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Structural and physico-mechanical properties of natural rubber/GTR composites devulcanized by microwaves: Influence of GTR source and irradiation time

Xavier Colom¹, Marc Marín-Genescà², Ramon Mujal³,
Krzysztof Formela⁴ and Javier Cañavate¹

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Abstract

Ground tire rubber from car and truck was modified using microwave irradiation at variable time. The irradiated ground tire rubber was used as filler in composites based on natural rubber. The composites, with high content of ground tire rubber, were prepared using an internal batch mixer and subsequently cross-linked at 160°C. The influence of the ground tire rubber source (car/truck) and irradiation time on structure, physico-mechanical behaviour, thermal properties and morphology of natural rubber/ground tire rubber composites was studied. The interfacial interactions between ground tire rubber and natural rubber as function of ground tire rubber source and irradiation time were evaluated by Fourier transform infrared spectroscopy, thermogravimetric analysis, tensile tests, swelling measurements and scanning electron microscopy. The results showed that irradiation of ground tire rubber slightly enhanced tensile properties and cross-link density of natural rubber/ground tire rubber composites. This effect was more evident in the case of ground tire rubber_{truck} because of its higher content of natural rubber and was reflected in changes in the interfacial adhesion, which were confirmed by the results of Fourier transform infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy analysis.

Keywords

Recycling, ground tire rubber, microwave irradiation, natural rubber, mechanical properties

Introduction

The dynamic development of the automotive industry produces an increasing amount of waste rubber, especially end-of-life tires. Estimated data show that more than 3.6 million tons of used car tires are discarded every year in the EU countries.¹ One of the issues is the increasing amount of illegally dumped or stockpiled waste tires, which is a serious threat to the natural environment and human health. For example, in May 2016, around 9000 people were evacuated from their homes in Seseña, a village near Madrid (Spain), because of the ignition of a big illegal tire dump which caused emissions of polycyclic aromatic hydrocarbons and other hazardous compounds.^{2,3} Therefore, the quest for economical and environment-friendly methods that allow potential application of waste tires in industry is very reasonable.^{4–6}

At present, one of the effective industrial-scale methods for recycling of used tires is the reclaiming/devulcanization of ground tire rubber (GTR). During the devulcanization process, the three-dimensional network of cross-linked rubber is destroyed by means of thermal, mechanical or chemical energy.^{7–9}

¹Department of Chemical Engineering, Universitat Politècnica de Catalunya BarcelonaTech, Spain

²Department of Mechanical Engineering, Universitat Rovira i Virgili, Spain

³Department of Electrical Engineering, Universitat Politècnica de Catalunya BarcelonaTech, Spain

⁴Department of Polymer Technology, Faculty of Chemistry, Gdansk University of Technology, Poland

Corresponding author:

Xavier Colom, UPC C/Colom I ESEIAAT, Terrassa 08222, Spain.
Email: xavier.colom@upc.edu

Compared to the GTR, the obtained reclaimed rubber can be easily processed, shaped and re-vulcanized. Many attempts have been focused on devulcanization of GTR for producing reclaimed rubber. They have been comprehensively described in the recent review work presented by Movahed et al.¹⁰ Under this approach, a very promising technique for devulcanization is the irradiation with microwaves. The use of microwaves for devulcanization of waste rubber was first proposed by Novotny et al.¹¹ from The Goodyear Tire & Rubber Company. Compared with other heating methods, based on convection or conduction, microwaves generate a more precise, faster and homogeneous increase of the temperature inside the material, allowing a better control avoiding excessive degradation of GTR. A high amount of energy is applied on the GTR in a short time, resulting in high efficiency. This reclaiming technology is environmental-friendly and can be easily improved using chemical agents.^{12–14}

In our previous work,¹⁵ we investigated the influence of the GTR composition on the microwave devulcanization mechanism. The results showed a strong correlation between the content of silica in the GTR and the achieved degree of devulcanization, which increased with higher content of silica. This suggests that the presence of silica fillers improve the reclaiming of GTR by microwaves.

Recently, Garcia et al.¹⁶ and de Sousa et al.¹⁷ analyzed the chemical and physical changes in GTR generated by the microwaves as a function of the time of exposure. The results showed that the temperature (determined by the irradiation time) is the main factor affecting devulcanization. Additionally, the phase constituted by the natural rubber (NR) present in the GTR showed more degradation than the styrene-butadiene rubber phase, because of the differences in thermal stability of these two elastomers. Similar observations were also reported by Thodesen et al.¹⁸ and Ghavibazoo et al.,¹⁹ which studied the effect of GTR composition on its interactions with bitumen at high temperature. Their results indicated that ground truck tires dissolve more into bitumen compared to ground car tires. This is related to the higher content of NR in truck tires, which as said above, is more prone to thermal degradation than synthetic rubber.

However, according to our best knowledge, there is no information about the microwave irradiation of GTR with different compositions and its possible influence on the properties of NR/GTR composites. This information would allow a better understanding of the interfacial interactions developed between NR and GTR, which would be very important from a technological point of view.

In this work, interfacial interactions between NR and GTR were studied as a function of the GTR

source (passenger car or truck tire) and the microwave irradiation time in the range 0–10 min (above 10 min, there is an evident degradation of the samples). The chemical structure (Fourier transform infrared spectroscopy, FTIR), thermal properties (thermogravimetric analysis, TGA), physico-mechanical properties (tensile strength, elongation at break, hardness, cross-link density, sol fraction) and morphology (scanning electron microscope, SEM) of NR/GTR composites were determined in order to develop a better understanding of the structure-properties relationship.

