Devulcanization of ground tire rubber: Physical and chemical changes after different microwave exposure times

P. S. Garcia[1], F. D. B. de Sousa[1], J. A. de Lima[1], S. A. Cruz[1], C. H. Scuracchio[2]*

[1]Center of Engineering, Modeling and Applied Social Science (CECS), Universidade Federal do ABC (UFABC), Santa Adelia 166, 09210-170 Santo André, SP, Brazil
[2]Materials Engineering Department (DEMa), Universidade Federal de São Carlos (UFSCar), Washington Luís (SP-310), Km 235, 13565-905 São Carlos, SP, Brazil

Abstract. Microwave devulcanization is known to be a promising and an efficient rubber recycling method which makes possible for the rubber to regain its fluidity, and makes it capable of being remolded and revulcanized. The focus of this work is to understand the physical and chemical changes that occur in the ground tire rubber after different microwave exposure periods. For this purpose chemical, thermal, rheological and morphological analyses were performed on the tire rubber, which contains natural rubber (NR) and styrene-butadiene rubber (SBR) as polymeric material. The results showed that the microwave treatment promoted the breaking of sulfur cross-links and consequently increased the rubber fluidity. However, long periods of exposure led to degradation and modification of some properties. At nanoscale, the deformation of the devulcanized NR domain under stress was observed, and the morphology obtained appears to be a droplet dispersion morphology. The most exposed samples presented only one glass transition temperature, and from this it was concluded that the treatment may have played an important role in the compatibilization of the elastomeric blend. Based on the results, it is required to control the microwave exposure time and polymeric degradation in order to achieve a regenerated rubber with satisfactory properties.

Keywords: recycling, ground tire rubber, devulcanization, microwaves, degradation

1. Introduction

The lack of recycling programs for vulcanized elastomers, such as scrap tire rubber, has become an environmental, social and economic problem. The rubber tires in landfills and dumps can create serious problems to the entire municipal solid waste (MSW) management system because of their low degradability and large volume. These scrap tires can also be responsible for the proliferation of mosquitoes and other disease-carrying vectors, besides potential soil contamination due to the presence of stabilizers, plasticizers and of other chemical substances leached from rubber [1, 2]. This situation could also impact the economic sphere due to higher sanitation and health system costs. Furthermore, if the rubbers were reused without incorporating technological solutions, the resulting materials would present low economic benefit, which would result in the depreciation of their final properties [3, 4].

However, there are methods that can be used to obtain recycled materials with enhanced properties, so that the rubber becomes processable and moldable. Once the rubber can flow, it can be revulcanized as the virgin rubber [5] or it can also be incorporated into thermoplastics to produce high toughness materials [6–9]. The technique known as devulcanization is used for regaining this fluidity. It is a physical or chemical method which has the objec-

tive to break the three-dimensional network, such as monosulfide, disulfide, and polysulfide present in the vulcanized rubber [10–12]. However, it should also be noted that the breaking of the main polymer chains might occur, leading to polymer degradation [13, 14].

Regarding devulcanization processes, there are currently many techniques available, such as chemical, thermal, mechanical, thermomechanical, microbial and by irradiation (ultrasound and microwaves) [1, 10–12, 15, 16]. The microwave devulcanization, used in this study, has proved to be an efficient technique. This method enables to apply large amounts of energy rapidly and uniformly to the rubber, without using chemical reagents during the process [17, 18], which makes it an eco-friendly process [19]. The energy used to heat the rubber promotes the breaking of sulfur cross-links [13]. However, nonpolar elastomers, such as tire rubber, are unable to absorb the microwave energy due to their low absorption and scattering, which requires adding some particles to absorb the energy, such as carbon black [13]. This filler is known to absorb electromagnetic radiation through a phenomenon known as Maxwell-Wagner polarization, and the devulcanization process can only be achieved through it [20–22]. According to Pistor *et al*. [23] the greater the presence of carbon black in the rubber, the more uniform and selective will be the devulcanization process.

Some studies have reported the use of microwave devulcanization in different types of elastomers. Zanchet *et al*. [24] noted that the microwave devulcanization enhanced the interfacial adhesion between devulcanized styrene-butadiene rubber (SBR) in a virgin SBR matrix. The results showed that this mixture can be used in automotive profiles obtained by compression molding. Other papers analyzed the influence of the amount of carbon black in the rubber during the microwave devulcanization and concluded that the degree of devulcanization increases as a function of the increase in the amount of carbon black [23, 25]. Paulo *et al*. [26] verified that the microwave devulcanization, using inorganic salts and nitric acid, promoted the breakup of sulfur cross-links and the oxidation in the SBR. Pistor and coworkers [23, 27, 28] evaluated the influence of the microwave devulcanization process in ethylene-propylene-diene (EPDM). As expected, the radiation was able to promote the breakage of the elastomeric three-dimensional network. The authors

also noticed that oil and additives present into EPDM influenced directly in the efficiency of the devulcanization process.

Despite the fact that microwave devulcanization is a known method, there are few studies addressing the chemical and physical aspects of the GTR after being exposed to radiation for different periods. Scuracchio and coworkers [13, 29] evaluated only the thermal and rheological aspects of the devulcanized GTR. According to the authors, with the technique, they were able to create a material with properties quite different from the original vulcanized rubber, due to the changes in the tire rubber structure and composition during the treatment.

The present study deals with these issues by proposing an in-depth study to better understand the chemical and physical changes occurred in the GTR structure after the microwave devulcanization process. The results of the chemical, morphological, thermal and rheological analysis were correlated with: (1) microwave exposure periods; (2) structural changes in GTR; (3) and the quantity of each element present in the GTR structure before and after the devulcanization process, such as natural rubber, synthetic rubber, carbon black, oils and additives.

2. Materials and methods
2.1. Materials
GTR from tread layers of truck tires, separated from non elastomeric components (as received), of 60 mesh particle size (about 75%) was supplied by Pirelli Ltda. (Brazil). The real composition of this rubber is unknown; however, the GTR usually contains polyisoprene (natural rubber – NR), synthetic rubber, which may contain styrene-butadiene rubber (SBR) and/or polybutadiene (BR), and other materials added during the tire manufacturing process, such as vulcanization additives, softeners and fillers. Interestingly, carbon black is the most widely used filler [18].

2.2. Recycling of ground tire rubber: Devulcanization process
Vulcanized ground tire rubber (GTRv) samples were recycled by devulcanization using microwaves. This system is comprised of a conventional microwave oven adapted with a motorized speed-control stirring system. It is very similar to the system used by Scuracchio [13, 29]. In this work, the microwave

oven used (Brastemp BMS35) has dimensions of approximately $0.35\times0.22\times0.34$ m. The power of the magnetron was set up at 820 W and 60 g of the sample was put in a 250 mL glass beaker with a stirring speed of 100 rpm. The devulcanization process was conducted using different periods, where GTRv samples were exposed to the microwaves for: 3 min (GTR3); 5 min (GTR5); 6 min (GTR6); and 7 min (GTR7). Then, each sample was homogenized in an open two-roll mill, which was operated at a friction ratio of 1:1.4 with a nip gap of 1 mm. The total mixing time was approximately 10 min for each sample at room temperature. It should be pointed out that all samples were exposed to the same treatment conditions and they were prepared the same way.

