FTIR SPECTROSCOPIC AND THERMOGRAVIMETRIC CHARACTERIZATION OF GROUND TYRE RUBBER DEVULCANIZED BY MICROWAVE TREATMENT

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Abstract

In this work the phenomena involved with the microwave devulcanization of ground tyre rubber (GTR) were investigated. During studies three types of GTR characterized by different content of organic compounds (elastomers, plasticizers, etc..), carbon black and ash have been analyzed. The chemical structure of GTR before and after microwave devulcanization process was studied by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Furthermore, efficiency of microwave devulcanization conducted at different time was evaluated based on the crosslinking density and sol content values. FTIR spectroscopy results shown that devulcanization of GTR causes a decrease in carbon black with generation of CO_2 due to its thermo oxidation, a decrease in structural groups of elastomeric components (mainly methylene and methine) and a breaking of C-S groups and S-S bridges. The presented results indicate the strong correlation between content of SiO_2 in GTR and its degree of devulcanization. It was observed that GTR with a high content of SiO_2 are easier devulcanized than samples with low content of SiO_2, which suggest the presence of silica fillers improve microwave devulcanization efficiency.

Keywords: Devulcanization, GTR, microwave, Recycling, FTIR, TGA

1.- Introduction

The development and rapid growth of the automotive industry has positive impacts on the economy and job creation. Nevertheless, this type of manufacturing presents also its downsides, including environmental issues. A specific problem is the generation of End-of-Life Tyres (ELT).

The global output of tyres is estimated at 1.5 billion units [1]. Only in 2013, 3.4 million tonnes of ELTs in Europe [2], 175.242 tonnes in Spain [3] and 200.000 tonnes in Poland were generated [4]. The disposal of waste tyres may affect human health because they provide a breeding ground for mosquitoes and rodents. The slow decomposition of tyres, produces some other environmental risks including spontaneous heating and fire. Unlike other materials such as paper, glass, or plastic, which have implemented processes that allow their reuse into new products, the three dimensional cross-linked structure of tyres causes difficulties with their recycling.

The basic components used during manufacturing of tyres are natural rubber or synthetic rubber, carbon black, sulphur, accelerators, plasticizers and other additives. They are cured at a high temperature and the result is a crosslinked structure formed by sulphur bridges that connect the carbons of the main chains of the rubber, enhancing the mechanical properties. However, the formation of sulphur bridges is irreversible, which causes significant difficulties with recycling of rubber goods.

From 1996 to 2010, the methods of disposal of ELTs in Europe have been substantially developed. The amount of ELTs that were dumped in landfills has reduced from 49% to 4% in that period [1]. The rest of the ELTs are sorted according to their physical features. The tyres that are in good condition or only partially worn out are rethreaded reused and exported. The idea of reusing the tyres by rethreading, usually applied for truck tyres, is considered as the best in environmental terms, because less energy and less raw materials (e.g. synthetic and natural rubber, plasticizers, curing agents, etc.) are used during production of new tyres [5].The tyres that are damaged and worn out are burned for energy generation in cement kilns and power plants. Other than energy generation, the ELTs can be recycled for their use in civil engineering and public facilities such as the rubber mats used in playgrounds, the flooring for running tracks or, blended with asphalt or other thermoplastics [6-11]. Unfortunately, some of these recycling methods are not enough friendly to the environment. The production of energy from combustion of old tyres has caused debates among the members of the scientific community because of the emission of hazardous pollutants that can have negative impact on health and environmental problems [12,13].

The mentioned recycling methods do not break the crosslinks produced by the vulcanization process inside the tyre, hindering the possibilities of applying recycling processes that require thermoplastic behaviour. In order to avoid the negative effects of a crosslinked structure in the recycling of the materials, the study of devulcanization of ground tyre rubber (GTR) becomes an interesting challenge. The devulcanizated

materials would be suitable for producing new composite materials by mixing them with fresh synthetic or natural rubber [14,15]. Nowadays, there are several research groups trying to devulcanize the GTR by different processes such as mechanical [16,17], thermomechanical [18], mechanochemical [15], supercritical CO_2 [19], microwave [20], microbial [21] or ultrasounds [22].

The aim of this work is to devulcanize three GTR samples with different composition by a microwave process and study the involved phenomena, including the changes in chemical structure of the rubber and the characterization of the resulting products. The efficiency of microwave devulcanization was evaluated based on the crosslinking density and sol content values. Furthermore was monitored the influence of the carbon black and other tyre components (SiO_2) of GTR in the microwave devulcanization process.

2. Methodology

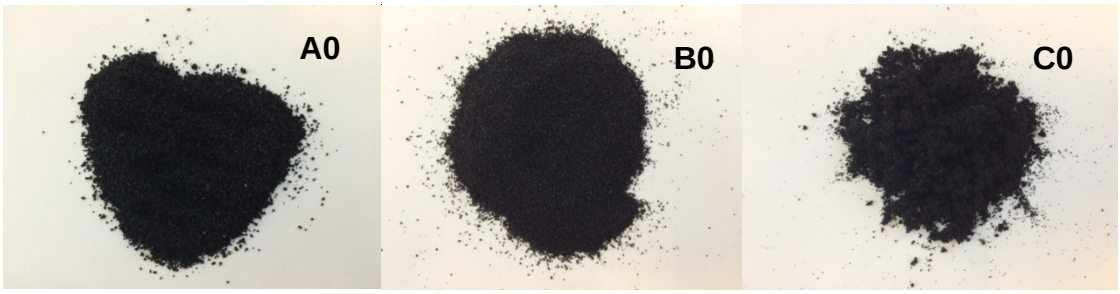
2.1. Materials

Three types of samples of GTR were used in this study. As shown in Table 1 each one of them presents different composition regarding to their percentage of elastomeric, carbon black and other inorganic components. Samples A and B show the same texture, feeling to touch like a fine powder. On the other hand sample C, is constituted by crumbs and is loosely packed, almost like a soft foam, turning into fine powder when little pressure is applied (see Picture 1). The GTR samples are obtained from Gestión Medioambiental de Neumáticos S. L. (GMN) from Maials (Spain).

Table 1.- Characteristics of ground tire rubber

Sample	Organic compounds content (%)	Carbon Black (%)	Ash content (%)	Average size of GTR (μm)
GTR A	61,88	32,09	6,03	400
GTR B	55,48	34,96	9,56	425
GTR C	57,87	36,89	5,25	275

Picture 1.- The GTR samples that has been used



2.2.- Sample preparation

The microwave devulcanization process was carried out by using a modified domestic microwave oven, Daewoo KOR-6L35, turned to the maximum power output of 700 W. A stirrer made of polytetrafluoroethylene (PTFE) has been added to the microwave in order to ensure homogeneous exposure of the GTR to the microwaves. During the devulcanization process, a sample of 15g of each GTR type was placed inside a 300ml PTFE beaker with a stirring speed of 20 rpm. The samples were then exposed to the microwave treatment for 0, 3 and 5 minutes at 700 W. In order to evaluated the effect of microwave treatment, chemical structure (FTIR analysis), thermal properties (TGA), physical properties (cross-link density, sol fraction), and morphology (SEM) have been analyzed.

To study the crosslinking density by swelling is needed a compacted sample, that has been obtained by using a hot plate press. 61g of each sample, without any other additive, was put into a square mould 16·16cm^2 with a thickness of 2,6 mm. To obtain a compact GTR sheet, the mould was pressed using a Collin P200E hot plate press at 220ºC and 120 bar for 4 min. The obtained sheet was removed from the mould and crosslinking density of those samples was determined. The effect of this procedure on the samples will be discussed later.

2.3.- Measurements

The size distribution of GTR particles were determined by sieving through ASTM E-11 standard sieves and weighing the respective fractions, using a Test sieve of Retsch (Germany).

Fourier transform infrared (FTIR) spectra were obtained by means of a Nicolet Avatar 320 FTIR spectrometer with CsI optics. Samples of the powdered rubber, with the average particle size showed in table 1, were ground and dispersed in a matrix of KBr

(9 mg of finely divided rubber in 300 mg KBr), followed by compression at 167 MPa to consolidate the formation of the pellet.

The determination of char and elastomeric components of GTR was obtained by thermogravimetric analysis by means of a Mettler Toledo TGA/SDTA 851, using alumina crucibles. The measurement was conducted in an inert environment, with a flow rate of 20 ml/min of nitrogen gas and a heating rate of 20^{o}C/min. The temperature started at 40^{o}C and ended at 600^{o}C.

The soluble (sol) fraction of each sample, before and after devulcanization process was determined by Soxhlet extraction by using toluene as solvent. Around 1,5 g of GTR was put inside a cellulose thimble and the extraction process was done for 24 h. After extraction, the samples were dried for 24 h at 80ºC to remove the solvent and their weight was measured. The sol fraction was determined as the ratio of the difference between weight of the sample before extraction (W_1) and weight of the sample after extraction (W_2), respect weight of the sample before extraction (W_1), according to equation (1):

$$\text{Sol Fraction} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (1)$$

In order to remove low molecular weight substance, the compacted samples described above were subjected to a preliminary extraction with acetone according to ASTM D297/13. Then, the crosslinking density of the samples was determined by equilibrium swelling in toluene (RT for 72h followed by drying to constant mass at 70ºC), according to Flory-Rehner equation (2) [23].

$$v_e = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{[V_1 (V_r^{1/3} - V_r / 2)]} \quad (2)$$

where V_e is crosslink density (mol/cm^3); V_1 is molar volume of solvent-toluene (106,13 cm^3/mol); χ is the rubber-solvent interaction parameter (0,39) [24] and V_r means volume fraction of rubber in swollen sample, which is calculated by using the Ellis and Welding equation (3) [25].

$$V_r = [(a_2/\rho_2)]/[((a_1 - a_2)/\rho_1) + (a_2/\rho_2)] \quad (3)$$

where a_1 is mass of swollen rubber sample (g), a_2 is mass of dry rubber sample (g) (24 hours at RT), ρ_1 is the density of solvent, toluene (0,8669 g/cm^3) and ρ_2 is the density of rubber sample.