Experimental

Materials

Natural rubber (NR) grade SVR 3L (Vietnam Natural Rubber) with ash content: 0.5% wt, volatile matter content: 0.8% wt and density: 0.92 g/cm³ was supplied by VIGAR Rubi (Spain). GTR from passenger car (GTR_{car}) and GTR from truck (GTR_{truck}) were supplied by GMN Maials (Spain). The particle size distribution of used GTR is presented in Figure 1. To eliminate the impact of particle size on the obtained results, particle size distribution for both type of GTR was similar with an average value of 390 μm. The differences in the composition of passenger car tires and truck tires are shown in Table 1. It is commonly known that truck tires contain more NR and less carbon black than passenger car tires, because of their specific requirements.

Carbon black N-330, vulcanization accelerators (TBBS- N-tert-butyl-2-benzothiazole sulfonamide, TMTD – tetramethylthiuram disulfide), stearic acid, zinc oxide and sulfur with technical purity were supplied by Vigar (Spain).

Microwave devulcanization of GTR

GTR was devulcanized in a prototype constructed at our lab. The system is based on a conventional

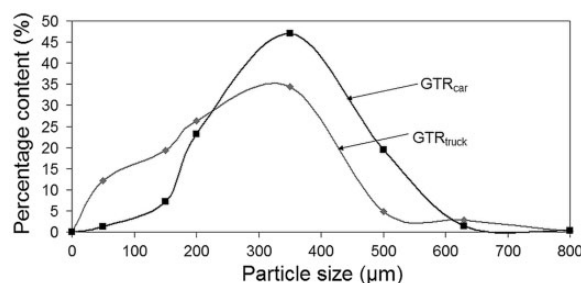


Figure 1. Particle size distribution as a function of content (%) for GTR_{car} and GTR_{truck}. GTR: ground tire rubber.

Table 1. Composition of passenger and truck tires obtained by TGA.

Composition	Passenger car tire	Truck tire
Natural rubber	25%	35%
Synthetic rubber	32%	25%
Carbon black	33%	30%
SiO ₂	5%	6%
Other additives (e.g. curing system, processing aids, etc.)	5%	4%

TGA: thermogravimetric analysis.

microwave oven adapted with a motorized stirring system designed in PTFE. The sample is placed in a container. The design of the container and the stirrer favours a homogeneous irradiation of the sample. Power and time of irradiation can be controlled independently. Samples of 30 g of GTR were used. Devulcanization process was performed at 700 W, 80 r/min and exposure times of 3, 5 and 10 min. This methodology is based on preliminary studies described in our previous work.¹⁵ Time was limited to 10 min, because preliminary studies show that longer irradiation resulted in evident degradation of GTR.

Samples preparation

NR/GTR composites were prepared at 70°C using a Brabender plastograph batch mixer. The rotational speed of the rollers was 100 r/min. The mixing time was 8 min which included 2 min of preliminary mastication of NR, 4 min of mixing with 50 parts per hundred of rubber (phr) of untreated or microwave devulcanized GTR (3, 5 and 10 min) and 30 phr of carbon black and 2 min of mixing the blend with the sulfur curing system. The same curing system was used for all samples. The curing system composition (phr) was zinc oxide 5.0; stearic acid 3.0; TBBS 1.0; TMTD 0.25; sulfur 2.0. A sample of NR without GTR with 30 phr of carbon black processed with the same curing system has been used as reference sample. From preliminary studies we have concluded that a good starting point in terms of equilibrium between properties and amount of GTR is situated around 50 phr.²⁰

The obtained NR/GTR composites were molded into 3-mm-thick samples at 160°C for 12 min under pressure 4.9 MPa using a laboratory plate press type P 200E from Dr. Collin GmbH (Germany). The samples were coded as NR/GTR-Z, where Z means the time of microwave devulcanization. For example, NR/GTR-5 is a sample of NR with 50 phr of GTR microwave irradiated for 5 min.

Measurements

Chemical structure of NR/GTR composites was determined using FTIR analysis performed by means of a Nicolet iS10 spectrometer from Thermo Scientific (USA). The device had an ATR attachment with a germanium crystal. Spectra were registered at 2 cm⁻¹ resolution and 40 scans in the range of 1800–750 cm⁻¹, in which typical signals for NR related to CH₂ deformation at 1450 cm⁻¹, CH₃ asymmetric deformation at 1375 cm⁻¹ and =CH out-of-plane bending at 831 cm⁻¹ can be observed.²¹

Tensile strength and elongation at break of the obtained vulcanized rubber composites were tested according to the standard ISO 37 using an Instron 3366 testing machine (USA) with cell load capacity of 20 kN. Tensile tests were performed at a cross-head speed of 500 mm/min at RH of 50 ± 5% and 23 ± 2°C of temperature. Direct extension measurements were conducted using an extensometer with sensor arms. Hardness was determined using a Zwick 3130 durometer Shore A (Germany) in accordance with the standard ISO 7619-1. Tensile and hardness results are the average of five measurements per sample.

Swelling degree of rubber composites (0.2 g samples) was determined by equilibrium swelling in toluene (room temperature) after immersing the samples in the medium for 72 h. According to our previous studies, after 72 h further changes in swelling behaviour are negligible. Swelling degree was calculated in accordance with the formula (1)

$$Q = \frac{m_t - m_o}{m_o} \times 100\% \quad (1)$$

where Q – swelling degree; m_t – mass of the sample swollen (g); m_o – initial mass of sample (g).

