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Revulcanization kinetics of waste tire rubber devulcanized by microwaves: Challenges in getting recycled tire rubber for technical application

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ABSTRACT

Recycling is a process towards sustainable development. However, it does not do any good to recycle a material trying to contribute to the environment, if the final properties of the recycled material do not point to a feasible application. In this sense, the purpose of the present study is to evaluate the kinetics parameters of the revulcanization reaction of ground tire rubber (GTR) devulcanized by microwaves using rheological (ODR) and differential scanning calorimetry (DSC) methods. For ODR, torque *versus* time curves was obtained at 160, 170, 180, 190 and 200°C and simulated. In general, occurred a decrease in activation energy values upon microwaves exposure time but all the samples showed an autocatalytic model from simulation curves. For DSC, three different models were used: Kissinger, Ozawa, and Flynn-Wall-Ozawa. All the methods showed a trend to decrease the activation energy by microwave exposure time as noticed in the rheological curves. Among the reasons, the carbon black and the viscosity of the system are the main contributors; the former by radiation tends to oxidize and facilitates the degradation process, and the latter achieves more facility to chain mobility, reducing the activation energy.

Keywords: ground tire rubber, devulcanization, revulcanization, kinetics, microwaves.

Highlights

- Revulcanization kinetics of ground tire rubber devulcanized by microwaves.
- Autocatalytic degradation mechanism obtained for all the samples.
- The higher the carbon black content, the lower the thermal energy for revulcanization.
- Revulcanization process was responsible for the oxidation of the carbon black.
- Successful simulation of rheometric curves using *F-test* powerful statistical tool.

Introduction

The production of elastomeric artifacts generates a large amount of vulcanized waste. Consequently, the environmental issue is a serious problem, involving high costs and the disposal of a material with high commercial value. Rubber waste recycling presents important consequences, including environmental protection, energy conservation, and supply of industrial raw material, being an example of sustainable action. In addition, recycling is considered a category of green chemistry, i.e., the use of renewable or recycled sources of raw material.[1] Especially concerning the incorrect final disposal of end-of-life tires, their recycling concerns not only to the attempt to reduce the environmental impact, but also it is a fundamental attitude on improving the quality of public health, since they are appropriate places to accumulate rainwater in which vectors, such as *aedes aegypti* mosquito can proliferate. It is known how dangerous this mosquito is, since it can transmit, until now, four different and serious diseases, such as dengue, chikungunya, zika and yellow fever.

An attractive recycling alternative is devulcanization by microwaves, bringing quite a lot of advantages such as: *(i)* a more uniform heating promoted by the volumetric heating of the material by microwaves than that one achieved by traditional heating methods, being that they depend on the conduction and/or convection;[2–4] *(ii)* it has physical nature, where chemicals are not involved in the process; *(iii)* a high productivity is reached due to the application of high amount of energy to the material in a short time;[2] and *(iv)* the possibility of a continuous process, and the easy modification of the process parameters.[5] Hence, the process is considered an eco-friendly technology in the present times.[6] One of the main features of the devulcanized elastomer is its ability to flow again, and therefore be remolded and revulcanized. Many works show the characteristics of the elastomers when subjected to the process of devulcanization by microwaves.[7–16]

However, the revulcanization is a process even more complex than the vulcanization itself, as new parameters are inserted into the process and can influence it.[17] So, several factors can influence the rate at which the vulcanization reaction occurs. In particular, the devulcanization process can cause the scission of the polymeric chains, which tends to increase the revulcanization reaction rate. A similar trend was observed by several authors.[18–23] Also, when considering a specific polymeric blend as ground tire rubber (GTR), the devulcanization may degrade an elastomeric phase in a higher degree,[9] and thus may, considerably, increase

the amount of carbon black in the sample (modifying the carbon black/elastomer ratio). The revulcanization process may oxidize the carbon black, and if it occurs, this oxidation favors the revulcanization due to the considerable increase in its surface area.[24,25] Therefore, the parameters of the devulcanization process need to be carefully studied for future reuse, since further polymeric degradation occurs during the revulcanization step.[26] In other words, it is essential to avoid excessive degradation during the devulcanization step so the final revulcanized material can be used in technical applications.

Vulcanization kinetics studies provide the kinetics coefficients necessary to predict possible responses of rubber compounds for any type of deformation encountered during the processing.[27] The vulcanization can be studied by several techniques including the differential scanning calorimetry (DSC) and oscillatory rheometry (ODR). Studies on the vulcanization kinetics by DSC have shown that the vulcanization enthalpy can be linearly related to the quantity of elementary sulfur of the formulation.[28] According to Ismail et al.,[29] the residual accelerator can act as a sulfur donor, which accelerates the early stages of the vulcanization process, but little is known about the influence of the devulcanization by microwaves in these compositions. The determination of kinetics parameters of the vulcanization is useful to predict its cross-linking profile, which plays a crucial role in the final properties of the artifact. The DSC technique is based on the hypothesis that the reaction heat is related solely to the reaction of the cross-linkings formation and it is proportional to the extent of the reaction, which in complex systems is often questionable. The chemical analysis involves a considerable number of reactions and excessive time consumption. On the other hand, the study by rheometry is based on the fact that the cross-linking density is proportional to the torque recorded during the vulcanization of the elastomeric compositions.[28] The apparent activation energy (E_a) for rubber compositions can be obtained from rheometric data, where it is assumed that the vulcanization follows a first-order kinetics.[28]

The importance of a complete kinetics analysis is widely known in the literature.[30–32] It allows predicting, among other parameters, the dependence of the Arrhenius parameters with conversion, degradation model and degradation mechanism. These parameters are of extreme importance since they allow to create a new model-fitting based on physical and/or chemical characteristic[33,34] of a determined material, and to predict the behavior of the material under specific use conditions[35] in times experimentally inaccessible. The majority of the studies consider a first-order model for kinetics considering the global

reaction. Nevertheless, they did not study kinetics models based on statistical tools as the *F-test* method which statistically compares each of the most solid-state kinetics models found in the literature.[36,37] Recent literature studies show that the study performing model-fitting methods as the *F-test* seems to have a more reasonable physical/chemical meaning in comparison to the model-free methods.[38–41]

The present study has as objective to evaluate the revulcanization kinetics study by ODR and DSC of GTR previously devulcanized by the action of microwaves, at different exposure times. In order to deeply understand the effect of the microwaves under GTR compounds, a complete investigation of the influence of the temperature and the carbon black/polymer ratio was performed since it has a great influence on the final properties as visualized in earlier studies.[9,26] The results depicted the influence of the carbon black amount, as well as the possible increase of its superficial area due to oxidative processes, on the revulcanization process of GTR. The recycling of GTR, according to parameters adopted in the present work, besides being a sustainable action, is included in different principles of green chemistry, presenting several advantages. However, for the recycled material to be used in technological applications, it is essential the deep knowledge of the aspects of the material/processing which influence its final properties. So, this is the major challenge of using GTR, since its initial real formulation is not known, being the main goal of this work.

Experimental

Materials

Ground waste truck tire (GTR), separated from non-elastomeric components (as received), rubber accelerator N-tert-butyl-2-benzothiazole sulfenamide (TBBS) and sulfur were kindly supplied by Prometeon Pneus Ltd. The exact recipe of the GTR is not known.

Devulcanization of GTR and mixture with vulcanization additives

The GTR was devulcanized in a system comprised of a conventional microwave oven adapted with a motorized stirring system with speed control. The whole devulcanization process was done by using the

maximum power of the oven, i.e., 820W. The time at which the material was exposed to microwaves ranged from 3, 4, 5, and 5.5 minutes.

The devulcanized GTR was mixed with the vulcanization additives by using a laboratory two roll mill PRENMAR for approximately 6 minutes at room temperature, in which were added 1 phr of accelerator TBBS and 1 phr of sulfur.

The nomenclature adopted is: for devulcanized samples, type GTRX; and for revulcanized samples, type GTRX+ad, where 'X' denotes the exposure time of the sample to the microwaves and '+ad' is related to the presence of the vulcanization additives.

Characterization

Rheological measurements were performed on the devulcanized samples to study their revulcanization characteristics, by using an RPA Tech Pro, model Rheo Tech MDPT, according to ASTM D 1646-07. Curves of torque *versus* time were obtained at 160, 170, 180, 190 and 200° C. Rheological properties were obtained from rheological tests at 180°C, such as optimum vulcanization time - t_{90} (time to achieve 90% of the maximum torque); scorch time - ts_1 (safety time); maximum torque - *MH* (related to the molecular stiffness); minimum torque - *ML* (proportional to the initial viscosity); and $\Delta M = MH - ML$, correlated to the cross-linking density.

