Microwave devulcanization of ground tire rubber and applicability in SBR compounds

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ABSTRACT: Rubber recycling is a major environmental challenge, as their covalently crosslinked structure makes it impossible to reprocess *via* conventional polymer processing technologies. Devulcanization of rubber waste, whereby crosslinks are selectively broken, may provide a solution, as it allows it to be remolded into new shapes. We used two types of ground tire rubbers (GTRs) for this study; mechanically ground and waterjet-milled GTRs with different particle sizes. First, we revealed the effects of GTR particle size on the devulcanization process. We examined the sol content of the samples before and after devulcanization with two different microwave ovens, a power-controlled conventional one, and a temperature-controlled laboratory oven. In the latter one, heating rate and maximum temperature were controlled. We studied the effects of temperature, atmosphere in which the rubber was treated, heating rate, and holding time at maximum temperature. We prepared styrene-butadiene rubber-based rubber compounds containing GTR and optimally devulcanized GTR (dGTR_WJ). The physical and mechanical properties of the samples were assessed. The results indicate that both GTR_WJ and dGTR_WJ have an accelerating and a mildly softening effect on curing and dGTR_WJ has a less significant negative effect on mechanical properties: 15 phr GTR_WJ has the same effect as 45 phr dGTR_WJ. © 2019 The Authors. *Journal of Applied Polymer Science* published by Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2020**, *137*, 48351.

INTRODUCTION

The expansion of the rubber industry is continuous. Global production of natural rubber (NR) and synthetic rubber is increasing steadily, which means the amount of rubber waste is growing as well. Rubber waste does not decompose easily, due to its crosslinked structure and the presence of stabilizers and other additives.[1,2] Large amounts of elastomeric waste, most prominently in the form of tires, are dumped to unsuitable places, generating escalating environmental hazards. Rubbers cannot be recycled like thermoplastics *via* relatively simple and cost-effective reprocessing (for example, remelting or remolding) methods. Currently, the recycling of tires is even harder, as their chemical composition is confidential. Therefore, recycling tire waste is a global problem and poses a great challenge to researchers. Reclaiming tires in the form of ground powder (ground tire rubber [GTR]) is considered to be the most attractive method of reusing rubber tire waste.[3] Consequently, GTR has been a commercially available product for

decades. There are a number of methods currently in industrial use to grind rubber waste: mechanical grinding at ambient or cryogenic conditions,[4] and waterjet milling. The latter incorporates a high-pressure water beam that grinds rubber waste. Compared with mechanical grinding, smaller particles with higher specific surface can be obtained by this method and rubber degradation can also be avoided, though the final material needs to be dried.

GTR can be blended with thermoplastic[3,5,6] or thermoset[7–9] polymers with or without compatibilization.[10,11] However, devulcanization is expected to bring a breakthrough for GTR recycling. During this process, new molecules are formed *via* crosslink scission. These molecules can form new bonds on the surface of the GTR particles,[1,3,12–15] which enhances adhesion between devulcanized GTR (dGTR) particles and the matrix. Consequently, the amount of recycled rubber in a new rubber product can be increased without compromising its mechanical properties. There

are various methods for rubber devulcanization, including thermomechanical,[16,17] thermochemical,[18] mechanochemical,[19] physical, and biological[20,21] techniques, as well as methods using microwaves[1,13,14,22] and ultrasound.[23,24]

Currently, microwave devulcanization is one of the most promising technologies because of the good properties of the treated material and the promise of high productivity as well as relative low costs.[25] Microwave heating takes advantage of volumetric heating: a fast and uniform rise of temperature can be achieved. The process does not require additional chemicals and is considered an eco-friendly technology. A disadvantage of microwave devulcanization is that nonpolar polymer chains are almost transparent for microwaves. Rubber additives, such as carbon black, can absorb microwaves and dissipate their energy in the form of heat due to their dielectric loss.[26] Therefore, rubber mixtures containing carbon black can be treated with microwaves. Fortunately, tires contain large amounts of carbon black. The process can be considered controlled degradation, so the parameters should be adjusted with care in order to avoid or minimize the chain scission of the polymer backbone.