Crosslinking density refers to presence of crosslinks inside the specimen. The solvent does not dissolve the crosslinked network, but swells it by entering the spaces inside the crosslinked cluster.

The determination of ash content of the devulcanizated samples was obtained according to the ASTM D297-13, where the sample is weighed and placed inside a crucible and then put inside a heat-treatment oven Optic Ivymen System at 550^{o}C for one hour. After this period the oven door is opened with a gap of 3 cm to introduce oxygen gas for 30 minutes in order to achieve the total oxidation of the sample. The remaining ashes corresponds to the part of inorganic components of the GTR, basically SiO_2, ZnO, and small quantities of Fe_2O_3 and $CaCO_3$ [26]. To determine the ash content percentage the equation (4) is used:

$$\text{Ash content} = \frac{m_2}{m_1} \times 100\% \quad (4)$$

where m_1 is the initial mass of sample (g) and m_2 is final mass (g) of sample after the oven treatment (ash)

3.- Results and discussion

3.1.- Particle size distribution

Figure 1 shows particle size distribution of different GTR used in this study. The particle size of GTR C is more homogeneous and lower than homogeneity and particle size of GTR A and GTR B; with an average value of 275 μm for GTR C and 400 and 425 μm for GTR A and GTR B respectively.

3.2.- Spectroscopy characterization

Figures 2a and 2b show the spectral areas comprised between 1500 to 800 cm-1 and 800 to 450 cm^{-1} of the three types of GTR samples without microwave treatment (A, B and C). Table 2 includes the most significant absorbance bands assigned to the components present in the samples according to previously published studies [27-29]. The 1500-800 cm^{-1} area includes the absorbance bands of elastomeric components, SiO_2 and carbon black. The 800-450 cm^{-1} area shows mainly the bands assigned to sulphur bonds.

Figure 3 shows the spectra of ash (mainly SiO2) and spectra of Carbon Black.

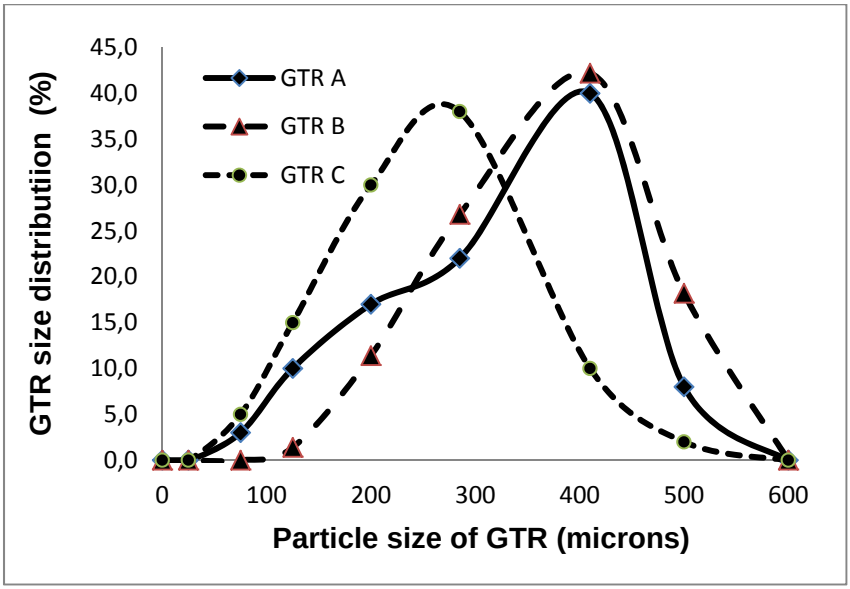


Figure 1.- Particle size distribution of GTR

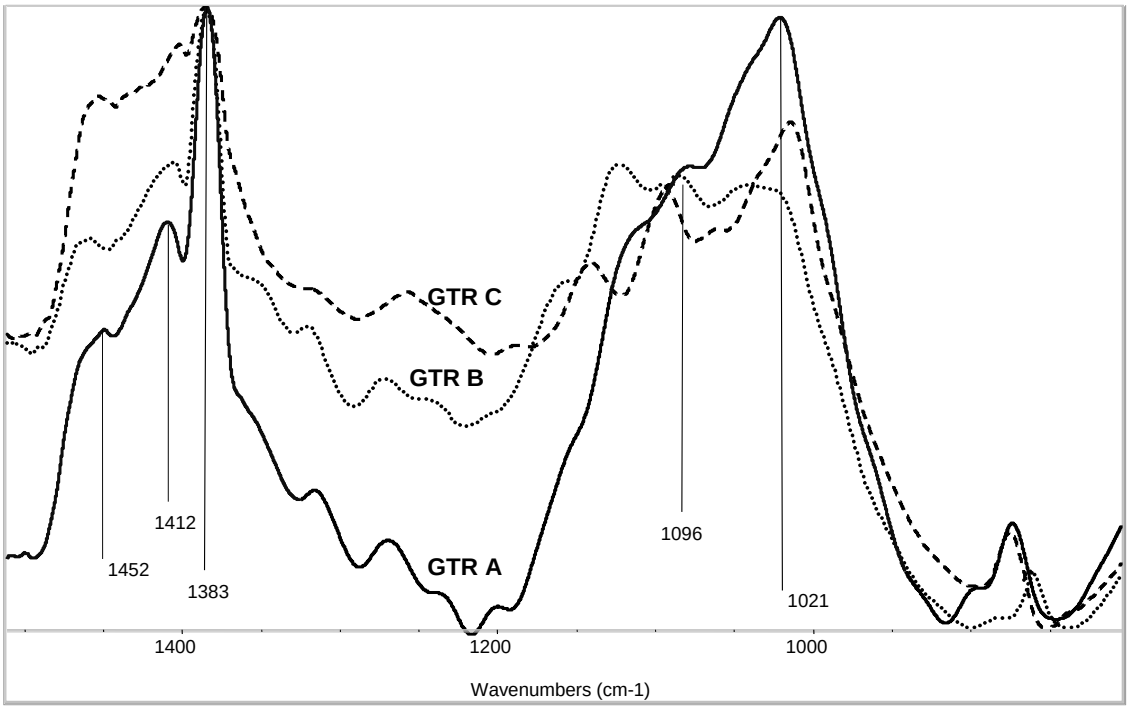


Figure 2a.- Spectral area comprised between 1500 and 800 of A, B and C samples

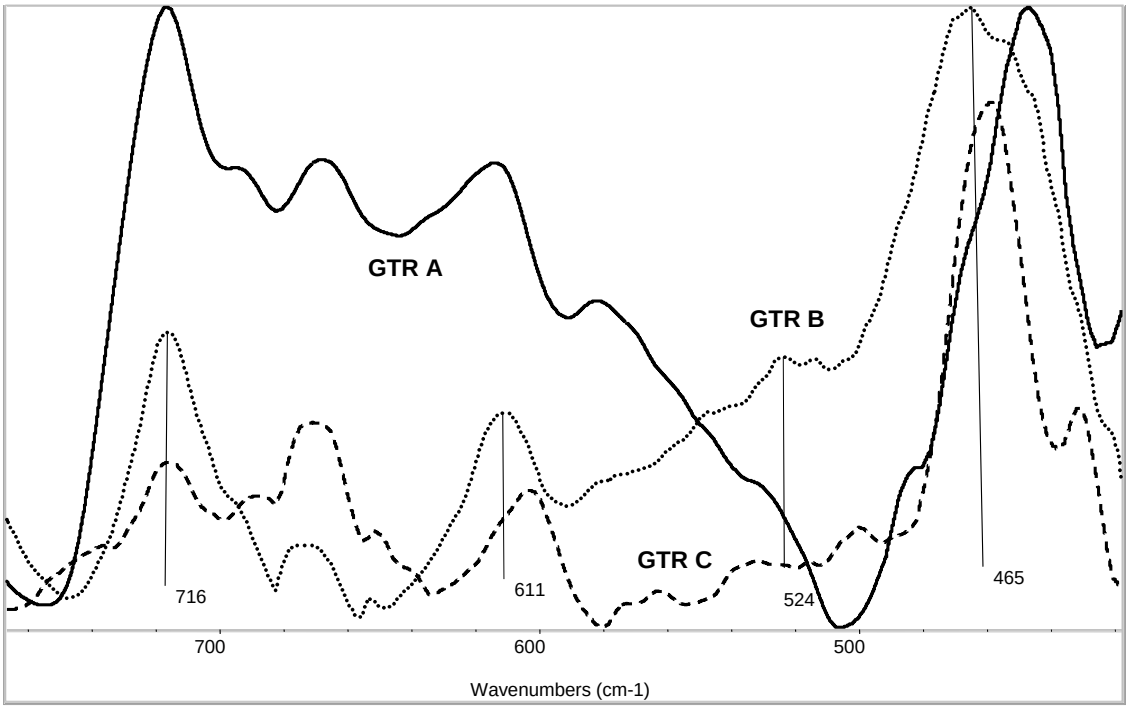


Figure 2b.- Spectral area comprised between 800 and 400 of A, B and C samples

Table 2.- Most significant bands of GTR and GTR MW devulcanized

Frequency (cm^{-1})	Assignments	Component
1452	$-CH_2-$ stretching	$R_1R_2-C=CH_2$
1412	-C=C-H in plane C-H bend	$R_1R_2-C=CH_2$
1383	$-CH_3$ symmetric bend	
1096	Si-O stretching	SiO_2 (reference band)
1021	-C-C- stretching	Black Carbon
874	-C=C-H out of plane	$R_1R_2-C=CH_2$
716	-C=C-H out of plane	$R_1H-C=CHR_2$
611	-C-S- stretching	
524	-S-S- stretching	
465	-S-S- stretching	

