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Research Article

Microwave Devulcanization of Ground Tire Rubber and Its Improved Utilization in Natural Rubber Compounds

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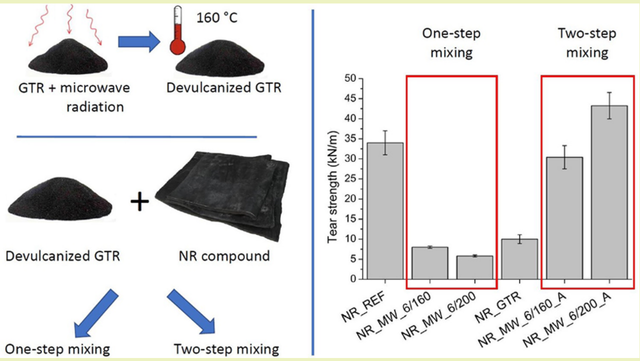
ABSTRACT: We devulcanized ground tire rubber (GTR) with microwaves at different temperatures (140−200 °C) and heating rates (2−18 °C/min). We measured the soluble content and the cross-link density of the samples, and then evaluated them by Horikx's analysis and determined the specific microwave energy during devulcanization and the selectivity parameter of the treatments. We also introduced the *K*·*D* number that can be calculated as the product of the selectivity parameter (*K*) and the relative decrease in the cross-link density (*D*). The results showed that GTR devulcanized at lower temperatures, selectivity was very high, and the degree of devulcanization was adequate. At higher temperatures (180−200 °C), the degree of devulcanization reached 85%, but the selectivity parameter was low, which indicates severe degradation at this temperature range. At lower temperatures (140−160 °C) and decreasing heating rate, i.e., increasing residence time, the degree of devulcanization showed an increase, but at higher temperatures, the heating rate had no significant effect on the degree of devulcanization. We introduced different devulcanized GTRs (dGTRs) to natural rubber-based mixtures and produced samples with two different mixing methods: conventional mixing and so-called two-step mixing. In the latter one, in the first mixing step, we added vulcanizing agents to the dGTR, and in the second mixing step, we added this mixture to the reference mixture. Two-step mixing helped recover mechanical properties, especially tear strength. Scanning electron microscopy−energy-dispersive spectroscopy and atomic force microscopy showed that microwave devulcanization and the vulcanizing agents mixed with dGTR acted in the cross-section of dGTR.



KEYWORDS: *recycling, microwave, devulcanization, GTR, tire, rubber, reclaiming*

INTRODUCTION

Tire recycling raises urgent environmental and economic issues. The amount of waste tires is increasing yearly, but their recycling remains a problem due to their cross-linked structure. Rubbers cannot be recycled like thermoplastics via remelting or remolding. Thus, the reclamation of tires in powder form is a widespread method. Waste tires can be ground by mechanical grinding at ambient or cryogenic conditions[1] and waterjet milling. Compared to mechanical grinding, waterjet milling produces smaller particles with a higher specific surface, and rubber degradation can also be avoided, though the final material needs to be dried.[2,3] Ground tire rubber (GTR) can be blended with both thermoplastics[4,5] and thermosets,[6−8] with or without compatibilization.[9,10]

The ultimate goal is to break up the cross-linked structure and thus allow the rubber to regain its processability. This can be achieved by devulcanization, which cleaves cross-link bonds while leaving the polymer chains intact.[11,12] There are various methods for rubber devulcanization, such as microwave,[13−15] thermomechanical,[16,17] thermochemical,[18] mechanochemical,[19] and biological[20] devulcanization. Furthermore, researchers have also used ultrasound[21] and supercritical carbon dioxide[22] as an auxiliary to help break down the cross-links.

Microwave devulcanization is a promising technology because the process is easily adjustable, the treated material has good properties, and it promises high productivity.[23] Thanks to the characteristics of microwave heating, GTR or other rubbers can be treated in minutes. The residence time influences the final temperatures, which determine the properties of the devulcanized GTR (dGTR) or rubber.[24−26] Several studies focused on the exposure time of microwave devulcanization. They reported that the soluble content of dGTR increased and its cross-link density decreased with

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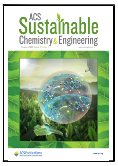

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increasing exposure time, i.e., with a higher temperature of the GTR.[25,27] For further analysis, Horikx's theory establishes a mathematical relationship between these two data.[28] The result of the analysis, the Horikx plot, shows whether the prominent phenomenon during devulcanization is the random scission of the polymer chains or the selective scission of the covalent cross-links.[13,29] Therefore, Horikx's analysis helps to understand the relationships between the soluble content, the decrease in the cross-link density, and the degradation of the dGTR. The results show that during microwave devulcanization, the dGTR became more degraded with increasing temperature.[13,30] The Horikx plot can be analyzed further with the calculation of the selectivity parameter (K), and it can also be quantitatively analyzed.[31]

The irradiated energy during devulcanization is an important parameter. Zanchet and de Sousa[32] calculated the specific microwave energy (E) during microwave devulcanization using the following equation: $E = P \cdot t/m$, where P is the power of the magnetron (W), t is the exposure time (h), and m is the mass of the sample (kg). They found a correlation between the specific microwave energy and the start of the degradation of styrene−butadiene rubber (SBR). Aoudia et al.[33] came to a similar conclusion during the devulcanization of GTR. They found a specific microwave energy limit above which devulcanization did not change significantly.

Garcia et al.[25] used atomic force microscopy (AFM) to analyze the fine morphology of dGTR. They distinguished the three main phases of GTR: natural rubber (NR), SBR, and carbon black. They found that longer microwave treatments reduced the amount of softer rubber phases and observed an increase in the amount of carbon black domains, which indicated a severe degradation of the rubber phases.

The quality of the dGTR can be determined in rubber mixtures indirectly. dGTR is usually blended with SBR[13,34] or NR[35,36] because these are the main elastomeric components of tires.

In this study, we devulcanized GTR with a laboratory microwave oven, studied the structural changes of GTR after the treatment with Horikx's analysis, and selected the ideal devulcanizates for further studies based on the results of the analysis. We produced NR-based mixtures incorporating 100 phr dGTR, based on our previous results.[37] Finally, we tested the mechanical and physical properties of the resulting rubber samples and studied their morphology and composition by scanning electron microscopy−energy-dispersive spectroscopy (SEM−EDS) and AFM.

EXPERIMENTAL SECTION

Materials. Waterjet-milled crumb rubber (particle size <400 μm) was provided by Aquajet Ltd. (Budapest, Hungary). The material originated from the tread part of truck tires. According to thermogravimetric analysis measurements,[37] it contains 33−38 wt % NR, 28−33 wt % synthetic rubber, 2−4 wt % oil, 24−28 wt % carbon black, and 8 wt % residual additives.

A general-purpose natural rubber, NR CV 60 (Sud Comoe Caoutchuc, Aboisso, Ivory Coast Mooney viscosity (ML, 1 + 4, 100 °C): 55−65), was chosen for our investigations. The additives of rubber mixtures were the following: zinc oxide (ZnO, S.C. Werco Metal S.r.l., Zlatna, Romania), stearic acid (Oleon, Ertvelde, Belgium), N772 carbon black (Omsk Carbon Group OOO, Omsk, Russian Federation), paraffin oil (Ipol Lubricants, Mumbai, India), tetramethyl thiuram disulfide (TMTD, Akrochem Corporation, Akron, Ohio, USA), N-cyclohexyl-2-benzothiazole sulfonamide (CBS, Rhein Chemie, Mannheim, Germany), and sulfur (Ningbo Actmix Rubber Chemicals Co., Ltd., Ningbo, China).

Devulcanization of GTR. Microwave devulcanization of GTR was carried out in a BP-125/50 (magnetron power: 1000 W, frequency: 2.45 GHz) laboratory microwave oven produced by Microwave Research Inc. (Carol Stream, Illinois, USA). 100 g of room temperature-GTR was treated at heating rates of 1, 2, 3, 6, 12, and 18 °C/min, and the final temperatures were 120, 140, 160, 180, and 200 °C. In some cases, we also applied a 30 min holding phase at the final temperature in the microwave oven after the heating cycle. In addition, we used heating profiles with two different heating rates within one devulcanization treatment. For example, in the case of the dGTR_MW_18/120_1/140 sample, the GTR was heated to 120 °C with 18 °C/min and then to 140 °C with 1 °C/min (Table 1).

