RECYCLING OF CHLOROBUTYL RUBBER USING GAMMA RADIATION

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Abstract

The management of solid waste is an important worldwide problem, which is becoming progressively worse as a byproduct of continuing economic growth and development. Polymeric materials (plastics and rubbers) comprise a steadily increasing proportion of the municipal and industrial waste going into landfill. Development of technologies for reducing polymeric waste, which are acceptable from the environmental standpoint, and which are cost-effective, has proven to be a difficult challenge due to a whole range of complexities inherent in the reuse of polymers. Establishing optimal processes for the reuse/recycling of polymeric materials thus remains a worldwide challenge. Due to the ability of ionizing radiation to alter the structure and properties of bulk materials, and the fact that it is applicable to essentially all polymer types, irradiation holds promise for managing effectively solid waste which can be used as raw-materials or chemical additives. Some progress has been made on the difficult problem of recycling rubber. Halogenated polymer has been used in large scale in a comprehensive variety of application, such as tires spare-parts (air chambers, tires internal coatings, etc.) and various artifacts (lids, gaskets, etc.). Due to low unsaturation of chlorobutyl rubber (around 3%), it exhibits significant degrees of degradation under radiation exposure. The major effect of high energy photon, such as gamma rays in polymers is the yielding of free-radicals along changes in electrical, optical and mechanical properties. This work has as objective the introduction of a recovering technique of chlorobutyl rubbers by characterization of non-irradiated and irradiated samples based on following properties: Mooney viscosity, tensile strength, elongation, hardness, rheological properties, Scanning Electron Microscopy (SEM), Infrared Spectroscopy and Thermogravimetric Analysis (TG). Doses used in degradation study via gamma ionizing radiation comprised: 0kGy, 25 kGy, 50 kGy, 100 KGy, 150 kGy and 200 KGy, in order to confirm the feasibility of chlorobutyl rubber for recycling. It was observed that doses higher than 100 kGy prejudice material recycling, due to the high level of degradation. Researches on recycling rubber into other useful products will reduce the negative impact upon the environment, including saving landfill space, eliminating harmful effects on humans and environment besides providing future lines of direction toward polymeric materials problem-solving.

Keywords: chlorobutyl rubber, recycling, gamma radiation, degradation, characterization.

1. Introduction

Chlorobutyl rubber (CIIR) is manufactured similarly to Butyl rubber (IIR) (isobutylene and isoprene copolymer) and is obtained from its chlorination, by varying chlorine contents within 1.1% a 1.3% range[1], by inserting chlorine in isoprene group. Rubber properties show various advantages, such as: high vulcanization speed, low permanent deformation and compatibility with other rubbers [2], making viable the combination between an excellent ozone resistance and permeability to gases besides a good thermal stability and elevated resistance to oxygen action. It has been used in a lot of applications such as tires spare-parts (air chambers, tires internal coatings, etc.) and various artifacts (lids, gaskets, etc.) [3].

In recent years, production of the rubber industry has increased and as polymeric materials do not easily decompose, the disposal of waste polymers into the environment is a major problem for municipalities and governments. Several global and national policies and proposals have been developed around the world related to the disposal of solid waste such as plastics and used tires. As most of the residues containing petroleum derivatives, re-use or recycling are very important to protect non-renewable natural resources. Unfortunately vulcanized rubbers are not re-usable, because of their dimensional network structure. Therefore, a de-vulcanization process or a controlled degradation can be applied toward the regeneration or recovery of these materials [4].

Rubber recycling is not recent and in fact, it is more than one hundred years ago, when rubber was very scarce. Practice of recycling was common, but it has been reducing up to now. The reason for that was a raise in consumption of synthetic rubber produced from poor quality imported petroleum. This reduced the value of recycled rubber, making it less profitable. Another reason is related o the development and spreading of radial tires with safety belts. This type of tires became no more serviceable, highly resistant and consequently extremely hard and expensive to recycle.

Based on rubber recycling decline came up the growth in the stock of non serviceable tires, prone to cause big fires, harmful to the environment and extremely hard to extinguish when initiated, besides the dissemination of illnesses from mosquito, usually found near to big tires stacks [5]. Even tires disposed in landfill generate environmental problems.

De-vulcanized rubber can be used in replacement of natural rubber, in some cases, when formulating a compound, concerned to their properties and manufacturing cost. De-vulcanized rubber can be re-vulcanized, using or not other compounds [6,7].

Recovering of rubber goods can be accomplished by following processes: chemical, in high pressure reactors with specific solvents[8]; biological [9] and physical, comprised of mechanicals, thermo-mechanicals, crio-mechanicals, ultra-sound (within a 16KHz to 1MHz range) [10,11] and micro-wave (within a 300MHz a 300GHz frequency range) [12].