dGTR can be rated based on its sol fraction, which can be measured by Soxhlet extraction or by studying the effect of its addition to virgin rubber mixtures: NR-based[27] or styrene-butadiene rubber (SBR)-based mixtures.[28–30] Many studies focused on the exposure time of GTR to microwaves. The general conclusion was that the longer the exposure time, the larger the soluble fraction (sol-fraction) of the samples, and hence the lower their gel fraction and crosslink density values. Garcia et al.[13] devulcanized GTR with microwave and used different exposure times. With 7 min, they were able to increase the sol-fraction from 14 to 31%. It was determined that in addition to breaking S—S and C—S bonds, the main chain was also degraded. De Sousa et al.[1] found that the higher the amount of energy absorbed during the treatment, the higher the temperature of the GTR, and hence the higher the degree of devulcanization. The temperature of the GTR is the primary factor responsible for devulcanization. Colom et al.[14] used Fourier-transform infrared spectroscopy to reveal the structural changes in GTR after devulcanization. They proved that S—S and C—S bonds break, which is the criterion for devulcanization. However, scission of the polymer backbone and of C—H bonds was also shown.

Zanchet et al.[29] incorporated dGTR in SBR-based rubber composites. The results showed that dGTR had a negative effect on tensile strength of the prepared composites. However, the negative effects of dGTR were minor compared with those of GTR. Furthermore, dGTR can increase the elongation at break. Karabork et al.[31] reached 34% of sol content in dGTR. SBR compounds containing 10 phr GTR and dGTR had enhanced tensile strength and elongation at break values in comparison with reference SBR compounds. At higher dGTR and GTR concentrations, however, these properties deteriorated. As a result of microwave devulcanization, SBR compounds with dGTR-content had better mechanical properties than the samples prepared with the same amounts of GTR.

Two types of crumb rubber (mechanical and waterjet-milled) were selected for this study in order to investigate the potential in microwave devulcanization of GTR. We used two different microwave ovens: a conventional power-controlled oven and a laboratory oven, in which the heating rate (°C min⁻¹) and the maximum temperature can be adjusted. We performed devulcanization both in an oxidative (air) and in an inert atmosphere (nitrogen). We prepared SBR-based rubber mixtures with various amounts of dGTR and examined the physical and mechanical properties of the resulting samples.

EXPERIMENTAL

Materials

Mechanically ground crumb rubber was provided by Euro-Novex Ltd. (Budapest, Hungary) and waterjet-milled rubber was provided by Aquajet Ltd. (Budapest, Hungary). The latter material originated from the tread area of truck tires; therefore, the waterjet-milled GTR is a high-purity material. Table I contains the manufacturers, types, and basic properties of GTRs and SBR.

The additives of rubber mixtures and their suppliers were the following: zinc oxide (ZnO, ZnO 99,7%, Werco Metal, Zlatna, Romania), stearic acid (Radiacid 0444, Oleon, Ertvelde, Belgium), N330 carbon black (Omsk Carbon Group, Omsk, Russia), 2,2-dibenzothiazole disulfide (MBTS, Ningbo Actmix Polymer, Ningbo, China), and sulfur (Powder Sulfur, Astrakhan, Russia). Toluene (purity: >95%), which was used for all Soxhlet extraction experiments, was supplied by Fischer Scientific UK.

The particle-size distribution of GTRs used is shown in Figure 1. The particle-size distribution of GTR_WJ was provided by the manufacturer. GTR_M was fractionated by a BA200N-type sieve shaker (CISA Cedaceria Industrial, Barcelona, Spain) for 45 min with an amplitude of 2 mm.