2.3. Characterization

In order to characterize the changes in the GTR structure after the devulcanization process, the chemical, thermal, rheological and morphological analysis were carried out.

2.3.1. Chemical analysis

The soluble (sol) and insoluble (gel) fractions of each sample, after the devulcanization process, were determined by Soxhlet extraction, by using toluene (Vetec – 99.5%; RJ, Brazil) as solvent. In the analysis, about 4 g of GTR was immersed in toluene for 6 h at 80°C. After extraction, the samples were dried for 24 h at 80°C to remove the solvent and their masses were measured. The gel content was calculated as the ratio of the dry weight of the samples after extraction to the weight of the samples before extraction.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy analyses were performed on all the samples to obtain information about chemical modifications on the GTR structure as a result of the devulcanization process. The spectra were recorded on a Perkin Elmer Frontier FTIR (Perkin Elmer, Waltham, MA, USA) with ATR accessory, from 4000 to 700 cm^{-1} at resolution of 4 cm^{-1} over 20 scans.

2.3.2. Thermal analysis

Thermogravimetric (TGA) analyses were conducted to provide information about thermo-oxidative degradation of the samples after devulcanization. The analyses were performed on a TGA Q500 (TA Instruments, New Castle, DE, USA) device. About 10–

15 mg of each sample was heated from room temperature to 560°C under nitrogen atmosphere at heating rate of 10°C/min to monitor the weight loss of oil and elastomers. At 560°C, the gas flow was changed to oxygen atmosphere and the samples were heated from 560 to 800°C in order to observe the carbon black degradation.

The glass transition temperatures of each sample were determined by using the differential scanning calorimetry (DSC; Q200, TA Instruments, New Castle, DE, USA). The experiments were performed according to the following program: (A) Initial temperature of 30°C; (B) Cooling: cooling rate of 30°C min^{-1} to –90°C; (C) Heating: heating rate of 30°C min^{-1} to 250°C. The results reported in this work correspond to the heating runs. All DSC curves were normalized according to the sample mass.

2.3.3. Rheological analysis

The rheometric measurements were determined at 190°C in an Oscillating Disk Rheometer (ODR; TechPro Rheotech, RheoTech MDpt, Akron, USA), according to ASTM D-2084-11. ODR was operated at the frequency of 1.67 Hz and 1° arc. This technique was a useful tool to monitor the rubber curing characteristics, as well as to verify the existence of revulcanization at high temperatures after microwave treatment.

The melt-viscosity of the devulcanized materials was measured by using a high pressure capillary rheometer Instron Ceast SR20 (SmartRHEO 2000, Pianezza, TO, Italy) with a capillary die of 1 mm and L/D ratio of 20. Measurements were performed at 190°C over a shear rate range between 300 and 15 000 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.

It should be pointed out that both rheological tests were conducted using rubber sheets obtained from the homogenizing and mixing process in the two-roll mill. For the capillary rheometer test, the sheets were cut in small pieces to facilitate their filling in the barrel.

2.3.4. Morphological analysis

The analysis of the surface morphology of the devulcanized samples, after being homogenized in a two-roll mill, was carried out using Scanning Electron Microscopy (SEM; JEOL, JSM-6010LA, Tokyo,

Japan) at an acceleration voltage of 5 kV. Surface sheets were coated with a thin layer of gold to attain some information about the flow behavior of each sample.

Atomic force microscopy (AFM; NX10, Park systems, Suwon, Korea) was applied to investigate the surface morphology of the devulcanized samples. Phase images were recorded in the tapping mode using a silicon tip. The probe oscillated at a resonance frequency of approximately 320 KHz with spring constant of 48 N/m.

3. Results and discussion

Before approaching the tests some preliminary observations were made about the texture samples. Figure 1 shows that the long exposure times to microwave caused drastic changes in their textures, and this observation was noted only after the mixing process. In the case of GTR3, small agglomerates were obtained, while in the GTR5 sample a tacky rubber sheet was formed. After these first observations, it was necessary to understand in depth the structural changes that occurred after the treatment, and their effects on the properties of the GTR.

3.1. Chemical properties

The percentage of soluble (sol) and insoluble (gel) contents after the devulcanization are shown in Table 1. The results show that longer microwave exposure times led to lower gel content. As described in the literature [12, 13], the devulcanization process can modify the chemical structure of vulcanized elastomers, mainly with the breaking of C–S and S–S bonds, forming materials with lower insoluble portions, as observed in this present study. Regarding the GTRv sample, a small amount of soluble materials could also be measured due to two possible reasons:

Table 1. Percentage of gel and sol contents

Samples	Gel content [%]	Sol content [%]
GTRv	86.0	14.0
GTR3	83.5	16.5
GTR5	73.0	27.0
GTR6	71.2	28.7
GTR7	69.0	31.0

either the oils/additives from rubber were solubilized in toluene, as described by Scuracchio *et al.* [29], and/or there were small amounts of polymer chains that were not cured.