Revulcanization kinetics study

The vulcanization process of elastomers is quite complex and various techniques have been developed to monitor and to analyze the formed products.[42] Some techniques which have been widely used are the oscillating disk rheometry (ODR) and differential scanning calorimetry (DSC).

Rheometric measurements are based on the fact that the cross-linking density is proportional to the stiffness of the rubber and its calculation is based on dynamic viscoelastic properties obtained in tests with equipment that accompany the vulcanization process. On the other hand, DSC follows through the enthalpy

changes in the physical and chemical events, being these fluxes endo- or exothermic, i.e., it determines the gain/loss of energy required during the vulcanization reactions.[43]

It is well known that the vulcanization reaction converts raw rubber into vulcanized rubber. So, it can be assumed that such reaction follows the stoichiometry of a simple first-order reaction of the type: R → P, where R denotes the reagents and P, the products of the chemical reaction.[44] In the case of the present work, R denotes devulcanized GTR, and P revulcanized GTR, through revulcanization reaction. Recent literature shows that the autocatalytic model achieved for other materials can be applied in our case because of a more realistic physical meaning,[38–41] following the same degradation model as mentioned before.

Revulcanization kinetics study by ODR

Rheometry can provide the apparent activation energy (E_a) of rubber compounds. If $n = 1$, i.e., a first-order reaction, the conversion equation of reagents in products can be expressed as:

$$\frac{dx}{dt} = k\,(1 - x) \qquad \text{Equation 1}$$

where dx/dt is the conversion rate of reagents to products and k is the rate constant for the reaction.[45]

Equation 1 can be written in terms of torques measured by rheometry:

$$\ln\left(\frac{MH - ML}{MH - M_t}\right) = kt \qquad \text{Equation 2}$$

where MH and ML are the maximum and minimum torques measured, respectively; M_t is the torque measured in a time t and k is the rate constant of the reaction.[28,46] To obtain Equation 3, Equation 2 is combined with Arrhenius equation, being used to calculate E_a:[28,46]

$$\frac{E_a}{R} = ln\left[\frac{ln\left(\frac{(t_{45\%} - t_{25\%})_\beta}{(t_{45\%} - t_{25\%})_\alpha}\right)}{\left(\frac{1}{T_\beta} - \frac{1}{T_\alpha}\right)}\right] \qquad \text{Equation 3}$$

where R is the gas constant, $t_{25\%}$ and $t_{45\%}$ are the times corresponding to 25% and 45% of the MH, respectively, and T_α and T_β are the isothermal temperatures.

Torque *versus* time curves were simulated by using Netzsch Thermokinetics Software using advanced statistical analysis and considering first-order kinetics as found in the literature.[44] The degradation mechanism models contain classic models for homogeneous reactions and for typical solid

reactions.[30,36,37,47,48] Fitting of selected model(s) is commonly accomplished by minimizing the difference between the experimental and theoretical data. To find the most probable kinetics model, the method of least squares and the *F-test* is used.[39,41,49] The use of a statistical model-fitting method for ODR to study kinetics revulcanization is a novelty in the literature.

Revulcanization kinetics study by DSC

For the analysis of the vulcanization reactions of the GTR, a dynamic method was performed using samples with a mass between 5-10 mg. Dynamic tests were carried out in heating rates of 5, 10, 20 and 40°C.min^{-1}, and from the obtained curves, were determined the vulcanization enthalpy (ΔH_v) and the maximum vulcanization temperature (T_{max}). The T_{max} values represent the temperature where the speed of reaction is at a maximum and they were used in the determination of the E_a of the vulcanization. The methods studied are described below.

Flynn-Wall-Ozawa method (FWO)

Flynn and Wall[50] and Ozawa[51] proposed the so-called isoconversional method (FWO) by using DSC curves aiming to determine kinetics parameters of reactions. This method is based on the Doyle approximation[52] for heterogeneous chemical reactions and it is represented by Equation 4:

$$log(\varphi) = log\left(\frac{AE_a}{R}\right) - log\left(g\big(\alpha(T)\big)\right) - 2.315 - 0.4567\ \frac{E_a}{RT} \qquad \text{Equation 4}$$

where: $g\big(\alpha(T)\big)$ is a function of the conversion, E_a is the apparent activation energy, R is the gas constant, A is a pre-exponential factor, φ is the heating rate and T is the absolute temperature. By the isoconversional principle of FWO, it assumes that the reaction rate is only a function of the temperature. So, for different heating rates, a linear relationship is observed through the graph of log (φ) *versus* $1/T$, and the apparent activation energy obtained from the slope of the linear fit.[53] The activation energy calculated by the FWO method, through the analysis of DSC, is called apparent activation energy, as it is the sum of the activation energies of the chemical reactions and the physical processes that occur.

Kissinger

The Kissinger method (Equation 5) is based on the peak temperature (T_p) of the derivative thermogravimetric (DTG) curves, where the reaction rate is maximum. By using this method, E_a is calculated from the slope of the graph $\ln\left(\frac{\beta}{T_{p^2}}\right)$ *versus* $1/T_p$, where the angular coefficient is $\frac{E_a}{RT_p}$. The Kissinger method provides highly reliable values of activation energy. DSC analyses conducted in multiple heating rates are carried out to estimate the peak temperature in exothermic curing.[54]

$$ln\left(\frac{\beta}{T_{p^2}}\right) = ln\left(\frac{AR}{T}\right) - \frac{E_a}{RT_p} \qquad \text{Equation 5}$$

Osawa

The Ozawa method is another way to obtain the kinetics parameters of the reaction. In this method, the logarithm of the heating ratio (β) is plotted as a function of the inverse of the temperature transition. The activation energy is also calculated by this method through the angular coefficient of the line between the points obtained by linear regression. Equation 6 is used in the Ozawa method for the calculation of the activation energy.[55]

$$ln\beta = \frac{E_a}{RT} - lnA \qquad \text{Equation 6}$$

Results and discussion

Revulcanization behavior

Representative torque *versus* time curves at 180°C of devulcanized GTRs containing vulcanization additives are shown in Fig. 1. This temperature was adopted since it was used to revulcanize the same samples in our earlier work.[26]

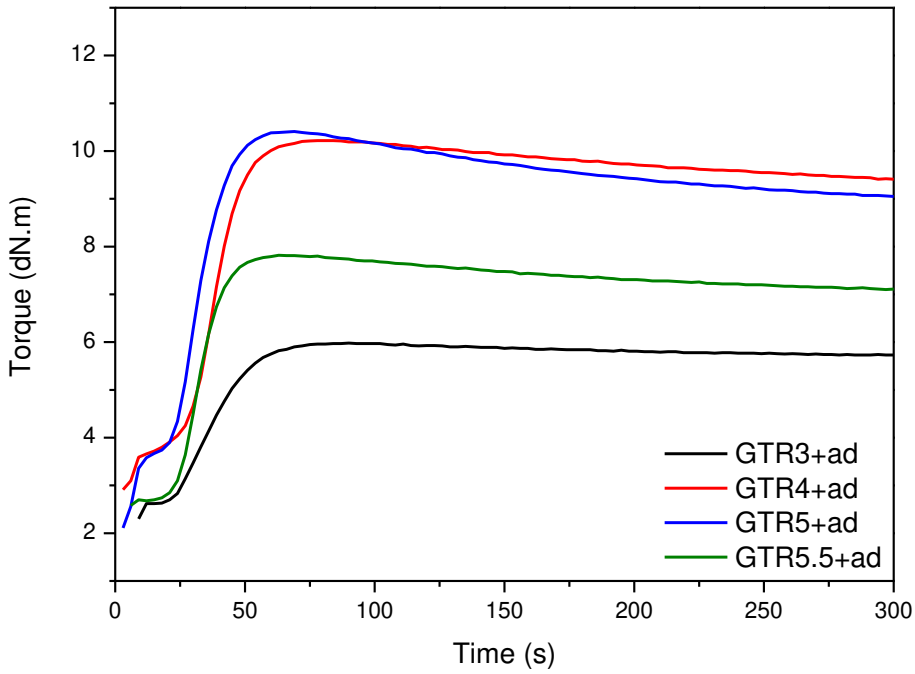


Fig. 1. Torque *versus* time curves of the devulcanized GTRs at 180°C.

