

THERMAL ANALYSIS OF GROUND TIRE RUBBER DEVULCANIZED BY MICROWAVES

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Ground tire rubber (GTR) was treated by microwaves at the same power and at different times of exposure, in order to improve their recycling characteristics. The resulting materials were characterized by thermogravimetric analysis (TG/DTG) and differential scanning calorimetry (DSC). DSC analysis showed that the microwaves treatment, specially for longer exposure times, changes the thermal behavior at low temperatures, that is to say, changing its glass transition (T_g), probably due to the modification in the chemical structure of the rubber. The TG/DTG analysis showed that the thermo-oxidation behavior of the sample after the microwaves treatment is different from the sample before the treatment. The thermo-oxidation temperature of the devulcanized rubber is shifted to lower temperatures, even for the rubber treated in short times.

Keywords: devulcanization, microwaves, rubber recycling

Introduction

Recycling of vulcanized rubber goods is, nowadays, a major environmental problem. The cross-links between the main polymer chains, formed during the vulcanization process, turns the thermoplastic into thermosets what makes impossible the reshape by heating [1, 2]. Therefore, to reuse these materials it is necessary to pass the material through some kind of physical or chemical treatment in order to destruct the three-dimensional network of the vulcanized rubber giving back to it, the thermoplastic behavior. These treatments are called devulcanization. This kind of rubber reclaim is currently receiving a special attention, since other disposal methods, like burning for energy generation, are pollutant and not environmentally friendly.

There are several physical and chemical devulcanization techniques described in the literature [3–12], but none of them is able to produce a material identical to the virgin rubber. This is caused by the fact that, during the devulcanization process, not only the cross-links are broken, but also the main chain, promoting the decrease in its molar mass and, consequently, the degradation of its properties [13]. Therefore, before using these materials, a complete characterization of their properties is necessary, not only to choose the best application for these materials, but also to understand what changes are induced to the rubber during the devulcanization process.

Despite that several devulcanization processes are available, one of the most promising is the microwave devulcanization [1, 4, 14–16]. In this technique, the cross-link breaking is promoted by heating of the vulcanized rubber by microwaves. The use of microwaves for heating purposes has the advantage of volumetric heating, which is faster and promotes a more homogeneous heating than other methods based on convection and conduction. However, the material to be heated is supposed to have some polarity, since the heating is mainly due to the dipole rotation induced by the microwaves [17]. This polarity can be an intrinsic characteristic of the material or can be induced by the addition of conductive fillers, such as carbon black, in an effect known as the Maxwell–Wagner polarization [18]. Carbon black is, by far, the most common filler used in rubber goods, specially in tire rubber. This fact makes possible to use the microwaves heating in tire rubber devulcanization.

Elastomeric systems have highly complicated formulations, which can contain, besides the base elastomers, process oil, plasticizers, fillers and additives such as process aid and curatives [2, 19]. In the specific case of tire rubber, the exact composition of the rubber depends on the manufacturer and the grade of the tire.

Since the devulcanization process can be classified as a controlled degradation method, the study of its thermal properties is a key factor to understand what is happening with the material structure during its treatment.

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Thermal analysis is a useful tool for the characterization of elastomer compound [20]. Thermogravimetry, for instance, is a powerful technique that shows the composition identification, degradation and thermo-oxidation behavior [21]. The differential scanning calorimetry is suitable to detect changes in thermal transitions and the kinetics of e.g. polymer thermo-oxidation [22].

In spite of the devulcanization process by microwaves being known since the later 70's, the literature describes the properties of the resulting material is very limited. The objective of this article is to describe the thermal behavior and thermo-oxidation characteristics of tire rubber treated by microwaves and to explain possible changes that occur in the structure of the rubber during the devulcanization.

Experimental

Materials

The ground tire rubber (GRT), supplied by Artgoma do Brasil, was a 20 mesh ground rubber obtained from the treads and sidewalls of passenger tires. The exact composition of the material is unknown, but it is well known that the major components of most tire rubbers are natural rubber (polyisoprene, NR), styrene-butadiene copolymer (SBR), polybutadiene (BR), as polymers, and carbon black, as filler.

The granulometric analysis of the ground rubber is shown in the Table 1.

