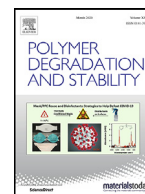


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Simon D. Á., Bárány T.

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Effective thermomechanical devulcanization of ground tire rubber with a co-rotating twin-screw extruder

Dániel Ábel Simon, Tamás Bárány*

Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

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ABSTRACT

We thermomechanically devulcanized ground tire rubber (GTR) in a co-rotating twin-screw extruder at different barrel temperatures and screw speeds. We measured the soluble content and the cross-link density of the samples and then evaluated them by Horikx's analysis. The results showed that at lower temperatures, selective cross-link scission is dominant, and screw speed has no effect. At higher temperatures and screw speeds, the degradation of the polymer chains becomes more and more severe. With the appropriate parameters, cross-link scission can be maximized without severe degradation of the main chains. Two devulcanized ground tire rubber (dGTR) samples were chosen for further study. Natural rubber (NR) based rubber mixtures were produced with conventional and two-step mixing. Tensile and tear strength decreased significantly with dGTR content. These results are in agreement with Horikx's analysis, i.e. the greater the degradation of dGTR, the more mechanical properties were impaired. However, elongation at break did not follow such a trend. With two-step mixing, mechanical properties improved, especially tear strength. Additional experiments were also conducted with Horikx's analysis. The aim was to reveal the accuracy and usability of the analysis, and it showed the theoretical maximum of devulcanization.

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1. Introduction

The continuous increase in the volume of rubber products began with vulcanization. This granted a stable cross-linked structure with broad applicability and customizable properties. In 2019, the global production of natural and synthetic rubber reached approximately 33 million tons. At the same time, the amount of waste is continuously increasing as well. The automotive industry uses 75% of global rubber production [1]. This means that most of the waste is made up of discarded tires. From 2015 to 2019, the worldwide increase in the total number of new vehicles was 7.9% [2]. Because of their cross-linked structure, rubbers and of course, tires cannot be recycled like thermoplastics. Therefore, recycling tire waste is a global problem and poses a great challenge to researchers. Despite the efforts made to recycle waste tires, a considerable part is land-filled, which poses serious environmental hazards [3,4]. Several tire recycling processes have been developed to solve these problems.

Recycling waste tires in the form of ground powder (ground tire rubber, GTR) is favoured [5]. GTR and other rubber waste can be used as fuel in cement industries, in asphalt as an additive, in playgrounds, or running track flooring. But these secondary recycling forms cannot accommodate the continuously increasing amount of waste. The aim is the primary recycling of GTR, and with devulcanization, it can be achieved. During the devulcanization process, cross-link scission occurs and new molecules are formed, which can form new bonds on the surface of the GTR particles; thus better adhesion can be developed with the matrix [6,7]. The amount of recycled tire and the devulcanized GTR (dGTR) can be increased without a significant worsening of mechanical properties. Several devulcanization processes have been developed over the years, e.g. microwave [8,9], thermomechanical [10,11]–[12], thermochemical [13], mechanochemical [14] and microbial devulcanization [15].

Thermomechanical devulcanization is mainly carried out in twin-screw extruders. It is a continuous process with high productivity potential. A further advantage is that the quality of the final product can be easily controlled with the barrel temperature and screw speed [16,17]. There is another important factor, screw

* Corresponding author.

E-mail address: barany@pt.bme.hu (T. Bárány).

configuration. Thanks to the modular design, the screw is entirely customizable, and the shear force also can be adjusted [10]. Mouri et al. [18] proposed that the devulcanization process with the optimal parameters could selectively break the cross-links in GTR. Formela et al. [19,20] found that barrel temperature and screw speed is a crucial factor of thermomechanical devulcanization and it greatly affect the properties of the final material. Higher barrel temperature causes severe degradation in the main chain, and mechanical properties deteriorate. The high-temperature process also generates volatile organic compounds (VOCs) [21]. In some applications, highly degraded GTR is better. Li et al. [22] found that asphalt with GTR reclaimed on higher barrel temperature, i.e. more degraded GTR has better processability, storageability, and anti-cracking properties. However, in most cases, the goal is to minimize degradation. Saiwari et al. [23] found that at a devulcanization temperature of 220°C, the cross-link density decreased by about 45–65% in the case of butadiene rubber (BR) and styrene-butadiene rubber (SBR). For natural rubber (NR), the polymer chains start to degrade above 170–180°C, and it is necessary to keep the processing temperature as low as possible. Tao et al. [24] used a co-rotating twin-screw extruder to devulcanize GTR. Screw speed was 80–160 rpm, and the temperature range was 160–240°C. They analyzed the relationship between soluble content and the tensile strength of the 100% revulcanized dGTR. The optimal parameters were 180°C and 100 rpm. However, they recorded that lower temperature leads to an increase in screw torque. Balasubramanian et al. [25] devulcanized GTR with a co-rotating twin-screw extruder at 150–200°C with a screw speed of 10–40 rpm. They determined that 170°C and 30 rpm were the optimum parameters. This dGTR (~36–80 wt%) was introduced in NR compounds (without additional carbon black). The mechanical properties were adequate. They introduced a four-parameter rheometric equation that represents the cure behaviour very well. Yazdani et al. [26] devulcanized GTR with a co-rotating twin-screw extruder at 220–280°C with a screw speed of 30–120 rpm. They introduced dGTR to NR/SBR virgin rubber in 15 wt%. The tensile strength slightly decreased with increasing temperature; the elongation at break showed opposite tendencies. They also determined that barrel temperature is a crucial parameter for devulcanization and the mechanical properties of the revulcanizates were acceptable. Barbosa et al. [27] produced NR compounds, then devulcanized them with a twin-screw extruder (L/D 44, diameter 35 mm) (210–270°C, 330 and 550 rpm) in the presence of polypropylene (PP) or ethylene-vinyl acetate copolymer (EVA). They found that the thermoplastics helped on the thermal stabilization of the extrusion process and to form better second phase incorporation in the compounds. Their results indicating thermoplastics, especially EVA, is a promising additive in the thermomechanical recycling of natural rubber compounds. However, tires contain significant amount of synthetic rubbers and other additives, fillers beside carbon black that affects the described beneficial effects. Nunes et al. [28] treated GTR shavings (stripes, ca. 2 × 0.5 cm) in a twin-screw extruder at 220 and 270°C with 150, 350 and 550 rpm (L/D 44, diameter 35 mm). They used different PPs, low-density polyethylene (LDPE) and antioxidants as devulcanization auxiliary. The results showed that GTR processed with LDPE has higher thermal stability than GTR processed with PPs. The soluble fraction of GTR/PP was considerably higher than GTR/LDPE, which indicates lower degradation.

The soluble content and the cross-link density are required to characterize the structural changes in dGTR. Horikx's analysis helps to understand structural changes in dGTR better [29]. It establishes a mathematical relationship between the sol fraction and the degree of devulcanization. Seghar et al. [30] verified Horikx's theory experimentally, and several other researchers used it successfully [6,16,31,32].

In our previous papers, we investigated the structural changes in GTR after microwave and thermomechanical devulcanization (with an internal mixer) and introduced the dGTRs in virgin SBR [33] and NR [34] based compounds. We found that dGTR has a better connection with the NR matrix.

In the present study, we devulcanized GTR with a co-rotating twin-screw extruder and characterized dGTR with Soxhlet extraction, a swelling test, and Horikx's analysis. We investigated the effect of different barrel temperatures (140–240°C), screw speeds (60–180 rpm). Based on the Horikx's analysis, two dGTR samples were chosen for further investigations and introduced in NR based compounds. In most of the literature, reclaimed GTR was introduced in fresh rubber in lower wt% [17,26,35,36]. Based on their results, these compounds have sufficient mechanical properties to use in various products, but because of the low reclaimed GTR content, this is not enough to accommodate the ever-increasing amount of tire waste. So we prepared NR compounds, where the fresh NR and dGTR ratio was 50/50 wt%. We introduce a so-called two-step mixing and recipe development to improve the mechanical properties.

The physical and mechanical properties of the rubber samples were assessed. Furthermore, we investigated the accuracy and usability of Horikx's analysis, as well and revealed the theoretical limit of devulcanization too.

2. Experimental

2.1. Materials

Waterjet-milled rubber powder was provided by Aquajet Ltd. (Budapest, Hungary). It only consists of the ground tread of truck tires. Therefore, this type of GTR is a high-purity material. According to TGA tests, it contains 50–55 phr of NR, 45–50 phr of synthetic rubber, 4–6 phr of oil, 33–37 phr of carbon black, and 7.5 phr of residual additives. We chose a general-purpose natural rubber for our investigations. Table 1 contains the main properties of the materials.