Table I. Types and Producers of Raw Materials

| Abbreviation	GTR_WJ	GTR_M	SBR
Manufacturer	Aquajet Ltd., Budapest, Hungary	Euro-Novex Ltd., Budapest, Hungary	JSC Sterlitamak Petrochemical Plant Sterlitamak, Russia
Main properties and composition	Waterjet-milled truck tire tread Particle size: 200–400 μm Moisture content: 0.99 wt % 4–6 phr oil, 50–55 phr NR, 45–50 phr synthetic rubber, 33–37 phr carbon black, and 7.5 phr residual additives (according to TGA measurements)	Mechanically ground truck tire Max. particle size: 0–4 mm Moisture content: 0.99 wt % 4–6 phr oil, 50–55 phr NR, 45–50 phr synthetic rubber, 33–37 phr carbon black, and 7.5 phr residual additives (according to TGA measurements)	Product name: SBR 1502, SKS-30 ARKPN Mooney viscosity (ML, 1 + 4, 100 °C): 48–58 Bound styrene content: 22–25 wt %
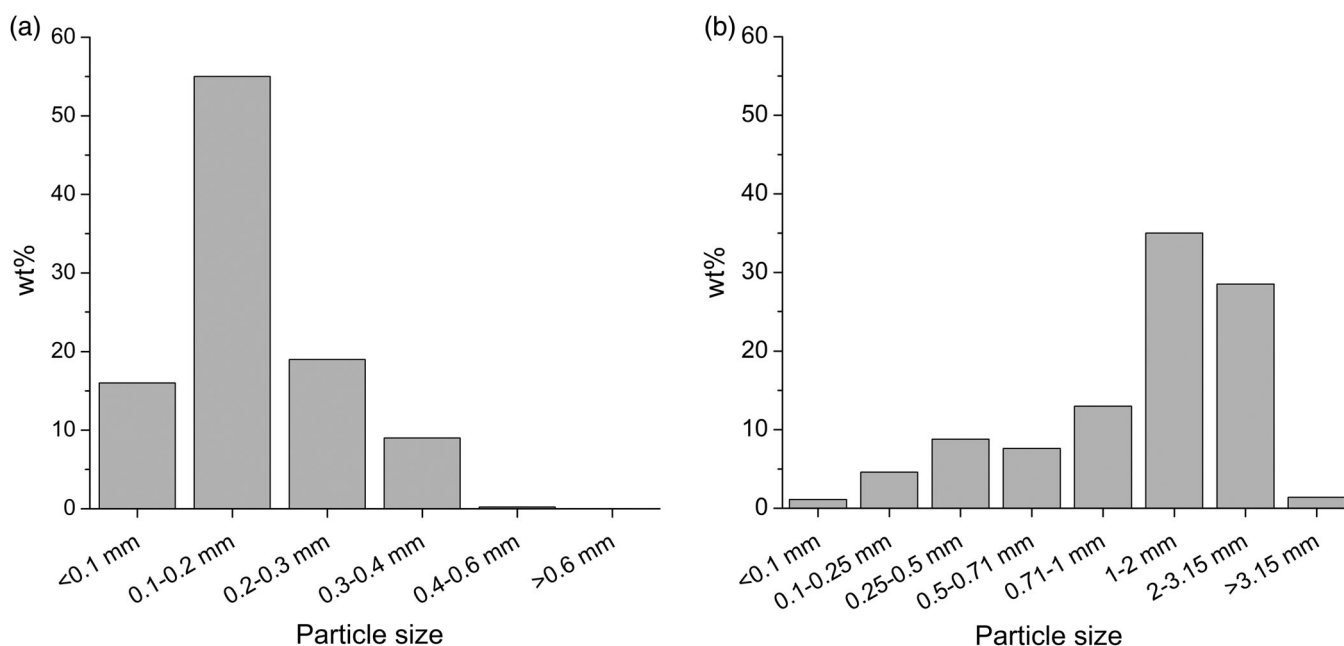
Figure 1. The particle size distribution of the GTRs: (a) the waterjet-milled GTR (GTR_WJ); (b) the mechanical GTR (GTR_M).

