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Chemical Surface Etching Methods for Ground Tire Rubber as Sustainable Approach for Environmentally-Friendly Composites Development– A Review

Mapoloko Mpho Phiri^{##}, Mohau Justice Phiri^{##}, Krzysztof Formela[§], Shanganyane Percy Hlangothi[#]

[#]Center for Rubber Science & Technology, Department of Chemistry, Nelson Mandela University, Port Elizabeth, South Africa

[§]Department of Polymer Technology, Faculty of Chemistry, Gdansk University of Technology, Gdansk, Poland

Corresponding authors: [*MapolokoMpho.Phiri@mandela.ac.za](mailto:MapolokoMpho.Phiri@mandela.ac.za), [*Mohau.Phiri@mandela.ac.za](mailto:Mohau.Phiri@mandela.ac.za)

Abstract

Ground tire rubber (GTR) has been used as a sustainable low-cost modifier in various composites. However, due to the hydrophobic nature of GTR, it is incompatible with most matrices and results in deterioration in both mechanical and physical properties of composites. This necessitates pre-modification of the powdered rubber to improve the interfacial bonding at the rubber-matrix interface. The most common GTR modification research relies on surface etching via use of various techniques. The current review aims to give a detailed overview of the surface etching chemical modification methods for GTR for incorporation into various matrices such as concrete, bitumen and polymers. The review will serve as a guide for engineers, chemists and manufacturers with interest of including GTR in any type of composite for achieving

compatibility with the main matrix. The surface chemical etching treatment methods such as acid etching, hydroxylation, oxidation, and radiation methods are discussed in this work. The characterization methods to confirm the functional groups on the modified GTR and the effect of the treatment on the resultant GTR composites are also highlighted. Finally, this review highlights the advantages and limitations of the chemical surface etching processes for GTR.

Keywords: Waste tire rubber; Recycling; Modification; Functionalization; Composites; Compatibilization

Abbreviations

C	Carbon
Ca(OH) ₂	Calcium hydroxide
Cl	Chlorine
DCP	Dicumyl peroxide
DSC	Differential scanning calorimetry
EA	Ethyl acetate
EVA	Ethylene vinyl acetate
FTIR	Fourier transform infrared spectroscopy
GTR	Ground tire rubber
HCl	Hydrochloric acid
HClO ₄	Perchloric acid
HNO ₃	Nitric acid
HDPE	High density polyethylene
H ₂ SO ₄	Sulfuric acid
KMnO ₄	Potassium permanganate

LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
MA	Maleic anhydride
MEK	Methyl ethyl ketone
MW	Microwave
N ₂	Nitrogen gas
NaClO	Sodium hypochlorite
NaOH	Sodium hydroxide
NBR	Nitrile butadiene rubber
NR	Natural rubber
O	Oxygen atom
O ₂	Oxygen gas
phr	parts per hundred parts of rubber
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
S	Sulfur
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscopy
TCI	Trichloroisocyanuric acid
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TMPTA	Trimethylolpropane triacrylate

TMPTMA	Trimethylolpropane trimethacrylate
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy

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1. Introduction

The 'during-use' performance of tires is measured by properties such as rolling resistance, endurance, traction, thermal stability and chemical resistance. These properties are known to be affected through the vulcanization process, which results in a complex three-dimensional network structure. Unfortunately, the same complex three-dimensional network structure is difficult to reverse and/or break, making it difficult to recycle tires and hence tires remain a huge environmental problem [1]. There are several widely adopted methods of dealing with waste tires, other than re-treading. These include energy generation through combustion in cement kilns [2–4], microbial fuel cells [5,6], pyrolysis [7–10], and shredding/grinding into various sizes. The shredded/ground rubber is usually applied in rubber compounds such as various engineering rubber parts, and for secondary applications such as artificial turfs and roads [11,12]. Other common waste tire recycling methods are reclaiming and devulcanization. Reclaiming is a process of depolymerisation and oxidation of the rubber component in tires as an elastic material which can be easily processed, compounded and vulcanised with or without the addition of either natural or synthetic rubbers [13–19]. Devulcanization is a selective scission of sulfide cross-linking bonds and results in increased plasticity of the obtained products [20–24]. The products from reclaiming and devulcanization show similar behavior during processing (sticky materials suitable for vulcanization with additional curing system). Therefore, currently in the literature, these two terms are used interchangeably. Several studies have been dedicated to formulating and understanding the properties of rubber that has been recycled through these processes either as rubber matrix [25–27] or as partial replacement of virgin rubber in rubber composites [28–30].

Among all the waste tires recycling approaches, grinding of tires into small particle sizes or granules has gained a lot of interest across a wide range of industries such as the automotive



sector, construction engineering and civil engineering [1,13,14]. Ground tire rubber (GTR) can be obtained via different processes, namely cryogenically [31,32], dry ambient mechanical grinding [33,34] and wet ambient mechanical grinding [35–37] of the waste tires to a desirable particle size [38]. GTR has been incorporated in various composites such as thermoplastics [39–45], thermosets [46–54], concrete [55–60], rubber [61–66] and asphalt/bitumen [67–74]. In turn, GTR in these composites has been found to improve impact strength [75], reduce the crack propagation in composites, [76] improve sound and heat damping properties [39,61,77] as well as promoting foamability of composites [78–80]. The growing interest in the use of GTR is related to advancement in research, the ease of GTR production and modification of GTR surface. The buy in by both the tire industry and government in terms of capital investment into research that promote GTR inclusion into composites and hence extending the useful life of waste tires also contributed to the interest. In most countries, this reaction was due to legislation which prohibited disposal of waste tires into landfills or dumpsites. However, these strict environmental legislations are more relevant in developed regions such as north America and Europe [81,82], and not so much for developing and underdeveloped countries [15].

Many research works confirmed that the hydrophobic and cross-linked nature of GTR makes it incompatible/immiscible with matrix, necessitating modification of the GTR surface to help improve its interaction with the matrix [83]. Treatment of GTR can be performed by mechanical [16,84–87], thermo–mechanical [88–93], mechano–chemical [94–99], biological [100–103], ultrasound [104–108] and chemical methods [109–114]. Such classification is generally used for reclaiming/devulcanization techniques comprehensively described in review papers [35, 85]. However, current interesting research approach trend is reclaiming/devulcanization combined with suitable modification of GTR. This solution allows easy tailoring final properties of treated



GTR by functionalization, grafting or other method. In this way, treated GTR can be dedicated as modifier or reinforcement for selected matrices. Additional treatment in combination with devulcanization significantly improves matrix-GTR interactions, which affects processing performance of prepared composites. Moreover, it should be pointed that treatment of GTR, especially degradation of three-dimensional network, main chain scission or suitable functionalization, enhance the migration of additives (e.g. accelerators, curing agents, etc.) and carbon black from treated GTR to fresh matrix. This phenomenon also affecting the final properties of obtained materials and should be consider during preparation of novel, environmentally friendly composites based on various matrices (e.g. polymers, bitumens, concretes, etc.).

As mentioned above, reclaiming/devulcanization combined with suitable treatment of GTR seems to be promising approach for sustainable development of waste tires recycling technologies. However, to the best of our knowledge, there is no recent review about the chemical treatment of GTR, which summarize achievement made in this field so far.

This work aims to review the literature data related to chemical surface modification methods for GTR, including surface chemical modification methods such as etching, oxidation, hydroxylation, and radiation. These methods allow etching the surface of the GTR particles and introducing functionalities such as hydroxyl, peroxy, hydroperoxyl, carbonyl groups, onto the surface of GTR. In turn, these groups modify the surface energy of the GTR, enhancing GTR particles compatibility with the fresh matrices, which have beneficial impact on the performance of obtained composites.

2. Chemical Surface Etching Methods for Ground Tire Rubber Prior to Composite Applications

There are several chemical methods used to modify the surface of waste tire rubber for different applications. The modification processes significantly increase the applicability of GTR in various industries and as such reduced the amount of waste tires generated directly to environment. Among the chemical methods, the etching, oxidation, hydroxylation and radiation methods have resulted in improved properties of the final composite product.

2.1. Acid Etching methods

Acid surface etching is a traditional technique that utilizes acids to modify the surface chemistry of various hydrophobic substances. Three different acids, namely 60 % nitric (HNO_3), 96 % sulfuric (H_2SO_4) and 60 % perchloric (HClO_4) acids have been used to treat 400–600 μm GTR particles [115]. GTR content used was in the range of 5–40 wt. % and after treatment with acid, the GTR was neutralized with hot water and 15 % ammonium hydroxide prior to the usage in high density polyethylene (HDPE) composites. The composites were prepared by a two-roll mill for 3 min with at 153 °C and they were compression moulded into sheets at 170 °C for 15 min. Fourier transform infrared spectroscopy (FTIR) showed a decrease in double bond, C=C, at 1640 cm^{-1} with H_2SO_4 and HNO_3 treatments; and new bonds, O=S=O, at 1408 cm^{-1} , and N–N=O at 1382 cm^{-1} appeared after treatment with H_2SO_4 and HNO_3 , respectively. Scanning electron microscopy (SEM) images, used to confirm and monitor the extent of the surface modification process, and showed a rough surface with micro pores and cavities after treatment with H_2SO_4 . However, HClO_4 had slight impact on the compatibility properties of HDPE/GTR composites. Tensile strength increased by 24 % with addition of 20 wt. % of GTR modified with either



H_2SO_4 or HNO_3 whereas HClO_4 produced composites with lowest tensile strength even lower than untreated GTR/HDPE composites, as presented in Figure 1. The authors concluded that the overall tensile strength of the composites is affected by GTR content and type of chemical modifier agent, and the order of surface treatment effectiveness was determined as follows: $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HClO}_4$.

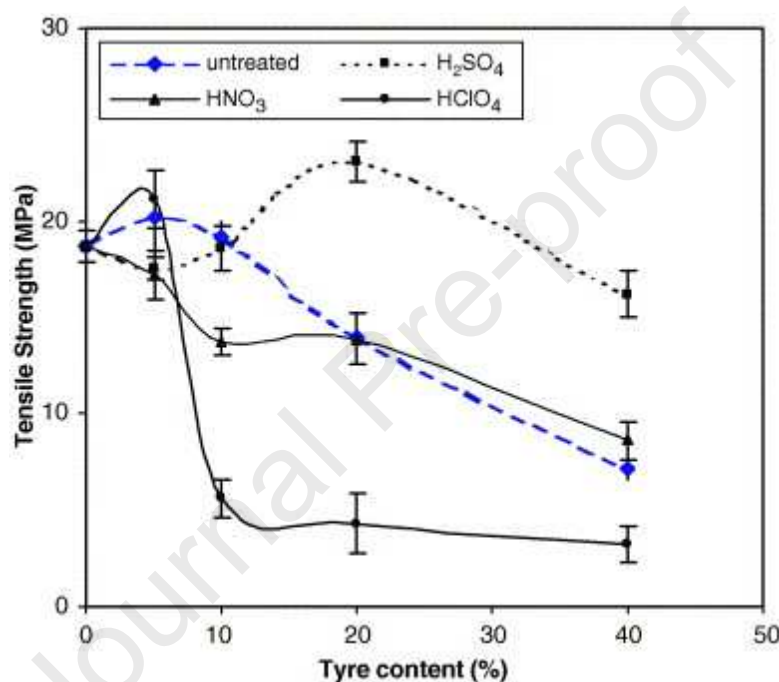


Figure 1: Tensile strength as a function of GTR content for untreated, and HNO_3 , H_2SO_4 and HClO_4 -treated HDPE/GTR composites. H_2SO_4 -treated composites show superior tensile strength for 10–40 wt. % GTR content studied. Reprinted with permission from Colom et al. 2007 [115].

Colom et al. 2009 [116] extended their work to evaluate the effect of particle size on the thermal, mechanical and morphological properties of HDPE/GTR composites and they treated three different sizes, $<200 \mu\text{m}$, $200\text{--}500 \mu\text{m}$ and $>500 \mu\text{m}$, of GTR with 50 % HNO_3 , 50 % H_2SO_4 and

acids blend in ratio 50/50 %. Subsequently, the treated GTR was neutralized with 3 M of sodium hydroxide. GTR content in HDPE/GTR composites was limited to 40 wt. % since above this limit, it was deemed practically impossible to process the composites. The composites were prepared by a two-roll mill at 153 °C for 3 min and they were compression moulded into sheets at 170 °C for 15 min. The authors also found that the smallest GTR particle size resulted in improved compatibility when blended with recycled HPDE as confirmed by an increase in melting enthalpy energy measured by differential scanning calorimetry (DSC). There was also an increase in tensile strengths of HPDE/GTR composites filled with the acid treated recycled rubber for particle size of <200 µm. However, an increase in unmodified and modified GTR content resulted in overall decrease in tensile strength and Young's modulus. SEM images were used to support the observed mechanical results and they showed a rough surface on GTR with pores and cracks after acid treatment. It was postulated that the pores and cracks gave rise to good adhesion between HPDE and GTR.

Elenien et al. 2018 [117] soaked 3–5 mm GTR particles in 97 % of H₂SO₄ for 1 min at room temperature and the etched GTR particles were neutralised with NaOH solution which was followed by final rinse with distilled water. The content of GTR was varied between 5–50 wt. % to produce polypropylene (PP)/GTR composites using a batch mixer at temperature of 180 °C for 10 min. The composite sheets were produced by compression moulding. Upon acid modification, the presence of sulfonic groups (S=O) was observed with appearance of peaks at 1057 cm⁻¹ wavenumbers as measured and confirmed by FTIR technique. In general, the compressive yield strength of the PP composites containing either treated or untreated GTR was observed to decrease as a function of increasing GTR amount in the composite. The rate of the decrease was much faster for the composite containing untreated GTR than for the treated one, thus the

modification process slightly improved the compressive yield strength of the composite, as presented in Figure 2. The authors attributed the slight improvement of the yield strength to the high roughness level and increased porosity on the surface of treated GTR aiding in better adhesion between the GTR and the PP matrix.

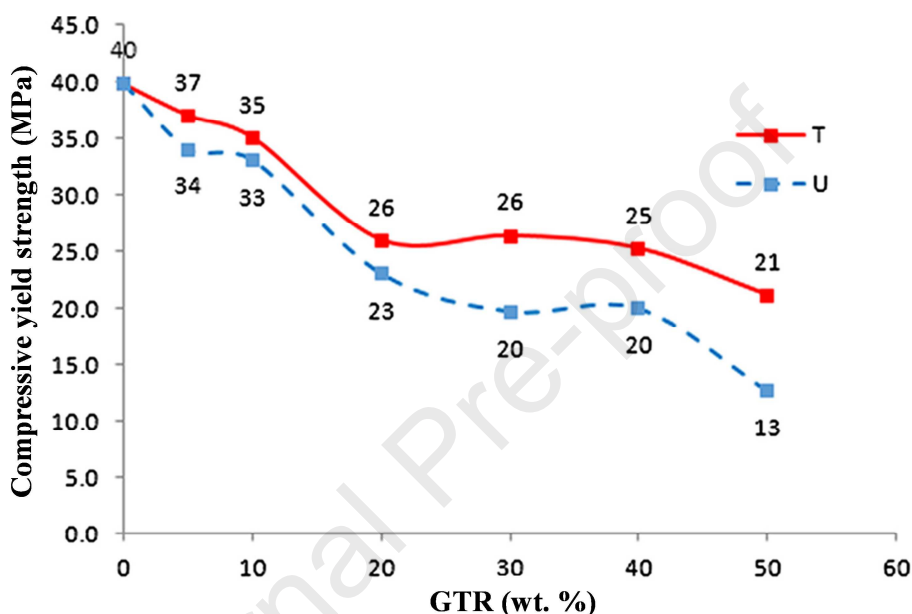


Figure 2: The effect of treated (T) and unmodified (U) GTR particles wt. % of size 5 mesh on the compressive yield strength of PP/GTR composites. Composites treated with 97 % H_2SO_4 have improved compressive yield strength and the content of GTR was varied between 5–50 wt. %. Reprinted with permission from Elenien et al. 2018 [117].

One of the rubber components in GTR is styrene–butadiene rubber (SBR). In a model study done by Cepeda-Jiménez et al. 2000 [118], a sulfur vulcanized SBR was treated with two concentrations, 50 and 95 wt. %, of sulfuric acid at 60 °C. The polyurethane (PU) solution was spread between two rubber sheets to make PU/GTR composites. They used contact angle experiments to confirm the existence of sulfonic moieties on the surface of SBR as well as a



decrease in contact angle after acid treatment; further reflecting the presence of polar groups on the SBR particles. The authors also reported that H₂SO₄ (95 wt. %) produced noticeable surface modification results as confirmed by the presence of carbonyl groups in FTIR region 1600–1700 cm⁻¹. The results showed improvement in adhesion properties with PU materials. However, there was a decrease in both tensile strength and elongation at break of the PU composites due to hardening of the rubber surface after acid treatment.

In another related model study, Pastor-Blas et al. 2000 [119] used 2, 5 and 7 wt. % trichloroisocyanuric (TCI) acid in ethyl acetate (EA), methyl ethyl ketone (MEK) and a mixture of EA and MEK solutions to modify the surface of sulfur vulcanized SBR. The composites were prepared by applying PU solution with a brusher on the surfaces of two rubber sheets. The modification process on the surface of rubber was studied and confirmed by both FTIR and SEM techniques. FTIR results showed the presence of chloro-ketone group (Cl-C=O) in the wavenumber region of 1680–1750 cm⁻¹. Chlorination of SBR surface increased with high percentage of TCI acid and in MEK and showed better results compared to EA solution while the mixture of EA and MEK did not show any modification behaviour. SEM images showed micro cracks and high degree of roughness on the surface of vulcanized SBR rubber, as such there was an increase in joint strength between the rubber and PU. However, there was poor adhesion noticeable between SBR and PU material when 7 wt. % TCI acid in EA solution due to a weak secondary layer caused by the by-product, cyanuric acid.