The additives in the rubber mixtures (and their suppliers) are zinc oxide (ZnO, S.C. Werco Metal S.r.l., Zlatna, Romania), stearic acid (Oleon, Ertvelde, Belgium), N330, N550 and 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 sulphur (Ningbo Actmix Rubber Chemicals Co., Ltd., Ningbo, China). The particle size distribution of GTR was published in our previous paper [33].

2.2. Devulcanization of GTR

Thermomechanical devulcanization of GTR was carried out in an LTE 26-44 type co-rotating twin-screw extruder (D=26 mm; L/D=44; Labtech Engineering Co., Ltd. (Thailand, Samutprakarn)). The extruder zone temperatures were 140, 160, 170, 180, 190, 200, 210, 220, 230 and 240°C (the temperature of all the zones and the die were the same). Screw speed was 60, 120 and 180 rpm. The feeding rate was 1.6, 2.4 and 2.7 kg/hour. The screw configuration can be seen in Fig. 1. The parameters of thermomechanical devulcanization and the nomenclature of the samples can be seen in Table 2.

Furthermore, we investigated the accuracy and usability of Horikx's analysis. Unfortunately, the exact recipe of the GTR is unknown. Therefore, we prepared a simplified rubber recipe based on truck tires. We named it model tire rubber (MTR), and it is expected to behave similarly to truck tires. The formulation was 30 phr NR, 70 phr SBR, 60 phr carbon black (N772), 5 phr ZnO,

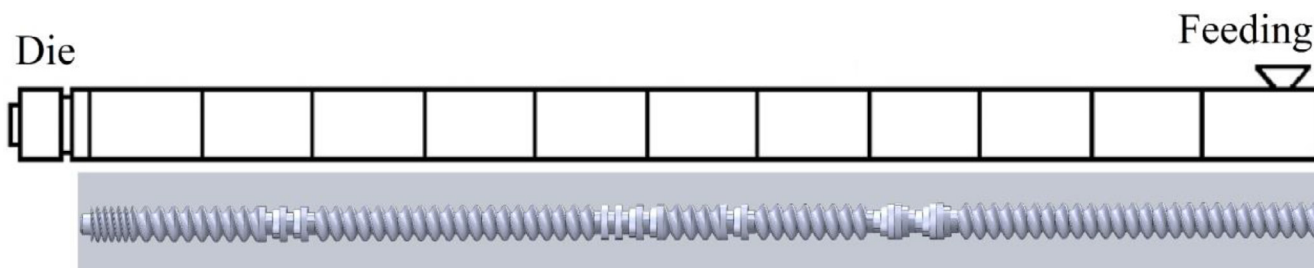


Fig. 1. The screw configuration.

Table 1

Types and producers of raw materials.

| Abbreviation | GTR | NR |
|--------------------|---|---|
| Manufacturer, type | Aquajet Ltd., Budapest, Hungary | NR TSR 10 Sud Comoe Caoutchuc, Aboisso, Ivory Coast |
| Main properties | Waterjet-milled truck tire tread, particle size between 200–400 μm | Mooney viscosity (ML, 1+4, 100°C): 55–65 |

Table 2

Parameters of thermomechanical devulcanization and the abbreviation of the samples.

| Abbreviations | Screw speed (rpm) | Temperature ($^{\circ}\text{C}$) |
|---------------|-------------------|------------------------------------|
| dGTR_60/140 | 60 | 140 |
| dGTR_120/140 | 120 | 140 |
| dGTR_180/140 | 180 | 140 |
| dGTR_60/160 | 60 | 160 |
| dGTR_120/160 | 120 | 160 |
| dGTR_180/160 | 180 | 160 |
| dGTR_60/170 | 60 | 170 |
| dGTR_120/170 | 120 | 170 |
| dGTR_180/170 | 180 | 170 |
| dGTR_60/180 | 60 | 180 |
| dGTR_120/180 | 120 | 180 |
| dGTR_180/180 | 180 | 180 |
| dGTR_60/190 | 60 | 190 |
| dGTR_120/190 | 120 | 190 |
| dGTR_180/190 | 180 | 190 |
| dGTR_60/200 | 60 | 200 |
| dGTR_120/200 | 120 | 200 |
| dGTR_180/200 | 180 | 200 |
| dGTR_60/210 | 60 | 210 |
| dGTR_120/210 | 120 | 210 |
| dGTR_180/210 | 180 | 210 |
| dGTR_60/220 | 60 | 220 |
| dGTR_60/230 | 60 | 230 |
| dGTR_60/240 | 60 | 240 |

1 phr stearic acid, 4.5 phr CBS, 4.5 phr TMTD, and 4.5 phr sulfur. Altogether, three samples were produced and investigated: the uncured rubber mixture (notation: MTR_m), the cured rubber (MTR), and a partially vulcanized sample (MTR_50s). The latter one was cured for only 50 sec (vulcanization was done at 150°C based on rheometer measurement).

Soxhlet extraction and swelling tests were performed on the samples. Based on their results, Horikx's analysis was performed. The reference was the cured rubber, and the uncured and partially vulcanized mixture was considered to be the final product of a theoretically 100% efficient devulcanization process. That way only the scission of the cross-link bonds occurred.

2.3. Characterization of GTR and dGTR

Thermogravimetric analyses (TGA) were performed on a TGA Q500 (TA Instruments, New Castle, DE, USA) device. About 5–6 mg of each sample was heated from room temperature to 700°C in air. Isothermal TGA tests were also conducted at 140–240°C. The “equi-

librate” setting was used. The heating rate varied as a function of maximum temperature (50–90°C).

The moisture content of the GTR was measured with an Aquatrac-3E (Brabender GmbH & Co. KG, Duisburg, Germany) device at 120°C.

The soluble fraction of the GTR and dGTR samples was determined by Soxhlet extraction in toluene, according to Eq. (1). Extraction time was 18 hours, and then we dried the samples for 12 hours at 80°C to remove the solvent.

$$\text{Sol Fraction (\%)} = \left(1 - \frac{M_f}{M_i}\right) \cdot 100 \quad (1)$$

where M_i and M_f stand for the mass of rubber before and after extraction, respectively.

The cross-link density of the GTR and dGTR samples was determined via swelling tests according to ASTM D 297-15. The Flory-Rehner Eq. (2) [37] with the Kraus correction [38] (4, 5) was used to calculate the cross-link density after equilibrium swelling (72 h followed by drying to constant mass at 80°C) in toluene.

$$v_e = \frac{-[\ln(1 - V_{r0}) + V_{r0} + \chi_1 \cdot V_{r0}^2]}{\left[V_1 \cdot (V_{r0}^{\frac{1}{3}} - V_{r0}) / 2\right]} \quad (2)$$

where v_e is 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), and V_{r0} is the equilibrium volume fraction of unfilled rubber in the swollen sample. V_{r0} can be determined with the Ellis and Welding Eq. (3) [39].

$$V_{r0} = \frac{\frac{m_r}{\rho_r}}{\frac{m_r}{\rho_r} + \frac{m_s}{\rho_s}} \quad (3)$$

where m_s is the mass of the solvent absorbed by rubber (g), m_r is the mass of the dry rubber sample (g), ρ_s is the density of the solvent, toluene (0.8669 g/cm^3 at 23°C) 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 4,(5) [38] is needed. The expression allows the determination of the degree of normal equilibrium swelling a vulcanisate would have achieved, if it had not contained any filler.