Table 1. Parameters of Microwave Devulcanization and the Abbreviation of the Samples

abbreviations	heating rate (°C/min)	achieved temperature (°C)	holding time at the final temperature (min)
dGTR_2/140	2	140	
dGTR_3/140	3	140	
dGTR_3/160	3	160	
dGTR_3/180	3	180	
dGTR_3/200	3	200	
dGTR_6/140	6	140	
dGTR_6/160	6	160	
dGTR_6/180	6	180	
dGTR_6/200	6	200	
dGTR_12/140	12	140	
dGTR_12/160	12	160	
dGTR_12/180	12	180	
dGTR_12/200	12	200	
dGTR_18/140	18	140	
dGTR_18/160	18	160	
dGTR_18/180	18	180	
dGTR_18/200	18	200	
dGTR_18/120_30	18	120	30
dGTR_3/140_30	3	140	30
dGTR_18/140_30	18	140	30
dGTR_18/160_30	18	160	30
dGTR_18/120_1/140	18; 1	140	
dGTR_18/120_3/140	18; 3	140	

The magnetron was controlled by a proportional−integral−derivative (PID) controller that used data from a thermocouple that continuously measured the temperature of the rubber inside the oven. A motorized stirring system (40 rpm) was installed in the microwave oven to ensure a homogeneous temperature. After the treatment, the material was taken out and cooled down.

We used eq 1 to calculate the specific microwave energy (E) of each treatment.

$$E = \frac{P \cdot t}{m}\ \text{(Wh/kg)} \tag{1}$$

where P is the power of the magnetron (W), t is the irradiation time (h), and m is the mass of the samples (kg).

Due to the control mechanics of the equipment, which controls the heating rate by switching the magnetron on and off (i.e., it switches on less frequently at low heating rates and more frequently at higher heating rates; hence, the total treatment time is not equal to the irradiation time), it was necessary to determine the irradiation time. We registered the electric consumption of the microwave oven to determine the irradiation time.

Characterization of GTR and dGTR. The soluble fraction of the dGTR samples was determined by Soxhlet extraction in toluene according to eq 2. We ran the extraction for 18 h and then dried the samples for 12 h at 80 °C to remove the solvent. We weighed each sample twice: before extraction and after drying.

$$S = \left(1 - \frac{M_f}{M_i}\right) \cdot 100 \tag{2}$$

where S is the soluble fraction (%), and M_i and M_f stand for the mass of rubber (g) before and after extraction, respectively.

The cross-link density of untreated GTR and devulcanizates was determined via swelling tests according to ASTM D 6814-02. We calculated the cross-link density using the Flory−Rehner equation (eq 3)[38] with the Kraus correction[39] after equilibrium swelling (72 h followed by drying to a constant mass at 80 °C) in toluene.

$$\nu_e = \frac{-[\ln(1 - V_{r0}) + V_{r0} + \chi_1 \cdot V_{r0}^2]}{[V_1 \cdot (V_{r0}^{1/3} - V_{r0})/2]} \tag{3}$$

where ν_e is the cross-link density (mol/dm^3), V_1 is the molar volume of the solvent (for toluene: 0.10613 dm^3/mol), χ_1 is the rubber−solvent interaction parameter (0.39),[30] and V_{r0} is the equilibrium volume fraction of unfilled rubber in the swollen sample. V_{r0} can be determined with the Ellis−Welding equation (eq 4).[40]

$$V_{r0} = \frac{\frac{m_r}{\rho_r}}{\frac{m_r}{\rho_r} + \frac{m_s}{\rho_s}} \tag{4}$$

where m_s is the mass of the swollen rubber sample (g), m_r is the mass of the dry rubber sample (g), ρ_s is the density of the solvent (for toluene: 0.8669 g/cm^3), and ρ_r is the density of the rubber sample (1.20 g/cm^3).

The Flory−Rehner equation can be used to calculate the cross-link density of unfilled vulcanizates. For filled vulcanizates, the Kraus correction (eqs 5 and 6)[39] is needed. With the expression, we can calculate the degree of normal equilibrium swelling a vulcanizate would have achieved if it had not contained any filler.

$$\frac{V_{r0}}{V_{rf}} = 1 - \frac{\mathrm{m}\varphi}{1 - \varphi} \tag{5}$$

In which

$$m = 3c(1 - V_{r0}^{1/3}) + V_{r0} - 1 \tag{6}$$

where V_{r0} is the assumed equilibrium volume fraction of unfilled vulcanizates in the swollen sample, V_{rf} is the equilibrium volume fraction of filled vulcanizates in the swollen sample, c is a constant for a given type of filler, and φ is the volume fraction of the filler. After V_{r0} is obtained, it can be introduced into the Flory−Rehner equation, which determines the cross-link density of the filled vulcanizate.

The degree of devulcanization (decrease in the cross-link density) D (%) was calculated with eq 7.[27]

$$D = \left(1 - \frac{\nu_f}{\nu_i}\right) \times 100 \tag{7}$$

where ν_f is the cross-link density of the devulcanized sample and ν_i is the cross-link density of untreated GTR.

We used Horikx's analysis to determine the relationship between the soluble fraction of rubber and the relative decrease in the cross-link density after devulcanization. There are two different scenarios: random chain scission and scission of the cross-links. In the case of main chain scission or degradation, eq 8 shows the relationship between the soluble fraction of the polymer and the relative decrease in the number of elastically active network chains.

$$1 - \frac{\nu_f}{\nu_i} = 1 - \frac{(1 - \sqrt{s_f})^2}{(1 - \sqrt{s_i})^2} \tag{8}$$

where ν_i stands for the initial cross-link density, ν_f stands for the cross-link density after degradation, s_i stands for the initial sol fraction of the polymer, and s_f stands for the sol fraction of the polymer after treatment.[28,41]

In the second scenario, only the cross-link bonds are cleaved, and the main chains of the polymer stay intact, as described by eq 9.[28]

$$1 - \frac{\nu_f}{\nu_i} = 1 - \frac{\gamma_f(1 - \sqrt{s_f})^2}{\gamma_i(1 - \sqrt{s_i})^2} \tag{9}$$

where γ_i and γ_f stand for the initial and final cross-linking indices, respectively. The cross-linking index tells the average number of cross-link bonds per polymer chain, and it can be determined with eq 10.[28,41]

$$\gamma_x = \nu_x \frac{M_n}{\rho} \tag{10}$$

where γ_x (−) is the cross-linking index, ν_x (mol/dm^3) is the cross-link density, M_n (g/mol) stands for the number-average molecular weight of the rubber, and ρ (g/cm^3) is the density of the rubber. In this paper, the initial cross-linking index is approximated with eq 11.[42]

$$S_i = \frac{(2 + \gamma_i) - \sqrt{\gamma_i^2 + 4\gamma_i}}{2\gamma_i} \tag{11}$$

where S_i is the initial soluble content of GTR (−), and the other notations are the same as mentioned before.

We calculated the selectivity coefficient (K) as a quantitative method to evaluate the selectivity of devulcanization.[31] There are two possible approaches: defining the selectivity parameter in the sol fraction (vertical) direction and the cross-link density (horizontal) direction. The sol fraction selectivity parameter (K_s) can be calculated with eq 12.[31]

$$K_s = \frac{S_c - s}{S_c - S_x} \tag{12}$$

where s is the measured sol fraction of the sample, S_x is the y-coordinate of the intersection of the vertical line set to each data point and the random scission curve, and S_x is the y-coordinate of the intersection of the vertical line set to each data point and the selective cross-link scission curve.

The selectivity parameter in the cross-link density direction (K_x) can be calculated with eq 13.[31]

$$K_x = \frac{X - X_c}{X_x - X_c} \tag{13}$$

where X is the percentage of devulcanization of the sample, X_c is the x-coordinate of the intersection of the horizontal line set to each data point and the random scission curve, and X_x is the x-coordinate of the intersection of the horizontal line set to each data point and the selective cross-link scission curve.

The overall selectivity parameter (K) is then defined according to eq 14.[31] Results range between 0 and 1. Random scission corresponds to $K = 0$, and selective scission corresponds to $K = 1$.

$$K = \frac{K_s + K_x}{2} \tag{14}$$

Figure 1 shows the derivation of the selectivity parameters.

Formulation and Preparation of Rubbers Containing GTR and dGTR. After evaluating the devulcanization experiments, we selected the dGTR_6/160 and dGTR_6/200 samples for further investigation. The formulations of rubber mixtures are shown in Table 2. In the case of samples ending with "A", mixing consisted of two steps. In the first step, the dGTR was compounded with vulcanizing agents (ZnO 10 phr, stearic acid 2 phr, paraffin oil 20 phr, CBS 1.25 phr, TMTD 0.6 phr, and sulfur 0.6 phr). Then, this untreated dGTR mixture was added to the original rubber mixture.

