



HAL
open science

Devulcanization of waste tire rubber by microwaves

Fabiula Danielli Bastos de Sousa, Carlos Henrique Scurrachio, Guo-Hua Hu,
Sandrine Hoppe

► **To cite this version:**

Fabiula Danielli Bastos de Sousa, Carlos Henrique Scurrachio, Guo-Hua Hu, Sandrine Hoppe. Devulcanization of waste tire rubber by microwaves. 32th International Conference of the Polymer Processing Society (PPS-32), Jul 2016, Lyon, France. hal-02521194

HAL Id: hal-02521194

<https://hal.science/hal-02521194>

Submitted on 22 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DEVULCANIZATION OF WASTE TIRE RUBBER BY MICROWAVES

Fabiula D. B. de Sousa^{1,3*}, Carlos H. Scuracchio², Guo-Hua Hu³ and Sandrine Hoppe³

¹ Technology Development Center (CDTec), Universidade Federal de Pelotas (UFPel), Rua Félix da Cunha, 809, Pelotas, Centro, 96010-000, Brazil, RS

² Materials Engineering Department (DEMa), Universidade Federal da São Carlos (UFSCar), Washington Luís (SP-310), Km 235, São Carlos, SP, 13565-905, Brazil

³ CNRS - Université de Lorraine, Laboratoire Réactions et Génie des Procédés (LRGP), 1 Rue Grandville, Nancy, BP20451, 54001, France

* fabiuladesousa@gmail.com

ABSTRACT

The disposal of solid residues is an enormous problem, especially in the case of vulcanized rubbers like tires. The old practice of landfilling is out of use due to the rising land costs, environmental concerns, fire risks and the possibility of proliferation of mosquitoes and other disease-carrying vectors. Devulcanization is shown to be an effective technique for making rubbers to flow and to be remolded. However, this process not only breaks down sulphur linkages, but also creates new other bonds, modifying the structure of the material as a whole.

In order to help understand structural modifications of ground tire rubbers (GTR) as a result of devulcanization by microwaves, this work proposes an in-depth study of the chemical modifications, flow and thermo-oxidative degradation behavior as a function of the exposure time of the GTR to microwaves. An important conclusion is that the final temperature reached by the sample is the primary factor responsible for the success of the process. Depending on the final temperature of the sample, different types of sulphur bonds can be broken. During the treatment there is a balance between break down and formation of new bonds. It is therefore important to well control the process in order to avoid degradation of the main chains. Tires usually are composed of a mixture of synthetic and natural rubbers, wherein natural rubbers could be more degraded by microwaves. This rubber has a higher number of cross-links which makes it more prone to degradation.

Keywords: ground tire rubber, recycling, devulcanization, microwaves, structure, modification.

1 - Introduction

Each year, large amounts of elastomeric wastes from automobile industries, especially tires, are discarded and accumulated in inappropriate places, generating environmental, social and economic problems. With the increasing production of tires, these problems are getting worst year by year.

Tire rubber residues do not decompose easily due to its cross-linked structure (they are not biodegradable) and the presence of stabilizers and other additives [1, 2]. The time required for them to degrade can be very long. They cannot be reprocessed like thermoplastic materials [3]. Currently, tire recycling is even harder due to the addition of new components in the mixture and additives in order to increase their performance and service life, safety, noise reduction, comfort and well-being of passengers. Moreover, their actual composition is unknown because it is proprietary. Therefore, recycling of tire residues is a global problem and is a challenge for researchers. In general, the recycling of waste tires has important implications such as environmental protection, energy conservation, use as raw materials for reducing costs and improving the behavior of rubber compounds [4].

Reclaiming is considered to be the most attractive method of utilizing waste tire rubbers [5]. Devulcanization of waste rubbers, as a reclaiming method, is a technique in which energy is provided to the material in order to destroy, totally or partially, their three-dimensional networks formed during vulcanization [6]. It aims to restore the flow capacity of the vulcanized rubber by breaking down its cross-links. The known methods that use different routes to promote the devulcanization of rubbers include thermo-mechanical, thermo-chemical and mechano-chemical [7-12], physical (by microwaves [13-29] and ultrasound [30-38]), and biochemical [39-42].

Microwave devulcanization is currently one of the most promising techniques because of good properties of devulcanized material and the possibility of high productivity [27]. The process takes advantage of volumetric heating of the material by microwaves, promoting a more uniform heating than that could be achieved by traditional heating methods which depend on conduction and/or convection [17, 18, 43]. The process is of physical nature, i.e., it does not involve chemicals during the process. It is a type of thermal devulcanization or controlled degradation [44]), allowing the application of high amount of energy to the material in a short time, resulting in high productivity [17], being considered as an ecofriendly technology in present times [45]. However, since the process is a kind of controlled degradation, parameters involved must be well controlled in order to avoid degradation of the material.

Some studies reported the importance of the exposure time of the sample to the microwaves. In general, the longer is the exposure time, the less are its gel fraction and cross-linking density. Those

studies were conducted by using different kinds of rubbers, like polystyrene-butadiene copolymer (SBR) [19-22, 46], ethylene-propylene-diene rubber (EPDM) [14-16], natural rubber (NR) [27], butyl rubber (IIR) [47] and ground tire rubber (GTR) [17, 18, 28]. All of them proved that devulcanization by microwaves is an effective technique, capable of breaking the cross-links of different kinds of vulcanized rubbers.

On the other hand, there are a very few studies addressing the chemical and physical aspects of the GTR after the exposure to microwaves. In a recent work, Garcia et al. [28] proved that the long exposure of GTR to microwaves changed its structure, including changes in the morphology at a nanoscale. This work proposes an in-deep study of the modifications of the structure of the GTR by microwave induced devulcanization. Chemical modifications are evaluated by solvent extraction and swelling as well as attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The effects of the chemical modifications on the flow behavior and thermo-oxidative degradation of the GTR are analyzed by capillary rheology and thermogravimetry (TGA), respectively. The results show that the microwave induced devulcanization may completely modify the structures of the GTR and consequently its properties.

2 - Experimental

2.1 - Materials

Ground waste truck tire (GTR) separated from non-elastomeric components was kindly supplied by Pirelli Pneus Ltda.

2.2 - Devulcanization of GTR

GTR was devulcanized in a system comprised of a conventional microwave oven adapted with a motorized stirring system with a speed control, as shown in Figure 1. The whole devulcanization process was done by using the maximum power of the oven, i.e. 820W. About 65 g of the GTR sample was put into a 250 mL glass beaker with a stirring speed of 100 rpm. The time at which the material was exposed to microwaves ranged from 1 to 5, and 5.5 minutes. The temperature after devulcanization was measured by using a rod thermometer.

After the devulcanization process, all the samples were homogenized in a laboratory two roll mill. They were designated as GTRX, where X represents the time the GRT is exposed to the microwaves (in minutes) mentioned above. The gel fractions of the samples after Soxhlet extraction were also analyzed. They were designated as GTRXg.

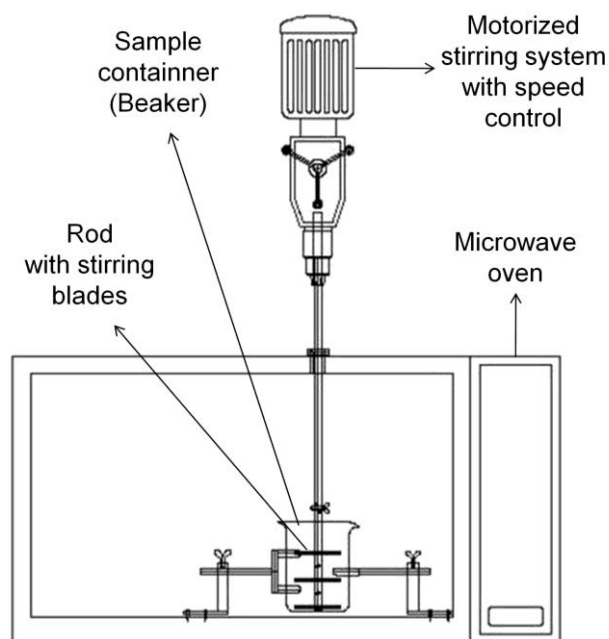


Figure 1 - Scheme of the devulcanization system used in this work.

2.5 - Characterization

The chemical modifications of the GTR after the different periods of exposure to microwaves were analyzed by solvent extraction and swelling as well as attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The details of each technique are given as follows.