$$\frac{V_{r0}}{V_{rf}} = 1 - \frac{m\varphi}{1 - \varphi} \quad (4)$$

In which,

$$m = 3c \left(1 - V_{r0}^{\frac{1}{3}}\right) + V_{r0} - 1 \quad (5)$$

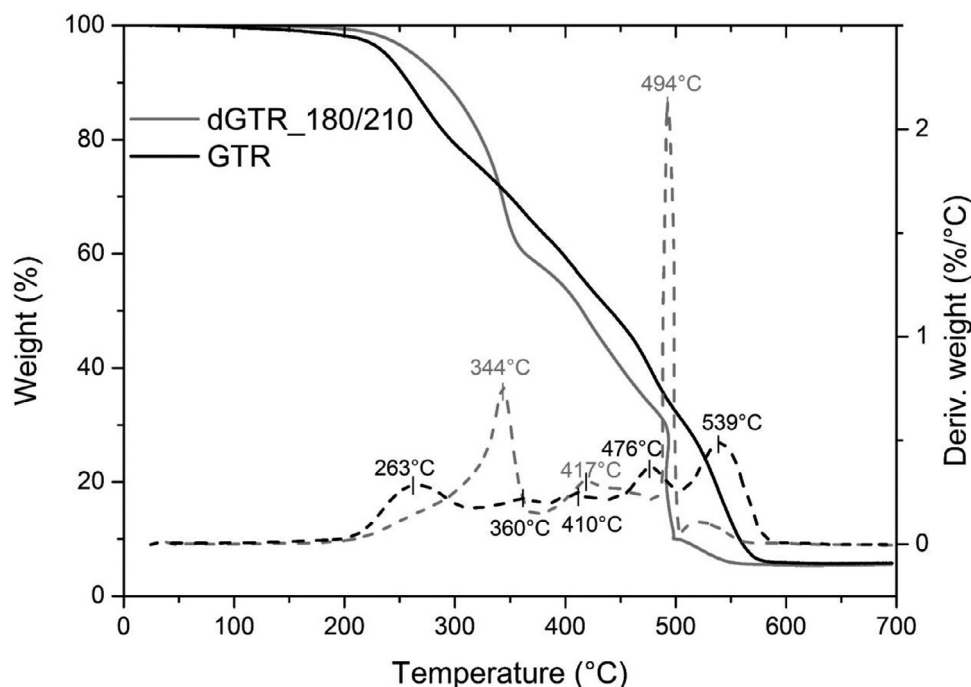


Fig. 2. TGA curves of the GTR and dGTR_180/210 samples.

Table 3

The dGTR-based compounds and their abbreviations (values in phr).

| Abbreviation | dGTR_60/190 | dGTR_180/190 | ZnO | Stearic acid | Paraffin oil | CBS | TMTD | Sulfur |
|----------------|-------------|--------------|-----|--------------|--------------|------|------|--------|
| dGTR_60/190_A | 100 | 0 | 10 | 2 | 20 | 1.25 | 0.6 | 0.6 |
| dGTR_180/190_A | 0 | 100 | 10 | 2 | 20 | 1.25 | 0.6 | 0.6 |

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 vulcanisate.

The degree of devulcanization, i.e. the decrease of cross-link density (in percentage) was calculated with Eq. (6) [6]:

$$Dev (\%) = \left(1 - \frac{v_f}{v_i}\right) \cdot 100 \quad (6)$$

where v_f is the cross-link density of the devulcanized sample, and v_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 cross-link density after devulcanization. The analysis can be used to identify and illustrate whether the degradation of a polymer is dominated by random chain scission or the selective breakdown of cross-links (i.e. 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. (7) shows the relationship between the soluble fraction of the polymer and the relative decrease in the number of elastically active network chains.

$$1 - \frac{v_f}{v_i} = 1 - \frac{(1 - \sqrt{s_f})^2}{(1 - \sqrt{s_i})^2} \quad (7)$$

where v_i stands for the initial cross-link density, v_f stands for 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 [29,31]. Using Eq. (7), a curve of random scission can be plotted (Fig. 4).

In the second scenario, only the cross-link bonds are cleaved, and the polymer main chain stays intact, as described by Eq. (8) [29].

$$1 - \frac{v_f}{v_i} = 1 - \frac{\gamma_f (1 - \sqrt{s_f})^2}{\gamma_i (1 - \sqrt{s_i})^2} \quad (8)$$

where γ_i and γ_f stand for the initial and final cross-linking index, respectively. The cross-linking index tells the average number of cross-link bonds per polymer chain [29,31], and it can be determined by Eq. (9) [29]. This curve contributes to selective cross-link scission (Fig. 2).

$$\gamma_x = v_x \frac{M_n}{\rho} \quad (9)$$

where γ_x (-) is the cross-linking index, v_x (mol/dm³) is the cross-link density, M_n (g/mol) stands for the number-average molecular weight of the rubber, and ρ is the rubber density.

In this paper, the initial cross-linking index is approximated by Eq. (10) [40].

$$Sol \text{ Fraction } (\%) = \frac{(2 + \gamma_i) - \sqrt{\gamma_i^2 + 4\gamma_i}}{2\gamma_i} \quad (10)$$

Based on Eqs. 5 and 6, the Horikx plot can be made (Fig. 4). The two curves represent the scission of the main chain and the selective cleavage of the cross-links. After the soluble fraction and the decrease of the cross-link density of the samples are determined, they can be plotted on the graph. Depending on which curve a data point is closer to, it is possible to infer the dominant phenomenon during the devulcanization process.

Table 4
The NR-based rubber compounds containing thermomechanically devulcanized ground tire rubber and their abbreviations (values in phr).

| Abbreviation | NR | ZnO | Stearic acid | Carbon black (N 772) | Carbon black (N 550) | Carbon black (N 330) | dGTR_60/190 | dGTR_180/190 | dGTR_60/190_A | dGTR_180/190_A | GTR | Paraffin oil | CBS | TMTD | Sulfur |
|------------------------|-----|-----|--------------|----------------------|----------------------|----------------------|-------------|--------------|---------------|----------------|-----|--------------|------|------|--------|
| NR_REF1 | 100 | 10 | 2 | 60 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF2 | 100 | 10 | 2 | 0 | 60 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF3 | 100 | 10 | 2 | 0 | 0 | 60 | 0 | 0 | 0 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF1_dGTR_60/190 | 100 | 10 | 2 | 60 | 0 | 0 | 100 | 0 | 0 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF1_dGTR_180/190 | 100 | 10 | 2 | 60 | 0 | 0 | 0 | 100 | 0 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF1_dGTR_60/190_A | 100 | 10 | 2 | 60 | 0 | 0 | 0 | 0 | 100 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF1_dGTR_180/190_A | 100 | 10 | 2 | 60 | 0 | 0 | 0 | 0 | 0 | 100 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF2_dGTR_60/190_A | 100 | 10 | 2 | 0 | 60 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF3_dGTR_60/190_A | 100 | 10 | 2 | 0 | 0 | 60 | 0 | 0 | 0 | 0 | 0 | 10 | 1.25 | 0.6 | 0.6 |
| NR_REF1_GTR_100 | 100 | 10 | 2 | 60 | 0 | 0 | 0 | 0 | 0 | 0 | 100 | 10 | 1.25 | 0.6 | 0.6 |

As a quantitative method to evaluate the selectivity of devulcanization, a selectivity coefficient (K) was calculated [41]. There are two possible approaches: defining the selectivity parameter in the sol fraction (vertical) direction and in the cross-link density (horizontal) direction. The sol fraction selectivity parameter (K_s) can be calculated by Eq. (11) [41].

$$K_s = \frac{S_c - s}{S_c - S_x} \quad (11)$$

where S_c is the theoretical sol fraction for random scission, S_x is the the theoretical sol fractions for selective cross-link scission and s is the measured sol fraction.

The selectivity parameter in the cross-link density direction (K_x) can be calculated by Eq. (12) [41].

$$K_x = \frac{X - X_c}{X_x - X_c} \quad (12)$$

where X is the devulcanization percentage, X_c is the the theoretical values of the relative decrease in cross-link density for random scission and X_x is the theoretical values of the relative decrease in cross-link density for selective scission.

The overall selectivity parameter (K) is then defined according to Eq. (13) [41]. Results range between 0 and 1. Random scission corresponds to $K=0$ and selective scission corresponds to $K=1$.

$$K = \frac{K_s + K_x}{2} \quad (13)$$

2.4. Formulation and preparation of rubbers containing GTR and dGTR

After Horikx's analysis and based on its results, we selected two types of dGTRs (dGTR_60/190 and dGTR_180/190) and introduced them in 100 phr in NR-based rubber samples to assess the usability of dGTR in rubbers. The recipes of the rubber compounds are shown in Table 4.

In the case of samples ending with "A", mixing consisted of two steps. In the first step, the dGTR was compounded with vulcanizing agents, according to Table 3. Then this untreated dGTR mixture was added to the original rubber mixture. In NR samples with the abbreviation ending in "A", the mixtures contain extra vulcanizing agents that were added to the dGTR beforehand. NR samples without "A" have dGTR without any additives.

The rubber ingredients were mixed in a Brabender Plasticorder (Brabender GmbH & Co. KG, Duisburg, Germany) internal mixer at 50°C and a screw speed of 40 rpm. The order of appearance of the components in Tables 3–4 (left to right) also reflects the order they were mixed in. 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.

2.5. Characterization of the rubber mixture and cured rubber sheets

The curing curves of the rubber compounds were recorded with a MonTech Monsanto R100S rheometer (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Germany) in isothermal ($T=160^\circ\text{C}$) time sweep mode (1.667 Hz, 1° angle) for 15 min.

