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Research article

Investigating the combined effects of devulcanization level and carbon black grade on the SBR/GTR composites

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Abstract. Carbon black migration between ground tire rubber (GTR) and rubber matrix is essential in developing high-performance rubber/GTR composites. In this work, carbon black N220 (surface area: 107.1 m^2/g, particle size: 20–25 nm) and N660 (surface area: 33.1 m^2/g, particle size: 49–60 nm) were used as the reinforcement fillers for styrene-butadiene rubber (SBR) blended with reclaimed GTR. The combined effects of GTR devulcanization level and carbon black grade on the properties of SBR/GTR composites were investigated considering curing characteristics, thermal stability, physico-mechanical properties, dynamic mechanical properties, swelling behavior, and morphology.
The results showed that, regardless of GTR devulcanization level and carbon black grade, application of GTR resulted in deterioration of mechanical properties compared to a reference sample without GTR. It was observed the reinforcement effect of carbon black in SBR/GTR composites was more visible with higher devulcanization level of GTR and lower particle sizes of carbon black fillers. SBR/GTR composites reinforced with carbon black N220 were characterized by tensile strength in the range of 15.3–16.3 MPa and abrasion resistance in the range of 120–123 mm^3, which justify their potential application in the manufacturing of technical rubber goods or footwear.

Keywords: *waste tires, recycling, devulcanization, rubber composites, carbon black, migration*

1. Introduction

In 2021, the European Tyre and Rubber Manufacturers' Association (ETRMA) and the European Recycling Industries' Confederation (EuRIC) announced that the rubber supply chain is ready to increase the amount of waste tire rubber in the production of new rubber goods, promoting the circular economy in the European Union [1]. This strategy fits well with global rubber manufacturers' current goals, resulting in the development and production of tires and other technical rubber goods made from renewable and recycled materials [2–4]. For example, Bridgestone Corporation announced that by 2050, it will use 100% sustainable materials in its products, while Michelin company is developing high-technology recycling to produce by 2048 tires that are 100% recycled [5].

Materials obtained from waste tires after mechanical disintegration can be divided into three streams: steel, textile cord fibers, and ground tire rubber (GTR), which should be considered as valuable source of raw materials [6]. Many attempts have focused on applying GTR in various rubber composites [7–9]. GTR is mainly composed of natural rubber, butadiene rubber, styrene-butadiene rubber as a rubber matrix, and carbon black as a reinforcement

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filler [10]. Therefore, the above-mentioned rubbers seem to be the most appropriate choice for the further development of rubber composites filled with GTR [11–13].

GTR is commonly considered for application in the rubber industry as a low-cost filler or partial replacement of rubbers. However, this approach usually results in the deterioration of obtained materials' processing and mechanical properties [14–16]. This is due to weak compatibility and limited interfacial adhesion between cross-linked GTR particles and rubber matrix. Therefore, suitable treatment of GTR before further use is strongly recommended [17–19] and seems crucial for developing high-value-added waste tire rubber-based materials.

In this field of research, GTR devulcanization and functionalization using a reactive extrusion have the highest potential, considering the possibility of upscaling and industrial application [20, 21].

Two important factors should be considered during the design of rubber composites filled with GTR. Firstly, it should be pointed out that using GTR in rubber composites affects the cross-link density of the rubber matrix due to competition for cross-linking agents between the rubber matrix and GTR. Gibala and Hamed [22] investigated the cure behavior of styrene-butadiene rubber (SBR)/ground rubber composites and observed the migration of sulfur from the rubber matrix to the ground rubber and the migration of accelerator fragments from the ground rubber to the matrix.

The second factor affecting rubber/GTR systems is the migration of carbon black particles from GTR into the rubber matrix, which significantly impacts the performance properties of obtained materials [23]. However, to our knowledge, the published information about this topic are still very limited [24, 25], especially considering the effect of carbon black migration in the rubber/GTR systems.

Carbon black is commonly used in the rubber industry as reinforcement filler, and its effectiveness depends on several parameters, such as primary particle size (specific surface area), structure, surface activity, or filler loading [26–28]. According to the ASTM D 1765 standard, rubber-grade carbon blacks should be classified using a four-character nomenclature system, *e.g.* N220. The first character in the nomenclature system for rubber-grade carbon blacks indicates the effect of carbon black on the cure rate of a typical rubber compound filled with carbon black. The letter 'N' stands for 'normal cure', meaning that the carbon black filler does not significantly affect the rubber vulcanization process, while the letter 'S' indicates that carbon black causes a 'slow cure' rate and, in this case suitable modification of used curing system is necessary. The second character in the four-character nomenclature system is a digit to designate the average surface area of the carbon black measured by nitrogen surface area, and the lower digit corresponds to the higher surface area. The last two digits in the four-character nomenclature system are assigned arbitrarily based on measurements of iodine adsorption, oil absorption number, and other specific properties.

Considering the above classification, carbon black fillers can also be divided into low and high structures. Low-structure carbon black has aggregates of spherical shape, usually made of fewer and larger particles (coarse structure), while high-structure carbon black has aggregates of branched shape, often made of more and smaller particles (fine structure) [29].

Recently, Zhang *et al.* [30] studied the effect of mechano-chemical devulcanization conditions on the quality of reclaimed rubber. The obtained results showed that rubber devulcanization enhances carbon black exfoliation. In this case, reclaimed rubber forms a micro-nano microstructure in natural rubber, which makes reinforcement of the natural rubber. The authors confirmed that this strategy is a promising approach for the production of high-strength and higher-value-added reclaimed rubber.

In this study, for a better understanding of the carbon black migration phenomenon in rubber/GTR systems, we aimed to examine the effects of GTR devulcanization level and carbon black grade on the curing characteristics (rubber process analyzer), thermal stability (thermogravimetric analysis), dynamic mechanical analysis, physico-mechanical properties (tensile test, hardness, abrasion resistance, density), swelling behavior and morphology (scanning electron microscopy) of styrene-butadiene rubber/GTR composites.

2. Materials and methods

2.1. Materials

GTR with a particle size up to 0.6 mm was supplied by Grupa Recykl S.A. (Śrem, Poland). GTR was prepared from a mix of passenger and truck tires using

Table 1. Specification of carbon black grades N220 and N660.

Property	ASTM standard	Carbon black*	
		N220	N660
Iodine adsorption number [g/kg]	D1510	122.0	37.3
Oil absorption number [cm^3/100 g]	D2414	112.5	89.0
Brunauer, Emmett, and Teller (BET) theory [m^2/g]	D6556	107.1	33.1
Average carbon black particle size [nm]	D1765-86	20–25	49–60
Average specific surface area of carbon black particles [m^2/g]		100–120	33–39

*Data provided by producer in technical data sheet.

an ambient grinding technology. GTR composition included organics (rubber and additives) – 63.1 wt%, carbon black – 28.4 wt%, and ash – 8.5 wt% [31].

Styrene-butadiene rubber (SBR) type KER® 1502, characterized by 22–25 wt% of bounded styrene and Mooney viscosity ML(1+4) 100 °C in the range: 45–55, was purchased from Synthos S.A. (Oświęcim, Poland).

Technical carbon black grades N220 and N660 were supplied by MAKROchem S.A. (Lublin, Poland), and their physical characteristics are summarized in Table 1. Carbon blacks N220 and N660 were selected for this study, considering their different surface characteristics and average particle size, which strongly affected their reinforcement effect in the rubber composites [32].

Curing additives, such as sulfur, stearic acid, zinc oxide, and *N*-tert-butyl-2-benzothiazolesulfenamide (TBBS), were obtained from P.P.H. Standard Sp. z o.o. (Lublin, Poland) and used as received.