High-energy irradiation offers unique solutions to the problem of recycling due to its ability in inducing crosslinking or scission in a wide range of materials without introducing any chemical initiators and without dissolving the sample, thus avoiding phase separation. This method can possess a significant economical and ecological advantage when compared to the conventional chemical, thermal and mechanical ones [13]. Radiation induced reactions in rubbers mean crosslinking and scission reactions [14].

Crosslinkings are intermolecular bonds and build polymeric chains. The build-up of these bonds is proportional to radiation dose. They occur during the radiation and do not require that polymeric chain is unsaturated or provided with reactive groups. Bond mechanism generally varies in accordance with the polymer that is being irradiated. Normally breaking mechanism involves carbon-hydrogen bonds(C-H) in a polymeric chain and builds a hydrogen atom, followed by the capture of a second hydrogen atom from a neighbor chain and produces free radicals. Afterwards two adjacent polymeric radicals combine themselves to build a crosslinking. Scission is the opposite of crosslinking, with the rupture of Carbon atoms bonds (C-C). Build-up of crosslinkings raises medium molecular weight while scission reduces molar mass. If radiation energy is elevated, it can occur a breaking in polymeric chain (de-polimerization) [4].The major and practically single effect of ionizing radiation in butyl rubber is the chain scission with a significant reduction in molar mass [15]. Unlike the majority of elastomers with high levels of unsaturation, butyl rubber exhibits significant degradation damage by ionizing radiation action.

Aliphatic halides, except fluorine, are among organic compounds, the most radiation sensitive; in these halogen compounds, carbon-chlorine (C-Cl) bonds are weaker than carbon-carbon (C-C) and carbon-hydrogen (C-H) bonds. The major radiation effect on chloro-butyl rubber is the scission in carbon-chlorine (C-Cl) bond, resulting in a free organic radical. High electrons affinity of halogens allows electron attachment reactions, leading to Cl^-, in addition to more usual reactions for hydrocarbons. Halogen atoms present a significant reduction in its reactivity: F> Cl> Br> I [3].

This work aims to the introduction of a recovering technique for chorobutyl rubber, by employing a basic compound used in automotive industry. Samples were gamma radiated within 25 to 200 kGy doses. Properties of irradiated samples were assessed and further compared to non-irradiated chlorobutyl rubber samples.

2. EXPERIMENTAL

2.1. MATERIALS

Chlorobutyl rubber used in this study was chlorobutyl Ht 1066 from Exxon Mobil Chemical, having as reference commonly formulations in tires and automotive spare-parts industry (Table 1). Admixtures were prepared in an open roll-mill (*Copê*), 40 kg capacity, according to ASTM D-3182.

Table 1- Formulation of chlorobutyl rubber

Ingredients	Sample 8 (phr)
Chlorobutyl Rubber	100
Zinc Oxide	5
Stearic Acid	1
Magnesium Oxide	0.5
Naphthenic oil	28
Carbon Black GPF 660	75
Sulfur	0.5
ZBEC	2

Samples were cured in an electrically heated HIDRAULIC-MAQ at 5 MPa pressure and $165^{\circ}C$ temperature to their optimum cure times (determined from a rheometer Monsanto R-100).

2.2. METHOD

Cure sheets in 11,5 x 11,5 x 0,1 cm³ dimension, 250g 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, 150 and 200 kGy doses range.

For the characterization of triplicate samples, there were assessed following properties, before and after radiations:

2.2.1 RUPTURE TENSILE

It is defined as the applied force by initial area unit of a specimen, at the rupture point (ASTM D 412). Tests were accomplished in an *EMIC* dynamometer, model DL 300, 300 kN maximum capacity.

2.2.2 ELONGATION OR ELASTIC STRESS

Generally it is expressed as the percentage between two marks in uniform cross section. Ultimate elongation is the elongation at which rupture occurs in the application of continued tensile stress (ASTM D 412).

Tests were accomplished in an *EMIC* dynamometer, model DL 300, 300 kN maximum capacity.

2.2.3 HARDNESS

Hardness numerical indexes represent the deepness of penetration or adequate arbitrary values, derived from ASTM D 2240. Hardness is one of the properties the most evaluated in rubbers, being the Shore A, *Instrutemp,* portable digital model Dp-100 the durometer used herein. This instrument is provided with a conical needle emerging from the apparatus, kept at zero level by means of a spring.