A study by Naskar et al. 2001 [120] showed improvement in mechanical properties of polyvinyl chloride (PVC) resin and 40 phr modified GTR with TCI acid. 160–205 µm GTR particles produced by cryogenic grinding method were treated with 1, 3 and 5 wt. % of TCI acid in methanol solution for 20 min at 25 °C, and rinsed with tap water to remove any residual by-

products from the GTR surface. To improve compatibility between PVC resin and GTR, acetone was used to extract soluble components from GTR prior to the modification process. The composites were prepared by a batch mixer at 170 °C and they were converted into sheets by using a two-roll mill. FTIR spectra for modified GTR showed increase in absorption peaks at 666 and 718 cm^{-1} for carbon–chlorine (C–Cl) stretching while the absorption peaks at 900–1050 cm^{-1} due to =C–H decreased with increase in amount of TCI acid. This reflected that hydrogen atoms were gradual replaced with Cl atoms from TCI acid. The results from carbon and oxygen X-ray photoelectron spectroscopy (XPS) experiments showed there were 3 types of carbon atoms and 2 types of oxygen atoms after modification of GTR, and the peak intensity increased with increasing amount of TCI acid. Based on the results of FTIR and XPS, the authors proposed a reaction mechanism for surface modification of GTR. The first step involved the hydrolysis of TCI acid to form hypochlorous (HOCl) acid which occurred during the rinsing with tap water. In the second step, HOCl acid reacted with carbon double bonds (C=C) via addition reaction to form chlorinated GTR. Mechanical results show that there was increased elongation at break of PVC/GTR composites with increase in amount of TCI acid. On other hand, tensile strength increased with TCI content up to 3 wt. % and thereafter it decreased due to hard shell of chlorinated layer formed on GTR surface.

2.2. Oxidation methods

In the research work done by Sonnier et al. 2007 [121], 2 wt. % of potassium permanganate (KMnO_4) solution in a mixture of water and acetone was used to oxidize the surface of 400–500 μm GTR. The ground tire rubber content used in the study was in the range of 0–70 wt.% in low density polyethylene (LDPE) and HDPE based composites. The composites were prepared by a batch mixer at 145 °C and they were injection moulded into specimens at 170 °C. FTIR analysis

confirmed the presence of carbonyl groups on the surface of the rubber as observed by absorption peaks at 1630 cm^{-1} . After modification, they found that there was no noticeable improvement in mechanical properties, tensile stress and impact energy of the HDPE/GTR or LDPE/GTR composites. Grafting maleic anhydride onto the polyethylene, did not result in any improvement of impact properties. The study concluded that there was no adhesion among the components of the blends. In an attempt to improve the compatibility of oxidised GTR, Sonnier et al. 2008 [122] performed a study using a 0.1–2.0 wt. % of dicumyl peroxide (DCP) in cyclohexane solvent. Cyclohexane was evaporated prior to melt blending of 50 wt. % of 400–500 μm GTR in HDPE composites. The composites were prepared by a batch mixer at $145\text{ }^\circ\text{C}$, followed by compounding with a twin screw extruder at $180\text{ }^\circ\text{C}$. High content of DCP promoted better mechanical properties, elongation at break and impact energy, of the composites whereas at lower content of DCP, there was a decline in the properties due to partially cured HDPE/GTR composite and opposite trend was observed for tensile strength (maximum stress) as presented in Figure 3. The in-situ SEM technique was used to monitor crack propagation of the sample as tensile test is performed and DSC analyses were employed to follow free radical mechanisms and it was found that the crystallinity of the composites as measured and calculated from DSC decreased with DCP content greater than 0.5 wt. %.



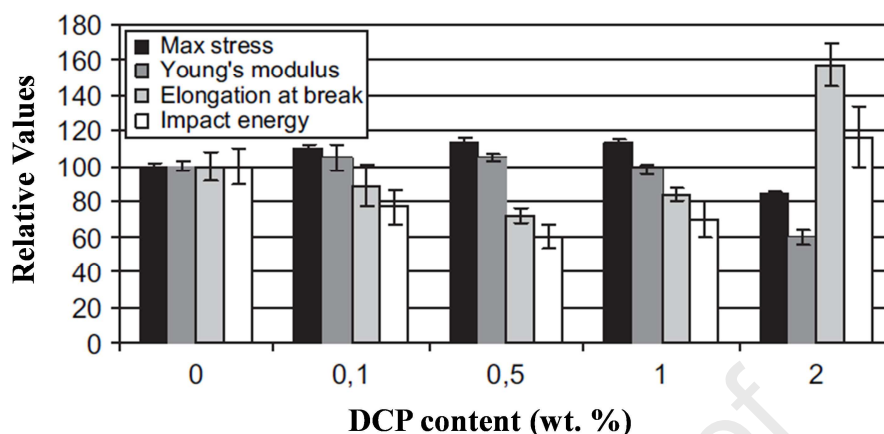


Figure 3: Mechanical properties of treated HDPE/GTR as a function of DCP content. Elongation at break and impact energy of the treated composites have increased with higher DCP content, 2 wt. %. Reprinted with permission from Sonnier et al. 2008 [122].

He et al. 2016 [123] used a three-stage modification process to perform surface treatment of 40 mesh GTR. The first step regarded as pre-treatment involved soaking GTR in NaOH solution, follow by the second step of using 5 wt. % KMnO_4 in acidic solution at 60 °C. In the final step, regarded as post-treatment, GTR was soaked in sodium hydrogen sulfite (NaHSO_3) solution at a temperature of 60 °C. The composites were prepared by curing cement paste and GTR at 20 °C for 28 d. The presence of hydrophilic carbonyl ($\text{C}=\text{O}$) and sulfonate ($-\text{SO}_3$) groups on the surface of GTR were confirmed by FTIR analysis at 1730 cm^{-1} and $1170\text{--}1080\text{ cm}^{-1}$ respectively. Contact angle was found to decrease from 95° to 90.5° with KMnO_4 oxidation and it even decreased further to 71° with post-treatment with NaHSO_3 due to more polar groups on GTR surface, see Figure 4. This three-stage treatment method resulted in good adhesion between GTR and cement matrix.



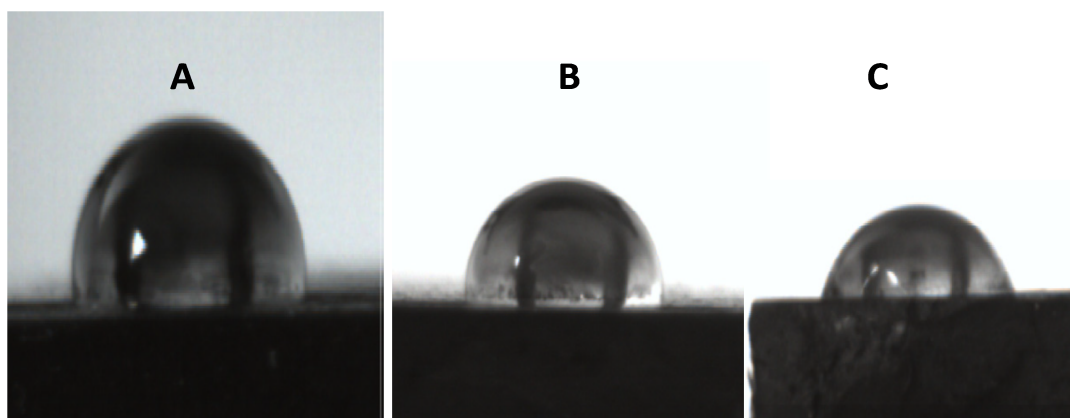


Figure 4: Water contact angle measurements for (a) original/unmodified, (b) oxidized and (c) sulfonated GTR rubber. The presence of polar groups after surface modification of GTR have resulted in a decrease of contact angle from 95° (unmodified GTR) to 71° (sulfonated GTR). Reprinted with permission from He et al. 2016 [123].

There was increase of $\sim 41\%$ in adhesion strength of cement/GTR composite after oxidation and sulfonation modification process. The impact energy values for neat cement, and cement composites with unmodified and treated GTR were determined to be 65.6, 102.6 and 124.8 J, respectively. The improved mechanical properties were attributed to new functional groups on GTR surface which resulted in good interfacial bonding between GTR and cement matrix as shown in Figure 5. From the study, it is evident that more than one modification step is needed to achieve effective surface treatment methods and the overall reaction mechanisms for the three stage is given in Figure 6.

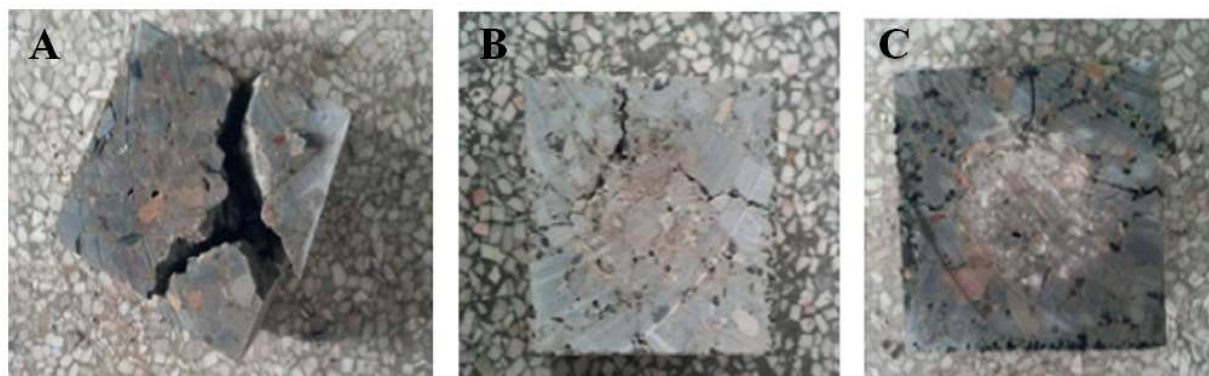


Figure 5: Failure modes of neat cement (a), and cement composite with 4 wt. % of untreated (b) and treated (c) GTR to ultimate impact. For the same GTR content, the impact energy of treated GTR composites increased by ~21 % as compared to untreated sample. There were fewer noticeable cracks on the treated composite surface. Reprinted with permission from He et al. 2016 [123].

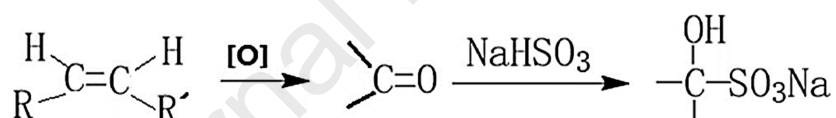


Figure 6: Reaction mechanisms for GTR surface modification using KMnO_4 and NaHSO_3 . Oxidation takes place on the double bond ($\text{C}=\text{C}$) from GTR to form the carbonyl group which further react with NaHSO_3 to result in sulfonated product. Reprinted with permission from He et al. 2016 [123].

In an attempt to improve the binder property of asphalt with GTR, Han et al. 2017 [124], used 1.41 M of sodium chlorite (NaClO) solution to perform oxidation surface treatment on 40–100 mesh GTR at a temperature of 40 °C for 3 h. The asphalt/GTR composites were prepared with a laboratory mixer by heating at temperatures between 170–190 °C for 20–30 min. FTIR analysis confirmed that surface modification did occur and showed carbonyl and hydroxyl groups at 1635



and 3410 cm^{-1} , respectively. SEM images showed the presence of more open pores on the modified GTR surface as compared to untreated GTR as shown in Figure 7 and the pores led to absorption of asphalt molecules, resulting in good interfacial bonding. The authors reported improved elastic recovery of up to 60 % for the modified asphalt binders with good compatibility due to the treatment of the GTR.

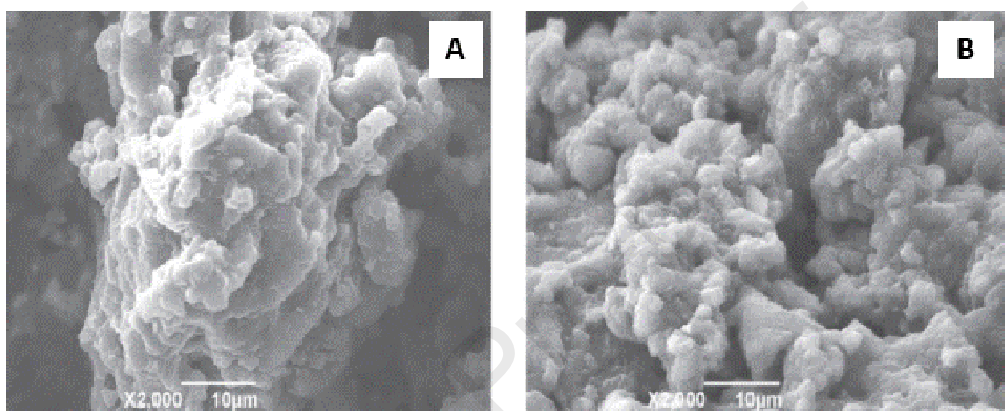


Figure 7: SEM images of (a) unmodified and (b) NaClO modified GTR. The image of modified GTR showed presence of more open pores which allowed asphalt to penetrate easily into GTR. Reprinted with permission from Han et al. 2017 [124]

The partial oxidation on the surface of GTR was done by using oxygen in nitrogen with the ratio of 0.04 and modification experiments were performed on 300–600 mesh GTR at three different temperature levels, 150 °C, 200 °C and 250 °C [125]. The mortar composite specimens were prepared in cubic moulders. SEM revealed that GTR changed to short and compact needle-like structure after the oxidation process. FTIR analysis showed the presence of hydrophilic functional groups, S=O and –S–O– at $1100\text{--}950\text{ cm}^{-1}$. The results obtained for the concrete/GTR composites prepared at 250 °C showed superior compressive strength compared to lower temperatures GTR treatments. The diffusion of oxygen into GTR was ineffective at lower

temperatures and it resulted into less formation of hydrophilic groups. Concrete/GTR composites treated at 250 °C was chosen for aging studies and compared concrete without GTR (control sample) and concrete composites made from untreated GTR, and results showed that 250 °C treated GTR/concrete composites gave superior properties at 28 and 56 d as depicted in Table 1. The method used in their study is considered ‘green’ since it did not involve use of solvents.

Table 1: Mechanical properties of neat concrete and concrete composites prepared with untreated and 250 °C–treated GTR at 28 and 56 d. The GTR treated with oxygen at 250 °C showed superior compressive strength over the aging period of 56 d. Adopted from Chou et al. 2010 [125].

Mechanical properties	Compressive Strength (MPa)		Flexural strength (MPa)		Tensile Strength (MPa)	
	28	56	28	56	28	56
Concrete without GTR (control sample)	34.8	39.2	6.1	6.2	3.2	3.3
Concrete composite with 6 wt. % of untreated GTR	16.3	19.4	3.8	4.2	1.8	1.9
Concrete composite with 6 wt. % GTR oxidized at 250 °C	41.2	42.1	6.2	6.6	3.3	3.3

Another “green” method used 6.5 mol % ozone in stream of oxygen to treat the surface of 420 μm GTR truck tire tread [126]. During the oxidation process, the GTR particles were mechanically shaken in a round-bottom flask for 1 h. FTIR spectroscopy was used to determine the rate of the ozonation reaction by monitoring the presence of carbonyl groups and the formation of CO_2 bond at 1710 cm^{-1} and 2360 cm^{-1} , respectively. Thermogravimetric analysis (TGA) demonstrated that the ozonation of GTR affected only the surface and not the bulk of the rubber. Similar decomposition behaviour was observed from TGA thermograms confirming that only volatile components were lost from the surface of GTR. However, the authors suggested solvent extraction with acetone to remove antioxidants from the GTR as they limited the consumption of ozone. Cao et al. 2014 [110] carried out deep ozonation on the surface of 100 mesh GTR from truck tire tread at room temperature with 1–6 hours exposure time and ozone concentration of 10 mg/L at 5 L/min flow rate. The oxidation process was carried out in a batch mixer at $150\text{ }^\circ\text{C}$ for 10 min. The FTIR showed an increase in carbonyl groups on the rubber surface at wavenumbers of 1710 and 1600 cm^{-1} . X-ray photoelectron spectroscopy (XPS) showed the formation of CO_2 bond due to ozone attack on the surface of GTR. Their results indicate that ozonation not only modify the GTR surface but also destroyed some cross-linking networks within the GTR as confirmed by the TGA results since the onset temperature of decomposition shifted from $267.5\text{ }^\circ\text{C}$ to $253.2\text{ }^\circ\text{C}$ after ozonation. A decreased gel content from 82 % to 65 % further validated the results of TGA to show that cross-link networks of GTR were destroyed. It was therefore postulated that important factors to consider for ozonation is the exposure time and ozone concentration as they determine the depth of penetration of the ozone into the GTR particles.



Fan and Lu 2011 [127] modified 60 mesh GTR particles by passing ozone of 1.4 mg/L concentration through a laboratory scale reactor at room temperature. Oils and additives were extracted from GTR powder using acetone prior to ozone treatment and the ozonation process was carried out at different times, 30, 60, 120 and 180 min. After the ozonation time of 180 min, the sol fraction of the modified GTR was determined to be 35 % as compared to 27 % of unmodified GTR particles. XPS, FTIR and contact angle were used for further characterization of modified GTR. FTIR spectra of the modified GTR verified the presence of carbonyl stretching (C=O) with absorption peak at 1710 cm^{-1} . Results of XPS technique, after 180 min, showed increased amount of oxygen of 11.9 % on the GTR surface as compared to 6.6 % before modification. In contrast, the XPS spectra peak of carbon, C_{1s} , showed a decreased amount of carbon for modified GTR from 90.6 % to 86.9 %. The authors postulated that the ozone attacked the unsaturated (C=C) part of GTR to form unstable complex which is further converted to either carbonyl or hydroxyl and their proposed a reaction mechanism of ozonolysis is presented in Figure 8 and was based on the original work of Criegee [128]. The study was concluded with contact angle measurements which confirmed the results of FTIR and XPS techniques since the contact angle values decreased from 115° to 87° for modified GTR. This observation reflected that there is increased wettability of GTR, hence it is suggested they would affect good adhesion between GTR and any polar matrix.