The rubber ingredients were mixed in a Plasti-corder internal mixer (Brabender GmbH & Co. KG, Duisburg, Germany) at 50 °C and 40 rpm. The order of appearance for the components in Table 2 (left to right) also reflects the order of mixing. We used a semi-efficient

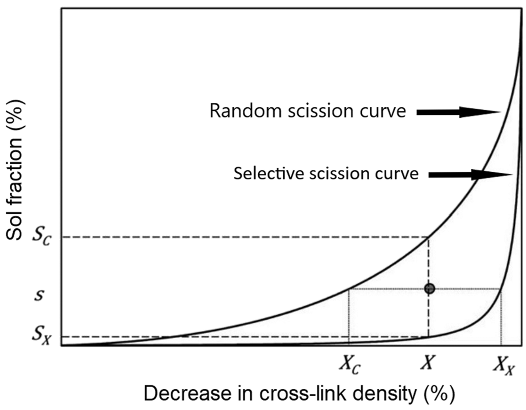


Figure 1. Derivation of the selectivity parameters.[31]

vulcanizing system. The compounds were vulcanized with a Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany) hot press. The pressure applied was 2.8 MPa, and the temperature was 160 °C. Each compound was cured for t_{90} (time necessary to reach 90% vulcanization). These time values were obtained from separate rheometer measurements.

Characterization of the Rubber Mixture and Cured Rubber Sheets. The curing curves of the rubber mixtures were recorded with a MonTech Monsanto R100S rheometer (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) in isothermal (T = 160 °C) time sweep mode (1.667 Hz, 1° angle) for 30 min.

Hardness was tested according to the ISO 7619-1:2010 Shore A method on a Zwick H04.3150.000 hardness tester (Zwick GmbH, Ulm, Germany) on the cured rubber sheets. Ten tests were performed on each compound, followed by the calculation of the average and standard deviation.

The compounds were tensile tested according to the ISO 37:2017 standard on a Zwick Z20 universal testing machine (Zwick GmbH, Ulm, Germany). Type 1 specimens with a clamping length of 60 mm were loaded at a crosshead speed of 500 mm/min. Tear tests were performed on the same testing machine. The test speed was set according to the ISO 34-1:2015 standard (Type C specimen), with a clamping length of 56 mm. Both tests were run at room temperature. The average and standard deviation of tensile strength, tear strength, and elongation at break were calculated based on five tests for each compound.

SEM–EDS was performed on the cross-section of the rubber samples with a JEOL 6380 LA scanning electron microscope (JEOL Ltd., Japan) after the sample surfaces were coated with a conductive carbon layer. The cross-section of the samples was produced by microtome cutting (Leica EM UC6, Wetzlar, Germany) at −120 °C.

AFM was performed on the cross-section of the rubber samples with a FlexAFM 5-type atomic force microscope (Nanosurf AG, Liestal, Switzerland) in tapping mode and a Tap-190AI-G type needle (BudgetSensors Inc., Sofia, Bulgaria) after microtome cutting and before carbon coating.

■ RESULTS AND DISCUSSION

Devulcanization of GTR. Table 3 lists the sol fraction, the decrease in the cross-link density, the selectivity parameter, the irradiation time (the duration when the magnetron was working), and the total treatment time of the microwave-devulcanized samples. The results show that higher treatment temperatures lead to an increase in the soluble content and degree of devulcanization, independent of the heating rate.

Irradiation time shows the duration when the magnetron was working during devulcanization. At lower heating rates (2−3 °C/min), the magnetron was working only approximately for a third of the total treatment time. At the highest heating rate (18 °C/min), this ratio reached 0.9. This means that a significant increase in the heating rate is not possible.

Horikx's analysis helps (Figure 1) evaluate the results further. The samples treated in one heating step (heating rate of 2−18 °C/min) have a very consistent trend in the position of the points. The trend shows that as the temperature increases, we get further and further away from the selective cross-link scission curve, the degradation becomes more severe, and selectivity (the selectivity parameter) decreases drastically. The heating rate of the samples devulcanized at 180 and 200 °C did not significantly affect the degree of devulcanization, but the soluble content decreased with increasing heating rates. We tried to take advantage of this trend and increased the heating rate to 50 °C/min, but the power of the magnetron was not enough to heat 100 g of GTR so fast.

The samples devulcanized at 140−160 °C have high selectivity but only a moderate degree of devulcanization, which increased with increasing residence time. It can be seen that the data points of the samples treated at 180−200 °C are in the 80−85% cross-link density decrease range. The heating rate did not significantly affect the decrease in the cross-link density, but the soluble fraction and the selectivity of these samples are low. The selectivity of the samples treated at 140−160 °C is very high, but the decrease in the cross-link density is moderate. In this temperature range, the heating rate did not significantly affect the soluble fraction, but the cross-link density decreased. The decrease in the cross-link density increased with decreasing heating rate, i.e., with increasing residence time.

In other publications,[27,33] with a power-controlled microwave oven, with low irradiation time (15−120 s), the temperature only reached 140−160 °C, but it was not sufficient—the degree of devulcanization was low. Increased irradiation times resulted in a large leap in temperature (it reached 220−260 °C), and the GTR was severely degraded. With a power-controlled microwave oven, it is not possible to increase the residence time without a temperature rise.

At lower temperatures (140−160 °C), the residence time is crucial, and we would have liked to increase the residence time.

Table 2. NR-Based Rubber Compounds Containing Microwave-Devulcanized GTR and Their Abbreviations (Values in phr)

abbreviation	NR	ZnO	stearic acid	carbon black (N772)	dGTR	dGTR mixture	GTR	paraffin oil	CBS	TMTD	sulfur
NR_REF	100	10	2	60	0	0	0	10	1.25	0.6	0.6
NR_dGTR_6/160	100	10	2	60	100	0	0	0	1.25	0.6	0.6
NR_dGTR_6/200	100	10	2	60	100	0	0	0	1.25	0.6	0.6
NR_dGTR_6/160_A	100	10	2	60	0	100	0	10	1.25	0.6	0.6
NR_dGTR_6/200_A	100	10	2	60	0	100	0	10	1.25	0.6	0.6
NR_GTR	100	10	2	60	0	0	100	10	1.25	0.6	0.6

Table 3. Sol Fraction of GTR after Microwave Devulcanization

sample	sol fraction (%)	decrease in the cross-link density (%)	selectivity parameter, K (−)	irradiation time (min)	total treatment time (min)
GTR	10.0 ± 1.2	0		0	0
dGTR_2/140	12.2 ± 0.7	68.9 ± 0.6	0.99 ± 0.01	17.3	60.0
dGTR_3/140	11.0 ± 0.8	63.4 ± 0.4	1.00 ± 0.02	12.1	40.0
dGTR_3/160	17.4 ± 0.7	72.8 ± 0.4	0.79 ± 0.01	14.4	46.7
dGTR_3/180	36.7 ± 0.6	79.4 ± 0.5	0.37 ± 0.02	16.8	53.3
dGTR_3/200	41.3 ± 0.6	81.7 ± 0.7	0.30 ± 0.02	18.6	60.0
dGTR_6/140	10.6 ± 0.7	55.4 ± 0.4	1.00 ± 0.02	7.1	20.0
dGTR_6/160	13.8 ± 0.6	68.8 ± 0.3	0.89 ± 0.01	8.9	23.3
dGTR_6/180	30.4 ± 0.8	80.4 ± 0.6	0.56 ± 0.02	10.5	26.7
dGTR_6/200	38.5 ± 0.6	80.0 ± 0.5	0.34 ± 0.02	11.9	30.0
dGTR_12/140	10.3 ± 0.7	53.5 ± 0.4	1.00 ± 0.02	6.5	10.0
dGTR_12/160	13.3 ± 0.5	66.1 ± 0.3	0.89 ± 0.01	7.5	11.7
dGTR_12/180	26.7 ± 0.7	79.8 ± 0.4	0.65 ± 0.01	8.9	13.3
dGTR_12/200	37.4 ± 0.9	82.0 ± 0.6	0.43 ± 0.01	9.9	15.0
dGTR_18/140	10.6 ± 0.6	37.9 ± 0.3	0.88 ± 0.01	5.5	6.7
dGTR_18/160	11.2 ± 0.6	51.2 ± 0.4	0.91 ± 0.01	6.4	7.8
dGTR_18/180	22.7 ± 0.8	77.5 ± 0.5	0.71 ± 0.02	7.6	8.9
dGTR_18/200	35.4 ± 0.7	82.4 ± 0.5	0.49 ± 0.01	8.4	10.0
dGTR_18/120_30	11.4 ± 0.6	54.0 ± 0.6	0.91 ± 0.01	10.7	35.6
dGTR_3/140_30	18.4 ± 0.7	73.0 ± 0.6	0.76 ± 0.02	20.9	70.0
dGTR_18/140_30	13.7 ± 0.6	57.4 ± 0.6	0.77 ± 0.01	14.6	36.7
dGTR_18/160_30	36.4 ± 0.8	84.0 ± 0.7	0.51 ± 0.01	15.8	37.8
dGTR_18/120_1/140	11.5 ± 0.6	66.7 ± 0.5	1.00 ± 0.02	12.7	25.6
dGTR_18/120_3/140	11.3 ± 0.7	64.3 ± 0.4	1.00 ± 0.02	7.2	12.2

