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The Role of Carbon Black on Devulcanization of Natural Rubber by Microwaves

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One of the greatest problems of the modern society is the recycling of vulcanized elastomers, like tires and industrial rejects. This work studies one of the techniques of devulcanization of natural rubber (NR), the devulcanization by microwaves, as well as the influence of the amount of carbon black on this process through devulcanization of the NR with controlled composition on it. The samples were analyzed by Soxhlet extraction and some important correlations could be made based on its results and also by the final temperature of the samples just after the time of exposure to microwaves. The results highlighted that the increase of the temperature is responsible for the occurrence of devulcanization, which is dependent on both the amount of carbon black present in the rubber and the time of exposure to microwaves. These factors can influence its degree of devulcanization, since they are important for the absorption of energy by the material.

Keywords: *NR, recycling, devulcanization, microwaves*

1. Introduction

Natural rubber (NR) is naturally produced through bio-synthesis by the *Hevea brasiliensis* tree. It is constituted by approximately 99.99% linear cis-1,4 polyisoprene. The average molecular weight of polyisoprene in the NR ranges from 200.000 to 400.000, with a broad distribution. As a result of this broad molecular weight distribution, NR has also a good performance during its processing[1].

To acquire properties like elasticity and damping, elastomers have to go through a complex process known as vulcanization; the process in which the elastomers are mixed with chemicals to reduce their plasticity, tackiness and sensitivity to heat and cold, as well as to aggregate the useful properties such as elasticity and mechanical resistance[2]. This process converts, chemically, independent polymeric chains of elastomers into a three-dimensional elastic network[1]. However, while the vulcanization provides improvements in the properties of the elastomers and, with it, the possibility of a wide use as consumer goods, it brings difficulties for recycling after use, once the vulcanized rubber becomes a thermoset polymer, preventing its subsequent molding into another product by heating[3].

Devulcanization is a way of providing energy to destroy, total or partially, the three-dimensional network formed during vulcanization[4]. The known methods that use different ways to promote the devulcanization of rubber include thermo-mechanical, thermo-chemical and mechano-chemical[5-9], physical (by microwaves[3,10-20] and ultrasound[21-29]) and biochemical[30-33]. All of them involve complex transformations that lead to depolymerization, oxidation, and in many cases, the degradation of polymeric chains of rubber, with the consequent reduction on its viscosity[34].

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The microwave devulcanization is currently one of the most promising techniques, because the good properties of the devulcanized material and the possibility of high productivity. The process takes advantage of volumetric heating of the material by microwaves, promoting a more uniform heating than that achieved by more traditional methods of heating, which depend on conduction and/or convection[14,15,35]. Materials behave differently when exposed to an electromagnetic field, like the one generated by microwaves. In polar materials, molecules or free ions can create a momentum of dipole, which results in the volumetric heating throughout the mass of the material. Elastomers such as NR, ethylene propylene diene monomer rubber (EPDM) and styrene-butadiene rubber (SBR) have low microwaves absorption capacity. This limitation can be overcome by the addition of a conductive filler like carbon black[36,37], that induces a phenomenon known as Maxwell-Wagner polarization[13,38]. The process has physical nature, i.e. it does not involve chemicals during the process and due to this reason is named ecofriendly[39]. Devulcanization of elastomers by microwaves shows promising results for recycling rubber[3,10,12-18,40].

The main technique of characterization of devulcanized rubber has been through Soxhlet extraction[41,42]. This technique is widely mentioned by the literature to detect the status of devulcanization of elastomers[4,5,14-16,24,31,32,39,41,43-52]. In general, the content of soluble material (sol) increases with the increasing of devulcanization degree, due to the breaks of the cross-linkings and, consequently, the release of these molecules from the three-dimensional network of vulcanized rubber. Although the insoluble part (gel) still makes part of the network, typically the devulcanization process tends to decrease the cross-linkings density, making even this part more easily moldable and breakable than the original

vulcanized rubber[21]. According to Yashin & Isayev[23], as a result of devulcanization, the rubber contains a significant amount of sol, that allows the rubber to be reprocessed and revulcanized in order to obtain a usable material with reasonably good mechanical properties.

Scuracchio et al.[14,15] studied the characteristics of ground tire rubber (GTR) after devulcanization by microwaves at different exposure times. It was noted that, the greater the exposure time of the sample to microwaves, the greater the final temperature just after the treatment and, also, the lower the gel content verified by Soxlhet extraction. In other words, the higher the time of exposure of the rubber to microwaves, the higher its degree of devulcanization. Similar results were obtained by Zanchet et al.[16], who analyzed the devulcanization of SBR by microwaves. According to the authors, the exposure time of the sample to the microwaves had a strong influence on the gel content, since for longer exposure times the material reached higher temperatures and generated materials with lower insoluble portion (gel content). A different behavior was observed by Pistor et al.[13], who analyzed the properties of EPDM devulcanized by microwaves. For exposure times until 4 minutes, no significant changes in the gel content values were observed. Only exposure times to 5 minutes showed some changes in gel content.