The "shoulder" at the beginning of the analysis (up to 25 s) is referred to the compression of the material, and the further increase in the torque is related to the revulcanization process. The revulcanization parameters from torque *versus* time curves are shown in Table 1.

Table 1

Revulcanization behavior parameters of the analyzed samples.

Sample	t_{90} (min)	t_{s1} (min)	*ML* (dN.m)	*MH* (dN.m)	Δ*M* (dN.m)	*CRI* (min^{-1})
GTR3+ad	0.94	0.53	2.62	5.99	3.37	2.44
GTR4+ad	0.86	0.50	3.71	10.22	6.51	2.78
GTR5+ad	0.76	0.42	3.67	10.41	6.74	2.94
GTR5.5+ad	0.73	0.45	2.64	7.82	5.18	3.57

In general, it could be observed that the optimum vulcanization time represented by t_{90} and the scorch time represented by ts_1 (time of the reaction onset) were lower with higher microwave exposure times. Several authors[12,13,18,19,29,56,57] attributed such behavior to the presence of residual vulcanization additives related to the first vulcanization reaction - a characteristic behavior of recycled rubbers. Carbon black contains a large number of other elements on its surface, such as oxygen, hydrogen, nitrogen and sulfur,[58,59] which may influence on the revulcanization reaction by reducing ts_1 and t_{90} values. According to Ismail et al.,[29] the residual accelerator can act as a sulfur donor, which speeds up the early stages of the vulcanization process and reduces ts_1 value. The behavior may also be due to the devulcanization itself, i.e., with the reduction of the cross-linking density, the mobility of polymeric chains increases promoting greater availability and number of effective collisions among the molecules, resulting in the larger speed of the revulcanization reaction.[12,13] Such behavior can also be attributed to carbon black/polymer ratio[9,60] due to the increase of the relative carbon black amount in the samples due to degradation processes of NR and styrene butadiene rubber (SBR) during the recycling processes (devulcanization and revulcanization).[26] In order to study this possibility, a correlation between the carbon black amount (from thermogravimetric analysis present in our earlier work[26]), ts_1 and t_{90} values is shown in Fig. 2. According to it, the revulcanization reaction is accelerated by the increase of the carbon black amount. The same behavior was previously observed by other authors, which facilitates the vulcanization reaction by promoting the reduction of the t_{90}.[61]

Also, the reduction of the ts_1 and t_{90} values may be due to the increase of the superficial area of carbon black due to the oxidation processes (more details will be given in the sequence). Li et al.[25] depicted that the surface area of carbon blacks strongly affects the vulcanization and the physical properties of ethylene-propylene-diene rubber (EPDM)/carbon black composites, due to physical cross-linkings between rubber/filler, which hinder the mobility of rubber chains and restrain its deformation.

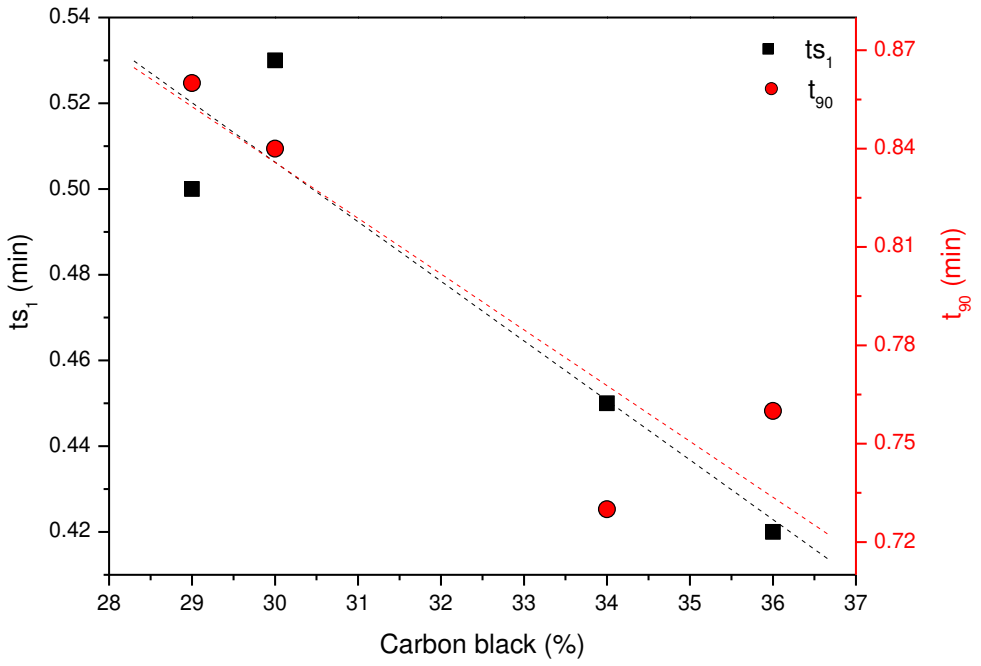


Fig. 2. Correlation between the carbon black amount, ts_1 and t_{90} values.

MH represents the measure of molecular stiffness, proportional to the formation of the cross-linkings.[57] *ML* is proportional to the initial viscosity. *MH* and *ML* reduction for GTR5.5+ad may be due to the degradation of the main polymeric chains and/or to the reduction in the amount of oil present in the sample due to its evaporation during the recycling processes. According to some authors,[57,62] *MH* and *ML* reduction can be attributed to the reduction of the size of the main polymeric chains during the devulcanization process (degradation), or due to the reduced initial viscosity of the rubber due to the breaking of the three-dimensional network of the vulcanized GTR.

The exposure of the carbon black to the microwaves possibly increased the amount of oxygen absorbed on its surface due to oxidative processes. Also, the interaction between the carbon black and the elastomer depends not only on the energy of the filler surface but also on the elastomer structure. Thus, polar elastomers have greater interaction with carbon black,[63] especially when oxidized. In our earlier work,[26] it was clearly demonstrated the change of the revulcanized GTR structure in relation to GTR devulcanized by microwaves, with lower thermal stability especially of the SBR phase and the formation of a new phase not yet completely known (450-465°C) which, among other possibilities, may result from the strong interaction

between SBR and the oxidized carbon black. In addition, Roychoudhury and De[58] showed that oxidized carbon black was more effective in the formation of additional bonding with epoxidized natural rubber (ENR) at elevated temperatures. Thus, the greater interaction of carbon black/elastomer and the possible formation of bonds, and the degradation of the polymeric chains may facilitate the dispersion of the carbon black in the elastomeric matrix, and reduce the viscosity of the compound, influencing the *ML* values. So, such values may not be correlated simply with the variation in the carbon black amount present in the compound (from results of thermogravimetric analysis[26]).

Devulcanization by microwaves results in a higher level of natural rubber (NR) phase degradation, due to its affinity by the carbon black.[9,60] Also our previous results[26] depicted the additional degradation on the NR phase, the degradation of the SBR phase during revulcanization, and the increase of the carbon black amount resulted from the adopted recycling processes (devulcanization and revulcanization), being that all of them may have influenced on the obtained results. Additionally, the GTR5+ad curve presents a reversal trend, which suggests degradation.[10] More attention on the reversion behavior will be given in the sequence. Besides, the increase of *MH* and *ML* values, observed in the GTR4+ad and GTR5+ad samples can be due, possibly, to the coexistence of two reticulation networks, the first one remained from the initial GTR cross-linkings (cross-linkings not broken during the devulcanization process) and the second from the revulcanization.[64]

ΔM followed the same trend of *MH* and *ML* values. This value is related to the cross-linking density. All the possibilities mentioned above to the *ML* and *MH* values are also valid here. In addition, our previous work[9] depicted the modification in the chemical structure of the GTR as a result of the devulcanization by the action of the microwaves, which probably influenced the revulcanization process of the samples.

CRI values (Cure Rate Index) increased as the exposure time of the samples to the microwaves increased. CRI values were calculated according to Equation 7:

$$CRI = \frac{1}{t_{90-}ts_1} \qquad \text{Equation 7}$$

where t_{90} is the optimum vulcanization time and ts_1 the scorch time.