Therefore, first, we decreased the heating rate from 3 to 2 °C/min (Figure 2a), and the cross-link density decreased without a significant change in selectivity, but a further decrease in the heating rate would have resulted in unreasonably long treatment times. Therefore, our idea was that we would only increase the residence time at the final temperature. We used a holding time of 30 min at the final temperature (Figure 2e, abbreviations ending with _30) and used two different heating rates (samples dGTR_18/120_3/140 and dGTR_18/120_1/140).

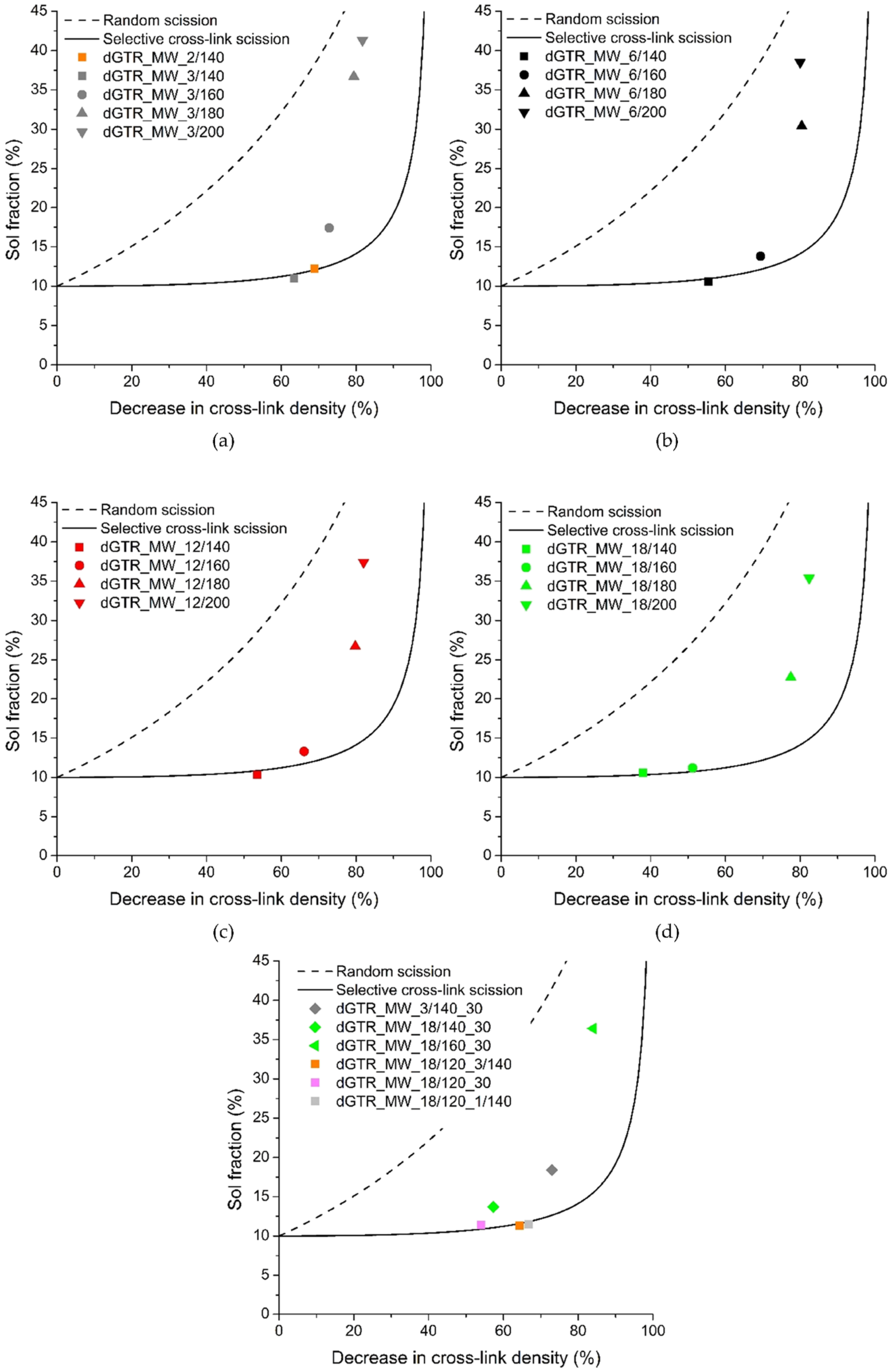
The holding phase took place in the microwave oven, and the equipment had to switch on the magnetron to counterbalance cooling. Our hypothesis was that it is equivalent to a slow heating cycle. The results show that a 30 min holding time at 140 °C, especially at 160 °C, caused degradation. A comparison of these samples with the dGTR_2/140 sample (highest selectivity and degree of devulcanization) shows that the main issue was the holding time at 140 °C; the temperature was too high. Therefore, in the low-temperature devulcanization range, the key parameter is the residence time of the GTR. With that in mind, we devulcanized GTR at 120 °C and used a 30 min holding time (dGTR_18/120_30) and two different heating rates (dGTR_18/120_3/140 and dGTR_18/120_1/140) in one treatment to increase the residence time near the final temperature. In the dGTR 18/120_30 sample, selectivity increased, thanks to the lower temperature, but the degree of devulcanization decreased compared to the dGTR_18/140_30 sample. In other samples, an increased residence time at 120−140 °C had a positive effect on the degree of devulcanization, which was still below that of the dGTR_2/140 sample.

Knowing the irradiation times, we were able to calculate the specific microwave energy based on eq 1. The plot of the decrease in the cross-link density or the selectivity parameter as a function of the specific microwave energy (Figure 3a) shows that a high degree of devulcanization (75−85%) was not only achieved with high absorbed energy but also with lower amounts of absorbed energy (between 1200 and 3400 Wh/kg). However, only samples devulcanized at 140−160 °C have high selectivity (>0.85) (Figure 3b).

In several publications, the researchers used conventional power-controlled microwave ovens, but we used a temperature-controlled oven; therefore, the irradiation times that we determined, compared to other publications, can be surprisingly long. For example, Aoudia et al.[33] devulcanized 2.7 g of GTR for 15−60 s, with power ranging from 350 to 900 W. With these parameters, the specific microwave energy ranged between 540 and 5556 Wh/kg, and the decrease in the cross-link density was 70−90%. Sadly, they did not present the final temperatures, but with Fourier transform infrared spectroscopy, they established severe degradation of the GTR samples treated for 60 s. In other publications,[13,26] irradiation times ranged between 2.5 and 7 min (700−1000 W), and the mass of the treated GTR was between 3.7 and 15 g. The decrease in the cross-link density was between 30 and 60%, and the measured maximum temperature was 170 °C.[13]

The degree of devulcanization alone is not enough for the evaluation of the results because only the selectivity parameter can show the distance of the data points from the selective cross-link scission curve in the Horikx plot. To overcome this, we introduced a parameter that considers both the degree of devulcanization and selectivity. This parameter is $K{\cdot}D$, a product of the relative value of devulcanization and selectivity (Figure 3c).

$K{\cdot}D$ can take values between 0 and 1 (the higher the value, the more effective devulcanization is). The figure shows that samples devulcanized at higher temperatures (180−200 °C) had a larger decrease in the cross-link density, but their $K{\cdot}D$



(a) (b)

(c) (d)

Figure 2. Horikx's plot: sol content of devulcanized samples versus decrease in the cross-link density. (a) Samples treated with 2 and 3 °C/min heating rates; (b) samples treated with 6 °C/min heating rate; (c) samples treated with 12 °C/min heating rate; (d) samples treated with 18 °C/min heating rate; and (e) samples with two different treatments in one treatment cycle.

values were low due to their low selectivity. Samples devulcanized at lower temperatures (140−160 °C) had very high selectivity, so their $K{\cdot}D$ values were high.