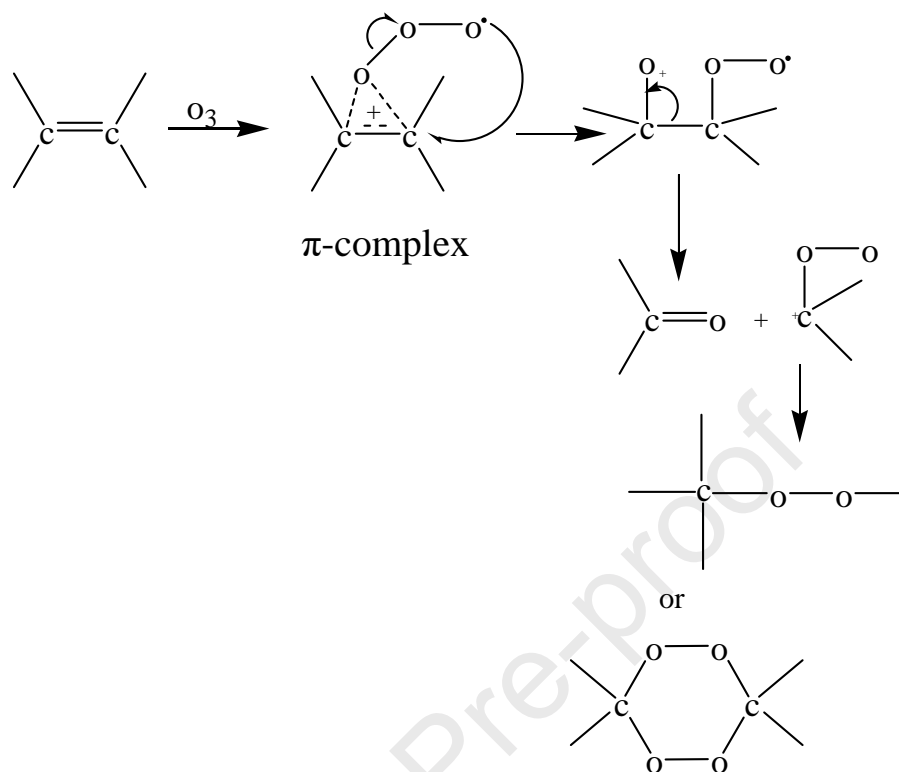


Figure 8: Ozonolysis of the double bond present in GTR material. In the reaction mechanism, ozone attacks the double bond (C=C) on the GTR to result into formation of unstable radical molecule which further dissociates into intermediate products, carbonyl and a radical molecule. The intermediate product reacts or combine together to form peroxide as a final product. Reprinted with permission from Fan and Lu 2011 [127].

2.3. Hydroxylation methods

In cement/concrete industrial applications, sodium hydroxide (NaOH) solution was used for surface treatment of the GTR to enhance adhesion properties between the rubber and cement [129–131]. Hydroxylation is one of the simplest methods used to modify the surface of GTR. Guo et al. 2017 [132] compared two different treatment methods, NaOH and silane, the amine functional Z-6020, and the epoxy functional Z-6040 trimethylsiloxanes, coupling agents for the

surface modification of GTR. They soaked 7–13 mesh GTR in NaOH solution (1 N) and the coupling agents were dissolved in water–ethyl alcohol solution. Different amounts of modified GTR ranging from 15–50 wt. % were used in cement composites and they reported increased compressive strength for 25 wt. % GTR treated with NaOH, as shown in Figure 9. Overall, their results revealed that NaOH-treated samples showed a long-term durability as compared to samples modified with silane coupling agent. The poor compatibility of silane coupling agents was thought to be a result of weak interaction between GTR and cement matrix. Furthermore, the addition of GTR resulted in decreased dynamic modulus of elasticity of the composites. However, there was no significant effect on dynamic modulus for different surface treatment methods.

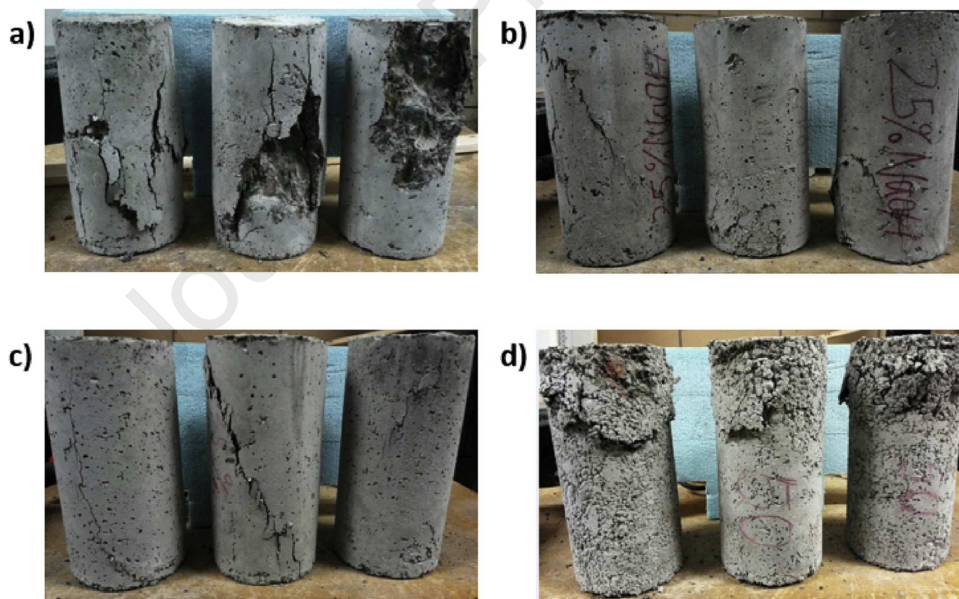


Figure 9: The appearance of samples after compressive strength tests for cement with NaOH-treated GTR aggregates at different content (a) 15 wt. %, (b) 25 wt. %, (c) 35 wt. % and (d) 50 wt. %. The treated sample with 25 wt. % of GTR showed superior compressive strength compared to other samples and at higher percentage there is poor compatibility between GTR

and cement due to agglomeration of GTR above 35 %. Reprinted with permission from Guo et al. 2017 [132].

Li et al. 2004 [133] used a saturated NaOH solution to modify the surface of GTR in form of chips (25.5 mm) and fibres (50.8 mm). The concrete composites were prepared by curing at room temperature for 28 d. The flexural strength and stiffness of cement composites were found to decrease after NaOH modification process due to crumb rubber acting as stress concentrator in the composites. It was reported that surface treatment failed with large sized chips of GTR as compared to the fibres since the large sized chips gave a lower flexural strength due to their decreased surface area. However, the presence of hydroxyl groups ($-OH$) had shown to provide a better wetting between GTR and cement matrix.

Segre and Joekes 2000 [130] modified 35 mesh GTR with saturated NaOH solution for 20 min at room temperature. The concrete composites were prepared by curing and GTR at 20 °C for 28 d. GTR, 10 wt. %, was used in concrete composites and the compressive strengths of both unmodified and NaOH treated GTR were similar. On the other hand, fracture energy of the NaOH treated GTR increased by a factor of 4 as compared to the unmodified GTR. The enhanced fracture energy and toughness properties were confirmed by SEM analyses showing that GTR did not pull out of the cement matrix, thus resulting in good interfacial adhesion. Segre et al. 2002 [131] extended their work on NaOH surface modification on 35 mesh GTR and studied the adhesion properties of cement matrix. The concrete composites were prepared by curing at 20 °C for 28 d. Surface modification was confirmed by FTIR analysis showing the presence of carboxylate vibration at 1600 cm^{-1} . The contact angle values greater than 90° were reported after NaOH treatment for period of 24 h, however a minor reduction to $\sim 87^\circ$ was

observed after 144 h (6 d). In addition, they showed that cement/NaOH treated GTR composites were resistant to hydrochloric (HCl) acid digestion at room temperature whereas the untreated GTR samples were completely degraded by HCl. This was postulated to the fact that NaOH could have reacted with zinc stearate in the GTR to form sodium stearate which is soluble in water and easily washable from the GTR surface. This meant that HCl did not have any material to react after NaOH treatment, on the other hand, HCl reacted with zinc stearate on the surface of untreated GTR.

Meddah et al. 2014 [11] reported improved adhesion properties for concrete/GTR composites to a much higher level by treating 5–30 wt. % of 4–6 mm GTR with NaOH solution for 24 h. GTR particles were rinsed with distilled water to remove any traces of NaOH and dried in oven at temperature of 60 °C for 24 h. The concrete composites were prepared by moulding at 25 °C for 24 h. The prepared concrete/GTR composites showed good water and acid resistance due to decreased porosity of the composite due to the strong adhesion between the hydrophilic GTR particles which made it difficult for water and acid to penetrate through the concrete composites. The density of the concrete composites decreased upon increasing the GTR content due to its low density compared to that of natural sand aggregates. Furthermore, compressive strengths of the concrete composites decreased with an increase in GTR content regardless of the treatment. Raghavan et al. 1998 [134] used two treatment methods with NaOH (pH = 10) and Ca(OH)₂ (pH = 12.5) solutions to treat the GTR at room temperature for 4 min. The modified GTR were rinsed with distilled water to obtain alkali-free GTR particles with two different sizes, 4.75 and 2.36 mm. They used 1–10 wt. % of GTR in cement paste and they found that flexural strength decreased with an increase in GTR content. The bigger particle size, 4.75 mm, showed promising results compared to 2.36 mm particle size, however a clear conclusion could not be reached due

limited number of replicates. Light microscopic experiments showed pull-out characteristics of GTR rubber particles from cement matrix and this behaviour was credited to have resulted in poor interfacial bonding between GTR and cement matrix as it was also reported elsewhere [135–137]. The authors suggested that a longer treatment time of GTR might be needed to achieve enhanced compatibility between GTR and the cement matrix.

The polymer applications of GTR treated with NaOH are rather poorly described in the literature. Recently, Nuzaimah et al. 2020 [138] modified waste rubber crumbs from NR gloves by soaking in 10 % NaOH solution for 2 h and finally rinsed with distilled water. The waste rubber particles were grinded using a cryogenic method to result with particle size of 0.85–1.70 mm. Polyester/waste rubber composites were prepared with 5 wt. % of waste rubber and cured in a stainless steel mould at ambient temperature using methyl ethyl ketone peroxide as accelerator. FTIR spectra of the modified crumb rubber showed the appearance of a broad peak at 3150–3600 cm^{-1} and it was assigned to OH groups. There was a decrease in contact angle from 64.95° to 45.10° post NaOH treatment, thus reflecting the formation of polar components on the rubber surface. The tensile strength of polyester/rubber composite was improved after NaOH treatment due to a better adhesion between the waste rubber and the polyester matrix. The authors postulated that the improvement in tensile strength was a result of NaOH reacting with zinc stearate in waste rubber to form sodium stearate which is washable from surface of rubber to create wider micro-crack and more micropores as compared to unmodified rubber as depicted in Figure 10. They suggested that polyester molecules penetrated through the micropores and micro-crack to increasing the physical interaction with waste rubber particles.



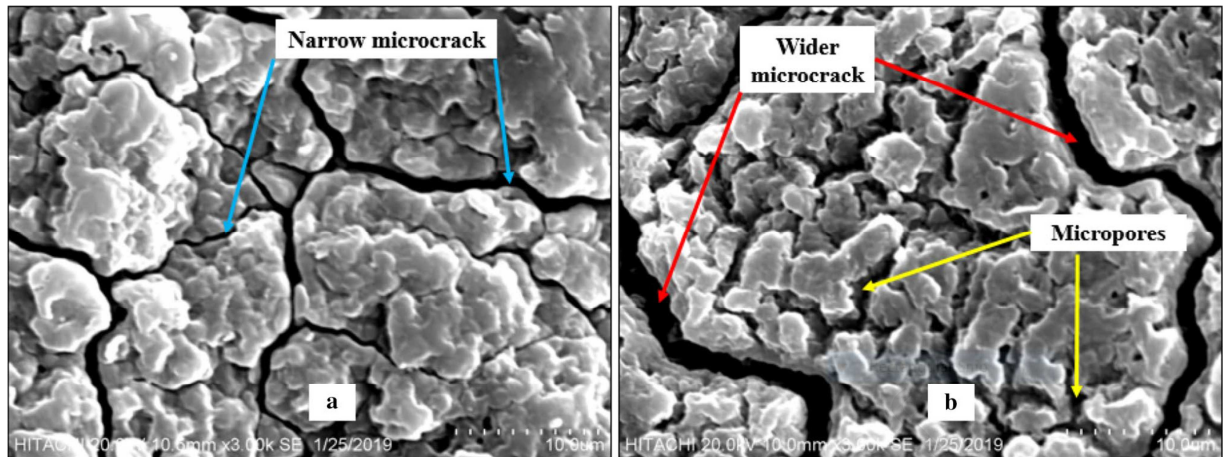


Figure 10: SEM images of (a) unmodified waste rubber and (b) NaOH modified waste rubber at the magnification of $\times 3000$. The image of modified sample showed wider micro-crack and more micropores which had allowed polyester to penetrate the rubber matrix. The improved tensile strength was noticed for treated composite. Reprinted with permission from Nuzaimah et al. 2020 [138].

Literature data showed, that the surface modification of GTR with NaOH solution resulted in improvement of mechanical properties of cement/concrete based composites dedicated for the construction applications. The proposed reaction mechanism for surface modification is presented in Figure 11, where NaOH react with hydrogen ion from carboxylic group attached to the GTR to form hydroxylated GTR product.

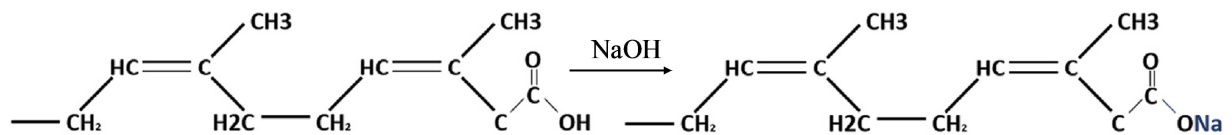


Figure 11: Reaction mechanism for GTR surface modification with NaOH solution. NaOH reacts with carboxylic acid group (—COOH) present on the GTR surface to form the

hydroxylated GTR product with sodium acetate group ($-\text{COONa}$). Reprinted with permission from Guo et al. 2017 [132].

2.4. Radiation methods

Radiation methods have been used to modify the surface chemistry of the GTR particles. The common denominator in all radiation methods is that they involve cleavage of the polymer chains especially at the sulfur–sulfur (S–S) cross-linking bonds to generate sulfidic radicals onto the surface of GTR. Once chain scission has occurred, the radicals can react further via oxidative reactions with the atmospheric oxygen to attain various hydrophilic functionalities such as carbonyl, peroxide and hydrogen peroxide groups [121,139]. The second type of reactions that the radicals generated during irradiation is cross-linking and this has been credited to the increase in the thermal stability of the polymer composites [140,141]. Radiation has also been used for reclaiming or devulcanization of GTR [142,143] as such radiation exposure time has to be precisely controlled to only etch the surface and not destroy the entire network structure [144]. In this subchapter, treatment of GTR with plasma [62,145,146], microwave [109,147], and gamma radiation [55,148–150] are covered as the main methods utilized for variable composites with GTR.

2.4.1. Plasma treatment

Cheng et al. 2012 [146] investigated the impact of plasma treatment on 120 μm GTR. The surface modification of GTR powder was carried out by using a plasma surface treatment apparatus (model DT-03 Suzhou OPS Plasma Technology, China). GTR particles were placed into the glassware evenly and positioned in plasma treatment apparatus chamber. The vacuum pump was closed until the vacuum reached <10 Pa, turned on the flow valve to let the air in.

While the flow quantity equaled the set value, the high-frequency generator was turned on for a 180 s modification. Furthermore, XPS analysis confirmed the presence of oxygen containing compounds on the surface of the irradiated GTR as indicated in Table 2 [146].

Table 2: Element content of the GTR powder before and after plasma treatment. The presence of oxygen compounds on GTR surface was confirmed by XPS analysis after treatment with plasma for 180 s. Adopted from Cheng et al. 2012 [146].

Element name	Untreated GTR	Plasma-treated GTR
C (%)	87.66	85.30
O (%)	11.00	13.47
O/C (%)	12.54	15.80

In the work of Vilela et al. 2018 [151], surface treatment of 1.19–4.76 mm GTR was done using air plasma of 12 kV power and 0.06 A for exposure time ranging from 5–20 min. The plasma treated GTR was included in the wood–cement composites by varying its content between 5–20 wt. % relative to the total weight of wood particles. The developed wood–cement panels were cured for 28 d at 20 °C for 24 h and using calcium chloride as an accelerator. FTIR technique was used to confirm modification process with peak appearance of C–O bonds at 1100–1200 cm^{-1} and a reduction in bands at 1400 cm^{-1} due to breaking of C=C bonds during post–treatment with air plasma. SEM images showed that the level of surface roughness increased with plasma exposure time and 20 min treatment was chosen to manufacture the panels. Compact ratio and dimensional stability of the panels were reported to be higher than the reference sample. The



overall mechanical properties of the panels improved because of good interfacial bonding between rubber and cement after air plasma treatment.