2.2. Sample preparation

2.2.1. GTR devulcanization in the planetary extruder

GTR devulcanization was performed at low temperature (180 °C) and high temperature (280 °C) using a lab-size planetary roller extruder model PLATEX 80 produced by Takımsan Disli Kesici Ltd. Sti. (Istanbul, Türkiye). Other extrusion parameters, such as screw speed and throughput, remained constant and were 15 rpm and 2 kg/h, respectively. The devulcanization level of prepared products was determined using a Mooney viscosity [33, 34], which is crucial for the processing of reclaimed rubbers. The obtained reclaimed rubbers were coded as LD-GTR (reclaimed GTR with a low devulcanization level) and HD-GTR (reclaimed GTR with a high devulcanization level). The LD-GTR had a form of granules, while HD-GTR agglomerates. In both cases, one pass through the two-roll mill was sufficient to combine rubber granules/agglomerates and create reclaimed rubber sheets. HD-GTR was more sticky than LD-GTR and left black marks on the silicone-coated paper used for the storage of material, which confirms its higher devulcanization level.

For tensile tests, reclaimed GTR (LD-GTR and HD-GTR) was mixed with sulfur-based curing system (in parts per hundred of rubber [phr]: zinc oxide – 2.5; stearic acid – 0.3; 2-mercaptobenzothiazole – 0.9; *N*-tert-butylbenzothiazole-2-sulphenamide – 0.8; sulfur – 1.5) and vulcanized at 150 °C according to previously determined optimal cure time.

2.2.2. Preparation of SBR/GTR composites

SBR composites with reclaimed GTR (LD-GTR or HD-GTR) were prepared using a Brabender internal mixer (model GMF 106/2) (Brabender GmbH & Co. K.G., Duisburg, Germany) with a chamber volume of approx. 55 cm^3, equipped with roller-type rotors. SBR/reclaimed rubber ratio was 80/20 wt%. Studied materials were reinforced by carbon black filler (N220 or N660), and the total carbon black content of each sample was 36 wt%. SBR/reclaimed GTR-based composites were mixed with a sulfur-based curing system, which consists in parts per hundred of rubber [phr]: ZnO – 3, stearic acid – 1, TBBS – 1, and sulfur – 1.75. The fill factor of the mixer was 0.7, and the rotor speed was 60 rpm. The mixing temperature was 60 °C, and total time of mixing was 9 min. Obtained SBR/reclaimed GTR-based composites were vulcanized according to previously determined optimal cure time (t_{90}) using a hydraulic press PH-90 ZUP (Nysa, Poland). Vulcanization temperature and pressure during the formulation of studied materials were 170 °C and 10 MPa, respectively. SBR without GTR and SBR/untreated GTR samples processed in the same conditions were used as reference samples. The composition and coding of prepared SBR/GTR composites are summarized in Table 2.

2.3. Methodology

Mooney viscosity ML(1+4) of reclaimed rubbers LD-GTR and HD-GTR was measured at 100 °C according to ISO 289-1 using a Mooney viscometer MV2000 (Alpha Technologies, Akron, OH, USA).

Curing characteristics of SBR/GTR composites were performed at 170 °C using a Premier RPA Alpha

Table 2. SBR/GTR composites composition and coding.

Sample composition*	Carbon black grade							
	N220				N660			
	SBR	SBR/GTR	SBR/LD-GTR	SBR/HD-GTR	SBR	SBR/GTR	SBR/LD-GTR	SBR/HD-GTR
SBR	100	80	80	80	100	80	80	80
GTR		20				20		
LD-GTR			20				20	
HD-GTR				20				20
N220	60	50	50	50				
N660					60	50	50	50

*For all samples, the same curing system was used. The curing system composition [phr]: ZnO – 3; stearic acid – 1; TBBS – 1 and sulfur – 1.75.

Technologies (Hudson, OH, USA) according to ISO 6502 standard.

Tensile strength, elongation at break, and modulus at 100% of studied samples were investigated according to the standard ISO 37 using a Zwick Z020 testing machine (Zwick/Roell, Ulm, Germany). Tensile tests were performed using a dumbbell sample type 2 and a cross-head speed of 500 mm/min.

Hardness was determined using a Zwick 3130 durometer Shore A from Zwick/Roell company (Ulm, Germany) following the standard ISO 7619-1. The reported results of tensile tests and hardness are the means of at least five measurements per sample.

The density of samples was measured based on the Archimedes method, as described in ISO 1183. Measurements were carried out at room temperature in a methanol medium using an analytical balance AS 110/C/2 from Radwag (Radom, Poland). At least three measurements were performed per sample.

Abrasion resistance was measured using an Abrasion Check equipment from Gibitre Instruments (Bergamo, Italy) according to the standard ISO 4649. The sample was weighed before the test and then abraded over an abrasive test paper of grade 60 at a constant force of 10 N. After the distance of 40 m, the loss of the sample's weight was determined. The abrasion resistance for the studied styrene-butadiene rubber composites was calculated using Equation (1):

$$\Delta V_{rel} = \frac{\Delta m_t \cdot \Delta m_{const}}{\rho_t \cdot \Delta m_r} \quad (1)$$

where ΔV_{rel} – the abrasion resistance [mm^3], Δm_t – the mass loss of the studied SBR/GTR composites [mg], Δm_{const} – the defined value of the mass loss for the reference compound (No. 1 was used) [mg]; ρ_t – the density of the composite [g/cm^3], and Δm_r – the mass loss of the reference compound [mg].

The swelling test was done by immersing the samples in toluene at room temperature. Studied samples (around 0.2 g) were initially weighed on an electronic balance. The samples were then immersed in toluene to reach an equilibrium swelling state (for 72 h) and weighed again. The swelling degree was calculated according to Equation (2):

$$Q = \frac{m_t - m_0}{m_0} \cdot 100\% \quad (2)$$

where Q – swelling degree [%]; m_t – a mass of the swollen sample after time t [g]; m_0 – an initial mass of the sample [g].

The sol fraction was estimated after the swelling test (toluene, room temperature, 72 h). It was determined based on the difference in mass of the initial sample and the dried sample after extraction according to Equation (3):

$$F_{sol} = \frac{w_1 - w_2}{w_1} \cdot 100\% \quad (3)$$

where F_{sol} – the content of the sol fraction [%], w_1 – the mass of the initial sample [g]; w_2 – the mass of the dried sample after extraction [g].

Dynamic mechanical analysis (DMA) was performed using the DMA Q800 model from TA Instruments (New Castle, DE, USA). Samples cut to the dimensions of 40×10×2 mm were loaded with a variable sinusoidal deformation force in the single cantilever bending mode at the frequency of 1 Hz under the temperature rising rate of 4 °C/min within the temperature range between –80 and 60 °C. DMA Q800 (TA instruments, New Castle, DE, USA) was also used for the strain sweep studies of the styrene-butadiene rubber-based composites at room temperature. The test was performed in tension mode using the strain amplitude range of 0.01 to 40% at 1 Hz.

Thermogravimetric analysis (TGA) for vulcanized SBR/GTR composites was performed using a Netzsch TG 209 apparatus from Netzsch Group (Selb, Germany). The samples of approximately 10 mg were investigated in the temperature range of 25–800 °C and under a nitrogen atmosphere at a heating rate of 20 °C/min.

The morphology of the surfaces created by breaking the samples in the tensile test at the speed of 500 mm/min was evaluated using a FlexSEM 1000 II scanning electron microscope from Hitachi Ltd. (Tokyo, Japan). During the analysis, the electron beam accelerating voltage was 20 kV. Before measurement, the samples were coated with a thin gold layer to increase their conductivity in the vacuum chamber using a 108 Auto Sputter Coater from Cressington Scientific Instruments (Watford, UK).

3. Results and discussion

3.1. Characteristics of GTR devulcanized in the planetary extruder

Reclaimed rubbers obtained in the planetary roller extruder were characterized by sol fraction, measured in toluene (room temperature, 72 h) and standardized methodology using a Mooney viscosity as processing parameter and tensile strength as mechanical properties indicator. The obtained results are presented in Figure 1. Sol fraction increased proportionally to a higher devulcanization level of GTR, confirming the destruction of the three-dimensional network in cross-linked rubber. It was observed that sample HD-GTR (reclaimed GTR with high devulcanization level) is characterized by much lower Mooney viscosity ML(1+4) 100 °C: 17.6±0.3 and tensile strength: 3.8±0.1 MPa, comparing to LD-GTR (reclaimed GTR with low devulcanization level) characterized by Mooney viscosity ML(1+4) 100°C: 119.2±1.6 and tensile strength: 7.0±0.4 MPa, respectively. The obtained results showed that a higher devulcanization level improves processing properties and, at the same time, deteriorates the mechanical properties of reclaimed rubber due to the main chain scission.