2.2.4 THERMOGRAVIMETRIC ANALYSIS (TG)

It was performed by using a *Mettler-Toledo* SDTA/851^{e} (10°C min^{-1} heating rate, within 25°C to 700°C, under O_2 and N_2 flow) apparatus. The analysis accomplished under O_2 atmosphere suffers decomposition effect by oxidation. At the present study was registered initial temperature for degradation (T_{onset}) and final temperature for degradation (T_{endset}), as well the temperature corresponding to the maximum value for the derivate (T_{peak}).

2.2.5 SCANNING ELECTRON MICROSCOPY (SEM)

This analysis aimed to study rubber morphology at different enlargements. It was used a PHILIPS XR-30 scanning electron microscope, located in Centro de Ciência e Tecnologia de Materiais (CCTM), IPEN-CNEN/SP. All samples were investigated by using enlargements of both 250 and 1,000 times.

3. RESULTS AND DISCUSSION

Chorobutyl rubber shows a significant degradation under ionizing radiation. The major and practically single effect of ionizing radiation on this type of rubber is the chain scission with a significant reduction in molar mass. The presence of halogens in butyl rubber induces a diminishing in material resistance to radiation action, due to different dissociation energies.

Results for tensile, ultimate elongation (elongation at break) and hardness at different radiation doses are presented in Figures 1 and 2, respectively.

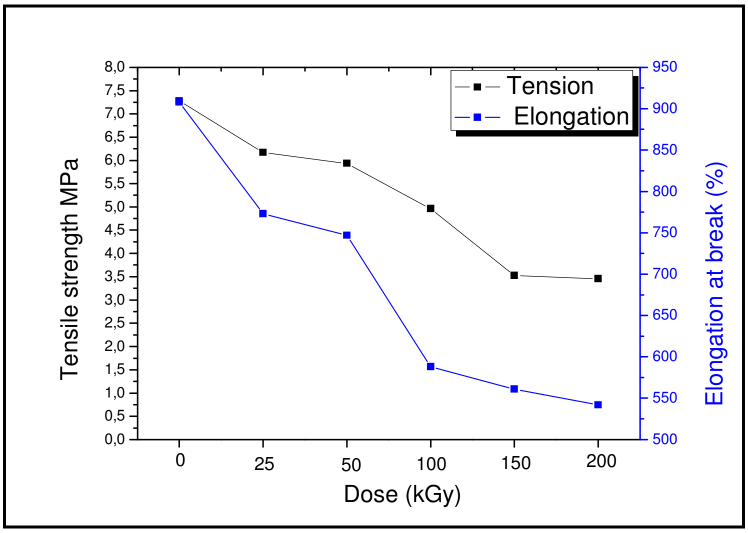

Figure 1- Tensile strength and Elongation at break values of Irradiated and non-irradiated rubber

According to Figure 1 it can be concluded that a raise in dose imparts a significant loss in properties of vulcanized compounds; a loss in rupture tensile is proportional to a reduction in elongation, indicating a less elastic and more rigid material, once the lower the elongation the higher the rigidity. It is observed too chain scission accompanied by sample softening, pointing toward doses higher than 100 kGy, with a more severe loss of properties and a high degree of degradation, suggesting so a de-polimerization in main chain.

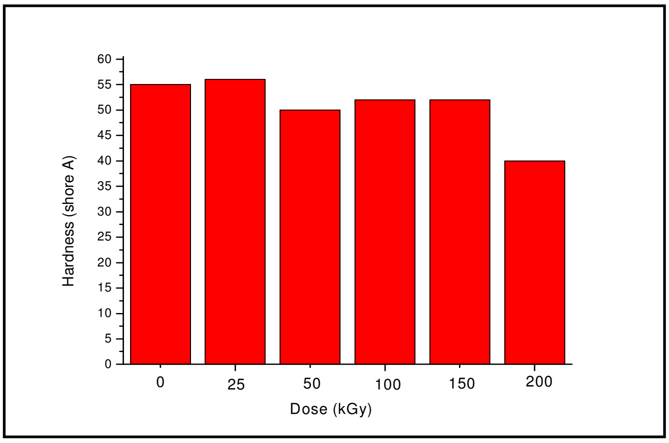

Figure 2- Effects of radiation doses on hardness of chlorobutyl rubber

Figure 2 shows hardness variation in function of radiation dose, with no significant changes in compound hardness when raising radiation dose. It was verified that for doses higher than 150 kGy, it takes place a softening in rubber, probably caused by compound degradation.