The hardness of the cured rubber samples was determined according to the ISO 48-4:2018 Shore A method on a Zwick H04.3150.000 hardness tester (Zwick GMBH., Ulm, Germany). Ten tests were performed on each compound.

The tensile mechanical properties of the compounds were investigated according to the ISO 37:2017 standard on a Zwick 2005 universal testing machine with a 10 kN load cell (Zwick GmbH,

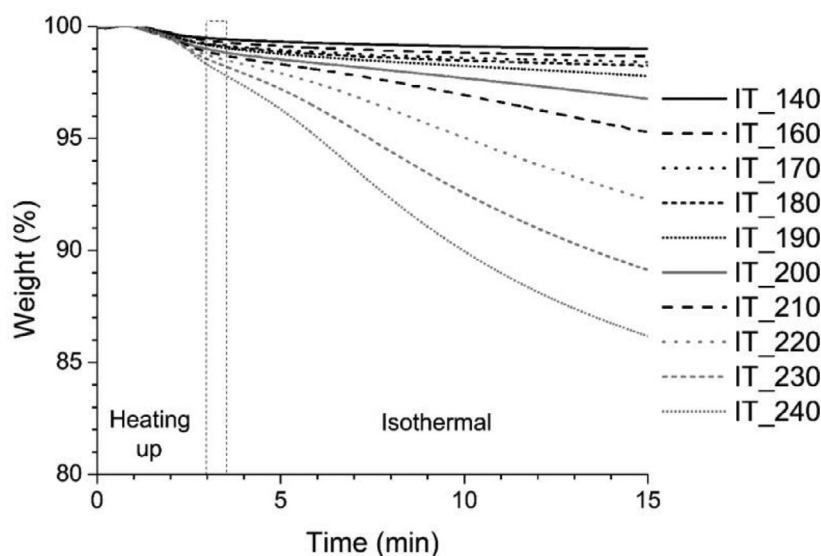


Fig. 3. Isothermal TGA curves of the GTR at 140...240°C.

Ulm, Germany). Type 1 specimens were used. Clamping length was 60 mm, and the crosshead speed was 500 mm/min. Tear tests were performed on the same testing configuration, and test speed was 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 for five tests each.

3. Results and discussion

3.1. Thermogravimetric analysis

The TG analysis of GTR and the dGTR_180/210 sample (Fig. 2) showed that the untreated GTR and the heavily degraded dGTR samples behaved differently. In the case of GTR, the volatilization of processing oils and additives can be observed around 150–200°C. At higher temperatures (250–500°C), the polymeric material decomposed. First, the natural rubber, followed by the synthetic rubbers. Carbon black decomposed around 500–600°C. In the case of the dGTR_180/210 sample, there is less weight loss around 200°C than in the case of the GTR. This can be attributed to the volatilization of processing oils and additives. This partially takes place during devulcanization. Therefore, there is an approximately 2% difference in the weight of decomposed materials in the initial section of the two curves around 200°C. The degradation of the NR phase shifts and it overlaps synthetic rubbers because of the severe degradation during devulcanization. Around 500°C, very intensive oxidation occurred with a sharp drop in the weight of the carbon black. The curve shows a temperature increase due to intensive oxidation. This temperature rise was compensated with lower heating, and that caused a slight temperature decrease after oxidation ended.

Isothermal TGA tests (Fig. 3) show a non-linear weight loss at increasing temperatures. We marked the time range when momentary temperature reached 95% of the final temperature. This is comparable with the residence time of the twin-screw extruder at 60 rpm. The weight loss during devulcanization can only be estimated due to different conditions. However, at lower temperatures (140–170°C) mainly the moisture content of the GTR (0.6–0.8%, determined from a separate moisture content measurement) evaporated during devulcanization. The evaporation of processing

oils and additives only becomes more significant at higher temperatures.

3.2. Devulcanization of GTR

Table 5 lists the soluble content, cross-link density, and the degree of devulcanization of the thermomechanically devulcanized samples. It can be seen that the cross-link density decreased with increasing temperature and screw speed. But at 190°C, and above, cross-link density increased with increasing screw speed. Soluble content increased with increasing temperature and screw speed. The TGA results showed that the reference values for the calculation of the sol content vary as a function of temperature, as shown in Fig. 3. Because the soluble processing oils and additives with low molecular mass started to evaporate, the reference soluble content shifted, i.e. evaporated materials can not be dissolved during Soxhlet extraction. At 140°C, this change is below the margin of error, but at 190 and 240°C, it exceeds this limit. The selectivity coefficient (K) also was calculated. In some cases, we excluded some of the devulcanized samples from this calculation due to the uncertainty in the sol fraction and cross-link density measurements. The data points of these samples are out of the range of the Horikx plot. Because of this, the K values were greater than one or less than zero. It can be seen that devulcanization is achievable with high selectivity at lower temperatures and screw speeds, but the decrease of the cross-link density was low. Increasing barrel temperature and screw speed promoted the reduction of selectivity. Because of this, high selectivity is achieved at relatively high temperatures and low screw speeds (dGTR_60/190 sample).

The Horikx plot (Fig. 4) gives more information about the structural changes that occurred during devulcanization. With the mildest devulcanization parameters, cross-link density decreased, and ~65 % devulcanization can be reached without a change in soluble content. It suggests effective devulcanization, i.e. the main phenomenon was selective cross-link scission. Different screw speeds did not have a significant effect on the devulcanization process at 140 and 160°C. At 170°C and above, on the other hand, the soluble content increased drastically with increasing screw speed, and the decrease of the cross-link density did not follow it. The Horikx plot shows that at 170°C and above, severe degradation occurs with increasing screw speed. We achieved the best result with a relatively high temperature (190°C) and the lowest screw speed (60 rpm). The Horikx plot shows that the main mechanism was

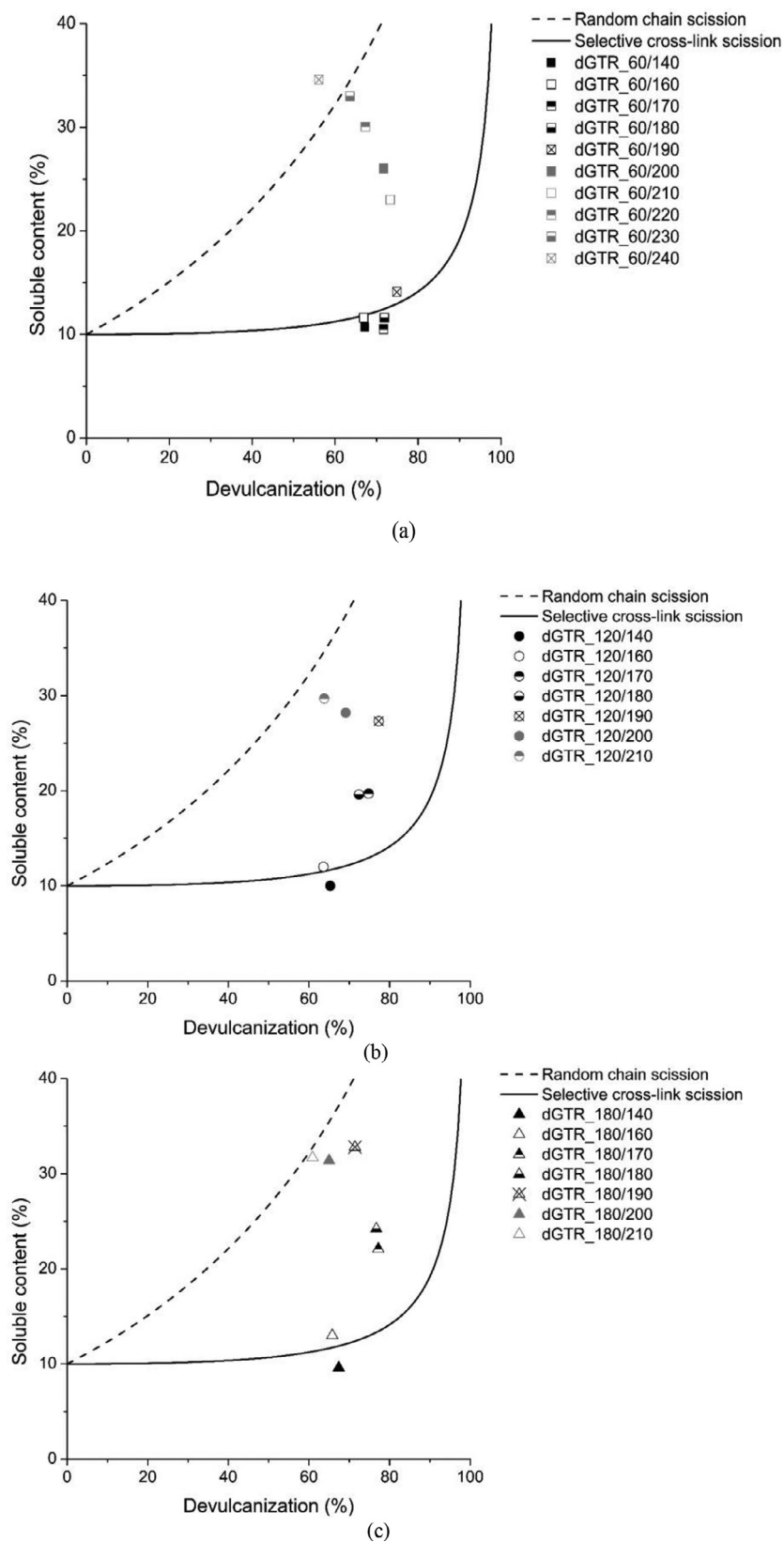


Fig. 4. Horikx plot of the devulcanized samples ((a) at 60 rpm, (b) at 120 rpm, (c) at 180 rpm): soluble content of the devulcanized samples as a function of devulcanization (decrease in cross-link density).