To better understand how the microwaves may have altered the chemical structures of the GTR, the ATR-FTIR technique was used. According to spectra (Figure 2), the intensities of some bands were altered with the devulcanization process. Previous studies have attributed these IR bands to: (1) 1537 cm^{-1}: stretching vibration of a methyl-assisted conjugated double bond ($v_{-(C=C)_n-}$, where $n > 6$) from both NR [30, 31] and SBR [32]; (2) 1435 and 1376 cm^{-1}: δ_{CH_2}
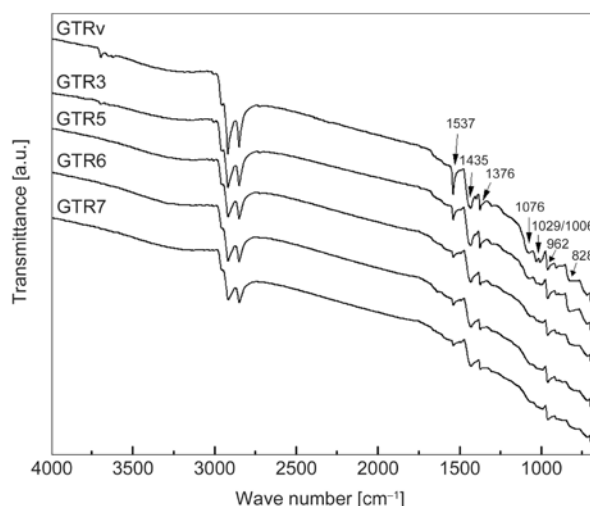
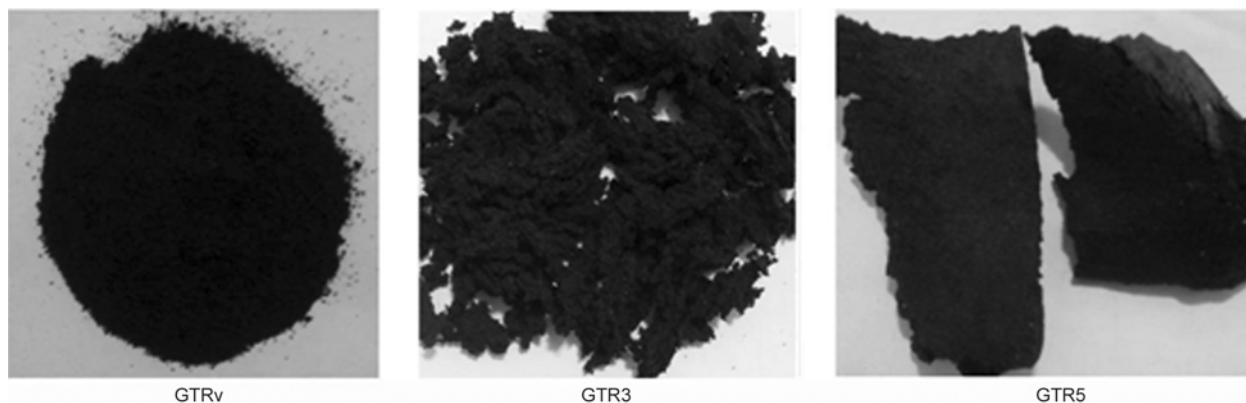**Figure 2.** FTIR spectra of vulcanized and devulcanized GTR samples

Figure 1. Photos of the GTRv, GTR3 and GTR5 samples after mixing process

deformation from NR rubber [31]; (3) 1076 cm^{-1}: symmetric C–S–C group stretching vibrations in the two C–S bonds [33]; (4) 1029 and 1006 cm^{-1}: C–S bonds [25]; (5) 962 cm^{-1}: –CH=CH– group vibrations of butadiene present in SBR [33, 34]; and (6) 828 cm^{-1}: γ_{C-H} bending from NR rubber [31]. The results reveal that the samples most exposed to microwaves had lower intensity bands, which was more evident in the GTR7 sample. It is also interesting to notice that the bands at 1076, 1029 and 1006 cm^{-1}, which are related to C–S bonds, are seen mainly in the GTRv and GTR3 samples. Hirayama and Saron [25] also noticed changes in the intensity bands in the SBR samples most exposed to microwaves. The authors observed that polysulfidic bonds were broken, however the monosulfidic bonds remained preserved.

So, the results obtained from both chemical techniques proved the existence of structural changes in GTR molecules when exposed to microwaves, especially with the breaking of C-S bonds. Moreover, it is expected that other GTR properties were also altered as a result of the chemical changes observed. Accordingly, an in-depth study of the thermal, rheological and morphological properties of the GTR was performed.

3.2. Thermal properties
The TGA-DTGA results shown in Figure 3 represent the events that occurred in the GTR3 sample, and the other samples presented similar behavior. Based on this, the following events are observed: (1) volatilization of processing oils and additives, or any other element with low molar mass and low boiling temperature; (2) decomposition of the polymeric material present in the tire rubber, where the first and the second peaks belong to the NR and synthetic rubber (SBR and/or BR) decomposition,
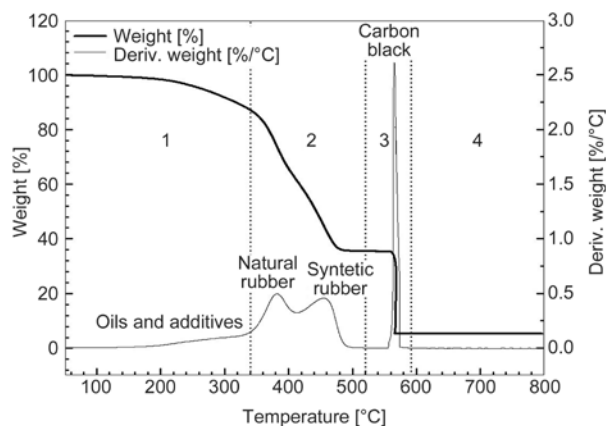

Figure 3. TGA-DTGA curves of the GTR3 sample

respectively [13, 35, 36]; (3) consumption of carbon black, and (4) the residual materials that correspond to the inorganic materials found after the pyrolysis process [35–37].

From the analyses, the temperature range (ΔT) and the weight loss percentage (Δm) of each element were measured (Table 2). According to the results, the longer the microwave exposure times, the lower the weight loss of processing oil, additives and NR, as previously observed by Scuracchio *et al.* [13]. During the devulcanization process, the samples were able to reach the thermal degradation temperatures of processing oils and additives, and these temperatures provided higher decomposition and scission of the NR chains. Therefore, the most degraded materials had smaller amounts of processing oils, NR and additives to be consumed during the thermogravimetric tests. Regarding the carbon black and residual materials, the samples most exposed to microwaves showed greater weight loss of these elements due to the degradation process. The samples most exposed also showed slight increase in the weight loss percentage of synthetic rubber. This indicates that the molecules of the synthetic rubbers were slightly consumed or not consumed at all.

Table 2. Parameter values obtained from TGA curves for vulcanized and devulcanized GTR

Samples	Data	Oils and additives	Natural rubber	Synthetic tubber	Carbon black	Residues
	ΔT [°C]	~ 35 to 320	320 to 410	410 to 520	520 to 600	600 to 800
GTRv	Δm [%]	10.31	28.35	26.05	29.88	5.41
	T_{max} [°C]	~253	381.02	454.60	569.65	–
GTR3	Δm [%]	10.37	27.91	26.24	30.20	5.28
	T_{max} [°C]	~253	382.03	456.40	565.59	–
GTR5	Δm [%]	10.08	25.36	26.67	32.36	5.52
	T_{max} [°C]	~256	384.55	453.30	566.99	–
GTR6	Δm [%]	9.97	22.47	28.26	33.62	5.65
	T_{max} [°C]	~256	387.46	449.05	566.98	–
GTR7	Δm [%]	8.84	19.41	28.63	36.92	6.20
	T_{max} [°C]	~256	391.03	447.78	567.94	–

It can also be observed that the temperatures at the maximum weight loss rate (T_{max}) of both elements (NR and synthetic rubber) were shifted (Table 2). The NR peaks of the most devulcanized samples shifted to higher temperatures. This phenomenon may have occurred due to the presence of higher amounts of carbon black. These fillers may have played the role of a physical barrier to the output of volatiles, increasing the tortuous and mean free path of these gases, as illustrated in Figure 4a [38]. Like the carbon black, the residual materials may have also played a part in delaying the output of gases. Shih and Jeng [39] reported that the structure of the carbon black pores can adsorb volatiles and liquid, all of them resulting from the pyrolysis process. Thus, in this work it is assumed that the carbon black could have acted as barrier (Figure 4a) and/or could have also adsorbed volatile products (Figure 4b). Fernandez-Berridi *et al*. [35] also observed an increase in the thermostability of the NR with the addition of the SBR in the blend. Once more, it is important to emphasize that the large amount of carbon black in GTR increased its thermostability, as seen in Figure 5.