The soluble (sol) and insoluble (gel) fractions of each GTRX sample, after the devulcanization process, were determined by extraction, according to ASTM 2765-11, using toluene as a solvent. About 1 g of GTRX was placed in a cage made of stainless steel blanket. They were completely immersed in boiling toluene for 24 h. About 1 g of Irganox 1010 of Dow Corning was added in to avoid degradation. After the extraction, the GTRXg sample was dried for 24h at 40°C to remove the solvent and its mass was measured. The percentages of the sol and gel fractions were calculated according to equations 1 and 2, respectively:

$$Extract (\%) = \frac{\text{Weight lost during extraction}}{\text{Weight of original specimen}} = \frac{(W_3 - W_4)}{(W_2 - W_1)} \quad \text{Equation 1}$$

where:

W_1 = weight of the pouch (sealed on three sides, one side open),

W_2 = weight of the specimen and the pouch (sealed on three sides, one side open),

W_3 = weight of the specimen and the cage, after being stapled shut,

W_4 = weight of the specimen and the cage after extraction and drying.

Gel content = 100 – Percent extract

Equation 2

After the extraction, the gel fractions of the GTRXg samples were pressed in a hydraulic press at 170°C using a circular mold (Ø25x1 mm) for 5 min. The pressed samples were immersed in 100 mL of toluene at controlled temperature (25°C) for 72 h, according to ASTM D6814-2. The excess of solvent on the surface of the samples was removed using an absorbent paper. The mass of the sample swelling was measured, and the cross-linking density was calculated by using the Flory-Rehner equation [48] (Equation 3):

$$v_e = \frac{-[\ln(1-V_r)+V_r+\chi_1 V_r^2]}{[V_1(V_r^{1/3}-V_r)/2]} \quad \text{Equation 3}$$

where: v_e is the cross-linking density (mol/cm³), V_r is the gel volume fraction in the swollen sample, V_1 is the solvent molar volume (106.2 cm³/mol [49]), and χ is the polymer-solvent interaction parameter (0.391 [50]).

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic analysis was performed on gel fraction samples, as well as on the samples before extraction, in order to obtain information about chemical modifications of the GTR as a result of the devulcanization process. The spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR with ATR accessory, from 4000 to 500 cm⁻¹ at a resolution of 4 cm⁻¹ over 20 scans at room temperature.

The melt-viscosity of the devulcanized materials was measured by using a high-pressure capillary rheometer Ceast SR20 (Instron) with a capillary die of 1 mm and an L/D ratio of 20. Measurements were performed at 180°C over a shear rate range between 100 and 5000 s⁻¹. The data were corrected according to Rabinowitsch corrections for non-Newtonian behavior. However, the Bagley correction was neglected due to the high L/D ratio.

A thermo gravimetric analyzer STA 449 F3 Jupiter device was used to carry out thermogravimetric analysis (TGA) was conducted to provide information about the thermo-oxidative degradation of the samples after the devulcanization. The analysis was performed on the extracted samples (gel fractions) and samples before the extraction. About 10 mg of each sample was heated from room temperature (25°C) to 550°C under nitrogen atmosphere to monitor the weight loss of oil and elastomers. At 550°C, the gas flow was changed to oxygen atmosphere and the samples were heated to 800°C in order to observe the carbon black degradation. Both ramps were heated at a rate of 10°C/min.

3 - Results

3.1 - Temperature measurements after devulcanization by microwaves

Table 1 shows the temperatures of the GTR samples just after their exposure to the microwaves. The temperature measurements were done immediately after the end of the treatment, by using a rod thermometer. The average temperature was calculated from the temperatures of 20 samples exposed to the same conditions of treatment.

The results show that the temperature increases with increasing exposure time of the sample to microwaves. , as also observed by other authors [17-22]. GTR is mainly composed of NR and SBR which are known as low microwave absorbers. On the other hand, GTR contains a high content of carbon black, a typical conductive filler [51, 52], which induces a phenomenon known as Maxwell-Wagner polarization [16, 27, 53].

Table 1 - Temperatures of the GTR samples immediately after their exposure to microwaves.

Sample	Temperature (°C)
GTR 1	72.6 (\pm 2.4)
GTR 2	114.7 (\pm 5.7)
GTR 3	145.8 (\pm 10.2)
GTR 4	160.3 (\pm 9.9)
GTR 5	200.4 (\pm 32.2)
GTR 5.5	219.5 (\pm 26.8)

In an earlier work [27], the influence of the carbon black content on the NR devulcanization by microwaves was studied. It was concluded that the factor that dictated the degree of devulcanization was the final temperature reached by the sample, which was dependent on the exposure time of the sample to microwaves and the amount of carbon black it contained. Another important observation was that the carbon black content allowing improving the devulcanization process by microwaves (in the case of NR) was as high as 45 phr. Hirayama and Saron [21] conducted a similar study using SBR. They also observed that the heating of the material during the exposure to microwaves was caused by the presence of carbon black, and that the final temperature achieved by the sample was influenced by the carbon black content in it. Garcia et al. [28] studied the change in morphology of GTR as a result of devulcanization by microwaves. They observed that the amount of carbon black in each of the phases of the material, i.e., NR and SBR, changed with the exposure time to microwaves. In samples exposed for 5 minutes, the carbon black was preferably located in the NR phase, while for a longer exposure time, it was preferably located in the SBR one.

According to Dubkov et al. [5], around 30% of a tire is composed of carbon black, which corresponds to around 40 phr of carbon black in the tire. Since carbon black is preferably in the NR phase, its content would be enough to devulcanize the sample, considering the fact that the minimum carbon black for improving the devulcanization process is 45 phr, as mentioned above. Another important observation is that if carbon black is preferably located in the NR phase, the probability for this phase to be overheated would be high. This observation is validated by TGA results, which will be presented later.

In summary, the degree of devulcanization of GTR increases with increasing exposure time to microwaves and increasing carbon black content in the GTR. The former provides more energy to the GTR and the later favors the transformation of the absorbed energy into heat. Both contribute to the heating and consequently the temperature rise of the GTR [27].

3.2 Gel content and cross-linking density

Table 2 shows the results of the gel content and cross-linking density of microwave treated GTR.

Table 2 - Gel contents and cross-linking densities of the GTR samples devulcanized by microwaves.

Sample	Gel content (%)	Cross-linking density ($U_e \times 10^{-5} \text{ mol.cm}^{-3}$)
GTR0	87.8	12.44
GTR1	88.0	NA
GTR2	87.9	12.65
GTR3	87.7	6.07
GTR4	86.3	5.52
GTR5	81.8	7.07
GTR5.5	73.8	6.07

NA: The cross-linking density of GTR1 was unavailable because it broke during the swelling in toluene.

The higher is the sol fraction, the more efficient is the devulcanization process [18, 54]. According to Table 2, the values of the gel fraction and cross-linking density of the samples decrease as the exposure time of the GTR to microwaves increases, confirming that the GTR was devulcanized by the action of microwaves [27]. The value of the gel fraction of GTR1 was slightly larger than that of

GTR0, due to experimental errors or possibly a real increase in the degree of vulcanization, as also observed by Hirayama and Saron [21].

According to some authors [21, 22], the degree of devulcanization (Equation 4) can be calculated by the difference in gel content between the devulcanized rubber (DR) and the vulcanized one (VR).

$$\text{Degree of devulcanization} = -(DR - VR) \quad \text{Equation 4}$$

Figure 2 shows the degree of devulcanization of the GTR as a function of the exposure time of the sample to the microwaves. The overall trend is that the degree of devulcanization became significant only when the time of exposure to the microwaves exceeded 3 min. It became significantly more important as the time of exposure to the microwaves further increased. GTRX1 and GTRX2 showed negative values for the degree of devulcanization, namely, the degree of formation of new bonds seems to be higher than the degree of breaking of cross-links during the time of exposure to microwaves. However, as discussed earlier, those values could also be within experimental errors.

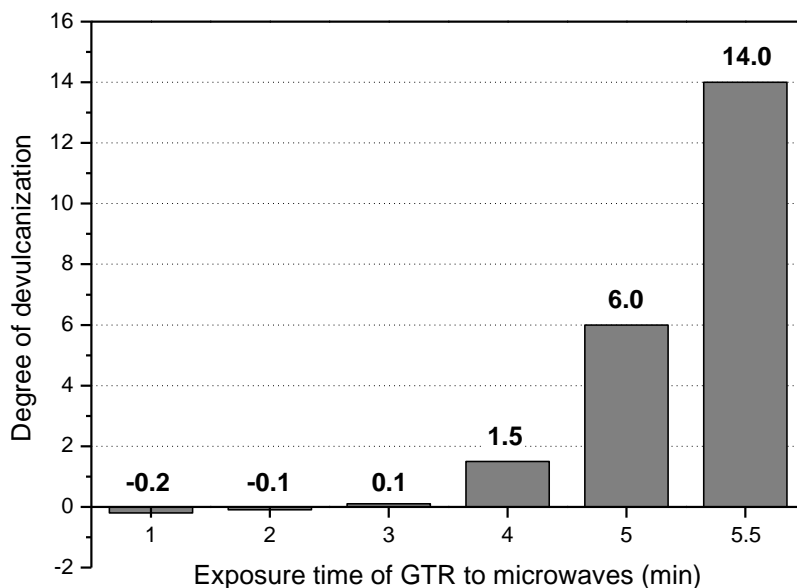


Figure 2 - Degree of devulcanization of the GTR as a function of its time of exposure to the microwaves.