Table II. Parameters of the Microwave Treatment

	Treatment time (min)	Heating rate ($^\circ$C min^{-1})	Achieved temperature ($^\circ$C)	Holding time at the maximum temperature (min)
Conventional microwave oven	8.5	~23[a]	~220	0
Laboratory microwave oven	~30 (+ the holding time)	6	150–250	0, 1, 3, 5
	~15	12	200	0
	~9	18	200	0

[a] Calculated average value.

Devulcanization of GTR

GTR was devulcanized in a BP-125/50-type temperature-controlled laboratory microwave oven, produced by Microwave Research Inc. (Carol Stream, IL), and in a conventional AVM561/WP/WH type (Whirlpool, Benton Harbor, MI) power-controlled microwave oven. In the latter oven, the power of the microwave treatment was set to 650 W. The batch size of the treated GTR was 50 g. A motorized stirring system with a speed control was attached to the microwave ovens in order to ensure uniform sample temperatures. The stirring speed was set at

Table III. The Rubber Compounds and Their Abbreviations (Values in phr)

Abbreviation	SBR	ZnO	Stearic acid	Carbon black	GTR_WJ	dGTR_WJ	MBTS	Sulfur
REF	100	3	2	60	0	0	1.5	2
GTR15	100	3	2	60	15	0	1.5	2
GTR30	100	3	2	60	30	0	1.5	2
GTR45	100	3	2	60	45	0	1.5	2
GTR60	100	3	2	60	60	0	1.5	2
dGTR15	100	3	2	60	0	15	1.5	2
dGTR30	100	3	2	60	0	30	1.5	2
dGTR45	100	3	2	60	0	45	1.5	2
dGTR60	100	3	2	60	0	60	1.5	2

Table IV. Microwave Devulcanization of GTR: Behavior and Temperature at the End of Treatment

Sample	Particle size (mm)	Time (s)			
		30	60	90	120
		Achieved temperature (°C)			
GTR_WJ	0–0.6	138	185	248	Ignition
GTR_M_0–1	0–1	145	190	Ignition	Ignition
GTR_M_1–2	1–2	Ignition			
GTR_M_2–4	2–4	Ignition			

Table V. The Sol Fraction of GTRs before and after Treatment in the Conventional Microwave Oven

Sample	Sol fraction (%)
GTR_WJ	10.1 ± 0.4
GTR_M_0–1	7.1 ± 0.5
dGTR_WJ	24.6 ± 2.0
dGTR_M_0–1	22.0 ± 1.4

100 rpm. Both instruments were equipped with a thermocouple to monitor the sample temperature. The parameters of the microwave treatment can be seen in Table II. Prior to the treatment, GTR was kept at ambient temperature.

Soxhlet Extraction

dGTR was characterized by Soxhlet extraction in toluene. The testing time was 18 h, during which the insoluble gel fraction was separated from the soluble fraction of the rubber sample. The sol content is a good indicator of processability, which is the ultimate goal of devulcanization.

Processing of GTR, dGTR-Containing Rubbers

In order to assess the usability of dGTR in rubbers, different amounts of dGTR and GTR (as reference) were added to SBR-based compounds. The recipes of the rubber compounds are shown in Table III. The rubber ingredients were mixed with an LRM-SC-110/T3E-type two-roll mill (Labtech Engineering Co. Ltd., Samutprakarn, Thailand) at 70 and 40 °C (front and rear roll) and 26 and 20 rpm (front and rear) roll speed, respectively. The order of the components in Table III (left to right) also reflects the order of mixing.

The compounds were vulcanized by a Teach-Line Platen Press 200E (Dr. Collin GmbH, Munich, Germany) hot press. The pressure applied was 2.8 MPa and the temperature was 165 °C.

