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Article

Mechanochemical treatment in high-shear thermokinetic mixer an alternative for tire recycling

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Abstract: This publication highlights the effect of mechanochemical treatment in a high-speed thermokinetic mixer as an alternative for recycling ground tire rubber (GTR). The GTR initially has an 80% gelled fraction and presented up to 50% gel fraction in the most intensive condition (5145 rpm, s_2). Processing at the lowest speed (2564 rpm, s_1) resulted in greater selectivity concerning the mechanochemical treatment (K~1). In the most intense processing condition (10 min. at s_2), more significant degradation was observed via random scission with a reduction of the glass transition temperature, T_g (11ºC), an increase of the soluble polymer fraction, and a more significant reduction in crosslink density. The artificial neural network could describe and correlate the thermal degradation profile and processing conditions with the physicochemical characteristics of the GTR. The approach presented here represents an alternative for mechanochemical treatment since it can reduce the crosslink density with selectivity and in short times (1–3 min.).

Keywords: GTR, mechanochemistry, recycling, thermokinetic mixer

1. Introduction

Car tires are the most relevant rubber items in terms of volume and importance, accounting for about 70% of the synthetic and natural rubber produced in the world. In general, they are composed of 40–50% elastomers such as raw rubber (NR, SBR, etc.), 20–30% fillers (carbon black, silica, etc.), 5–10% fibers and reinforcement (rayon, polyester, steel, etc.) and finally a tiny percentage of vulcanizing agents [1,2]. Unfortunately, the search for products with high performance, durability, and long life results in a polymer that is difficult to discard and complex to recycle[1].

At the end of the tire's cycle life, its destination can be recovery, incineration, pyrolysis, or landfill. In incineration, waste tires are completely burned for energy generation in cement kilns and for producing steam, electricity, pulp, paper, lime, and steel [1,2]. In pyrolysis, the rubber component decomposes in the presence of heat and in the absence of oxygen, which prevents oxidation, and makes it possible to obtain pyrolysis oil, carbon black, and others. [1,2]. Finally, in devulcanization, the focus is on selective scission, or in a way that allows the elastomer to be reprocessed. When scission is selective, the sulfide bonds undergo scission using specific conditions, which reduces the crosslinked fraction and often allows revulcanization [3]. Overall, these processes require rubber separation, and the wire and steel mesh are recovered as qualified iron scrap, and the nylon fabric is recovered and can be used as reinforcement in cardboard packaging [4].

Devulcanization or recovery methods have particularities, and their acceptability must be associated with the final destination of the treated product. Regarding devulcanization, the most efficient methods are the chemical method [5], the microwave-assisted method, the ultrasonic method, the biological method, the thermal method, and the mechanical method [4,5]. Mechanical processes are those in which the rubber is subjected to

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high shear stress forces [1,2,4,5]. Thermo-mechanical processes can be carried out continuously or in batches. In the continuous process, a twin screw extruder is commonly used, in which the thread profile must be precisely adjusted to promote a good balance of bond breaks that allows the reuse of the elastomer. The batch process is usually done in roller mixers or some other equipment specifically designed to generate the high levels of shear that benefit this process [1-3,5]. Furthermore, these methods can be aided by chemical agents to aid in processing conditions or chain breaking.

Ujianto and coworkers compared elastomer devulcanization using single and twin screw extruders. They reported that the twin screw extruder operating at 300°C and 100 rpm reduced the gel content by 50% for an elastomer with an initial gel content of 85%, while for the single screw, the reduction was 40%[6]. Diaz et al. performed thermomechanical devulcanization of waste tires and compared two mixers, one with high shear and the other with pressure. In the study, the authors varied the temperature of the rubber and the mechanical energy consumed in operation, feeding the instrument with large pieces of rubber [7]. The machine reduced the particle size by rotating the rotor, thus increasing the content of soluble material in the rubber by 5% and decreasing its crosslink density by five times for the smallest particle size (100 μm) [7,8]. Studies show that using shear forces can reduce the particle size and the fraction of gelled material.

WO 2011/113148 deals with a method and equipment used to regenerate ground vulcanized rubber. The equipment consists of a thermokinetic mixer with a hermetic stationary chamber with a non-uniform internal surface, a rotor shaft that extends coaxially into the chamber, and a speed controller that varies up to at least about 2,000 rpm. The method comprises pre-mixing the shredded rubber with oil at room temperature and then transfer the mixture to the thermokinetic mixer. The speed is increased until a devulcanization temperature is reached (300 to 330°C for 0.25 to 3 seconds). After this condition, the speed is reduced until a new mixture temperature condition is reached (150 to 250°C for 2 to 30 seconds). The best devulcanization condition leads to a 61% reduction in crosslink density. One of the advantages of this method is that there is no need to use auxiliary devulcanization chemicals, making this method ecologically correct or "green" [9].

Cavalieri and coworkers evaluated the effect of mechanochemical activation on the surface of solid-state devulcanized mid-tire rubber [10]. The authors show a reduction of 3% in the gel content and more than 50% in the crosslink density in 15h of treatment in a ball mill. Interestingly, surface activation often allows the GTR to be reincorporated into fabrics with other elastomers and thermoplastics polymers more easily. Furthermore, during the GTR recovery process, shear forces increase friction between particles and exothermic reactions. Consequently, it can generate self-heating in the elastomer during its recovery [11].

Thermokinetic mixers can be used to generate heat and often melt the material. A crosslinked PU recovery approach was used by Gonela and coworkers, in which PU particles were depolymerized in a thermokinetic mixer. For the processing time of 90% to 30% reduction in gel content occurred [12]. Subsequently, the authors use PU after thermomechanical treatment to obtain blends with TPU and PA12. Other studies for the use of thermokinetic mixers deal with obtaining blends with crosslinked PE and EVA with high amounts (>60wt.%) of crosslinked material [13,14]. Tire waste generally has a high gel content (>60%) and a more significant limitation for production if blended with thermoplastics or reused in industrial processes. In addition, high vulcanization limits adhesion between phases when used in mixtures and results in products with poor surface finish. Thus, thermokinetic mixers represent good opportunities to be used to treat crosslinked elastomers to improve and expand their use in the polymer and elastomers industry.