Although all these factors contributed to the shift of T_{max}, the effect of the breaking of cross-links on the thermostability should be considered. This breakage can thermally destabilize the rubber, promoting its degradation at lower temperatures. However, the effect of the presence of carbon black was still more intense.

Regarding the thermostability of the synthetic rubber, the samples with longer microwave exposure times shifted their T_{max} to lower temperatures (Table 2). Although there is the effect of carbon
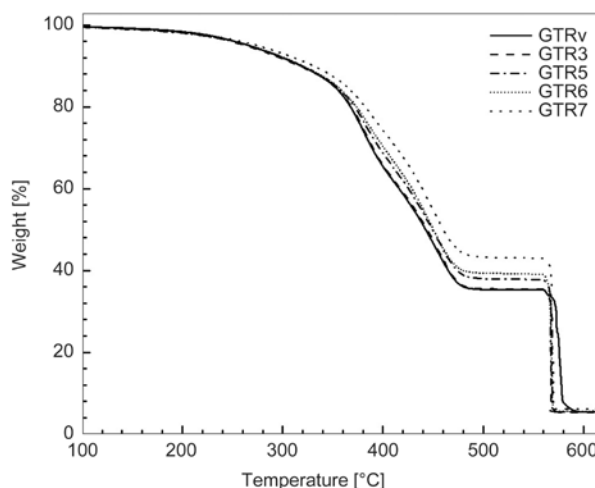

Figure 5. TGA curves of the vulcanized and devulcanized samples

black on the material, it is believed that the effect of the breaking of cross-links stood out. Another possibility is that the devulcanization process played a role in improving the adhesion between the mixture phases. Karger-Kocsis *et al*. [12] reported that this treatment can act on the compatibility of devulcanized molecular structures. Zanchet *et al*. [24] noted that the microwave treatment enhanced the interfacial adhesion between devulcanized SBR and virgin SBR matrix.

So, in this work, molecular entanglements could have occurred between the devulcanized molecules of the NR and synthetic rubber, and it would result in the shift of this T_{max} to lower values.

The DSC technique was employed to determine the T_g of each elastomeric phase, as shown in Table 3. In general, two distinct glass transitions can be observed, called T_{g1} and T_{g2}, which are related to the presence of the NR and SBR in the GTR, respec-
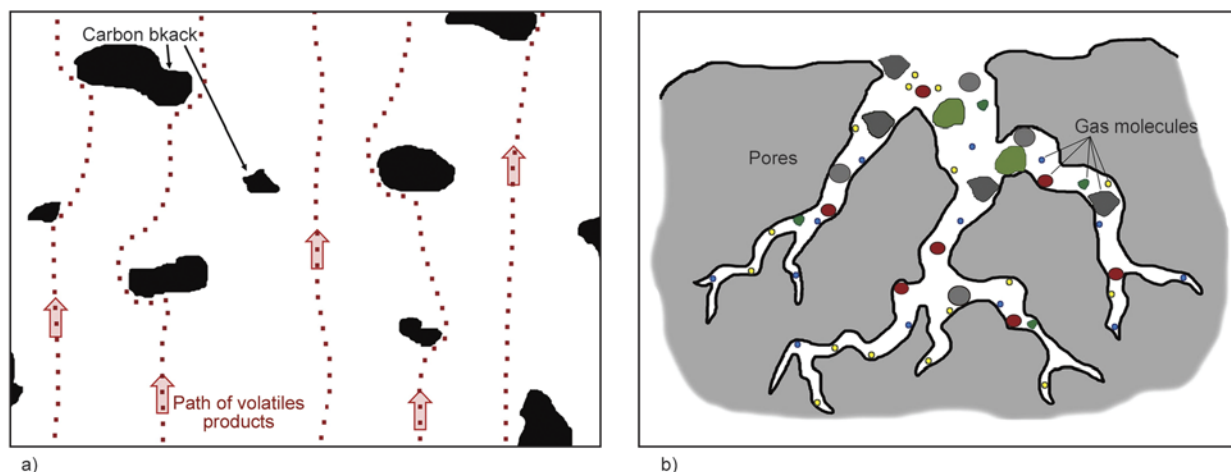

Figure 4. Schema of barrier effect and increase of mean free path of volatiles (a) and adsorption of gas molecules in the carbon black pores (b)

Table 3. Glass transition temperature (T_g) and glass transition width (ΔL) of the samples

Sample	T_{g1}	ΔL_1	T_{g2}	ΔL_2
GTRv	−57	5.7	−46	8.1
GTR3	−56	7.2	−44	9.0
GTR5	−65	10.5	−44	11.4
GTR6	−64	12.4	−	−
GTR7	−62	15.7	−	−

tively [40]. The results shown in Table 3 indicate that the T_{g1} values of the most degraded samples were shifted to lower values, since the cross-links were broken and the polymer chains gained mobility. Pistor *et al.* [23] also noted the same tendency toward lower T_g values with the increase in the exposure time of the ethylene-propylene-diene rubber (EPDM) to microwaves. The authors related these results to the rupture of covalent bonds.

It was also expected that the GTR7 sample had the lowest T_{g1} value. However, in this case, it is likely that the carbon black acted by restricting the segmental motion of the NR molecules, increasing the T_{g1} value, as reported by Scuracchio *et al.* [13]. The literature [13, 29, 41] also showed that the devulcanization process, in these case, by ultrasound, can lead to the formation of cyclic sulphur structures in the polymer chains of the devulcanized SBR, increasing the T_g.

Thus, these factors (breaking of cross-links and carbon black) are expected to counterbalance themselves.

GTR5, GTR6 and GTR7 samples had only a single glass transition in their DSC curves, so that the T_{g2} could not be determined by this technique in this particular case. There are two factors that can explain what took place: (1) the largest amount of carbon black found in these samples could have restricted the segmental motion of the SBR molecules, and/or (2) the devulcanization process might have acted as a compatibilizing agent through molecular entanglement of the devulcanized molecular structures, as previously mentioned.

Table 3 also shows the width values of the glass transition (ΔL), which is defined as the difference between the initial and final temperatures of the transition. These values reflect the number or the distribution modes and relaxation times associated with the transition temperature. For the polymer blends, it can be related to the concentration gradient, also called microheterogeneity. According to Table 3, the ΔL_1 and ΔL_2 values increase with

devulcanization, indicating an increase in the relaxation numbers that may be associated to different microenvironments (regions with dimensions of the order of a few chain segments with different neighborhoods). Pistor *et al.* [27] also noticed the width values of glass transition (ΔL) in the most exposure samples to microwaves. These results were associated to the break of the three-dimensional network, where some molecules could acquire mobility at lower temperatures.