For a better assessment of reclaimed rubbers' quality, their properties were compared with those of products on the market. For commercially available reclaimed rubbers, Mooney viscosity ML(1+4) 100 °C might vary in the range of 65–90 [35]. Reclaimed rubber offered by Tyromer Inc. (Waterloo, Canada) is characterized by Mooney viscosity ML(1+4) 100 °C: 45±15, and according to the producer, this parameter can be optimized for individual request and application. On the other hand, reclaimed rubber's tensile strength strongly depends on the devulcanization method [36], and cross-linking system used [37] and might vary in the range of 2.5–11 MPa. Mooney viscosity and tensile strength parameters for samples LD-GTR and HD-GTR prepared using a planetary extruder are comparable to the commercially available reclaimed rubbers based on waste tires.

3.2. Thermal stability of SBR/GTR composites

Thermogravimetric analysis was used to investigate the thermal stability of SBR/GTR composites. TGA results are presented in Figure 2 and summarized in Table 3. As can be observed, the trends in TGA curves for studied materials are very similar. It was noticed that applying GTR improves the thermal stability of SBR/GTR composites filled with carbon black N660, which increased with a higher devulcanization level of GTR. On the other hand, SBR/GTR composites with carbon black N220 and HD-GTR showed decreased $T_{-2\%}$ and $T_{-5\%}$ (temperatures

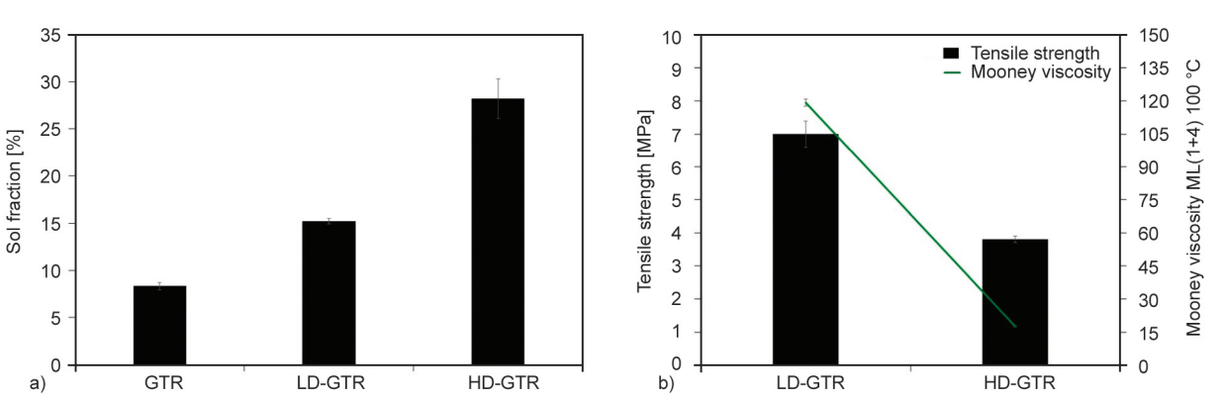

Figure 1. Characteristics of reclaimed rubbers: a) sol fraction; b) tensile strength and Mooney viscosity.

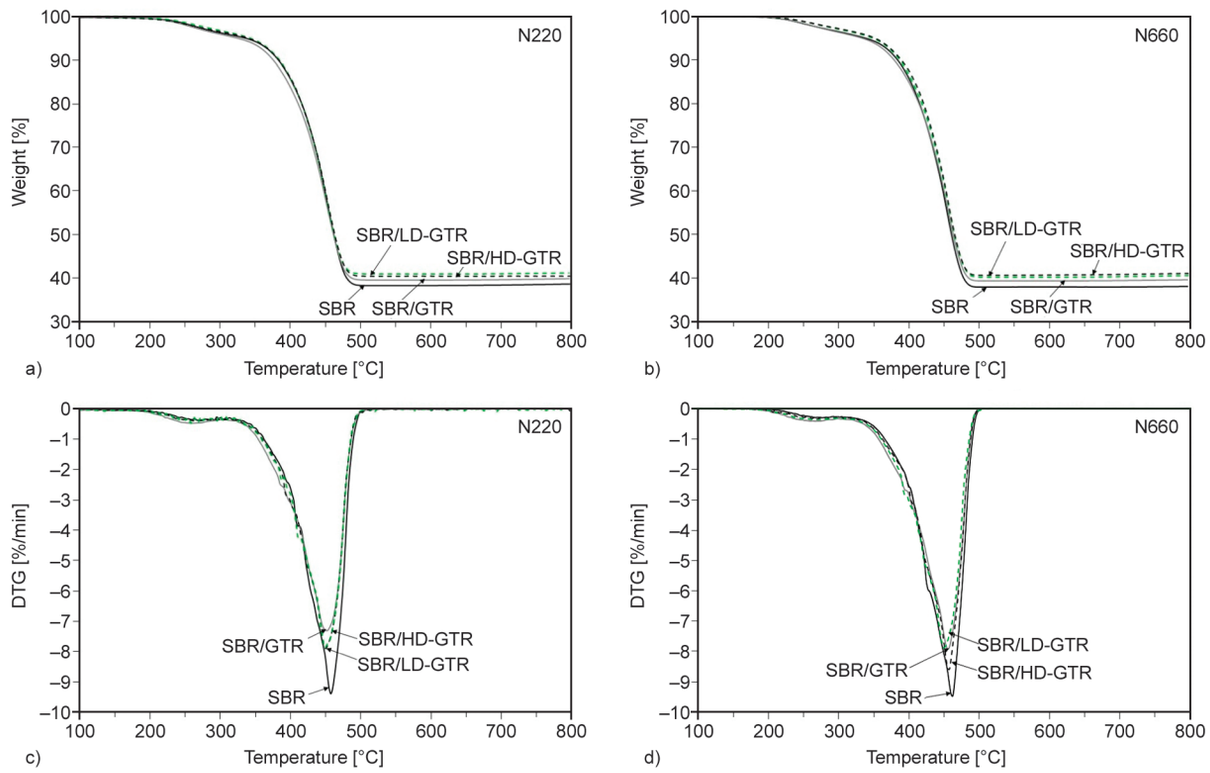

Figure 2. TGA and DTG curves of SBR/GTR composites with: a), c) N220 and b), d) N660.

related to 2 and 5% weight loss of sample) decomposition temperature compared to SBR as a reference sample. This can be due to carbon black migration between GTR particles and the SBR matrix, which seems to be limited in the case of SBR/GTR composites filled with carbon black N220.

Furthermore, the degradation temperature may be related to the volatile content of carbon black filler. Sam *et al.* [38] showed that carbon black N660 (surface area: 35 m^2/g, particle size: 70 nm) contains less volatile matter compared to carbon black N330 (surface area: 80 m^2/g, particle size: 28 nm), which increased the degradation temperature of studied composites.

As presented in Figure 2, SBR/GTR composites showed one maxima (T_{max}) on derivative thermogravimetry (DTG) curves. T_d values are summarized in Table 3. It was observed that SBR/GTR composites with carbon black N660 have higher degradation temperatures than those with carbon black N220, which confirms better thermal stability of those systems. Garcia *et al.* [39] indicated that carbon black in GTR can act as a barrier and/or adsorb volatile organic compounds formed during devulcanization or pyrolysis. The dual action of carbon black particles affects the thermo-stability of GTR and the blends of GTR with fresh rubber.

The residue mass of studied samples was very similar and in the range of 38.1–41.1%, confirming the

Table 3. Thermal decomposition temperatures and residue mass of SBR/GTR composites.