The cross-link density was determined by equilibrium swelling in toluene (room temperature, 72 h, refreshing the solvent every 24 h), according to the Flory-Rehner²² equation (2)

$$v_e = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{[V_1(V_r^{1/3} - V_r/2)]} \quad (2)$$

where: v_e – cross-link density, mol/cm³; V_r – gel volume in the swollen sample; V_1 – solvent molar volume (toluene = 106.2, cm³/mol); χ – polymer-solvent interaction parameter (in the calculations, it was assumed to be 0.39)

Gel volume in the swollen sample was calculated according to equation (3)

$$V_r = \frac{\frac{m_p}{\rho_p}}{\frac{m_p}{\rho_p} + \frac{m_s}{\rho_s}} \quad (3)$$

where m_p – the weight of the dry polymer, g; ρ_p – the density of the dry polymer, g/cm³; m_s – the weight of solvent absorbed by polymer, g; ρ_s – the density of the solvent, g/cm³

The Flory-Rehner equation can be applied for non-filled compounds, while studied samples contain carbon black. Kraus correction for filled compounds was applied in order to calculate the actual remaining cross-link density according to equations (4) and (5)^{23,24}

$$v_{\text{after correction}} = \frac{v_e}{1 + K \times \Phi} \quad (4)$$

$$\Phi = \frac{\phi_f \times \rho_r \times m_0}{\rho_f \times m_{\text{dry}}} \quad (5)$$

where v_e – the measured chemical cross-link density, mol/cm³; $v_{\text{after correction}}$ – the actual chemical cross-link density, mol/cm³; K – constant characteristic of the filler but independent of the solvent; ϕ_f – the volume fraction of filler in the sample which is calculated for each sample and depends of GTR source; ρ_r – the density of studied compound, g/cm³; m_0 – the weight of sample before extraction, g; ρ_r – the density of filler, g/cm³; m_{dry} – the weight of sample after extraction, g.

Sol fraction was calculated as mass difference of NR/GTR composites before swelling (W_1) and after extraction (W_2), according to equation (6)

$$\text{Sol fraction} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (6)$$

TGA was performed on a Mettler Toledo TGA/SDTA 851 apparatus (USA). NR/GTR composite weighing approximately 10 mg was placed in a corundum dish. The measurement was conducted in the temperature range 50–600°C and under nitrogen atmosphere (30 ml/min), at a heating rate of 20°C/min. Obtained results are the average of three measurements per sample.

The morphology of NR/GTR fracture surfaces created by the tensile test of the composites at the speed of 500 mm/min was observed with a JEOL 5610 scanning electron microscope (Japan). Before observation the samples were covered with a fine gold–palladium layer in order to increase their conductivity in a vacuum chamber.

Results and discussion

FTIR analysis

According to our previous studies the spectral area that provides more information is comprised between 1800

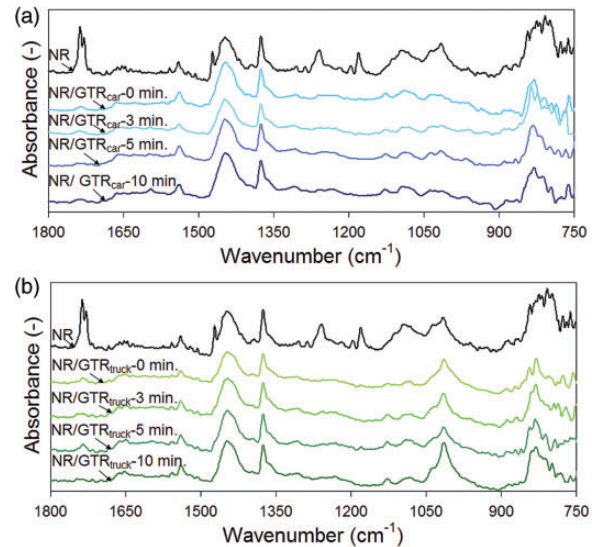


Figure 2. FTIR spectra in the range 1800–750 cm⁻¹: (a) NR/GTR_{car} samples and (b) NR/GTR_{truck} samples. NR/GTR: natural rubber/ground tire rubber.

Table 2. Most significant FTIR bands of NR/GTR composites.

Wavenumber (cm ⁻¹)	Assignments	Component
1736	–C = O free	Stearic acid
1728	–C = O bonded water	Stearic acid
1660	–CH = CH–	NR
1538	Zn carboxylic salts	ZnSt ₂
1450	–CH ₂ – stretching	NR
1375	–CH ₃ symmetric bend	NR
1018	–C–C–	Carbon black
831	–C = C–H out of plane	NR

FTIR: Fourier transform infrared spectroscopy; NR/GTR: natural rubber/ground tire rubber.

and 750 cm⁻¹ and it is shown in Figure 2. FTIR spectra of the surface of NR filled with 50 phr of GTR_{car} and GTR_{truck} devulcanized by microwaves at variable times (0–10 min) have been compared. Table 2 includes the most significant absorbance bands assigned to the components of the samples. The absorbance bands at 1736 cm⁻¹ and 1728 cm⁻¹ are related to the unreacted stearic acid present in the samples, which migrates from the core to the surface.²⁵ The above-mentioned bands are higher for NR than for NR/GTR composites, regardless of the GTR type. This indicates that carbon black present in the GTR acts as an impediment to diffusion and limits the migration of the stearic acid molecules through the NR matrix.