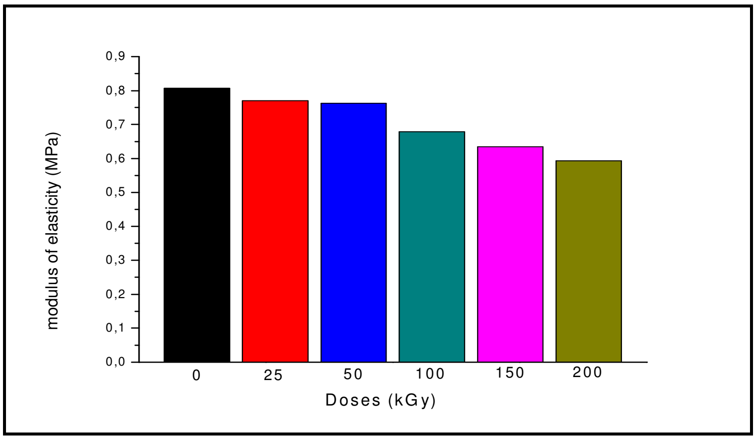

Figure 3- Radiation effects on elasticity modulus

Figure 3 shows that the variation in elasticity modulus is proportional to dose: the higher the dose the lower the modulus.

It was observed too effects caused by irradiation in rubber morphology, being this study performed by SEM (Scanning Electron Microscopy), within a raise between 250 and 1,000 times. Micrographies obtained are shown in Figures 4 and 5.

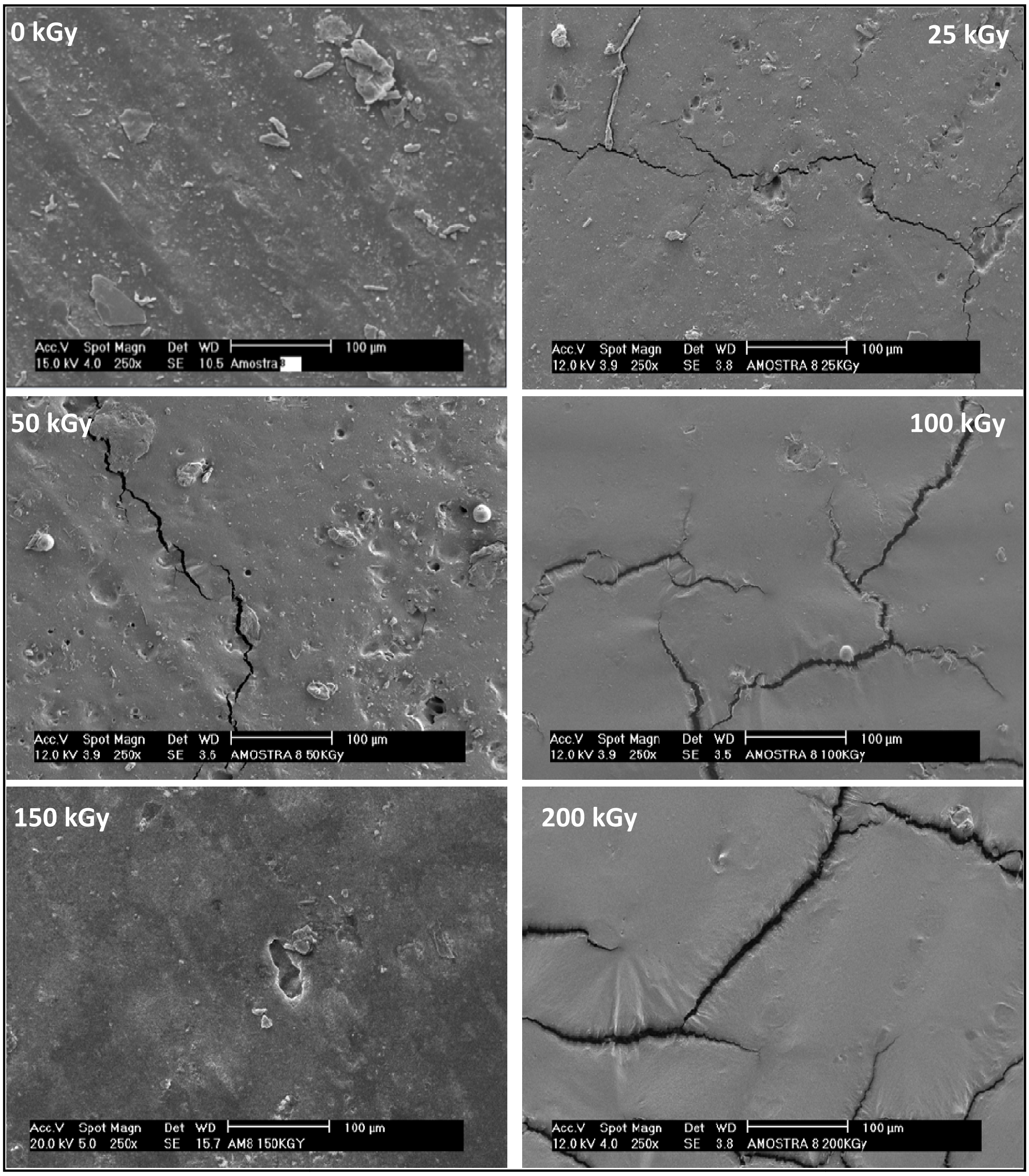

Figure 4 - Micrographies for irradiated and non irradiated samples (250 X)