Sample code	Carbon black grade	Decomposition temperature [°C]				T_{max} from DTG [°C]	Residue mass at 750 °C [%]
		$T_{-2\%}$	$T_{-5\%}$	$T_{-10\%}$	$T_{-50\%}$		
SBR	N220	259.2	337.4	383.1	461.5	457.3	38.6
SBR/GTR		250.2	324.6	375.8	461.6	451.8	39.8
SBR/LD-GTR		266.7	343.8	385.1	463.2	449.7	41.1
SBR/HD-GTR		256.3	339.2	383.1	462.8	448.9	40.4
SBR	N660	258.3	337.8	383.7	460.4	461.2	38.1
SBR/GTR		260.7	334.6	379.4	463.3	455.2	39.6
SBR/LD-GTR		274.7	349.5	387.6	465.0	456.2	40.6
SBR/HD-GTR		275.4	351.7	389.4	465.3	456.3	41.0

constant carbon black content in SBR/GTR composites. The total content of carbon black in studied materials was 36% while the remaining part in char residue is related to the presence of ZnO (present in curing additives) and inorganic impurities present in GTR (*e.g.*, dust, sand).

3.3. Curing characteristics of SBR/GTR composites

Curing curves of SBR/GTR composites as a function of carbon black grade are presented in Figure 3, while determined curing parameters are summarized in Table 4. As can be observed, reversion of studied SBR/GTR composites was negligible, which indicates that all studied materials showed good thermal resistance during vulcanization.

It was observed that the application of carbon black N660 instead of N220 to SBR/GTR reduces the minimal torque value. Minimal torque value decreased from 4.2–4.8 dN·m for samples with N220 to 2.2–2.8 dN·m for SBR/GTR systems with N660. This result indicates better processing properties (lower viscosity) of SBR/GTR composites with N660 than samples reinforced with carbon black N220. Carbon black N220 has more reactive functional groups on the filler surface and a smaller particle size than carbon black N660 (Table 1), enhancing matrix-filler and filler-filler interactions. Similar findings were described by Aghajan *et al.* [40], who studied the effect of carbon blacks N220 (surface area: 120 m^2/g, particle size: 20–25 nm) and N550 (surface area: 45 m^2/g, particle size: 40–48 nm) on the properties of SBR-based composites. A higher devulcanization level of GTR also reduces minimal torque value; however, this effect was less visible than for the carbon black grade used in the SBR/GTR system. Maximal torque and torque increment parameters correspond with the vulcanized samples' stiffness, shear modulus, and cross-link density. Regardless of GTR devulcanization level, applying GTR (untreated and treated) decreased maximal torque and torque increment parameters. The effect of GTR devulcanization level on the maximal torque and torque increment parameters of SBR/GTR system was affected by carbon black grade. For samples with carbon black N220, a higher devulcanization level of GTR resulted in decreased maximal torque and torque increment parameters compared to untreated GTR, while for the SBR/GTR system with N660, the opposite tendency was observed. This phenomenon can be related to competition for cross-linking agents between rubber matrix and GTR [22] and the reinforcement effect of carbon black, whose efficiency might be affected by rubber compound viscosity (rubber chains mobility). In the studied case, viscosity was higher for SBR/GTR composites with N220 carbon black,

Table 4. Curing characteristics of SBR/GTR composites (measurement performed at 170 °C).

	Carbon black grade							
	N220				N660			
	SBR	SBR/GTR	SBR/LD-GTR	SBR/HD-GTR	SBR	SBR/GTR	SBR/LD-GTR	SBR/HD-GTR
Minimal torque [dN·m]	4.4	4.8	4.6	4.2	2.8	2.2	2.7	2.2
Maximal torque [dN·m]	29.3	23.4	20.3	20.4	28.8	16.9	20.5	19.4
Torque increment [dN·m]	24.9	18.6	15.7	16.2	26.0	14.7	17.8	17.2
Scorch time [min]	2.4	1.2	1.6	1.4	2.4	1.6	1.3	2.1
Optimal cure time [min]	10.5	6.7	9.6	6.5	7.0	6.5	5.5	5.5

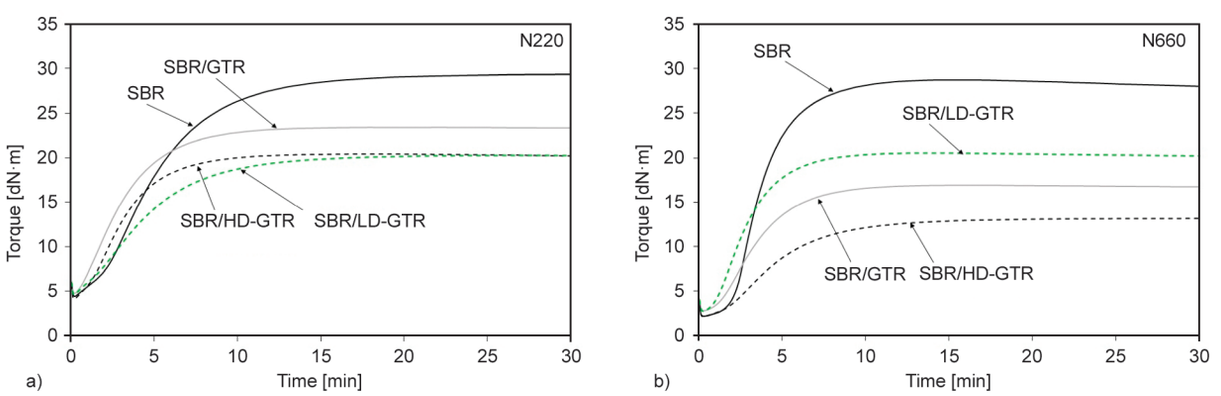

Figure 3. Curing curves for SBR/GTR composites determined at 170 °C as function of carbon black grade: a) N220, b) N660.

which was confirmed by the higher value of minimal torque determined for these materials compared to composites with N660 carbon black.

Regardless of GTR devulcanization level and carbon black grade, scorch time and optimal cure time decreased with adding GTR to the SBR matrix. Similar trends were observed in other works [41, 42]. This effect is due to the presence of carbon black and curing additives (*e.g.*, zinc stearate, vulcanization accelerators) in GTR, which can migrate to accelerate the vulcanization of rubber compounds. Phadke and De [43] investigated natural rubber/cryoground reclaimed rubber composites and indicated that the presence of carbon black can limit sulfur diffusion, which can reduce the optimal curing time of studied materials. This is due to the longer diffusion route of curing agents, reduced flexibility of the elastomer chains, and adsorption of accelerators on the surface of carbon black particles. In this study, such a phenomenon was observed only for sample SBR/LD-GTR filled with carbon black N220.

3.4. Physico-mechanical properties of SBR/GTR composites

The results of the physico-mechanical properties of SBR/GTR composites, including tensile strength [MPa], elongation at break [%] modulus at 100% [MPa], hardness [Shore A], density [g/cm^3], abrasion resistance [mm^3], swelling degree [%] and sol fraction [%] as a function of carbon black grade are summarized in the graphs presented in Figure 4. SBR/GTR system filled with N220 was characterized by tensile strength in the range of 15.3–16.3 MPa (22.4 MPa for SBR); elongation at break in the range of 392–486% (378% for SBR); modulus at 100% in the range of 3.6–4.0 MPa (5.6 MPa for SBR); hardness in the range of 73.1–75.2 Shore A (77.9 Shore A for SBR); density in the range of 1.173–1.179 g/cm^3 (1.172 g/cm^3 for SBR), abrasion resistance in the range of 120–123 mm^3 (106 mm^3 for SBR), a swelling degree in the range of 180–192% (157% for SBR) and sol fraction in the range of 3.5–6.4% (1.8% for SBR). It was observed that regardless of devulcanization level and carbon black grade, adding GTR (untreated and treated) to SBR matrix filled with carbon black resulted in the deterioration of the mechanical properties of SBR/GTR composites. However, the deterioration of tensile properties was lower for SBR/GTR filled with N660 characterized by a lower surface area (see Table 1).