The absorbance maximum at 1538 cm⁻¹ can be related to the presence of zinc stearate (ZnSt₂), which

is a product of the reaction of zinc oxide and stearic acid that takes place during the manufacturing process of the rubber compounds.²⁶ Other interesting bands appear from 1596 to 1660 cm^{-1} , related to C=C bonds and, as the 1538 cm^{-1} , are indicative of the cross-link density of the samples. The correlation between cross-link density and intensity of absorbance (I_A) at 1538 cm^{-1} and 1660 cm^{-1} for NR/GTR composites is presented in Figure 3. The I_A at 1538 cm^{-1} and 1660 cm^{-1} in the spectra of NR/GTR_{truck} composites are lower than those for NR/GTR_{car} composites. The irradiation time of GTR had a significant impact on the I_A parameters. In case of NR/GTR_{car}

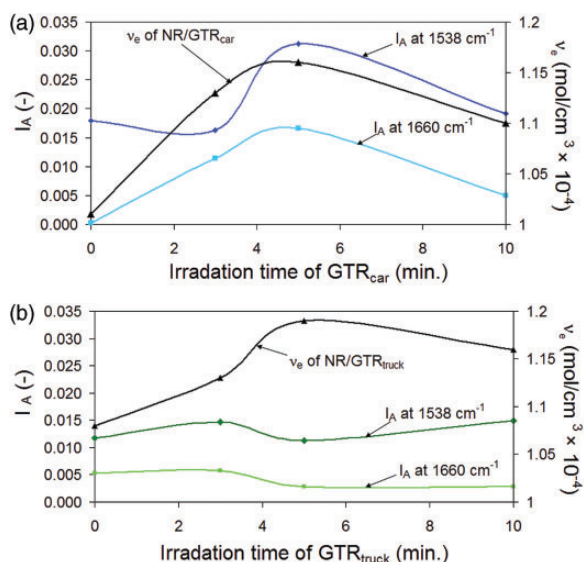


Figure 3. The correlation between cross-link density (v_e) and intensity of absorbance (I_A) at 1538 cm^{-1} and 1660 cm^{-1} as function of GTR irradiation time for: (a) NR/GTR_{car} samples and (b) NR/GTR_{truck} samples. NR/GTR: natural rubber/ground tire rubber.

composites, the highest value of I_A at 1538 cm^{-1} and 1660 cm^{-1} was obtained for samples with GTR_{car} irradiated for 5 min (Figure 3(a)), while for NR/GTR_{truck} composites I_A decreased with increasing irradiation time (Figure 3(b)). This suggests, that regardless of GTR source, longer microwave devulcanization time resulted in partial degradation of GTR. Moreover, it was found that the source of GTR (car/truck) had significant impact on formation of unsaturated C=C bonds which are generated after microwave irradiation of GTR.¹⁷

Additionally, absorbance band at 1016 cm^{-1} , characteristic of carbon black,¹⁵ was more intense for the NR/GTR_{truck} samples than for NR/GTR_{car} samples (see Figure 2). Carbon black present in NR²⁷ and styrene-butadiene rubber²⁸ samples affect their microwave devulcanization efficiency. The devulcanization degree of GTR has influence on its further processing and the possibility of developing interactions with other elastomers.^{29,30}

Figure 4 shows SEM images of NR/GTR_{car}-0 min and NR/GTR_{car}-5 min. On the surface of NR filled with untreated GTR the particles of ZnSt₂ can be observed. The magnification ($\times 8000$) in whole frame reveals the structural morphology of ZnSt₂, which appears as random plate-like crystals with a size comprised between 1 and 3 microns.³¹ On the other hand, on the sample NR/GTR_{car}-5 min these crystals were not detected, which indicates a better dispersion of ZnSt₂ into the NR filled with irradiated GTR.

These observations are in agreement with the results of the cross-link density measurements. It was found that cross-link density of NR/GTR_{truck} composites was slightly higher than for NR/GTR_{car} composites. These results confirm that for GTR_{truck}, the microwave devulcanization is more efficient, allowing subsequently the formation of sulfur bridges during co-vulcanization, than in case of GTR_{car}.

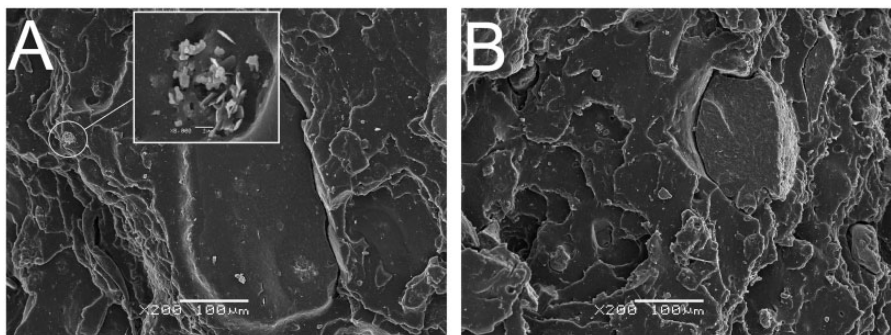


Figure 4. SEM images of surface: (a) NR/GTR_{car}-0 min and (b) NR/GTR_{car}-5 min (magnification $\times 200$, presented in white frame crystals of zinc stearate was observed at $\times 8000$ magnification). NR/GTR: natural rubber/ground tire rubber.

TGA characterization

TGA of NR and NR/GTR composites was conducted in nitrogen atmosphere. These conditions allow only thermal degradation, avoiding the combined effect of thermal and thermo-oxidative degradation in the presence of oxygen. This experiment was carried out to complete degradation of the organic components of the sample, in order to determine the stability of the composites and the amount of inorganic residua.