Table 5
The soluble content of GTR after thermomechanical devulcanization.

| Sample | Soluble content(%) | Cross-link density(mol/dm ³) | Devulcanization(%) | K(-) |
|--------------|--------------------|--|--------------------|------|
| GTR | 10.0±1.2 | 0.659±0.025 | - | - |
| dGTR_60/140 | 10.7±0.6 | 0.216±0.030 | 67.2 | - |
| dGTR_120/140 | 10.0±0.8 | 0.229±0.025 | 65.3 | - |
| dGTR_180/140 | 9.6±0.9 | 0.215±0.019 | 67.4 | - |
| dGTR_60/160 | 11.6±0.9 | 0.218±0.020 | 66.9 | - |
| dGTR_120/160 | 11.2±1.1 | 0.240±0.022 | 63.6 | 0.98 |
| dGTR_180/160 | 12.0±0.7 | 0.226±0.017 | 65.8 | 0.97 |
| dGTR_60/170 | 10.5±0.7 | 0.187±0.029 | 71.7 | - |
| dGTR_120/170 | 19.7±0.5 | 0.166±0.024 | 74.8 | 0.75 |
| dGTR_180/170 | 22.1±0.8 | 0.150±0.023 | 77.2 | 0.72 |
| dGTR_60/180 | 11.6±0.6 | 0.228±0.016 | 71.9 | - |
| dGTR_120/180 | 19.6±0.6 | 0.182±0.024 | 72.4 | 0.72 |
| dGTR_180/180 | 24.2±0.5 | 0.154±0.028 | 76.7 | 0.65 |
| dGTR_60/190 | 14.1±0.8 | 0.166±0.018 | 74.9 | 0.94 |
| dGTR_120/190 | 27.3±0.8 | 0.150±0.021 | 77.3 | 0.58 |
| dGTR_180/190 | 32.8±1.0 | 0.189±0.017 | 71.4 | 0.28 |
| dGTR_60/200 | 26.2±0.5 | 0.187±0.020 | 71.7 | 0.50 |
| dGTR_120/200 | 28.2±0.6 | 0.204±0.030 | 69.1 | 0.38 |
| dGTR_180/200 | 31.4±0.8 | 0.231±0.012 | 65.0 | 0.17 |
| dGTR_60/210 | 23.9±0.7 | 0.176±0.025 | 73.3 | 0.60 |
| dGTR_120/210 | 29.7±0.5 | 0.239±0.018 | 63.8 | 0.21 |
| dGTR_180/210 | 31.7±0.8 | 0.258±0.022 | 60.9 | 0.05 |
| dGTR_60/220 | 30.1±0.6 | 0.216±0.027 | 67.3 | 0.28 |
| dGTR_60/230 | 33.0±0.6 | 0.240±0.019 | 63.6 | 0.07 |
| dGTR_60/240 | 34.6±0.5 | 0.290±0.026 | 56.1 | - |

Table 6
The main parameters of the cure characteristics of model tire rubber (MTR).

| | |
|----------------------------------|----------|
| Maximum torque | 70.4 dNm |
| Minimum torque | 1.3 dNm |
| Scorch time | 70 sec |
| t ₁₀ | 97 sec |
| t ₉₀ | 494 sec |
| Time to reach the minimum torque | 30 sec |

selective cross-link scission with minimal degradation. A further increase in barrel temperature caused severe degradation in the samples even at 60 rpm. At 120 and 180 rpms, the sol content did not increase further, even decreased a bit, and cross-link density started to increase. This behaviour shows that degradation became more dominant and severe. The continuous rise of cross-link density can be attributed to the fact that during devulcanization, in addition to the breaking of the bonds, new bonds are also formed. The final cross-link density is the sum of these processes. At higher temperatures, the formulation of new bonds is accelerated.

If we compare the residence time (60 rpm: ~225 s, 120 rpm: ~120 s, 180 rpm: ~70 s) with the local temperature of the GTR, the results suggest that local temperature is the crucial factor for thermomechanical devulcanization. Local temperature is composed of external heating and heat generation due to shear. The higher screw speed is, the more intense heat generation is. At 180 rpm, the duration of the devulcanization process is only one-third of that at 60 rpm, but degradation is more severe at 180 rpm. Based on the Horikx analysis, we chose the dGTR_60/190 and dGTR_180/190 samples for further investigation.

3.3. Further examination of Horikx's analysis

Table 6 shows the cure characteristic of the model tire rubber (MTR) mixture. Fig. 5 shows the registered curing curve of the model tire rubber at 150°C. We chose this relatively low temperature to prolong the induction phase of the curve.

Table 7 shows the results of Soxhlet extraction and swelling tests. The soluble content of MTR is relatively high compared to GTR. However, in the case of the MTR_m sample, the measured

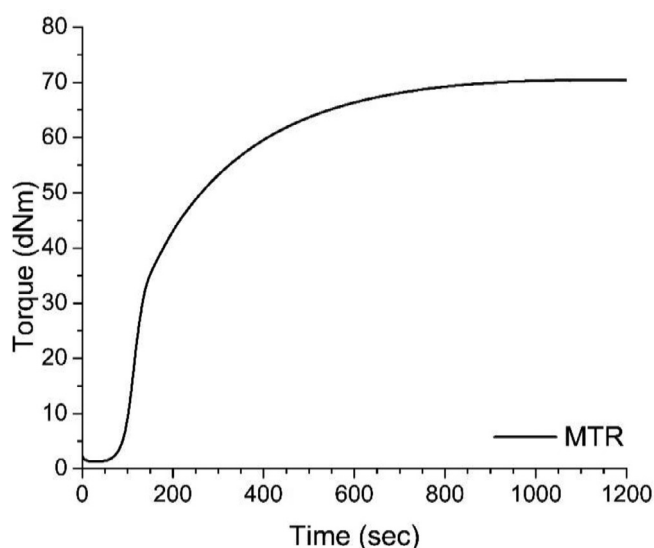


Fig. 5. Vulcanization curves of the model tire rubber (MTR).

soluble content (63.5%) was similar to the theoretical soluble content (68.4%) calculated based on the recipe. The MTR_50s sample was cured for 50 sec, so curing had already started, but the sample was slightly vulcanized. Therefore the sol content of the MTR_50s sample was quite high compared to dGTR samples. The results of the swelling test show a significant drop in cross-link density in the MTR_50s sample, compared to the MTR sample; the calculated devulcanization rate is very high. The uncured rubber sample (MTR_m) dissolved completely during the swelling tests, so its cross-link density can be considered zero, i.e. the devulcanization rate is ~100%.