Thus, in this study, an alternative for treating ground tire rubber (GTR) has been proposed using mechanochemical treatments based on a high-speed mixer. It has been investigated processing parameters that affect gel content, crosslink density, and particle morphology. Furthermore, the selectivity of chain scission has been evaluated using Horikx analysis. Finally, an artificial neural network (ANN) was used to correlate the samples' thermal degradation characteristics after mechanochemical treatment. For the system studied, it is noted that random scission dominates the degradation process from processing times of 10 min. at speeds of 5145 rpm.

2. Materials and Methods

The ground tire rubber (GTR) with a particle size of 0.5–0.7mm from the car, truck, tractors, and others, free of metallic parts, ground, and sieved was supplied by a recycling industry located in the Rio Grande do Sul (Brazil). Acetone P.A. (Neon, Brazil), ethanol 92.8 INP (Factor 1, Brazil), hexane P.A. (Neon, Brazil), and Toluene P.A. (Anhydrol, Brazil).

2.1. Mechanochemical treatment

GRT samples containing 200g were added to the mixing chamber of the DRAIS thermokinetic M.H. Equipment Ltd (Brazil) mixer model MH-50. This type of equipment heats the sample through the friction of the system and the material. In the mixer, it is possible to use two speeds in which its blades rotate at s_1=2565 rpm and s_2=5145 rpm. The mixing chamber was constantly cooled with circulating water at 25°C. Different processing conditions were used at speeds 1 (s_1) and 2 (s_2), in which the time was varied (1–60min.). Immediately after processing, the temperature of the samples was read and cooled for further analysis.

2.2. Characterizations

The glass transition (T_g) was determined using a TA Instruments DSC model Q 20 and some 6 mg of sample, and the temperature ranged from -80 to 250°C, with a heating rate of 10°C/min under an inert atmosphere (N_2, 50 ml.min^{-1}). Next, the thermal degradation profile and the filler content were determined with a TA Instruments TGA model Q 50. The analysis was performed in an inert atmosphere (nitrogen) and an oxidizing atmosphere after 600°C for the determination of carbon black (synthetic air) (50 ml.min^{-1}). The heating rate was 20°C/min, from 30°C to 900°C, using ~10 mg.

The gel content was determined using about 7 g of samples using extraction (soxhlet) in acetone and hexane. Extraction with acetone was carried out for 16h and in hexane for 24h, then the samples were dried [15]. The gel content was considered the load fraction of the sample after the mechanochemical treatment. The density of the samples was determined according to ASTM D 792.

The crosslink density (equation 1) was determined according to the standard ASTM D6814 and using the Kraus correction (equation 3) [16]. The swelling was performed with 2–3 g) samples packed in paper bags. This determination was made on the samples after extraction in acetone and hexane. The equilibrium of swelling was reached after 20 days. Then, the excess solvent was removed from the sample's surface, and the mass measurement was performed. The crosslink density according to:

$$\nu_e = \left\{ \frac{-[\ln(1 - V_r) + V_r + \chi_1 V_r^2]}{\left\lceil \dfrac{V_{m1}(V_r^{1/3} - V_r)}{2} \right\rceil} \right\} \qquad (1)$$

where ν_e is the crosslink density per unit volume; V_r is the polymer volume fraction in a swollen network in equilibrium with pure solvent; χ_1 is the polymer-solvent interaction parameter (Flory-Huggins), and V_{m1} is the molar volume of the solvent.

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$$V_r = \left[\frac{\left(\frac{m_e}{\rho_b}\right)}{\left(\frac{m_e}{\rho_b}\right) + \left(\frac{m_s}{\rho_s}\right)} \right] \tag{2}$$

where m_e is the mass of extracted rubber, ρ_b is the density of the extracted rubber, m_s is the mass of solvent adsorbed by the sample, and ρ_s is the density of the solvent. The interaction parameter χ_1 used in this work was considered 0.391 at 25°C for Cis-polyisoprene-toluene [17].

$$\frac{V_r}{V_R} = 1 - \frac{\Phi\left[3c\left(1 - \sqrt[3]{V_r}\right) + V_r - 1\right]}{1 - \Phi} \tag{3}$$

where V_r is calculated according to equation 4, V_R is the volume fraction of polymer in a swollen network in equilibrium with charge-corrected pure solvent. Φ is the volumetric fraction of the filler in the sample, determined by TGA, and calculated according to equation 4, and c is a constant relative to the fillers present in the solvent-independent composition (for fillers such as carbon black, the value is 1.17) [16,18].

$$\Phi = \frac{m_c \times \rho_g \times m_i}{\rho_c \times m_f} \tag{4}$$

m_c is the mass of fillers, m_i is the mass of the polymer before swelling, m_f is the mass of the polymer after swelling, ρ_g is the density of the polymer, and ρ_c is the density of the fillers. The efficiency of the mechanochemical treatment, X was made by comparing the crosslink densities before and after the treatment.

$$X = \left[1 - \left(\frac{\nu_e}{\nu_{ec}}\right)\right] \times 100 \tag{5}$$

where ν_e is the crosslink density per unit volume and ν_{ec} is the crosslink density per unit volume of the sample without mechanochemical treatment.