As expected, SBR/GTR composites filled with N220 were characterized by higher performance properties than composites filled with N660, which is related to significant differences in the particle size and surface area of used carbon blacks (see Table 1). It was observed that higher devulcanization level of GTR enhanced tensile strength and elongation at break and modulus at 100% of SBR/GTR composites (see Figures 4a–4c). Similar findings were observed by Mangili *et al.* [44], which shows that a higher devulcanization level of GTR treated by twin screw extruder combined with ultrasounds improves the tensile properties of natural rubber/GTR composites. The authors indicate that the soluble phase formed during GTR devulcanization provides enough active sites that can be co-cross-linked with the natural rubber matrix. This effect improves compatibility between rubber matrix and reclaimed GTR particles, resulting in better final mechanical properties. Figures 4d and 4e showed that, regardless of GTR devulcanization level, SBR/GTR composites filled with carbon black N220 are characterized by higher hardness and better abrasion resistance compared to composites with carbon black N660. This is related to the particle size and surface area of used fillers (see Table 1), which affects matrix-filler interfacial interactions. Figure 4f indicated that the combined effects of devulcanization level and carbon black grade on the density of SBR/GTR composites were negligible.

As presented in Figures 4g and 4h, regardless of carbon black grade, swelling degree increased, and sol fraction has a tendency to increase with a higher devulcanization level of reclaimed GTR. This confirmed that the application of reclaimed GTR affects the cross-link density of studied SBR/GTR composites, which is inversely related to the swelling degree. Sobhy *et al.* [45] performed comprehensive studies on the effect of waste rubber powder in SBR formulations on the swelling of different organic solvents. The results showed that the cross-link density of styrene-butadiene rubber decreases with the waste rubber content for 125 μm particle size. Meanwhile, waste rubber loading (<50 phr) increases with higher particle size. This phenomenon can be explained by competition for cross-linking agents and carbon black filler between the rubber matrix and GTR, as well as the diffusion rate of these components in the system. For a better understanding, combined effects of GTR and carbon black on the processing (minimal torque,

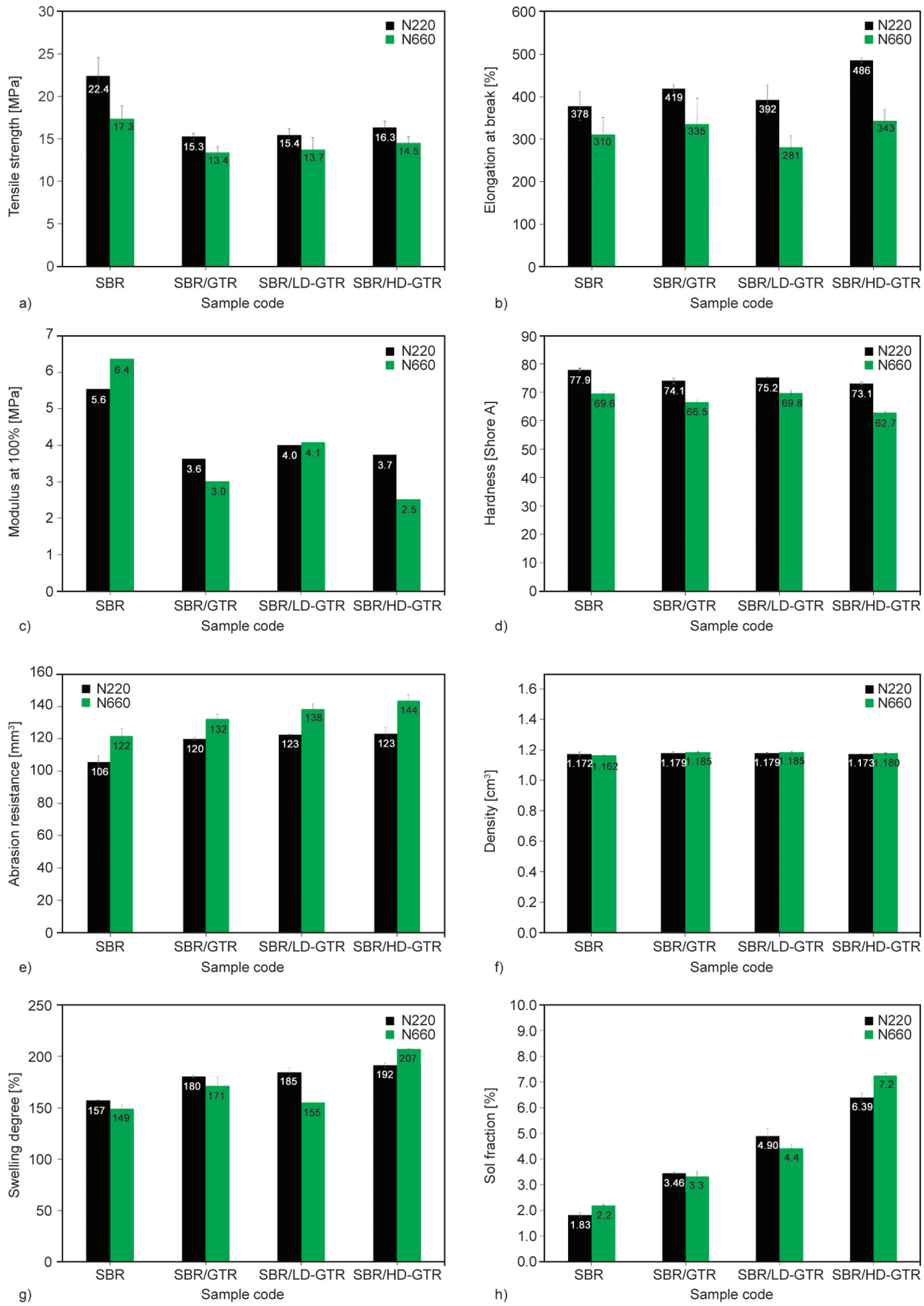

Figure 4. Physico-mechanical properties of SBR/GTR composites: a) tensile strength; b) elongation at break; c) modulus at 100%; d) hardness; e) abrasion resistance; f) density; g) swelling degree and h) sol fraction.

optimal cure time) and mechanical properties (tensile strength, elongation at break, hardness) of SBR/GTR composites with carbon black investigated by other research groups were summarized in Table 5. Samples without GTR (references samples with values in the brackets) and 10–20 wt% of GTR and 30–60 phr of carbon black filler were considered during literature data analysis. As can be noticed, adding GTR or devulcanized GTR (D-GTR) reduces optimal cure time and usually increases minimal torque in all studied cases. One of the factors affecting huge differences in minimal torque value is the methodology used: oscillating disc rheometer (higher values) or moving die rheometer (lower values). In most of the studied cases, the application of GTR or D-GTR resulted in the deterioration of mechanical properties. According to the literature, SBR/GTR composites reinforced with carbon black are characterized by tensile strength in the range of 7.2–19.3 MPa, elongation at break in the range of 350–618% and hardness in the range of 56–70 Shore A. The results presented in this research work fit these ranges. As observed, a broad range of mechanical properties can be tailored by using appropriate composition (*e.g.* carbon black grade/content or curing system used) and preparation method (mixing conditions, vulcanization temperature).

3.5. Dynamic mechanical properties of SBR/GTR composites

Figures 5a and 5b present the Payne effect of SBR/GTR composites, which is related to the formation of the filler network. The decrease in the storage modulus with strain is attributed to the progressive destruction of the filler-filler and matrix-filler interactions [51, 52] with the dominant role of filler-filler contacts [53]. According to the literature, carbon black grade significantly affected the Payne

Table 5. The comparison of processing and mechanical properties of SBR/GTR composites filled with carbon black described in the literature [46–50].