High selectivity or a high degree of devulcanization alone is not a sufficient criterion for effective devulcanization, and the two values must be treated together. For example, dGTR_MW_3/200 has a high degree of devulcanization but low selectivity, and dGTR_MW_18/140 has high selectivity and a low degree of devulcanization. Therefore, the $K{\cdot}D$ of both samples is low, and the efficiency of devulcanization is low.

The specific microwave energy does not follow the $K{\cdot}D$ value. The specific microwave energy does not affect effective devulcanization, which is only influenced by the temperature and residence time. Devulcanization at 140 °C, with a long residence time, i.e., high specific microwave energy, and at a

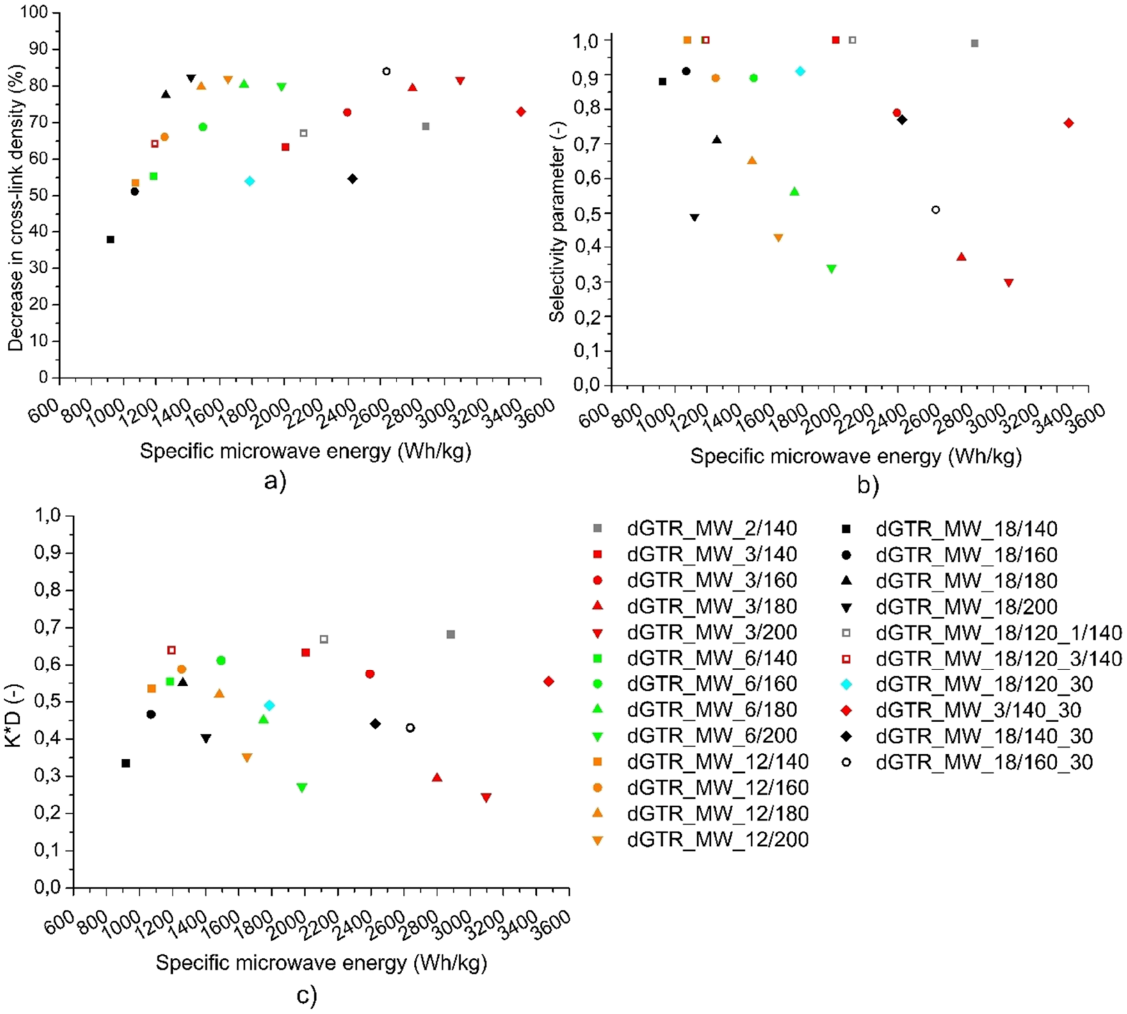


Figure 3. (a) Degree of devulcanization, (b) selectivity, and (c) *K·D* as a function of the specific microwave energy.

higher temperature of 160 °C, with a shorter residence time, i.e., lower specific microwave energy, can both result in a high *K·D* value.

For further analysis, we selected the dGTR_MW_6/160 and dGTR_MW_6/200 samples and introduced them into NR-based rubber mixtures. In the selection of the dGTR samples, we considered Horikx's analysis, the *K·D* value, and the decrease in the cross-link density. dGTR_MW_6/160 had high selectivity, and dGTR_MW_6/200 suffered severe degradation.

Cure Characteristics of the Rubber Compounds. Figure 4 shows the recorded vulcanization curves of the samples. dGTR has a softening effect on the mixtures, and the maximum torque is significantly decreased. Also, the more degraded the dGTR in the sample, the more the torque decreased. GTR acts as a filler—it significantly increased the torque in the induction phase, so it is more difficult to process NR_GTR than the other mixtures. With extra vulcanizing agents, it was possible to recover the torque without the initial torque increasing because more cross-links formed during curing.

Table 4 shows the main parameters of the vulcanization curves. dGTR reduced the vulcanization times of the samples, and the extra amount of vulcanizing agents further reduced it. The hardness of the samples decreased with increasing dGTR content, but the extra vulcanizing agents helped to recover it.

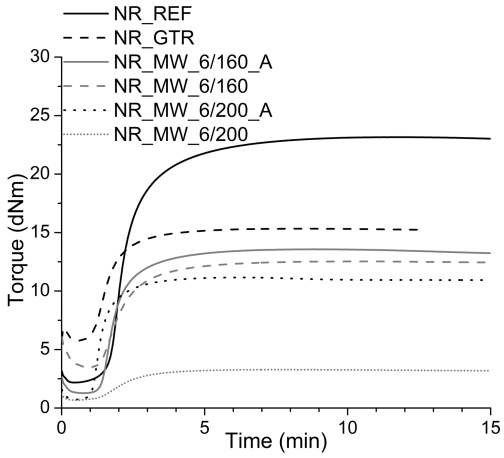


Figure 4. Vulcanization curves of the samples.

Mechanical Properties of the Cured Rubber Compounds. The dGTR added to the rubber mixture drastically decreased tensile strength (Figure 5a). The more degraded the dGTR, the more it decreased the tensile strength. However, elongation at break did not follow this trend (Figure 5b); it showed a moderate decrease, and all samples exceeded 300% elongation. Comparing our results to other literature data may suggest that the deterioration of tensile strength (~65%) is

Table 4. Cure Characteristics and Hardness of the Samples

sample	t_{90} (min)	t_{s2}/t_{10} (min)	minimum torque (dNm)	maximum torque (dNm)	Shore A hardness (−)
NR_REF	4.2	1.7	2.2	23.2	57.3 ± 0.7
NR_dGTR_6/160	3.8	1.5	3.5	12.5	47.2 ± 0.3
NR_dGTR_6/200	3.7	1.3	0.7	3.3	34.1 ± 0.6
NR_GTR	2.9	1.1	5.7	15.3	52.9 ± 0.4
NR_dGTR_6/160_A	3.3	1.4	1.3	13.6	50.4 ± 0.5
NR_dGTR_6/200_A	2.4	1.1	0.7	11.2	43.3 ± 0.6