Figure 3 shows the gel content, cross-linking density and average temperature of the GTR as a function of the time of exposure to microwaves. The overall trend is that the longer the exposure time of the sample to the microwaves, the higher is the final average temperature and the lower is the gel fraction, confirming the occurrence of devulcanization. In other words, the longer the time

of the microwave treatment, the higher the degree of devulcanization degree (as observed from Figure 2), due to the greater amount of energy absorbed by the GTR. As mentioned above, the final temperature reached by the sample is the primary factor responsible for the degree of devulcanization which depended on the time of exposure of the sample to microwaves and the amount of carbon black in the sample [27].

On the other hand, the cross-linking density reached a plateau after 3 minutes of microwaves treatment. As observed in Figure 2, in the samples which were exposed to the microwaves in a short time, the values of the degree of devulcanization were negative, showing that the number of new bonds formed likely exceeded that of bonds which were broken. Also the FTIR spectra to be shown later indicate that the exposure of GTR to microwaves changed its chemical structure. Some crosslinks were broken down and new ones were formed at the same time.

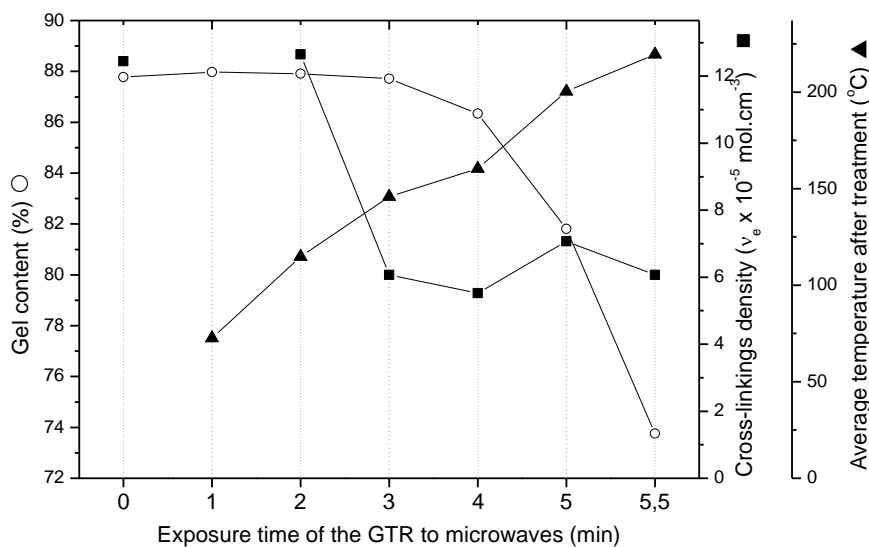


Figure 3 - Gel content, cross-linking density and average temperature after microwave treatment *versus* exposure time of the GTR to microwaves.

Figure 4 shows the gel content and cross-linking density of the GTRX as a function of its average temperature. There is an obvious correlation between them, suggesting that the temperature rise is responsible for the devulcanization [27], and that it is likely that there were no additional mechanisms of interaction between the microwaves and the GTR.

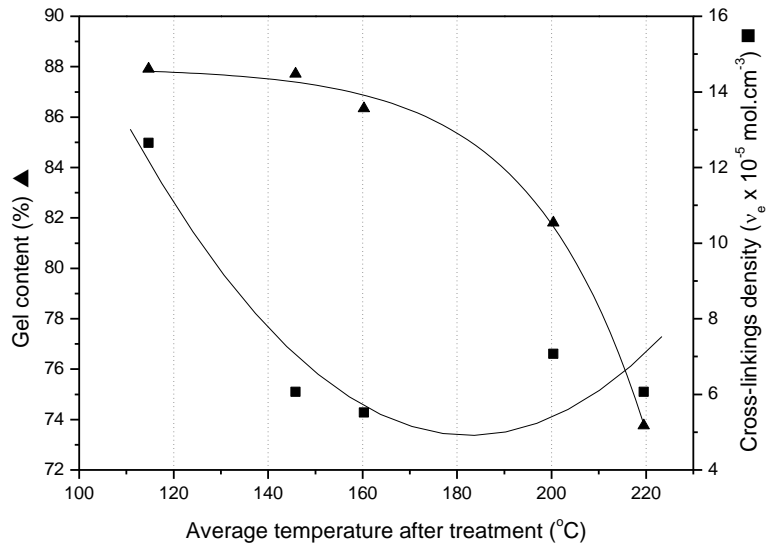
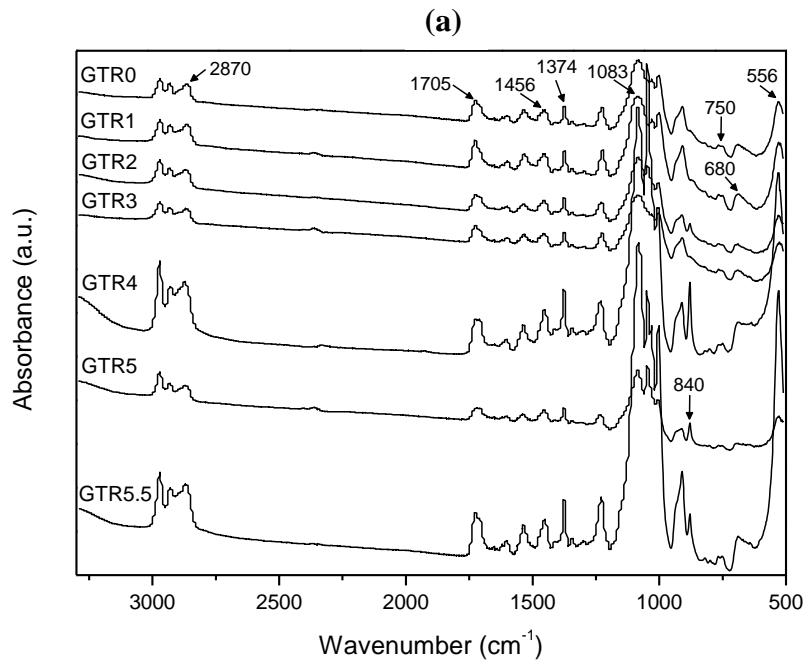


Figure 4 - Gel content and cross-linking density of the GTRX as a function of its average temperature.

3.3 – Characterization of chemical modification by ATR-FTIR

Figure 5 shows the FTIR spectra of the devulcanized GTRX before solvent extraction and of their gel fractions obtained under different times of exposure to microwaves.



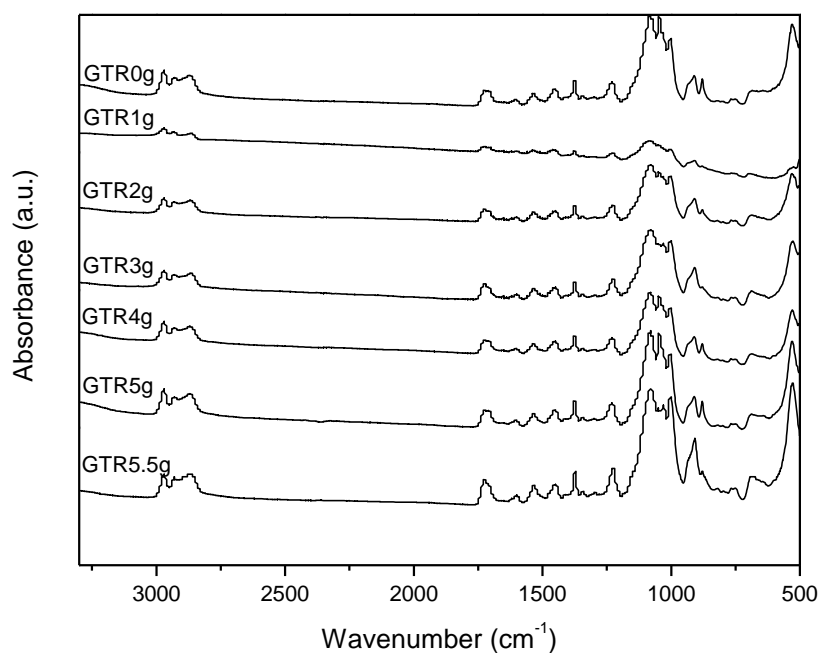


Figure 5 - FTIR spectra of (a) the devulcanized GTRX before solvent extraction and (b) their gel fractions.