The *CRI* value is proportional to the average slope of the torque *versus* time curve, i.e., proportional to the speed of rubber revulcanization.[65] The results of extraction and swelling of the devulcanized samples[9] corroborated to *CRI* values, since the higher level of cross-linkings breakup probably has increased the freedom degree of the chains during the revulcanization reaction, which speeded up the reaction. The increase may also be influenced by the presence of residual additives from the first vulcanization process. As mentioned above, the increase of the carbon black amount as a result of the recycling processes[26] may have influenced the reaction rate as well, since this filler has a high specific surface.

The carbon black porosity can be divided into two categories, open and closed porosity. The open porosity may be in the form of small pores on the nanometric order, an undefined shape on the surface that may or not lead to internal voids. This type of porosity strongly influences the increase in the external surface of the filler.[66] As observed in our early work,[26] it is possible that carbon black has suffered some oxidation degree as a result of the GTR recycling processes. Kamegawa et al.[24] have studied the oxidative degradation of carbon black and the main conclusions were: (*i*) increase of the density of carbons upon oxidation; (*ii*) formation of oxygenated functional groups; (*iii*) removal of amorphous carbon; and (*iv*) change of closed pores into open ones. According to Papirer et al.,[59] by oxidation processes of carbon black in air, the surface area of the carbon black increased dramatically due to the generation of microporosity. The increase of the cross-linking density would be caused by the change of the closed pores into open pores by crevasses formation, which increased the surface area. All the mentioned factors may have influenced the obtained results. In the same way, the reduction of ts_1 and t_{90} values may be due to the increase of the superficial area of the carbon black, as a result of the oxidation processes.

The percentage of reversion *R* is defined as (Equation 8)[67]:

$$R = \frac{(MH-Mt).100}{(MH-ML)} \qquad \text{Equation 8}$$

where: MH is the maximum torque, Mt is the torque at a time t (300 s) and ML is the minimum torque on the rheometer.

A correlation between the carbon black amount (from the thermogravimetric analysis presented in our earlier work[26]) and the percentage of reversion is shown in Fig. 3.

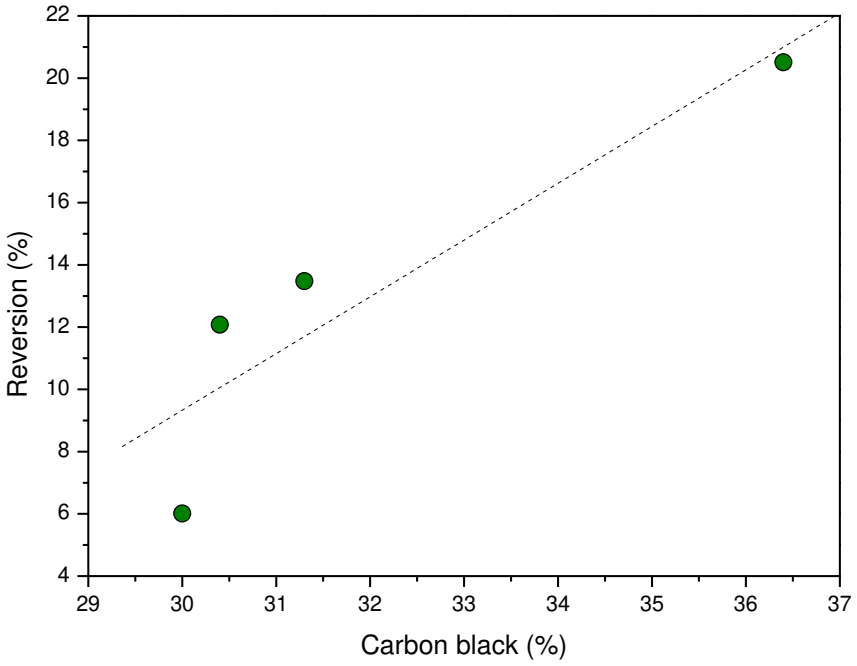


Fig. 3. Correlation between the carbon black amount and the percentage of reversion of the analyzed samples.

It is known that the higher the ratio accelerator/sulfur, the greater the mono and disulfidic bonds proportion.[68] Besides, literature[23,69] has shown that carbon black enhances the formation of polysulfidic bonds and, consequently, these compounds usually present reversion trend. This behavior was observed in the correlation presented, due to the possible increase of the polysulfidic bonds, favored by the increase of the carbon black amount present in the samples. Our previous results[26] have shown the presence of polysulfidic bonds in the revulcanized GTR samples through the results of attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. According to the literature,[70] the relationship between the density of polysulfidic bonds and the reversion percentage is real, noticeably showing that the less thermal stable bonds (polysulfidic ones) are responsible for the reversion trend in NR. Consequently, in the present work, the reversion trend is related to the degradation of the samples during the devulcanization process since it is the responsible by the increase of the relative amount of carbon black in the samples.

During the devulcanization by microwaves, it is known that is necessary that the material has some polarity to interact to the microwaves, since the heating is mainly due to the dipole rotation induced by the

microwaves.[71] In the case of NR and SBR rubbers, the polarity is induced by the addition of a conductive filler, in this case, the carbon black, by an effect known as the Maxwell-Wagner polarization.[72] The higher the carbon black amount present in the sample, the higher the temperature just after the microwaves treatment, resulting in higher devulcanization levels (higher devulcanization efficiency)[7] and, also, higher the degradation levels.

According to Seghar et al.,[73] the maximal microwave specific energy to perform a controlled reclaiming of SBR is 440 Wh/kg. The corresponding microwave specific energy E of the devulcanized samples was evaluated from Equation 9[73]. The results are present in Fig. 4.

$$E = \frac{P.t}{m} \qquad \text{Equation 9}$$

where P is the magnetron power of the oven (820 watts), t is the exposure time of the sample to the microwaves (h) and m is the mass of the sample (65 g).

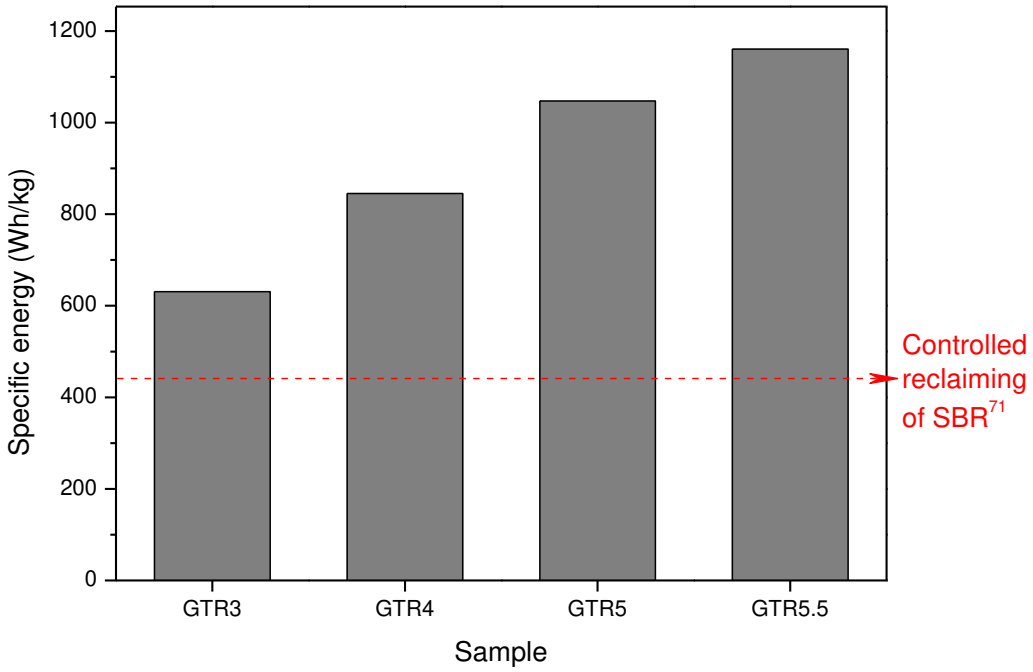


Fig. 4. Corresponding medium microwave specific energy of the devulcanized GTR samples. A controlled reclaiming dotted line was inserted as a guide for the eyes.