The theoretical relationship between the soluble fraction generated after degradation of a polymeric network and the relative decrease in crosslink density as a result of main-chain scission or crosslink scission [18,19] was based on Horikx's approach, using the Flory-Huggins theory as a basis [20]. However, when the polymer is degraded through the statistically random distribution of chain scission events, equation 6 is adopted. In this scenario, where the degradation consists only of the crosslinks' selective scission, strictly corresponding to an ideal devulcanization process, the equation used is the 7 [19].

$$1 - \frac{\nu_f}{\nu_i} = 1 - \frac{\left(1 - \sqrt{s_f}\right)^2}{\left(1 - \sqrt{s_i}\right)^2} \tag{6}$$

$$1 - \frac{\nu_f}{\nu_i} = 1 - \frac{\gamma_f\left(1 - \sqrt{s_f}\right)^2}{\gamma_i\left(1 - \sqrt{s_i}\right)^2} \tag{7}$$

where ν_i and ν_f are the crosslink densities in mol.cm^{-3}; s_i and s_f the sol fractions. γ_i and γ_f are the crosslinking indices, computed according to equation 8. The subscripts "i" and "f" represent the samples before and after devulcanization, respectively [18,19].

$$\gamma = \nu_x \frac{M_n}{\rho} \tag{8}$$

where ρ is the density in $g.cm^{-3}$ of the polymer, v_x is the crosslink densities in $mol.cm^{-3}$, Mn is the original polymer chains' average molecular weight ($g.mol^{-1}$) before the crosslink formation.

It was proposed to correlate these characteristics with the thermal degradation profile (TGA) using an artificial neural network (ANN) after the mechanochemical treatment from the assumption that there is a reduction in the crosslink density and gel content. The ANN was conventionally constructed with three layers: an input layer, an output layer, and a hidden layer. Each layer has a different number of neural elements. In the present study, information from TGA curves, speed of mechanochemical treatment, processing time, gel content, and bond density were input vectors. Thus, the generated network will modify the weight of the interconnections between neurons to reproduce the parameters provided to obtain the mass loss curves. Figure 1 shows a schematic of the network used.

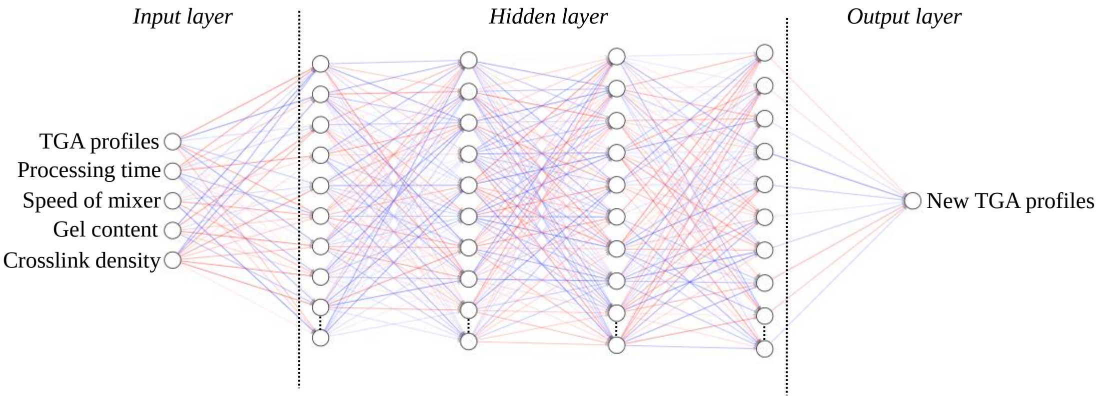

Figure 1. Scheme of the ANN used.

In this procedure, the initial information to be considered includes the number of initial TGA curves and other characterizations of the GTR after the mechanochemical treatment. With network training, it is possible to predict new TGA curves between the lower and upper ranges and obtain information about new experimental conditions to avoid accumulating errors. The ANN fit was created with 4 layers, 20 hidden neurons in each layer, k-fold cross validation = 5, error summation squared error function, activation function = ReLU, learning rate = 0.001 and loss tolerance = 1E-6. The algorithm used was resilient backpropagation with tracking.

Fourier Transform Infrared Spectroscopy (FTIR) was used to evaluate the possible degradation of the GTR after mechanochemical processing. Measurements were made with the soluble fraction in Perkin Elmer equipment, model 1000 in KBr pellets (4000–400 cm^{-1}, 32 scans, and 4 cm^{-1} of the resolution).

The morphology of the samples was investigated by scanning electron microscopy (FEG-SEM, Tescan MIRA3, Czech Republic) with a dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments). The samples were fixed on carbon tapes, and a thin layer of gold was deposited by sputtering.

3. Results and discussion

Table 1 shows the temperature, acetone, and hexane soluble fractions for GTR samples before and after mechanochemical treatment. As the processing time was increased, the temperature increased proportionally from 32°C for 1 min in s1 to 68°C in 60min. This result is expected since the thermokinetic mixer generates heat by friction. However, as the speed has practically doubled, a much more significant increase in temperature is noted, reaching 185°C in 10 min. for s_2. Although, the soluble fractions presented constant values in s1 and 1 min. processing in s_2, an increase in these fractions was later noticed.

This increase in the soluble fraction may be related to chain scission that produces smaller fragments that can be extracted.

Table 1. Processing conditions, the temperature at final processing, and solubles fractions for GTR after and before mechanochemical treatment

Processing speed	Time (min.)	Temperature (°C)	Solubles fraction in acetone	Solubles fraction in Hexane
-	-	-	0.11	0.12
s_1	1	32	0.11	0.12
s_1	3	43	0.11	0.12
s_1	6	59	0.11	0.12
s_1	10	54	0.11	0.12
s_1	30	38	0.10	0.13
s_1	60	68	0.10	0.13
s_2	1	51	0.11	0.12
s_2	3	169	0.13	0.16
s_2	6	179	0.14	0.19
s_2	10	185	0.18	0.27

s_1=2565 rpm and s_2=5145 rpm

The gel fraction (ξ) and crosslink density (ν) are important parameters to characterize the efficiency of the mechanochemical process of GTR recovery. However, the gel fraction is less sensitive to structural changes. Therefore, it is often possible to activate the surface of the GTR particle with faster treatments and reincorporate it into a production process. Although some approaches, such as using ball mills, produce exciting results [10], the thermokinetic mixer is capable of generating high shear rates [21] ($>10^4$ s^{-1}), and it plays an essential role in reducing the crosslink density. On the other hand, at higher shear rates, the oxidation of the elastomeric compound may increase [11]. Thus, depending on which application the recovered elastomer will be used, the best processing conditions for recovery will be defined.