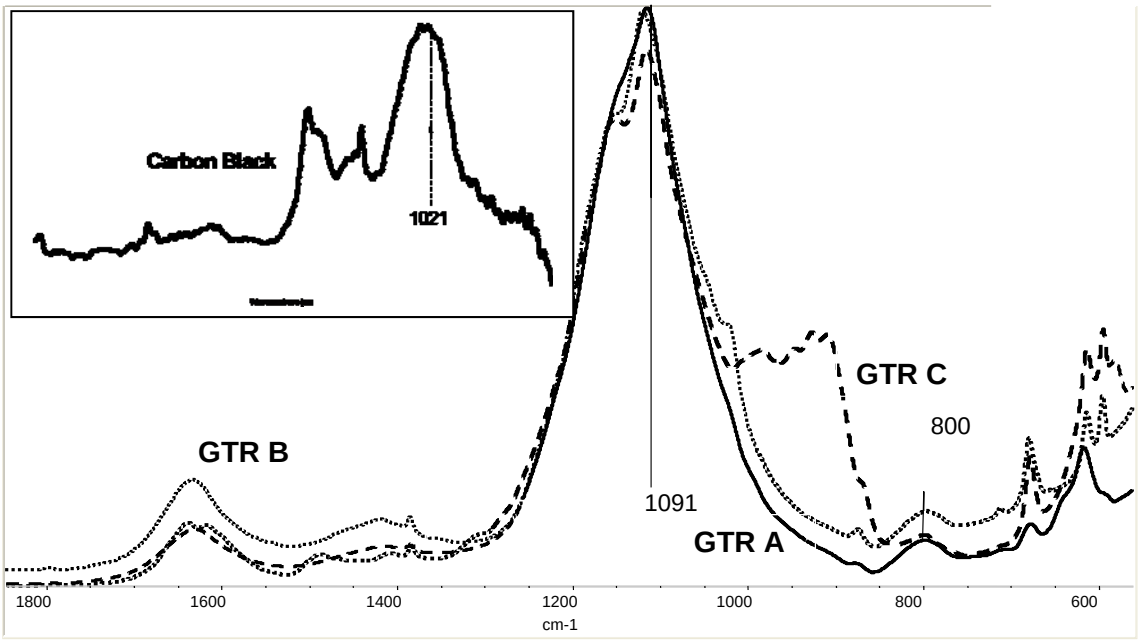


Figure 3.- Spectral area comprised between 1800 and 600 of ashes of GTR A, GTR B and GTR C samples (continuous line A, dotted line B and dashed line C). The inset shows the characteristic spectra of carbon black, with the band at 1021 cm^{-1}.

According to Miller and Wilkins [30] the FTIR bands assigned to SiO_2 appear at 1090 cm^{-1} and 800 cm^{-1}, and the bands assigned to ZnO at 1540 cm^{-1} and 1400 cm^{-1} [28], the spectra of figure 3 corresponding to the ashes of samples A, B and C show mainly a high band at 1090 cm^{-1} corresponding to SiO_2, and no band appears at 1540 or at 1400 cm^{-1}. The inorganic nature and thermal stability of SiO_2 does that it will remain unaltered after the treatment. For that reason, the band assigned to this substance has been used as reference in order to monitor the spectral changes of the other bands that may experience alterations. By dividing the absorbance of the spectral bands by that of the SiO_2 band, the magnitude of the observed changes is relative to the amount of SiO_2 component included in the sample. The absorbance processed that way is called reduced absorbance. Moreover, the inset shows the characteristic spectra of carbon black with the band at 1021 cm^{-1}, which is in agreement with different references [31-33].

Figure 4 shows reduced absorbance values of GTR A, GTR B and GTR C. As already can be observed sample C has higher reduced absorbance values comparatively than A and overall B. This is due to the differences in composition cited above. The composition of each sample is different, and the proportion between inorganic component and organic compounds are variable. B tyre has lower amount of organic

compounds (55,48%) and also has the maximum percentage of ash content (9,56%) as it shows in Table 1.

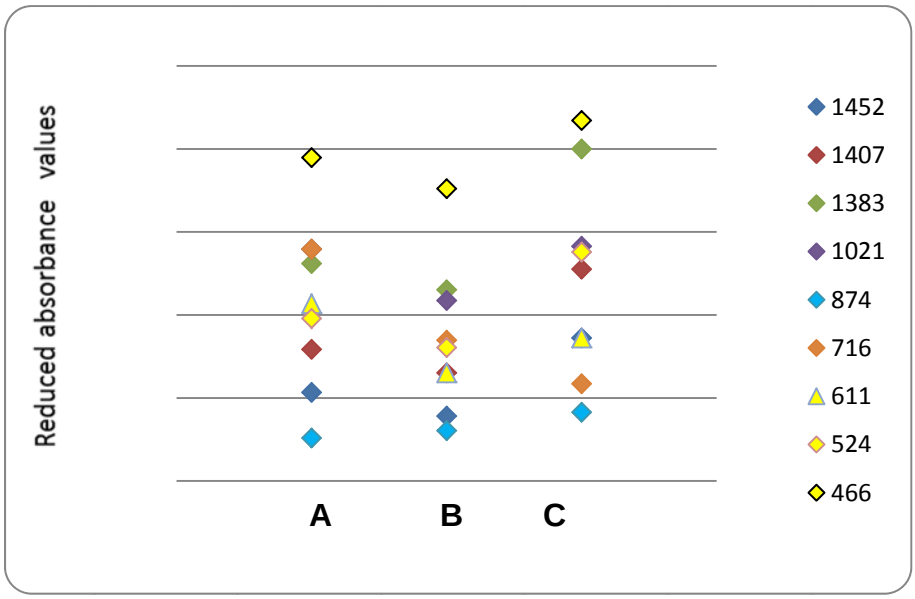


Figure 4.- Comparative values of reduced absorbance of A, B and C samples

Spectra shown at Figures 5a and 5b allow the analysis of the structural changes that take place in sample GTR A when is submitted to microwave treatment for 3 minutes (A3) and for 5 minutes (A5). Figure 6 shows the evolution of reduced absorbance values of different bands as a function of microwave exposure time.

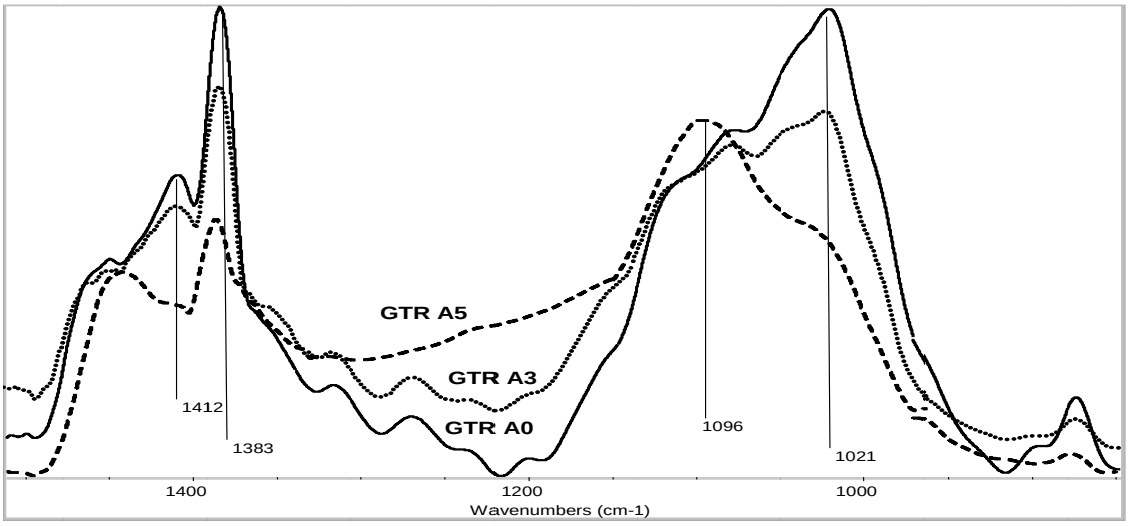


Figure 5a.- Evolution of 1500-850 cm^{-1} spectral area of samples A as a function of microwave exposure time (continuous line A0, dashed line A3 and dotted line A5)

The reduced values of the bands at 1452 cm^{-1}, 1412 cm^{-1} and 1383 cm^{-1} assigned to methylene $–CH_2$-, methine $–RC=CH_2$ and methyl $–CH_3$ groups respectively show different evolution: methylene group of the backbone remains constant meanwhile methine and methyl groups decrease significantly. The band at 1383 cm^{-1} assigned to methyl specially shows a big decrease of 42,5% (see Figure 5a). These bands are related to elastomeric components of the tyre and imply that the microwave treatment breaks the hydrogen bonds of the groups =CH of the main chain and those of the groups CH_3 present in the branches of the polymer, but the CH_2 of main chain remains practically constant. This behaviour is related to the difference in the -CH bond energy of these groups, which is 607 kJ/mol for $-CH_2$, higher than this value for =CH (around 418 kJ/mol) and $-CH_3$ (335 kJ/mol) [34]. The amount of energy provided by the treatment is enough to modify the methine and methyl groups but not enough to break the CH_2 (most important chemical group) of main chain of the elastomeric component. According to these data, the microwave treatment causes degradation of the elastomeric macromolecular chains of GTR, basically located on the branching and the double bonds.