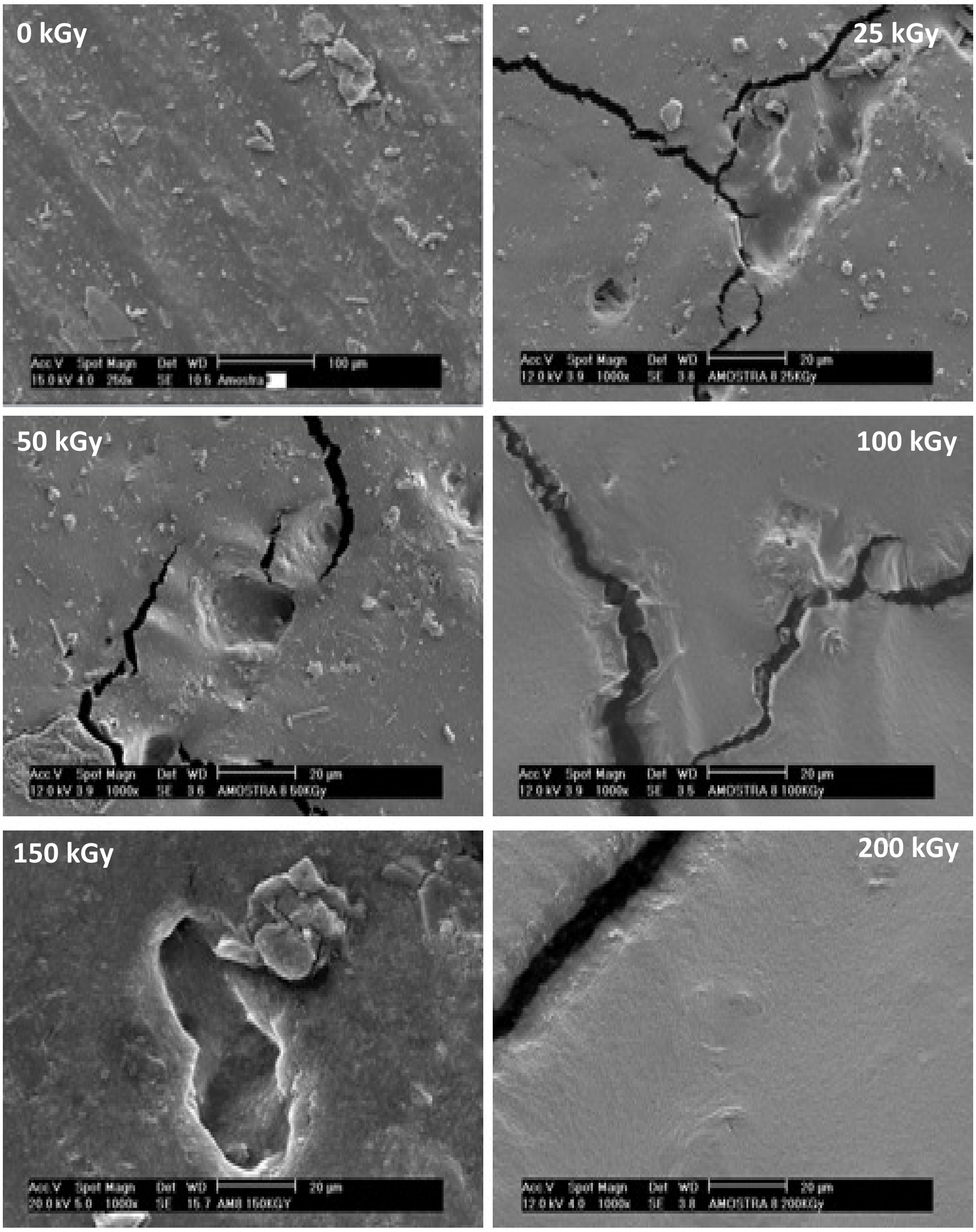

Figure 5- Micrographies for irradiated and non irradiated samples (1000 X)

Figures 4 and 5 indicate the occurrence of failures in surface of irradiated samples and a certain rugosity caused by irregular dispersion of fillers in mixtures. Fractures and wrinkles in material surface for high doses indicate that radiation can damage polymer surface. Fractures observed in micrographies point toward polymer degradation in function of gamma rays. Apparently the application of radiation does not produce morphological modifications in the material, but makes it fragile, causing wrinkles on the surface.