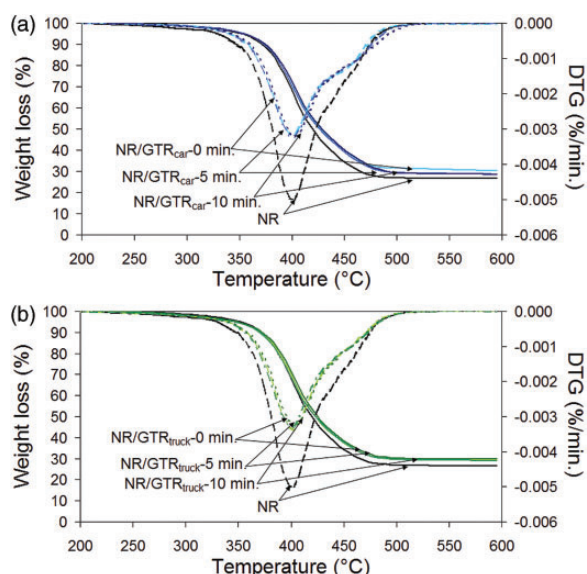


Figure 5. TGA and DTG curves measured in N_2 atmosphere and heating rate of $20^\circ\text{C}/\text{min}$: (a) NR/GTR_{car} samples and (b) NR/GTR_{truck} samples. DTG: derivative thermogravimetry; TGA: thermogravimetric analysis; NR/GTR: natural rubber/ground tire rubber.

Obtained results are presented in Figure 5 and summarized in Table 3. The data showed that $T_{-2\%}$ and $T_{-5\%}$ temperatures, which corresponded to the 2 and 5% weight loss, were higher for NR/GTR_{car} composites than for NR/GTR_{truck} composites. This is due to the mentioned higher thermal stability of GTR_{car} compared to GTR_{truck}. As the derivative thermogravimetry (DTG) curves show, in case of NR, one maximum ($T_{\text{max}1}$) was detected, while the NR/GTR composites showed two peaks. These peaks of DTG curves are related to the maximum rate of thermal degradation of NR ($T_{\text{max}1}$) and styrene-butadiene rubber ($T_{\text{max}2}$).³² The presence of synthetic rubber in the particles of GTR increases its thermal stability, because the styrene-butadiene rubber has higher decomposition temperature than the NR. As could be expected, regardless of GTR source and irradiation, addition of GTR to NR matrix increased char residue values at 550°C . At this temperature, the remaining residua are related to the content of carbon black and SiO_2 in GTR, 38 and 36% wt for GTR_{car} and GTR_{truck}, respectively. Furthermore, it was observed that irradiation time of GTR has negligible influence on the thermal stability of NR/GTR composites. Some minor differences in thermal stability may be related to the heterogeneous composition of the ground rubber obtained from waste tires.

These results may cause confusion because the literature, in some cases, concludes that the devulcanization of GTR affects its thermal stability.^{33,34} According to Garcia et al.,¹⁶ the carbon black included in the devulcanized rubber can adsorb low-molecular-weight volatile products formed during thermal degradation (barrier effect), improving the thermal stability of devulcanized GTR. However, in this case, NR/GTR composites were obtained at elevated temperature

Table 3. Thermal decomposition characteristics of prepared NR/GTR composites.

Sample	Weight loss (%)				$T_{\text{max}1}$ ($^\circ\text{C}$)	$T_{\text{max}2}$ ($^\circ\text{C}$)	Char residue at 550°C (%)
	2	5	10	50			
	Temperature ($^\circ\text{C}$)						
NR	316 ± 1	355 ± 2	373 ± 1	420 ± 1	401	–	26.6
NR/GTR _{car} -0 min	321 ± 2	356 ± 3	374 ± 2	430 ± 2	401	443	30.8
NR/GTR _{car} -5 min GTRcar. ...	321 ± 1	356 ± 3	374 ± 2	429 ± 2	401	445	28.9
NR/GTR _{car} -10 min	316 ± 3	356 ± 2	377 ± 2	430 ± 1	404	446	28.7
NR/GTR _{truck} -0 min	306 ± 2	350 ± 2	373 ± 2	424 ± 3	402	440	29.4
NR/GTR _{truck} -5 min GTRcar. ...	305 ± 1	349 ± 3	372 ± 2	424 ± 2	401	441	29.2
NR/GTR _{truck} -10 min	306 ± 2	350 ± 2	373 ± 2	425 ± 2	405	442	29.8

NR/GTR: natural rubber/ground tire rubber.

Table 4. Physico-mechanical properties of NR/GTR composites.

Item	Sample								
	NR	NR/GTR _{car}				NR/GTR _{truck}			
		GTR _{car} irradiation time (min.)				GTR _{truck} irradiation time (min)			
		0	3	5	10	0	3	5	10
Tensile strength (MPa)	26.1 ± 1.9	15.5 ± 1.0	16.4 ± 1.3	15.8 ± 1.4	16.0 ± 0.9	14.0 ± 1.0	14.6 ± 0.9	15.2 ± 0.78	15.6 ± 1.14
Elongation at break (%)	854 ± 68	695 ± 81	705 ± 78	671 ± 94	728 ± 60	675 ± 61	717 ± 71	702 ± 68	779 ± 60
Modulus at 300% (MPa)	2.2 ± 0.1	2.1 ± 0.1	2.1 ± 0.1	2.2 ± 0.3	2.2 ± 0.1	2.0 ± 0.1	2.2 ± 0.1	2.2 ± 0.1	2.1 ± 0.1
Hardness (Shore A)	49 ± 3	48 ± 2	48 ± 2	48 ± 4	48 ± 3	45 ± 2	46 ± 3	46 ± 3	47 ± 3
Cross-link density (mol/cm ³ × 10 ⁻⁴)	1.30	1.01	1.13	1.16	1.10	1.08	1.13	1.19	1.16
Swelling degree (%)	219	245	243	230	229	243	236	225	227
Sol fraction (%)	3.1	6.0	6.9	5.9	6.5	8.1	8.2	7.4	7.5

NR/GTR: natural rubber/ground tire rubber.

