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Preliminary studies of the rubber from unserviceable tires irradiated by electron beam

Clécia M. Souza[1a], Leonardo G. Andrade e Silva[1b]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
[a]cleciamsouza@ymail.com
[b]lgasilva@ipen.br

ABSTRACT

Nowadays there is a growth in the developing processes for modification of polymers with ionizing radiation (gamma rays, electron beam) for several industrial applications. An option is ionizing radiation process due to their capacity of inducing crosslinking and scission on a wide range of polymeric materials without initiators or chemicals products. This method has significant advantages on economical and ecological fields, when compared to chemical, thermal and mechanical process. The rubber recycling has been extensively discussed, mainly related to tire. There are reports with data about production and consumption of rubber and unserviceable tire. There is very few information about the destination of others rubber items, incineration and landfill are the main methods for elimination of unserviceable tire, however those methods are not environmentally friendly. It is necessary to study better and effective methods to recycle and to give value to rubber residue. This work is about the use of ionizing radiation for the recovery and/or reuse and processing rubber of unserviceable tire. The samples were irradiated with 200, 400 and 600kGy radiation dose, 22.39 kGy/s dose rates, at room temperature and in the presence of air using an 1.5MeV electron beam accelerator. The irradiated and non-irradiated samples were studied by thermogravimetry (TG). The analyses were performed from room temperature up to 600ºC, heating rate of 10ºC/min in the presence of nitrogen (N_2) and air. By this technique it was possible to observe the effects of the radiation dose on the weight loss.

1. INTRODUCTION

Recycling process became important to preserve natural resources, avoid waste and prevent pollution of rivers which would be detrimental to 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 as raw material to benefit or to reduce the use of amount of virgin raw material [1, 2].

Recycling also includes the steps of segregation, that are the intermediates activities that takes the waste to the point of being transformed and it is the step of transformation in the reprocessing industry [2].

By its own thematic condition, the recycling process, its development and the technology used have guided the discussion and the work of several researchers in multiple areas of scientific, business and professionals in recycling field [3].

A major problem faced in preserving the environment is the management of waste polymeric materials before and after consumption such as production´s remains and used artifacts. Most of these materials are plastic usually as food packaging, bags, bottles and tires. They are found in dumps, landfills, or even in everyday life, in rivers, lakes and ponds. Usually as food packaging, bags, bottles and tires. Among all these materials, the rubber of automotive unserviceable tire is the subject of investigation of this work [4].

In several countries, most of these old tires are thrown into landfills, dumps, land and areas without any control. The most controlled and licensed landfills are those used by industries. For example, the industrial reuse of rubber that produces cars mats and use recovered rubber tires as part of their composition, burns old tires in cement kilns.

Typically, the composition of the tires consists of different types of rubber: natural rubber, synthetic rubber, butyl rubber, and fillers, carbon black, and also as reinforcements, nylon and steel mesh [4].

Tires are one of the main components of the cars to be considered to 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 (BR), styrene-butadiene rubber (SBR), vary according to the manufacturer and the end use. For example, the compositions of the tires used in cars and in trucks are not the same. The tires of cars represent 80% against 20% of truck tires [5, 6].

In passenger cars, dominates the petroleum derivatives and chemical products, constituting 36%; natural rubber 36% and metallic material (or steel) with 18%. These are designed to withstand high speeds, while truck tires are for load and provide support more weight, due to this, the amount of natural rubber in truck tires is over 40% [6].

Only in the U.S., 250 million unserviceable tires are produced every year and it reaches the amount of billions of units considering earlier years. For this reason the unserviceable tires is subject of investigation and they have been attracting the attention of environmentalists and academics [5].

In Brazil, the amount of tires/year reaches 68 million on the market. The data from the National Association of the Tire Industry (ANIP) indicates that exist around the country about 900 million unserviceable tires, and only 50% of the total are discarded properly [7].

Several methods have being developed to solve the problem of waste tires in Brazil, for example, they are reused in various ways, as an alternative fuel for cement industry, the manufacture of soles of shoes, rubber seal, rainwater pipes, for blocks courts, industrial floors, asphalt and rubber mats for automobiles. Reciclanip is an organization dedicated to the collection and disposal of unserviceable tires (those that are no longer capable of being used for circulation or retreading). They collected and disposed environmentally correct 107,104 tons of unserviceable tires in the first quarter of 2011, the equivalent to 214 million units of tires for passenger cars [8].