The CH₂ bands (1475-1450 cm⁻¹) [20, 41, 54-56] refer to the vibrations of stretching and aromatic bending of the SBR, and the CH₃ bands (1390-1372 cm⁻¹) [20, 54, 57] are groups of the NR [58]. Those bands were observed in all the FTIR spectra, indicating that the GTR did not undergo significant degradation when exposed to the microwaves [20]. In other words, whatever the time of exposure of the GTR to microwaves, it did not degrade completely by the action of the microwaves.

A peak around 680 cm⁻¹ refers to the presence of C-CH₃ group which is characteristic of the deformational vibration of the styrene ring [54], which also confirms the presence of SBR in the composition of the GTR. A peak around 1705 cm⁻¹ is related to the lactone ring (C=O), confirming the presence of carbon black in the GTR [59]. It is important to mention that this peak is present in all samples, both in the devulcanized GTR and their gel fractions. This means that the carbon black present in the samples remains in the gel fractions after the extraction of the sol fraction by toluene. This result is in agreement with that of Dubkov et al. [5] who analyzed the sol and gel fractions of the GTR after devulcanization by nitrous oxide. According to them, the gel fraction contained that carbon black which was present in the initial GTR.

In GTR2, GTR5 and GTR5.5, there was a new peak around 840 cm⁻¹ which, according to Rooj et al. [57], refers to C=C links of the NR of the GTR. The formation of this new peak would have a positive effect since they are active sites for the revulcanization of the devulcanized GTR during subsequent processing [21]. However, this peak cannot be clearly observed in the gel fractions of the devulcanized samples (see Figure 5b), indicating a possible degradation of the main chains of

the NR of the GTR. According to Dubkov et al. [5] who performed Nuclear Magnetic Resonance (NMR) analysis on the sol fraction of the GTR, the signal of the internal double bonds ($>C=CH-$) in 1,4-units of polyisoprene indicates that the sol fraction contained isoprene oligomers.

In order to perform a quantitative analysis on the sulphur links, the peaks related S-S, C-S and S-O bonds (556 , 750 and 1083 cm^{-1} respectively) were normalized by dividing their heights by that of the absorbance peak at 2870 cm^{-1} which corresponds to the C-H bonds of the main chains of the NR of the GTR (Figure 6). From Figure 6, as the time of exposure to microwaves increased, the intensity ratio of the S-S (556 cm^{-1}) [57, 60] bond (especially for gel fraction samples) and that of the S-O (1083 cm^{-1}) bond [21] (especially for GTR5.5) slight increased, and that of the C-S bond (750 cm^{-1}) [21, 60] slightly decreased. The absorbance peaks of the S-S and C-S bonds were more obvious for samples with longer exposure times to microwaves (Figure 5), which indicates that the exposure to microwaves led to the disappearance of less stable cross-linking bonds [21].

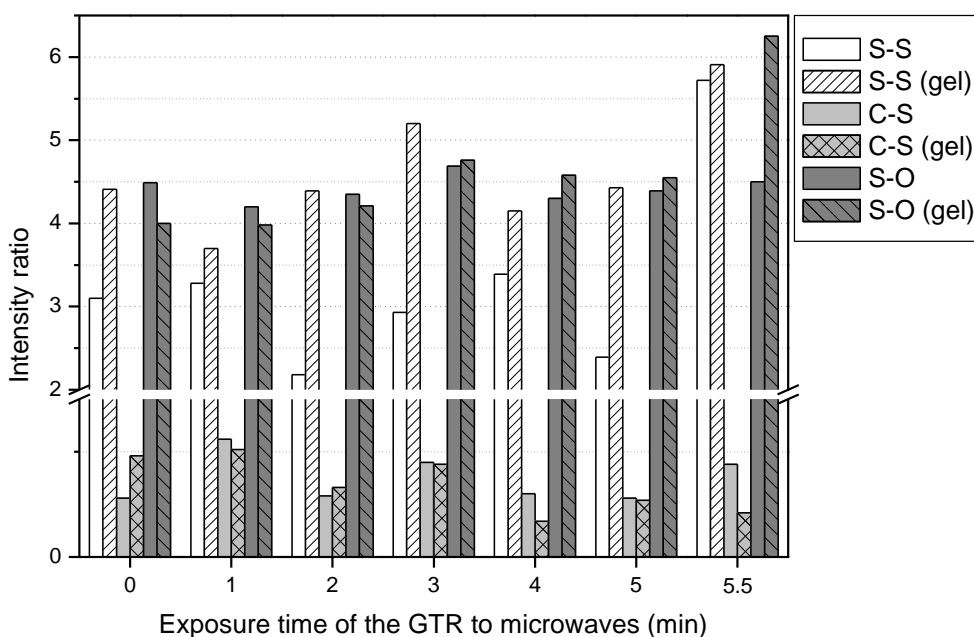


Figure 6 - Intensity ratio of chemical bonds as a function of exposure time of the GTR to microwaves.

Similar to the degree of devulcanization (Equation 4), the degree of bonding which is the difference in intensity ratio of a bond between a devulcanized GTR and the initial one (Equation 5), can be used to quantify the degree of chemical modifications of the GTR after the exposure to the microwaves.

$$\text{Degree of bonding} = IR_{\text{Sample}} - IR_{\text{GTR0}}$$

Equation 5

where IR_{Sample} and IR_{GTR0} are the intensity ratios of a devulcanized GTR and GTR0, respectively. In the case of the gel fractions, IR_{GTR0g} was used instead of IR_{GTR0} .

As some authors concluded [21, 47], heating as a result of the exposure to the microwaves may induce the breaking of sulphur bonds and the formation of new ones. The resulting degree of devulcanization is related to the balance between them. The swelling results showed that the longer the exposure time of the GTR to the microwaves, the less its cross-linking density. However, this is an overall result and does not imply that all different kinds of cross-links in the GTR were broken. This is clearly shown in Figure 7. The degree of bonding depends on the exposure time of the sample to the microwaves and the energy necessary to break each kind of sulphur bond.

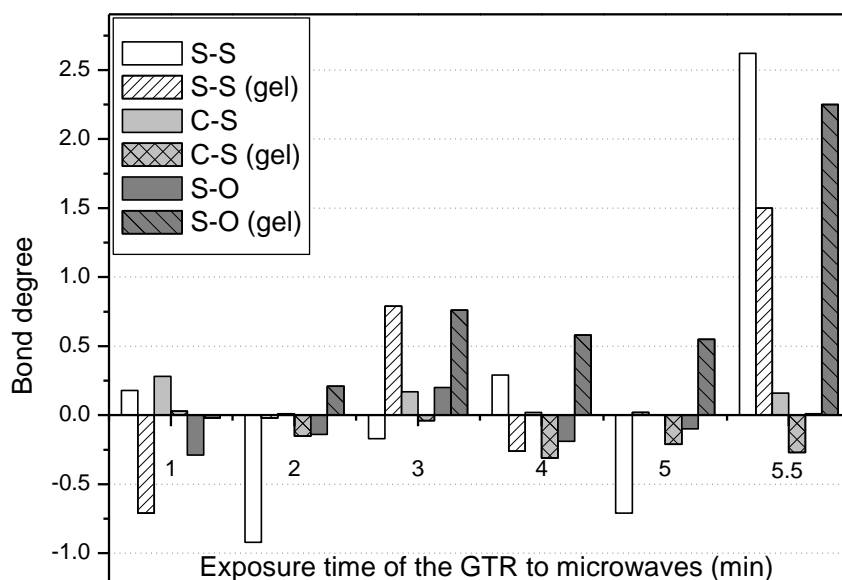


Figure 7 - Degree of bonding from intensity ratio values of the devulcanized samples.

The analysis of the gel fraction allows better understanding of chemical modifications of the GTR as a result of the exposure to the microwaves. In general, the formation of S-S bonds outperformed their breaking in samples which were less exposed to microwaves, whereas the breaking of C-S bonds outperformed their formation in those which were exposed to microwaves for longer times. In the latter cases, S-S and S-O bonds were formed. The formation of the new S-S bonds in the samples with longer exposure times to microwaves would likely result from the breaking of the C-S bonds. Another possibility would be the reaction of an excess of unconsumed sulphur in the first vulcanization process (free sulphur) which would tend to form polysulfide links. On the other hand, the formation of the S-O new bonds would result from rearrangement of the sulphur free radicals

from the devulcanization of the GTR in the presence of oxygen. Those results confirm that the GTR was indeed subjected to devulcanization upon exposure to microwaves and that different types of sulphur bonds could be broken and formed as a result of the microwave radiation, depending on the exposure time and consequently the final temperature of the sample. In the case of the IIR devulcanization by microwaves, disulfidic bonds were broken, releasing sulphurs which were transformed into new mono and polysulfidic bonds [47].