Table 1 Granulometric analysis of the GTR

Mesh	Mass/%
20	0.67
80	80.76
Residue	18.57

Methods

Microwave treatment of the rubber

The rubber was treated in an adapted microwave apparatus consisting of a home style microwave oven Electrolux 27E and a stirring system, as schematically showed below, in Fig. 1. The power of the magnetron was set up to 700 W and 60 g of the GTR were put in a 250 mL Becker with a stirring speed of 40 rpm.

The processing variable adopted here was the exposure time, which was varied from 1 to 5 min. The samples were identified as GTR followed by a number corresponding to the exposure time in minutes and the temperature of the samples was measured after each treatment.

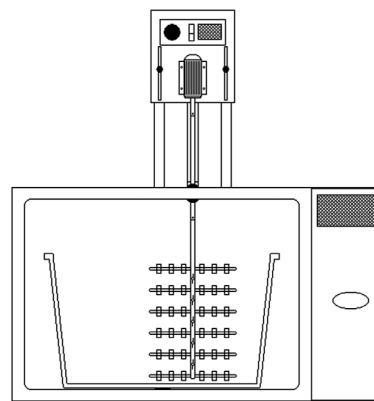


Fig. 1 Microwave apparatus used in the present work

Gel content determination

The gel content of each sample was determined by Soxhlet extraction using toluene as solvent. The extraction took about 24 h and it was done with approximately 5 g of the material. After the extraction, the material and the thimble filter were dried for 24 h at 80°C and their mass was measured.

Thermogravimetric analysis (TG)

The thermogravimetric analyses (TG/DTG) were done in a Shimadzu TGA 50. About 8 mg of the sample were weighed and heated from room temperature up to 800°C, under 50–50 v/v% N₂ and 50% O₂ atmosphere, at a heating rate of 10°C min⁻¹.

Differential scanning calorimetry (DSC)

The DSC analysis were done in a DSC QA-100 from TA Instruments, from -75 up to 400°C, under N₂ atmosphere, at a heating rate of 10°C min⁻¹.

Results and discussion

Temperature measurements after treatment

Temperatures of the samples after the exposure to the microwaves are shown in Table 2. It can be observed that as expected, the temperature of the sample just after the microwaves exposure increases almost linearly.

Table 2 Temperatures of the samples immediately after the microwave treatment

Sample	Temperature/°C
GTR 1	95
GTR 2	141
GTR 3	236
GTR 4	282
GTR 5	312

The exception to this linearity is the sample with 5 min of treatment. This can be explained by the high extent of the degradation of the rubber. Tests executed in inert atmosphere [23] showed that the more intensive the microwaves treatment, the lower is the relative amount of rubber. The high amount of carbon black probably changed the microwave absorption behavior of the rubber compound at the end of the treatment, influencing also the final temperature of the sample.

Gel content

Table 3 shows the results of Soxhlet extraction for the samples.

Table 3 Gel content of the samples

Sample	Gel content/%
GTR without treatment	85
GTR 1	85
GTR 2	84
GTR 3	64
GTR 4	54
GTR 5	*

*The sample turned to char

In spite of the Soxhlet extraction only evaluates the fraction of soluble matter present in the sample; it remains a good parameter to evaluate the efficiency of the devulcanization process [13]. In general, the lower the gel content, the more efficient the devulcanization process is. It can be observed that the time of treatment has a high influence on the gel content. This was already expected, since for longer times the material reached higher temperatures and generated materials with lower insoluble portion.

Thermogravimetric analysis (TG)

Figures 2a and b show the mass loss recorded by TG analysis and the DTG curves as well. Curves of the GTR samples without treatment and after 1 and 4 min of microwaves treatment are shown.

Table 4 shows the results obtained by TG/DTG curves.