When compared to the literature,[73] the microwave specific energy of the GTR samples was superior. Since SBR presents higher thermal stability than NR, this result depicts the high degradation levels of the GTR samples, and that the higher the exposure time of the sample to the microwaves, the higher its degradation level. As depicted before, this result is favored by the carbon black amount present in the samples. However, the carbon black amount present in the GTR0 (no devulcanized sample) is around 30%,[9] which demonstrates that the increase of the concentration of carbon black as a result of the degradation of the elastomeric phases was observed only in the samples GTR5 and GTR5.5, since the others also present about 30% of carbon black, according to thermogravimetric analysis present in our earlier work.[26] The samples GTR5 and GTR5.5 presented higher degradation levels according to Horikx's theory,[9] corroborating to the present results.

As a result of the possible oxidation of the carbon black, the higher concentration of oxygen on the surface of the filler, which is polar by nature, tends to interact more with the microwaves, which facilitates the processes of devulcanization/degradation of the polymeric chains during the microwave devulcanization process. Thus, with the increase of the microwaves exposure time, the highest degree of degradation observed, especially in the NR phase (which has greater interaction with the carbon black)[9] is also, probably, due to the oxidation of the carbon black occurred during the devulcanization itself, being that the process did not occur with controlled atmosphere. De Sousa et al.[9] demonstrated, from the results of FTIR of the devulcanized GTR samples, the formation of S–O bonds in the samples, as a form of rearrangement of the sulfur from the break of the cross-linkings (S–S and C–S), which corroborates with the described previously.

Revulcanization kinetics study by ODR

The experimental results of E_a calculated according to Equation 3 obtained for the GTR devulcanized under different exposure times to the microwaves are shown in Fig. 5. The column height represents the average of three measurements and the error bars are also shown.

As the chemical reaction occurs, it is essential that the effective shocks of the reagents form an intermediate structure known as activated complex which is generated by the favorable collision of the

molecules of reagents and by their energy. This energy (E_a) is the smallest amount of energy needed to generate an activated complex and, hence, for the reaction to occur.[74]

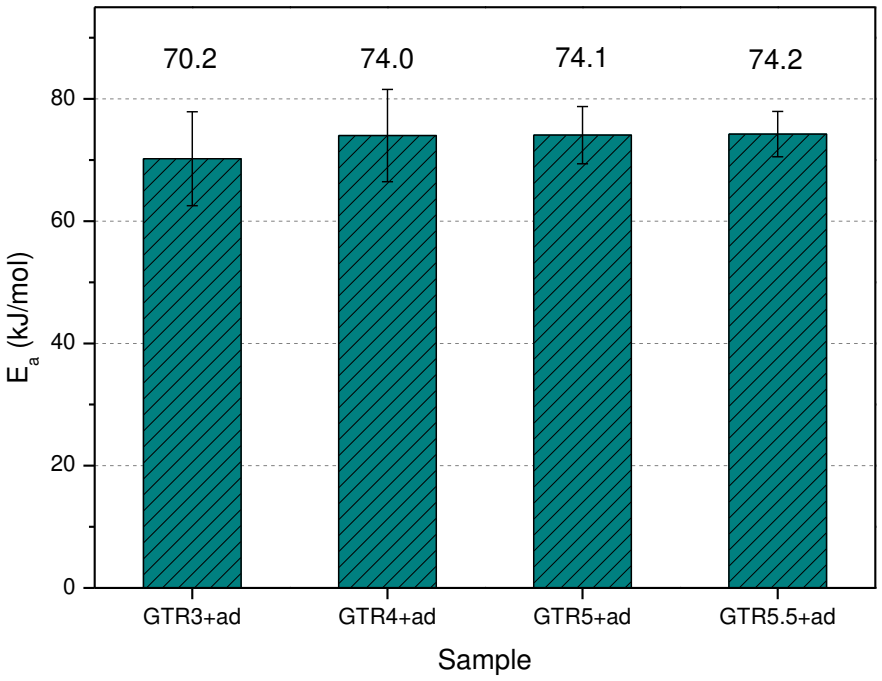


Fig. 5. Activation energies of GTR devulcanized under different exposure times to the microwaves.

The results presented in Fig. 5 suggest that the devulcanization of the GTR by microwaves did not notably influence E_a values obtained according to the proposed equation, and the order of the revulcanization reaction, in spite of higher degradation for higher exposure times and the increased amount of carbon black as a result of degradation.

According to Sirqueira and Soares,[75] when plotting a curve $100/T$ *versus* log (CRI), the behavior of linearity of the resulting curve is related to the trend of first-order reaction kinetics of vulcanization. The resulting curves are shown in Fig. 6, and they suggest first-order reaction kinetics of revulcanization under different exposure times.

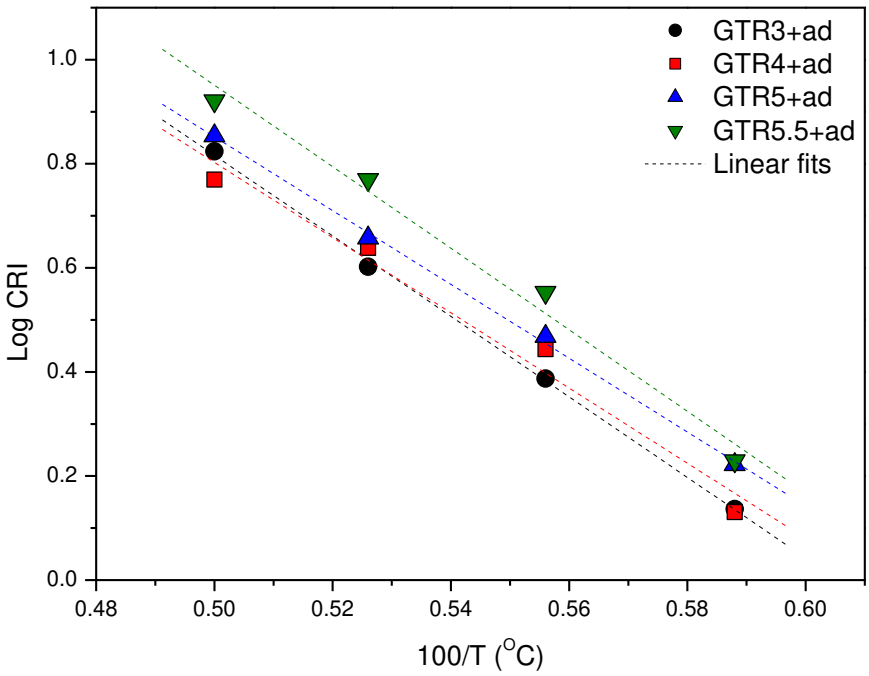


Fig. 6. Dependence of *CRI* as a function of the inverse of the temperature of the devulcanized GTRs.

Rheometric thermal simulation

Simulation of experimental data is extremely important in academic and industrial fields since it allows us to determine the degradation and the mechanism models, as well as the activation energy and the pre-exponential factor (last two from Arrhenius equation using different methods[30,47,76]). From these parameters, reliable results are obtained by simulating and statistically comparing each typical degradation mechanism (from geometrical contraction (*R*-type) to diffusion in three dimensions (*D*-type), for example).

All experimental torque *versus* time curves were simulated and compared to using the *F* statistics method using all the classic models from the solid state (presented in Table 2). The second derivative of the torque *versus* square temperature (allows better visualization of the results) is presented in Fig. 7. All the curves presented similar behavior, i.e., at higher isothermal temperatures a shift for lower square temperature is observed due to reaction proceeds faster. However, the mean activation energy decreased with the exposure time, and it can be attributed to the activated complex responsible for accelerating the reaction. The results suggest that up to 5 minutes the exposition time is enough to facilitate the chain reaction. At higher exposure times (for GTR5.5+ad), a reversal trend seems to occur.