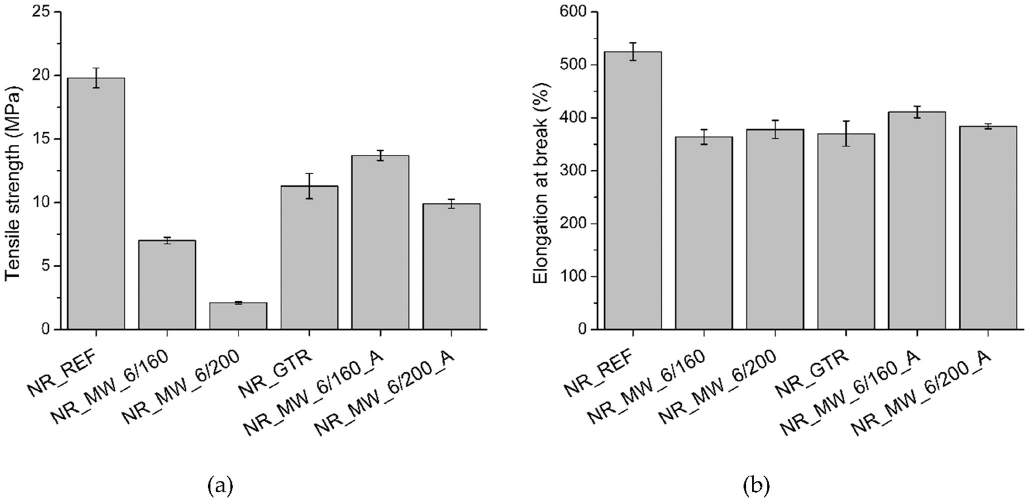


Figure 5. (a) Tensile strength and (b) elongation at break of the samples.

more considerable,[35,36] but in these cases, the typical amount of dGTR added to the mixtures was below 50 phr. The deterioration of tensile strength was ∼30 to 40% in these publications. We successfully improved the tensile strength of mixtures containing dGTR with the development of the recipe and mixing method. Two-step mixing and the extra vulcanizing agents helped to recover tensile strength, but there was no significant effect on elongation at break. It is important to note that properties can be improved further. We only modified the amount of vulcanizing agents but replacing carbon black with more active carbon black can recover mechanical properties more. Furthermore, additives can be used to compatibilize dGTR and NR. For example, TOR (trans-polyoctenamer) is a promising candidate to improve adhesion between the phases.[43]

dGTR drastically reduced tear strength as well (Figure 6), but due to the additional vulcanizing agents introduced by two-step mixing, tear strength increased and exceeded the reference value. Samples with more degraded dGTR showed a higher increase in tear strength. It may be due to the fact that the fragmented molecular chains are more mobile and form bonds more easily, resulting in even better interfacial contact.

Morphology of the Cured Rubber Compounds. We compared the morphology of the rubber mixtures by AFM and SEM−EDS. We used AFM to investigate the modulus, or damping, to see how the different phases separate from each other. The behavior of extra vulcanizing agents was examined by SEM−EDS. Do they act only at the surface of the dGTR particles or in the particles as well? We also wanted to investigate the homogeneity of devulcanization and revulcanization.

Figure 7a,b shows the AFM images of the cross-section of the NR_REF and the NR_GTR samples. The cross-section of NR_REF shows a uniform morphology. In Figure 7b, a GTR particle can be seen with bright yellow color, and the darker area is the rubber matrix. From the uniformity of the color shade of the GTR particle, we can infer uniform properties along the cross-section.

The sample containing dGTR (Figure 8a) and the sample produced by two-step mixing with dGTR (Figure 8b) show that the change in properties along the cross-section of the particles is negligible. Devulcanization and the vulcanizing agents during the mixing acted uniformly along the whole cross-section of the particles. With conventional mixing, the vulcanizing agents had a uniform but small effect on the dGTR. They rather had an impact on the matrix. In comparison, with

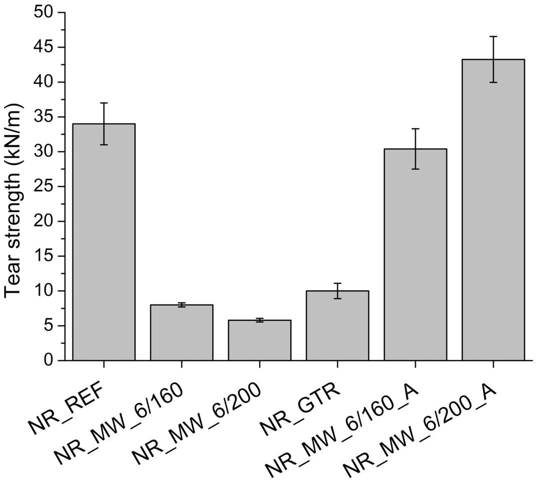
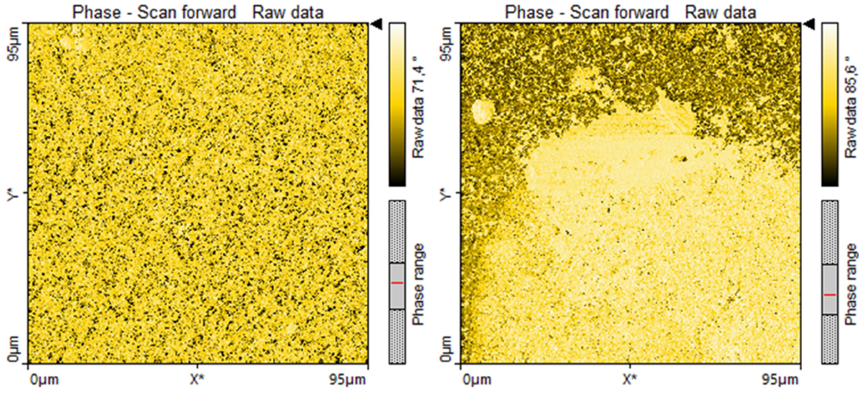
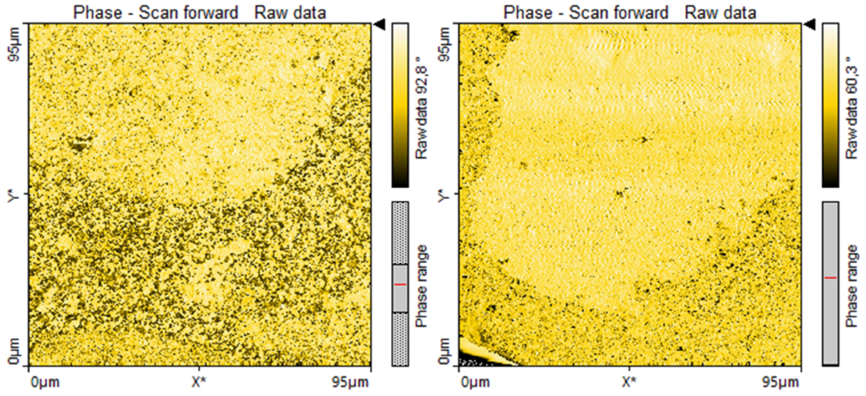


Figure 6. Tear strength of the samples.



a) b)

Figure 7. AFM image of (a) NR_REF and (b) NR_GTR samples.

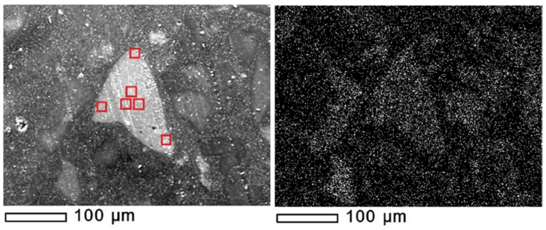


a) b)

Figure 8. AFM image of (a) NR_dGTR_6/160 and (b) NR_dGTR_6/160_A samples.

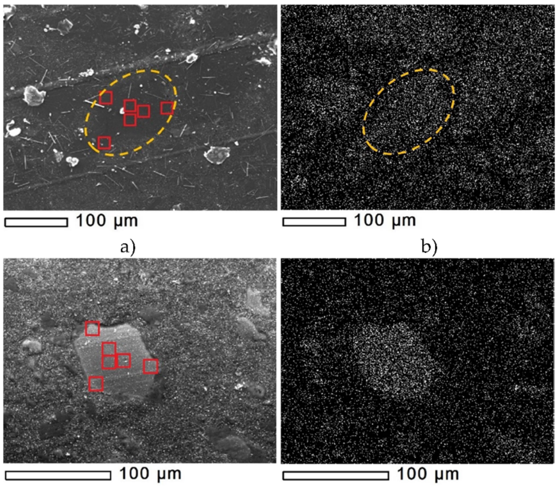
two-step mixing, the extra vulcanizing agents affected the dGTR particles more.

We used SEM−EDS to support the AFM results. We detected carbon, oxygen, sulfur, and zinc atoms (Figures 9 and 10), but we only present the distribution of the sulfur atoms because our goal was to compare the sulfur content and how it changes in the GTR and dGTR particles. Figure 10a shows the SEM image of the cross-section of the NR_GTR sample. The red squares show the areas examined in more detail and where EDS was performed. We compared the atomic composition on the edge and in the middle of the cross-section of the GTR particle. The results are summarized in Table 5.



a) b)

Figure 9. SEM image of (a) NR_GTR and (b) distribution of the detected sulfur atoms (SEM−EDS).



a) b) c) d)

Figure 10. SEM image of (a) NR_dGTR_6/160 and (c) NR_dGTR_6/160_A, and the distribution of sulfur atoms in (b) NR_dGTR_6/160 and (d) NR_dGTR_6/160_A samples (SEM−EDS).