(70°C) using an internal mixer and then compression molded at 160°C for 12 min. These conditions allow the evaporation of low-molecular-weight volatile products formed during the thermal degradation of GTR, which explain the lack of correlation between irradiation time of GTR and thermal stability of NR/GTR composites.

Physico-mechanical properties

Table 4 shows physico-mechanical properties of the NR/GTR composites as a function of the microwave irradiation time of GTR. As could be expected, the application of 50 phr of GTR to NR matrix resulted in noticeable decrease of tensile strength, from 26.4 MPa for NR sample to 14.0–16.4 MPa for NR/GTR composites. A similar trend was observed for elongation at break, which decreased from 854% for NR to 671–779% for NR/GTR samples. These results corresponded with the values obtained by Ismail et al.,³⁵ who studied the effect of carbon black on properties of NR filled with GTR/carbon black hybrid filler. The deterioration of tensile properties of NR/GTR composites could be due to the weak interactions between the NR matrix and GTR filler. The partially cross-linked structure of GTR does not disperse well in the continuous elastomeric matrix, which creates weak sites in terms of stress-transmission, resulting in a decrease of tensile properties. The tensile properties of NR-based composites containing microwave irradiated GTR were slightly higher than those with untreated GTR. This is related to partial devulcanization of GTR, which increases the roughness and specific surface of the devulcanized GTR particles and provides better adhesion between GTR and polymer matrix.^{36,37} This effect was more visible in the case of

NR/GTR_{truck} composites, because of higher content of NR and consequently higher degree of devulcanization in this GTR_{truck} filler.¹⁷

Additionally, the GTR source and irradiation time have small impact on modulus at 300% elongation and hardness of NR/GTR composites, which were surprisingly comparable to the NR sample. This behaviour could be related to the cross-link density values of the studied composites, which were lower than the ones of NR sample (see Table 4). Compared to the NR sample, the number of unsaturated bonds in the composites increased with the addition of GTR. The unsaturated bonds present in GTR are able to cross-link and compete against the unsaturated bonds in the NR matrix. These results could support an observation by Kim et al.,³⁸ who suggested that the decrease of mechanical properties in the rubber compounds filled with GTR might be affected by changes in the cross-link density of the rubber matrix, not by low adhesion between the matrix and GTR.

Furthermore, the studied samples showed similar swelling behaviour, regardless of the type of used GTR (car or truck). Increasing irradiation time of GTR resulted in decreased swelling degree. The effect of irradiation time on swelling degree and sol fraction of GTR was studied in a previous work.¹⁵ The reduction of swelling degree as function of irradiation time could be attributed to higher interfacial interactions between NR matrix and GTR filler. These interactions restrict the mobility of polymer chains, which prevented the penetration of the solvent into the studied samples.^{20,39} Additionally, it was found that NR/GTR_{truck} composites were characterized by slightly higher content of sol fraction than NR/GTR_{car} composites, which is due to the differences in composition of GTR_{truck} and GTR_{car} (see Table 1).

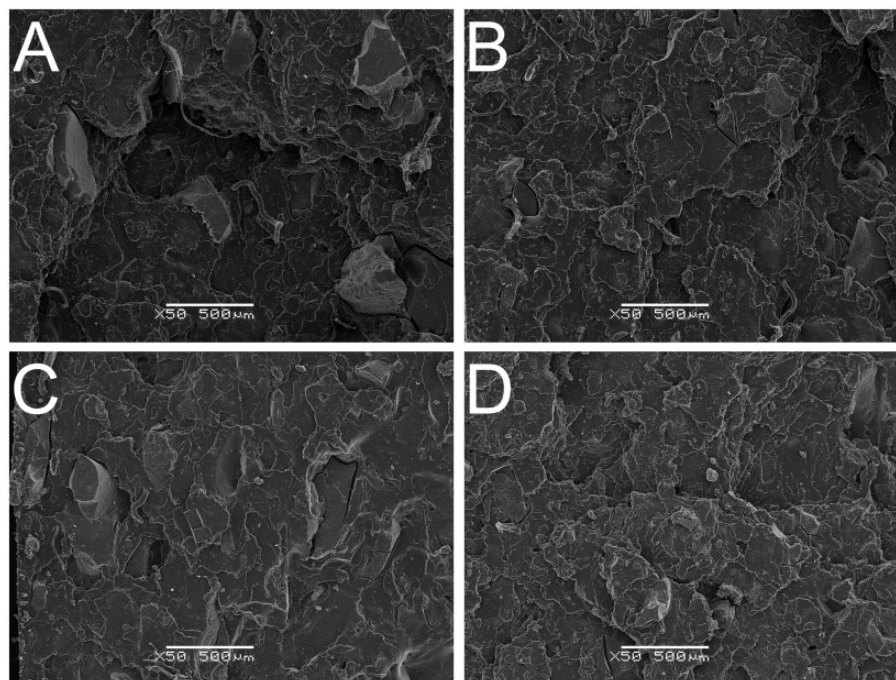


Figure 6. SEM images of selected samples: (a) NR/GTR_{car}-0 min; (b) NR/GTR_{car}-10 min; (c) NR/GTR_{truck}-0 min and (d) NR/GTR_{truck}-10 min (magnification $\times 50$). SEM: scanning electron microscope; NR/GTR: natural rubber/ground tire rubber.