Sample composition	Sample preparation	Minimal torque [dN·m]	Optimal cure time [min]	Tensile strength [MPa]	Elongation at break [%]	Hardness [Shore A]	References
SBR +D-GTR (devulcanized GTR) (20 wt%) +N220–N660 (50 phr) Curing system ([phr]): ZnO (3), StAc (1), TBBS (1), S (1.75)	Mixing in an internal batch mixer Curing at 170 °C	2.2–4.8 (2.8–4.4)	5.5–9.6 (7.0–10.5)	13.4–16.3 (17.3–22.4)	281–486 (310–378)	63–75 (70–78)	This study
SBR +N220–N660 (40–60 phr) Curing system ([phr]): ZnO (3), StAc (1), TBBS (1), S (1.75)	Mixing on a two-roll mill Curing at 145 °C	1.8–4.3	11.5–15.4	13.1–24.6	390–592	58–67	[46]
SBR +GTR/D-GTR (15 phr) +N330 (60 phr) Curing system ([phr]): ZnO (3), StAc (2), MBTS (1.5), S (2)	Mixing on a two-roll mill Curing at 165 °C	11.9–12.1 (11.4)	14.1–17.4 (18.3)	~17.5–19.0* (~20.5)	~365–380* (~355)	68–70 (70)	[47]
SBR +GTR/D-GTR (10 wt%) +N330 (66.85 phr) Curing system ([phr]): ZnO (3), StAc (1), CBS (1.8), S (1.75)	Mixing on a two-roll mill Curing at 170 °C	11.9–13.5 (10.8)	2.9–3.0 (3.3)	7.2–9.2 (7.5)	595–618 (525)	56–58 (57)	[48]
SBR +D-GTR (20 wt%) +N330 (40 phr) Curing system ([phr]): ZnO (5), StAc (2), TMTD (1.6), S (0.5)	Mixing on a two-roll mill Curing at 160 °C	–	4.5 (10.0)	12.6 (12.0)	509 (537)	65 (65)	[49]
SBR +D-GTR (10–20 wt%) +high abrasion furnace carbon black (30 phr, no information about specification) Curing system ([phr]): ZnO (5), StAc (1), CBS (1.25), S (2)	Mixing on a two-roll mill Curing at 152 °C	11.5 (11.5)	15.5 (16.5)	17.5–19.3 (20.6)	350–375 (400)	–	[50]

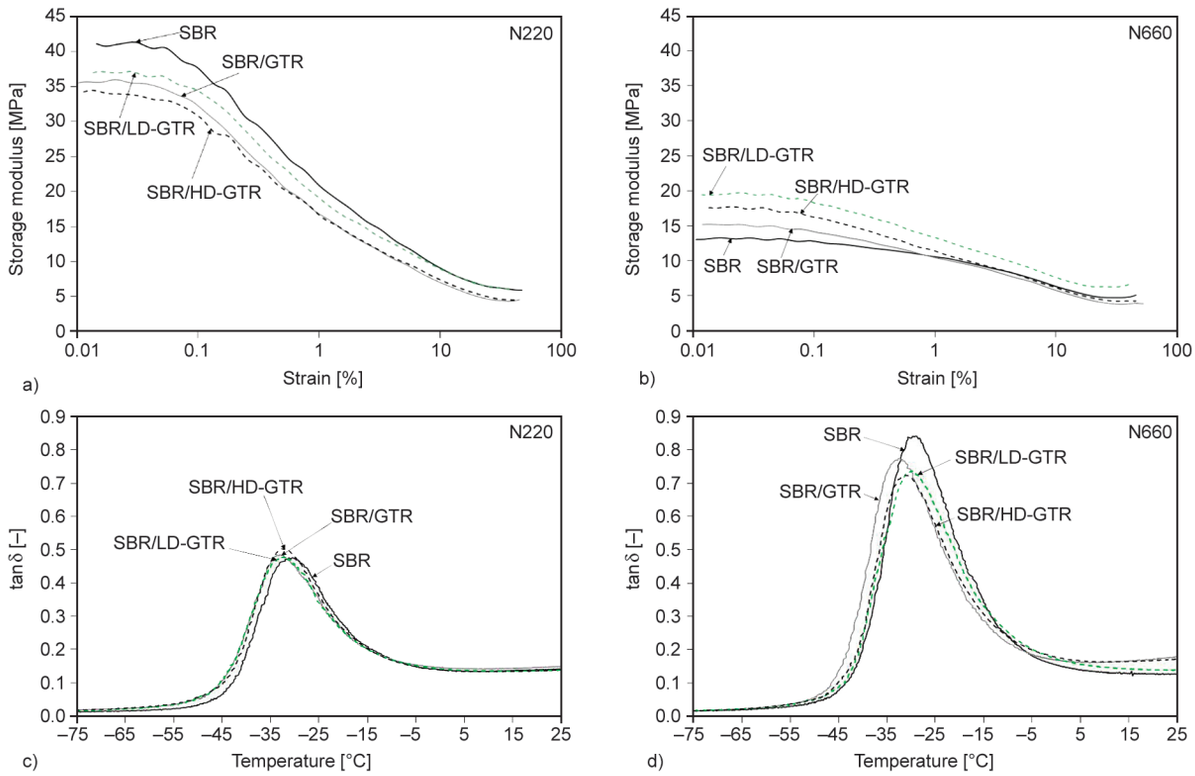

Figure 5. Dynamic mechanical analysis of SBR/GTR composites as a function of carbon black grade: a), b) Payne effect; c), d) loss tangent (tan δ).

effect, and generally, rubber compounds reinforced with carbon blacks characterized by high surface area (smaller particles) showed higher Payne softening compared to rubber composites filled with carbon blacks with lower surface area (bigger particles) [54]. For a deeper understanding of structural changes in studied of SBR/GTR composites, dynamic mechanical analysis-related parameters as a function of carbon black grade are summarized in Table 6. The Payne effect can be quantified by the difference in the storage modulus (E') measured at 0.01 and 10% tensile strains (denoted as $M_{0.01}$–M_{10}) [55, 56]. SBR/GTR composites with carbon black N220 were characterized by lower E' than reference sample SBR, while an opposite trend was observed for SBR/GTR composites with carbon black N660. This effect is due to the more uniform dispersion of carbon black N220 (higher surface area) than carbon black N660 (lower surface area) into SBR/GTR composites. As can be noticed in Table 6, the samples with more active carbon black (in this case, N220) resulted in lower tan δ values, which is in agreement with the literature [57].

Moreover, it was found that for SBR/GTR composites with carbon black N660 the Payne effect was more affected by GTR devulcanization level, which suggests easier migration of carbon black for these systems.

Ren *et al.* [58] showed that the Payne effect of natural rubber/reclaimed rubber blends (without carbon black) gradually weakened with higher devulcanization level of GTR. The authors pointed out that higher

Table 6. Dynamic mechanical analysis-related parameters of SBR/GTR composites as a function of carbon black grade.

DMA parameter	Carbon black grade							
	N220				N660			
	SBR	SBR/GTR	SBR/LD-GTR	SBR/HD-GTR	SBR	SBR/GTR	SBR/LD-GTR	SBR/HD-GTR
T_g [°C] according to $\tan\delta_{max}$	–30.6	–33.2	–32.1	–32.2	–28.9	–32.4	–29.8	–31.4
tan δ at T_g [–]	0.48	0.49	0.48	0.50	0.84	0.77	0.74	0.72
Payne effect ($M_{0.01}$–M_{10}) [MPa]	32.3	28.4	28.0	27.1	6.7	9.4	11.7	11.3
E' at 0.01% strain ($M_{0.01}$) [MPa]	41.2	35.5	37.0	34.2	13.0	15.2	19.4	17.6

degradation of cross-linked networks in GTR resulted in easier separation of carbon black particles from the cross-linked rubber network, which improves the compatibility of reclaimed rubber and natural rubber matrix. In the studied case, the carbon black migration from GTR to the SBR matrix and from SBR to GTR can be affected by the surface area and particle size of carbon black used during SBR/GTR preparation. Consequently, the devulcanization level of GTR had a much lower effect on the Payne effect than the surface area and particle size of carbon black.

Loss tangent ($\tan\delta$) as a function of temperature plotted for SBR/GTR composites is presented in Figures 5c and 5d. It was noticed that regardless of carbon black grade and GTR devulcanization level, glass transition temperature (T_g) (see Table 5) determined according to $\tan\delta_{max}$ decreased with the addition of GTR, corresponding to the swelling degree results (see Figure 4g). Decreased T_g is due to natural rubber in GTR [59] and competition for cross-linking agents between the rubber matrix and GTR [22]. It was noticed that higher T_g characterizes SBR/LD-GTR and SBR/HD-GTR samples compared to SBR/GTR, which confirms that GTR devulcanization is a good strategy to improve the compatibility of polymer composites [60].