Table 2 shows the results of the gel fraction, crosslink density, and mechanochemical treatment efficiency for samples treated under different conditions in a thermokinetic mixer. Here the gel fraction was estimated after extractions in acetone and hexene. The gel content is less sensitive to the mechanochemical treatment since some crosslinks on the surface are initially broken, and only when the medium is more aggressive is there a chain thermomechanical degradation by random scission, which results in changes in the gel content. In the crosslink density, it can be verified that they already produce efficiency of approximately 50% in milder processing conditions. These results show that depending on where the elastomer will be used, as in mixtures with other elastomers or thermoplastics, there may not be a need for further degradation of the polymer chain, as reported by Cavalieri and coworkers [5].

Table 1. Gel fraction (ξ), crosslink density (ν) and mechanochemical efficiency, X

Processing speed	Time (min.)	Gel fraction (wt.%)	Crosslink density (mol.cm^{-3})	X (%)
-	-	77.3	0.00107	-
s_1	1	77.4	0.00075	29

s_1	3	77.1	0.00061	43
s_1	6	77.1	0.00055	49
s_1	10	77.2	0.00056	48
s_1	30	77.1	0.00057	46
s_1	60	77.1	0.00051	52
s_2	1	77.3	0.00051	53
s_2	3	70.5	0.00045	58
s_2	6	66.5	0.00044	59
s_2	10	55.7	0.00039	63

Zhang et al. (2009), used a mechanochemical pan-mill reactor in the devulcanization experiments realized at room temperature, 30 rpm, and cycles of 25 to 40 seconds. They obtained a gel content of approximately 75% in the most aggressive condition. On the other hand, Ujianto et al. [6], using twin screw extruders, reached gel values of approximately 50%, from samples with 85% gel content at 300°C and 100 rpm. Taking as a basis that the speed used in the extrusion is 100 rpm, and resulted in a rate of the same magnitude as that in the thermokinetic mixer, the speeds are about 50 times more significant, but the temperature reached in the times studied is much lower than at 300°C, the shear rate is believed to play an essential role in reducing the gel content as it results in greater chain scissions. When performing the devulcanization of rubber, Simon and coworkers [22,23] originated from ground tire tread in a laboratory microwave oven and an internal mixer. For a sample treated at 120 rpm, which reached a temperature of 200°C, the sol content was 30.2wt.%, and the crosslink density was 3.7 x 10^{-4} mol.cm^{-3}, whereas a sample treated at 40 rpm, which reached a temperature of 160°C, the sol content was 14.4%, and the crosslink density was 7.3 x 10^{-4} mol.cm^{-3}.

The DSC results not shown here show only a glass transition (T_g) for the GTR at -58.9°C, which agrees with the literature [22,23]. Note that there is no variation for the processing times of 1 and 3 min. at speed s1. On the other hand, when GTR was processed for 10 minutes. in s2 there was a reduction to -69.8°C. Thus, when there is a reduction in T_g, there is an increase in the segmental mobility of the chains. This may be related to the possible scission of chains under more severe shear conditions for a longer time.

Figure 2 (a) illustrates the TGA curves for the GTR sample after processing in a thermokinetic mixer. Here it was chosen to present the conditions in 10 min. in s_1, 60 min. in s1, and 10 min. in s_2. Along with the experimental data, the neural network's prediction for the behavior of the thermal degradation profile of the samples and an experimental prediction is being shown. All samples presented the temperature of the beginning of thermal degradation ~250ºC, with maximum rates around 500ºC. Due to the GTR being formed by different elastomers, the thermal loss mass profile occurs in multiple steps, as can be seen for a maximum around 350ºC which can be related to natural rubber, and at 470ºC it is related to styrene-butadiene rubber, which are the main elastomers used in the manufacture of automobile tires [1,4]. In addition, chain scission forms molecules of a lower molecular mass composed of hydrocarbon species ($-CH_2-$) and CO_2 [1]. For the samples processed in s_1, a carbon black content of around 31wt.% was found. However, when they were processed in s_2 a change was noticed, and this amount increased to 36wt.% as well as the other relative amounts of fillers (silica and others). This change in the mass loss profile is associated with the fact that during the mechanochemical process, chain scission and volatilization of low molecular mass compounds occur. As a result, there is a change in the relative fraction of carbon black and inorganic compounds.

The ANN was used to predict the observed behavior of the complex mass loss profile. First, experimental data were compared with predicted theoretical data, as shown in Figure 2 (b), and a good agreement $R^2>0.999$ was noted. Subsequently, it was possible to predict the experimental data for other conditions (blue curve, Fig. 2(a)). It is also noted that the cross-validation (Fig. 2(c)) results in low dispersion.