Figure 6 and Table 2 show results of thermogravimetric analyses for chlorobutyl rubber compound under O_2 atmosphere.

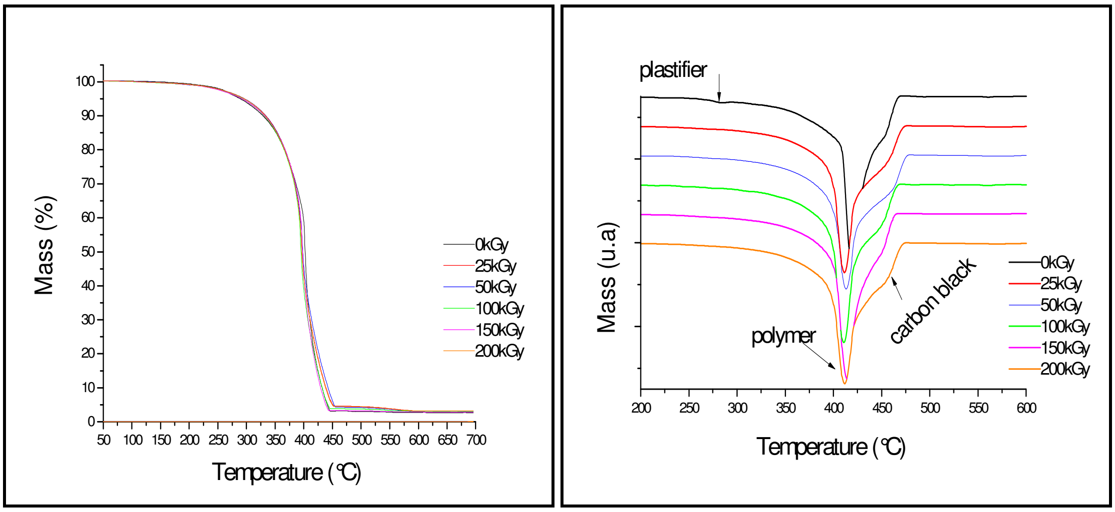

Figure 6 - TG and DTG curves on O_2 atmosphere

Table 2- TG under O_2 atmosphere

	T_{ONSET} 1st peak (°C)	T_{ENDSET} 1st peak (°C)	ΔT 1st peak (°C)	T_{ONSET} 2nd peak (°C)	T_{ENDSET} 2nd peak (°C)	ΔT 2nd peak (°C)	T_{PEAK} (°C)	**Residue** (%)
0 kGy	249.88	270.60	20.72	281.74	458.60	176.86	420.37	2.62
25 kGy	0	0	0	225.25	464.39	239.14	411.04	3.73
50 kGy	0	0	0	210.97	467.10	256.13	413.11	3.08
100 kGy	0	0	0	220.31	457.00	236.69	410.00	3.05
150 kGy	0	0	0	227.15	455.79	228.64	414.32	2.97
200 kGy	0	0	0	235.00	463.12	228.12	411.73	3,20

T_{onset} = initial temperature of thermal degradation, at each stage;
T_{endset} = final temperature of thermal degradation, at each stage;
T_{peak} = peak temperature of thermal degradation, at each stage;
Residue = amount of remaining degradated samples, in temperatures higher than 600°C;
ΔT = T_{endset} - T_{onset} temperature interval where takes place sample degradation.

Thermogravimetric analysis allowed the identification of sample mass loss in function of temperature; in Figure 6 it is possible the identification of 3 stages for losses, the first one within 250°C to 300°C range, due to the presence of volatile agents as plastifiers and antioxidants[38], the second one at 420°C temperature for non-irradiated rubber and within 410°C to 415°C range for irradiated rubbers. The third stage is observed at more elevated temperatures, that is, higher than 450°C. Mass loss within 300°C to 500°C corresponds to polymeric contents and loss above these temperatures corresponds to inorganic additives, pigments or metallic oxides [2, 16]. It can be noted too that decomposition temperatures for irradiated samples is slightly lower than those ones verified for non irradiated samples. Residual mass at 700°C varied within a 1% to 3% range, due to the almost complete oxidation for carbon black.

Figure 7 and Table 3 show thermogravimetric analyses results for chorobutyl rubber compound under N_2 inert atmosphere.