As discussed above, the degree of bonding depends on the exposure time of the sample to the microwaves or the temperature in the sample during the microwave treatment. Figure 8 shows the intensity ratios of S-S and C-S bonds as a function of the average temperature of the sample after the microwave treatment. Despite the scattering of the data, there seems to be an overall trend that the intensity ratio of the S-S bonds increases with increasing average temperature while that of the C-S bonds decreases. This seems to show that as the average temperature increased, more C-S bonds broke while new S-S bonds were formed. According to the literature [23, 57, 61], the energy necessary for breaking C-S, S-S and S_x bonds is 285, 268 and 251 kJ/mol, respectively, while it is 346 kJ/mol for C-C bonds. Therefore the breaking of the C-S bonds is more sensitive to temperature than that of the S-S bonds.

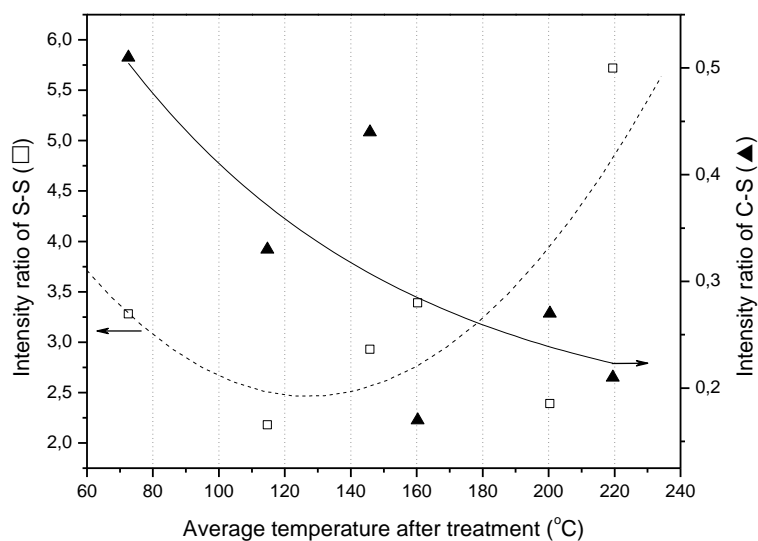


Figure 8 - Intensity ratios of the S-S and C-S bonds as a function of the average temperature after the microwave treatment for all devulcanized samples.

3.4 - Thermo-oxidative degradation of devulcanized GTR by TGA

According to Cui et al. [62], when using TGA, a problem associated with the identification of mixtures of rubbers is encountered. Fernández-Berridi et al. [63] reported that the first mass reduction under N₂ atmosphere between 200 and 300 °C (about 9% of the total mass) corresponded to the volatilization of the processing oil and/or other components of low boiling points. The next

mass reduction, still under N₂ atmosphere (about 37% of the total mass), corresponded to the NR, and the subsequent mass reduction corresponded to the SBR. Hassan et al. [54] also reported two mass reduction stages that occurred between 300 and 500°C and corresponded to the decomposition of elastomeric components of the GTR.

Figure 9 shows the TGA curves of the devulcanized GTR after different times of exposure to microwaves before and after Soxhlet extraction (gel fraction). According to Figure 9, the first mass loss (from room temperature to approximately 300°C) refers to the decomposition of processing oil and other organic polymeric additives [18], the second mass loss corresponds to the decomposition of NR (from approximately 300 to 400°C), the third one corresponds to the decomposition of the synthetic rubber (from 400 to 550°C) and the last one (from 550 to 800°C) refers to the decomposition of the carbon black, which occurs under oxidizing atmosphere.

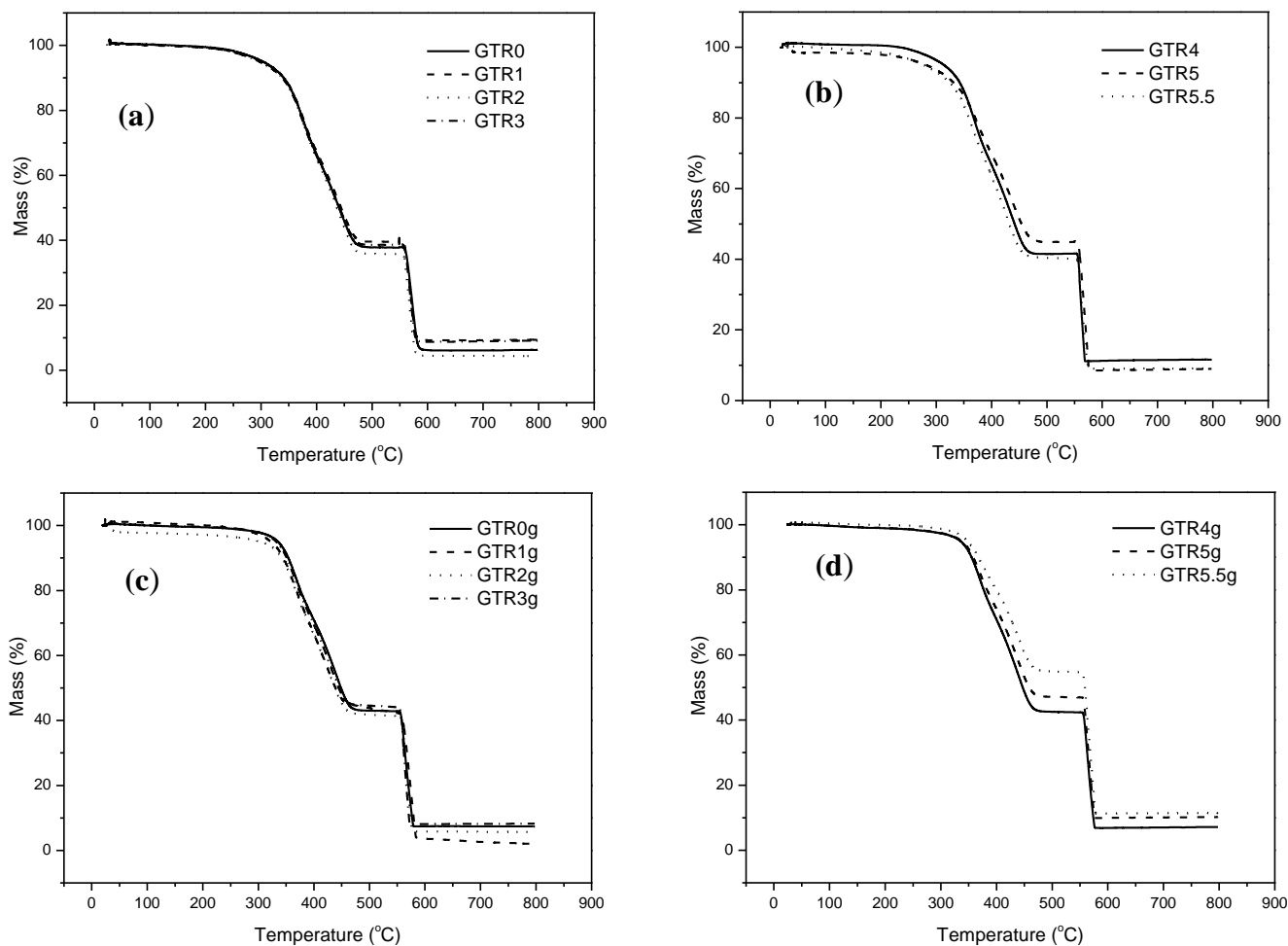


Figure 9 - TGA curves of the devulcanized GTR (a) and (b), and their gel fractions (c) and (d). The curves are separated for the sake of clarity.

Table 3 – Mass loss values (Δm) and the temperature ranges (ΔT) from TGA curves of the devulcanized samples (left column) and the gel fractions after Soxhlet extraction (right column).

Sample	Δm (%)	ΔT (°C)	Sample	Δm (%)	ΔT (°C)
GTR0	3,4	25-280	GTR0g	2,9	25-315
	30,8	280-400		25,4	315-400
	27,8	400-550		28,9	400-550
	31,9	550-800		35,4	550-800
	Residue: 6,1			Residue: 7,4	
GTR1	4,8	25-300	GTR1g	3,4	25-300
	28,5	300-400		25,8	300-390
	27,5	400-550		28,7	390-550
	30	550-800		38,2	550-800
	Residue: 9,2			Residue: 3,9	
GTR2	5	25-300	GTR2g	5	25-300
	30,3	300-400		24,4	300-400
	28,9	400-550		28,9	400-550
	31,5	550-800		35,8	550-800
	Residue: 4,3			Residue: 5,9	
GTR3	6,4	25-300	GTR3g	3	25-320
	29,3	300-400		22,5	320-390
	25,7	400-550		30,3	390-550
	30	550-800		36	550-800
	Residue: 8,6			Residue: 8,2	
GTR4	4,3	25-300	GTR4g	4,5	25-320
	27,8	300-400		23	320-400
	26,3	400-550		30,1	400-550
	30,4	550-800		35,4	550-800
	Residue: 11,2			Residue: 7	
GTR5	6,6	25-300	GTR5g	4,4	25-330
	22,9	300-400		19,6	330-400
	25,5	400-550		29,2	400-550
	36,4	550-800		36,8	550-800
	Residue: 8,6			Residue: 10	
GTR5.5	5,6	25-290	GTR5.5g	3,2	25-330
	26,7	290-390		16,2	330-400
	27,4	390-550		25,7	400-550
	31,3	550-800		43,6	550-800
	Residue: 9			Residue: 11,3	

Table 3 shows the mass loss values and the temperature ranges from TGA curves of the devulcanized samples (left column) and the gel fractions after Soxhlet extraction (right column).