In this work, special attention is paid to the influence of the carbon black amount present in the NR in the devulcanization process by microwaves, through the study of the devulcanization of NR with controlled composition of carbon black. It is important to bear in mind that the carbon black in the rubber is the responsible for the heating of these materials when exposed to microwaves, and the understanding of the mechanisms that occur during the devulcanization includes the role of the carbon black during the process.

2. Experimental

2.1. Materials

NR with controlled composition of carbon black (0, 20, 45, 60 and 80 phr) was kindly supplied by IPAB SA. The carbon black used was type N330 according to ASTM classification (ASTM D1765-14)[53]. The exact composition of the samples is not known, except the amount of carbon black. All composites have the same additives and the same amount for all the samples; they are vulcanized.

2.2. Devulcanization of NR

NR was devulcanized in a system comprised of a conventional microwave oven adapted with a motorized stirring system with speed control[14]. The speed of stirring was set at 40 rpm. The devulcanization process was done by using the maximum power of the oven (700 W). The time at which the material was exposed to microwaves ranged from 2 to 5 minutes. The temperature after devulcanization was measured by using a rod thermometer.

The nomenclature used in this work is type NRX, where NR represents the type of rubber used and X represents the amount of carbon black present in the sample (in phr), ranged in 0 (NR0), 20 (NR20), 45 (NR45), 60 (NR60) and 80 phr (NR80).

2.3. Characterization

Granulometric analysis of the samples of NR0 and NR80 was performed according to ASTM D5644-01[54].

In order to verify the influence of the amount of carbon black and the exposure time of NR to microwaves on devulcanization, gel content of devulcanized NR with controlled composition of carbon black was analyzed by performing Soxhlet extraction, by using toluene as solvent. The extraction time was 24 h and it was performed by using approximately 5 g of material. After the extraction, the material and the thimble filter were dried for 24 h at 80 °C and its mass was measured.

3. Results and Discussion

3.1. Granulometry

The granulometric analysis of the NR0 and NR80 is shown in the Figure 1.

According to the Figure 1, it can be seen that the NR80 has a more refined granulometry in comparison to the compound NR0. Due to the presence of carbon black in NR80, rubber was probably more rigid and, thereby, easier to grind, resulting in a rubber with smaller particle sizes. So, the higher stiffness promoted by the presence of carbon black in the vulcanized sample, the easier the grinding process.

However, the difference of the particle sizes (Figure 1) is supposed not to have a significant effect on the devulcanization process, since the microwave heating is volumetric and less dependent on heat conduction.

3.2. Temperature measurements after treatment

Temperatures of the NR with controlled composition of carbon black after the time of exposure to microwaves are shown in Table 1.

In general, it can be observed the increase of the temperature of the samples with the increase of the time of exposure to microwaves, as also observed by other authors[3,14,15,18]. Besides, it can be verified a trend towards the increase of the temperature of NR after the treatment as the amount of

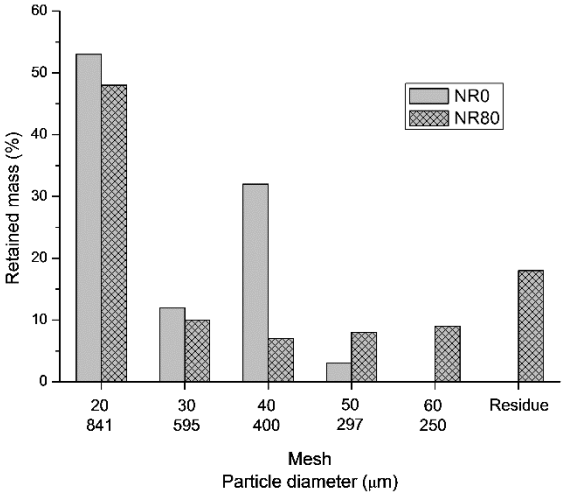

Figure 1. Granulometric analysis of the NR0 and NR80.

carbon black in the rubber got higher. As carbon black is a conductive filler[13,36,37], it can absorb microwave radiation and converts this energy into heat[3,18]. So, by increasing the amount of carbon black in the NR, more microwave energy is absorbed.

Even in the sample containing no carbon black, heating was observed, but it was much smaller in comparison to the samples containing this filler. The heating of the NR0 probably happened due to the presence of some residue of any other chemical substance used during vulcanization, since the real composition of the rubber is not known.

3.3. Gel content

Table 2 shows the results of Soxhlet extraction of the samples.