Cheng et al. 2015 [152] investigated the time effects of modifying surface of car and truck GTR with low temperature plasma. The low temperature plasma, model OPS-OMEGA-DT03 was employed to modify the GTR particles. The thin and even layer of the GTR sample was placed inside the reaction chamber. The copper sulfate was used to dry the air that was used during plasma discharging and the 60 and 100 W power was employed for 150 s at each power level. The concrete/GTR composites were cured at 30 °C for 7 d. SEM images of the treated GTR showed an increase in surface roughness for the samples with samples that were treated for longer times displaying decreased hydrophilicity as indicated by decreased dispersity in water. The FTIR result of the raw GTR and of the treated GTR after 1, 10 and 20 d of storage time were run and analyzed. All characteristic peaks were observed including -C=C- at 1640 cm^{-1} , -C=O at 1720 cm^{-1} and a broad -OH absorption band at 3440 cm^{-1} as previously reported [62,153]. The -OH band was stronger for treated samples than the one for untreated samples and increased in strength with time. XPS results presented in Figure 12 showed a 0.36 % increase in the oxygen carbon ratio on the GTR sample after plasma treatment, this ratio was observed to increase after 10 and 20 d which was ascribed to increasing -OH groups on the GTR surface [152]. Additionally, results showed presence of two peaks, O1sA and O1sB, which were assigned to reduced binding energy of -C=O and higher binding energy of -C-O- , respectively and O1sB content increased with storage time.



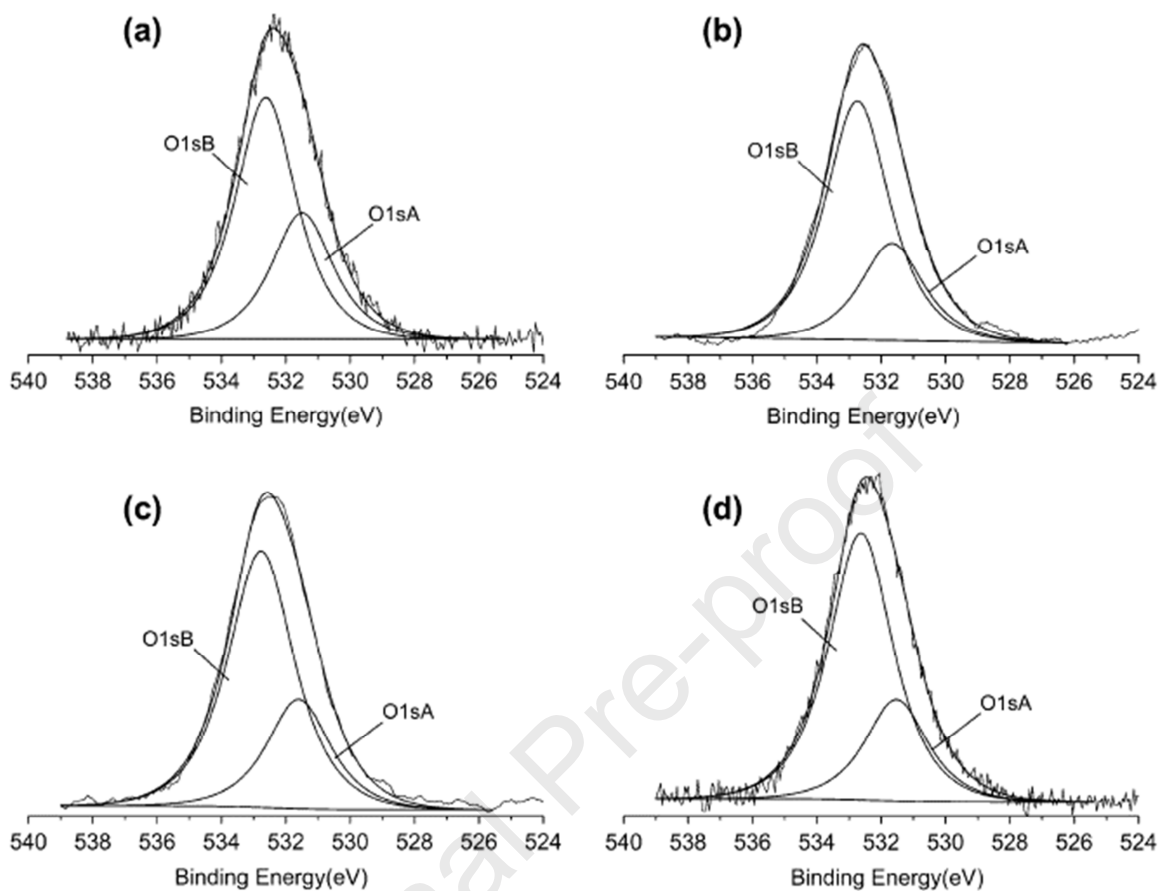


Figure 12: XPS of unmodified GTR (a) and of the treated GTR after 1 (b), 10 (c) and 20 (d) d of storage time. The oxygen to carbon ratio increased with storage time after low plasma treatment due to presence of $-OH$ groups on the surface of GTR. Reprinted with permission from Cheng et al. 2015 [152].

2.4.2. Microwave treatment

Microwave has also been successfully used in the treatment of the surface of GTR and its efficiency is depended on the chemical composition and carbon content of GTR, exposure time and magnetron power [154–158]. All these factors affect the extent of devulcanization process including both devulcanization and post-devulcanization temperatures [144,159–161].

Colom et al. 2016 [144] studied the impact of microwaves on GTR with three different particle sizes, 275, 400 and 425 μm , with carbon black content of 32.1, 34.9 and 36.9 %, respectively. Microwave energy of 700 W was applied to 15 g of GTR and the sample was stirred at 20 rpm with exposure times of 3 and 5 min and the recorded temperature values after the treatment were 225 $^{\circ}\text{C}$ and 297 $^{\circ}\text{C}$ respectively. The char obtained after microwave treatment was analyzed using FTIR technique and the results showed that zinc oxide decomposed whereas silicon oxide (SiO_2) did not degrade. SiO_2 absorption bands at 1096 cm^{-1} was chosen and used as a reference peak as suggested by other studies [162,163] and the relative absorbance of other components in treated GTR were determined based on it. Based on FTIR spectra of treated GTR for both 3 and 5 min, there was chain scissions of methine ($=\text{CH}-$) group (1412 cm^{-1}) on the main polymer backbone and methyl ($-\text{CH}_3$) groups (1383 cm^{-1}) on the side chains, however methylene ($-\text{CH}_2$) groups (1452 cm^{-1}) remained intact after the treatment as presented in Figure 13. This observation was related to the bond energy values of the groups with $-\text{CH}_2$ having the highest energy compared to the two groups. Furthermore, the absorption peaks of carbon-sulfur ($-\text{C}-\text{S}$) bond and S-S bridges at 603 and 524 cm^{-1} , respectively decreased significantly post-treatment with microwave. Cross-link density increased with microwave treatment exposure time for all the particle size, for example, 425 μm particle size increased from 4.4×10^{-4} – 8.8×10^{-4} mol/cm^3 . The expectation was a reduced cross-link density since the bonds or chain are being broken, however, the authors postulated that there is revulcanization taking place which rebuilt the S-S bridges due to residual sulfur in the GTR. TGA provided more insight about chemical composition of treated GTR as oils and additives evaporated at temperature of 50–320 $^{\circ}\text{C}$ and NR decomposed at 320–410 $^{\circ}\text{C}$, whereas SBR peak remain constant with exposure time. The content of carbon black decreased as a function of microwave exposure time due to thermo-

oxidation of the main chain which resulted with a release of CO_2 during the treatment. SEM images showed increased level of roughness on the surface of treated three particle sizes with increase in exposure time and 400 μm size had some pores and holes. This behavior suggested that microwave has ability to modify surface of GTR for further application in composites.

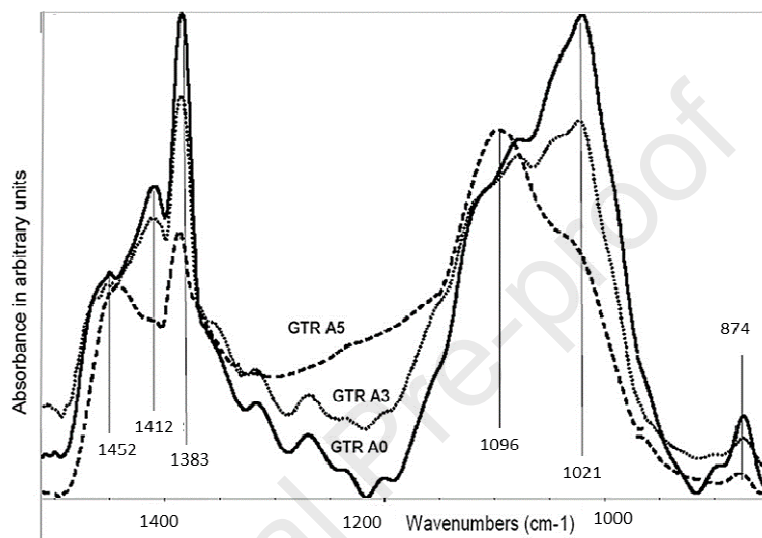


Figure 13: FTIR spectra of 400 μm GTR particle size (GTR A) as a function of microwave exposure time for wavenumber region of 1500–850 cm^{-1} . GTR A0, GTR A3 and GTR A5 are samples treated for 0, 3 and 5 min, respectively. FTIR results showed that methyl ($-\text{CH}_3$) groups on the side chains are destroyed as indicated by their decreasing concentration, however methylene ($-\text{CH}_2$) on the main polymer chain remained intact after the microwave treatment. Reprinted with permission from Colom et al. 2016 [144]

Garcia et al. 2015 [164] used longer microwave exposure time and treated 60 g of 60 mesh GTR with a higher microwave energy of 820 W for 3, 5, 6 and 7 min. Prior to the treatment, GTR particles were homogenized for 10 min using a twin-roll mill at room temperature. Gel content of the treated GTR was decreased with a longer microwave exposure times due to chain scission of



–C–S bond and S–S bridges. The results of FTIR showed that the absorption peak of –C–S bond at 1076 and 1006 cm^{-1} were only observed in untreated and 3 min-treated GTR and the authors further observed that polysulfidic bonds decreased whereas monosulfidic bonds were unaffected as the latter have higher bond energy [165]. Glass transition temperature (T_g) of the treated GTR samples decreased with increasing microwave exposure time and it was postulated that carbon black had restricted the movement of NR molecules shifting the mobility of the chains to higher temperatures as it was suggested by another study [166]. SEM images showed smoother surfaces for treated GTR samples with increase in microwave exposure time, and small pores and large voids were noticed for a sample treated for 6 and 7 min. The study concluded that the microwave exposure time determines the degree of devulcanization process and a special efforts should be taken to avoid revulcanization during microwave treatment of GTR.

In bitumen application, 40 mesh GTR particles were treated in microwave oven at energy of 800 W for 90 s [167]. GTR content in 10–20 wt. % was mixed with asphalt in high-shear mixer at temperature of 180–190 °C and stirred at 2000 rpm for 60 min. FTIR revealed that there was a weak chemical reaction post-treatment with microwave as there was disappearance of absorption peak for sulfur additives and partial breakage of S–S bonds of vulcanization cross-links at 1031 cm^{-1} . The gel permeation chromatography results showed that modified GTR/asphalt binders had higher molecular weight due to swelling reaction between GTR rubber and asphalt molecules. It was suggested that asphalt migrated into the rubber particles of rubber using a reaction mechanism shown in Figure 14. The onset temperatures from TGA shifted to lower values and there was a decrease in thermal enthalpy of treated GTR samples due to broken cross-linked bonds during microwave treatment. Atomic force microscopy (AFM) images showed a ‘bee-like’ structure for a neat asphalt but upon adding the treated GTR, smooth surface of the binder was



obtained. There were several micropores and cracks on GTR surface which increased contact area for asphalt molecules and this behavior had little effect on storage, loss modulus, complex modulus and pavement rutting parameter of the binders.

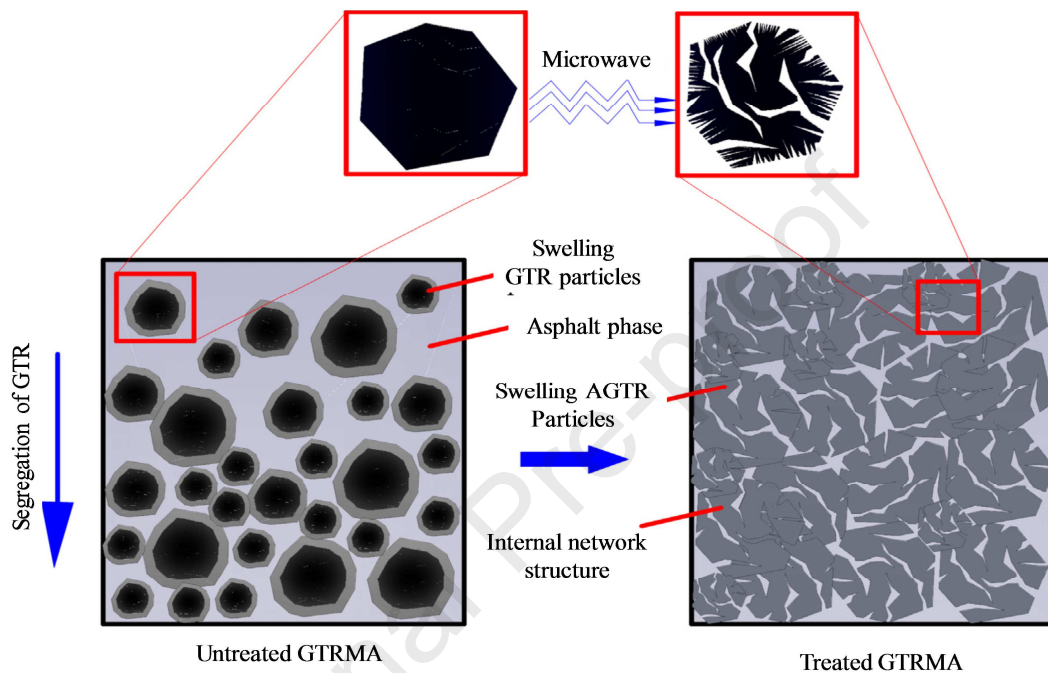


Figure 14: Reaction mechanism for crumb rubber modified asphalt (GTRMA) before and after microwave treatment, where AGTR is activated GTR. The micropores and cracks were observed for microwave treated GTR and asphalt molecules was assumed to penetrate through them into the rubber matrix. Reprinted with permission from Yang et al. 2020 [167].

Microwave radiation of GTR from truck and passenger car tires was done for different exposure times [158]. To achieve homogeneity on to the GTR particles, the microwave was fitted with a motorized stirrer. 30 g sample of 390 μm GTR was placed in the microwave oven with magnetron power 700 W at 80 rpm for 3, 5, and 10 min exposure times. The 50 phr modified GTR was incorporated in NR matrix using a batch mixer at 70 $^{\circ}\text{C}$, and the composites were

cross-linked at 160 °C and characterized. The microwave energy was reported to result in partial devulcanization of GTR and generated unsaturated carbon–carbon (C=C) bonds which partake in cross-linking. FTIR showed that absorption peak of C=C bond from 1596–1600 cm^{-1} decreased with irradiation time regardless of GTR source. However, the microwave treatment was more efficient for truck tire GTR and resulted in NR/GTR composites with higher cross-linking density. The thermal stability of NR/GTR composites with GTR from passenger car tires was increasing slightly with increase in GTR while the opposite was seen for the GTR from truck tires due to higher SBR content in passenger car tires. The tensile properties of the truck tire GTR/NR composites improved after microwave treatment because of high NR content in truck tires making adhesion much stronger.

In other work, microwave energy was used to modify the surface of 390 μm GTR for inclusion into composites of nitrile butadiene rubber (NBR) and NR [109]. In this work, 60 g of GTR was treated with 700 W and 80 rpm using a microwave oven fitted with a custom-made stirrer for 3, 5 and 10 min. GTR content used in the composites was 10, 30 and 50 phr and GTR was mixed with NBR and NR at 70 °C in batch mixer. The sulfur curing occurred at 160 °C for 12 min and these optimum cure conditions were determined elsewhere [158]. The microwave energy was found to devulcanize the surfaces of GTR and these modified GTR proved to partake in the vulcanization reactions with the virgin NBR and NR matrix. There was 19 % increase in Young's modulus for composites with 50 phr of GTR treated for 5 min and this behavior was attributable to good adhesion among modified GTR, NBR and NR components. However, GTR treated for 10 min resulted into reclaiming of rubber as C–C bonds of polymer backbone were also destroyed and could not be revulcanized. SEM images for composites with high amount of NBR revealed that NBR provided a lower compatibility with GTR as compared to NR.



Aoudia et al. 2017 [168] treated 2.7 g of 125–630 μm GTR with microwave power of 350, 500, 650, 750 and 900 W for exposure time of 15 and 60 s and 10 wt. % of GTR was mixed with bisphenol epoxy resin for 15 min with the addition of 45 wt. % of hardener. The composites were prepared by mixing epoxy resin and GTR in a batch mixer for 15 min and compounded and using the glass molder. FTIR showed a decrease of the C–S and S–S absorption peaks in the region $750\text{--}400\text{ cm}^{-1}$ with increase in the microwave power. This decrease was associated with the scission of the cross-links on the GTR surface by the microwave energy. Flexural stress at break for epoxy/GTR composites increased with increase in microwave treatment energy as shown in Figure 15. The improvement in mechanical properties was attributed to a better adhesion between epoxy resin and GTR due to chemically induced functional groups on GTR surface post-treatment.