3.6. Microstructure and reinforcement mechanism in SBR/GTR composites

The microstructure of surfaces created at the break-ing of SBR/GTR composites subjected to static ten-sile test at 500 mm/min was investigated by scan-ning electron microscopy (SEM). SEM images on the surface area perpendicular to the direction of strain are presented in Figure 6. Regardless of the carbon black grade, used SBR reference samples without GTR show many tear lines, indicating good carbon black dispersion and high tensile strength value [61]. Tear lines after the tensile test were also created on the surface of SBR/HD-GTR samples filled with carbon blacks N220 and N660, characterized by the highest tensile strength among studied materials.

It was found that prepared SBR/GTR composites are characterized by uniform dispersion, and the GTR particles are not observed on the fracture surfaces. This result indicates that the breaking mechanism occurred directly through the SBR matrix and not through the interfaces between the SBR matrix and GTR particles. Similar findings were described in work [62]. Moreover, the contours of GTR particles under the SBR matrix can be observed, especially for SBR/GTR samples. The number of GTR particle contours is reduced with a higher devulcanization level of GTR. This is due to the destruction of the three-dimensional network present in GTR, which resulted in a lower molecular weight of reclaimed GTR (LD-GTR and HD-GTR) as confirmed by sol fraction and Mooney viscosity measurements (see Figure 1).

In Figure 7, SEM images of samples SBR/GTR and SBR/HD-GTR filled with carbon black N220 and N660 at magnification 3500× are presented. As can be observed, regardless of GTR devulcanization level, carbon black N220 showed better dispersion in the SBR/GTR matrix compared to carbon black N660, which is related to the particle size of used fillers (see Table 1).

The possible reinforcement mechanism by carbon black migration in SBR/GTR composites is proposed in Figure 8. Higher devulcanization level of GTR resulted in a more uniform SBR/GTR composite morphology. This result is due to the destruction of the three-dimensional cross-linked network in GTR and the exfoliation of carbon black from reclaimed rubber [25]. Therefore, carbon black migration from reclaimed rubbers (LD-GTR and HD-GTR) towards fresh rubber matrix and in the opposite direction is more efficient, and as a consequence, an enhanced compatibility and reinforcing effect in the SBR/GTR system is observed. Moreover, this reinforcing effect is more visible in carbon black N220, characterized by lower particle size (higher surface area), which is related to its better dispersion in rubber matrix compared to carbon black with larger particle size (lower surface area) [63].

4. Conclusions

This study investigated the combined effects of GTR devulcanization level and carbon black grade on the properties of SBR/GTR composites using a rubber process analyzer, thermogravimetric analysis, tensile test, hardness, abrasion resistance, density, swelling measurements, dynamic mechanical analysis, and scanning electron microscopy. During investigations, SBR/GTR composites were reinforced with two grades of commercially available carbon blacks: N220 (surface area: 107.1 m^2/g, particle size: 20–25 nm) and N660 (surface area: 33.1 m^2/g, particle

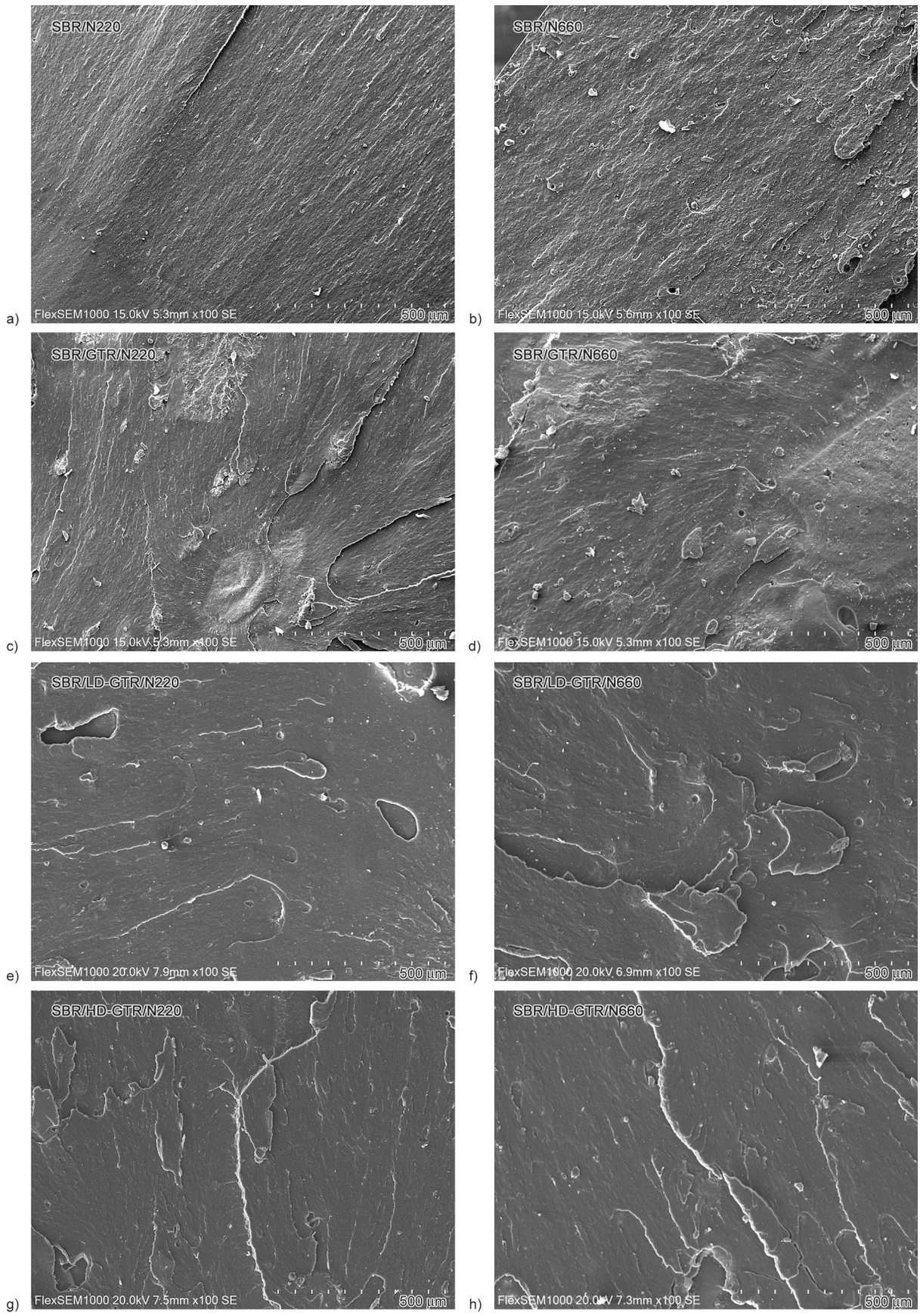

Figure 6. Microstructure of SBR/GTR composites determined by SEM (magnification 100×): a) SBR/N220; b) SBR/N660; c) SBR/GTR/N220; d) SBR/GTR/N660; e) SBR/LD-GTR/N220; f) SBR/LD-GTR/N660; g) SBR/HD-GTR/N220; h) SBR/HD-GTR/N660.