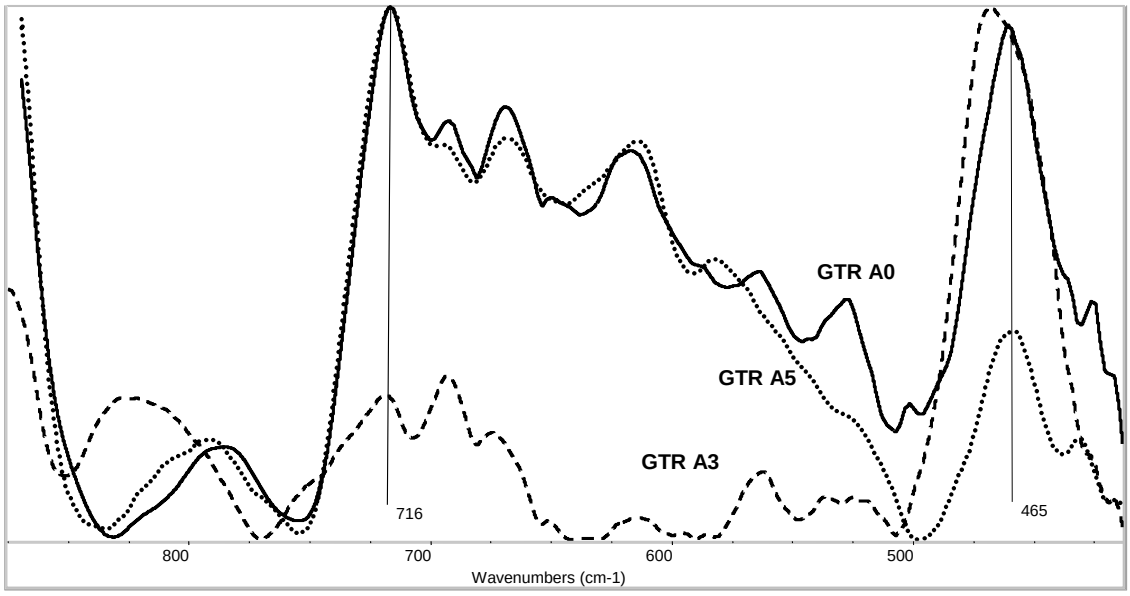


Figure 4b.- Evolution of 850-400 cm^{-1} spectral area of samples A as a function of microwave exposure time (continuous line A0, dashed line A3 and dotted line A5).

The band at 1021 cm^{-1} assigned to carbon black decreases notably (see figure 5a and figure 6) in all the samples as a function of exposure time (from 1.397 to 0691 that corresponds to 50%). This means that the treatments affect and reduce the amount of carbon black, due mostly at increase of temperature produced by the friction of the

polar components of GTR and also the induced dipoles of the elastomeric macromolecules, which results in oxidation, and CO_2 generation (*).

The evolution of the bands at 874 and 716 cm^{-1} assigned to -C=C-H follows the same trend observed in the bands at 1407 and 1383 cm^{-1} discussed above, confirming the previous results. The band at 603 cm^{-1} assigned to -C-S- and the bands at 524 and 465 cm^{-1} assigned both at S-S also decrease a lot. This means that the microwave process not only affects to the -C-H bonds of elastomeric components, but the microwave treatment also breaks the S-S bridge that were generated by the original vulcanization in tyre manufacturing process. The decrease of the reduced absorbance value at 524 cm^{-1} is from 0.966 to 0.745 and the decrease of band 466 cm^{-1} is from 1.948 to 1.273 (34.6%)

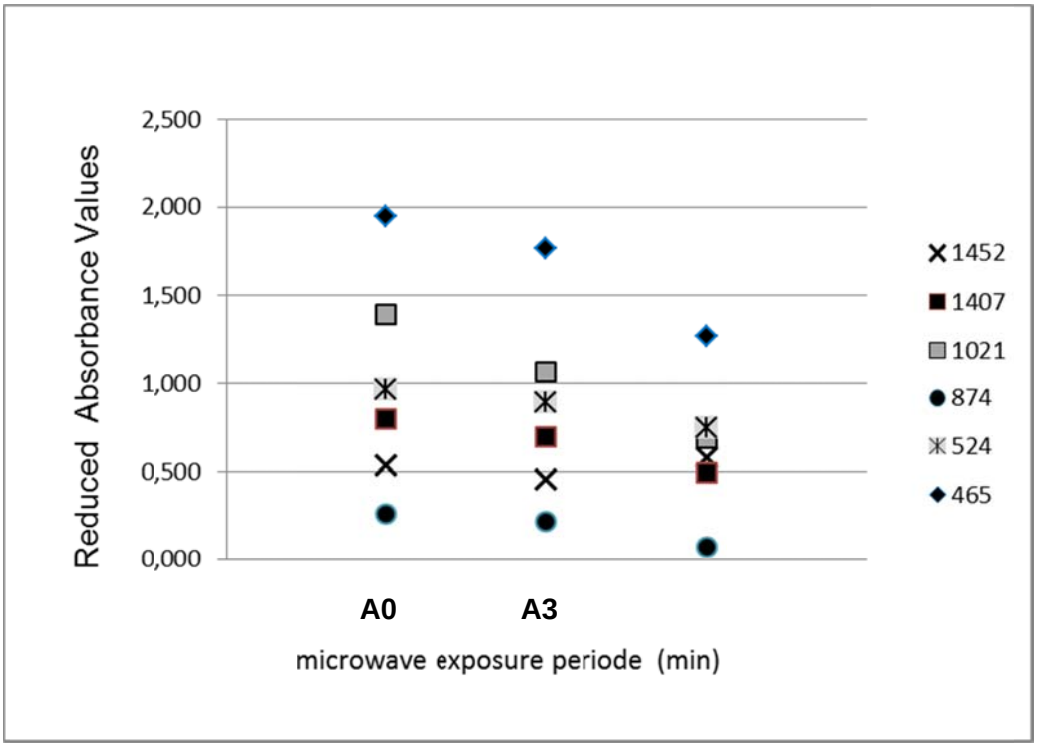


Figure 6.- Comparative values of reduced absorbance of A0, A3 and A5 samples

Figures 7a and 7b show the spectral evolution of different B GTR samples when they have been summited to microwave process. As appears at Figure 8, the behaviour of all B bands are similar at bands of samples A, except the bands assigned to S groups where the decrease is higher than the values of samples A (69,4% band at 524 cm^{-1} and 46,96% band at 466 cm^{-1} in front of 22,87% and 34,65% for samples A). There is a decrease of bands assigned to elastomeric components (methylene $–CH_2-$, methine $–RC=CH_2$ and methyl $–CH_3$ groups), and a decrease (41%) of the band at 1021 cm^{-1}

assigned to carbon black component, due also at the increase of temperature and generation of CO_2.