Characterization of the Rubber Mixture and Cured Rubber Sheets

Curing curves for each rubber compound were recorded with a MonTech Monsanto R100S rheometer (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) in isothermal ($T = 165$°C) time sweep mode (1.667 Hz, 3° angle) for 30 min.

Hardness was tested according to the ISO 868 Shore D method on a Zwick H04.3150.000 hardness tester (Zwick GmbH, Ulm, Germany) on the cured rubber sheets. Each compound was

tested 10 times in order to obtain average and standard deviation values.

The tensile mechanical properties of the compounds were investigated according to the ISO 527 standard on a Zwick Z250 universal testing machine with a 20 kN load cell (Zwick GmbH, Ulm, Germany). Type 1 specimens of DIN 53504 standard with a clamping length of 60 mm were loaded at a crosshead speed of 500 mm min^{-1}. Tear tests were made on the same testing machine and test speed was according to the ASTM D624 standard (Type C specimen), with a clamping length of 56 mm. Both tests were run at room temperature. The average and standard deviation of the tensile strength, tear strength, and elongation at break were determined with five tests on each compound.

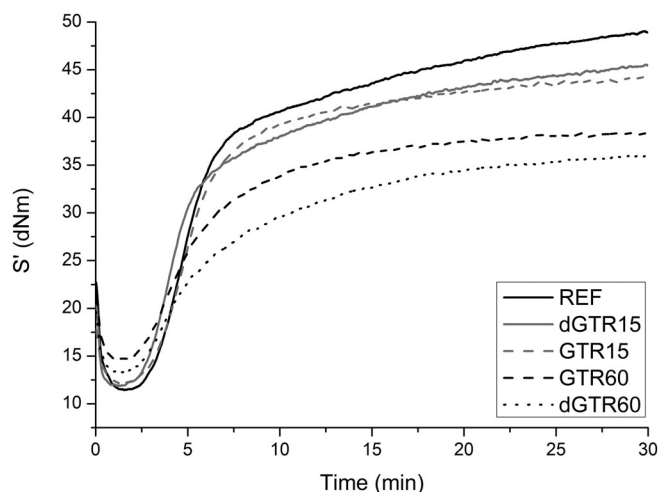## RESULTS

Devulcanization of GTRs

As preliminary experiments, both types of GTR were treated in a conventional microwave oven at 650 W without stirring, in order to determine the potential of GTR for microwave devulcanization. The temperatures (Table IV) were measured with a Testo 875-type thermal camera (Testo SE, Lenzkirch, Germany). Samples with particle sizes exceeding 1 mm were no longer considered for investigation as they ignited rapidly within the first 30 s of treatment. On the other hand, a steady rise in temperature was observed for both GTR_WJ with a particle size range of 0–0.6 mm and GTR_M with a particle size range of 0–1 mm. Therefore, we chose these samples for further studies.

GTR_WJ and GTR_M_0–1 samples were then treated in the same conventional microwave oven with constant stirring. After several devulcanization attempts, 8.5 min was set as treating time, in order to keep temperatures below 248 °C and thus to avoid ignition. The soluble content of the samples was determined by Soxhlet extraction before and after devulcanization (Table V) and no significant difference was detected between the two samples. However, the process was more consistent and stable in the case of GTR_WJ, and less smoke was generated during those experiments. Consequently, GTR_WJ was chosen for further devulcanization experiments.

Process control can be improved by using a temperature-driven microwave device. We studied the effects of heating rate, set maximum temperature, holding time, and type of atmosphere on the soluble content of dGTR and such results are summarized in Table VI. Devulcanization parameters were set to reveal the minimum temperature of efficient devulcanization, and also to

Table VI. The Results of the Soxhlet Extraction before and after the Treatment of GTR_WJ in the Laboratory Microwave Oven