3.3. Rheological properties

Table 4 shows the rheometric measurements obtained in the ODR. Scorch time (t_{s1}, the starting time of the vulcanization reaction) and minimum torque (M_L, parameter related to the Mooney viscosity of the material prior to the reaction) were evaluated. According to the results, the absence of revulcanization in the devulcanized samples was observed during analysis (5 min), since the torque did not exceed the minimum of 1 lbf·in (= 0.113 Nm). In relation to M_L values, the decrease of this parameter in the samples GTR5 and GTR6 showed the decrease of the three-dimensional network generated by devulcanization (since M_L value is related to the viscosity and, consequently, to the cross-link density), as shown earlier. The increase of this parameter for the GTR7 sample is probably related to the increasing amount of carbon black and the lowest amount of oil in its structures, as shown by thermogravimetric data (Table 2). So, the increasing in the torque during analysis indicates its flow difficulty in these shear rates.

To determine the storage modulus (G') and the loss modulus (G'') as a function of time (min), the ODR analysis was also used, as seen in Figure 6. Before analyzing the results, it should be noted that both G' and G'' are dependent on the length and on the level of entanglement of the polymer chains [42]. Furthermore, the higher the cross-link density, the higher the G' values. According to Figure 6, the devulcanized samples show three distinct behaviors. Sample GTR3 had the highest G' value due to its elevated

Table 4. Rheological parameters of the devulcanized samples

Samples	t_{s1} [min]	M_L [lbf·in]
GTR3	>5	6.3
GTR5	>5	4.1
GTR6	>5	4.1
GTR7	>5	6.2

Figure 7. Viscosity versus shear rate for devulcanized samples
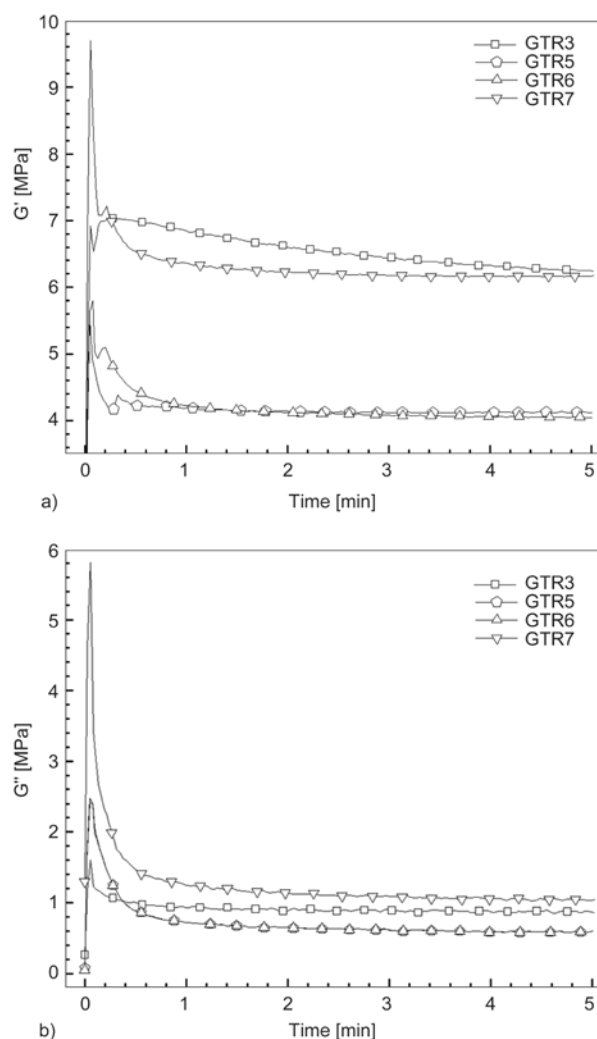

Figure 6. Storage (a) and loss modulus (b) as a function of the time [min] for devulcanized samples

cross-link density. GTR5 and GTR6 had the lowest G' values due to its decreasing stiffness by increasing the mobility of the polymer chains, as a result of the devulcanization process. However, sample GTR7 exhibited values very close to those of GTR3. As mentioned before, GTR7 was the sample with the highest amount of carbon black and inorganic residues in its structure, and considered as fillers, its stiffness increased. This sample also presented a low concentration of oils, which also favored the increase of G'. Note that the values G'' followed the same trend observed for G'. The breaking of the cross-links increased the G'' value, especially for GTR7. However, GTR3 displayed distinct behaviors during the test. The G'' values varied between the values of GTR7 and GTR5/GTR6. It is possible that the large amount of oil benefited the sliding of its polymer chains, which were not cross-linked or were broken during the treatment. Thus, G'' was

higher than the G'' of the GTR5 and GTR6 samples. It is also a possibility that this result may not be reliable. It is known that the G' and G'' values strongly depend on the sample morphology, and in this case, probably, GTR3 morphology may not be uniform. As mentioned earlier, after the mixing process, GTR3 presented small agglomerates, whereas GTR5, GTR6 and GTR7 presented tacky rubber sheets.

Regarding the capillary rheometry analysis, Figure 7 shows the flow curves of the devulcanized rubber as a function of shear rate. The results reveal that the flow characteristics of the samples were affected by microwaves. At higher shear rates, the increased exposure to microwaves makes the rubber more fluid, since the microwave radiation affected the rubber molecular structures, leading to the scission of the molecules and the decrease of its molar mass. Consequently, the shear viscosity was decreased, as reported by Scuracchio *et al*. [29]. All samples heated more than 5 min presented a pseudoplastic behavior, similar to a thermoplastic polymer. Regarding sample GTR5, the curve did not show linearity by reducing the shear viscosity at higher shear rates. Somehow, its high cross-link density (in comparison to the others) appears to have affected its viscosity. It is worth noting that sample GTR3 could not be analyzed, since it did not flow at high shear stresses and high temperatures due to its high cross-link density.