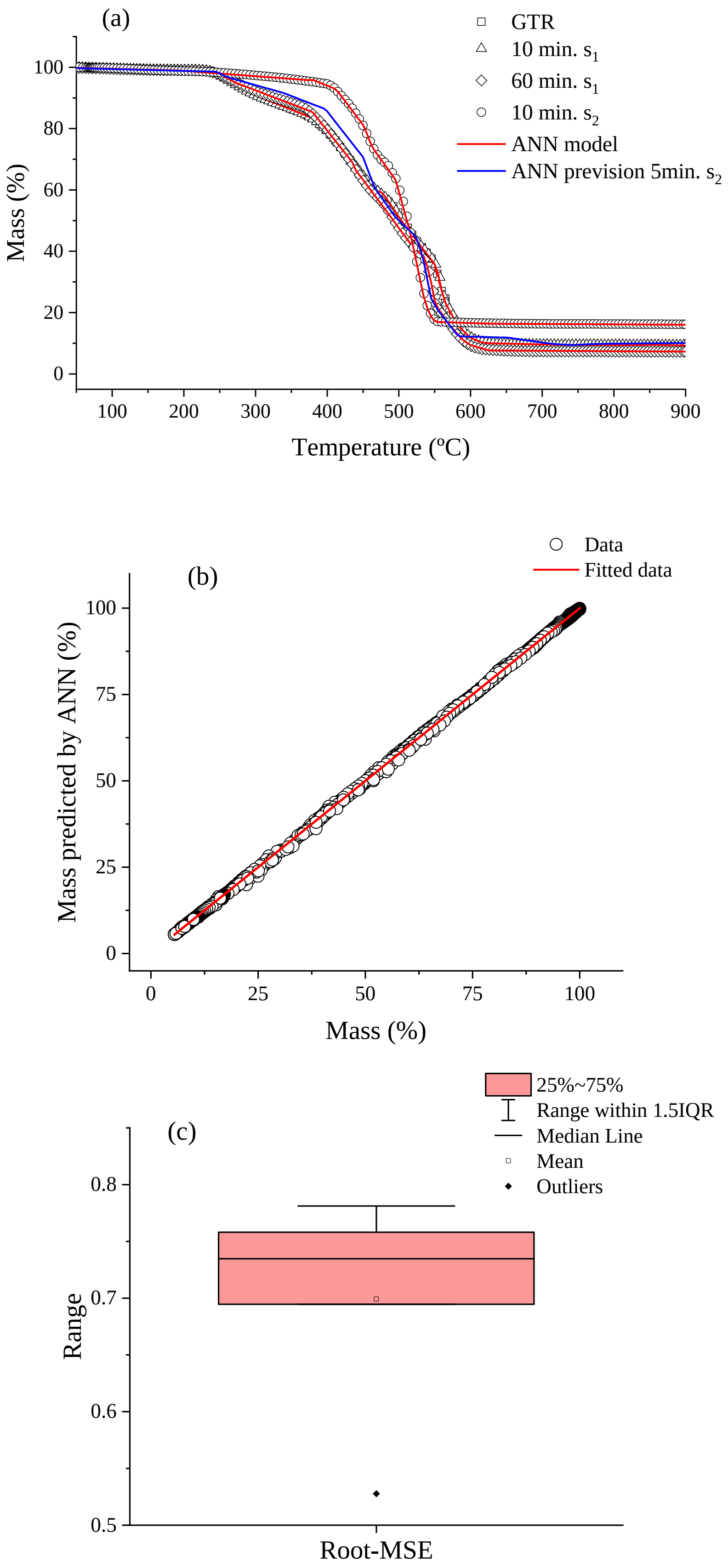
(a)
GTR
10 min. s_1
60 min. s_1
10 min. s_2
ANN model
ANN prevision 5min. s_2
Mass (%)
0
20
40
60
80
100
100
200
300
400
500
600
700
800
900
Temperature (ºC)
(b)
Data
Fitted data
Mass predicted by ANN (%)
0
25
50
75
100
0
25
50
75
100
Mass (%)
(c)
25%~75%
Range within 1.5IQR
Median Line
Mean
Outliers
Range
0.5
0.6
0.7
0.8
Root-MSE

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Figure 1. (a) TGA curves (20 ºC.min^{-1}) for GTR samples in different treatment times and speeds. The open dots symbols refer to experimental data, the solid red line to the ANN predicted data, and the solid blue line to a 5min. predicted condition in s_2. (b) Comparison of the data fitted by ANN and experimental data and (c) Cross-validation box plot, R^2>0.9999.

The selectivity of the scission of chains generated by the mechanochemical process in a thermokinetic mixer, the Horikx method, was used, which allows distinguishing whether the scission of chains tends to be more selective or random. For this analysis, it is necessary to carry out a mass balance in the material since the filler and polymer fractions are altered during the treatment.

The theoretical lines in Figure 3 were constructed using equations 6 and 7, respectively, varying the fraction of solubles from 0.10 to 0.99 concerning the decrease in crosslink density. The crosslinking index was obtained through equation 8, considering the numerical average molecular weight of the NR polymer of 200,000 g.mol^{-1}, according to the literature [18,19]. Based on the proximity of the curve (random or selective), it is possible to infer whether the dominant phenomenon during the mechanochemical process is more selective or random [18,24]. Selectivity can be done using a coefficient (K). Two possible approaches are to set the selectivity parameter towards the soluble fraction (vertical) or the crosslink density (horizontal). The selectivity parameter of the soluble fraction (K_s) can be calculated by equation 9[18].

$$K_s = \frac{S_c - S}{S_c - S_x} \tag{9}$$

where S_c is the theoretical sol fraction for random scission, S_x is the theoretical sol fraction for selective crosslinking scission, and S is the measured soluble fraction. The selectivity parameter in the crosslink density direction (K_x) can be calculated by equation 10 [15].

$$K_x = \frac{X - X_c}{X_x - X_c} \tag{10}$$

where X is the devulcanization degree, X_c is the theoretical values related to the relative decrease in crosslink density for random scission, and X_x is the theoretical values of the relative decrease in crosslink density for selective scission. The general selectivity parameter (K) is then defined according to equation 11 [18].

$$K = \frac{K_s + K_x}{2} \tag{11}$$

Thus, when random chain scission is dominant, K=0, and when selective K=1.