SEM analysis

The morphology of the fracture surfaces of the samples subjected to static tensile test at the rate of 500 mm/min was evaluated. The micrographs show the surface area perpendicular to the direction of strain. In Figure 6 the effects of source of GTR and microwave devulcanization (for 10 min) on the NR/GTR composite breaking mechanism are presented. Figure 6(a) and (b) showed the surface of NR/GTR_{car}-0 min. and NR/GTR_{car}-10 min samples. In both micrographs, the GTR_{car} particles embedded in the NR matrix could be observed. However, in the case of NR/GTR_{car}-0 min sample, some cracks, pores and many cavities are visible, which means that the adhesion between NR and untreated GTR is rather poor. It was noticed that surface of NR/GTR_{car}-10 min sample after tensile test was smoother due to stronger interactions between NR matrix and GTR filler, when devulcanization degree of GTR increased. The results suggest enhanced cross-linking efficiency between NR and GTR, related to the presence of active sites in GTR_{car} after irradiation, which are able to participate in the revulcanization process. Micrographs for NR/GTR_{truck} composites (Figure 6(c) and (d)) showed a similar trend, although it should be noticed that the NR/GTR_{truck}-0 min sample is more homogeneous than the NR/GTR_{car}-0 min. This is due to the different composition of GTR from car and truck, as discussed previously.

Conclusions

GTR prepared from passenger car tires (GTR_{car}) and truck tires (GTR_{truck}) were irradiated at different times in the range: 0–10 min using a prototype based on a commercial microwave oven. NR-based composites were highly filled with carbon black (30 phr) and GTR (50 phr). The effects of GTR source and its irradiation time on structure, physico-mechanical, thermal and morphological properties were determined. The following conclusions on the effects of studied variables in NR/GTR composites may be drawn:

Increasing irradiation time of GTR has significant influence on structure, mechanical and thermal properties of the NR/GTR composites, which is related to the changes in the interfacial adhesion, and cross-link density was also affected by the GTR source (car/truck).

FTIR results suggest that, regardless of the source, microwave irradiation resulted in partial devulcanization/degradation of the GTR and simultaneously in generation of unsaturated bonds able to further reactions of revulcanization:

Irradiation of GTR affects the migration of the stearic acid and zinc stearate from the core to the surface of studied NR/GTR composites. This was confirmed by FTIR and SEM analysis;

Regardless of the irradiation time of GTR, the addition of GTR_{car} to the NR matrix increases its thermal stability, while for NR/GTR_{truck} composites the opposite trend was observed. This is due to higher content of

synthetic rubbers in GTR_{car} than in GTR_{truck} and also by the possible evaporation of low-molecular-weight volatile products formed during thermal degradation of GTR, which affected thermal stability of studied NR/GTR composites;

Compared to samples with untreated GTR, irradiation of GTR slightly enhanced tensile properties and cross-link density of studied composites. This effect is more evident in the case of GTR_{truck}, because of the higher interfacial interaction between NR and GTR_{truck} confirmed by SEM images.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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References