Fig. 6 shows the Horikx's diagram of the model tire rubber samples. The cured MTR sample is the reference. The MTR_m and MTR_50s samples can be considered the end product of a theoretical devulcanization process where only cross-link scission occurs. The Horikx plot of MTR_m is the theoretical maximum of the devulcanization process. To reach this value is an ideal scenario, but

Table 7
The sol fraction and cross-link density of the model tire rubber samples.

| Sample | Sol fraction (%) | Cross-link density (mol/dm ³) | Devulcanization (%) |
|---------|------------------|---|---------------------|
| MTR | 20.0±0.6 | 0.890±0.020 | 0 |
| MTR_m | 63.5±2.4 | ~0 | ~100 |
| MTR_50s | 37.3±0.4 | 0.048±0.006 | 94.6 |

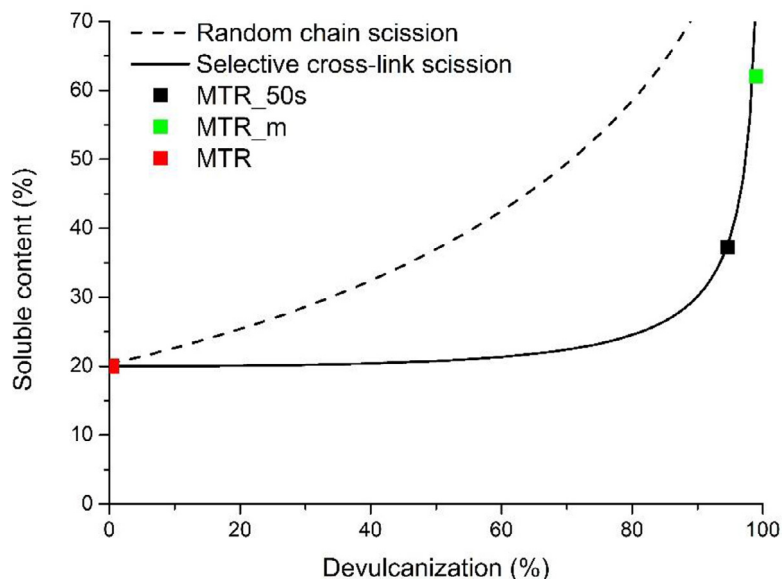


Fig. 6. Horikx plot of the additional rubber mixtures.

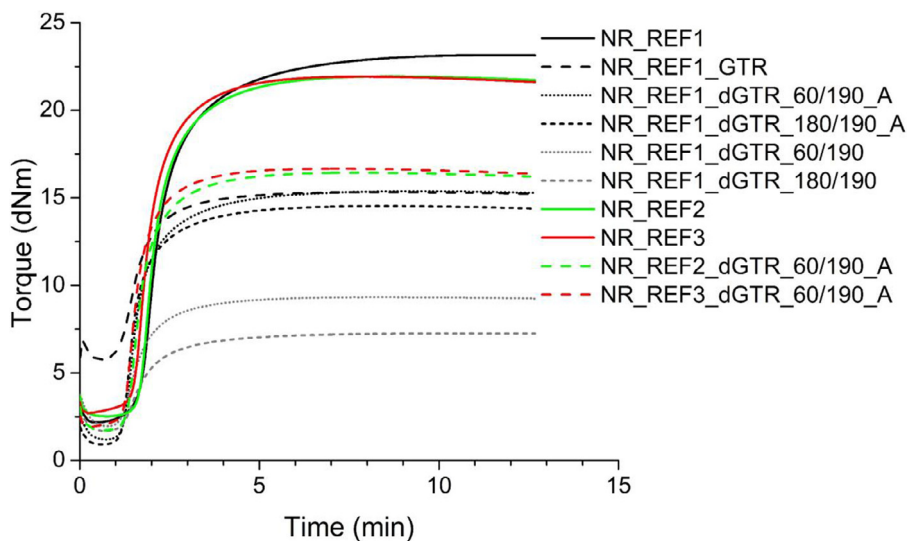


Fig. 7. Vulcanization curves of the samples.

unfortunately, it is impossible during the real devulcanization process. MTR_50s and MTR_m samples both fit nicely on the selective scission curve. With other samples cured for different times, the whole selective scission curve could be covered.

3.4. Cure characteristics of the rubber compounds

Fig. 7 shows the cure characteristics of the prepared samples; the main parameters of the curves are listed in Table 6. The cure characteristics of the REF samples do not show significant difference, i.e. carbon black has no significant effect. The maximum torque values decreased significantly with the introduction of dGTR. It has a softening effect, and vulcanization time was also re-

duced. The hardness (Table 8) shows similar results. With two-step mixing (_A samples), when extra vulcanizing agents were added to dGTR, the maximum torque was recovered because of the re-vulcanization of dGTR. This trend was also reflected in hardness. In the case of samples containing GTR, the maximum torque did not decrease as much as the maximum torque of samples containing dGTR, because of the harder GTR particles. They showed greater resistance, as can be seen in the minimum torque.

3.5. Mechanical properties of the cured rubber compounds

The reference samples (REF1, 2, 3) followed our expectation (Fig. 8). The more active carbon black was used, the higher the

Table 8
Cure characteristics and hardness of the samples.

| Sample | t_{90} (min) | t_{2}/t_{10} (min) | Min. torque (dNm) | Max. torque (dNm) | Shore A Hardness (-) |
|------------------------|----------------|----------------------|-------------------|-------------------|----------------------|
| NR_REF1 | 4.2 | 1.7 | 2.2 | 23.2 | 57.3±0.7 |
| NR_REF2 | 3.6 | 1.7 | 2.4 | 21.9 | 59.2±0.6 |
| NR_REF3 | 3.2 | 1.5 | 2.7 | 22.0 | 60.7±0.5 |
| NR_REF1_dGTR_60/190 | 3.0 | 1.2 | 1.9 | 9.3 | 44.6±0.5 |
| NR_REF1_dGTR_180/190 | 3.5 | 1.2 | 1.7 | 7.2 | 38.8±0.8 |
| NR_REF1_GTR | 2.9 | 1.1 | 5.7 | 15.3 | 52.9±0.4 |
| NR_REF1_dGTR_60/190_A | 3.1 | 1.1 | 1.2 | 15.4 | 48.9±0.2 |
| NR_REF1_dGTR_180/190_A | 2.8 | 1.2 | 0.9 | 14.5 | 48.1±0.5 |
| NR_REF2_dGTR_60/190_A | 2.9 | 1.3 | 1.7 | 16.4 | 49.7±0.7 |
| NR_REF3_dGTR_60/190_A | 2.6 | 1.3 | 1.9 | 16.7 | 51.0±0.6 |

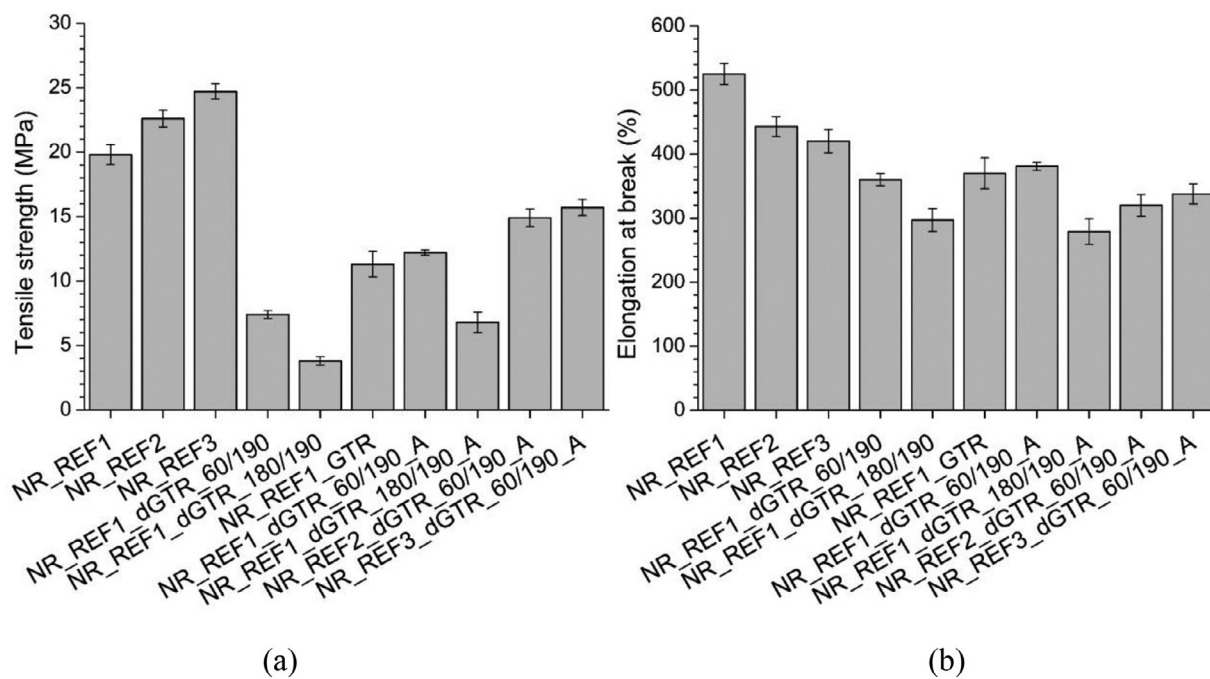


Fig. 8. The results of tensile tests, tensile strength (a) and elongation at break (b).