As mentioned before, extraction technique is able to separate the insoluble fraction of the rubber (known as gel fraction - vulcanized part) of the soluble fraction (sol fraction - devulcanized part). So, the gel content is an index to evaluate the degree of vulcanization of the rubbers[18]. In general, the higher the sol fraction, the more efficient the devulcanization process is[5,15,55].

According to the Table 2, in general, it could be observed that the gel contend decreased with the increasing of the exposure time of the NR to microwaves, as well as with the increasing of carbon black content present in the sample. These results show that the vulcanized rubbers were devulcanized by the action of microwaves, and the carbon black acting as a conductive filler was really efficient, increasing the efficiency of the process in the samples as its content increases.

It is important to point out that, during heating, the oil can evaporate when the rubber reaches high temperatures. As the exact quantity of oil is the one detected for the untreated sample, the value of the soluble phase can be even greater than the one obtained through the analysis of Soxhlet extraction, being that the process has been, in fact, more efficient. According to Scuracchio et al.[14], the existence of some part soluble in toluene even for the sample with no treatment by microwaves is probably due to the presence of auxiliary process oils in the rubber.

The interaction of charged particles in some materials with the electric field component of electromagnetic radiation causes heating on the material[38]. Carbon black presents a sufficient electrical conductivity to promote this interaction between the wave and the material[36]. In the case of dielectric solid materials with charged particles, which are free to move in a delimited region of the material (such as π-electrons in carbon black), a current traveling in phase with the electromagnetic field is induced. As the electrons cannot couple to the changes of phase of the electric field, heat is the result of dissipated energy (Maxwell-Wagner effect[56,57]).

The ability of a microwave absorber material to be heated in the presence of a microwave field is defined by its dielectric loss tangent (Equation 1):

$$\tan \delta = \varepsilon'' / \varepsilon' \quad (1)$$

The dielectric loss tangent is composed of two parameters, the dielectric constant (or real permittivity), ε′, and the dielectric loss factor (or imaginary permittivity), ε″. ε' quantifies the efficiency with which the electromagnetic energy is converted to heat[38,58,59]. The tan δ value of carbon black is between 0.35-0.83[60,61].

Pistor et al.[12] studied the devulcanization of EPDM by microwaves and the influence of paraffinic oil in the process. They observed higher temperatures in the samples without paraffinic oil due to an increase in carbon black content and absence of evaporation or degradation of oil. According to the authors, carbon black has high thermal conductivity and heat capacity, what permit greater accumulation of internal energy and a better distribution of energy in the material. In the same way, some authors analyzed the conductivity of elastomers or blends based on elastomers containing carbon black. The conductivity got higher as the amount of filler present in the samples increased[62-67], especially after

Table 1. Temperatures of the samples immediately after the microwaves treatment.

Exposure time of NR to microwaves (min)	Temperature (°C)				
	NR0	NR20	NR45	NR60	NR80
2	56	66	101	109	166
3	74	94	153	175	244
4	80	117	185	271	250
5	103	138	217	280	307

Table 2. Gel content of the samples of NR with controlled composition of carbon black.

Exposure time of NR to microwaves (min)	Gel content (%)				
	NR0	NR20	NR45	NR60	NR80
0	83.04	80.38	89.52	82.70	80.09
2	79.19	80.31	82.26	79.77	79.66
3	78.43	79.37	79.91	76.74	64.93
4	78.29	78.82	77.71	65.45	59.17
5	77.51	77.84	60.32	53.61	55.09

achieving the percolation threshold, showing its efficiency as a conductive filler.

The presented results are in agreement with other authors[3,18,68], who studied the influence of variation of the carbon black content present in SBR on its devulcanization by microwaves. According to them, the degree of devulcanization by microwaves is proportional to the amount of carbon black on the rubber. In other words, the electrical conductivity of rubber increases with the increase of the amount of carbon black due to the higher energy absorbance.

In order to deepen the analysis of the results, Figure 2 presents the correlation between temperature of the samples after exposure to microwaves and gel content.

From the results presented in the Figure 2, a correlation between the temperature of the samples just after the treatment and the gel content obtained by Soxhlet extraction technique can be seen. In general, the higher the final temperature of the sample, the smaller its gel content, what proves that the devulcanization of the rubber was obtained. Then, the temperature rise is responsible for the occurrence of devulcanization. According to Hirayama & Saron[18], "the heating of material, due to the presence of carbon black, is the main factor that leads to devulcanization, which is confirmed by an increase in the temperature of the rubber as a function of carbon black content in the material". Based on the results found, it could be concluded that the time of exposure of the sample to microwaves has also great value, what can be highlighted from the analysis of the Figure 3.