The soluble fraction showed a practically linear variation for the experiments at s_1 $(S = 0.20 + 1.46E - 4 * t, R > 0.98)$ and s_2 $(S = 0.19 + 0.02 * t, R > 0.98)$. Thus, the gel fraction changes much more intensely when shear is increased. Regarding the decrease in crosslinks $(1 - \frac{\nu_f}{\nu_i})$ can be fitted by logistic equations. For s_1 $(1 - \frac{\nu_f}{\nu_i} = 0.49 + \frac{6.69E-5-0.49}{1+(\frac{t}{t_0})^{1.53}}$, R>0.98) and for s_2 $(1 - \frac{\nu_f}{\nu_i} = 3.30 + \frac{1.50E-5-3.30}{1+(\frac{t}{t_0})^{0.08}}$, R>0.99). This observation may be related to the reduction of crosslinks following a sigmoidal process [25]. That is, there is an initial period plus reading, a period of acceleration, and a limit is reached for the processing technique employed in the mechanochemical treatment.

Figure 3 shows the results of the Horikx analysis for the two speeds (s_1 and s_2) and times of mechanochemical processing. The blue line illustrates the region in which the process is selective, while the red line illustrates the random scission. A comparison was also made with the data generated by ANN. All samples processed at s_1 show selective chain scission with K=0.98–1) and at 1min. in s_2. Subsequently, there is an increase in thermomechanical degradation by the random scission in the mechanochemical treatment with K, going from 0.80 to 0.39 in the 10 min. in s_2 condition, which indicates that the high shear induces the scission of the C-C bonds of the backbone chain.

Edwards and coworkers [18], used Horikx analysis to indicate the selectivity of crosslink scission during the devulcanization of GTR by mechanical shear at elevated temperatures in a twin screw extruder. The extruder used operated at 30 - 80 rpm and 175–275°C. The best selectivity condition found by the authors was obtained in the sample submitted to 275°C and 55 rpm. This best shear condition is about forty-six times lower than the best condition in this study. Furthermore, the working temperature was five times higher than the final temperature of the best condition evaluated by Horikx in the study in the thermokinetic mixer. Simon et al. [24,26], compared the thermomechanical treatment in a mixing chamber (Brabender Plasti-corder) with microwave processes. They noticed that chain scissions are more selective in the internal mixer. However, when there is an increase in temperature, there is a tendency for the polymer chain to degrade, as reported by the same authors. The literature [8] reports that the devulcanization process will occur extremely slowly if the operating temperature is below 50°C. This observation is in line with the data presented in this study, in which similar conditions and greater selectivity are achieved in s_1.

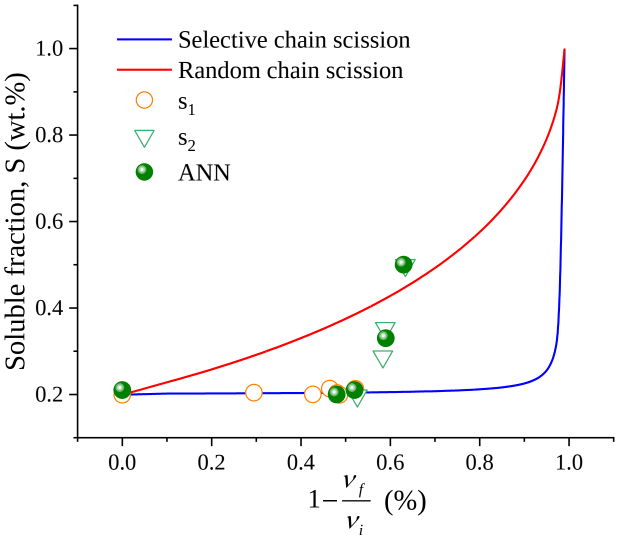


Figure 3. Soluble fraction as a function of the decrease in crosslinks $(1-\frac{\nu_f}{\nu_i})$ (Horikx analysis). The red line represents the theoretical random scission curve, the blue line selective scission, and ANN-generated green dots.

Figure 4 shows that the normalized gel fraction (ξ/ξ0) as a function of the normalized crosslink density (ν/ν0) can be correlated by the empirical model proposed by Isayev, according to equation 12 [27]

$$\frac{\xi}{\xi_0} = \left(1+\psi ln\frac{\nu}{\nu_0}\right) H\left[\frac{\nu}{\nu_0} - exp\left(-\frac{1}{\psi}\right)\right] \qquad (12)$$

where H is the Heavi-side step function because the gel fraction is always positive and negative values and has no physical meaning, such that $1+\psi ln\frac{\nu}{\nu_0} > 0\ if\ \frac{\nu}{\nu_0} - exp\left(-\frac{1}{\psi}\right) > 0$. The parameter ψ represents the scales of the relative change in gel fraction concerning the change in ν0) should be controlled by the relative to chain scission probability.

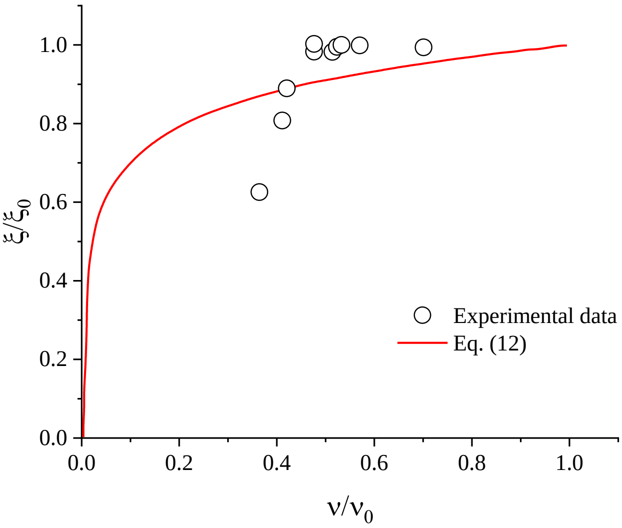


Figure 4. Normalized gel fraction versus normalized crosslink density for GTR processed in a thermokinetic mixer. Symbols are experimental data, and the solid line in red is the fit of Equation 12.