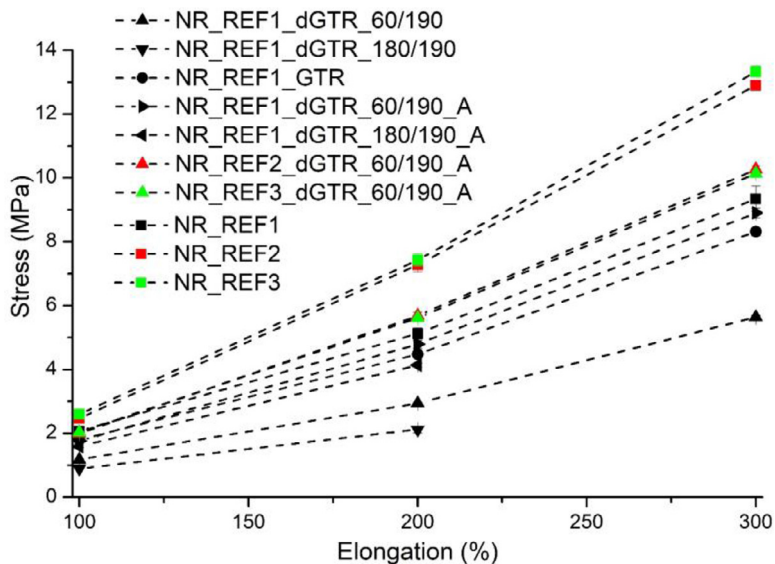


Fig. 9. Stress at 100%, 200% and 300% elongation.

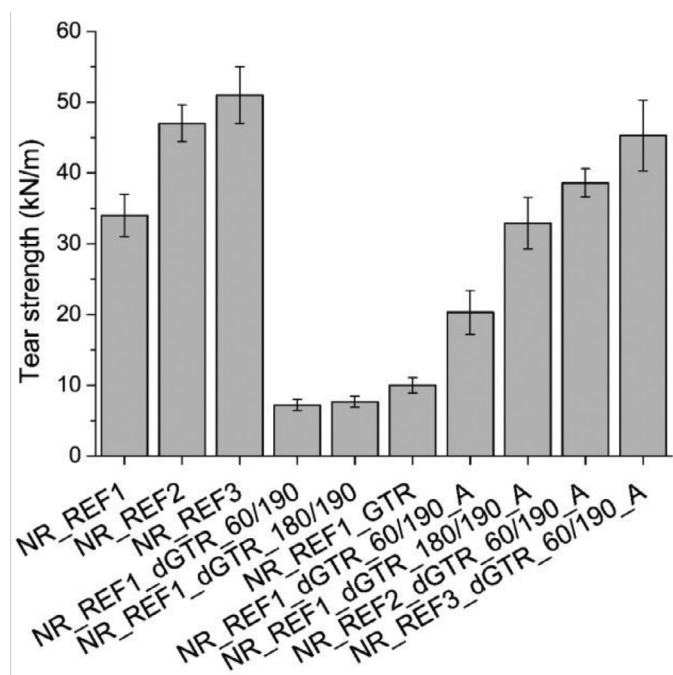


Fig. 10. The tear strength of the samples.

tensile strength was. At the same time, the elongation at break decreased. The dGTR added to the rubber mixture drastically decreased tensile strength. But elongation at the break did not follow this trend; it showed a moderate decrease. Almost all samples exceeded 300% elongation. Two-step mixing and the extra vulcanizing agents helped to recover tensile strength and elongation at break. The effect of different carbon blacks is also evident in these samples. Furthermore, the results of the tensile tests reflect the results of Horikx's analysis. The dGTR_60/190 sample achieved better results than the dGTR_180/190 sample. dGTR_60/190 has the highest devulcanization and lowest degradation against the dGTR_180/190 sample.

Fig. 9 shows the stress values of samples at 100%, 200% and 300% elongation. The measured stress values follow the trend of tensile strength with two exceptions; the NR_REF2_dGTR_60/190_A and NR_REF3_dGTR_60/190_A samples performed better than REF1, which is quite favourable because most rubber products are used in this elongation range.

Fig. 10 shows the results of tear tests. In the REF samples, with more active carbon black, tear strength also increased significantly. When 100 phr dGTR was introduced in the mixtures, tear strength decreased drastically, regardless of the quality of the dGTR. The results also show the beneficial effect of the two-step mixing and extra vulcanizing agents. The results show that the sample with more degraded dGTR has better tear strength. It can be attributed to the fact that during more powerful devulcanization, shorter and more mobile molecules formed. During revulcanization, more cross-links formed between the rubber matrix and the surface of the dGTR particles with the aid of extra vulcanization agents and two-step mixing. The improved adhesion between the phases and the different load mode of the tear test caused excellent tear strength in these samples [34]. The tear strength can be increased further with N550 or N330 carbon black, and the reference values can be approached.

4. Conclusions

We devulcanized ground tire rubber (GTR) thermomechanically with a twin-screw extruder with different barrel temperatures and

screw speeds. We characterized the devulcanized GTR (dGTR) samples by Soxhlet extraction and swelling tests to determine their soluble content and cross-link density. We evaluated these results with Horikx's analysis. It showed that the local temperature is the key factor in devulcanization. Local temperature is a result of external heating and shear-generated heat. The higher screw speed is, the more heat is generated by shear. At lower temperatures ($\leq 160^\circ\text{C}$), screw speed had no significant effect on soluble content and cross-link density because local temperature was relatively low even with the heat generated at high screw speeds. Horikx's analysis and the calculated selectivity parameter (K) showed that devulcanization was effective—mostly cross-links scission occurred with minimal degradation. At higher temperatures ($\geq 160^\circ\text{C}$), the effect of screw speed, i.e. heat generated by shear, was crucial. Local temperatures greatly increased with increasing screw speed, and the samples suffered severe degradation. These results show that treatment at lower screw speeds but higher temperatures may be more expedient and suggest that the intense shear-generated heat due to higher screw speeds mainly causes chain breakage, despite the shorter residence time. At 60 rpm, the soluble content does not increase exponentially with increasing temperature, so the points are located close to the selective scission curve. However, there is a temperature limit at 190°C . Below this limit, the effectiveness of devulcanization continuously increases with temperature, but above that, degradation becomes more prominent.

When dGTR was introduced in NR-based rubber mixtures, physical and mechanical properties decreased significantly. In agreement with Horikx's analysis, the more degraded dGTR the mixture contained, the more mechanical properties worsened. However, when the recipe was modified, and the mixtures were prepared by two-step mixing, the physical and mechanical properties improved. With this method, extra vulcanizing agents were added directly to dGTR, and this mixture was added to the reference. They helped cross-link generation. Therefore better adhesion was achieved between the dGTR particles and the rubber matrix.

When the reference mixture was improved with N550 or N330 carbon black, the mechanical properties improved as expected. The reduction of the tensile strength of samples containing dGTR and processed by two-step mixing can be calculated because it is approximately a fixed percentage. Based on this, a specific target tensile strength of the mixture containing dGTR can be achieved with further improvements to the reference mixture.

Declaration of Competing Interest

None.

CRediT authorship contribution statement

Dániel Ábel Simon: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Visualization. **Tamás Bárány:** Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration.

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References

- [1] T.M. Lechter, D.A. Vallero, Waste editors, 2nd Edition, Academic Press, Cambridge, 2019.

