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CHARACTERIZATION OF IRRADIATED AND NON-IRRADIATED RUBBER FROM AUTOMOTIVE SCRAP TIRES

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Abstract

The aim of this work was to characterize the samples of irradiated and non-irradiated rubber from automotive scrap tires. Rubber samples from scrap tires were irradiated at irradiation doses of 200, 400 and 600kGy in an electron beam accelerator. Subsequently, both the irradiated and non-irradiated samples were characterized by thermogravimetry (TG), differential scanning calorimetry (DSC), tensile strength mechanical test, and Fourier transform infrared (FTIR) spectrophotometry.

Introduction

Recycling process has become important to preserve natural resources, to avoid waste and prevent pollution of the rivers it would be harmful to the health, safety or welfare of the population. Recycling is the recovery of waste through a series of operations that allow processed material to be reused or to reduce the amount of virgin material used [1, 2].

Tires are one of the main components of the automotive to be considered by recycling process because they are the combination of raw materials, such as petroleum derivatives, natural rubber, steel and chemicals. The concentrations of natural rubber (BN), butadiene rubber (BR), styrene-butadiene rubber (SBR), vary according to the manufacturer and the end use. Several methods have been developed to solve the tires problem in Brazil. For example, they have been reused in various ways, as an alternative fuel for cement industry, the manufacture of shoes soles, rubber seal, rainwater pipes, for blocks courts, industrial floors, asphalt and rubber mats for automotive [3].

One of the most widely used elastomers in the manufacture of tires is SBR (styrene-butadiene copolymer) containing 25% by weight of styrene. Other kinds of rubbers used in the manufacture of tires are poly (cis-isoprene), which is natural rubber, and synthetic poly (cis-butadiene) [4].

Current legislation establishes that improperly disposed tires are environmental liabilities that may result in serious risk to the environment and public health. Also in accordance with this resolution, for each new tire sold to the aftermarket, the manufacturers or importers should dispose properly the waste tire.

The main problem faced by preserving environment is the management of waste polymeric materials before and after consumption such as production remains and used artifacts. Generally food packaging, bags, bottles and tires are the most materials founded in dumps, landfills, rivers, lakes every day without any control [5]. The rubber from automotive scrap tires tire is the subject of investigation of this current work.

Material and Methods

This current work was used granules and rubber powder from automotive scrap tires, density of 0.907g/cm^3 supplied by Reciclanip which is an institution responsible for the collection and disposal of scrap tires in Brazil. Rubber granules samples were prepared with2 mm for TG and DSC analysis. The mechanical tests were used powder of rubber from automotive scrap tires of 250 m and natural rubber matrix not vulcanized. Additives and accelerators were used for rubber samples vulcanization. The samples compositions were: zinc oxide, stearic acid, sulphur, MBTS: mercapto benzothiazol sulfenamide, TMTD: tetramethyl tiuran disulfides.

Thermogravimetry

The TG curves were obtained using the thermo balance model TGA-51 (Shimadzu) with the temperature range 25°C to 600°C, dynamic air atmosphere (50 mL/min), heating rate 10°C min^{-1} and Pt crucible containing approximately 5mg of sample. The TGA-51 equipment was calibrated according to ASTM (1582-04) and conducted by the measures conditions evaluation where it was used a standard of calcium oxalate monohydrate with 99.99% purity, origin Merck.

Differential Scanning Calorimetry (DSC)

DSC curves were obtained using the DSC cell model DSC-50 (Shimadzu), with dynamic N_2 atmosphere (50 mL/min) in the temperature range 25ºC to 550°C, heating rate 10°C min^{-1}. Al partially enclosed crucible containing approximately 2 mg of the sample. In additional, it was necessary to obtain blank curves in these experiments to evaluate the baseline system with the same conditions of the measures. However, it was not necessary to use the reference capsules sample. Because the cell DCS was calibrated using standard substances indium (T_m = 156.6°C; H_m = 28.7J/g) and zinc (T_m = 419.5°C) metal purity 99.99%.

Fourier Transform Infrared (FTIR) Spectrophotometry

Infrared spectra with Fourier transform infrared (FTIR) were registered in the Perkin Elmer, spectrometer, Spectrum model One, coupled with Universal device ATR ("Sampling Accessory"), employing solid samples and wavelength spectral range from 500 to 4000cm^{-1}. The equipment has a comparison program that allows correlate the spectral differences occurred between the samples analyzed.

Irradiation of samples

The samples were irradiated in air at room temperature with electron beam using an electron accelerator Dynamitron JOB 188 power 0,5 to 1,5MeV and 0,3 to 25mA current, and subjected to irradiation dose of 200kGy to 600kGy, at 22.39kGy/s dose rate.

Results and Discussion

Thermogravimetry

The results for non-irradiated and irradiated samples at doses of 200, 400 and 600kGy heated in air atmosphere showed different mass losses with temperature increase and the occurrence of several events (see Figure 1).