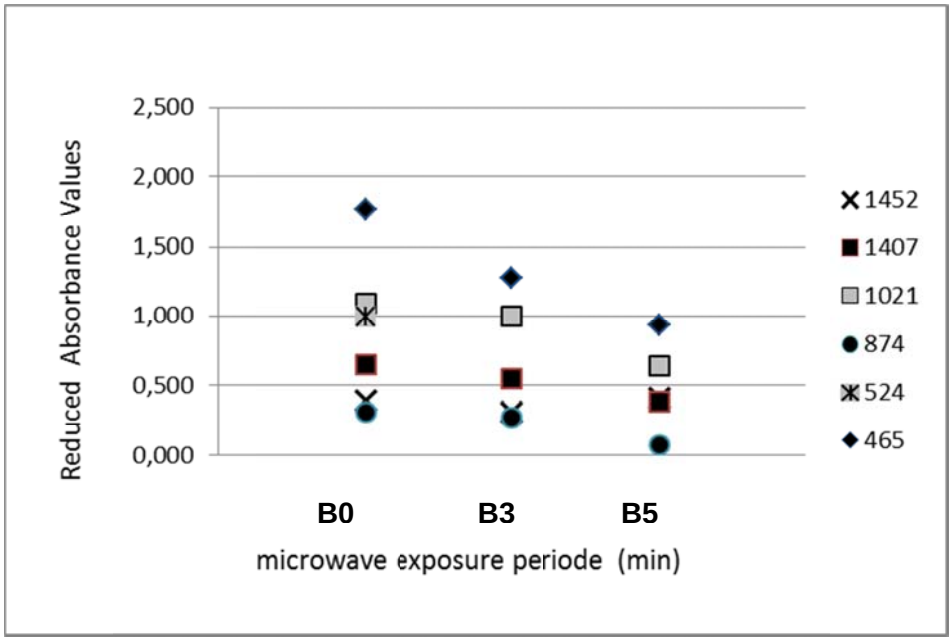


Figure 8.- Comparative values of reduced absorbance of B0, B3 and B5 samples

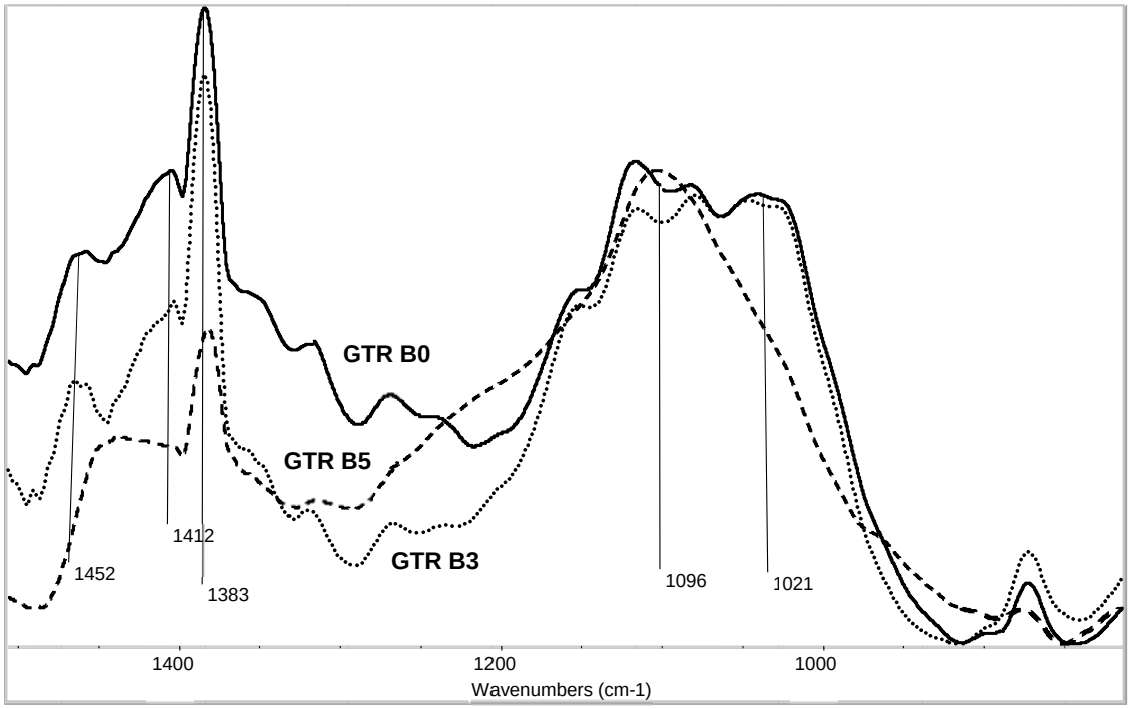


Figure 7a.- Evolution of 1500-850 cm^{-1} spectral area of samples B as a function of microwave exposure time (continuous line B0, dashed line B3 and dotted line B5).

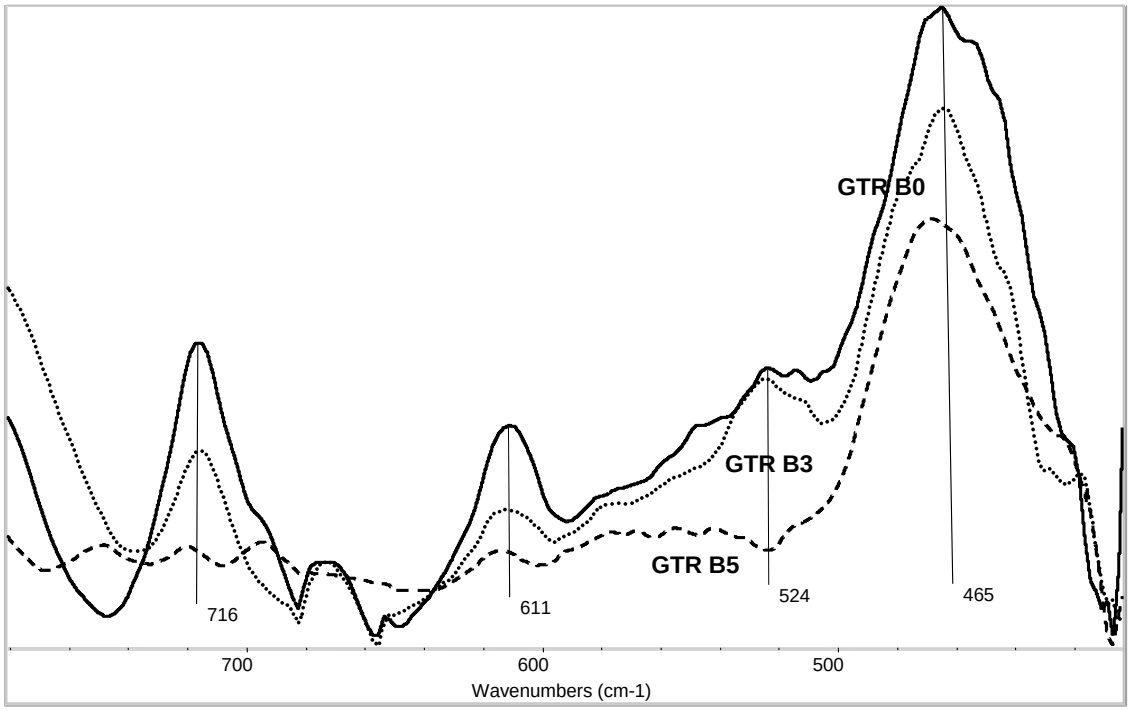


Figure 7b.- Evolution of 800-400 cm^{-1} spectral area of samples B as a function of microwave exposure time (continuous line B0, dashed line B3 and dotted line B5).

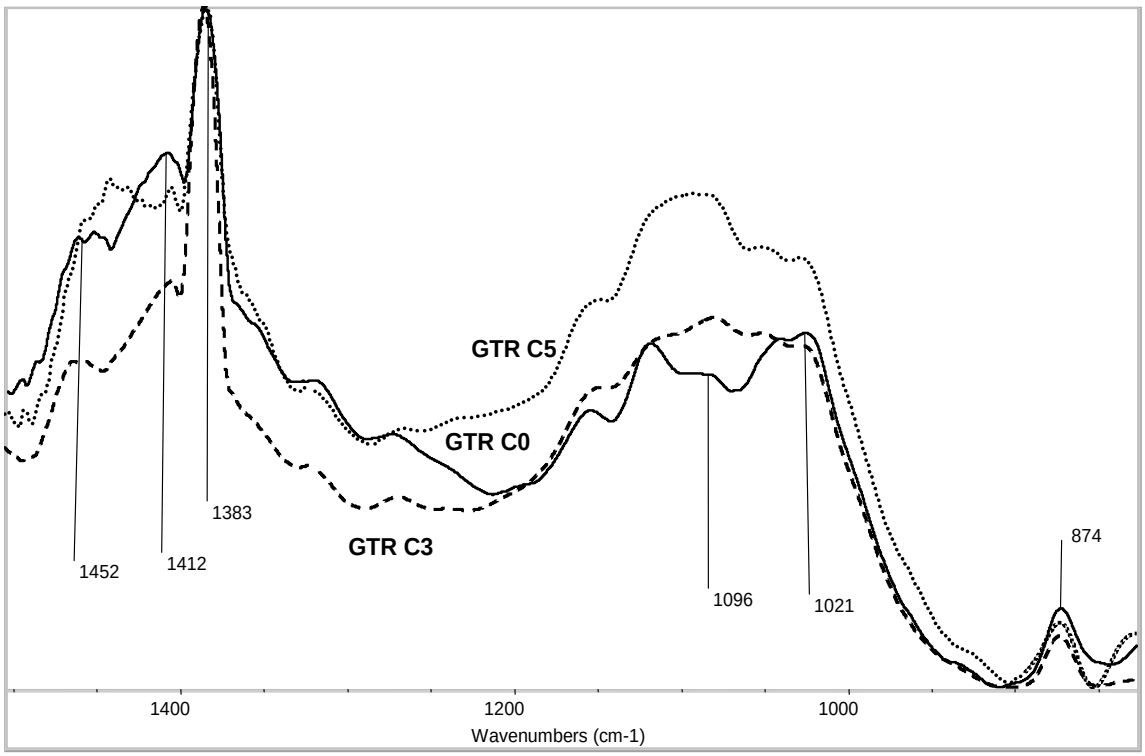


Figure 9a.- FTIR spectra of samples C as a function of microwave exposure time (continuous line C0, dashed line C3 and dotted line C5) spectral area of 1500-850 cm-1.