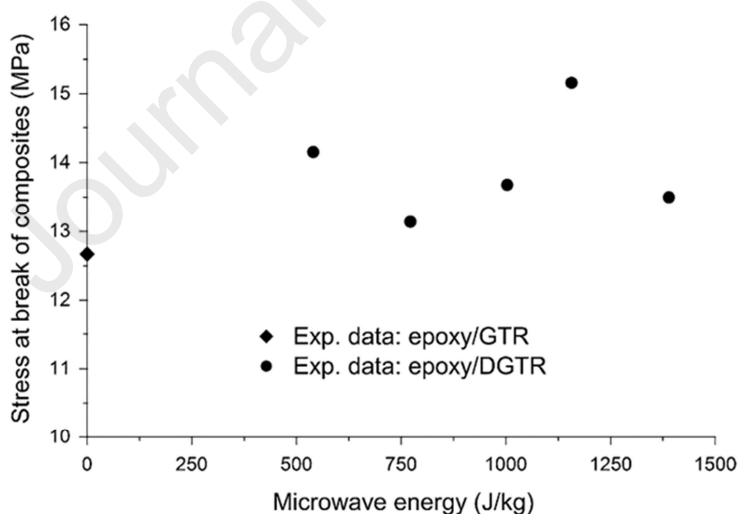


Figure 15: Flexural stress at break for the epoxy resin/GTR composites as a function of microwave treatment. The results of untreated GTR and devulcanized ground tire rubber (DGTR) are presented. Microwave treatment on GTR surface introduced polar components that

were compatible with epoxy resin to enhance flexural stress of the treated composites. Reprinted with permission from Aoudia et al. 2017 [168].

Microwave treatment of waste tires for recycling has been recently reviewed by Formela et al. [169]. This work was focused on the processing parameters, devulcanization/pyrolysis efficiency and quality of obtained products. Most of papers confirmed that the optimization of microwave power and exposure time are key parameters for efficient modification of GTR for environmental friendly composites. The main advantages and limitations of this method have been summarized in Table 3.

Table 3: Advantages and limitations of microwave treatment of GTR. Adopted from Formela et al. 2019 [169].

Advantages	Limitations
Heating in the material volume	High cost of professional microwave reactors
Short-time of process	Problems with efficient mixing
Solvent-free and environmental-friendly process	Hot spots issue
Precise control of MW energy dosage by	Problems with volatile degradation

magnetron power and time settings

products emission

Possible to perform in continuous manner

Possible functionalization/modification of GTR

Improvement of the matrix-GTR interactions

Preparation of novel products, such as reclaimed
rubber, oligomers, oils, carbon black and gases

2.4.3. Gamma radiation

Gamma radiations are high energy photons emitted by a reactor as a result of radioactive decay of an atomic nucleus, this energy has been used to etch the surface of GTR introducing hydrophilic groups which help improve compatibility with polar matrices. Ethylene vinyl acetate (EVA) modified with gamma irradiated GTR exhibited improved mechanical properties with increase in irradiation dose [139]. In the work of Herrera-Sosa et al. 2015 [55] GTR was irradiated with gamma radiation source at 200 and 300 kGy with a ratio of 4 kGy/h using irradiator Gamma Beam 651-PT loaded with ^{60}Co . 7–20 mesh GTR was incorporated in the concrete mix, followed by casting into molds. The samples were cured for 28 d prior to mechanical testing. Effects of GTR loading, GTR mesh size and irradiation dose on the properties of the samples were investigated. In this study, it was observed that concrete containing untreated GTR had much lower unit weights as opposed to the control samples while concrete samples containing irradiated GTR showed an increase in the unit weight which slightly

decreased upon increasing the irradiation dose but still higher than the control sample; up to 5 % increase was reported [55]. The increase in the unit volume was ascribed to poor mixing because of lumps formed during mixing of the concrete mixture with unmodified GTR. Both compressive strength and splitting tensile strength were found to decrease as a function of increasing in GTR content for both irradiated and non-irradiated concrete samples, as presented in Figure 16. This was ascribed to the promotion of aeration levels of concrete containing GTR and as such prone to micro-cracking hence lowering the compressive strength of the concrete samples containing GTR. The increase in radiation dose resulted in gradual rise in the compressive strength due to hardening because of irradiation and as such resulting in increased compressive strength while for splitting tensile, a slight decrease was observed at 200 kGy and upon increasing the irradiation dose to 300 kGy. This was ascribed to high functionality imparted onto the GTR particles at high irradiation doses meaning compatibility between the GTR and concrete was better at 300 kGy. The surface morphology of GTR modified concrete was evidently rough for non-irradiated samples as evidenced by non-uniformly distributed particles on the surface. Post irradiation at 200kGy, the surfaces of concrete samples appeared smoother due to cross-linking between the GTR surfaces and the concrete and the GTR particle distribution was much more improved. However, upon increasing the radiation dose further, the surfaces showed some cracks which were associated with possible polymer chain scission on the surfaces of GTR.



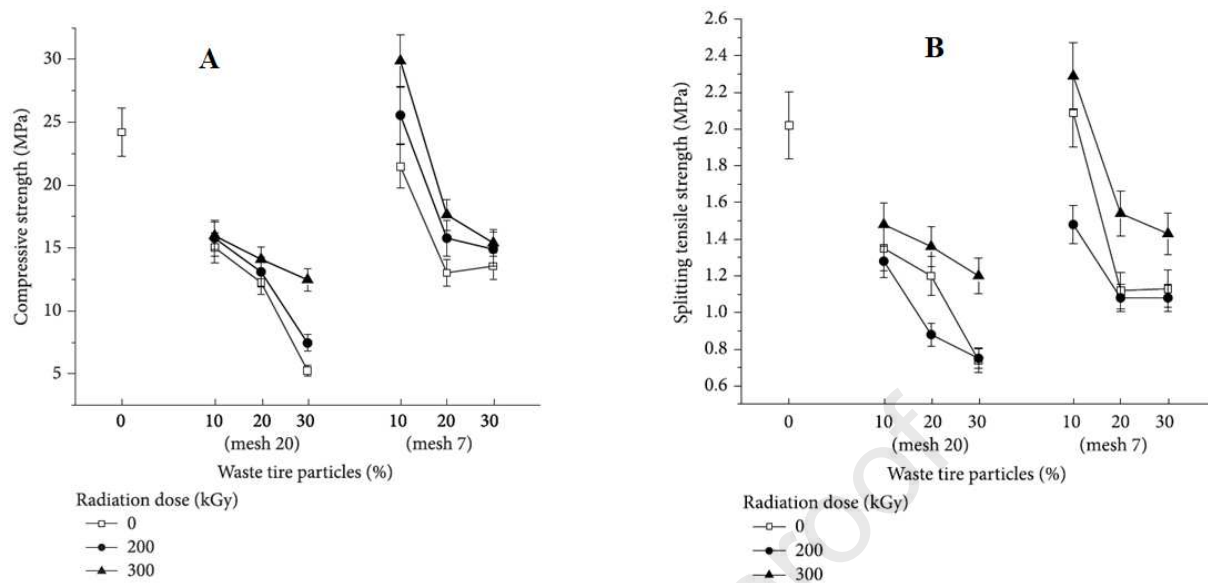


Figure 16: Compressive strength (a) and splitting tensile strength (b) of concrete with waste tire particles of 0.85 mm (20 mesh) and 2.8 mm (7 mesh). The increase in radiation dosage resulted in gradual increase in compressive strength of the composites due to hardening. Reprinted with permission from Herrera-Sosa et al. 2015 [55].

Gamma irradiation dose ranging from 200, 250 and 300 kGy have been used to ionize the surfaces of the GTR to improve its adhesion properties when used as partial replacement for silica aggregate in cement composites [148]. The use of the irradiator Transelektro LGI-01 IZOTOP with ^{60}Co , at a dose rate of 2.5 kGy/h, was employed and the irradiated GTR particles were mixed and cured into cement concrete composites at concentrations of 1, 3 and 5 wt. %. The GTR particle sizes studied were 0.85 mm and 2.8 mm. Table 4 shows the cement concrete formulations used and the various amounts of irradiated GTR incorporated, where the masses of cement concrete, water and crushed rock were kept constant at 78.7 g, 51.2 g and 196.8 g, respectively. This study reported that improvement of the mechanical properties of irradiated

GTR modified concrete was strongly dependent on the irradiation dose, thus, improvement of up to 108 % and 13 % were reported for the elasticity modulus and deformation respectively [148].

Table 4: Concrete mix proportions and 28 d compressive strength for 2.8 mm GTR. The radiation dosage and GTR content resulted in improved compressive strength for gamma radiation-treated GTR composites. Reprinted with permission from Martínez-Barrera et al. 2020 [148].

Code	Silica Sand (g)	Waste tire particles (g)	Waste tire particles (%)	Compressive strength (MPa) [#]
C0	118.1	0	0	18.6
C-1GTR	116.9	1.2	1	20.2
C-3GTR	114.6	3.5	3	18.0
C-5GTR	112.2	5.9	5	17.2

[#]data was extracted from Figure 1 of Martínez-Barrera et al. 2020 [148].

Blends of SBR, GTR and polyfunctional monomers namely trimethylolpropane trimethacrylate (TMPTMA) and trimethylolpropane triacrylate (TMPTA) were prepared and cross-linked via gamma radiation of up to 100 kGy [170]. The composites were prepared by a two-roll mill at 60 °C and a batch mixer at 120 °C for 15 min, followed by compression molding at 150 °C. The study reported an increase in the tensile strength and hardness with radiation dosage up to 100 kGy. However the gel content of the composites increased with an increase in radiation dosage

up to 75 kGy and levelled off at 100 kGy. Composites containing TMPTA had higher gel contents compared to the composites with TMPTMA.

In other study, GTR was exposed to gamma irradiation at 100, 200 and 300 kGy doses and incorporated into asphalt at 5 wt. % and 10 wt. % [171]. It was found that the results of the 10 % of GTR treated with gamma rays at 300 kGy had higher temperature stability, low temperature ductility and good anti-aging performance. This observation was with the highest adsorption of asphalt molecules by GTR treated with gamma rays.

3. Advantages and Limitations of Surface Modification of GTR Composites

The chemical surface etching modification methods for GTR discussed in this study are very diverse and some are proven to compatibilize GTR in various matrices (e.g. polymer, bitumen or concrete). Table 5 presents the effects of GTR source, its particle size, mixing techniques and treatment methods on the obtained results and observations of GTR composites. Several acids have been used for surface etching of GTR and high concentration H_2SO_4 has been found to be the most effective. Based on Table 5, ozonation and radiation treatment methods have been preferred as they are solvent-free. The effectiveness of these treatment methods depends on higher temperature for ozone, higher radiation dosages and longer exposure time in both cases.

There are challenges with regards to some GTR chemical modification methods, for instance, most of the methods require complex reaction set ups, processes and long treatment times. For gamma irradiation, it must be noted that some studies recommended extended periods for treatment of GTR, up to 3 d, before it could be incorporated in the matrix [55]. This method is clearly not ideal for industrial applications as it leads to prolonged waiting times which could potentially mean economic losses to the company. The aged GTR has carboxylic acid

functionality on its surface hence when incorporated in the concrete mixture, it is known to react with the alkaline content of the cement, eg. $\text{Ca}(\text{OH})_2$, hence contaminating its structure. This necessitates pre-treatment of GTR with bases such as NaOH is common to convert the acid on the surface to a sodium salt. Another issue with both acid etching and hydroxylation treatment methods is post-treatment step that requires neutralization. This step always adds cost to the surface treatment of GTR.

The summary of the matrices modified with GTR of various surface functionalities is shown in Table 6. From the studies examined in the current review, most research works have focused on construction and thermoplastic industries. Overall, the potential applications of modified GTR composites are in automotive, construction and building applications such as road pavements, roofing, isolations, and vibration absorbance.

Table 5: Summary of the effects of GTR source, particle size, mixing techniques and treatment methods on the results and observations of GTR composites.

Application	Matrix	GTR particle size & source	Mixing technique	Treatment method	Results and observations of the on composites	Ref
Construction	Concrete	300–600 μm of the rubber tire.	Compression molding	Oxidation	The optimal conditions for oxidation reaction were temperature of 250 $^{\circ}\text{C}$ and O_2/N_2 ratio of ≤ 0.04 .	[125]
	Cement	25.5–50.8 mm of the car and truck tires.	Cast, demolded and cured	Hydroxylation	The flexural strength of the composites decreased after NaOH treatment, and it was noticeable with larger GTR particle size.	[133]
	Concrete	7 and 20 mesh of the rubber tire.	Compression molding	Gamma radiation	For similar GTR content in the composites, splitting strength increased with smaller particle size (7 mesh) and increase in radiation dosage to maximum of 300 kGy.	[55]
Thermoplastic	HDPE	400–600 μm the of rubber tire.	Two-roll mill; Compression molding	Acid etching.	The surface roughness, micro pores and cavities of GTR increased with H_2SO_4 treatment compared to HNO_3 and HClO_4 .	[115]



	PP	3–5 mm of the rubber particle.	Batch mixer; Compression molding	Acid etching	Compressive yield strength of the H ₂ SO ₄ - treated GTR composites was superior to untreated ones for the similar GTR content. [117]
	HDPE	400–500 μm of the car and truck tires.	Batch mixer; Injection molding	Oxidation	The optimum DCP content for GTR surface oxidation was 2 wt. %. The lower and higher DCP contents gave partially cured and over-cured composites, respectively. [122]
Elastomers	NBR & NR	Average value of 390 μm for car and truck tires.	Batch mixer; Compression molding	Microwave	The microwave exposure time of 10 min resulted into surface modification and reclaiming of polymer backbone of GTR. [109]
	NR	Average value of 390 μm for car and truck tires.	Batch mixer; Compression molding	Microwave	The tensile properties of the truck tire composites improved after microwave treatment compared to car tire composites due to high NR content in truck tires. [158]
	SBR	80 mesh of the rubber tire.	Two-roll mill; Batch mixer; Compression	Gamma radiation	The gel content of the composites increased with an increase in radiation dosage up to 75 kGy and levelled off at [170]



			molding		100 kGy.	
Thermosets	PVC resin	160–205 μm of the cryogenic rubber tire.	Batch mixer; Two-roll mill	Acid etching	The tensile strength of the composites increased with TCI content up to 3 wt. % and thereafter it decreased due to formation of chlorinated layer on the GTR surface.	[120]
	Polyester resin	0.85–1.70 mm of the cryogenic rubber particle.	Compression molding	Hydroxylation	NaOH reacted with zinc stearate in waste rubber to form washable sodium stearate that created wider micro-crack and more micropores on rubber surface.	[138]
	Bisphenol epoxy resin	160–205 μm of the side wall rubber tire.	Batch mixer; Glass molding	Microwave	Flexural stress at break of the composites increased with microwave power up to 750 W and thereafter it decreased at 900 W.	[168]



Table 6: Summary of GTR modification methods for a specific matrix and resulting composite properties. Most studies on the surface modification of GTR have been employed in construction industry and followed by thermoplastic applications.

Application	Matrix	Modification methods	Improved Composite Properties	Ref
Construction	Concrete	Hydroxylation; gamma radiation; Oxidation	Elastic modulus; compressive strength; fracture energy; flexural strength; splitting tensile strength.	[11] [55] [125] [130] [133] [148]
		Cement paste	Oxidation; hydroxylation	Adhesion strength; compressive strength.
	Wood-cement	Plasma	Compact ratio and dimensional stability of the panels	[151]
Thermoplastic	HDPE	Oxidation; acid etching.	Tensile strength; elongation at break; impact energy; adhesion strength; melting enthalpy energy	[75] [115] [116] [122]



	LDPE	Oxidation	Elongation at break; impact energy.	[122]
	PP	Acid etching	Compressive yield strength; adhesion strength.	[117]
Road Pavement	Paving binder	Oxidation; microwave.	Elastic recovery; storage modulus.	[124]
	Asphalt binder	Microwave	storage stability; Loss modulus; pavement rutting parameter	[167]
Rubbers	NBR and NR	Microwave	Adhesion strength; Young's modulus.	[109]
	NR	Microwave	Tensile properties	[158]
	SBR	Gamma radiation	Tensile strength; hardness; gel content	[170]
Thermoset	PVC resin	Acid etching	Elongation at break; tensile strength.	[120]
	Polyester resin	Hydroxylation	tensile strength; adhesion strength	[138]



Bisphenol	Microwave	Flexural stress at break increased with	[168]
epoxy resin		microwave energy	

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4. Conclusions and Future Trends in GTR Composites

Uncontrolled disposal of waste tires into the environment is a huge, global problem, which enforced industry and researchers to searching new direction of waste tire recycling. Application of ground tire rubber (GTR) into various matrices and development of environmentally-friendly composites is one of possibility to solve this burning issue. Unfortunately, GTR is incompatible with most matrices, especially hydrophobic matrices such as cement, concrete and hydrophilic polymers, due to its hydrophobicity and cross-linked nature.

In this work, an overview of surface chemical modification methods for GTR was reviewed as summarized in Table 7. The chemical modification of the GTR with simple bench top chemicals such as acids, bases, and with strong oxidizing agents proved to compatibilize the GTR with various matrices. The research evolved into radiation methods for surface modification. These methods introduce, among others, the peroxides and the hydroperoxides groups onto the GTR surface, making GTR compatible with most polar matrices such as cement. It has also been found that various approaches can be considered in modifying the surface of GTR for compatibilization with the same matrix. For instance, compatibilization of GTR with cement/concrete has been achieved via hydroxylation and radiation methods. However, we found the literature to be lacking in studies that assesses various GTR modification methods on one type of matrix in the same study. We believe that such studies could further advance knowledge and aid the end user in making the decision pertaining to the GTR surface modification method that gives better properties without incurring extra manufacturing costs.