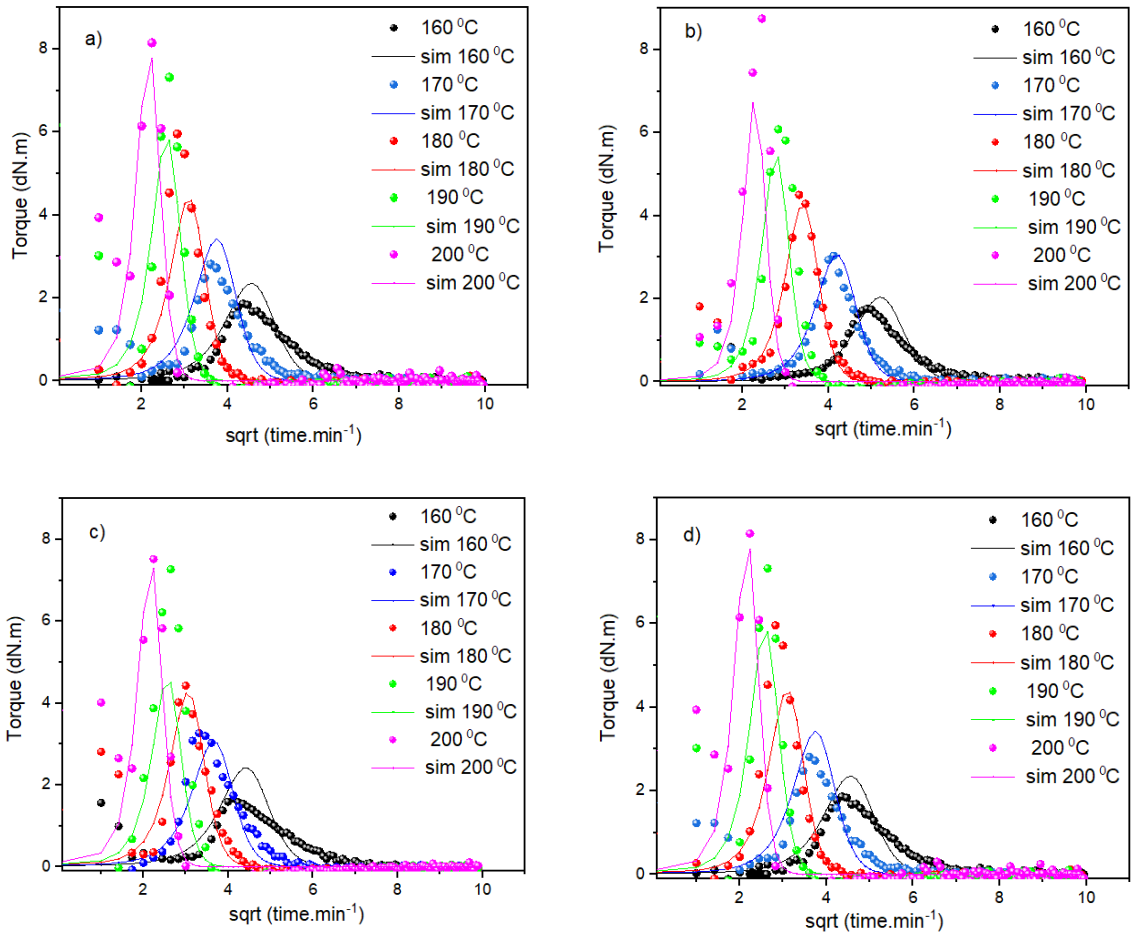


Fig 7. Experimental and simulated data obtained from torque *versus* square root time.min^{-1} curves using the advanced *F* statistic method for: a) GTR3+ad, b) GTR4+ad, c) GTR5+ad, and d) GTR5.5+ad.

Degradation mechanisms follow, basically, two degradation types: autocatalytic (*C*-type and *B*-type) and nucleation (*A*-type) models, according to the advanced statistics method. Diffusion (*D*-type), geometrical contraction (*R*-type) and reaction order (*F*-type) models showed very poor F_{exp} and, so, it can be discarded from a statistical point of view.

Table 2

Kinetics models tested with respective activation energy and pre-exponential values. Shaded lines mean values below the respective F_{test}.

Sample	Model f(α)	E_a (kJ/mol)	Log A (s^{-1})	F_{exp}	Sample	Model f(α)	E_a (kJ/mol)	Log A (s^{-1})	F_{exp}
GTR3+ad	An (n=3.43)	73.03	6.84	1.00	GTR4+ad	C	71.07	4.58	1.00
	Cn (n=0.84)	72.61	5.71	1.00		Bna(n=1.02 a=0.90)	70.84	7.42	1.06
	Bna (n=0.68 a=0.71)	73.34	7.41	1.01		An (n=5.71)	71.50	6.58	1.14
	C	71.86	5.48	1.01		B1	68.14	7.29	2.61
	A3	73.53	6.90	1.07		A3	73.19	6.83	2.71
	A2	75.97	7.18	2.28		Cn (n=2.18E-4)	83.83	7.63	2.81
	Fn (n=2.51E-5)	96.84	9.42	3.16		A2	74.30	6.95	5.05
	R2	84.77	7.78	4.86		Fn (n=8.85E-5)	87.79	8.42	6.05
	R3	85.61	7.69	5.27		R2	78.42	7.02	8.15
	F1	86.52	8.26	5.95		R3	80.15	7.04	8.61
	D1	123.55	12.38	6.50		F1	82.17	7.74	9.33
	B1	124.86	13.63	6.97		D1	124.29	12.41	10.27
	F2	88.53	8.49	7.28		F2	86.03	8.17	10.71
	D2	126.49	12.34	7.58		D2	123.07	11.91	11.21
	D4	125.91	11.60	7.84		D4	124.27	11.37	11.45
	D3	126.90	11.70	8.22		D3	128.14	11.80	11.81
GTR5+ad	C	61.13	3.88	1.00	GTR5.5+ad	C	63.87	4.13	1.00
	An (n=4.57)	62.25	5.63	1.05		Cn (n=1.04)	63.75	4.05	1.01
	Bna (n=0.91, a=0.84)	60.97	6.25	1.05		Bna (n=1.10, a=0.88)	63.11	6.57	1.04
	Cn (n=0.18)	67.20	5.62	1.18		An (n=4.73)	64.69	5.90	1.09
	A3	64.86	5.96	1.34		A3	66.85	6.17	1.54
	A2	68.63	6.38	2.11		B1	64.59	6.98	2.54
	B1	61.75	6.66	2.30		A2	70.16	6.54	2.55
	Fn (n=1.54E-3)	82.77	7.94	2.31		Fn (n=2.72E-5)	85.27	8.20	2.85
	R2	78.68	7.15	3.23		R2	82.03	7.52	3.94
	R3	80.33	7.16	3.44		R3	85.17	7.69	4.17
	F1	83.07	7.95	3.76		F1	89.78	8.70	4.55
	D1	104.40	10.34	3.91		D1	119.87	12.05	4.75
	F2	89.92	8.74	4.37		F2	100.82	9.97	5.28
	D2	120.72	11.81	4.43		D2	138.35	13.78	5.35
	D4	122.44	11.34	4.56		D4	141.00	13.42	5.50
	D3	127.15	11.88	4.74		D3	147.98	14.21	5.72

According to Khawam and Flanagan,[37] *A*-type mechanism, in special, Avrami-Erofeev model considers that in any solid-state decomposition, there are certain restrictions on nuclei growth. Two of them are: (a) ingestion – elimination of a potential nucleation site by the growth of an existing nucleus, and (b) coalescence – loss of reactant/product interface when reaction zones of two or more growing nuclei merge. According to literature,[77] n values of Avrami-Erofeev equation depends on the mechanism of the reaction based on the constant nucleation rate or growth of a constant number of nucleation mechanism (zero nucleation rate): for the former, n = 2 is referred to one dimensional growth, n = 3 to two-dimensional growth, and n = 4 to three-dimensional growth; for the latter n = 1 is referred to one-dimensional growth, n = 2 two-dimensional growth, and n = 3 for three-dimensional growth. So, in considering literature and the most common n values found in the present simulation, the *A*-type degradation mechanism was discarded.

Autocatalytic models are physically justified since sulfur is released from the first vulcanization process, forming less stable links. This favoring can degrade the mixture depending on the isothermal temperature and exposure time to the microwaves (observed from t_{90}) since carbon black can degrade due to microwaves exposure, which also accelerates the degradation process. Therefore, the process of mixture occurs from different velocities depending on two main factors: isothermal temperature of mixture and microwave exposure time. Independently of these two factors, the results suggest that, statistically, the autocatalytic model is the most probable model for torque *versus* time curves since the process occurs from heat diffusion inside the sample, the process occurs randomly along the sample from the autocatalytic process. In general, the autocatalytic model found for all the compounds can be explained, among other factors, by the cleavage of the rubber chain segments generated during the mixture process, producing oligomers that accelerate the reaction. This acceleration shifts the reaction (in this case, increase in torque) to lower times. As a consequence, the curing process (width of the curve) occurs in a narrower range because the residual accelerator acts as a sulfur donor,[47] and as the number of effective collision among the molecules is increased by increasing the chain mobility, the reaction tends to occur faster and generates a greater torque maximum. As the temperature decreases, the number of effective collisions among the molecules decreases, shifting the maximum torque for higher times and broadening the reaction process.