The number of atoms detected varies little depending on the location of the test, and the composition of the GTR particles along the cross-section is uniform (Table 5). It is hard to compare the results with the recipe of GTR because the formulation of the GTR is unknown. According to the literature,[44,45] zinc oxide is used in more weight percent than sulfur in tire tread mixtures. It is true, but we measured a higher sulfur content than zinc content. It is due to the much

Table 5. Atomic Composition of the GTR Particle

element	middle of the particle (%)	edge of the particle (%)
carbon	88.89 ± 0.08	88.78 ± 0.06
oxygen	5.01 ± 0.09	4.95 ± 0.10
zinc	2.72 ± 0.07	2.80 ± 0.06
sulfur	3.38 ± 0.07	3.47 ± 0.06

higher accelerating voltage required to detect zinc in the EDS test compared to the carbon, oxygen, and sulfur atoms. In addition, an increased electron beam diameter is required for EDS compared to SEM. Despite the carbon layer applied, the high accelerating voltage and wide electron beam caused degradation of the samples. We reduced both the accelerating voltage and the diameter of the electron beam to avoid it, but this made the detection of zinc more difficult.

Figure 10 shows the SEM−EDS images of the NR_dGTR_6/160 and NR_dGTR_6/160_A samples. In the SEM image of the NR_MW_6/160 sample, the particles are relatively harder to distinguish from the matrix, (Figure 10a), but the detected sulfur atoms roughly outline them (Figure 10b). We marked the investigated dGTR particle with a yellow dashed curve. In the NR_MW_6/160_A sample, produced by two-step mixing, the detected sulfur atoms show a sharper boundary with the dGTR particle due to the additional vulcanizing agents.

Table 6 shows a summary of the results of EDS made with higher magnification marked with red squares. A comparison of the sulfur content of the GTR particles in the NR_GTR sample and the dGTR particles in the NR_MW_6/160 sample shows a decrease in the sulfur content, which proves devulcanization. Song et al.[46] achieved similar results with hot air treatment (150 °C, 4 h). The decrease in the number of sulfur atoms was 25%, but Horikx's analysis showed severe degradation. Araujo-Morera et al.[47] showed using SEM−EDS that mechanochemical devulcanization was uniform on the surface of the GTR particles. From the measured sulfur content in the middle and at the edge of the dGTR particles, we can assume that devulcanization and sulfur (during mixing) act uniformly in the whole cross-section of the particles (less than 200 μm).

The detected sulfur and oxygen content increased in the NR_MW_6/160_A sample due to the extra vulcanizing agents introduced by two-step mixing, but the zinc content did not increase as much for the reason mentioned above.

CONCLUSIONS

We devulcanized GTR with microwaves in a laboratory oven at 140−200 °C and used a heating rate between 2 and 18 °C/min. We then characterized the dGTR samples by Soxhlet extraction and swelling tests to determine their soluble content and cross-link density and performed Horikx's analysis. We also determined the selectivity parameter and specific microwave energy of the samples. The results showed that with GTR devulcanized at lower temperatures (140−160 °C), selectivity was very high, and the degree of devulcanization was adequate (∼50 to 70%). At higher temperatures (180−200 °C), the degree of devulcanization reached 85%, but selectivity was low, which indicates severe degradation in this temperature range. At lower temperatures and decreasing heating rate, i.e., increasing residence time, the degree of devulcanization increased, but at higher temperatures, the heating rate had no significant effect on the degree of devulcanization. An adequate degree of devulcanization and high selectivity can be achieved below the degradation temperature of NR. Near, at, or above the degradation temperature of NR, degradation occurs, and an increasing residence time also increases degradation.

The degree of devulcanization and selectivity should be treated together, so we introduced the *K·D* number. It can be calculated as the product of the relative decrease in the cross-link density and selectivity. We rated the samples based on *K·D*. Comparing these results with the specific microwave energy showed that degradation does not depend on the specific microwave energy. It depends only on the temperature and the heating rate.

We selected two dGTR samples and introduced them in 100 phr into NR-based mixtures. In addition, we produced samples with two-step mixing with extra vulcanizing agents (first adding vulcanizing agents to dGTR, and then mixing it with the reference rubber mixture). The physical and mechanical properties of the mixtures containing dGTR became considerably worse, but two-step mixing helped recover tensile strength, especially tear strength.

The SEM−EDS and AFM results showed that microwave devulcanization and the vulcanizing agents mixed with the dGTR acted in the whole cross-section of the dGTR.

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Notes

The authors declare no competing financial interest.

Table 6. Atomic Composition of the dGTR Particles

	NR_MW_6/160		NR_MW_6/160_A	
element	middle of the particle (%)	edge of the particle (%)	middle of the particle (%)	edge of the particle (%)
carbon	90.76 ± 0.09	90.60 ± 0.08	88.15 ± 0.08	87.80 ± 0.07
oxygen	4.72 ± 0.07	4.94 ± 0.09	5.53 ± 0.09	5.72 ± 0.08
zinc	2.36 ± 0.08	2.43 ± 0.07	2.51 ± 0.08	2.59 ± 0.07
sulfur	2.16 ± 0.08	2.03 ± 0.06	3.81 ± 0.08	3.89 ± 0.07

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■ REFERENCES

(1) Adhikari, B.; De, D.; Maiti, S. Reclamation and recycling of waste rubber. *Prog. Polym. Sci.* **2000**, *25*, 909−948.

(2) Loderer, C.; Partl, M. N.; Poulikakos, L. D. Effect of crumb rubber production technology on performance of modified bitumen. *Constr. Build. Mater.* **2018**, *191*, 1159−1171.

(3) Forrest, M. J.*Recycling and re-use of waste rubber*, 2nd ed.; De Gruyter: Berlin, 2019.

(4) Nunes, A. T.; de Santos, R. E.; Pereira, J. S.; Barbosa, R.; Ambrósio, J. D. Characterization of waste tire rubber devulcanized in twin-screw extruder with thermoplastics. *Prog. Rubber, Plast. Recycl. Technol.* **2018**, *34*, 143−157.

(5) Jiang, C.; Zhang, Y.; Ma, L.; Zhou, L.; He, H. Tailoring the properties of ground tire rubber/high-density polyethylene blends by combining surface devulcanization and in-situ grafting technology. *Mater. Chem. Phys.* **2018**, *220*, 161−170.

(6) Hejna, A.; Korol, J.; Przybysz-Romatowska, M.; Zedler, Ł.; Chmielnicki, B.; Formela, K. Waste tire rubber as low-cost and environmentally-friendly modifier in thermoset polymers − A review. *Waste Manage.* **2020**, *108*, 106−118.

(7) Karabork, F. Investigation of the mechanical, tribological and corrosive properties of epoxy composite coatings reinforced with recycled waste tire products. *Express Polym. Lett.* **2022**, *16*, 1114−1127.

(8) Fazli, A.; Rodrigue, D. Recycling waste tires into ground tire rubber (GTR)/rubber compounds: A review. *J. Compos. Sci.* **2020**, *4*, 103.

(9) Colom, X.; Carrillo, F.; Cañavate, J. Composites reinforced with reused tyres: Surface oxidant treatment to improve the interfacial compatibility. *Composites, Part A* **2007**, *38*, 44−50.

(10) Lu, Y.; Yang, Y.; Xiao, P.; Feng, Y.; Liu, L.; Tian, M.; Li, X.; Zhang, L. Effect of interfacial enhancing on morphology, mechanical, and rheological properties of polypropylene-ground tire rubber powder blends. *J. Appl. Polym. Sci.* **2017**, *134*, 45354.

(11) Ramarad, S.; Khalid, M.; Ratnam, C. T.; Chuah, A. L.; Rashmi, W. Waste tire rubber in polymer blends: A review on the evolution, properties and future. *Prog. Mater. Sci.* **2015**, *72*, 100−140.

(12) Bockstal, L.; Berchem, T.; Schmetz, Q.; Richel, A. Devulcanisation and reclaiming of tires and rubber by physical and chemical processes: A review. *J. Cleaner Prod.* **2019**, *236*, 117574.