Sol content (%)									
Atmosphere		Air	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen
Holding time (min)		0		1		3		5	
Heating rate (°C min⁻¹)	Maximum temperature (°C)								
GTR_WJ		10.1 ± 0.3	10.2 ± 0.4	-	-	-	-	-	-
6	150	11.5 ± 0.4	10.6 ± 0.3	7.9 ± 0.5	10.7 ± 0.6	10.4 ± 0.5	9.3 ± 0.9	6.7 ± 0.7	9.9 ± 0.5
6	170	11.8 ± 0.2	11.1 ± 0.3	11.0 ± 0.7	10.8 ± 0.3	9.4 ± 0.6	11.2 ± 0.6	6.7 ± 0.9	11.7 ± 0.3
6	190	19.8 ± 0.6	12.5 ± 0.6	13.1 ± 0.5	11.0 ± 0.7	11.3 ± 0.4	11.9 ± 0.5	9.6 ± 0.5	10.1 ± 0.6
6	200	21.2 ± 0.9	13.0 ± 1.2	11.8 ± 0.9	11.1 ± 0.5	13.4 ± 0.7	13.4 ± 1.0	16.5 ± 1.1	10.8 ± 0.8
6	210	18.3 ± 1.2	12.9 ± 0.7	-	-	-	-	-	-
6	230	21.5 ± 1.1	-	-	-	-	-	-	-
6	250	18.4 ± 1.3	-	-	-	-	-	-	-
12	200	10.5 ± 0.4	-	-	-	-	-	-	-
18	200	10.9 ± 0.6	-	-	-	-	-	-	-

Figure 2. Vulcanization curves of the samples containing GTR, dGTR.

minimize the degradation of main polymer chains and smoke generation. To ensure the latter, the experiments were repeated in nitrogen atmosphere. The results showed that devulcanization required high temperatures (around 200 °C), but keeping the samples above 200 °C after the treatment would cause a decrease in sol content, indicating a reverse devulcanization.

The process was tested in nitrogen to investigate GTR devulcanization with no oxidation reactions. As shown in Table VI, smaller sol contents were achieved in nitrogen atmosphere and there is no significant change in the sol fraction of the samples treated at different temperatures.

After heating GTR, the maximum temperature was held for different durations (1, 3, 5 min). The results revealed that holding time in an oxidative atmosphere, independently of its duration has a decreasing effect on the sol content. In the case of inert atmosphere, there is no significant effect of holding time. In conclusion, microwave heating causes partial decomposition of the GTR matrix, and its rate and final temperature are the most important factors of the process. At higher heating rates, lower sol contents were obtained, which may be justified by reduced treatment times and nonuniform sample temperatures, due to the formation of hotspots.

Cure Characteristics of the Rubber Compounds

Vulcanization curves of the rubber mixtures are presented in Figure 2. In the samples containing GTR, the S'$_{min}$ values increased with increasing GTR content, whereas S'$_{max}$ values decreased. GTR caused the vulcanization times to decrease compared with the REF sample, but the amount of the GTR added had no effect on the vulcanization time of the samples. Altogether, GTR had a mildly softening effect on the samples, as samples with increasing GTR content had gradually lower vulcanization plateaus, corresponding to lower moduli. For samples containing dGTR, the same trends can be observed, though vulcanization times were shortened by GTR to a greater extent, compared with dGTR, indicating some accelerating behavior for GTR.