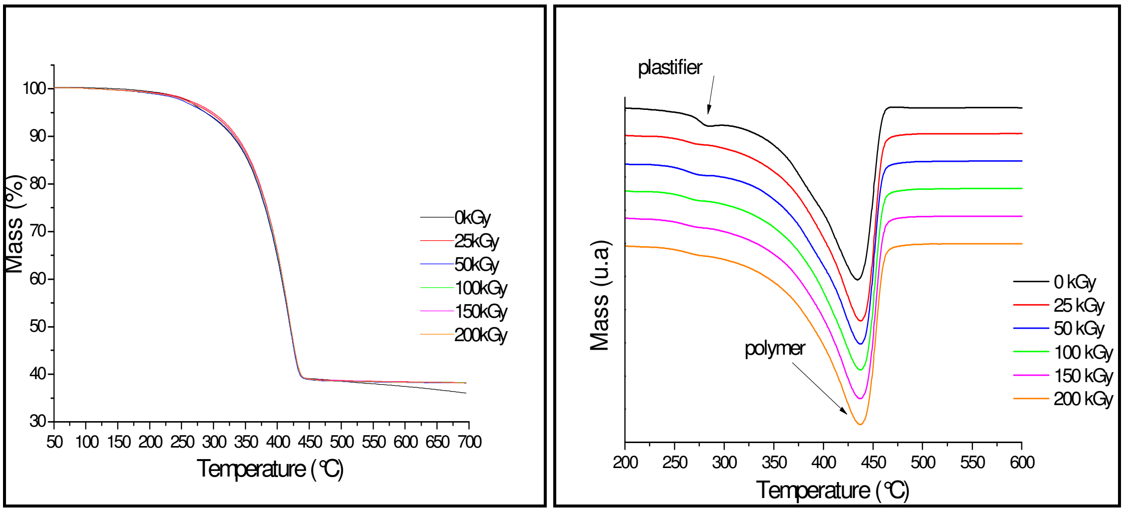

Figure 7 - TG e DTG curves under N_2 atmosphere

Table 3 – TG under N_2 atmosphere

	T_{ONSET} 1st peak (°C)	**T_{ENDSET}** 1st peak (°C)	**ΔT** 1st peak (°C)	**T_{ONSET}** 2nd peak (°C)	**T_{ENDSET}** 2nd peak (°C)	**ΔT** 2nd peak (°C)	**T_{PEAK}** (°C)	**Residue** (%)
0 kGy	252.5	267.7	15.7	287.9	451.8	163.9	434.8	36.03
25 kGy	269.5	329.1	59.6	282.7	474.9	192.2	437.8	38.73
50 kGy	236.9	273.8	36.8	285.8	470.9	185.0	437.8	38.74
100 kGy	239.8	280.1	40.2	287.7	477.9	190.1	437.8	38.50
150 kGy	232.3	266.3	34.0	283.55	479.9	196.3	437.8	38.42
200 kGy	231.8	272.6	40.8	273.85	466.6	192.9	437.8	38.35

T_{onset} = initial temperature of thermal degradation, at each stage;
T_{endset} = final temperature of thermal degradation, at each stage;
T_{peak} = peak temperature of thermal degradation, at each stage;
Residue = amount of remaining degradated samples, in temperatures higher than 600°C;
$\Delta T = T_{endset} - T_{onset}$ temperature interval where it takes place sample degradation.

Figure 7 shows results obtained under N_2 atmosphere, similar to those ones found for O_2 atmosphere, where it is possible to be identified mass loss into two different stages: the first one within 230°C to 280°C and the second one within 430°C range. Due to inert atmosphere used for the experiment, residual mass is 38%, that is, non-oxidized carbon black residue is 38%. It is possible to conclude too that results variation presented for irradiated and non-irradiated samples is not significant.

Thermogravimetric analyses performed under N_2 and O_2 atmospheres showed the same behavior, that is, mass loss stages and degradation temperatures were similar, demonstrating that independently of applied dose, the obtained result did not present significant variations. The major difference was found for residual mass under O_2 and N_2 atmospheres, due to the different behavior of carbon black oxidation in both of them.

Molecular changes, that is, carbonyl and unsaturated groups formation in CIIR during irradiation are shown in Figure 8.