One of the most widely used elastomers in the manufacture of tires is SBR (styrene-butadiene copolymer) containing 25% by weight of styrene. Other rubbers used in the manufacture of tires are poly (cis-isoprene), which is natural rubber, and synthetic poly (cis-butadiene) [9]. An example of composition of tire rubber is shown in Table 1.

Table 1: Example of a tire rubber composition, percentage used and the purpose of adding the fillers [9, 10].

Component	Percentage (%)	Composition/Purpose
SBR	62.1	[-CH2-CH=CH-CH2 – ran –CH2-CH-(Ph) -] $_n$
carbon black	31.5	strength the rubber, increase resistance to abrasion, heat dissipating
modified oil	1.9	aromatic hydrocarbon mixture / soften the rubber, give workability
zinc oxide	1.9	control the vulcanization process, better rubber properties
stearic acid	1.2	control the curing process, enhance physical properties of rubber
sulfur	1.1	produce the crosslink between the polymer chains, prevent excessive deformation at high temperatures
accelerators	0.7	organic sulfur compound / catalyze the curing

Due to its chemical composition, tire can be considered as a fuel and it burs at high temperatures leading to large amounts of black smoke and oils that contaminate soil and groundwater. In addition, the accumulation of used tires may generate mosquito breeding, and becomes a major problem for public health in the control of disease [11, 12].

Current legislation establishes that improperly disposed tires are environmental liabilities that may result in serious risk to the environment and public health [4, 5].

In order to find an effective way for the disposal of unserviceable automobile tires it was created the Resolution No. 416 of 30 September 2009 published in the Official Gazette on October 1, 2009, published by the National Council on the Environment - CONAMA Ministry of Environment, provides for the prevention of environmental degradation caused by waste tires and their environmental adequate disposal, and other measures [7]. Manufacturers and importers of new tires, with weight exceeding 2.0kg, are required to collect and dispose waste tires appropriately in the national territory.

Also in accordance with this resolution, for each new tire sold to the aftermarket, the manufacturers or importers should dispose properly the waste tire.

2. MATERIALS AND METHODS

It was used in this work crumb rubber from waste tires donated by RECICLANIP which is an institution responsible for collection and disposal of waste tires in Brazil. The tire rubber was washed and separated from the steel mesh and, afterwards from the nylon. This rubber is cut to a thickness of 2mm crumb rubber by grinding process. The specific gravity of the crumb rubber is 0.907 g/cm^3.

The samples were separated into glass containers and irradiated in air from 200kGy up to 600kGy, at 22.39 kGy/s dose rate, at room temperature. The irradiation process was carried out using a 1.5MeV electron accelerator. The dosimetry of total absorbed dose was performed using cellulose triacetate dosimeters. The samples irradiated were placed in plastic bags, stored in a dry container and protected from light to avoid the influence of natural light and consider the effects of post-irradiation.

The samples irradiated and non irradiated were analyzed with thermogravimetry (TG), using a TGA 50, from Shimadzu Co in Thermal Analysis Laboratory located at Radiation Technology Center (CTR). Analysis were performed in accordance with ISO 11358, DIN ASTM 1131e 51 006, from room temperature to 600ºC, heating rate of 10°C/min, in air 50 mL/min. The irradiated and not irradiated samples were also studied by the same technique, in the laboratory LATIG, IQ/USP [13] using nitrogen as a gas flow, 50 mL/min.

3. RESULTS AND DISCUSSION

Figure 1 shows the TGA results for non irradiated and electron beam irradiated samples at doses of 200, 400 and 600kGy heated under oxygen atmosphere. The results showed different weight losses with increasing of temperature all the samples. The first weight loss around 250ºC can be attributed to humidity and oil, consequently it is not decomposition. It is evaporation or volatilization of the oil and water.