Table VII. Cure Characteristics and Hardness of the Samples

Sample	t_{90} (min)	t_{s2}/t_{10} (min)	S'_{min} (dNm)	S'_{max} (dNm)	Shore A Hardness (–)
REF	18.3	2.9	11.4	49.1	70.3 ± 0,6
GTR_15	14.1	2.9	12.1	44.3	68.2 ± 0,3
GTR_30	13.3	2.5	13.1	43.8	67.6 ± 0,5
GTR_45	13.5	2.8	13.7	39.9	66.3 ± 0,3
GTR_60	14.0	2.8	14.6	38.4	65.9 ± 0,5
dGTR_15	17.4	2.6	11.9	45.5	69.9 ± 0,3
dGTR_30	16.4	2.3	11.8	39.6	69.5 ± 0,3
dGTR_45	17.0	2.5	13.4	39.8	69.2 ± 0,2
dGTR_60	17.8	2.8	13.2	36.2	68.7 ± 0,4
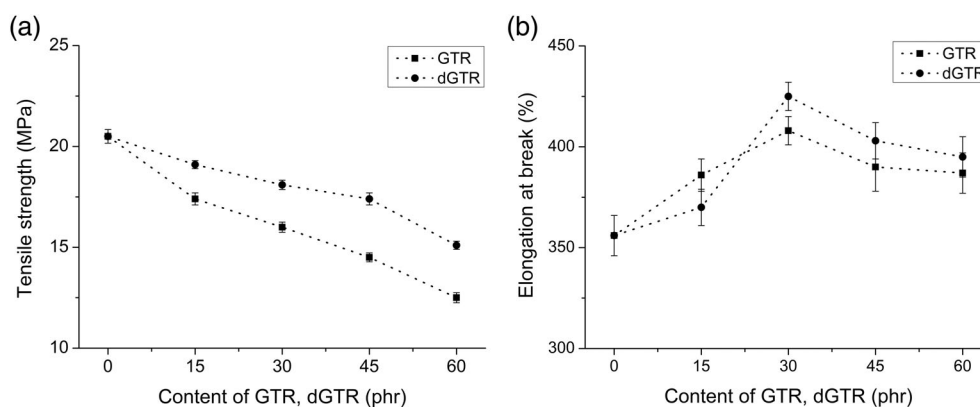
Figure 3. Effects of GTR and dGTR content on (a) the tensile strength and (b) the elongation at break values.

Table VII contains the main parameters of the vulcanization curves and hardness values. There was no significant effect of the additional GTR and dGTR content on hardness, while doping had a mildly softening effect.

Mechanical Properties of the Cured Rubber Compounds

Figures 3–5 show the mechanical properties of the SBR mixtures with different concentrations of GTR and dGTR. Tensile strength decreased at increasing GTR and dGTR content (Figure 3). However, the use of dGTR can reduce this effect. Samples with a 45 phr dGTR content had the same tensile strength as the ones with

15 phr GTR content. This suggests that the microwave treatment improved the adhesion between the rubber matrix and the dGTR particles. Additional GTR and dGTR content had a positive effect on the elongation at break values due to the increase in the amount filler materials. The maximum value was reached at 30 phr GTR and dGR content.

Figure 4 shows stresses at 100, 200, and 300% elongation. The same trends can be observed as in the case of tensile strength. Higher stress values were observed for samples with dGTR, compared with their GTR counterparts, yet none of these stress values matched those of the reference rubber sample.
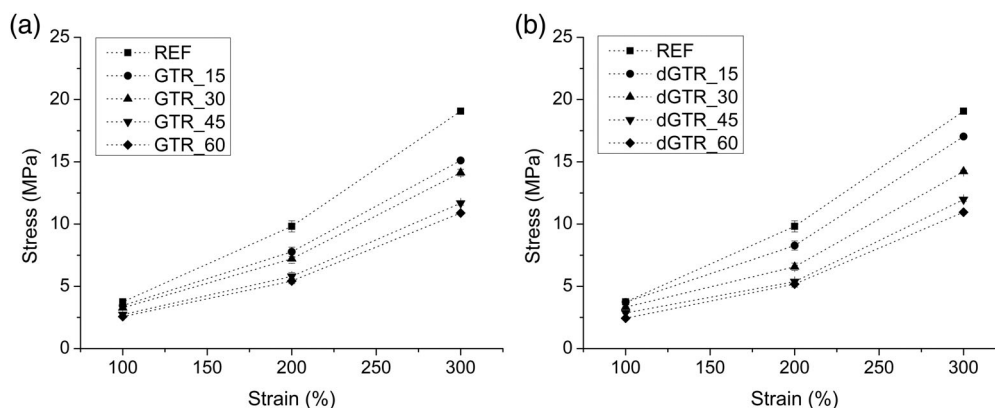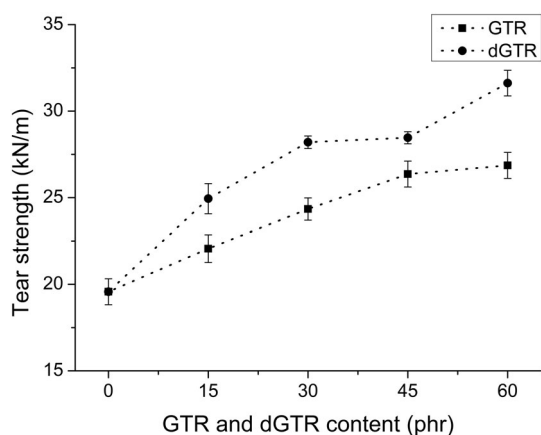