All the samples showed a thermal event in the temperature range between 200 and 350°C. The mass loss in this temperature range is due to the evaporation or decomposition of extender oil and other organic non-polymeric additives present in the rubber compound. The extender oil is, generally, a mixture of hydrocarbons which serves to soften the rubber and improve workability [19]. Thermogravimetric compositional analysis done by Ginic-Markovic *et al.* [20] also showed this temperature range as the decomposition temperature of

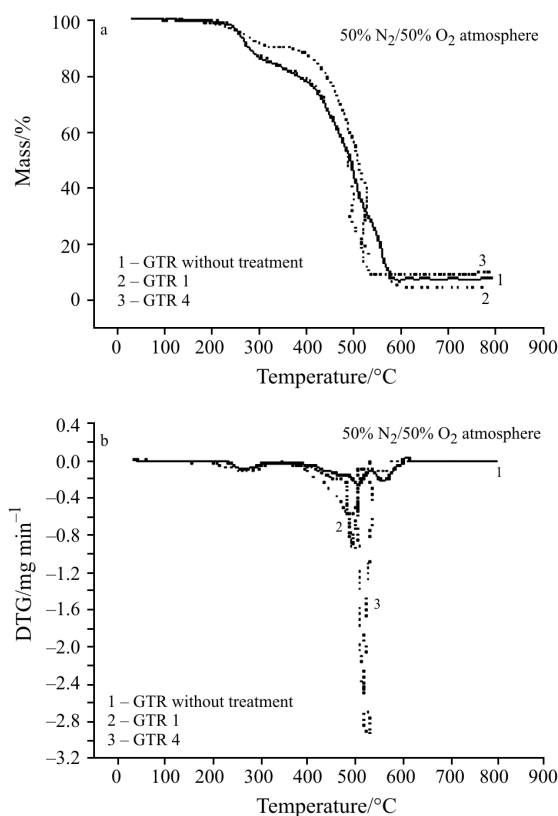


Fig. 2 a – TG and b – DTG curves obtained for the GTR samples before and after microwave treatment

extender oil. To confirm this assumption, in our case, the oil was separated from the original GTR, using solvent extraction with toluene, and thermogravimetric analysis was done under the same conditions as it has been done for the GTR. The decomposition range of this material matched with the decomposition temperature range of the first peak in the GTR. As expected, the amount of extender oil detected in the rubber without

Table 4 Mass loss, Δm , temperature range, ΔT , from TG curves and peak position, T_p , from DTG curves for GTR samples

Sample	Δm /%	ΔT /°C	T_p /°C
GTR without treatment	17.1	200–350	266
	52.4	350–530	504
	22.0	530–600	558
GTR 1	16.6	200–350	262
	64.0	350–530	492
	77.9	530–600	564
GTR 2	12.3	200–350	251
	82.3	350–600	496
GTR 3	10.1	200–350	263
	82.8	350–600	486
GTR 4	10.3	200–350	272
	82.5	350–600	520
GTR 5	4.89	200–350	nd
	82.8	350–600	529

treatment by TG is similar to the soluble fraction found in Soxhlet extraction, that is, between 15 and 17%. The mass loss due to the oil release decreases as the exposure time is increased. This effect was expected, since the microwave treatment promotes the heating of the rubber and part of the oil can evaporate or decompose during this step. Actually, it was observed, during the microwaves treatment, that the sample released a large amount of smoke. There are also two thermal events between the 350 and 600°C for the GTR without treatment. The first event, with a peak at 504°C is probably due to the thermo-oxidation of the polymeric phase of the material and the second event, with a peak at 558°C is due to the thermo-oxidation of the carbon black. It is interesting to observe that the microwave treated samples showed only one thermal event in this temperature range. In addition, this single event occurs at temperatures below the thermo-oxidation of both, the rubber and the carbon black, in comparison with the sample without treatment. This suggests that the microwave treatment promoted some chemical modification in the components, accelerating their decomposition. Kleps *et al.* [22] observed the same behavior. They attributed this overlap in the decomposition of polymer and carbon black phases to the existence of polymer with lower molar mass than the original rubber, as a result of degradation of the polymer chains under the influence of microwaves. Another observed behavior in Fig. 2 is the shift of the maximum decomposition temperature to lower temperatures up to 3 min of treatment, being lower than both, polymer and carbon black of the rubber without treatment. For the samples treated for 4 min or longer, the maximum decomposition temperature increases, approaching to the thermo-oxidation of the carbon black in comparison with the rubber without treatment. This indicates that the rubber phase was decomposed and the carbon black is the main component, that is, the carbon black rules the overall decomposition of the material.

Williams and Besler [24] found a two-stage decomposition of the polymer during TG analysis of tire rubber under inert atmosphere. They attributed these two thermal events to the differences in the decomposition temperature of natural and synthetic rubber. In our work, it was not possible to differentiate the decomposition of the synthetic and the natural rubber, probably due to the use of an oxidative atmosphere, which is expected to change the decomposition behavior of the elastomers.