The empirical model was able to describe all data in a universal curve. Thus, using the same assumptions as Isayev[27], it is possible to infer that the mechanochemical treatment can be described by a network percolation model, in which the ratio between the amounts of intermolecular bond breakage and main chain bond breakage resulting in the formation of the fraction soluble [27,28]. This model implies that devulcanization and degradation coincide at random throughout the rubber network, a condition believed to be sufficiently satisfied during processing in a thermokinetic mixer. The value of the parameter ψ found was 0.13 ± 0.05, which is in agreement with the values found by Isayev [27] for ultrasonic devulcanziation of GTR ($\psi = 0.17$).

Figure 5 shows the FTIR spectra for the hexane-extracted GTR samples. In the 2950 and 2853 cm^{-1}, the asymmetric and symmetrical stretching bands of the C-H bonds present in NR methyl groups are observed. At 1450 and 1375 cm^{-1} it is possible to observe the symmetrical deformation bands in the CH_2 and CH_3 planes and the cis-isoprene bands, around 885 cm^{-1}, 1370 cm^{-1}, and 1630 cm^{-1}. At 700 cm^{-1} and 775 cm^{-1} characteristic bands of SBR were found, and at 965 cm^{-1} to butadiene [29,30]. The band that characterizes the vibration absorption related to the S-S bond in the GTR is found close to 462 cm^{-1} and can reach 495 cm^{-1} [30]. Regarding the effect of processing time and speed, it is noted that the region between 2950 and 2853 cm^{-1} increases proportionally with the intensity of the mechanochemical treatment.

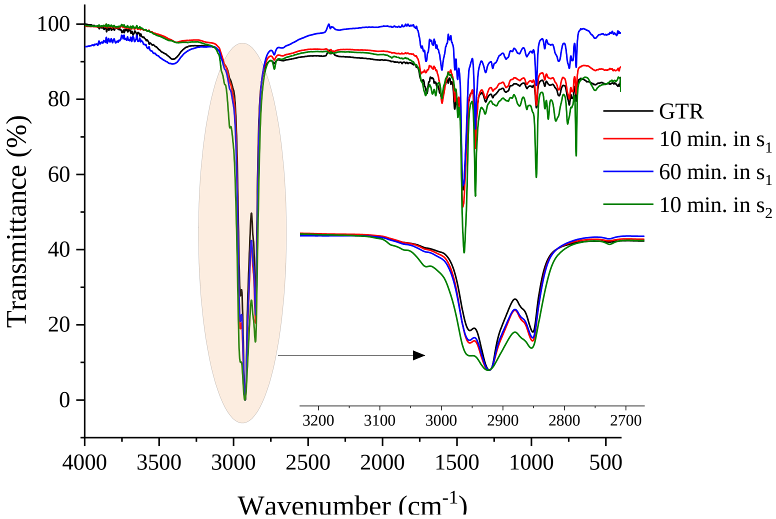
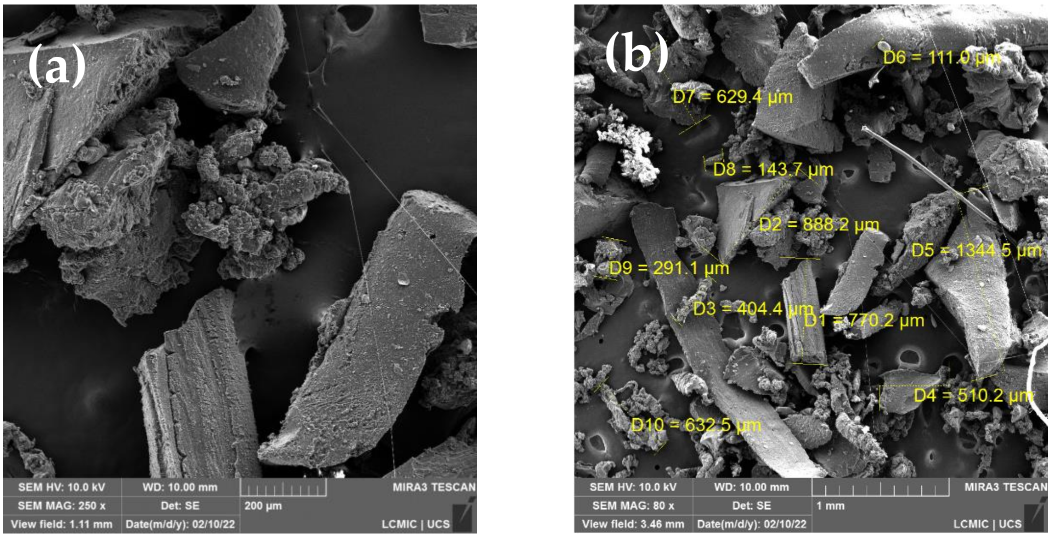


Figure 5. FTIR spectra for soluble fraction of GTR after mechanochemical treatment.

The intensive mechanochemical treatment results in degradation and almost always oxidation. The oxidative process can result in the formation of new crosslinks, but it is counterbalanced by the high shear that results in chain scission, as noted by the samples processed in s$_2$. The relative increase in bands at 1800 to 1500 cm^{-1} can relate to this effect (C=C and C=O), as well as the appearance of bands at 1500 to 750 cm^{-1} (C-O, S-O-C, C-O-C, S=O, C-C) [29-31].

Figure 6 (a) – (f) illustrates SEM micrographs of the GTR samples before (Fig. 6 (a) and (b)) and after treatment in the thermokinetic mixer. The particles have elongated sizes, typical of a non-cryogenic milling process. Sizes range from 111 μm to 1345 μm, with a higher incidence of particles larger than 400 μm. The EDX analyses in the supplementary files show the presence of carbon, sulfur, silicon, aluminum, calcium, oxygen, zinc, and sodium. These elements are part of the compounds commonly used to manufacture tires [4]. After 3 min. and 60 min. of processing at s$_1$, it is noted that the beginning of the fragmentation of the sample occurs ((Fig. 6 (c) and (d)). The increase in the processing speed (s$_2$) resulted in the formation of a sample with a smoother and more continuous surface. This characteristic is related to the increase in the amount of soluble phase. These results are similar to those found in the literature [30] using mechanochemical treatment in extrusion. As the conditions are intensified, the rubber particles present smooth contours.