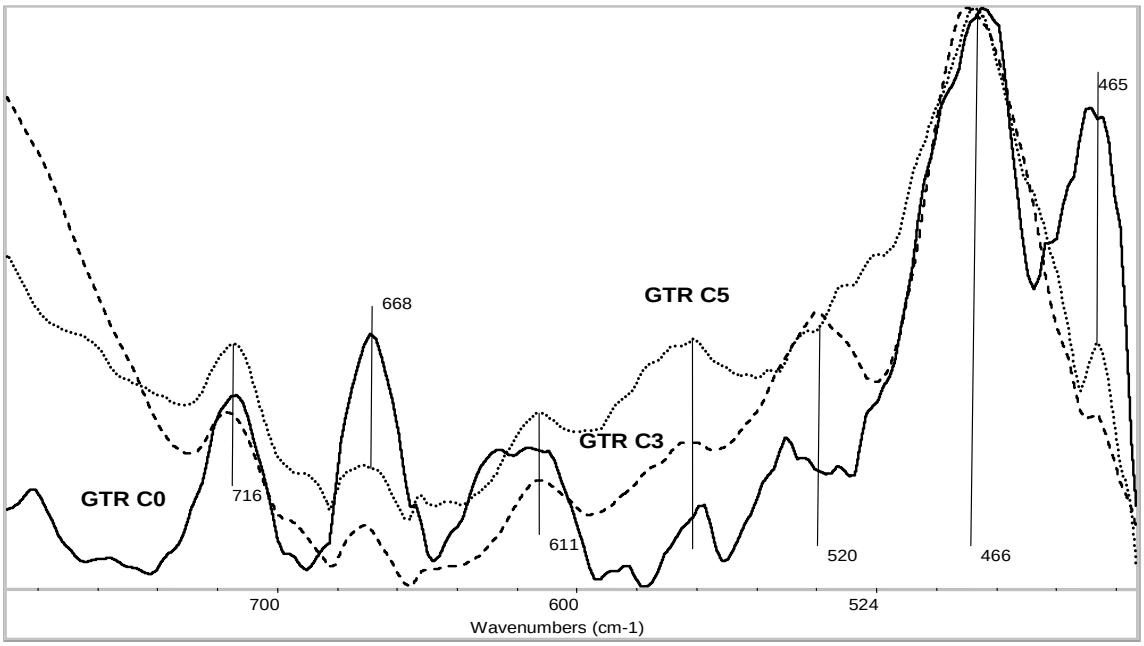


Figure 9b.- FTIR spectra of samples C as a function of microwave exposure time (continuous line C0, dashed line C3 and dotted line C5). spectral area of 800-500 cm-1.

Sample C, with the minimum content of ashes (5.25%) and maximum content of carbon black (36.89%) as presented in Table 1, shows a behaviour similar to other samples (A and B) when are treated with microwave process: decrease of bands assigned to elastomeric components, decrease of bands assigned to S-S linkage and decrease of carbon black content (Figures 8a, 8b and 9). However, the decrease of carbon black of the sample C is lower than samples A and B (34.7% in front of 50% and 41% respectively). The evolution of the band at 465 cm^{-1} follows also a similar behavior, where the decrease is higher in A and overall B respect C (34,65%, 46,96% and 25,3%).

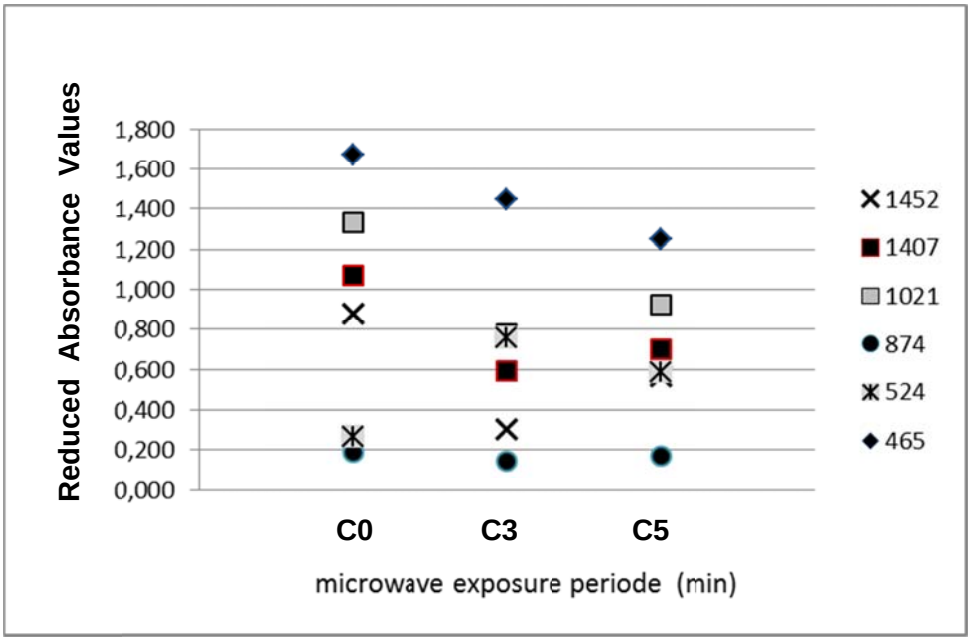


Figure 10.- Comparative values of reduced absorbance of C0, C3 and C5 samples

3.3.- Sol Fraction and Crosslinking density

The results of sol fraction determined by Soxhlet extraction, before and after devulcanization process, and crosslinking density obtained after samples were compacted are summarized at Table 3.

Table 3.- Values of different components for each GTR samples as a function of MW treatment process

Samples	Organic compound (*Char at 520ºC*) (%)	Ash content *(Carbon Black)* (%)	Crosslinking Density (mol/cm^3 x10^{-4})	Sol fraction (%)
A0	61,88 *(38,12)*	6,03 *(32,09)*	3,66	13,23
A3	63,15 *(36,85)*	6,56 *(29,29)*	4,83	18,48
A5	64,73 *(35,27)*	6,41 *(28,86)*	5,80	25,85
B0	55.48 *(44,52)*	9,56 *(34,96)*	4,40	13,95
B3	56,16 *(43,83)*	10,49 *(33,34)*	5,50	14,85
B5	58,05 *(41,94)*	10,62 *(31,32)*	8,82	29,26
C0	57,86 *(42,14)*	5,25 *(36,89)*	3,40	9,54
C3	58,33 *(41,66)*	5,39 *(36,26)*	3,39	10,05
C5	60,30 *(39,70)*	5,46 *(34,24)*	3,73	15,87

As described above, the compaction process was intended as a way to produce a solid sample, suitable for swelling test. However, the high temperature of the treatment (around 220ºC) produces a revulcanization and crosslinking due at the existence of residual sulphur in the samples. This process of revulcanization is reflected in the crosslinking data.

Samples A, B, and C, submitted to 0 (reference), 3 and 5 min of treatment present differences in crosslinking attributed to the effect of the microwave action. The crosslinking density increases as a function of the time of microwave treatment in all the samples. These results are a consequence of the process of revulcanization, cited above. The revulcanization produces the heating of the samples beyond that value producing the vulcanization of the residual sulphur that remains in the GTR, generating S-S linkages and increasing the crosslinking density as schematized at image 1.

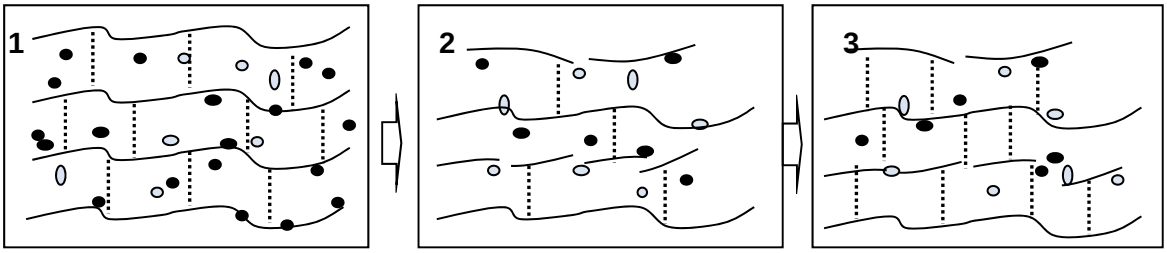


Image 1.- Evolution of devulcanized by MW and revulcanized process: 1) GTR previous to devulcanized, 2) MW process break some branches, few parts of backbone and S-S bridges of elastomeric components and decreasing the carbon black particles generating CO_2 and 3) vulcanization process of devulcanized GTR (black points represents Carbon Black, white points represent SiO_2, yellow lines represents sulphur bridges)

The cross linking density achieved after this revulcanization is higher in samples submitted to longer microwave treatment. For example Sample A (no microwave treatment) presents a crosslinking density of $3.66 \cdot 10^{-4}$ mol/cm^3 and the sample A5 $5.80 \cdot 10^{-4}$, an increase of about 60%. This increase appears also in samples B and in a lower degree at samples C. As showed in the FTIR study, the microwave treatment breaks the -S-S- bonds and the longer the treatment, the more possibilities of rebuilding these disulphur bridges by revulcanization. Returning to the values obtained by samples A, the difference between the values $3.66 \cdot 10^{-4}$ mol/cm^3 and the sample A5 $5.80 \cdot 10^{-4}$, could be attributed to the breaking of the disulphur bridges related to the microwave treatment. Sol fraction, which increases as a function of microwave treatment, follows the same trend and corroborates the FTIR results. Samples C show also lower increase than the others (9,54% to 15,87%), meaning that the devulcanization process by microwave in samples C is the lowest comparatively with A and B samples.