In our opinion, future research work on surface chemical modification should be focused on four main targets: i) research and development of novel, low-cost and green modifiers of GTR; ii)



studies of scaling up from batch methods to continuous methods in order to verify laboratory results and their possible industrial applications; iii) investigation of efficiency of modified/functionalized GTR as function of time (to solve the storage stability issues); iv) characterization of liquid and volatile by-products formed during modification/functionalization of GTR and evaluation of their impact on environment and human health (lack of such data can be a strong limitation in application of selected method at industrial scale).

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Table 7: Summary of the surface etching chemical methods, experimental conditions and analysis techniques used to confirm surface modification of GTR. Plasma, microwave and gamma radiation are solvent-free and environmental friendly surface modification methods for GTR.

Chemical Methods	Modifier agent	Experimental Conditions	Test to confirm modification and attained properties	Ref
Acid etching	H ₂ SO ₄ , HNO ₃ and blend of the two acids	GTR particles with size of < 200, 200–500 and >500 μm were immersed in acidic solutions for 2 min at room temperature and neutralized by NaOH solution.	DSC and SEM were used. Tensile strength increased with < 200 μm GTR particle size for HDPE composites.	[116]
	H ₂ SO ₄ acid	GTR with particle size of 3–5 mm was immersed in 97 wt. % of acid for 1 min and neutralized by NaOH solution at room temperature.	SEM and FTIR were used. Slight improvement in yield strength of PP composites.	[117]
	TCI acid	160–205 μm GTR was immersed in methanol solution of 1, 3 and 5 wt. % of acid for 20 min and rinsed with distilled water at 25 °C.	FTIR and XPS were used. Elongation at break improved with 5 wt.% acid for thermoset composites.	[120]



Oxidation	DCP	400–500 μm GTR was immersed in cyclohexane solvent with 0.1–2.0 wt. % of peroxide for 2 h and the solvent was evaporated.	In-situ SEM and DSC were used. There was improvement of fracture energy for HDPE composites.	[122]
	KMnO ₄	40 mesh GTR was immersed in (1) acidic medium of 5 wt. % of KMnO ₄ for 2 h and (2) sodium bisulfite solution for 0.5–1 h at 60 °C.	FTIR and contact angle were used. There was 41 % increase in adhesion strength for concrete composites.	[123]
	NaClO	40–100 mesh GTR was stirred in 1.4 M of NaClO solution for 3 h at 40 °C. GTR was dried and grinded prior to use.	SEM and FTIR were used. Elastic recovery improved by 60 % for asphalt composites.	[124]
Hydroxylation	NaOH	35 mesh of GTR was immersed in saturated solution of hydroxide for 20 min and rinsed with distilled water at room temperature.	FTIR and contact angle were used. Enhanced fracture energy and toughness properties for cement composites.	[130]
	NaOH and Ca(OH) ₂	GTR with particle size of 2.36 and 4.75 mm was immersed in NaOH and Ca(OH) ₂ solutions with	Light microscope was used. There was a poor interfacial bonding for cement	[134]



		pH=10 and 12, respectively for 4 min.	composites.	
	NaOH	Waste rubber crumb with size of 0.85–1.70 mm was soaked in 10 wt. % of NaOH solution for 2 h and rinsed with distilled water at room temperature.	Contact angle, FTIR and SEM were used. Improvement of tensile strength for polyester composites.	[138]
Plasma	Plasma model DT-03 Suzhou OPS Plasma Technology	120 μ m GTR powder was carried out by using a plasma surface treatment apparatus model. The high-frequency generator was turned on for 180 s.	Treated GTR dispersed better in water and XPS confirmed the presence of oxygen containing species on the GTR surface.	[146]
	Air plasma of 12 kV power	GTR was treated with air plasma of 12 kV power and 0.06 A for 5–20 min.	FTIR technique was used to confirm modification of GTR. Surface roughness increased with plasma exposure time. Compact ratio and dimensional stability of the panels increased after treatment.	[151]
	Low Temperature Plasma of 60 and	The low temperature plasma was employed to modify the GTR powder at 60 and 100 W power	Surface roughness for the treated GTR powder increased. The FTIR and XPS	[152]



	100 W power	was employed for 150 s at each power level.	results showed new functional groups on GTR sample after plasma treatment.	
Microwave (MW)	MW power of 700 W	MW Exposure time of 3, 5 and 10 min. 60 g of GTR with average particle size of 390 μm was stirred with speed of 80 rpm	FTIR and SEM were used. There was 19 % increase in Young's modulus for NBR/NR composites.	[109]
	MW power of 800 W	MW Exposure time of 90 s. GTR with particle size of 0.35 mm was stirred with speed of 2000 rpm.	FTIR, TGA and AFM were used. There was a slight improvement in pavement rutting parameter for asphalt composites	[167]
	MW power of 350–900 W	MW Exposure time of 15 and 60 s. 2.7 g of GTR with particle size of 200–250 μm was used.	SEM and FTIR were used. There was increase in flexural stress at break for epoxy resin composites.	[168]
Gamma radiation	Gamma Beam 651–PT with ^{60}Co .	200, 250 and 300 kGy at a dose rate of 2.5 kGy/h was used to treat GTR of both 7 mesh and 20 mesh	Increased unit volume, improved aeration, decreasing compressive and splitting tensile strength for composite.	[55]



Transelektro LGI- 200, 250 and 300 kGy at a dose rate of 2.5 kGy/h Improved elastic modulus and [148]
01 IZOTOP was used to treat 7 mesh and 20 mesh GTR. deformation with increase in radiation
dose

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References

- [1] Fortman DJ, Brutman JP, De Hoe GX, Snyder RL, Dichtel WR, Hillmyer MA. Approaches to sustainable and continually recyclable cross-linked polymers. *ACS Sustain Chem Eng* 2018;6:11145–59. <https://doi.org/10.1021/acssuschemeng.8b02355>.
- [2] Nakomcic-Smaragdakis B, Cepic Z, Senk N, Doric J, Radovanovic L. Use of scrap tires in cement production and their impact on nitrogen and sulfur oxides emissions. *Energy Sources, Part A Recover Util Environ Eff* 2016;38:485–93. <https://doi.org/10.1080/15567036.2013.787473>.
- [3] Sharma VK, Fortuna F, Mincarini M, Berillo M, Cornacchia G. Disposal of waste tyres for energy recovery and safe environment. *Appl Energy* 2000;65:381–94. [https://doi.org/10.1016/S0306-2619\(99\)00085-9](https://doi.org/10.1016/S0306-2619(99)00085-9).
- [4] Czajczyńska D, Krzyżyńska R, Jouhara H, Spencer N. Use of pyrolytic gas from waste tire as a fuel: A review. *Energy* 2017;134:1121–31. <https://doi.org/10.1016/j.energy.2017.05.042>.
- [5] Chen W, Feng H, Shen D, Jia Y, Li N, Ying X, et al. Carbon materials derived from waste

- tires as high-performance anodes in microbial fuel cells. *Sci Total Environ* 2018;618:804–9. <https://doi.org/10.1016/j.scitotenv.2017.08.201>.
- [6] Al-Rahbi AS, Williams PT. Production of activated carbons from waste tyres for low temperature NO_x control. *Waste Manag* 2016;49:188–95. <https://doi.org/10.1016/j.wasman.2016.01.030>.
- [7] Martínez JD, Cardona-Urbe N, Murillo R, García T, López JM. Carbon black recovery from waste tire pyrolysis by demineralization: Production and application in rubber compounding. *Waste Manag* 2019;85:574–84. <https://doi.org/10.1016/j.wasman.2019.01.016>.
- [8] Fernández-Berridi MJ, González N, Mugica A, Bernicot C. Pyrolysis-FTIR and TGA techniques as tools in the characterization of blends of natural rubber and SBR. *Thermochim Acta* 2006;444:65–70. <https://doi.org/10.1016/j.tca.2006.02.027>.
- [9] Williams PT. Pyrolysis of waste tyres: A review. *Waste Manag* 2013;33:1714–28. <https://doi.org/10.1016/j.wasman.2013.05.003>.
- [10] Martínez JD, Puy N, Murillo R, García T, Navarro MV, Mastral AM. Waste tyre pyrolysis – A review. *Renew Sustain Energy Rev* 2013;23:179–213. <https://doi.org/10.1016/j.rser.2013.02.038>.
- [11] Meddah A, Beddar M, Bali A. Use of shredded rubber tire aggregates for roller compacted concrete pavement. *J Clean Prod* 2014;72:187–92. <https://doi.org/10.1016/j.jclepro.2014.02.052>.

- [12] Ho AC, Turatsinze A, Hameed R, Vu DC. Effects of rubber aggregates from grinded used tyres on the concrete resistance to cracking. *J Clean Prod* 2012;23:209–15. <https://doi.org/10.1016/j.jclepro.2011.09.016>.
- [13] Adhikari B, De D, Maiti S. Reclamation and recycling of waste rubber. *Prog Polym Sci* 2000;25:909–48. [https://doi.org/10.1016/S0079-6700\(00\)00020-4](https://doi.org/10.1016/S0079-6700(00)00020-4).
- [14] Dubkov KA, Semikolenov SV, Ivanov DP, Babushkin DE, Panov GI, Parmon VN. Reclamation of waste tyre rubber with nitrous oxide. *Polym Degrad Stabil* 2012;97:1123–30. <https://doi.org/10.1016/j.polymdegradstab.2012.04.006>.
- [15] Jacob P, Kashyap P, Suparat T, Visvanathan C. Dealing with emerging waste streams: Used tyre assessment in Thailand using material flow analysis. *Waste Manag Res* 2014;32:918–26. <https://doi.org/10.1177/0734242X14543554>.
- [16] De D, Das A, De D, Dey B, Debnath SC, Roy BC. Reclaiming of ground rubber tire (GRT) by a novel reclaiming agent. *Eur Polym J* 2006;42:917–27. <https://doi.org/10.1016/j.eurpolymj.2005.10.003>.
- [17] Rani S, Agnihotri R. Recycling of scrap tyres. *Int J Mater Sci Appl* 2014;3:164. <https://doi.org/10.11648/j.ijmsa.20140305.16>.
- [18] Gagol M, Boczkaj G, Haponiuk J, Formela K. Investigation of volatile low molecular weight compounds formed during continuous reclaiming of ground tire rubber. *Polym Degrad Stabil* 2015;119:113–20. <https://doi.org/10.1016/j.polymdegradstab.2015.05.007>.
- [19] Formela K, Bogucki M. Use of response surface methodology in characterization of

- properties of recycled high density polyethylene/ground tire rubber compositions. *Polimery/Polymers* 2014;59:488–94. <https://doi.org/10.14314/polimery.2014.488>.
- [20] Zhang X, Saha P, Cao L, Li H, Kim J. Devulcanization of waste rubber powder using thiobisphenols as novel reclaiming agent. *Waste Manag* 2018;78:980–91. <https://doi.org/10.1016/j.wasman.2018.07.016>.
- [21] Zhang X, Lu Z, Tian D, Li H, Lu C. Mechanochemical devulcanization of ground tire rubber and its application in acoustic absorbent polyurethane foamed composites. *J Appl Polym Sci* 2013;127:4006–14. <https://doi.org/10.1002/app.37721>.
- [22] Padella F.; D’Uva, G.; La Barbera, A.; Cataldo, F. F. C. Recycling of scrap tires rubber by mechanochemical devulcanization. *Polym Recycl* 2001;6:16.
- [23] Cavalieri F, Padella F, Cataldo F. Mechanochemical surface activation of ground tire rubber by solid-state devulcanization and grafting. *J Appl Polym Sci* 2003;90:1631–8. <https://doi.org/10.1002/app.12829>.
- [24] Ghorai S, Bhunia S, Roy M, De D. Mechanochemical devulcanization of natural rubber vulcanizate by dual function disulfide chemicals. *Polym Degrad Stabil* 2016;129:34–6. <https://doi.org/10.1016/j.polymdegradstab.2016.03.024>.
- [25] Phiri MM, Sibeko MA, Phiri MJ, Hlangothi SP. Effect of free foaming and pre-curing on the thermal, morphological and physical properties of reclaimed tyre rubber foam composites. *J Clean Prod* 2019;218:665–72. <https://doi.org/10.1016/j.jclepro.2019.02.051>.
- [26] Gumede JI, Carson J, Hlangothi SP, Bolo LL. Effect of single-walled carbon nanotubes on

- the cure and mechanical properties of reclaimed rubber/natural rubber blends. *Mater Today Commun* 2020;23:100852. <https://doi.org/10.1016/j.mtcomm.2019.100852>.
- [27] Phiri MJ, Phiri MM, Mpitso K, Hlangothi SP. Curing, thermal and mechanical properties of waste tyre derived reclaimed rubber–wood flour composites. *Mater Today Commun* 2020;101204. <https://doi.org/10.1016/j.mtcomm.2020.101204>.
- [28] Satapathy S, Nag A, Nando GB. Thermoplastic elastomers from waste polyethylene and reclaim rubber blends and their composites with fly ash. *Process Saf Environ Prot* 2010;88:131–41. <https://doi.org/10.1016/j.psep.2009.12.001>.
- [29] De D, Panda PK, Roy M, Bhunia S. Reinforcing effect of reclaim rubber on natural rubber/polybutadiene rubber blends. *Mater Des* 2013;46:142–50. <https://doi.org/10.1016/j.matdes.2012.10.014>.
- [30] Ramarad S, Ratnam CT, Khalid M, Chuah AL. Improving the properties of reclaimed waste tire rubber by blending with poly(ethylene-co-vinyl acetate) and electron beam irradiation. *J Appl Polym Sci* 2015;132:41649. <https://doi.org/10.1002/app.41649>.
- [31] Liang SB, Hao YC. A novel cryogenic grinding system for recycling scrap tire peels. *Adv Powder Technol* 2000;11:187–97. <https://doi.org/10.1163/156855200750172303>.
- [32] Wang Q, Huang Z, Liu Z. Overview of high-value reuse and grinding at sub-zero temperature of scrap rubber tires. *IOP Conf Ser Mater Sci Eng* 2019;472:12071. <https://doi.org/10.1088/1757-899x/472/1/012071>.
- [33] Sienkiewicz M, Borzędowska-Labuda K, Zalewski S, Janik H. The effect of tyre rubber

- grinding method on the rubber-asphalt binder properties. *Constr Build Mater* 2017;154:144–54. <https://doi.org/10.1016/j.conbuildmat.2017.07.170>.
- [34] Thives LP, Pais JC, Pereira PAA, Trichês G, Amorim SR. Assessment of the digestion time of asphalt rubber binder based on microscopy analysis. *Constr Build Mater* 2013;47:431–40. <https://doi.org/10.1016/j.conbuildmat.2013.05.087>.
- [35] Asaro L, Gratton M, Seghar S, Aït Hocine N. Recycling of rubber wastes by devulcanization. *Resour Conserv Recycl* 2018;133:250–62. <https://doi.org/10.1016/j.resconrec.2018.02.016>.
- [36] Gyorgy M. Apparatus for regular grinding rubber vehicle tires and other elastic materials by ultra high-pressure fluid. Patent Number: PCT/HU2009/000061, 2009.
- [37] Adhikari J, Das A, Sinha T, Saha P, Kim JK. Chapter 1: Grinding of waste rubber. *Rubber Recycl. Challenges Dev. R. Soc. Chem.*, Cambridge: 2018, p. 1–23. <https://doi.org/10.1039/9781788013482-00001>.
- [38] Sienkiewicz M, Janik H, Borzędowska-Labuda K, Kucińska-Lipka J. Environmentally friendly polymer-rubber composites obtained from waste tyres: A review. *J Clean Prod* 2017;147:560–71. <https://doi.org/10.1016/j.jclepro.2017.01.121>.
- [39] Haworth B, Chadwick D, Chen L, Ang YJ. Thermoplastic composite beam structures from mixtures of recycled HDPE and rubber crumb for acoustic energy absorption. *J Thermoplast Compos Mater* 2016;31:119–42. <https://doi.org/10.1177/0892705716681836>.
- [40] Karger-Kocsis J, Mészáros L, Bárány T. Ground tyre rubber (GTR) in thermoplastics,

- thermosets, and rubbers. *J Mater Sci* 2013;48:1–38. <https://doi.org/10.1007/s10853-012-6564-2>.
- [41] Fazli A, Rodrigue D. Waste rubber recycling: A review on the evolution and properties of thermoplastic elastomers. *Materials* (Basel) 2020;13:782. <https://doi.org/10.3390/ma13030782>.
- [42] da Costa HM, Ramos VD, da Silva WS, Sirqueira AS. Analysis and optimization of polypropylene (PP)/ethylene–propylene–diene monomer (EPDM)/scrap rubber tire (SRT) mixtures using RSM methodology. *Polym Test* 2010;29:572–8. <https://doi.org/10.1016/j.polymertesting.2010.04.003>.
- [43] Céspedes, R., Gámez, J., Velázquez, M., Belmontes, F., León, R., Fernández, O., Orta, C., Hernández E. Thermoplastic elastomers based on high-density polyethylene, ethylene–propylene–diene terpolymer, and ground tire rubber dynamically vulcanized with dicumyl peroxide. *J Appl Polym Sci* 2014;131:39901–8. <https://doi.org/10.1002/app.39901>.
- [44] Egodage SM, Harper JF, Walpalage S. Effect of maleimide curing on mechanical properties of ground tyre rubber/waste polypropylene blends. *Plast Rubber Compos* 2012;41:332–40. <https://doi.org/10.1179/1743289811Y.0000000042>.
- [45] Formela K, Cysewska M, Korol J. Effect of compounding conditions on static and dynamic mechanical properties of high density polyethylene/ground tire rubber blends. *Int Polym Process* 2014;29:272–9. <https://doi.org/10.3139/217.2849>.
- [46] Ratna D, Banthia AK. Rubber toughened epoxy. *Macromol Res* 2004;12:11–21. <https://doi.org/10.1007/BF03218989>.