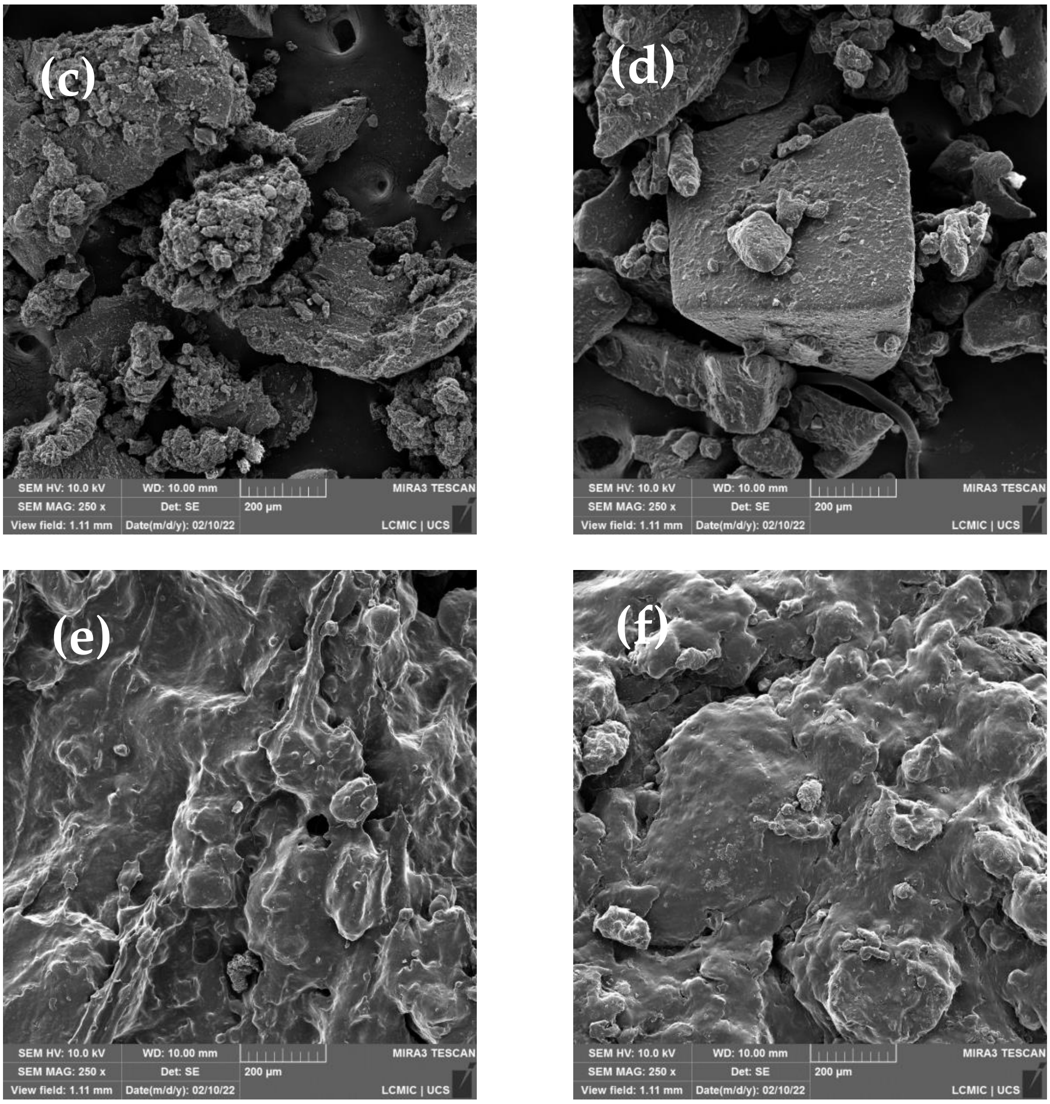


Figure 6. SEM micrographs for GTR: before mechanical treatment (a) and (b); 3 min. (c) and 60 min. (d) in s_1; 6 min. (e) and 10 min. (f) in s_2.

5. Conclusions

GTR was submitted to mechanochemical treatment in a thermokinetic mixer under different processing conditions and experimentally characterized by physical, chemical, thermal, and morphological methods. Experimental techniques allowed for establishing relationships with processing conditions. Models based on an artificial neural network (ANN), Horikx, and Isayev analysis were used to describe how the ~~effects of~~ different processing conditions affect the mechanochemical process. The most aggressive processing condition resulted in a reduction of 11ºC in the glass transition temperature. The crosslink density, as well as the gel content, respond directly to the effect in the processing conditions. That is, the more intense, the smaller the number of crosslinks and the greater the soluble fraction. Horikx analysis indicates that samples processed in s_1 showed the highest concentration of selective chain scissions. However, when the thermokinetic mixer speed is increased, there is a greater tendency for random scission. The highest efficiency in the mechanochemical treatment was 53%, with one minute of processing in s_2. The Artificial Neural Network (ANN), was able to predict thermal degradation behavior and correlate with the mechanochemical treatment in a thermokinetic mixer. Both chain scission and devulcanization are processes that coincide. When chain scission increases, materials with smoother and more continuous surface textures are formed.

We conclude that the GTR produced by the thermokinetic process has great potential for use due to its short processing time and efficiency concerning selectivity. The treatment intensity is critical in using mechanochemical techniques as a "green" and sustainable approach to recovering waste tires. The technique discussed here represents an exciting alternative to contribute to the circularity and reuse of these materials.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: EDS analysis for GTR sample, Figure S2: Compositional map for GTR sample.

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Data Availability Statement: The raw data needed to reproduce these findings can be shared if the authors request.

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