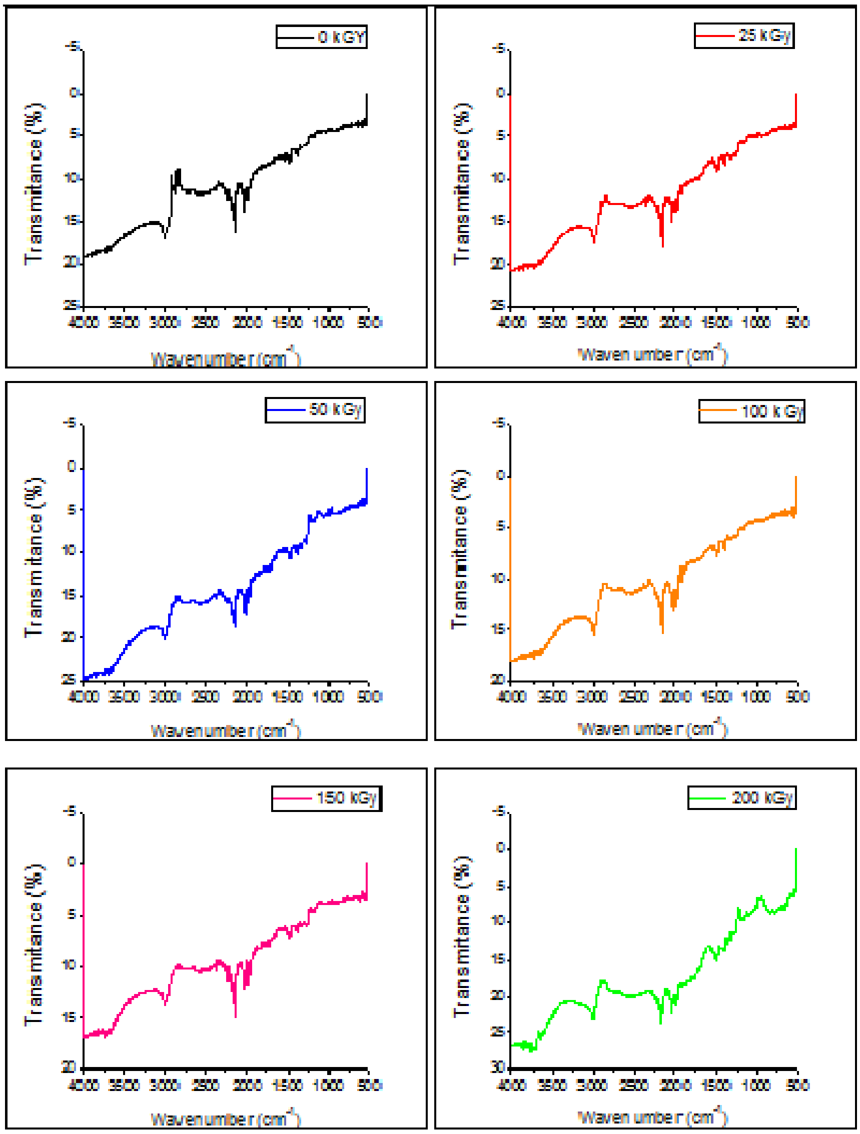

Figure 8 - Characteristic IR spectra for non irradiated rubber and 25, 50, 100,150 and 200 kGy gamma irradiated.

Different and small carbonyl bands (C=O) are seen in 1690 - 1500 cm^{-1} region, for doses higher than 100 kGy. Weak bonds between C-Cl are broken during irradiation, with a molecular rearrangement from electrons donation for the build-up of carbonyl group. It is noted too the presence of small bands within 3500 - 3200 cm^{-1} range attributed to OH groups vibration. 2 peaks in non irradiated samples within 2920-2810 cm^{-1} range correspond to the stretching of C-H group bond and almost disappear in irradiated samples, at high doses. Bands within 1000-940 cm^{-1} and 930-860 cm^{-1} in irradiated rubber are due to the presence of some olephinic bands in CIIR molecular chain [17]. The presence of unsaturation in olephinic bonds (C=C) shows that the low concentration of these groups in non irradiated sample and chain scission in irradiated rubber is a clue of polymer degradation.

4. CONCLUSION

The study and the application of the method showed that gamma radiation can be used for recycling chlorobutyl rubber in replacement of conventional methods. The advantages of radiation method are the following ones:

- Good quality presented by recovered chorobutyl rubber. It can be used in original formulation of rubber sample and replace a few parts of natural rubber in the manufacturing of final products.
- Simple recovering processing. Radiation source Cobalt-60 (γ rays) offers a deep penetration in the material and makes feasible the irradiation of rubber residues in great dimensions, thus avoiding a pre-process of rubber cutting or milling.
- Chlorobutyl rubber degradation is controlled basically according to the applied dose.
- None pollution to environment is caused.
- Energy saving.
- Improvement of processing properties related to mixing and extrusion, by shortening vulcanizing time.

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