- [47] Piszczyk Ł, Hejna A, Danowska M, Strankowski M, Formela K. Polyurethane/ground tire rubber composite foams based on polyglycerol: Processing, mechanical and thermal properties. *J Reinf Plast Compos* 2015;34:708–17. <https://doi.org/10.1177/0731684415579089>.
- [48] Piszczyk Ł, Hejna A, Formela K, Danowska M, Strankowski M. Effect of ground tire rubber on structural, mechanical and thermal properties of flexible polyurethane foams. *Iran Polym J* 2015;24:75–84. <https://doi.org/10.1007/s13726-014-0301-4>.
- [49] Nikje MMA, Tehrani ZM. Thermal and mechanical properties of polyurethane rigid foam/modified nanosilica composite. *Polym Eng Sci* 2010;50:468–73. <https://doi.org/10.1002/pen.21559>.
- [50] Müller M, Valášek P, Rudawska A, Chotěborský R. Effect of active rubber powder on structural two-component epoxy resin and its mechanical properties. *J Adhes Sci Technol* 2018;32:1531–47. <https://doi.org/10.1080/01694243.2018.1428040>.
- [51] Jun Z, Xiang-ming W, Jian-min C, Kai Z. Optimization of processing variables in wood–rubber composite panel manufacturing technology. *Bioresour Technol* 2008;99:2384–91. <https://doi.org/10.1016/J.BIORTECH.2007.05.031>.
- [52] Formela K, Hejna A, Zedler Ł, Przybysz M, Ryl J, Saeb MR, et al. Structural, thermal and physico-mechanical properties of polyurethane/brewers' spent grain composite foams modified with ground tire rubber. *Ind Crops Prod* 2017;108:844–52. <https://doi.org/10.1016/j.indcrop.2017.07.047>.
- [53] Abu-Jdayil B, Mourad A-H, Hussain A. Thermal and physical characteristics of



- polyester–scrap tire composites. *Constr Build Mater* 2016;105:472–9. <https://doi.org/10.1016/j.conbuildmat.2015.12.180>.
- [54] Hejna A, Korol J, Przybysz-Romatowska M, Zedler Ł, Chmielnicki B, Formela K. Waste tire rubber as low-cost and environmentally-friendly modifier in thermoset polymers – A review. *Waste Manag* 2020;108:106–18. <https://doi.org/10.1016/j.wasman.2020.04.032>.
- [55] Herrera-Sosa ES, Martínez-Barrera G, Barrera-Díaz C, Cruz-Zaragoza E, Ureña-Núñez F. Recovery and modification of waste tire particles and their use as reinforcements of concrete. *Int J Polym Sci* 2015;2015:8. <https://doi.org/10.1155/2015/234690>.
- [56] Zhang H, Gou M, Liu X, Guan X. Effect of rubber particle modification on properties of rubberized concrete. *J Wuhan Univ Technol Sci Ed* 2014;29:763–8. <https://doi.org/10.1007/s11595-014-0993-5>.
- [57] Pacheco-Torgal F, Ding Y, Jalali S. Properties and durability of concrete containing polymeric wastes (tyre rubber and polyethylene terephthalate bottles): An overview. *Constr Build Mater* 2012;30:714–24. <https://doi.org/10.1016/j.conbuildmat.2011.11.047>.
- [58] Thomas BS, Gupta RC. A comprehensive review on the applications of waste tire rubber in cement concrete. *Renew Sustain Energy Rev* 2016;54:1323–33. <https://doi.org/10.1016/j.rser.2015.10.092>.
- [59] Sofi A. Effect of waste tyre rubber on mechanical and durability properties of concrete – A review. *Ain Shams Eng J* 2018;9:2691–700. <https://doi.org/10.1016/j.asej.2017.08.007>.
- [60] Eiras JN, Segovia F, Borrachero MV, Monzó J, Bonilla M, Payá J. Physical and

- mechanical properties of foamed Portland cement composite containing crumb rubber from worn tires. *Mater Des* 2014;59:550–7. <https://doi.org/10.1016/j.matdes.2014.03.021>.
- [61] Zedler Ł, Colom X, Saeb MR, Formela K. Preparation and characterization of natural rubber composites highly filled with brewers' spent grain/ground tire rubber hybrid reinforcement. *Compos Part B Eng* 2018;145:182–8. <https://doi.org/10.1016/j.compositesb.2018.03.024>.
- [62] Zhang X, Zhu X, Liang M, Lu C. Improvement of the properties of ground tire rubber (GTR)-filled nitrile rubber vulcanizates through plasma surface modification of GTR powder. *J Appl Polym Sci* 2009;114:1118–25. <https://doi.org/10.1002/app.30626>.
- [63] Yehia AA, Mull MA, Ismail MN, Hefny YA, Abdel-Bary EM. Effect of chemically modified waste rubber powder as a filler in natural rubber vulcanizates. *J Appl Polym Sci* 2004;93:30–6. <https://doi.org/10.1002/app.20349>.
- [64] Formela K, Formela M, Thomas S, Haponiuk J. Styrene-butadiene rubber/modified ground tire rubber blends co-vulcanization: Effect of accelerator type. *Macromol Symp* 2016;361:64–72. <https://doi.org/10.1002/masy.201500024>.
- [65] Formela K, Haponiuk J. Characterization and properties of LDPE/(ground tire rubber)/crosslinked butyl rubber blends. *J Vinyl Addit Technol* 2014;20:237–42. <https://doi.org/10.1002/vnl.21363>.
- [66] Formela K, Haponiuk JT. Curing characteristics, mechanical properties and morphology of butyl rubber filled with ground tire rubber (GTR). *Iran Polym J* 2014;23:185–94. <https://doi.org/10.1007/s13726-013-0214-7>.

- [67] Lo Presti D. Recycled tyre rubber modified bitumens for road asphalt mixtures: A literature review. *Constr Build Mater* 2013;49:863–81. <https://doi.org/10.1016/j.conbuildmat.2013.09.007>.
- [68] López-Moro FJ, Moro MC, Hernández-Olivares F, Witoszek-Schultz B, Alonso-Fernández M. Microscopic analysis of the interaction between crumb rubber and bitumen in asphalt mixtures using the dry process. *Constr Build Mater* 2013;48:691–9. <https://doi.org/10.1016/j.conbuildmat.2013.07.041>.
- [69] Yousefi Kebria D, Moafimadani SR, Goli Y. Laboratory investigation of the effect of crumb rubber on the characteristics and rheological behaviour of asphalt binder. *Road Mater Pavement Des* 2015;16:946–56. <https://doi.org/10.1080/14680629.2015.1042015>.
- [70] Cao W. Study on properties of recycled tire rubber modified asphalt mixtures using dry process. *Constr Build Mater* 2007;21:1011–5. <https://doi.org/10.1016/j.conbuildmat.2006.02.004>.
- [71] Ali AH, Mashaan NS, Karim MR. Investigations of physical and rheological properties of aged rubberised bitumen. *Adv Mater Sci Eng* 2013;2013:7. <https://doi.org/10.1155/2013/239036>.
- [72] Cong P, Xun P, Xing M, Chen S. Investigation of asphalt binder containing various crumb rubbers and asphalts. *Constr Build Mater* 2013;40:632–41. <https://doi.org/10.1016/j.conbuildmat.2012.11.063>.
- [73] Behl A, Kumar G, Sharma G. Performance of low energy crumb rubber modified bituminous mixes. *Procedia - Soc Behav Sci* 2013;104:49–58.



- <https://doi.org/10.1016/j.sbspro.2013.11.097>.
- [74] Formela K, Sulkowski M, Saeb MR, Colom X, Haponiuk JT. Assessment of microstructure, physical and thermal properties of bitumen modified with LDPE/GTR/elastomer ternary blends. *Constr Build Mater* 2016;106:160–7. <https://doi.org/10.1016/j.conbuildmat.2015.12.108>.
- [75] Kim JI, Ryu SH, Chang YW. Mechanical and dynamic mechanical properties of waste rubber powder/HDPE composite. *J Appl Polym Sci* 2000;77:2595–602. [https://doi.org/10.1002/1097-4628\(20000919\)77:12<2595::AID-APP60>3.0.CO;2-C](https://doi.org/10.1002/1097-4628(20000919)77:12<2595::AID-APP60>3.0.CO;2-C).
- [76] Laun G, Hallak T, Strecker K, Luis A, Paine K. Investigations on cementitious composites based on rubber particle waste additions 2013;16:259–68. <https://doi.org/10.1590/S1516-14392012005000177>.
- [77] Siddique R, Naik TR. Properties of concrete containing scrap-tire rubber – an overview. *Waste Manag* 2004;24:563–9. <https://doi.org/10.1016/j.wasman.2004.01.006>.
- [78] Shao L, Ji Z-Y, Ma J-Z, Xue C-H, Ma Z-L, Zhang J. The synergy of double cross-linking agents on the properties of styrene butadiene rubber foams. *Sci Rep* 2016;6:36931. <https://doi.org/10.1038/srep36931>.
- [79] Phiri MM, Sibeko MA, Hlangothi SP, John MJ. Chapter 4: Waste rubber based composite foams. vol. 1. 2019. <https://doi.org/10.1039/9781788013482-00083>.
- [80] Piszczyk L, Hejna A, Formela K, Danowska M, Strankowski M. Rigid polyurethane foams modified with ground tire rubber - mechanical, morphological and thermal Studies.

- Cell Polym 2015;34:45–62. <https://doi.org/10.1177/026248931503400201>.
- [81] Directive 2006/12/EC. Directive 2006-12-12-EC of the European Parliament and of the Council of 5 April 2007 on waste 2006.
- [82] ETRma. Europe - 92% of all end of life tyres collected and treated in 2017 2019.
- [83] Coiai, S., Passaglia, E., Ciardelli, F., Tirelli, D., Peruzzotti, F. and Resmini E. Modification of cross-linked rubber particles by free radical polymerization. *Macromol Symp* 2006;234:193–202. <https://doi.org/doi:10.1002/masy.200650225>.
- [84] De D, De D. Processing and material characteristics of a reclaimed ground rubber tire reinforced styrene butadiene rubber. *Mater Sci Appl* 2011;2:486–95. <https://doi.org/10.4236/msa.2011.25066>.
- [85] Bockstal L, Berchem T, Schmetz Q, Richel A. Devulcanisation and reclaiming of tires and rubber by physical and chemical processes: A review. *J Clean Prod* 2019;236:117574. <https://doi.org/10.1016/j.jclepro.2019.07.049>.
- [86] Formela K, Cysewska M, Haponiuk J, Stasiak A. 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. *Polimery/Polymers* 2013;58:906–12. <https://doi.org/10.14314/polimery.2013.906>.
- [87] Formela K, Cysewska M, Haponiuk JT. Thermomechanical reclaiming of ground tire rubber via extrusion at low temperature: Efficiency and limits. *J Vinyl Addit Technol* 2016;22:213–21. <https://doi.org/10.1002/vnl.21426>.



- [88] Formela K, Cysewska M. Efficiency of thermomechanical reclaiming of ground tire rubber conducted in counter-rotating and co-rotating twin screw extruder. *Polimery/Polymers* 2014;59:231–8. <https://doi.org/10.14314/polimery.2014.231>.
- [89] Yazdani H, Karrabi M, Ghasmi I, Azizi H, Bakhshandeh GR. Devulcanization of waste tires using a twin-screw extruder: The effects of processing conditions. *J Vinyl Addit Technol* 2011;17:64–9. <https://doi.org/10.1002/vnl.20257>.
- [90] Li Y, Shen A, Lyu Z, Wang S, Formela K, Zhang G. Ground tire rubber thermo-mechanically devulcanized in the presence of waste engine oil as asphalt modifier. *Constr Build Mater* 2019;222:588–600. <https://doi.org/10.1016/j.conbuildmat.2019.06.162>.
- [91] Formela K, Wąsowicz D, Formela M, Hejna A, Haponiuk J. Curing characteristics, mechanical and thermal properties of reclaimed ground tire rubber cured with various vulcanizing systems. *Iran Polym J* 2015;24:289–97. <https://doi.org/10.1007/s13726-015-0320-9>.
- [92] Balasubramanian M. Cure modeling and mechanical properties of counter rotating twin screw extruder devulcanized ground rubber tire—natural rubber blends. *J Polym Res* 2009;16:133–41. <https://doi.org/10.1007/s10965-008-9211-5>.
- [93] Zedler Ł, Kowalkowska-Zedler D, Vahabi H, Saeb MR, Colom X, Cañavate J, et al. Preliminary investigation on auto-thermal extrusion of ground tire rubber. *Materials (Basel)* 2019;12:1–16. <https://doi.org/10.3390/ma12132090>.
- [94] Hassan MM, Aly RO, Abdel Aal SE, El-Masry AM, Fathy ES. Mechanochemical devulcanization and gamma irradiation of devulcanized waste rubber/high density



- polyethylene thermoplastic elastomer. *J Ind Eng Chem* 2013;19:1722–9. <https://doi.org/10.1016/j.jiec.2013.02.012>.
- [95] Yehia AA, Ismail MN, Hefny YA, Abdel-Bary EM, Mull MA. Mechano-chemical reclamation of waste rubber powder and its effect on the performance of NR and SBR vulcanizates. *J Elastomers Plast* 2004;36:109–23. <https://doi.org/10.1177/0095244304039896>.
- [96] Wang X, Shi C, Zhang L, Zhang Y. Effects of shear stress and subcritical water on devulcanization of styrene-butadiene rubber based ground tire rubber in a twin-screw extruder. *J Appl Polym Sci* 2013;130:1845–54. <https://doi.org/10.1002/app.39253>.
- [97] Grigoryeva O, Fainleib A, Starostenko O, Danilenko I, Kozak N, Dudarenko G. Ground tire rubber (GTR) reclamation: virgin rubber / reclaimed GTR (RE)vulcanizates. *Rubber Chem Technol* 2004;77:131–46. <https://doi.org/10.5254/1.3547806>.
- [98] Hassan AA, Formela K, Wang S. Reclaimed rubber in situ grafted with soybean oil as a novel green reactive plasticizer in SBR/silica compounds. *ACS Sustain Chem Eng* 2019;7:14991–5001. <https://doi.org/10.1021/acssuschemeng.9b03339>.
- [99] Formela K, Klein M, Colom X, Saeb MR. Investigating the combined impact of plasticizer and shear force on the efficiency of low temperature reclaiming of ground tire rubber (GTR). *Polym Degrad Stabil* 2016;125:1–11. <https://doi.org/10.1016/j.polymdegradstab.2015.12.022>.
- [100] Li Y, Zhao S, Wang Y. Microbial desulfurization of ground tire rubber by *Thiobacillus ferrooxidans*. *Polym Degrad Stabil* 2011;96:1662–8.



- <https://doi.org/10.1016/j.polymdegradstab.2011.06.011>.
- [101] Romine RA, Romine MF. Rubbercycle: Abioprocess for surface modification of waste tyre rubber. *Polym Degrad Stab* 1998;59:353–8. [https://doi.org/10.1016/S0141-3910\(97\)00202-4](https://doi.org/10.1016/S0141-3910(97)00202-4).
- [102] Tatangelo V, Mangili I, Caracino P, Bestetti G, Collina E, Anzano M, et al. Microbial desulfurization of ground tire rubber (GTR): Characterization of microbial communities and rheological and mechanical properties of GTR and natural rubber composites (GTR/NR). *Polym Degrad Stabil* 2019;160:102–9. <https://doi.org/10.1016/j.polymdegradstab.2018.12.021>.
- [103] Cui X, Zhao S, Wang B. Microbial desulfurization for ground tire rubber by mixed consortium-*Sphingomonas* sp. and *Gordonia* sp. *Polym Degrad Stabil* 2016;128:165–71. <https://doi.org/10.1016/j.polymdegradstab.2016.03.011>.
- [104] Isayev AI, Liang T, Lewis TM. Effect of particle size on ultrasonic devulcanization of tire rubber in twin-screw extruder. *Rubber Chem Technol* 2013;87:86–102. <https://doi.org/10.5254/RCT.13.87926>.
- [105] Oh JS, Isayev AI. Ultrasonically treated polypropylene/ground tire rubber blends. *Rubber Chem Technol* 2002;75:617–25. <https://doi.org/10.5254/1.3544988>.
- [106] Feng W, Isayev AI. Blends of ultrasonically devulcanized tire-curing bladder and butyl rubber. *J Mater Sci* 2005;40:2883–9. <https://doi.org/10.1007/s10853-005-2423-8>.
- [107] Hong CK, Isayev AI. Plastic/rubber blends of ultrasonically devulcanized GRT with

- HDPE. *J Elastomers Plast* 2001;33:47–71. <https://doi.org/10.1106/5AMQ-XEAY-A05B-P1FY>.
- [108] Albano C, Camacho N, Reyes J, Feliu JL, Hernández M. Influence of scrap rubber addition to Portland I concrete composites: Destructive and non-destructive testing. *Compos Struct* 2005;71:439–46. <https://doi.org/10.1016/j.compstruct.2005.09.037>.
- [109] Cañavate J, Colom X, Saeb MR, Przybysz M, Zedler L, Formela K. Influence of microwave treatment conditions of GTR on physico-mechanical and structural properties of NBR/NR/GTR composites. *AFINIDAD* 2019;76:171–9. <https://doi.org/www.raco.cat/index.php/afinidad/article/view/361403>.
- [110] Cao X-W, Luo J, Cao Y, Yin X-C, He G-J, Peng X-F, et al. Structure and properties of deeply oxidized waste rubber crumb through long time ozonization. *Polym Degrad Stabil* 2014;109:1–6. <https://doi.org/10.1016/j.polymdegradstab.2014.06.014>.
- [111] Sadaka F, Campistron I, Laguerre A, Pilard J-F. Controlled chemical degradation of natural rubber using periodic acid: Application for recycling waste tyre rubber. *Polym Degrad Stabil* 2012;97:816–28. <https://doi.org/10.1016/j.polymdegradstab.2012.01.019>.
- [112] Ateeq M, Al-Shamma'a A. Experimental study on the optimisation of chemical treatment to reduce waste rubber aggregates absorption properties. *Constr Build Mater* 2016;126:274–85. <https://doi.org/10.1016/j.conbuildmat.2016.09.021>.
- [113] Colom X, Marín-Genescà M, Formela K, Cañavate J. Chapter 2. Surface treatment of rubber waste. *Rubber Recycl. Challenges Dev.*, vol. 1, 2018, p. 24–55. <https://doi.org/10.1039/9781788013482-00024>.