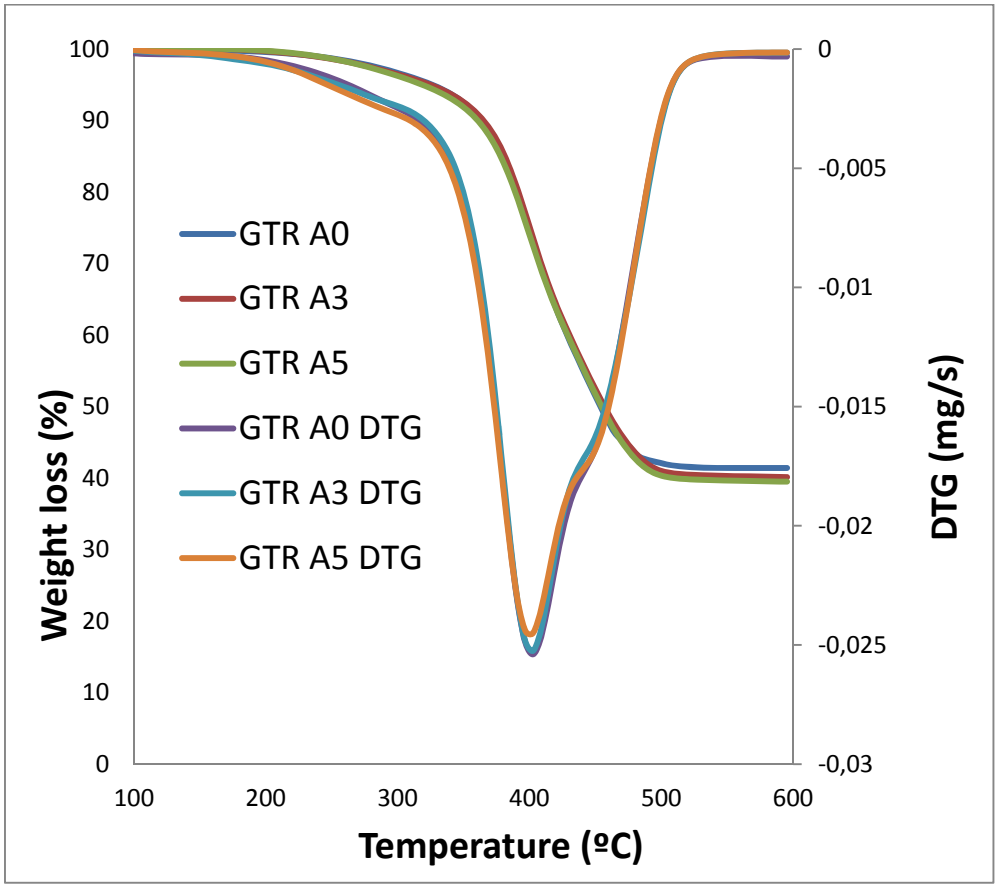
3.4.- Thermogravimetric analysis

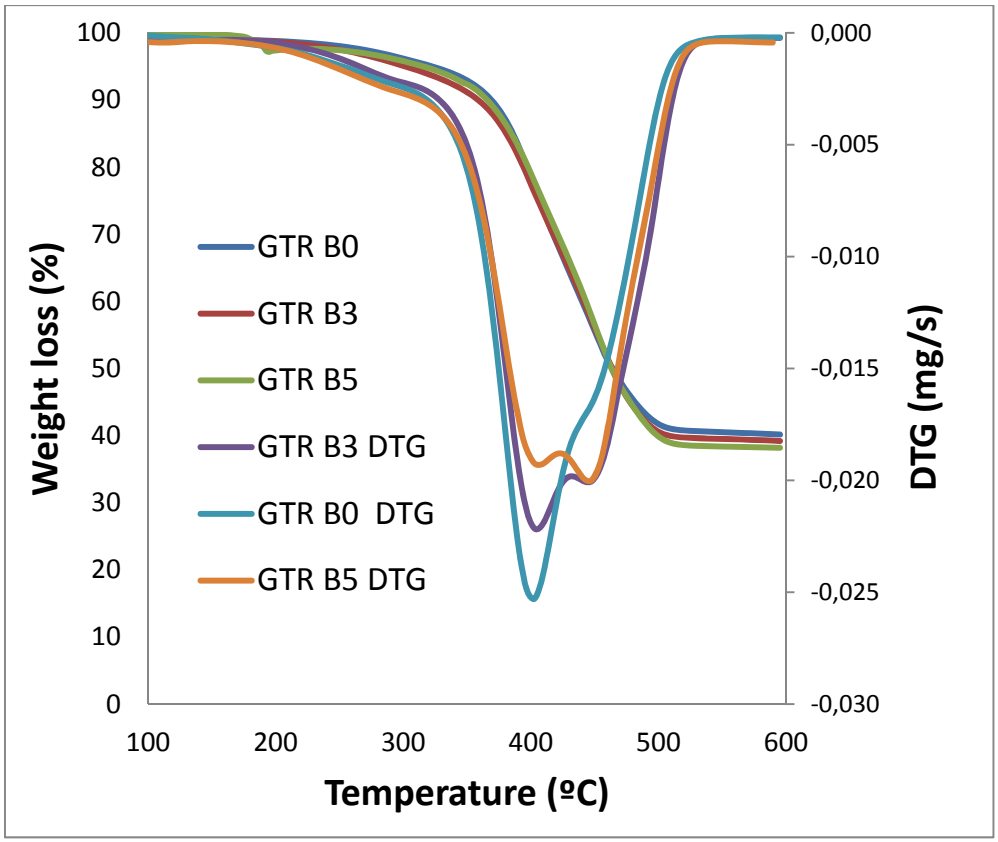
Table 4.- Parameter values from TGA and DTG curves for vulcanized and devulcanized samples

Samples	Data	Oils and Additives	Natural Rubber	Synthetic Rubber	Chart
	ΔT (ºC)	**50-320 ºC**	**320-410 ºC**	**410-520 ºC**	**>520ºC**
A0	**ΔT (ºC)**	4.7	36,33	20,85	38.12
	Δm (%)		401,34	445,4	
A3	**ΔT (ºC)**	4.3	35,98	22,87	36.85
	Δm (%)		401,71	442,98	
A5	**ΔT (ºC)**	4.1	35,77	22,86	35.27
	Δm (%)		402,27	439,15	
B0	**ΔT (ºC)**	4.8	31,19	19,49	44.52
	Δm (%)		402,66	436,76	
B3	**ΔT (ºC)**	4.6	28,95	22,62	43.83
	Δm (%)		407,98	442,17	
B5	**ΔT (ºC)**	4.0	26,29	27,77	41.94
	Δm (%)		408,16	442,17	
C0	**ΔT (ºC)**	5.1	34,10	18,66	42.14
	Δm (%)		387,34	443,56	
C3	**ΔT (ºC)**	3.9	35,32	19,12	41.66
	Δm (%)		399,65,	443,76	
C5	**ΔT (ºC)**	3.6	36,16	20,54	39.70
	Δm (%)		402,33	448,26	

The results of the thermogravimetric analysis of devulcanized samples A, B and C are presented in Figure 11a, 11b and 11c and summarized in Table 4 and its allow to determinate the parameter values of different samples. According to the results the microwave process reduces the weight of oils and additive in all the samples and also reduce natural rubber component in sample A and especially in sample B. The

devulcanization process by microwave heats the samples to its thermal decomposition temperature and then produces the volatilization of oils and decomposition of additive in all the samples and, the decomposition of natural rubber in samples A and mainly in samples B, while the weight loss of synthetic rubber increase slightly (20). The increase of the relative content of synthetic rubber, is due to the modification of the percentages of the components of the sample caused by the treatment. The absolute amount of synthetic rubber of the sample remains constant, but a decrease of the contents of carbon black or other component will be traduced in a higher proportion of synthetic rubber. Moreover there is a decrease of the amount of carbon black in all the samples caused by a thermo oxidation reaction with generation of CO_2. This decrease is similar in samples A and B and lower in samples C (10,06; 10,41 and 7,18% for samples A,B and C respectively. By submitting the samples to oxidation according to the conditions of the test of ashes content, it is possible to determine the weight corresponding to ash for each sample. The obtained values are summarized in second column of table 3, and ashes are constituted basically by SiO_2, as we have demonstrate previously.





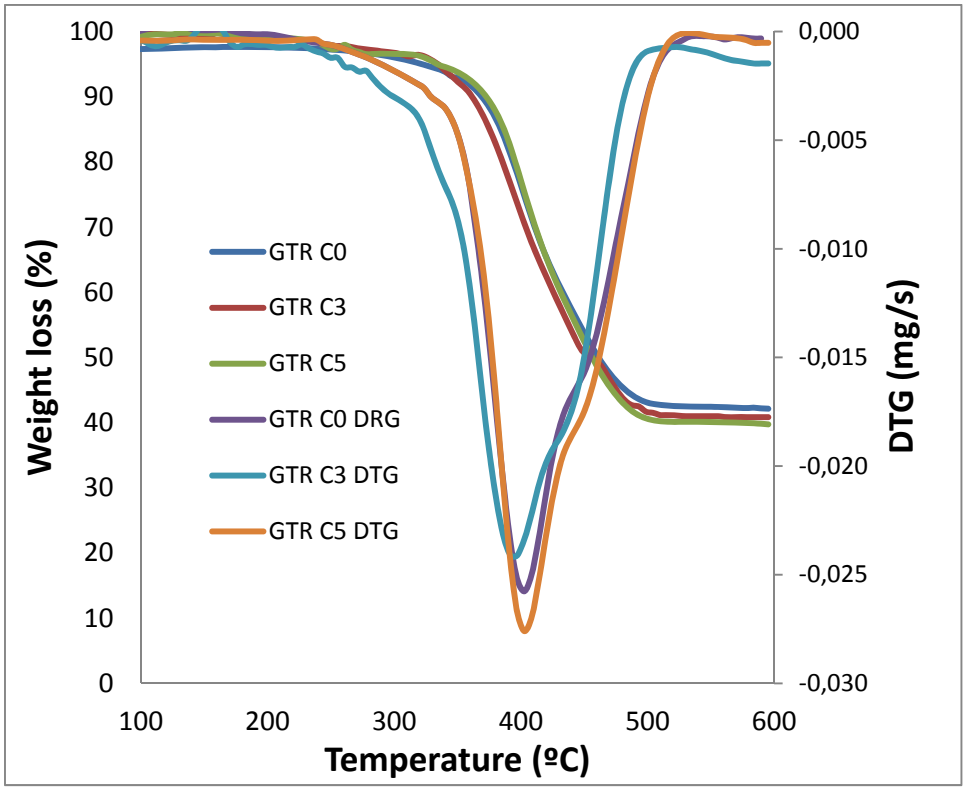


Figure 11a, 11b and 11c.- TGA and DTG curves obtained for the GTR samples before and after microwave treatment