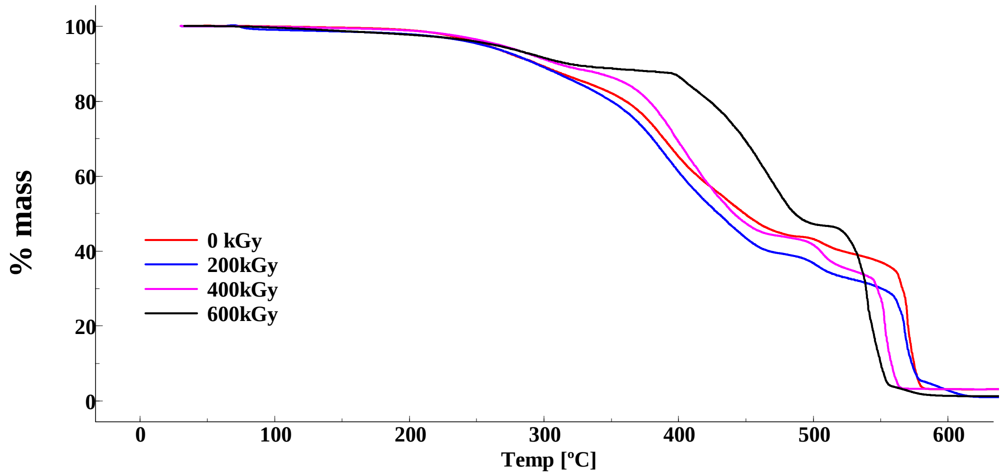

Figure 1: Thermogravimetric curves obtained in a dynamic atmosphere in air for samples of unserviceable automobile tires at different doses.

As shown in Table 2, the mass reduction was around 97% for the non-irradiated samples and samples irradiated at 200kGy and 400kGy. At dose of 600kGy, the mass reduction was around 99%, the remaining residue may be zinc oxide as shown in Table 1 and Table 2. The Table 2 also illustrates the range of temperature where occurred higher weight loss for each dose. The non irradiated samples and samples irradiated at 200 kGy and 400 kGy degraded at lower temperatures compared to the samples irradiated at 600 kGy. The 600 kGy irradiated sample presented higher degradation temperature due to radiation process. The 200kGy irradiated samples presented a decrease of thermal stability and it can be conclude a rubber degradation occurred.

Table 2: Comparison in the percentage (%) of the weight losses of samples with increasing temperature to 600°C at different doses.

Dose (kGy)	Range of temperature (°C)	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 presents the TGA results for non irradiated and electron beam irradiated samples under nitrogen atmosphere. The results showed the weight loss as a function of radiation dose, with increasing temperature. The mass reduction was 71% for non-irradiated samples, 58% for 200 kGy irradiated samples, 60% for 400kGy irradiated samples and 69% for 600 kGy irradiated samples. It can be observed a small decrease on weight loss with increasing radiation dose as shown in Table 3.

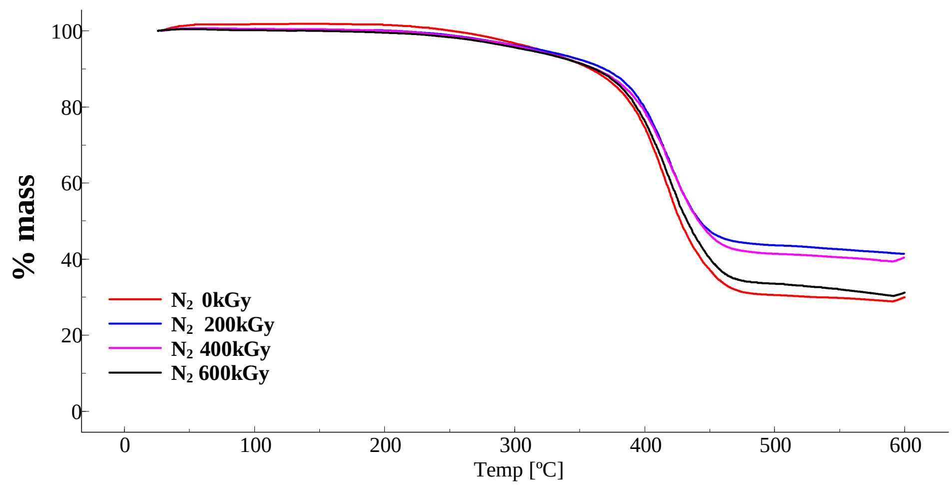

Figure 2: Thermogravimetric curves obtained in a dynamic atmosphere of N_2 for samples of unserviceable automobile tires at different doses.

Table 3: Comparison of percentage (%) of the weight losses of samples with increasing temperature to 600ºC of the samples at different doses.

Dose (kGy)	**Range of temperature (ºC)**	**Higher weight loss (%)**	**Total weight loss (%)**	**Residue (%)**
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

CONCLUSION

This study showed different weight losses with increasing temperature for non irradiated and the irradiated samples. In addition, on the samples irradiated at 200kGy the degradation process is predominant. The samples irradiated at 600kGy presented higher onset degradation temperature on due to crosslink formed by irradiation process. It was possible to observe presence residue that may be zinc oxide. In inert atmosphere rubber seemed to undergo to depolymerization because weight loss occurred in one step. The residue in N_2 atmosphere could be attributed to carbon black content and zinc oxide.

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