(13) Buitrago-Suescún, O.; Britto, R. Devulcanization of ground tire rubber: thermo-oxidation followed by microwave exposure in the presence of devulcanizing agent. *Iran. Polym. J.* **2020**, *29*, 553−567.

(14) Molanorouzi, M.; Mohaved, S. O. Reclaiming waste tire rubber by an irradiation technique. *Polym. Degrad. Stab.* **2016**, *128*, 115−125.

(15) de Sousa, F. D. B.; Zanchet, A.; Scuracchio, C. H. From devulcanization to revulcanization: Challenges in getting recycled tire rubber for technical applications. *ACS Sustainable Chem. Eng.* **2019**, *7*, 8755−8765.

(16) Diaz, R.; Colomines, G.; Peuvrel-Disdier, E.; Deterre, R. Thermo-mechanical recycling of rubber: Relationship between material properties and specific mechanical energy. *J. Mater. Process. Technol.* **2018**, *252*, 454−468.

(17) Seghar, S.; Asaro, L.; Rolland-Monnet, M.; Aït, H. N. Thermo-mechanical devulcanization and recycling of rubber industry waste. *Resour., Conserv. Recycl.* **2019**, *144*, 180−186.

(18) Ghorai, S.; Bhunia, S.; Roy, M.; De, D. Mechanochemical devulcanization of natural rubber vulcanizate by dual function disulfide chemicals. *Polym. Degrad. Stab.* **2016**, *129*, 34−46.

(19) Zhang, X.; Saha, P.; Cao, L.; Li, H.; Kim, J. Devulcanization of waste rubber powder using thiobisphenols as novel reclaiming agent. *Waste Manage.* **2018**, *78*, 980−991.

(20) Ghavipanjeh, F.; Rad, Z. Z.; Pazouki, M. Devulcanization of ground tires by different strains of bacteria: optimization of culture condition by Taguchi method. *J. Polym. Environ.* **2018**, *26*, 3168−3175.

(21) Hong, Y. J.; Jeong, K. M.; Saha, P.; Suh, J.; Kim, J. K. Processing and characterization of microwave and ultrasonically treated waste-EPDM/LDPE polymer composites. *Polym. Eng. Sci.* **2015**, *55*, 533−540.

(22) Asaro, L.; Gratton, M.; Poirot, N.; Seghar, S.; Aït, H. N. Devulcanization of natural rubber industry waste in supercritical carbon dioxide combined with diphenyl disulfide. *Waste Manage.* **2020**, *118*, 647−654.

(23) Formela, K.; Hejna, A.; Zedler, Ł.; Colom, X.; Cañavate, J. Microwave treatment in waste rubber recycling − recent advances and limitations. *Express Polym. Lett.* **2019**, *13*, 565−588.

(24) Scuracchio, C. H.; Waki, D. A.; da Silva, M. L. C. P. Thermal analysis of ground tire rubber devulcanized by microwaves. *J. Therm. Anal. Calorim.* **2007**, *87*, 893−897.

(25) Garcia, P. S.; de Sousa, F. D. B.; de Lima, J. A.; Cruz, S. A.; Scuracchio, C. H. Devulcanization of ground tire rubber: Physical and chemical changes after different microwave exposure times. *Express Polym. Lett.* **2015**, *9*, 1015−1026.

(26) Colom, X.; Faliq, A.; Formela, K.; Cañavate, J. FTIR spectroscopic and thermogravimetric characterization of ground tyre rubber devulcanized by microwave treatment. *Polym. Test.* **2016**, *52*, 200−208.

(27) de Sousa, F. D. B.; Scuracchio, C. H.; Hu, G.-H.; Hoppe, S. Devulcanization of waste tire rubber by microwaves. *Polym. Degrad. Stab.* **2017**, *138*, 169−181.

(28) Horikx, M. M. Chain scissions in a polymer network. *J. Polym. Sci.* **1956**, *19*, 445−454.

(29) Khavarnia, M.; Movahed, S. O. Butyl rubber reclamation by combined microwave radiation and chemical reagents. *J. Appl. Polym. Sci.* **2016**, *133*, 11.

(30) de Sousa, F. D. B.; Zanchet, A.; Scuracchio, C. H. Influence of reversion in compounds containing recycled natural rubber: In search of sustainable processing. *J. Appl. Polym. Sci.* **2017**, *134*, 45325.

(31) Edwards, D. W.; Danon, B.; van der Gryp, P.; Görgens, J. F. Quantifying and comparing the selectivity for crosslink scission in mechanical and mechanochemical devulcanization processes. *J. Appl. Polym. Sci.* **2016**, *133*, 43932.

(32) Zanchet, A.; de Sousa, F. Elastomeric composites containing SBR industrial scraps devulcanized by microwaves: Raw material, not a trash. *Recycling* **2020**, *5*, 3.

(33) Aoudia, K.; Azem, S.; Aït, H. N.; Gratton, M.; Pettarin, V.; Seghar, S. Recycling of waste tire rubber: Microwave devulcanization and incorporation in a thermoset resin. *Waste Manage.* **2017**, *60*, 471−481.

(34) Debapriya, D.; Debasish, D. Processing and material characteristics of a reclaimed ground rubber tire reinforced styrene butadiene rubber, Materials Sciences and Applications. *Mater. Sci. Appl.* **2011**, *2*, 486−496.

(35) Colom, X.; Marín-Genescà, M.; Mujal, R.; Formela, K.; Cañavate, J. Structural and physico-mechanical properties of natural rubber/GTR composites devulcanized by microwaves: Influence of GTR source and irradiation time. *J. Compos. Mater.* **2018**, *52*, 3099−3108.

(36) Luo, M.; Liao, X.; Liao, S.; Zhao, Y. Mechanical and dynamic mechanical properties of natural rubber blended with waste rubber powder modified by both microwave and sol−gel method. *J. Appl. Polym. Sci.* **2013**, *129*, 2313.

(37) Simon, D. Á.; Pirityi, D. Z.; Bárány, T. Devulcanization of ground tire rubber: microwave and thermomechanical approaches. *Sci. Rep.* **2020**, *10*, 16587.

(38) Flory, P. J.; Rehner, J. Statistical mechanics of cross-linked polymer networks II. swelling. *J. Chem. Phys.* **1943**, *11*, 521−526.

(39) Kraus, G. Swelling of filler-reinforced vulcanizates. *J. Appl. Polym. Sci.* **1963**, *7*, 861−871.

(40) Ellis, B.; Welding, G. N. Estimation, from swelling, of the structural contribution of chemical reactions to the vulcanization of natural rubber. Part II. Estimation of equilibrium degree of swelling. *Rubber Chem. Technol.* **1964**, *37*, 571−575.

(41) Verbruggen, M. A. L.; van der Does, L.; Noordermeer, J.; van Duin, M.; Manuel, H. J. Mechanisms involved in the recycling of NR and EPDM. *Rubber Chem. Technol.* **1999**, *72*, 731−740.

(42) Verbruggen, M. A. L.; van der Does, L.; Dierkes, W. K.; Noordermeer, J. W. M. Experimental validation of the Charlesby and Horikx models applied to de-vulcanization of sulfur and peroxide vulcanizates of NR and EPDM. *Rubber Chem. Technol.* **2016**, *89*, 671−688.

(43) Zedler, Ł.; Kowalkowska-Zedler, D.; Colom, X.; Cañavate, J.; Saeb, M. R.; Formela, K. Reactive sintering of ground tire rubber (GTR) modified by a trans-polyoctenamer rubber and curing additives. *Polymer* **2020**, *12*, 3018.

(44) Waddell, W. H.; Evans, L. R. Use of nonblack fillers in tire compounds. *Rubber Chem. Technol.* **1996**, *69*, 377−423.

(45) Wang, M.-J.; Lu, S. X.; Mahmud, K. Carbon−silica dual-phase filler, a new-generation reinforcing agent for rubber. Part VI. Time−temperature superposition of dynamic properties of carbon−silica-dual-phase-filler-filled vulcanizates. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 1240−1249.

(46) Song, P.; Wan, C.; Xie, Y.; Formela, K.; Wang, S. Vegetable derived-oil facilitating carbon black migration from waste tire rubbers and its reinforcement effect. *Waste Manage.* **2018**, *78*, 238−248.

(47) Araujo-Morera, J.; Verdugo-Manzanares, R.; González, S.; Verdejo, R.; Lopez-Manchado, M. A.; Hernández, S. M. On the use of mechano-chemically modified ground tire rubber (GTR) as recycled and sustainable filler in styrene-butadiener ubber (SBR) composites. *J. Compos. Sci.* **2021**, *5*, 68.