Figure 4. Stress at 100, 200, and 300% strain.

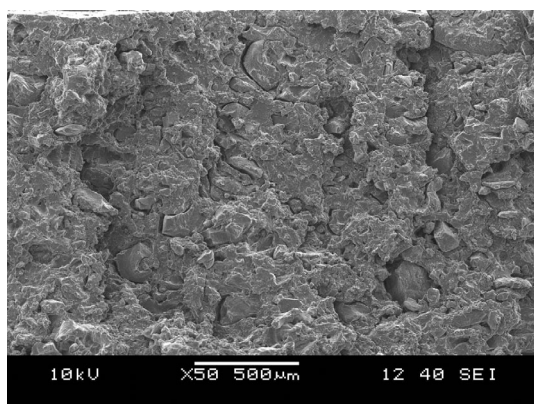**Figure 5.** The tear strength of the rubber composites.

Figure 6. Scanning electron micrograph of the fracture surface of a tear specimen.

Tear strength (Figure 5) increased with increasing GTR and dGTR content, which can be justified by the higher structural integrity of GTR and dGTR particles, compared with the bulk rubber matrix. Consequently, whenever a crack reached a hard GTR, or dGTR particle, it was forced to change its direction of propagation. This theory is supported by Figure 6, where the crack on the right-hand side has a zigzag pattern around GTR particles.

CONLUSIONS

We tested the recycling potential of microwave devulcanization on GTR in this work. Based on our preliminary experiments, a waterjet-milled truck tire sample (GTR_WJ) was selected for our research, as mechanically ground samples of larger particle sizes were more prone to ignition and smoke generation. Two microwave devices were compared, a conventional power-controlled oven and a temperature-controlled oven. In the latter one, heating rate ($°C min^{-1}$) and maximum temperature values were adjustable. Soxhlet extraction results revealed no significant difference in terms of devulcanization power between the two ovens. However, the process was easier to control, the experiments were more repeatable, and the quality of the dGTR was more uniform in the case of the temperature-controlled oven.

We analyzed the effects of various process parameters on the soluble content of the devulcanizate. The results showed that an inert atmosphere inhibits the generation of soluble material. Keeping the samples at the maximum devulcanization temperature would decrease the sol content, indicating devulcanization; 200 °C was obtained as optimal devulcanization temperature with a heating rate of 6°C min^{-1}.

We also prepared SBR-based rubber compounds with GTR and dGTR (GTR_WJ and dGTR_WJ, respectively) and tested their physical and mechanical properties. Both GTR and dGTR contents had accelerating and softening effects on curing. Tensile strength results showed that dGTR had a positive impact on values compared with samples containing GTR. Elongation at break and tear strength increased when GTR and dGTR were incorporated in the compounds because of the amount of additives present in GTR and dGTR. Considering that the addition of dGTR deteriorated the mechanical properties of the reference rubber mixture to a lesser extent, compared with GTR, it can be anticipated that a fully optimized microwave treatment of GTR would allow even larger recycled rubber content in the future.

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