The mass loss in percentage of each organic component of the GTR (processing oils and rubbers) tends to decrease as the exposure time of the GTR to microwaves increases, while the opposite trend is observed for the percentage of the carbon black.

In the case of the gel fractions, the same trends were observed. It turns out that the devulcanization process adopted acted more strongly in the breaking of the NR cross-links (mass loss from about 300 to 400°C). As found by Garcia et al. [28], carbon black is preferably located in the NR phase of the GTR. Recently, Hong et al. [45] analyzed devulcanized EPDM by microwaves and found that the devulcanization effect was limited to the surroundings of polar fillers due to the ion polarization effect. In our work, the NR phase was shown to be the most degraded, since there was no big variation in the synthetic rubber content in the GTR before and after the extraction (gel fraction).

Horikx's theory [64] is used to deepen the study of microwave devulcanization process and its consequences. It is commonly adopted to determine the relationship between the sol fraction after the degradation of the network structure of a rubber and relative decrease in the cross-linking density [65]. This theory investigates two limited cases:

(i) when main chain scission occurs, the relative decrease in the cross-linking density is calculated by using Equation 6:

$$1 - \frac{\vartheta_f}{\vartheta_i} = 1 - \frac{(1 - s_2^{1/2})^2}{(1 - s_1^{1/2})^2} \quad \text{Equation 6}$$

where ν_i and ν_f are the cross-linking densities before and after the devulcanization. S_1 and S_2 are the sol fractions before and after the devulcanization, respectively.

(ii) When cross-linking scission occurs, the relative decrease in the cross-linking density is calculated by using Equation 7:

$$1 - \frac{\vartheta_f}{\vartheta_i} = 1 - \frac{\gamma_f (1 - s_2^{1/2})^2}{\gamma_i (1 - s_1^{1/2})^2} \quad \text{Equation 7}$$

Where γ_i and γ_f are the cross-linking indexes which refer to the average number of cross-links per chain in the residual gel before and after the devulcanization, respectively.

Figure 10 shows Horikx's diagram for the devulcanized GTR. The NR phase of the GTR3, GTR4, GTR5 and GTR5.5 (Figure 10) also degraded. However, the SBR phase only showed scission of cross-links.

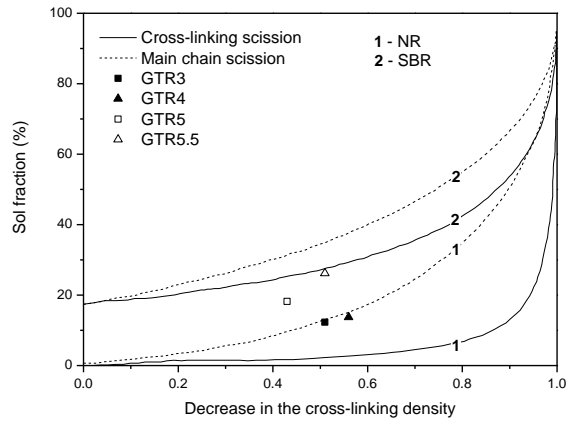


Figure 10 - Sol fractions of GTR3, GTR4, GTR5 and GTR5.5 *versus* relative decrease in the cross-linking density.

It can be concluded that the NR phase of the samples which were more exposed to the microwaves was subjected to random scission, i.e., the break of the cross-links and the main chains took place. However, their SBR phase was only subjected to the breaking of the cross-links, whatever the exposure time of the sample to the microwaves.

3.5 – Viscosity of devulcanized GTR by Capillary Rheometry

Figure 11 shows the viscosity of GTR5 and GTR5.5 as a function of shear rate at 180°C. Both samples were able to flow as a result of the devulcanization by microwaves. They showed a shear-thinning behavior [28]. The viscosities of both samples were very close. GTR4 was unable to flow. Therefore, GTR with an exposure time to the microwaves less than 4 minutes were not analyzed.

It is worthy to point out the texture of the devulcanized samples after remixing in a two-roll mill. Figure 12 shows the appearances of GTR0, GTR5 and GTR5.5. The difference between GTR5 and GTR5.5 is likely due to a higher relative amount of carbon black and a smaller amount of processing oil in GTR5.5, as shown in the TGA results (Table 3).

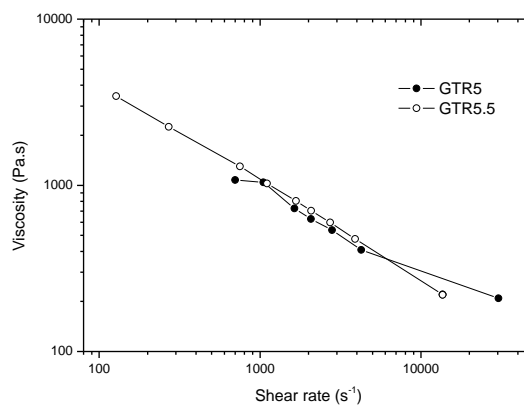


Figure 11 - Viscosity *versus* shear rate for GTR5 and GTR5.5 samples.



Figure 12 - Photos of GTR0, GTR5 and GTR5.5 after remixing in a two roll mill.

Based on all the results of this work, Figure 13 proposes a scheme of structural changes in C-S and S-S bonds which may occur in the GTR as a function of exposure time to microwaves. The break of each type of sulphur bond depends on the temperature of the GTR during the devulcanization process. This is because it requires a specific amount of energy to break. Also bonds are broken and formed at the same time. However, the degree of devulcanization characterized by the sol fraction increases with increasing exposure time of the GTR to the microwaves.

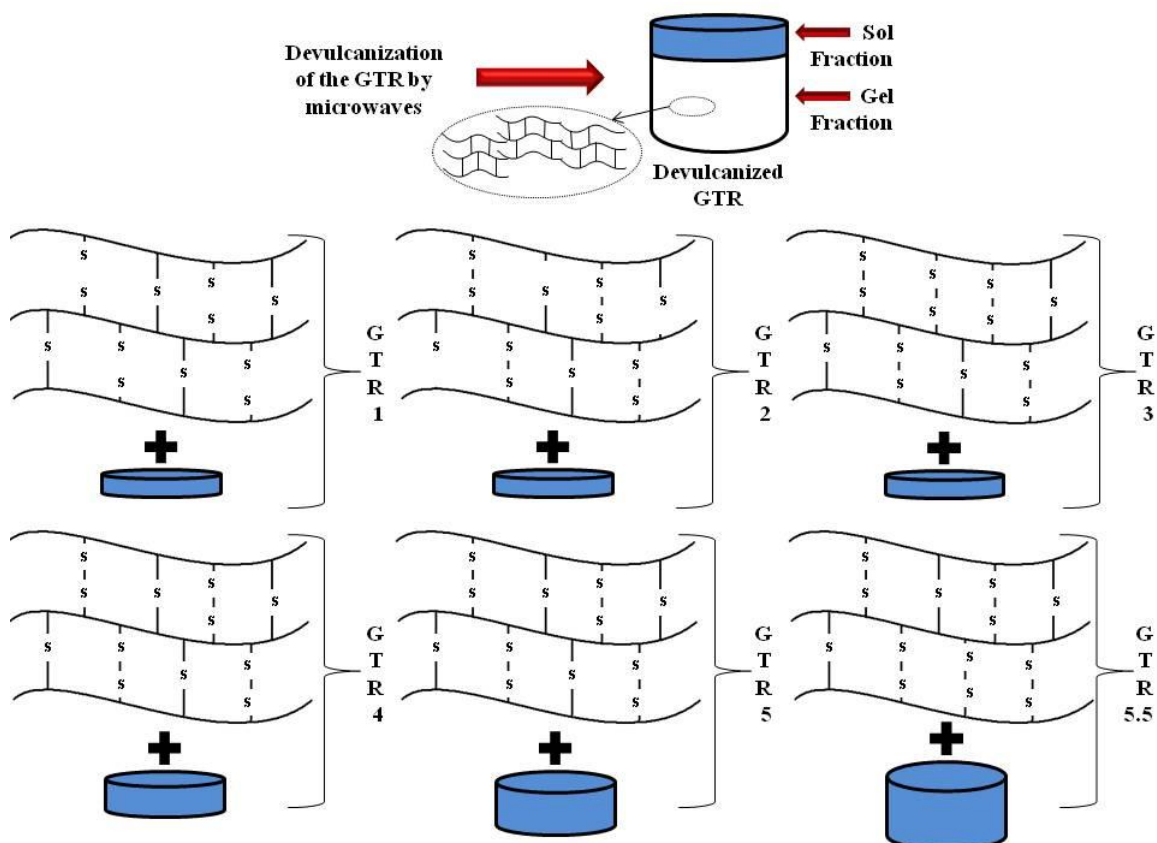


Figure 11 – Structural (C-S and S-S bonds) changes and gel fraction as a function of the exposure time to the microwaves.