Revulcanization kinetics study by DSC

In general, both mechanical and thermal properties are directly related to the vulcanization degree of the elastomeric matrix, as well as the amount and the filler type. Vulcanization involves multiple and complex reactions with the additives present in the matrix, significantly affecting the properties mentioned above. Thus, the study of the vulcanization reactions and the respective kinetics provide knowledge about the mechanism and its effects on the mechanical properties.

As a general procedure, the activation energy was determined through the slope of the curves present in Fig. 8 using the FWO, Kissinger, and Osawa methods.

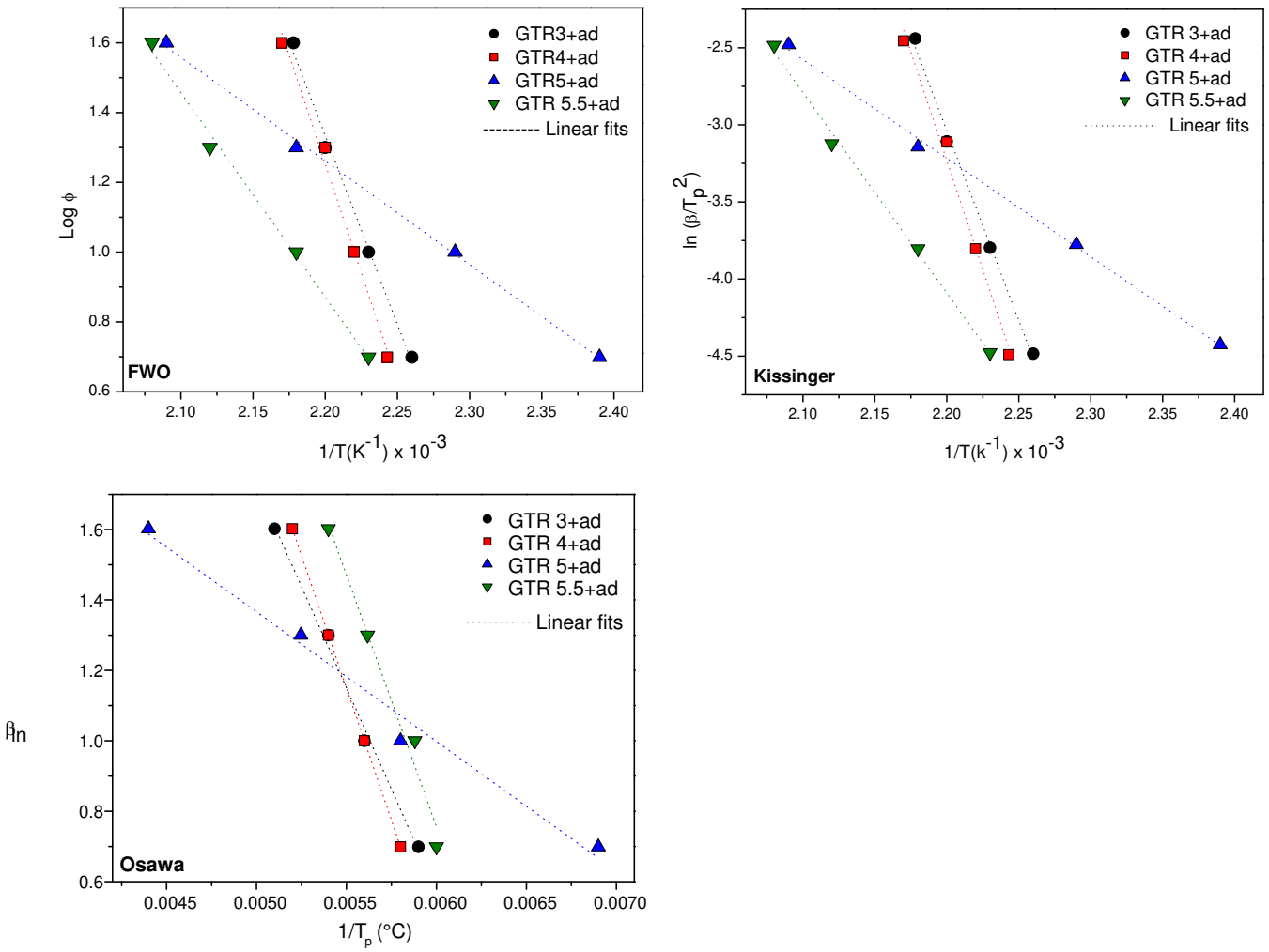


Fig. 8. Dependence of *log* ϕ (FWO method), *ln* β/T_p^2 (Kissinger method) and *ln* β (Osawa method) as a function of the inverse of the DSC peak temperature of the GTRs.

In Table 3 are presented the values of the activation energy, as well as the correlation coefficients (R^2) obtained from the slope of the curves from Fig. 8.

Table 3

E_a and R^2 values of the analyzed samples by the FWO, Kissinger and Osawa methods.

Method	GTR3+ad		GTR4+ad		GTR5+ad		GTR5.5+ad	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
FWO	89.97	0.99265	103.67	0.98910	24.67	0.99796	48.67	0.99201
Kissinger	20.43	0.99399	23.42	0.98608	5.31	0.99685	10.80	0.99456
Osawa	9.56	0.99410	12.50	1.00000	3.06	0.97679	11.88	0.97131

The activation energy represents the amount of energy necessary to start (onset) the reaction, the barrier in which the molecules must overcome to initiate the reaction.[78,79] Thus, higher E_a values suggest higher energy necessary for the occurrence of the reaction and the formation of the activated complex.

It is observed that all samples presented low E_a values, according to all the methods, except the sample GTR4+ad. Activation energy has a close relationship with the network structure formed during the vulcanization process.[80] As earlier mentioned, the presence of residual vulcanization additives (especially sulfur) related to the first vulcanization reaction is characteristic of recycled rubbers, and it favors the formation of less stable links.[17] On the other hand, according to Hirayama and Saron,[81] sulfur present in chemical groups ruptured by microwave radiation is released in the form of volatile organic compounds with low molecular weights and SO_2. So, as GTR4+ad was not exposed for a long time to the microwaves during the devulcanization process, sulfur from the sulfidic bonds broken during devulcanization step probably was kept in the samples. By increasing the exposure time to the microwaves, increased the number of new S–S and S–O type bonds formation as a result of the rearrangement of the sulfur free radicals from the devulcanization of the GTR in the presence of oxygen.[9] In addition, the rigidity of the devulcanized sample can lead to increased activation energy during the subsequent revulcanization process. According to previous results,[9] GTR4 was unable to flow during capillary rheometry analysis, as well as to its high gel content, which demonstrated that the sample was not devulcanized at a level capable of enabling the flow, which is necessary more energy to begin/continue the process.

In a very recent work, de Sousa et al.[26] showed, based on thermogravimetric analysis, that the decrease of the degradation degree of the elastomeric phases is attributed to a lower carbon black amount on its composition, being that GTR4+ad is the sample containing the lesser carbon black amount. Also, GTR4+ad presents the higher oxidation level, according to the FTIR results.[26] All these mentioned points possibly influenced in the higher E_a value of this sample.

The effect of carbon black on the dynamic properties of elastomers differs quantitatively from one elastomer to another, and depends on the processing type. The effect is mainly a function of the state of the carbon black dispersion, both concerning the size and number of agglomerates, as to the distance of separation between them.[82]

To deepen the understanding of the carbon black amount in the samples[26] in the revulcanization step (E_a), a correlation between them is proposed (by using the E_a values from the FWO method) (Fig. 9), and it showed a clear correlation. The results suggested that the amount of filler/degree of degradation can strongly influence the revulcanization of GTR previously devulcanized by the action of the microwaves.