3.4. Morphological properties

Based on the texture changes after the devulcanization and mixture processes (Figure 1), the SEM analyses were performed. According to Figure 8,
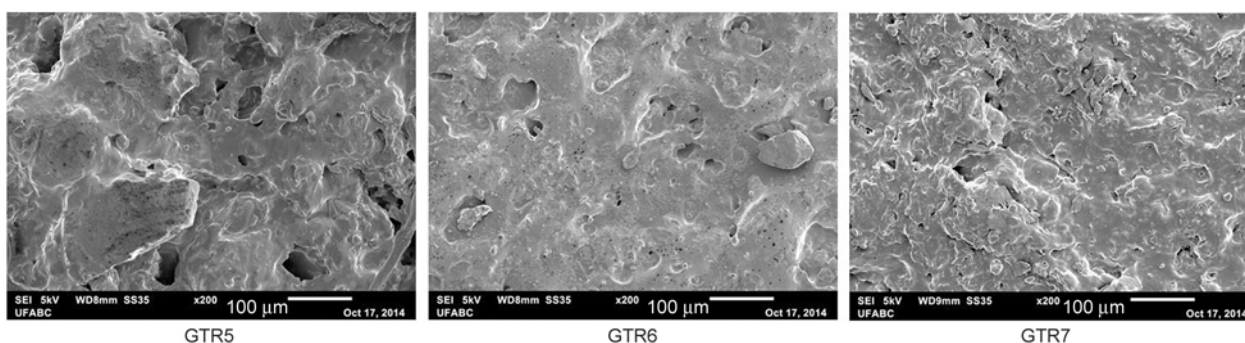
Figure 8. SEM of the surface sheets of the GTR5, GTR6 and GTR7 samples

the micrographs reveal differences amongst themselves regarding voids and particles. It is believed that as this rubber went through the roll mills, the sol phase could have wet the gel phase more effectively. Thus, the most devulcanized samples (GTR6 and GTR7), which have higher amount of the sol phase in their structures, exhibited smoother sheets with smaller voids. It was deducted that the wettability of the sol phase can be related to its fluidity when it is submitted to shear stress during the mixing process. On the other hand, GTR5 exhibited larger voids, indicating that this material possibly did not flow like the others. Also, this sample exhibited stiff particles (i.e cross-link fraction) that were not deformed under mechanical stress.

It should also be noted that GTR7 revealed the presence of some other small particles, which are carbonized materials from the thermo-oxidative degradation process. These data support the thermal analysis results, showing an increase of residual materials in the samples that received higher microwave exposures. The data are also in agreement with the results of rheological properties, since the viscosity of the samples tends to decrease with the increase of the exposure time of GTR to microwaves, increasing the rubber fluidity.

Additionally, phase images obtained from AFM (Figure 9) were used to provide information about the composition of the polymeric blends at nanoscale [43, 44]. Assuming that GTR is a blend composed by NR, SBR and carbon black (according to the previous results presented in this work), its morphology could be analyzed, where three phases were clearly distinguished by the different colors in the images.

Regarding the color scale, which represents the scale of hardness in the images, hard and soft segments can be seen in the mixture. Some studies have represented the dark domains as being the softer materials and the clear domains the harder ones [45, 46]. Similarly, in the present work the carbon black particles are represented by clearer domains. As this filler is the hardest phase found in the blends and as it has a specific shape and nanometric sizes [46], it was easy to single it out in the images. Consequently, the darkest and middle color areas are the NR and the SBR domains, respectively. Thus, the phase images (GTR5 → GTR7) show the consumption of the darker phase and the increase of the clearer phase with the increase of exposure time of GTR to microwaves, and in the same way an increase in the amount of carbon black domains can be also observed. These data validate the results obtained mainly from TGA analysis, where there was a reduction in the amount of the NR and the relative increase in the amount of carbon black and residual materials with higher
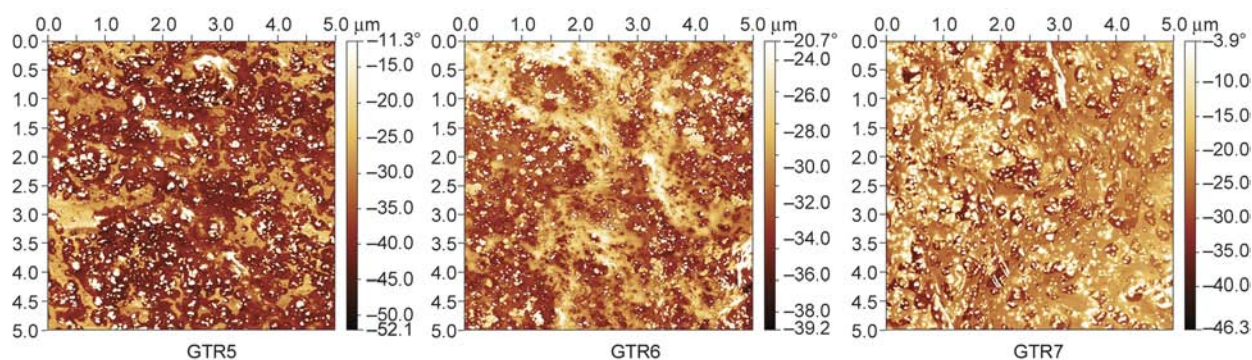

Figure 9. Tapping mode AFM phase images of the samples

exposure times. Although some studies have shown that SBR is softer than NR [46], it should be remembered that the NR molecular structures were changed with radiation, where their main chains and cross-links were broken, and it is possible that this allowed the NR to become softer.

Regarding the dispersion of carbon black particles in elastomeric blends, GTR5 showed peculiar results about the localization of these fillers in the elastomeric phases. It can be observed that in this sample the carbon black is located in the NR, and in samples GTR6 and GTR7 these particles were transferred to the SBR phase. Le *et al*. [47] showed that there are two factors that cause carbon black to remain in one of the phases: (1) the effect of the matrix viscosity, and (2) the polarity. The authors reported that although NR chains are more capable of wetting the carbon black, fillers migrate to the SBR over time due to chemical affinity. However, in this work, in addition to the fact that NR underwent degradation and was able to enhance its degree of wettability, its polarity also changed. These factors may have contributed to the preference for carbon black by NR. However, while the NR phases decreased with increasing exposure times, carbon black particles were being transferred from NR to the SBR phases.

Another peculiar result was seen in the GTR7. It appears that the devulcanized NR domains were deformed during mixing in the two-roll mill, even under small stresses, and they were oriented in the flow direction. The obtained morphology is very similar to droplet dispersion morphology, frequently seen in thermoplastic blends, as illustrated in Figure 10.
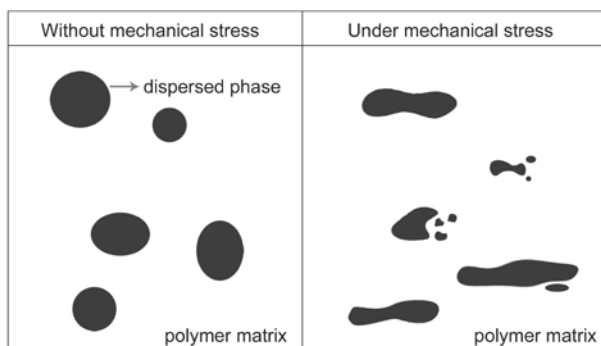

Figure 10. Illustration of the droplet dispersion morphology during melt-mixing of immiscible polymer blends. Deformation and breakup of dispersed phase in shear flow.