According to the Figure 3, it is clear the dependence of the degree of devulcanization with the time of exposure of NR to microwaves. The devulcanization process is efficient from 3 minutes (or more) of exposure to microwaves, and depending on the content of carbon black present in the sample, the efficiency level of the process can be improved.

According to some authors[3,18], the degree of devulcanization (Equation 2) can be calculated by the difference between gel content of the devulcanized rubber (DR) and the one of vulcanized rubber (VR).

$$Degree\ of\ devulcanization = -(DR - VR) \quad (2)$$

The results of the degree of devulcanization of the NR with controlled composition of carbon black are showed in the Figure 4. It is noted, in general, that there is a tendency of the increase of the degree of devulcanization values as function of the amount of carbon black present in the rubber, and as function of the increasing of the exposure time of NR to microwaves. In addition, according to the Figures 2 and 3, it could be observed that the relevant amount of carbon black able to improve the process of devulcanization by microwaves is from 45 phr. Smaller quantities seem not to have influence on the process. According to Paulo et al.[3], the amount of carbon black is an important factor to achieve a successful recycling by using devulcanization by microwaves.

As the increase of the final temperature of the compound is the responsible for devulcanization, the amount of carbon black and exposure time of the sample to microwaves are able to cause its increase, which is reflected in the degree of devulcanization. The final temperature reached by the sample is the determining factor for the degree of devulcanization, being dependent on the time of exposure of the sample to microwaves and the amount of carbon black present on it.

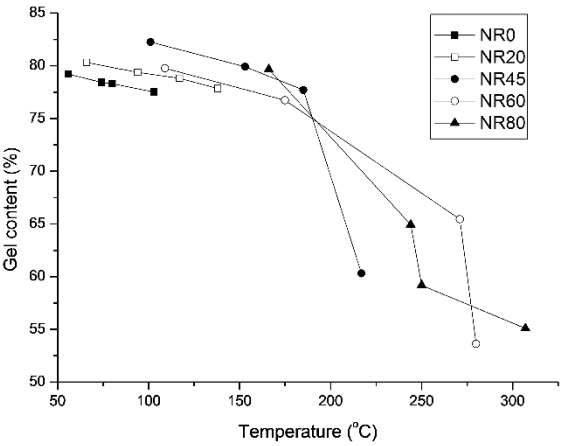

Figure 2. Gel content *versus* temperature of the samples after exposure to microwaves.

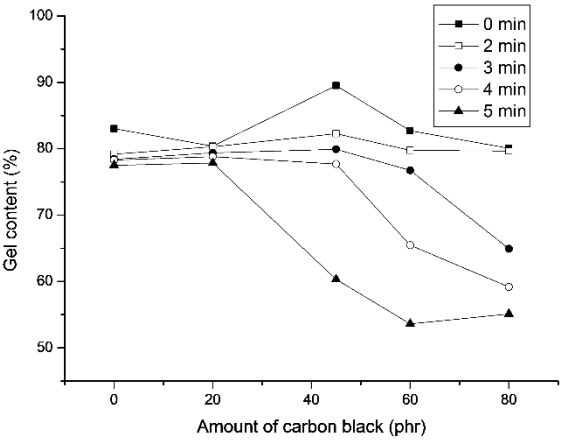

Figure 3. Gel content *versus* amount of carbon black of the samples after different times of exposure to microwaves.

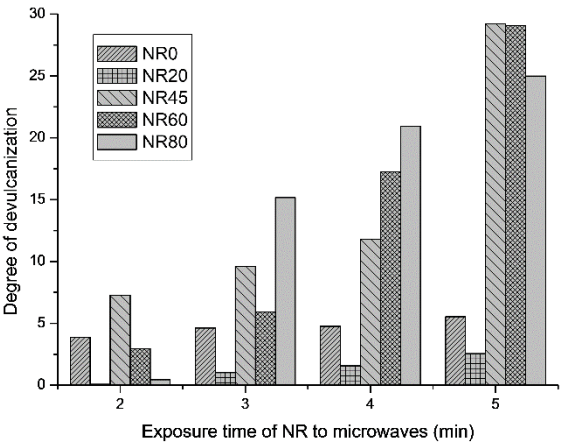

Figure 4. Degree of devulcanization of the NR with controlled composition of carbon black.

4. Conclusions

The compound containing carbon black (NR80) was easily ground and presented a more refined granulometry in comparison to the compound containing no carbon black (NR0).

The amount of carbon black present in the rubber, as well as the time of exposure of NR to microwaves, are able to influence its devulcanization degree. The temperature of the NR, immediately after the time of exposure to microwaves, increased as the amount of carbon black present in the sample, as well as the time of exposure to microwaves got higher. As the increase of the temperature is the responsible for the occurrence of devulcanization, both factors are important. The gel content of the samples decreased as the treatment time and carbon black content increased.

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