4 - Conclusions

This work presented an in-deep analysis of the devulcanized and gel fraction samples, allowing for the identification of the main chemical transformations which occurred during the exposure time of GTR to the microwaves.

According to the results of solvent extraction and swelling, the longer the exposure time of GTR to microwaves, the higher is degree of devulcanization due to the decrease of cross-links. In other words, the higher the amount of energy absorbed during the microwave treatment due to the presence of carbon black, the higher the temperature of the GTR, and the higher the degree of devulcanization. The temperature of the GTR is the primary factor responsible for the devulcanization.

Sulphur bonds can be broken or formed during the microwave treatment. In the samples whose exposure to microwaves is long, S-O new bonds are formed as a result of the rearrangement of the sulphur free radicals from the devulcanization of the TGR in the presence of oxygen.

Sufficient break of the sulphur bonds by devulcanization, GTR5 and GTR5.5 can flow and consequently can be remolded and revulcanized. The NR phase of the GTR is more degraded than the SBR phase.

Acknowledgements

The authors would like to thank Pirelli Pneus for the material donation, Capes, FAPESP (process number 2010/15799-6) and CNPq (process number 201891/2011-5) for the financial support.

References

- [1] B. Wu, M.H. Zhou, Recycling of waste tyre rubber into oil absorbent, *Waste Management* 29(1) (2009) 355-359.
- [2] N. Roche, M.N. Ichchou, M. Salvia, A. Chettah, Dynamic Damping Properties of Thermoplastic Elastomers Based on EVA and Recycled Ground Tire Rubber, *Journal of Elastomers and Plastics* 43(4) (2011) 317-340.
- [3] K. Masaki, S.I. Ohkawara, T. Hirano, M. Seno, T. Sato, Devulcanization of nitrile butadiene rubber in nitrobenzene, *Journal of Applied Polymer Science* 91(5) (2004) 3342-3353.
- [4] J. Scheirs, Rubber tyre recycling, in: J. Scheirs (Ed.), *Polymer recycling: science, technology and applications*, Wiley, London, 1998, pp. 125-137.
- [5] K.A. Dubkov, S.V. Semikolenov, D.P. Ivanov, D.E. Babushkin, V.D. Voronchikhin, Scrap tyre rubber depolymerization by nitrous oxide: products and mechanism of reaction, *Iranian Polymer Journal* 23(11) (2014) 881-890.
- [6] X.M. Sun, A.I. Isayev, Continuous ultrasonic devulcanization comparison of carbon black filled synthetic isoprene and natural rubbers, *Rubber Chemistry and Technology* 81(1) (2008) 19-46.
- [7] X.X. Zhang, Z.X. Lu, D. Tian, H. Li, C.H. Lu, Mechanochemical devulcanization of ground tire rubber and its application in acoustic absorbent polyurethane foamed composites, *Journal of Applied Polymer Science* 127(5) (2013) 4006-4014.
- [8] D. De, D. De, Processing and Material Characteristics of a Reclaimed Ground Rubber Tire Reinforced Styrene Butadiene Rubber, *Materials Sciences and Applications* 2 (2011) 486-496.

- [9] B. Maridass, B.R. Gupta, Performance optimization of a counter rotating twin screw extruder for recycling natural rubber vulcanizates using response surface methodology, *Polymer Testing* 23(4) (2004) 377-385.
- [10] B. Maridass, B.R. Gupta, Process Optimization of Devulcanization of Waste Rubber Powder From Syringe Stoppers by Twin Screw Extruder Using Response Surface Methodology, *Polymer Composites* 29(12) (2008) 1350-1357.
- [11] H. Yazdani, M. Karrabi, I. Ghasmi, H. Azizi, G.R. Bakhshandeh, Devulcanization of Waste Tires Using a Twin-Screw Extruder: The Effects of Processing Conditions, *Journal of Vinyl & Additive Technology* 17(1) (2011) 64-69.
- [12] K. Formela, M. Klein, X. Colom, M.R. Saeb, Investigating the combined impact of plasticizer and shear force on the efficiency of low temperature reclaiming of ground tire rubber (GTR) Polymer degradation and stability 125 (2016) 1-11.
- [13] A. Bani, G. Polacco, G. Gallone, Microwave-Induced Devulcanization for Poly(ethylene-propylene-diene) Recycling, *Journal of Applied Polymer Science* 120(5) (2011) 2904-2911.
- [14] V. Pistor, A.J. Zattera, Degradation kinetics of ethylene propylene diene terpolymer residues devulcanized by microwaves, *Journal of Elastomers and Plastics* 44 (2012) 1-15.
- [15] V. Pistor, C.H. Scuracchio, P.J. Oliveira, R. Fiorio, A.J. Zattera, Devulcanization of Ethylene-Propylene-Diene Polymer Residues by Microwave-Influence of the Presence of Paraffinic Oil, *Polymer Engineering and Science* 51(4) (2011) 697-703.
- [16] V. Pistor, F.G. Ornaghi, R. Fiorio, A.J. Zattera, P.J. Oliveira, C.H. Scuracchio, Devulcanization of Ethylene-Propylene-Diene Polymer Residues (EPDM-r) by Microwaves, *Polimeros-Ciencia E Tecnologia* 20(3) (2010) 165-169.
- [17] C.H. Scuracchio, D.A. Waki, R.E.S. Bretas, Caracterização Térmica e Reológica de Borracha de Pneu Desvulcanizada por Microondas, *Polímeros: Ciência e Tecnologia* 16(1) (2006) 46-52.
- [18] C.H. Scuracchio, D.A. Waki, M. da Silva, Thermal analysis of ground tire rubber devulcanized by microwaves, *Journal of Thermal Analysis and Calorimetry* 87(3) (2007) 893-897.
- [19] A. Zanchet, L.N. Carli, M. Giovanela, J.S. Crespo, C.H. Scuracchio, R.C.R. Nunes, Characterization of Microwave-Devulcanized Composites of Ground SBR Scraps, *Journal of Elastomers and Plastics* 41(6) (2009) 497-507.
- [20] A. Zanchet, L.N. Carli, M. Giovanela, R.N. Brandalise, J.S. Crespo, Use of styrene butadiene rubber industrial waste devulcanized by microwave in rubber composites for automotive application, *Materials & Design* 39 (2012) 437-443.
- [21] D. Hirayama, C. Saron, Chemical Modifications in Styrene-Butadiene Rubber after Microwave Devulcanization, *Industrial & Engineering Chemistry Research* 51(10) (2012) 3975-3980.
- [22] G.D. Paulo, D. Hirayama, C. Saron, Microwave devulcanization of waste rubber with inorganic salts and nitric acid, 2012, pp. 1072-1075.
- [23] T. Kleps, M. Piaskiewicz, W. Parasiewicz, The use of thermogravimetry in the study of rubber devulcanization, *Journal of Thermal Analysis and Calorimetry* 60(1) (2000) 271-277.
- [24] L. Landini, S.G. de Araujo, A.B. Lugao, H. Wiebeck, Preliminary analysis to BIIR recovery using the microwave process, *European Polymer Journal* 43(6) (2007) 2725-2731.
- [25] F.D.B. de Sousa, J.R. Gouveia, P.M.F. de Camargo, S.E. Vidotti, C.H. Scuracchio, L.G. Amurin, T.S. Valera, Blends of ground tire rubber devulcanized by microwaves/HDPE - Part A: influence of devulcanization process, *Polimeros-Ciencia E Tecnologia* 25(3) (2015) 256-264.
- [26] F.D.B. de Sousa, J.R. Gouveia, P.M.F. de Camargo Filho, S.E. Vidotti, C.H. Scuracchio, L. Amurin, T.S. Valera, Blends Ground Tire Rubber devulcanized by microwaves/HDPE - Part B: Influence of clay addition, *Polimeros-Ciencia E Tecnologia* 25(4) (2015) 382-391.
- [27] F.D. de Sousa, C.H. Scuracchio, The Role of Carbon Black on Devulcanization of Natural Rubber by Microwaves, *Materials Research-Ibero-American Journal of Materials* 18(4) (2015) 791-797.
- [28] P.S. Garcia, F.D.B. de Sousa, J.A. de Lima, S.A. Cruz, C.H. Scuracchio, Devulcanization of ground tire rubber: Physical and chemical changes after different microwave exposure times, *Express Polymer Letters* 9(11) (2015) 1015-1026.
- [29] F.D.B. de Sousa, C.H. Scuracchio, G.H. Hu, S. Hoppe, Effects of processing parameters on the properties of microwave-devulcanized ground tire rubber/polyethylene dynamically devulcanized blends *Journal of applied polymer science* 133(23) (2016).
- [30] C.H. Scuracchio, R.E.S. Bretas, A.I. Isayev, Blends of PS with SBR devulcanized by ultrasound: Rheology and morphology, *Journal of Elastomers and Plastics* 36(1) (2004) 45-75.
- [31] S. Ghose, A.I. Isayev, E. von Meerwall, Effect of ultrasound on thermoset polyurethane: NMR relaxation and diffusion measurements, *Polymer* 45(11) (2004) 3709-3720.
- [32] V.V. Yashin, A.I. Isayev, The effect of polydispersity on structure of ultrasonically treated rubbers, *Polymer* 45(17) (2004) 6083-6094.
- [33] W.L. Feng, A.I. Isayev, High-power ultrasonic treatment of butyl rubber gum: Structure and properties, *Journal of Polymer Science Part B-Polymer Physics* 43(3) (2005) 334-344.
- [34] W.L. Feng, A.I. Isayev, Blends of ultrasonically devulcanized tire-curing bladder and butyl rubber, *Journal of Materials Science* 40(11) (2005) 2883-2889.
- [35] A.I. Isayev, B. Sujun, Nonisothermal vulcanization of devulcanized GRT with reversion type behavior, *Journal of Elastomers and Plastics* 38(4) (2006) 291-318.