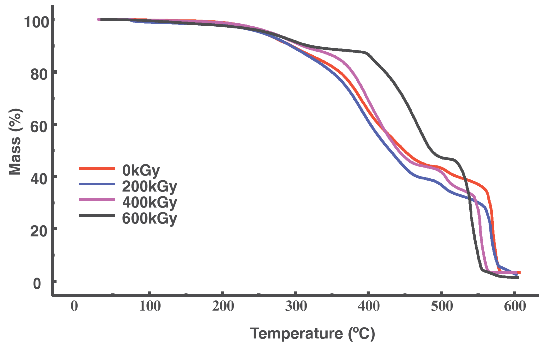

Figure 1. Thermogravimetric curves obtained in a dynamic atmosphere in air for automotive scrap tires samples at different doses.

Table I shows obvious changes of weight loss in the temperature ranges at varying irradiation doses.

Table I. Comparison in the percentage (%) of the weight losses of samples with temperature increase to 600ºC at different doses.

Dose (kGy)	Range of temperature (ºC)	Higher weight loss (%)	Total weight loss (%)	Residue (%)
0	530 – 599	36	96.9	3.0
200	518 – 599	36	97.1	2.8
400	471 – 599	41	97.8	2.1
600	382 – 599	86	99.6	1.3

Figure 2 and Table II present the TGA results for non-irradiated and irradiated samples under nitrogen atmosphere. The results showed the weight loss as a function of irradiation dose, with temperature increase.

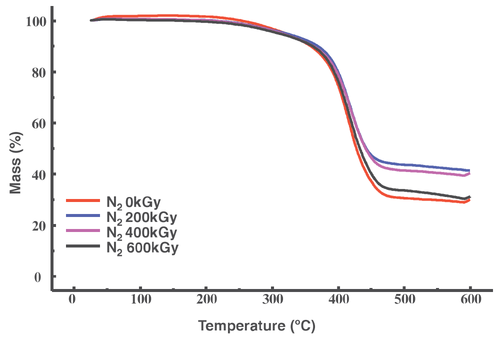

Figure 2. Thermogravimetric curves obtained in a dynamic atmosphere of N_2 for automotive scrap tires samples at different doses.

Table II. Comparison of percentage (%) of the weight losses of samples with temperature increase to 600ºC of the samples at different doses.

Dose (kGy)	Range of temperature (ºC)	Higher weight loss (%)	Total weight loss (%)	Resídue (%)
0	300 – 499	66	70.5	29.4
200	211 – 485	56	58.7	41.2
400	179 – 489	58	60.0	39.9
600	162 – 490	66	69.1	30.8

Differential Scanning Calorimetry

DSC curves show the thermal behavior of the rubber samples from automotive scrap tires. The component of the sample chemically reacts due to heat energy. It was observed that the peaks area it is proportional to the enthalpy involved in the reactions.

In the case of exothermic events, it is judged in the DSC heat flow. In general the difference TA (sample temperature) – TR (reference temperature) serves as the basis for heat calculation absorbed or released by the sample, and the result is positive ($\Delta T>0$) for exothermic events.

DSC curves obtained in dynamic N_2 atmosphere for automotive scrap tires samples non-irradiated, irradiated at dose of 200kGy, 400kGy, 600kGy show a peak at approximately 393ºC, 395ºC, 383ºC, 381ºC and another peak at approximately 435ºC, 439ºC, 437ºC, 435ºC, respectively.

It is revealed that the peaks observed in the DSC curves are exothermic because the energy produced in the process can be regarded as materials decomposition. The enthalpy was calculated from peak area in the temperature range.

Tensile Strenght Mechanical Test

Figure 3 shows the results of the percentage of maximum elongation at break for the samples without tire powder and with different percentages of 10, 30 and 50% of tires powder non-irradiated and irradiated with 200, 400 and 600kGy. Figure 3 shows a reduction in maximum elongation at break with irradiation dose increase. These results are shown in Table III.

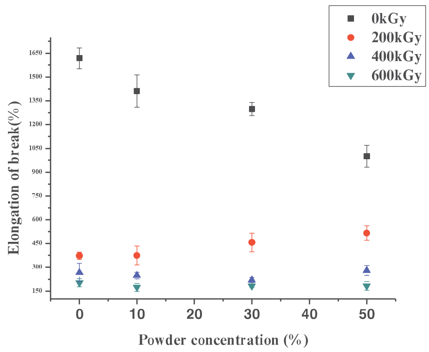

Figure 3. Variation of the maximum elongation at break of the non-irradiated and irradiated at doses of 200kGy, 400kGy and 600kGy with increasing concentration of tire rubber powder.

As shown in Figure 3, when comparing the samples without powder and samples with powder non-irradiated, sample without powder has a 1618% order behavior in maximum elongation at break while all other samples 10, 30 and 50% of powder had a loss at maximum elongation at break, 1411%, 1298% and 999% respectively. However for the samples non-irradiated can be possible to add 10 to 30% of rubber powder from automotive scrap tires for residue recovery purposes.