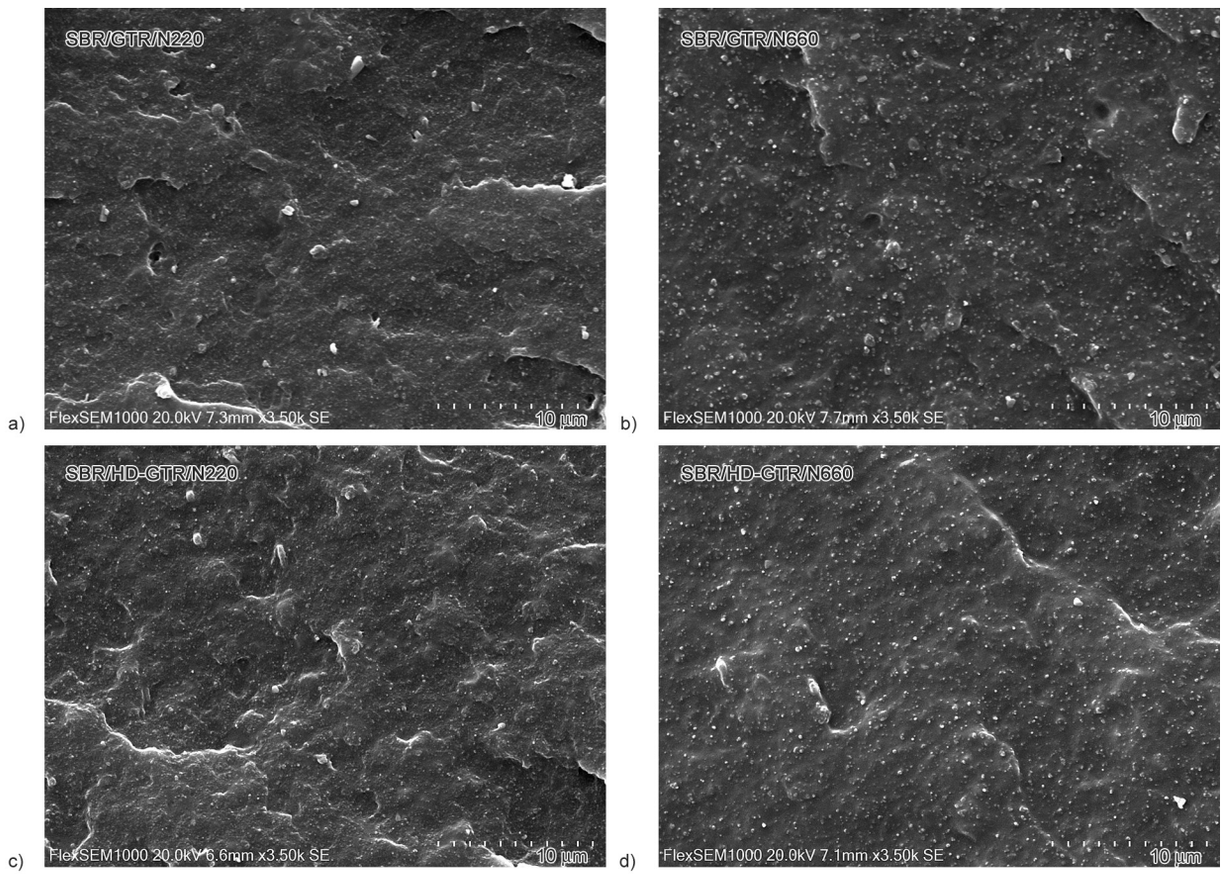

Figure 7. Microstructure of samples: a), b) SBR/GTR and c), d) SBR/HD-GTR filled with carbon black N220 and N660 (magnification 3500×).

size: 49–60 nm). Reclaimed rubbers characterized by different devulcanization level were prepared using a planetary roller extruder.

The obtained results showed that the application of reclaimed GTR (regardless of devulcanization level) to SBR reinforced with carbon black resulted in the deterioration of the mechanical properties of SBR/GTR composites, which was lower for SBR/GTR filled with N660 characterized by lower surface area and bigger particles. It was observed that GTR devulcanization level and carbon black grade affect carbon black migration between GTR and SBR matrix and, consequently, formulation of filler network. The reinforcement effect of carbon black in SBR/GTR composites was more visible for samples with a higher devulcanization level of GTR and smaller particle size of carbon black filler, which was confirmed by static and dynamic mechanical properties. The best mechanical properties were determined for sample SBR/HD-GTR composites filled with carbon black N220, which showed relatively good tensile strength (16.3 MPa), elongation at break (486%), hardness (73 Shore A) and abrasion resistance (123 mm^3). The performance properties of prepared SBR/GTR composites allow their application during technical rubber goods or footwear production.

Further investigations about the reinforcement effect of GTR on rubber composites should be mainly focused on: i) improvement of mixing and processing efficiency (*e.g.* latex dispersion processing, application of continuous methods, screw/rotors with unique design, reduced energy consumption, *etc*.); ii) optimization of vulcanization process as a function of GTR devulcanization level and resulting exfoliation of carbon black (*e.g.* modification of sulfur-based curing system, co-cross-linking using organic peroxides, reduction of vulcanization temperature, *etc*.) and iii) application of hybrid filler systems which allows tailoring high-performance GTR-based rubber composites (*e.g.* application of highly dispersed silica, cellulose-derivative reinforcement, conductive carbon fillers, inorganic flame retardants, *etc*.).

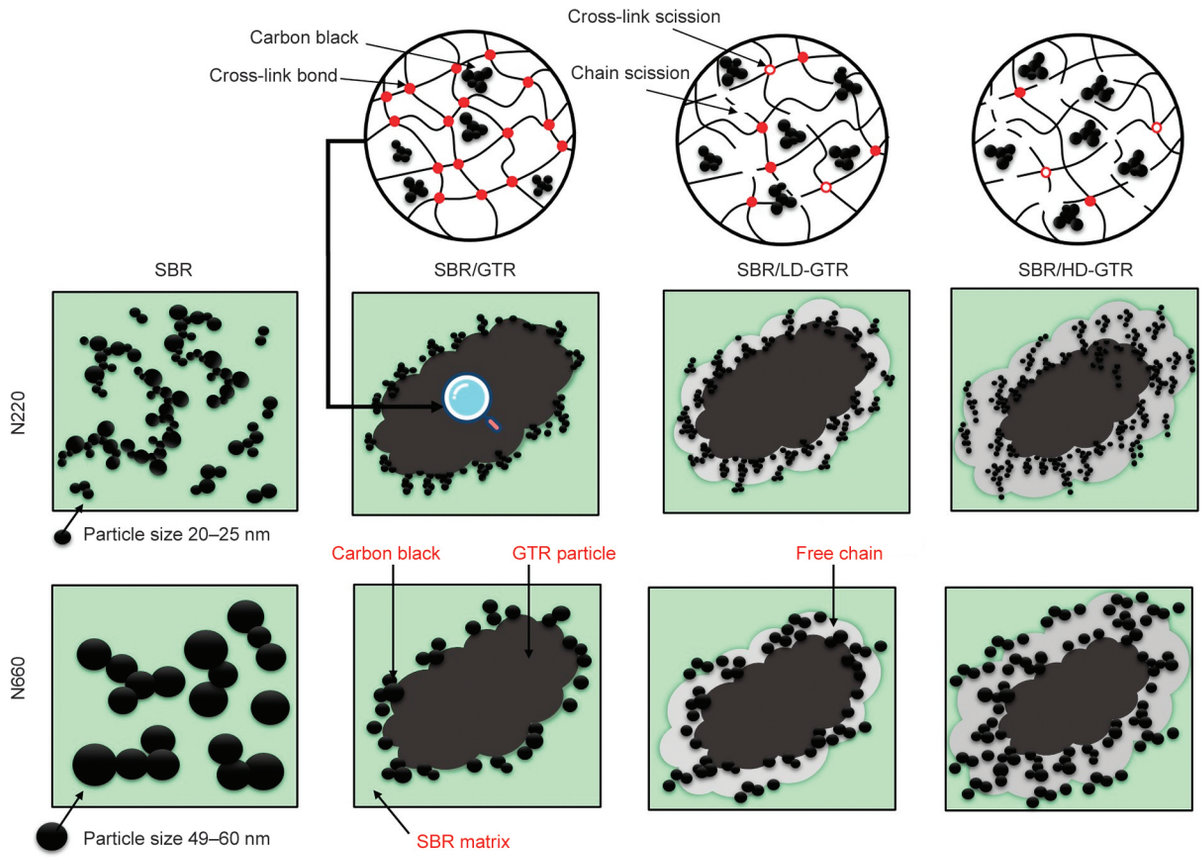

Figure 8. Possible mechanism of carbon black migration in SBR/GTR composites.

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