- [2] R. Saputra, R. Walvekar, M. Khalid, N.M. Mubarak, M. Sillanpää, Current progress in waste tire rubber devulcanization, *Chemosphere* 265 (2021) 129033.
- [3] A. Molino, A. Donatelli, T. Marino, A. Aloise, J. Rimauro, P. Iovane, Waste tire recycling process for production of steam activated carbon in a pilot plant, *Resour. Conserv. Recycl.* 129 (2018) 102–111.
- [4] J. Burlakovs, M. Kriipsalu, M. Klavins, A. Bhatnagar, Z. Vinc vi a-Gaile, J. Steinis, Y. Jani, V. Mykhaylenko, G. Denafas, T. Turkadze, M. Hogland, V. Rudovica, F. Kaczala, R.M. Rosendal, W. Hogland, Paradigms on landfill mining: from dump site scavenging to ecosystem services revitalization, *Resour. Conserv. Recycl.* 123 (2017) 73–84.
- [5] J. Karger-Kocsis, L. Mészáros, T. Bárány, Ground tyre rubber (GTR) in thermoplastics, thermosets, and rubbers, *J. Mater. Sci.* 48 (1) (2013) 1–38.
- [6] F.D.B. de Sousa, C.H. Scuracchio, G.-H. Hu, S. Hoppe, Devulcanization of waste tire rubber by microwaves, *Polym. Deg. Stab.* 138 (2017) 169–181.
- [7] X. Colom, A. Faliq, K. Formela, J. Cañavate, FTIR spectroscopic and thermogravimetric characterization of ground tyre rubber devulcanized by microwave treatment, *Polym. Test.* 52 (2016) 200–208.
- [8] P.S. Garcia, F.D.B. de Sousa, J.A. de Lima, S.A. Cruz, C.H. Scuracchio, Devulcanization of ground tire rubber: physical and chemical changes after different microwave exposure times, *Express Polym. Lett.* 9 (11) (2015) 1015–1026.
- [9] K. Aoudia, S. Azem, N. Ait Hocine, M. Gratton, V. Pettarin, S. Seghar, Recycling of waste tire rubber: microwave devulcanization and incorporation in a thermoset resin, *Waste Manage.* 60 (2017) 471–481.
- [10] K. Formela, M. Cysewska, Efficiency of thermomechanical reclaiming of ground tire rubber conducted in counter-rotating and co-rotating twin screw extruder, *Polimery* 59 (3) (2014) 231–238.
- [11] B. Maridass, B.R. Gupta, Performance optimization of a counter rotating twin screw extruder for recycling natural rubber vulcanizates using response surface methodology, *Polym. Test.* 23 (4) (2004) 377–385.
- [12] B. Maridass, B.R. Gupta, Effect of extruder parameters on mechanical properties of devulcanized ground rubber tire powder, *Polimery* 52 (6) (2007) 456–460.
- [13] B. Sripornsawat, S. Saiwari, S. Pichaiyut, C. Nakason, Influence of ground tire rubber devulcanization conditions on properties of its thermoplastic vulcanizate blends with copolyester, *Eur. Polym. J.* 85 (2016) 279–297.
- [14] X. Zhang, C. Lu, M. Liang, Properties of natural rubber vulcanizates containing mechanochemically devulcanized ground tire rubber, *J. Polym. Res.* 16 (2009) 411–419.
- [15] B. Kaewpetch, S. Prasongsuk, S. Poompradub, Devulcanization of natural rubber vulcanizates by *Bacillus cereus* TISTR 2651, *Express Polym. Lett.* 13 (10) (2019) 877–888, doi:10.3144/expresspolymlett.2019.76.
- [16] K. Formela, M. Cysewska, J.T. Haponiuk, Thermomechanical reclaiming of ground tire rubber via extrusion at low temperature: Efficiency and limits, *J. Vinyl Addit. Technol.* 22 (3) (2016) 213–221.
- [17] S. Seghar, L. Asaro, M. Rolland-Monnet, N. Ait Hocine, Thermo-mechanical devulcanization and recycling of rubber industry waste, *Resour. Conserv. Recycl.* 144 (2019) 180–186.
- [18] H.O.M. Mouri, M. Matsushita, H. Honda, K. Nakashima, K. Takeushi, Y. Suzuki, M. Owaki, De-vulcanisation conditions and mechanical properties of re-vulcanised rubber for EPDM. Continuous activation of rubber by shear flow reaction control technology (Part 2), *Int. Polym. Sci. Technol.* 27 (2000) 23–28.
- [19] K. Formela, M. Cysewska, J. Haponiuk, A. Stasiak, The influence of feed rate and shear forces on the devulcanization process of ground tire rubber (GTR) conducted in a co-rotating twin screw extruder, *Polymery-W* 58 (2013) 906–912.
- [20] K. Formela, M. Cysewska, J. Haponiuk, The influence of screw configuration and screw speed of co-rotating twin screw extruder on the properties of products obtained by thermomechanical reclaiming of ground tire rubber, *Polymery-W* 59 (2014) 170–177.
- [21] M. Gagol, G. Boczkaj, J. Haponiuk, K. Formela, Investigation of volatile low molecular weight compounds formed during continuous reclaiming of ground tire rubber, *Polym. Deg. Stab.* 119 (2015) 113–120.
- [22] Y. Li, A. Shen, Z. Lyu, S. Wang, K. Formela, G. Zhang, Ground tire rubber thermo-mechanically devulcanized in the presence of waste engine oil as asphalt modifier, *Const. Build. Mater.* 222 (2019) 588–600.
- [23] S. Saiwari, W. Dierkes, J. Noordermeer, Comparative investigation of the devulcanization parameters of tire rubbers, *Rubber Chem. Technol.* 87 (2014) 31–42.
- [24] G. Tao, Q. He, Y. Xia, G. Jia, H. Yang, W. Ma, The effect of devulcanization level on mechanical properties of reclaimed rubber by thermal-mechanical shearing devulcanization, *J. Appl. Polym. Sci.* 129 (5) (2013) 2598–2605.
- [25] M. Balasubramanian, Cure modeling and mechanical properties of counter rotating twin screw extruder devulcanized ground rubber tire–natural rubber blends, *J. Polym. Res.* 16 (2009) 133–141.
- [26] H. Yazdani, M. Karrabi, I. Ghasmi, H. Azizi, G.R. Bakhshandeh, Devulcanization of waste tires using a twin-screw extruder: The effects of processing conditions, *J. Vinyl Addit. Technol.* 17 (1) (2011) 64–69.
- [27] R. Barbosa, J. Ambrósio, Devulcanization of natural rubber compounds by extrusion using thermoplastics and characterization of devulcanized compounds, *J. Polym. Res.* 26 (2019) 160.
- [28] A.T. Nunes, R.E.d.D. Santos, J.S. Pereira, R. Barbosa, J.D. Ambrósio, Characterization of waste tire rubber devulcanized in twin-screw extruder with thermoplastics, *Prog. Rubber Plast. Recycl. Technol.* 34 (3) (2018) 143–157.
- [29] M.M. Horikx, Chain scissions in a polymer network, *J. Polym. Sci.* 19 (93) (1956) 445–454.
- [30] S. Seghar, L. Asaro, N. Ait Hocine, Experimental validation of the Horikx theory to be used in the rubber devulcanization analysis, *J. Polym. Environ.* (2019) 27.
- [31] M.A.L. Verbruggen, L.v.d. Does, J.W.M. Noordermeer, M.v. Duin, H.J. Manuel, Mechanisms Involved in the recycling of NR and EPDM, *Rubber Chem. Technol.* 72 (4) (1999) 731–740.
- [32] V. Tatangelo, I. Mangili, P. Caracino, M. Anzano, Z. Najmi, G. Bestetti, E. Collina, A. Franzetti, M. Lasagni, Biological devulcanization of ground natural rubber by *Gordonia desulfuricans* DSM 44462T strain, *Appl. Microbiol. Biot.* 100 (20) (2016) 8931–8942.
- [33] D.Á. Simon, D.Z. Pirytyi, P. Tamás-Bényei, T. Bárány, Microwave devulcanization of ground tire rubber and applicability in SBR compounds, *J. App. Polym. Sci.* (2019) 8.
- [34] D.Á. Simon, D.Z. Pirytyi, T. Bárány, Devulcanization of ground tire rubber: microwave and thermomechanical approaches, *Sci. Rep.-UK* 10 (1) (2020) 16587.
- [35] S. Saiwari, J.W. van Hoek, W.K. Dierkes, L.E.A.M. Reuvekamp, G. Heideman, A. Blume, J.W.M. Noordermeer, Upscaling of a batch de-vulcanization process for ground car tire rubber to a continuous process in a twin screw extruder, *Materials* 9 (9) (2016) 724.
- [36] H. Si, T. Chen, Y. Zhang, Effects of high shear stress on the devulcanization of ground tire rubber in a twin-screw extruder, *J. App. Polym. Sci.* 128 (2013).
- [37] P.J. Flory, J. Rehner Jr., Statistical mechanics of cross-linked polymer networks II. Swelling, *J. Chem. Phys.* 11 (11) (1943) 521–526.
- [38] G. Kraus, Swelling of filler-reinforced vulcanizates, *J. App. Polym. Sci.* 7 (3) (1963) 861–871.
- [39] B. Ellis, G.N. Welding, 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.* 37 (2) (1964) 571–575.
- [40] M.A.L. Verbruggen, L. van der Does, W.K. Dierkes, J.W.M. Noordermeer, Experimental validation of the Charles by and Horikx models applied to de-vulcanization of sulfur and peroxide vulcanizates of NR and EPDM, *Rubber Chem. Technol.* 89 (4) (2016) 671–688.
- [41] D.W. Edwards, B. Danon, P. van der Gryp, J.F. Görgens, Quantifying and comparing the selectivity for crosslink scission in mechanical and mechanochemical devulcanization processes, *J. App. Polym. Sci.* 133 (37) (2016).