- ETRMA – European Tyre & Rubber Manufacturers' Association (Belgium). End-of-life Tyre Report 2015, <http://www.etrma.org/uploads/Modules/Documentsmanager/elt-report-v9a—final.pdf> (2016, accessed February 2018).
- Chen SJ, Su HB, Chang JE, et al. Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires. *Atmos Environ* 2007; 41: 1209–1220.
- Gagol M, Boczkaj G, Haponiuk J, et al. Investigation of volatile low molecular weight compounds formed during continuous reclaiming of ground tire rubber. *Polym Degrad Stab* 2015; 119: 113–120.
- Formela K and Haponiuk J. Curing characteristics, mechanical properties and morphology of butyl rubber filled with ground tire rubber (GTR). *Iran Polym J* 2014; 23: 185–194.
- Piszczyk Ł, Hejna A, Formela K, et al. Effect of ground tire rubber on structure, mechanical and thermal properties of flexible polyurethane foams. *Iran Polym J* 2015; 24: 75–84.
- Karahrodi MH, Jazani OM, Paran SMR, et al. Modification of thermal and rheological characteristics of bitumen by waste PET/GTR blends. *Constr Build Mater* 2017; 134: 157–166.
- Yazdani H, Karrabi M, Ghasemi I, et al. Devulcanization of waste tires using a twin-screw extruder: the effects of processing conditions. *J Vinyl Addit Techn* 2011; 17: 64–69.
- Mangili I, Lasagni M, Huang K, et al. Modeling and optimization of ultrasonic devulcanization using the response surface methodology based on central composite face-centered design. *Chemometr Intell Lab* 2015; 144: 1–10.
- Saiwari S, van Hoek JW, Dierkes WK, et al. Upscaling of a batch de-vulcanization process for ground car tire rubber to a continuous process in a twin screw extruder. *Materials* 2016; 9: 724.
- Movahed SO, Ansarifar A and Estagy S. Review of the reclaiming of rubber waste and recent work on the recycling of ethylene-propylene-diene rubber waste. *Rubber Chem Technol* 2016; 89: 54–78.
- Novotny DS, Marsh RL, Masters FC, et al. Microwave devulcanization of rubber. Patent 4104205, USA, 1978.
- Seghar S, Ait Hocine N, Mittal V, et al. Devulcanization of styrene butadiene rubber by microwave energy: effect of the presence of ionic liquid. *Exp Polym Lett* 2015; 9: 1076–1086.
- Molanorouzi M and Mohaved SO. Reclaiming waste tire rubber by an irradiation technique. *Polym Degrad Stab* 2016; 128: 115–125.
- Khavarnia M and Movahed SO. Butyl rubber reclamation by combined microwave radiation and chemical reagents. *J Appl Polym Sci* 2016; 133: 43363.
- Colom X, Faliq A, Formela K, et al. FTIR spectroscopic and thermogravimetric characterization of ground tyre rubber devulcanized by microwave treatment. *Polym Test* 2016; 52: 200–208.
- Garcia PS, de Sousa FDB, de Lima JA, et al. Devulcanization of ground tire rubber: physical and chemical changes after different microwave exposure times. *Exp Polym Lett* 2015; 9: 1015–1026.
- de Sousa FDB, Scuracchio CH, Hu GH, et al. Devulcanization of waste tire rubber by microwaves. *Polym Degrad Stab* 2017; 138: 169–181.
- Thodesen C, Shatanawi K and Amirkhanian S. Effect of crumb rubber characteristics on crumb rubber modified (CRM) binder viscosity. *Constr Build Mater* 2009; 23: 295–303.
- Ghavibazoo A and Abdelrahman M. Composition analysis of crumb rubber during interaction with asphalt and effect on properties of binder. *Int J Pavement Eng* 2013; 14: 517–530.
- Colom X, Sans J, Norazman ASB, et al. Characterization of elastomeric matrix of SBR reinforced with GTR devulcanized by microwave. *Afinidad* 2017; 77: 9–17.
- Nallasamy P and Mohan S. Vibrational spectra of cis-1,4-polyisoprene. *Arab J Sci Eng* 2004; 29: 17–26.
- Flory PJ and Rehner J. Statistical mechanics of cross-linked polymer networks I. rubberlike elasticity. *J Chem Phys* 1943; 11: 512–520.
- Kraus GJ. Swelling of filler-reinforced vulcanizates. *J Appl Polym Sci* 1963; 7: 861–871.
- Saiwari S, Dierkes WK and Noordermer JWM. Devulcanization of whole passenger car tire material. *KGK Kaut Gummi Kunst* 2013; 66: 20–25.
- Arabiti J and Pajarito BB. Effect of ingredient loading on surface migration of additives in a surfactant-loaded natural rubber vulcanizate. *Adv Mat Res* 2015; 1125: 64–68.
- Heideman G, Datta RN, Noordermer JWM, et al. Influence of zinc oxide during different stages of sulfur vulcanization. Elucidated by model compound studies. *J Appl Polym Sci* 2005; 95: 1388–1404.

27. de Sousa FDB and Scuracchio CH. The role of carbon black on devulcanization of natural rubber by microwaves. *Mat Res* 2015; 18: 791–797.
28. Hirayama D and Saron C. Chemical modifications in styrene–butadiene rubber after microwave devulcanization. *Ind Eng Chem Res* 2012; 51: 3975–3980.
29. Mangili I, Lasagni M, Anzano M, et al. Mechanical and rheological properties of natural rubber compounds containing devulcanized ground tire rubber from several methods. *Polym Degrad Stab* 2015; 121: 369–377.
30. Formela K, Cysewska M and Haponiuk J. Thermomechanical reclaiming of ground tire rubber via extrusion at low temperature: efficiency and limits. *J Vinyl Addit Techn* 2016; 22: 213–221.
31. Gönen M, Balköse D, İnal F, et al. Zinc stearate production by precipitation and fusion processes. *Ind Eng Chem Res* 2005; 44: 1627–1633.
32. Kleps T, Piaskiewicz M and Parasiewicz W. The use of thermogravimetry in the study of rubber devulcanization. *J Therm Anal Calorim* 2000; 60: 271–277.
33. Scuracchio CH, Waki DA and da Silva MLCP. Thermal analysis of ground tire rubber devulcanized by microwaves. *J Therm Anal Calorim* 2007; 87: 893–897.
34. Formela K, Cysewska M and Haponiuk J. 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. *Polimery* 2014; 59: 170–177.
35. Ismail H, Omar NF and Othman N. Effect of carbon black loading on curing characteristics and mechanical properties of waste tyre dust/carbon black hybrid filler filled natural rubber compounds. *J Appl Polym Sci* 2011; 121: 1143–1150.
36. Colom X, Cañavate J, Carrillo F, et al. Effect of the particle size and acid pretreatments on compatibility and properties of recycled HDPE plastic bottles filled with ground tire powder. *J Appl Polym Sci* 2009; 112: 1882–1890.
37. Colom X, Carrillo F and Cañavate J. Composites reinforced with reused tyres: surface oxidant treatment to improve the interfacial compatibility. *Compos Part A Appl Sci Manuf* 2007; 38: 44–50.
38. Kim SW, Hong KH and Seo KH. Effects of ground rubber having different curing systems on the crosslink structures and physical properties of NR vulcanizates. *Mat Res Innovat* 2003; 7: 149–154.
39. Kumnuanti C and Sombatsompop N. Dynamic mechanical properties and swelling behaviour of NR/reclaimed rubber blends. *Mater Lett* 2003; 57: 3167–3174.