4. Conclusions

GTRv samples were devulcanized using different microwave exposure times. Long microwave exposure periods resulted in many structural changes, such as the decrease of the insoluble phase content (gel phase), breaking of chemical bonds (C=C and C–S) and increase in the fluidity of rubber. Even though the goal was achieved, the breaking of the main polymer chain also occurred. Substantial amounts of the NR chain were decomposed and broken during the treatment, and likewise there was an increase in the relative amount of carbon black and residual materials with the polymer degradation. However, this amount of carbon black led to the samples' enhanced thermostability and increased stiffness. The treatment proved to be efficient in the compatibilization of the elastomeric phases. Despite all structural changes, the devulcanized samples could not to be revulcanized during the rheological analyses. Regarding the analyses, it is very important to emphasize that the AFM technique proved to be an interesting and effective tool in monitoring changes in GTR using the devulcanization process. This technique revealed the morphology of the blends at nanoscale. The method enabled to observe the increasing wettability of the NR domain in the carbon black, and also its increasing fluidity in the blend, which was similar to a droplet dispersion (NR) in a continuous phase of the SBR.

References

[1] Adhikari B., De D., Maiti S.: Reclamation and recycling of waste rubber. Progress in Polymer Science, **25**, 909–948 (2000).
   DOI: 10.1016/S0079-6700(00)00020-4
[2] Wolsky A. M., Gaines L. L.: Discarded tires: A potential source of hydrocarbons to displace petroleum. Resources and Energy, **3**, 195–206 (1981).
   DOI: 10.1016/0165-0572(81)90023-2
[3] Celauro B., Celauro C., Lo Presti D., Bevilacqua A.: Definition of a laboratory optimization protocol for road bitumen improved with recycled tire rubber. Construction and Building Materials, **37**, 562–572 (2012).
   DOI: 10.1016/j.conbuildmat.2012.07.034

[4] Guillamot F., Goujard L., Simard D., Boulangé L.: Influence of interface energy on compatibility between ground tyre rubber and bitumen used in asphalt pavement. Road Materials and Pavement Design, **14**, 372–383 (2013).
DOI: 10.1080/14680629.2013.796890

[5] Oh J. S., Ghose S., Isayev A. I.: Effects of ultrasonic treatment on unfilled butadiene rubber. Journal of Polymer Science Part B: Polymer Physics, **41**, 2959–2968 (2003).
DOI: 10.1002/polb.10606

[6] Scuracchio C. H., Bretas R. E. S., Isayev A. I.: Blends of PS with SBR devulcanized by ultrasound: Rheology and morphology. Journal of Elastomers and Plastics, **36**, 45–75 (2004).
DOI: 10.1177/0095244304039913

[7] Hassan M. M., Aly R. O., Abdel Aal S. E., El-Masry A. M., Fathy E. S.: Mechanochemical devulcanization and gamma irradiation of devulcanized waste rubber/high density polyethylene thermoplastic elastomer. Journal of Industrial and Engineering Chemistry, **19**, 1722–1729 (2013).
DOI: 10.1016/j.jiec.2013.02.012

[8] Hassan M. M., Badway N. A., Elnaggar M. Y., Hegazy E-S. A.: Thermo-mechanical properties of devulcanized rubber/high crystalline polypropylene blends modified by ionizing radiation. Journal of Industrial and Engineering Chemistry, **19**, 1241–1250 (2013).
DOI: 10.1016/j.jiec.2012.12.024

[9] Garcia P. S., Cruz S. A., Scuracchio C. H.: Composição para obtenção de blenda polimérica tenacificada, processo para a preparação da composição, blenda polimérica tenacificada, e, uso da mesma. BR 10 2014 021424 0, Brazil (2014).

[10] De S. K., Isayev A. I., Khait K.: Rubber recycling. CRC Press, New York (2005).

[11] Bandyopadhyay S., Agrawal S. L., Ameta R., Dasgupta S., Mukhopadhyay R., Deuri A. S., Ameta S. C., Ameta R.: An overview of rubber recycling. Progress in Rubber, Plastics and Recycling Technology, **24**, 73–112 (2008).

[12] Karger-Kocsis J., Mészáros L., Bárány T.: Ground tyre rubber (GTR) in thermoplastics, thermosets, and rubbers. Journal of Materials Science, **48**, 1–38 (2013).
DOI: 10.1007/s10853-012-6564-2

[13] Scuracchio C. H., Waki D. A., da Silva M. L. C. P.: Thermal analysis of ground tire rubber devulcanized by microwaves. Journal of Thermal Analysis and Calorimetry, **87**, 893–897 (2007).
DOI: 10.1007/s10973-005-7419-8

[14] Isayev A. I., Sujan B.: Nonisothermal vulcanization of devulcanized GRT with reversion type behavior. Journal of Elastomers and Plastics, **38**, 291–318 (2006).
DOI: 10.1177/0095244306067424

[15] Myhre M., MacKillop D. A.: Rubber recycling. Rubber Chemistry and Technology, **75**, 429–474 (2002).
DOI: 10.5254/1.3547678

[16] Myhre M., Saiwari S., Dierkes W., Noordermeer J.: Rubber recycling: Chemistry, processing, and applications. Rubber Chemistry and Technology, **85**, 408–449 (2012).
DOI: 10.5254/rct.12.87973

[17] Novotny D. S., Marsh R. L., Masters F., Tally D. N.: Microwave devulcanization of rubber. U.S. Patent US 4104205 A, USA (1978).

[18] Isayev A. I.: Recycling of rubbers. in 'Science and technology of rubber' (eds.: Mark J. E., Erman B., Eirich F. R.) Elsevier, New York, vol 3, 663–701 (2005).

[19] Hong Y. J., Jeong K. M., Saha P., Suh J., Kim J. K.: Processing and characterization of microwave and ultrasonically treated waste-EPDM/LDPE polymer composites. Polymer Engineering and Science, **55**, 533–540 (2015).
DOI: 10.1002/pen.23916

[20] Menéndez J. A., Arenillas A., Fidalgo B., Fernández Y., Zubizarreta L., Calvo E. G., Bermúdez J. M.: Microwave heating processes involving carbon materials. Fuel Processing Technology, **91**, 1–8 (2010).
DOI: 10.1016/j.fuproc.2009.08.021

[21] Kwon S. K., Ahn J. M., Kim G. H., Chun C. H., Hwang J. S., Lee J. H.: Microwave absorbing properties of carbon black/silicone rubber blend. Polymer Engineering and Science, **42**, 2165–2171 (2002).
DOI: 10.1002/pen.11106

[22] Yacubowicz J., Narkis M.: Dielectric behavior of carbon black filled polymer composites. Polymer Engineering and Science, **26**, 1568–1573 (1986).
DOI: 10.1002/pen.760262207

[23] Pistor V., Scuracchio C. H., Oliveira P. J., Fiorio R., Zattera A. J.: Devulcanization of ethylene-propylene-diene polymer residues by microwave – Influence of the presence of paraffinic oil. Polymer Engineering and Science, **51**, 697–703 (2011).
DOI: 10.1002/pen.21875