The peak associated to the thermo-oxidation of rubber plus carbon black for the samples treated by microwaves happens at lower temperatures than both, the carbon black and the rubber decomposition, of the untreated rubber. This behavior was also observed by Kleps *et al.* [22] and can be attributed to changes in the molecular structure of the material.

Differential scanning calorimetry (DSC)

Figure 3 shows the DSC curves for the GTR with and without microwaves treatment.

The inflection point at low temperatures can be attributed to the glass transition (T_g) of the material. The peaks at high temperatures represent the exothermal decomposition reactions of the material. Table 5 shows the T_g and the decomposition peak position of the samples.

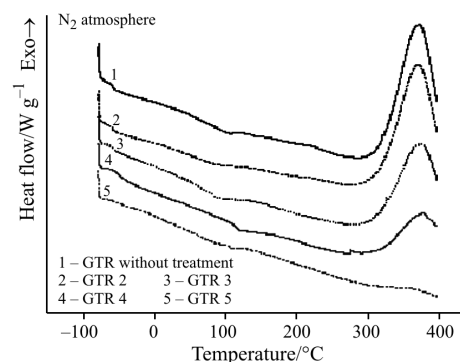


Fig. 3 DSC results for the samples of GTR before and after the microwave treatment

The results of the GTR 5 sample did not show neither the T_g nor the decomposition peak. It is probably due to the fact that the polymer phase of the sample was completely decomposed during the microwave treatment. Actually, the sample turned to a black powder, similar to carbon black after 5 min of treatment.

The values of T_g of the GTR samples without treatment, GTR 2, GTR 3, were almost the same, indicating that there is no significant changes in the thermal behavior at low temperature until 3 min of microwave treatment. However, there was a significant change in T_g value for the GTR 4 sample. Comparing these data to the gel fraction results, it can be observed that these samples had the higher soluble content, that is to say, they were submitted to the most aggressive treatment. The shift of the T_g to higher temperatures was also detected by Isayev *et al.* for

Table 5 Glass transition (T_g) and decomposition temperatures of the samples measured from DSC curves

Sample	$T_g/^\circ\text{C}$	Decomposition peak temperature/ $^\circ\text{C}$
GTR without treatment	-59.7	373
GTR 2	-59.6	371
GTR 3	-60.1	375
GTR 4	-46.8	377
GTR 5	nd	nd

nd – not detected

devulcanization of sulphur vulcanized rubber by ultrasound [13]. In the case of ultrasound devulcanization, this change in T_g was attributed to the formation of cyclic sulphur structures in the polymer chains. These structures limit the mobility of the chains, increasing the T_g of the elastomer. Another possibility of this difference in the T_g values is the higher carbon black content of both GTR 4 and GTR 5 samples. A similar behavior was also observed in TG curves. As it can be seen in TG curves, for the untreated sample, the thermo-oxidation of the polymer occurs at lower temperature than the carbon black. Therefore, the higher the treatment time of the material, the higher the temperature and the exposure time at this temperature and the higher the relative amount of the carbon black in the sample. There is, also, the volatilization of the extender oil, which works as a plasticizer for the rubber molecules. The higher amount of carbon black and the lower amount of the extender oil tends to diminish the molecular mobility of the rubber, increasing its T_g [22].

Conclusions

The microwave treatment of rubber tire promotes some changes in the tire rubber structure and composition, which is reflected on the thermal properties of the rubber.

The thermo-oxidative behavior of the samples is completely changed. The untreated rubber showed two distinct thermo-oxidation peaks, due to the decomposition of the rubber and the carbon black. Although, for treatment times as short as 1 min, these two peaks cannot be distinguished anymore and this situation remains until the treatment times long enough to completely decomposed the rubber. It is interesting to notice that, for the sample exposed to the microwaves for 1 min, other properties like gel content and thermal properties measured by DSC was the same as the properties of the untreated one. This suggests that a chemical modification happened during the microwaves treatment which favored the thermo-oxidation of the system rubber+carbon black.

The T_g obtained by DSC was higher for the material treated for 4 min, probably due to structural changes in the rubber. This behavior is also found in rubber devulcanized by ultrasound [13].

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