Table III. Maximum elongation at break (%) for samples without powder and with 10%, 30% and 50% of tire rubber powder irradiated and non-irradiated

Doses	0kGy	200kGy	400kGy	600kGy
Samples without powder	1618	372	267	202
Samples 10% powder	1411	374	248	173
Samples 30% powder	1298	456	219	183
Samples 50% powder	999	515	279	182

FTIR

Figures 4-6 show the FTIR spectra for beads samples automotive scrap tires non-irradiated and irradiated at doses of 200, 400 and 600kGy respectively.

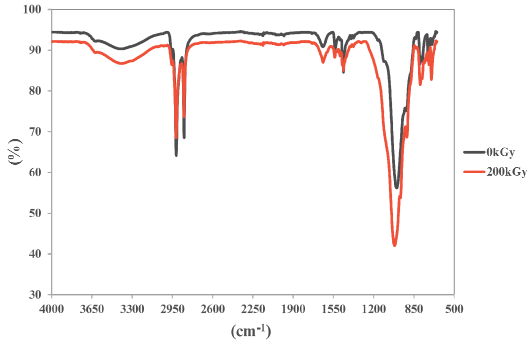

Figure 4. Absorption spectra in the infrared region for samples of automotive scrap tires non-irradiated and irradiated at a dose of 200kGy.

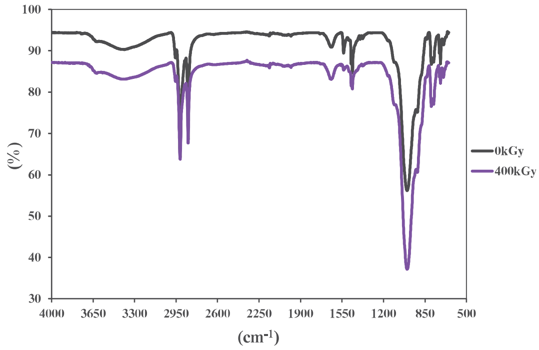

Figure 5. Absorption spectra in the infrared region for samples of automotive scrap tires non-irradiated and irradiated at a dose of 400kGy.

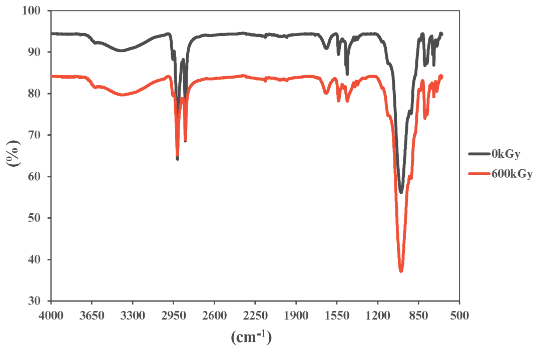

Figure 6. Absorption spectra in the infrared region for samples automotive scrap tires non-irradiated and irradiated at a dose of 600kGy.

These spectra show no changes and shifts of the peaks due to irradiation and it was not possible detect changes caused by irradiation for beads samples automotive scrap tires.

Conclusion

This study showed different weight losses with temperature increase for non-irradiated and the irradiated samples. From the results of the thermogravimetric curves obtained in the presence of air it can be concluded that in the non-irradiated and irradiated samples at different irradiation doses, there was a probable oxidation of the components of the rubber from automotive scrap tires in relation to the temperature increase. The thermogravimetric curves showed that various events occurred. These events occurred at different temperatures. It can be observed that there was a possible degradation when the samples were irradiated and the thermal behavior of the samples remained unchanged at each irradiation dose.

The granules rubber samples from automotive scrap tires when subjected and characterized by thermogravimetric analysis in nitrogen (N_2) have demonstrated a single event. It has not oxidation because it is an inert atmosphere, possibly with increasing radiation dose may have occurred changes in thermal behavior of the sample, but the thermal stability did not change with increasing irradiation dose.

Through the thermal evaluation of these samples, it can be seen that the thermal behavior varies according to each irradiation dose. The thermal behavior of the sample is a sum of the thermal degradation curves. However, increased temperature promotes not only the chemical reactions but also the fractions of volatilization of components. Besides, the differential scanning calorimetry, DSC, was adequate to determine the degradation behavior, and this degradation is different as irradiation doses.

In the mechanical tests maximum elongation at break was observed degradation with respect to all the irradiated samples when compared to non-irradiated. Therefore, for non-irradiated samples it is possible to add 10 to 30% of rubber powder from automotive scrap tires for residue recovery purposes.

Regarding FTIR spectra, it can be concluded that there was not changes and shifts of the peaks due to irradiation, that is, the technique lacks sensitivity to detect changes caused by the irradiation rubber samples from automotive scrap tires.

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