[24] Zanchet A., Carli L. N., Giovanela M., Brandalise R. N., Crespo J. S.: Use of styrene butadiene rubber industrial waste devulcanized by microwave in rubber composites for automotive application. Materials and Design, **39**, 437–443 (2012).
DOI: 10.1016/j.matdes.2012.03.014

[25] Hirayama D., Saron C.: Chemical modifications in styrene–butadiene rubber after microwave devulcanization. Industrial and Engineering Chemistry Research, **51**, 3975–3980 (2012).
DOI: 10.1021/ie202077g

[26] Paulo G. D., Hirayama D., Saron C.: Microwave devulcanization of waste rubber with inorganic salts and nitric acid. Advanced Materials Research, **418–420**, 1072–1075 (2012).
DOI: 10.4028/www.scientific.net/AMR.418-420.1072

[27] Pistor V., Ornaghi F. G., Fiorio R., Zattera A. J., Oliveira P. J., Scuracchio C. H.: Devulcanization of ethylene-propylene-diene polymer residues (EPDM-r) by microwaves (in Portuguese). Polímeros, **20**, 165–169 (2010).
DOI: 10.1590/S0104-14282010005000027

[28] Pistor V., Zattera A. J.: Degradation kinetics of ethylene propylene diene terpolymer residues devulcanized by microwaves. Journal of Elastomers and Plastics, **46**, 69–83 (2014).
DOI: 10.1177/0095244312462159

[29] Scuracchio C. H., Waki D. A., Bretas R. E. S.: Thermal and rheological characterization of ground tire rubber devulcanized by microwaves (in Portuguese). Polímeros, **16**, 46–52 (2006).
DOI: 10.1590/S0104-14282006000100011

[30] Zhang X., Lu C., Liang M.: Properties of natural rubber vulcanizates containing mechanochemically devulcanized ground tire rubber. Journal of Polymer Research, **16**, 411–419 (2009).
DOI: 10.1007/s10965-008-9243-x

[31] Tripathy A. R., Morin J. E., Williams D. E., Eyles S. J., Farris R. J.: A novel approach to improving the mechanical properties in recycled vulcanized natural rubber and its mechanism. Macromolecules, **35**, 4616–4627 (2002).
DOI: 10.1021/ma012110b

[32] Jiang G., Zhao S., Li W., Luo J., Wang Y., Zhou Q., Zhang C.: Microbial desulfurization of SBR ground rubber by *Sphingomonas sp*. and its utilization as filler in NR compounds. Polymers for Advanced Technologies, **22**, 2344–2351 (2011).
DOI: 10.1002/pat.1769

[33] Gunasekaran S., Natarajan R. K., Kala A.: FTIR spectra and mechanical strength analysis of some selected rubber derivatives. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **68**, 323–330 (2007).
DOI: 10.1016/j.saa.2006.11.039

[34] Mangili I., Collina E., Anzano M., Pitea D., Lasagni M.: Characterization and supercritical CO_2 devulcanization of cryo-ground tire rubber: Influence of devulcanization process on reclaimed material. Polymer Degradation and Stability, **102**, 15–24 (2014).
DOI: 10.1016/j.polymdegradstab.2014.02.017

[35] Fernández-Berridi M. J., González N., Mugica A., Bernicot C.: Pyrolysis-FTIR and TGA techniques as tools in the characterization of blends of natural rubber and SBR. Thermochimica Acta, **444**, 65–70 (2006).
DOI: 10.1016/j.tca.2006.02.027

[36] Mui E. L. K., Lee V. K. C., Cheung W. H., McKay G.: Kinetic modeling of waste tire carbonization. Energy and Fuels, **22**, 1650–1657 (2008).
DOI: 10.1021/ef700601g

[37] Yang J., Kaliaguine S., Roy C.: Improved quantitative determination of elastomers in tire rubber by kinetic simulation of DTG curves. Rubber Chemistry and Technology, **66**, 213–229 (1993).
DOI: 10.5254/1.3538307

[38] Chrissafis K., Paraskevopoulos K. M., Stavrev S. Y., Docoslis A., Vassiliou A., Bikiaris D. N.: Characterization and thermal degradation mechanism of isotactic polypropylene/carbon black nanocomposites. Thermochimica Acta, **465**, 6–17 (2007).
DOI: 10.1016/j.tca.2007.08.007

[39] Shih Y-F., Jeng R-J.: Carbon black-containing interpenetrating polymer networks based on unsaturated polyester/epoxyII. Thermal degradation behavior and kinetic analysis. Polymer Degradation and Stability, **77**, 67–76 (2002).
DOI: 10.1016/S0141-3910(02)00080-0

[40] Prasertsri S., Lagarde F., Rattanasom N., Sirisinha C., Daniel P.: Raman spectroscopy and thermal analysis of gum and silica-filled NR/SBR blends prepared from latex system. Polymer Testing, **32**, 852–861 (2013).
DOI: 10.1016/j.polymertesting.2013.04.007

[41] Levin V. Y., Kim S. H., Isayev A. I., Massey J., von Meerwall E.: Ultrasound devulcanization of sulfur vulcanized SBR: Crosslink density and molecular mobility. Rubber Chemistry and Technology, **69**, 104–114 (1996).
DOI: 10.5254/1.3538350

[42] Garcia P. S., Scuracchio C. H., Cruz S. A.: Effect of residual contaminants and of different types of extrusion processes on the rheological properties of the post-consumer polypropylene. Polymer Testing, **32**, 1237–1243 (2013).
DOI: 10.1016/j.polymertesting.2013.08.002

[43] Dikland H. G., Sheiko S. S., van der Does L., Möller M., Bantjes A.: A scanning force microscopy study on the morphology of elastomer-coagent blends. Polymer, **34**, 1773–1775 (1993).
DOI: 10.1016/0032-3861(93)90341-7

[44] de Sousa F. D. B., Scuracchio C. H.: The use of atomic force microscopy as an important technique to analyze the dispersion of nanometric fillers and morphology in nanocomposites and polymer blends based on elastomers. Polímeros, **24**, 661–672 (2014).
DOI: 10.1590/0104-1428.1648

[45] Le H. H., Sriharish M. N., Henning S., Klehm J., Menzel M., Frank W., Wießner S., Das A., Stöckelhuber K-W., Heinrich G., Radusch H-J.: Dispersion and distribution of carbon nanotubes in ternary rubber blends. Composites Science and Technology, **90**, 180–186 (2014).
DOI: 10.1016/j.compscitech.2013.11.008

[46] Jeon I. H., Kim H., Kim S. G.: Characterization of rubber micro-morphology by atomic force microscopy (AFM). Rubber Chemistry and Technology, **76**, 1–11 (2003).
DOI: 10.5254/1.3547733

[47] Le H. H., Ilisch S., Kasaliwal G. R., Radusch H-J.: Filler phase distribution in rubber blends characterized by thermogravimetric analysis of the rubber-filler gel. Rubber Chemistry and Technology, **81**, 767–781 (2008).
DOI: 10.5254/1.3548231