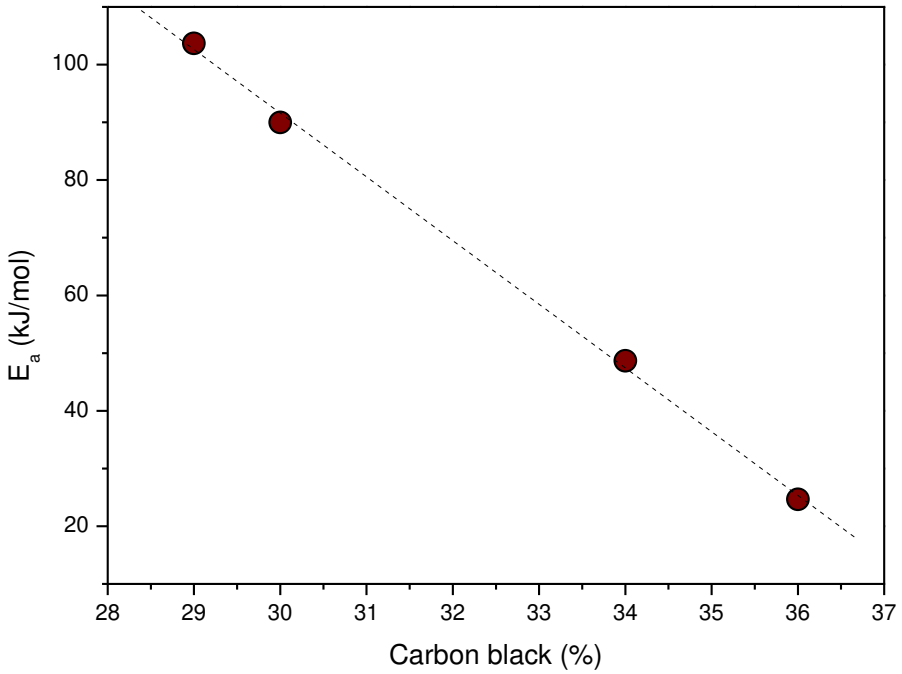


Fig. 9. Correlation between carbon black amount in the sample and E_a.

Some fundamental understandings concerning the reduction of the environmental impact must be incorporated in the product design, such as the principles of the green chemistry. It is defined as the design, development, and application of chemical processes and products to reduce or eliminate the use and generation of substances hazardous to human health and the environment.[1] Some principles of the green chemistry will be discussed, concerning the present work, to deepen the discussion.

In addition to being considered a process of an eco-friendly technology,[6] the method of devulcanization of elastomers by microwaves can be considered an ally of the green chemistry, since one of the principles highlights the reduction of the energy needed to minimize environmental and economic impacts, and the use of microwaves is one of the strategies to increase the energy efficiency.[83]

Some authors[83] consider polymeric wastes as renewable materials: "While traditional discussions of renewable feedstocks exclude the wastes, they are eminently renewable (they are being renewed whether we like it or not) and are available in much larger quantities than biomass." Thus, materials derived from plants and other renewable biological sources or recycled should be used whenever possible.[1] Accordingly, the use of recycled materials in new applications is encouraged by one of the principles of the green chemistry. However, it is known that polymers, in general, degrade during recycling processes and, especially in the case of end-of-life tires, the challenge of using them into technological applications is to deeply know the aspects of the material/processing that influence their final properties (the real formulation is not known), which proposes the present work.

The use of catalytic reagents is included in the principles of the green chemistry.[83] In this sense, the revulcanization of GTR devulcanized by the action of the microwaves was catalyzed by carbon black, being that this vastly used filler in elastomeric compounds was already contained in the recycled GTR. In general, the results showed the influence of the amount increasing, as well as the possible increase of the surface area due to oxidative processes in the revulcanization reaction of GTR, with reduction in the activation energy of the reaction (i.e., less energy is necessary as the carbon black amount increased), as well as a reduction in the ts_1 and t_{90} values. The influence of carbon black in the results is schematically shown in Fig. 10.

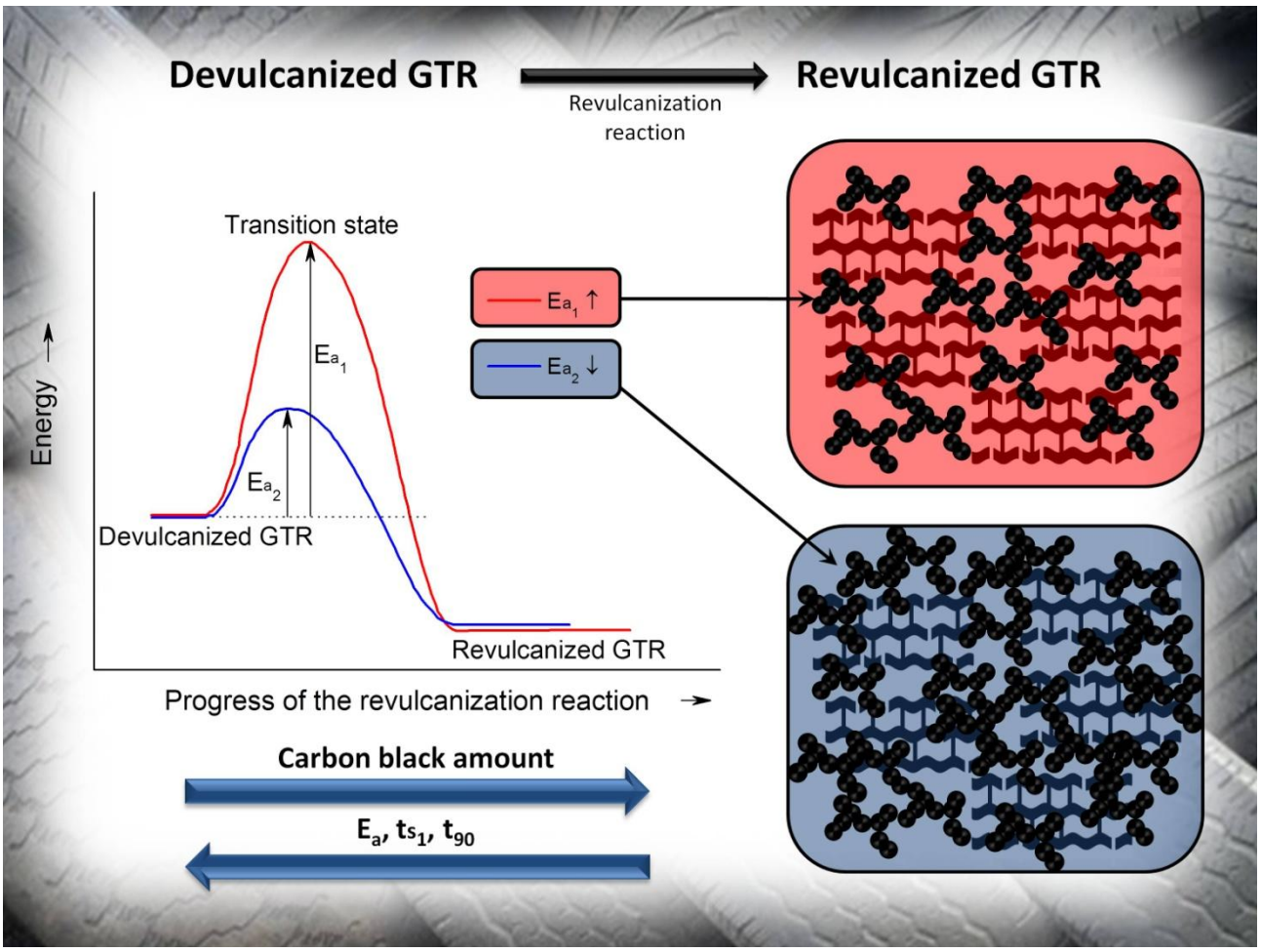


Fig. 10. Influence of the carbon black amount on the progress of the revulcanization reaction of the GTR devulcanized by microwaves.

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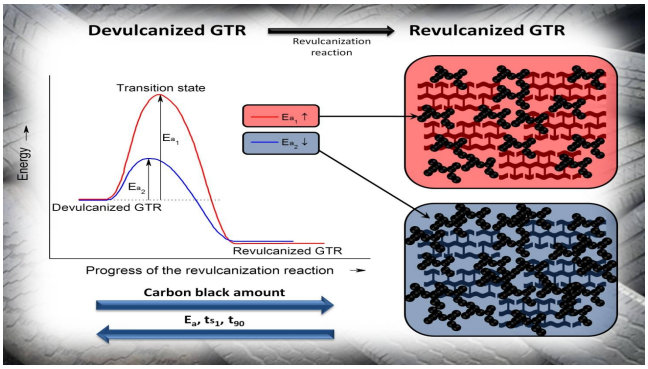
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TOC/Abstract Graphic



Revulcanization kinetics of eco-friendly devulcanized ground tire rubber for technical application of waste tire towards sustainable development.