- [114] Zedler Ł, Przybysz M, Klein M, Saeb MR, Formela K. Processing, physico-mechanical and thermal properties of reclaimed GTR and NBR/reclaimed GTR blends as function of various additives. *Polym Degrad Stabil* 2017;143:186–95. <https://doi.org/10.1016/j.polymdegradstab.2017.07.004>.
- [115] Colom X, Carrillo F, 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. <https://doi.org/10.1016/j.compositesa.2006.01.022>.
- [116] Colom X, Cañavate J, Carrillo F, Sunol JJ. Effect of the particle size and acid pretreatments on compatibility and Properties of recycled HDPE plastic bottles filled with ground tyre powder. *J Appl Polym Sci* 2009;112:1182–890. <https://doi.org/10.1002/app.29611>.
- [117] Elenien KFA, Abdel-Wahab A, ElGamsy R, Abdellatif MH. Assessment of the properties of PP composite with addition of recycled tire rubber. *Ain Shams Eng J* 2018;9:3271–6. <https://doi.org/10.1016/j.asej.2018.05.001>.
- [118] Cepeda-Jiménez CM, Pastor-blas MM, Ferrándiz-Gómez TP, Martín-Martínez JM. Surface characterization of vulcanized rubber treated with sulfuric acid and its adhesion to polyurethane adhesive. *J Adhes* 2000;73:135–60. <https://doi.org/10.1080/00218460008029303>.
- [119] Pastor-Blas MM, Ferrándiz-Gómez TP, Martín-Martínez JM. Chlorination of vulcanized styrene-butadiene rubber using solutions of trichloroisocyanuric acid in different solvents. *J Adhes Sci Technol* 2000;14:561–81. <https://doi.org/10.1163/156856100742744>.



- [120] Naskar AK, De SK, Bhowmick AK. Surface chlorination of ground rubber tire and its characterization. *Rubber Chem Technol* 2001;74:645–61. <https://doi.org/10.5254/1.3544964>.
- [121] Sonnier R, Leroy E, Clerc L, Bergeret A, Lopez-Cuesta JM. Polyethylene/ground tyre rubber blends: Influence of particle morphology and oxidation on mechanical properties. *Polym Test* 2007;26:274–81. <https://doi.org/10.1016/j.polymertesting.2006.10.011>.
- [122] Sonnier R, Leroy E, Clerc L, Bergeret A, Lopez-Cuesta JM, Bretelle AS, et al. Compatibilizing thermoplastic/ground tyre rubber powder blends: Efficiency and limits. *Polym Test* 2008;27:901–7. <https://doi.org/10.1016/j.polymertesting.2008.07.003>.
- [123] He L, Ma Y, Liu Q, Mu Y. Surface modification of crumb rubber and its influence on the mechanical properties of rubber-cement concrete. *Constr Build Mater* 2016;120:403–7. <https://doi.org/10.1016/j.conbuildmat.2016.05.025>.
- [124] Han L, Zheng M, Li J, Li Y, Zhu Y, Ma Q. Effect of nano silica and pretreated rubber on the properties of terminal blend crumb rubber modified asphalt. *Constr Build Mater* 2017;157:277–91. <https://doi.org/10.1016/j.conbuildmat.2017.08.187>.
- [125] Chou L-H, Yang C-K, Lee M-T, Shu C-C. Effects of partial oxidation of crumb rubber on properties of rubberized mortar. *Compos Part B Eng* 2010;41:613–6. <https://doi.org/10.1016/j.compositesb.2010.09.009>.
- [126] Cataldo F, Ursini O, Angelini G. Surface oxidation of rubber crumb with ozone. *Polym Degrad Stabil* 2010;95:803–10. <https://doi.org/10.1016/j.polymdegradstab.2010.02.003>.

- [127] Fan P, Lu C. A study on functionalization of waste tire rubber powder through ozonization. *J Polym Environ* 2011;19:943–9. <https://doi.org/10.1007/s10924-011-0352-y>.
- [128] Criegee R. Mechanism of ozonolysis. *Angew Chemie Int Ed English* 1975;14:745–52. <https://doi.org/10.1002/anie.197507451>.
- [129] Chou LH, Lu C-K, Chang J-R, Lee MT. Use of waste rubber as concrete additive. *Waste Manag Res* 2007;25:68–76. <https://doi.org/10.1177/0734242X07067448>.
- [130] Segre N, Joekes I. Use of tire rubber particles as addition to cement paste. *Cem Concr Res* 2000;30:1421–5. [https://doi.org/10.1016/S0008-8846\(00\)00373-2](https://doi.org/10.1016/S0008-8846(00)00373-2).
- [131] Segre N, Monteiro PJM, Sposito G. Surface characterization of recycled tire rubber to be used in cement paste matrix. *J Colloid Interface Sci* 2002;248:521–3. <https://doi.org/10.1006/jcis.2002.8217>.
- [132] Guo S, Dai Q, Si R, Sun X, Lu C. Evaluation of properties and performance of rubber-modified concrete for recycling of waste scrap tire. *J Clean Prod* 2017;148:681–9. <https://doi.org/10.1016/j.jclepro.2017.02.046>.
- [133] Li G, Stubblefield MA, Garrick G, Eggers J, Abadie C, Huang B. Development of waste tire modified concrete. *Cem Concr Res* 2004;34:2283–9. <https://doi.org/10.1016/j.cemconres.2004.04.013>.
- [134] Raghavan D, Huynh H, Ferraris CF. Workability, mechanical properties, and chemical stability of a recycled tyre rubber-filled cementitious composite. *J Mater Sci* 1998;33:1745–52. <https://doi.org/10.1023/A:1004372414475>.



- [135] Lee BI, Burnett L, Miller T, Postage B, Cuneo J. Tyre rubber/cement matrix composites. *J Mater Sci Lett* 1993;12:967–8. <https://doi.org/10.1007/BF00420187>.
- [136] Huynh H, Raghavan D. Durability of simulated shredded rubber tire in highly alkaline environments. *Adv Cem Based Mater* 1997;6:138–43. [https://doi.org/10.1016/S1065-7355\(97\)90021-3](https://doi.org/10.1016/S1065-7355(97)90021-3).
- [137] Raghavan D, Tratt K, Wool RP. Recycled rubber in cement composites. *MRS Proc* 1994;344:177. <https://doi.org/10.1557/PROC-344-177>.
- [138] Nuzaimah M, Sapuan SM, Nadlene R, Jawaid M. Effect of surface treatment on the performance of polyester composite filled with waste glove rubber crumbs. *Waste and Biomass Valorization* 2020. <https://doi.org/10.1007/s12649-020-01008-2>.
- [139] Ratnam CT, Ramarad S, Khalid M, Noraini N. Effect of pre-irradiation of waste tire dust on the properties of ethylene vinyl acetate/waste tire dust blend (EVA/WTD) blends. *J Compos Biodegrad Polym* 2013;1:16–22. <https://doi.org/10.12974/2311-8717.2013.01.01.3>.
- [140] Moustafa AB, Mounir R, El Miligy AA, Mohamed MA. Effect of gamma irradiation on the properties of natural rubber/styrene butadiene rubber blends. *Arab J Chem* 2016;9:S124–9. <https://doi.org/10.1016/j.arabjc.2011.02.020>.
- [141] Wang W, Jiao Y, Cheng A, Lu Y, Liu J, Zeng X, et al. Enhanced thermal stability of gamma radiation vulcanized polybutadiene rubber (PBR)/nature rubber (NR) blends with sulfur added. *Mater Lett* 2017;186:186–8. <https://doi.org/10.1016/j.matlet.2016.09.128>.

- [142] Hirayama D, Saron C. Chemical modifications in styrene-butadiene rubber after microwave devulcanization. *Ind Eng Chem Res* 2012;51:3975–80. <https://doi.org/10.1021/ie202077g>.
- [143] Molanorouzi M, Mohaved SO. Reclaiming waste tire rubber by an irradiation technique. *Polym Degrad Stabil* 2016;128:115–25. <https://doi.org/10.1016/j.polymdegradstab.2016.03.009>.
- [144] Colom X, Faliq A, Formela K, Cañavate J. FTIR spectroscopic and thermogravimetric characterization of ground tyre rubber devulcanized by microwave treatment. *Polym Test* 2016;52:200–8. <https://doi.org/10.1016/j.polymertesting.2016.04.020>.
- [145] Xiaowei C, Sheng H, Xiaoyang G, Wenhui D. Crumb waste tire rubber surface modification by plasma polymerization of ethanol and its application on oil-well cement. *Appl Surf Sci* 2017;409:325–42. <https://doi.org/10.1016/j.apsusc.2017.03.072>.
- [146] Cheng X, Chen H, Huang S, Li Z, Guo X. Improvement of the properties of plasma-modified ground tire rubber-filled cement paste. *J Appl Polym Sci* 2012;126:1837–43. <https://doi.org/10.1002/app.36907>.
- [147] Zedler Ł, Klein M, Saeb MR, Colom X, Cañavate J, Formela K. Synergistic effects of bitumen plasticization and microwave treatment on short-term devulcanization of ground tire rubber. *Polymers (Basel)* 2018;10:1265. <https://doi.org/10.3390/polym10111265>.
- [148] Martínez-Barrera G, del Coz-Díaz JJ, Álvarez-Rabanal FP, López Gayarre F, Martínez-López M, Cruz-Olivares J. Waste tire rubber particles modified by gamma radiation and their use as modifiers of concrete. *Case Stud Constr Mater* 2020;12:e00321.

<https://doi.org/10.1016/j.cscm.2019.e00321>.

- [149] Herrera-Sosa ES, Martínez-Barrera G, Barrera-Díaz C, Cruz-Zaragoza E. Waste tire particles and gamma radiation as modifiers of the mechanical properties of concrete. *Adv Mater Sci Eng* 2014;2014:1–8. <https://doi.org/10.1155/2014/327856>.
- [150] Mohamed MA, EL-Zayat MM, Shaltout NA, Zeid MMA. Effect of glycidyl methacrylate as compatibilizer on physico-chemical properties of gamma irradiated composites of ethylene propylene diene monomer rubber / styrene butadiene rubber/ground tire rubber. *Radiat Eff Defects Solids* 2019;174:248–59. <https://doi.org/10.1080/10420150.2018.1552961>.
- [151] Vilela AP, Silva DW, Mendes LM, Martins MA, Brandão Vaz, L. E. V., Mendes RF. Surface modification of tire rubber waste by air plasma for application in wood-cement panels. *BioResources* 2018;13:6409–27. <https://doi.org/10.15376/biores.13.3.6409-6427>.
- [152] Cheng X, Long D, Huang S, Li Z, Guo X. Time effectiveness of the low-temperature plasma surface modification of ground tire rubber powder. *J Adhes Sci Technol* 2015;29:1330–40. <https://doi.org/10.1080/01694243.2015.1026958>.
- [153] Feldman D, Denes F, Zeng Z, Denes AR, Banu D. Polypropylene fiber–matrix bonds in cementitious composites. *J Adhes Sci Technol* 2000;14:1705–21. <https://doi.org/10.1163/156856100742500>.
- [154] Yin J, Wang S, Lv F. Improving the short-term aging resistance of asphalt by addition of crumb rubber radiated by microwave and impregnated in epoxidized soybean oil. *Constr Build Mater* 2013;49:712–9. <https://doi.org/10.1016/j.conbuildmat.2013.08.067>.

- [155] Yu G-X, Li Z-M, Zhou X-L, Li C-L. Crumb rubber-modified asphalt: Microwave treatment effects. *Pet Sci Technol* 2011;29:411–7. <https://doi.org/10.1080/10916460903394102>.
- [156] Seghar S, Aït Hocine N, Mittal V, Azem S, Al-Zohbi F, Schmaltz B, et al. Devulcanization of styrene butadiene rubber by microwave energy: Effect of the presence of ionic liquid. *Express Polym Lett* 2015;9:1076–86. <https://doi.org/10.3144/expresspolymlett.2015.97>.
- [157] de Sousa FDB, Scuracchio CH, Hu G-H, Hoppe S. Devulcanization of waste tire rubber by microwaves. *Polym Degrad Stabil* 2017;138:169–81. <https://doi.org/10.1016/j.polymdegradstab.2017.03.008>.
- [158] Colom, X., Marín-Genescà, M., Mujal, R., Formela, K., & Cañavate J. Structural and physico-mechanical properties of natural rubber/GTR composites devulcanized by microwaves: Influence of GTR source and irradiation time. *J Compos Mater* 2018;52:3099–3108. <https://doi.org/10.1177/0021998318761554>.
- [159] Xu O, Cong L, Xiao F, Amirkhanian SN. Rheology investigation of combined binders from various polymers with GTR under a short term aging process. *Constr Build Mater* 2015;93:1012–21. <https://doi.org/10.1016/j.conbuildmat.2015.05.051>.
- [160] Liang M, Ren S, Fan W, Wang H, Cui W, Zhao P. Characterization of fume composition and rheological properties of asphalt with crumb rubber activated by microwave and TOR. *Constr Build Mater* 2017;154:310–22. <https://doi.org/10.1016/j.conbuildmat.2017.07.199>.
- [161] Liang M, Xin X, Fan W, Ren S, Shi J, Luo H. Thermo-stability and aging performance of



- modified asphalt with crumb rubber activated by microwave and TOR. *Mater Des* 2017;127:84–96. <https://doi.org/10.1016/j.matdes.2017.04.060>.
- [162] Bradley M. Carbon black analysis comparison with diamond ATR and germanium crystals. Appl. Note 50829, Madison Wi (USA): Thermo Electron Corporation; 2005.
- [163] Xue P, Bao Y, Li Q, Wu C. Impact of modification of carbon black on morphology and performance of polyimide/carbon black hybrid composites. *Phys Chem Chem Phys* (Incorporating Faraday Trans 2010;12:11342. <https://doi.org/10.1039/B924178G>.
- [164] Garcia PS, de Sousa FDB, de Lima JA, Cruz SA, Scuracchio CH. Devulcanization of ground tire rubber: Physical and chemical changes after different microwave exposure times. *Express Polym Lett* 2015;9:1015–26. <https://doi.org/10.3144/expresspolymlett.2015.91>.
- [165] Paulo GD, Hirayama D, Saron C. Microwave devulcanization of waste rubber with inorganic salts and nitric acid. *Adv Mater Res* 2011;418–420:1072–5. <https://doi.org/10.4028/www.scientific.net/AMR.418-420.1072>.
- [166] Scuracchio CH, Waki DA, da Silva MLCP. Thermal analysis of ground tire rubber devulcanized by microwaves. *J Therm Anal Calorim* 2007;87:893–7. <https://doi.org/10.1007/s10973-005-7419-8>.
- [167] Yang X, Shen A, Li B, Wu H, Lyu Z, Wang H, et al. Effect of microwave-activated crumb rubber on reaction mechanism, rheological properties, thermal stability, and released volatiles of asphalt binder. *J Clean Prod* 2020;248:119230. <https://doi.org/10.1016/j.jclepro.2019.119230>.

- [168] Aoudia K, Azem S, Aït Hocine N, Gratton M, Pettarin V, Seghar S. Recycling of waste tire rubber: Microwave devulcanization and incorporation in a thermoset resin. *Waste Manag* 2017;60:471–81. <https://doi.org/10.1016/j.wasman.2016.10.051>.
- [169] Formela K, Hejna A, Zedler L, Colom X, Canavate J. Microwave treatment in waste rubber recycling – recent advances and limitations. *Express Polym Lett* 2019;13:565–88. <https://doi.org/10.3144/expresspolymlett.2019.48>.
- [170] Yasin T, Khan S, Shafiq M, Gill R. Radiation crosslinking of styrene–butadiene rubber containing waste tire rubber and polyfunctional monomers. *Radiat Phys Chem* 2015;106:343–7. <https://doi.org/10.1016/j.radphyschem.2014.08.017>.
- [171] Ibrahim IM, Fathy ES, El-Shafie M, Elnaggar MY. Impact of incorporated gamma irradiated crumb rubber on the short-term aging resistance and rheological properties of asphalt binder. *Constr Build Mater* 2015;81:42–6. <https://doi.org/10.1016/j.conbuildmat.2015.01.015>.

Highlights

- Ground tire rubber (GTR) used as an efficient modifier for green composites.
- Radiation as environmentally friendly method for surface etching of GTR.
- Functionalization of GTR for construction, automotive and road composites.
- Efficiency of different modification methods should be evaluated on one matrix.
- Low-cost sustainable composite materials developed from waste tires.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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