that causes a remarkable decrease in the viscosity of gamma or electron beam processed substrates.

4. Conclusions

The radiation exposure of three sorts of butyl rubber (pristine structure and chlorinated or brominated materials) show different thermal resistances that depend on their susceptivity to generate fragments. The FTIR investigation reveals the accumulation of carbonyl compound due to the reactions of intermediates radicals with diffused oxygen. This behavior differentiates the studied butyl rubbers placing then in the following stability sequence:

IIR > IIR-Cl > IIR-Br

The higher stability of chlorinated material in respect to the brominated one is explained taking into account their electronegativity difference. The nonisothermal CL analysis carried out for the characterization on the thermal stability of γ-irradiated rubbers points out the influence of irradiation doses that is responsible by the decrease in the values of onset oxidation temperature, as well as in the increase of the photoemission intensities characterizing the scission of the C – C bond in the vicinity of unsaturation of isobutylene segments. The isothermal chemiluminescence measurements allow to calculate the activation energies required photooxidative degradation of studied rubbers confirming the stability order previously established.

This paper provides the background information for the recycling of butyl rubber-based composites by radiation processing that may be produced for the manufacture of several sealing products with the foreseen elasticity and hardness. All the presented results are important for the evaluation of the contribution of butyl rubber components, when they are blended with other polymers, even though they are raw materials or wastes. The present results may be considered as the pertinent recommendations for the compatibilization of polymer mixtures under the action of high energy radiation due to the formation of active radicals by the breaking simultaneously occurredC – C, C – X and double bonds.

This study provides basic details for the manufacture of addition components in several rubbery materials for the decrease of their viscosity. The results present intrinsic value, because they are shown as a comparative analysis. The radiation processing of these butyl rubbers indicatesthe way, which may be followed, when a preirradiation treatment creates the reaction centers in the recycling technologies.

5. Author’s Contribution

- **Conceptualization –** Traian Zaharescu; Ademar Benévolo Lugao.
- **Data curation –** NA.
- **Formal analysis –** NA.
- **Funding acquisition –** Ademar Benévolo Lugao.
- **Investigation –** Traian Zaharescu; Ademar Benévolo Lugao; Heloisa Augusto Zen; Radu Mirea; Dorel Buncianu.
- **Methodology –** Traian Zaharescu; Ademar Benévolo Lugao.
- **Project administration –** Traian Zaharescu; Ademar Benévolo Lugao.
- **Resources –** NA.
- **Software –** NA.
- **Supervision –** Traian Zaharescu.
- **Validation –** Heloisa Augusto Zen.
- **Visualization –** Radu Mirea; Dorel Buncianu.
- **Writing – original draft –** Traian Zaharescu; Ademar Benévolo Lugao.
- **Writing – review & editing –** Heloisa Augusto Zen; Radu Mirea; Dorel Buncianu.

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