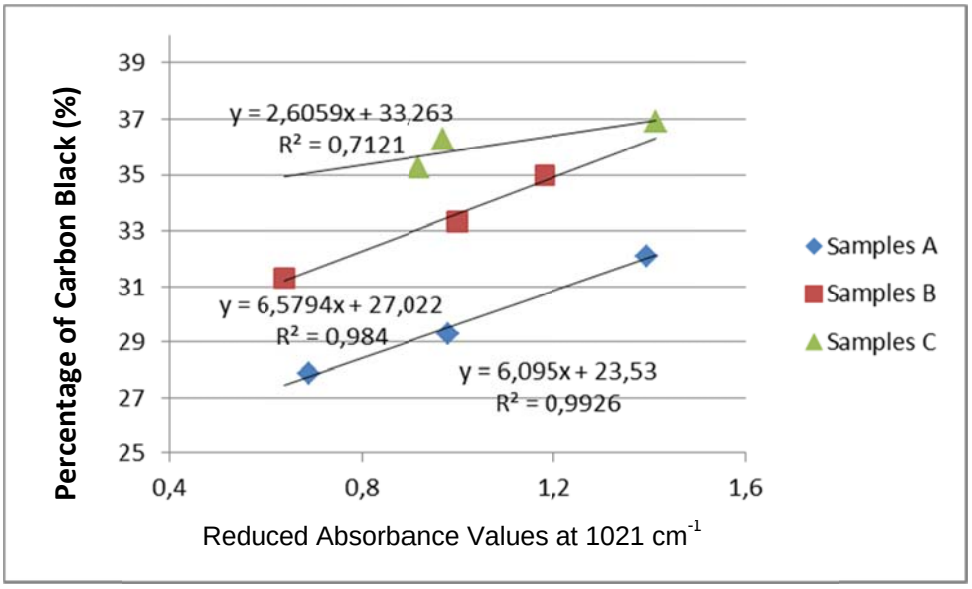


Figure 12.- Decrease of Carbon Black content as a function of MW process for A, B and C samples (maxim value of reduced absorbance at 0 min of MW treatment and minimum value at 5 min of MW treatment, in correspondence with the values of column 3 of table 3)

Figure 12 shows the existing correlation between percentages of carbon black (CB) obtained by TGA and reduced absorbance values of 1021 cm^{-1} obtained by FTIR. Furthermore the figure shows the decrease of carbon black content as a function of the time of microwave process for A, B and C samples. Samples B and A have the maximum decrease with a slope of 6,57 and 6,09 respectively and the slope for samples C is 2.6, that relates with the minimum decrease of carbon black (from 36,89 to 34%). Another interesting result is the correlation between the content of ashes and the degree of devulcanization process by microwave. When the values of content ashes (mainly SiO_2) increase the value of reduced absorbance assigned to S-S decrease. Samples with high content of SiO_2 such as B are easier to devulcanize than those with lower content of SiO_2 such as C. The decrease of reduced absorbance value of band at 466 cm-1 for sample B is 46,96%, for sample A is 34,65% and for

sample C (minimum percentage of ashes) is 25,3%. This means that SiO_2 acts as a catalysed in the devulcanization process by microwave.

3.5.- Scanning Electron Microscopy

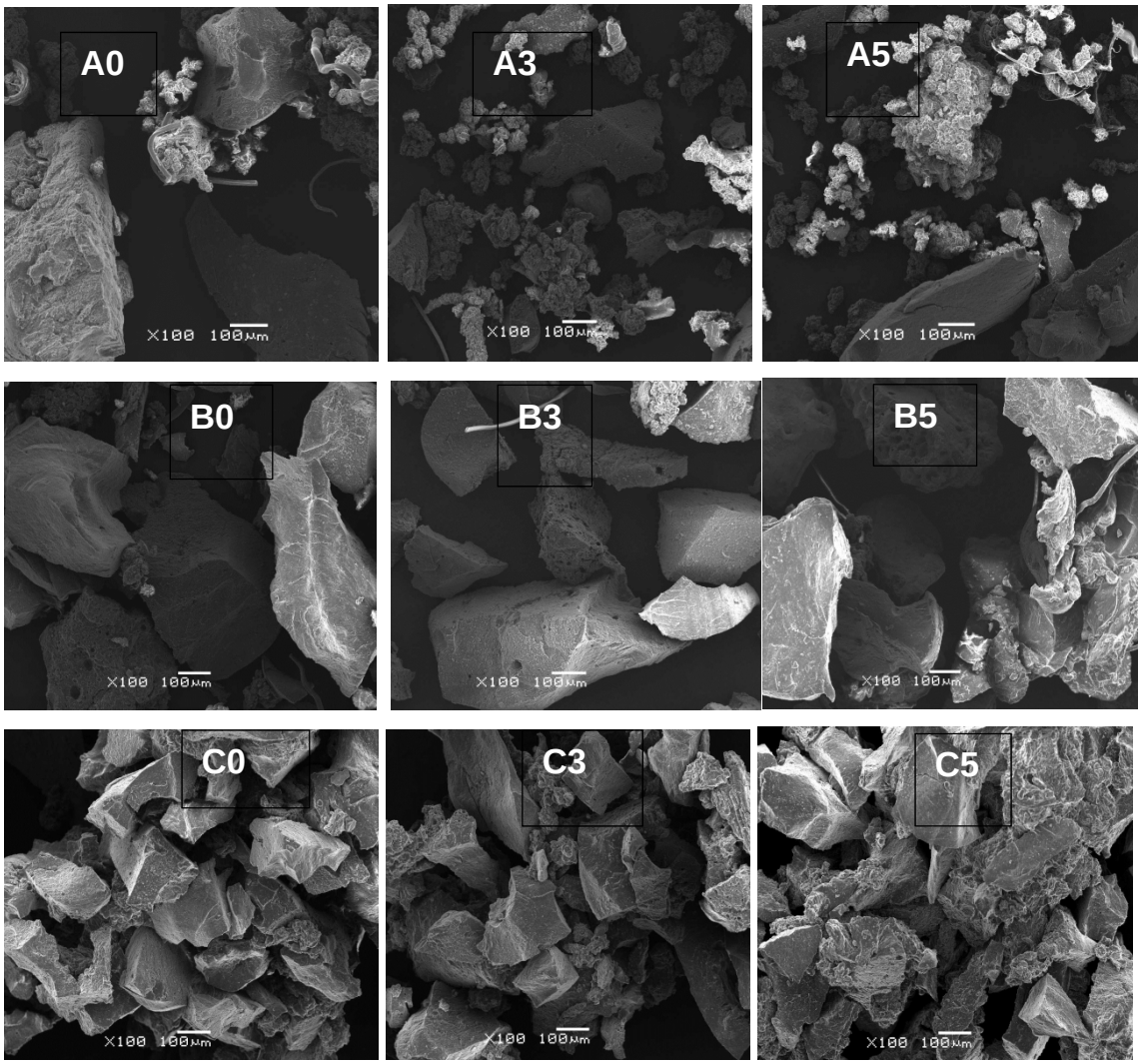


Figure 13.- SEM microphotography of GTR samples A,B and C before and after devulcanization.

The SEM pictures of figure 13 show the surface morphology, particle size and homogeneity of different samples before and after the devulcanization process by microwaves. The sample C shows particles more homogeneous and smaller than samples A and B. Most of the GTR particles present in sample C were smaller than 300 microns, while samples A and B have particles either bigger than 400 microns or smaller than 200 microns. The shapes of particles C appear more regular than particles A and B, but all of them show a polished surface. When the particles are submitted to the microwave process, the size of the particles remain more or less constant but the

surface aspect changes as a function of the exposure time. When the GTR particles are submitted at 5 minutes of microwave treatment the surface shows roughness and sometimes even holes and pores. The effect is particularly noticeable in the case of samples A. The degree of roughness achieved with this treatment is related to the ability of the microwave to degrade and remove part of different components of the GTR inside or on the surface of the particle. This includes volatilization of oils, decomposition of some elastomers (mainly natural rubber), additives and, as mentioned previously oxidation of carbon black in CO_2.

4.- Conclusion

Three different types of GTR and has been characterized by using FTIR. The results show that has each sample present different percentage of elastomeric matrix, carbon black and other inorganic components (basically constituted by SiO_2). Furthermore, these results have been corroborated by thermo gravimetric analysis, cross linking density and sol content value. FTIR spectroscopy was also used to analyse the devulcanization process obtained by microwave method, and results indicate that there is a decrease of black carbon caused by a thermo oxidation reaction with generation of CO_2. This decrease has also been assessed by TGA. The change in absorbance of the spectral bands show that the microwave treatment produce degradation of the elastomeric component with a decrease of structural groups located on the branching and double bonds (methylene and methine). Microwave not only affect the C-H bonds, but and more important produce a breaking of C-S groups and S-S bridges that were generated by the original vulcanization process. Finally, a correlation between the amount of SiO_2 present in the sample and the degree of devulcanization (breaking of S-S), obtained by the microwave treatment, has been observed. GTR samples with a high content of SiO_2 are easier devulcanized than samples with low content of SiO_2. This means that SiO_2 acts as a catalysed in the devulcanization process by microwave.

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