- [36] J.L. Massey, J.C. Parr, T.A. Wagler, E. von Meerwall, C.K. Hong, A.I. Isayev, Ultrasound devulcanization of unfilled natural rubber networks, studied via component molecular mobility, *Polymer International* 56(7) (2007) 860-869.
- [37] X. Sun, A.I. Isayev, Ultrasound devulcanization: comparison of synthetic isoprene and natural rubbers, *Journal of Materials Science* 42(17) (2007) 7520-7529.
- [38] C.K. Hong, A.I. Isayev, Plastic/rubber blends of ultrasonically devulcanized GRT with HDPE, *Journal of Elastomers and Plastics* 33(1) (2010) 47-71.
- [39] Y.H. Li, S.H. Zhao, L.Q. Zhang, Y.Q. Wang, W.Y. Yu, The effect of different Fe²⁺ concentrations in culture media on the recycling of ground tyre rubber by *Acidithiobacillus ferrooxidans* YT-1, *Annals of Microbiology* 63(1) (2013) 315-321.
- [40] Y.H. Li, S.H. Zhao, Y.Q. Wang, Microbial Desulfurization of Ground Tire Rubber by sp.: A Novel Technology for Crumb Rubber Composites, *Journal of Polymers and the Environment* 20(2) (2012) 372-380.
- [41] Y.H. Li, S.H. Zhao, Y.Q. Wang, Microbial desulfurization of ground tire rubber by *Thiobacillus ferrooxidans*, *Polymer Degradation and Stability* 96(9) (2011) 1662-1668.
- [42] C. Yao, S.H. Zhao, M.H. Hu, B.W. Wang, L.Q. Zhang, Half-Submerged Cultivation Method for the Microbial Desulfurization of Waste Latex Rubber, *Journal of Applied Polymer Science* 131(21) (2014).
- [43] D.S. Novotny, R.I. Marsh, F.C. Masters, D.N. Tally, Microwave devulcanization of rubber, 1978.
- [44] M. Myhre, D.A. MacKillop, Rubber recycling, *Rubber Chemistry and Technology* 75(3) (2002) 429-474.
- [45] Y.J. Hong, K.M. Jeong, P. Saha, J. Suh, J.K. Kim, Processing and Characterization of Microwave and Ultrasonically Treated Waste-EPDM/LDPE Polymer Composites, *Polymer Engineering and Science* 55(3) (2015) 533-540.
- [46] S. Seghar, N. Ait Hocine, V. Mittal, S. Azem, F. Al-Zohbi, B. Schmaltz, N. Poirot, Devulcanization of styrene butadiene rubber by microwave energy: Effect of the presence of ionic liquid, *eXPRESS Polymer Letters* 9(12) (2015) 1076-1086.
- [47] M. Khavarnia, S.O. Movahed, Butyl rubber reclamation by combined microwave radiation and chemical reagents *Journal of applied polymer science* 133(17) (2016).
- [48] F.P. J., J. Rehner Jr, Statistical mechanics of cross-linked polymer networks. II. Swelling, *Journal of Chemical Physics* 11 (1943) 521-526.
- [49] D.A. Baeta, J.A. Zattera, M.G. Oliveira, P.J. Oliveira, THE USE OF STYRENE-BUTADIENE RUBBER WASTE AS A POTENTIAL FILLER IN NITRILE RUBBER: ORDER OF ADDITION AND SIZE OF WASTE PARTICLES, *Brazilian Journal of Chemical Engineering* 26(1) (2009) 23-31.
- [50] A.J. Marzocca, Evaluation of the polymer-solvent interaction parameter χ for the system cured styrene butadiene rubber and toluene 43 (2007) 2682-2689.
- [51] T. Amari, N.J. Themelis, I.K. Wernick, Resource recovery from used rubber tires, *Resources Policy* 25(3) (1999) 179-188.
- [52] X. Sun, A.I. Isayev, T.R. Joshi, E. von Meerwall, Molecular mobility of unfilled and carbon-black-filled isoprene rubber: Proton NMR transverse relaxation and diffusion, *Rubber Chemistry and Technology* 80(5) (2007) 854-872.
- [53] J.A. Menendez, A. Arenillas, B. Fidalgo, Y. Fernandez, L. Zubizarreta, E.G. Calvo, J.M. Bermudez, Microwave heating processes involving carbon materials, *Fuel Processing Technology* 91(1) (2010) 1-8.
- [54] M.M. Hassan, R.O. Aly, S.E.A. Aal, A.M. El-Masry, E.S. Fathy, Mechanochemical devulcanization and gamma irradiation of devulcanized waste rubber/high density polyethylene thermoplastic elastomer, *Journal of Industrial and Engineering Chemistry* 19(5) (2013) 1722-1729.
- [55] R. Rios, M. Gontijo, V.P. Ferraz, R.M. Lago, M.H. Araujo, Devulcanization of styrenebutadiene (SBR) waste tire by controlled oxidation, *Journal of the Brazilian Chemical Society* 17(3) (2006) 603-608.
- [56] A. Kebritchi, H. Firoozifar, K. Shams, A. Jalali-Arani, Effect of pre-devulcanization and temperature on physical and chemical properties of waste tire pyrolytic oil residue, *Fuel* 112 (2013) 319-325.
- [57] S. Rooj, G.C. Basak, P.K. Maji, A.K. Bhowmick, New Route for Devulcanization of Natural Rubber and the Properties of Devulcanized Rubber, *Journal of Polymers and the Environment* 19(2) (2011) 382-390.
- [58] S. Yagneswaran, W.J. Storer, N. Tomar, M.N. Chaur, L. Echegoyen, D.W. Smith, Surface-grafting of ground rubber tire by poly acrylic acid via self-initiated free radical polymerization and composites with epoxy thereof, *Polymer Composites* 34(5) (2013) 769-777.
- [59] A.P. Izhik, N.B. Uriev, Surface properties and specific features of structurization of disperse carbon black with different degrees of oxidation, *Colloid Journal* 64(5) (2002) 562-566.
- [60] G. Socrates, *Infrared characteristic group frequencies*, John Wiley & Sons, New York, 1980.
- [61] K.S. Loganathan, *Rubber engineering*, McGraw-Hill, New York, 2000.
- [62] H. Cui, J.L. Yang, Z.Y. Liu, Thermogravimetric analysis of two Chinese used tires, *Thermochemica Acta* 333(2) (1999) 173-175.
- [63] M.J. Fernandez-Berridi, N. Gonzalez, A. Mugica, C. Bernicot, Pyrolysis-FTIR and TGA techniques as tools in the characterization of blends of natural rubber and SBR, *Thermochemica Acta* 444(1) (2006) 65-70.
- [64] M.M. Horikx, Chain scissions in a polymer network, *Journal of polymer science Part A - Polymer chemistry* 19(93) (1956) 445-454.
- [65] M. Sabzekar, M.P. Chenar, S.M. Mortazavi, M. Kariminejad, S. Asadi, G. Zohuri, Influence of process variables on chemical devulcanization of sulfur-cured natural rubber *Polymer degradation and stability* 118 (2015) 88-95.