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1 **An overview on the recycling of waste ground tyre rubbers in thermoplastic matrices:**  
2 **effect of added fillers**

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12

13 **Abstract**

14 The increasing generation and accumulation of waste tyres threaten the ecosystem. Waste  
15 tyre landfills create potential fire hazards, environmental pollutions, and threats to human  
16 health, as waste tyre pileups harbor rodents, mosquitoes and reptiles, generating harmful  
17 diseases. Moreover, there is a great economic loss associated with the disposal of waste tyre  
18 rubbers. Therefore, this approach is not sustainable, making the recycling of waste tyre  
19 rubber necessary. Accordingly, several recycling strategies are being developed to obtain  
20 value-added waste tyre rubber. One of such strategies, which is of environmental  
21 conservative and consumes an appreciable quantity of the waste tyres, is the blending of  
22 thermoplastics with ground tyre rubber (GTR). However, achieving homogenous dispersion  
23 of GTR in matrix poses a great challenge owing to little or no affinity between GTR and  
24 thermoplastics. To overcome this problem, surface treatments of GTR, compatibilizers,  
25 additives, and energy treatments are used. Most recently, incorporation of rigid nanoparticles  
26 with or without combination of other techniques are adopted to facilitate GTR dispersion. In  
27 this review, we discuss the recycling of GTR in thermoplastic matrices. Specific attention

28 was paid to the effect of fillers, and more particularly nanofillers, on the dispersion of GTR  
29 within thermoplastic matrices for achieving competitive materials.

30 **Keywords:** Waste tyre rubbers, recycling, thermoplastics, blend, rigid fillers,  
31 nanocomposites.

## 32 **1. Introduction**

33 Industrially, tyre rubbers are manufactured at a low cost through an efficient but  
34 irreversible process called vulcanization. Vulcanization can be defined as the creation of  
35 three-dimensional crosslinked network between rubber macromolecules via irreversible  
36 reactions, in the presence of curing agents (sulphur, peroxides), activators (stearic acid, zinc  
37 oxide), accelerators (thiazoles, sulphonamide), retarders (*N*-cyclohexylthio phthalimide) and  
38 other additives (Luna et al., 2020; Junkong et al., 2020). The sulphur vulcanization creates  
39 strong chemical bonds, and the sulphur content strongly dictates the resulting structural and  
40 physical properties of the rubber vulcanizates (Sienkiewicz et al., 2017; Yangthong et al.,  
41 2020). Hence, rubber products like tyres are insoluble and infusible, which makes them  
42 difficult to be reprocessed unlike thermoplastics (Sienkiewicz et al., 2012). Meanwhile,  
43 global industrialization is driving the rapid expansion of the automotive sector, leading to an  
44 increase in the production of tyres, about 1.5 billion units per year worldwide (Czajczyńska et  
45 al., 2017; Simon-Stöger and Varga, 2021). This consequently generates a large volume of  
46 end-of-life tyres, since they do not degrade naturally for centuries (Gupta et al., 2012; Liu et  
47 al., 2020). The traditional dumping or unchecked burning of waste tyres pose great hazards to  
48 man and its environment, and thus raising attention from all nations (Ghosh et al., 2020).  
49 Unlike thermoplastic waste used to obtain value-added new products, there is no known  
50 effective process to completely regain elastomeric waste monomers (Adhikari et al., 2000).  
51 This makes the reclaimed rubber less viable commercially. Thus, the disposal of large  
52 quantity of such elastomeric materials, which alters the conservation of environment.  
53 Nevertheless, a laudable alternative means of using worn-out tyres is simply the  
54 incorporation of the GTR in thermoplastic matrices to form blends (Simon-Stöger and Varga,  
55 2021). This approach is gaining scientific research momentum because it serves as the most  
56 straightforward rubber recycling means. It is cheap, easy and environmentally friendly.

57 Moreover, it consumes an appreciable quantity of waste tyres in the form of GTR (Karger-  
58 Kocsis et al., 2013). More importantly, the renewability and recyclability of thermoplastic  
59 matrices support the ecosystem sustainability targets (Ramarad et al., 2015; Nuzaimah et al.,  
60 2018; Sanusi et al., 2020, 2021a).

61 There are some reviews on the recycling of tyres in thermoplastics and other matrices  
62 focusing on different methods of treatments, preparations or applications. For instance, the  
63 review by Karger-Kocsis et al. (2013) covers the recycling of waste tyre in thermoset,  
64 thermoplastic and elastomer matrices. Ramarad et al. (2015) discuss incorporation of waste  
65 tyre rubber in both natural rubber and thermoplastics. Sienkiewicz et al. (2017) focus on the  
66 methods of generation and treatment of rubber granules as well as implications on the  
67 properties of final composites. Beside waste tyre rubber, Nuzaimah et al. (2018) extend their  
68 review to include waste condom and shoe rubbers. The paper by Fazli and Rodrigue (2020)  
69 emphasizes the chemistry and kinetics of the compatibilization methods for rubber dispersion  
70 in thermoplastics. In this review, a distinctive effort is made to summarize, principally, the  
71 works dealing with the recycling of treated or untreated waste tyre particles in thermoplastic  
72 matrices, with or without additional phases (coupling agents, fillers), aiming at developing  
73 composites with competitive properties. Particular attention is paid to the effects of rigid  
74 micro and nanofillers on the structure and properties of thermoplastic/waste tyre blends.

## 75 **2. Challenges and methods of waste tyre rubbers recycling**

### 76 **2.1 Challenges of waste tyre rubbers recycling**

77 Over 70% of total natural and synthetic rubber materials are utilized for tyre  
78 manufacturing (Myhre and MacKillop, 2002; Karger-Kocsis et al., 2013). When a tyre is no  
79 longer efficient or satisfactorily safe to be used, it becomes a waste tyre, that is equally  
80 referred to as end-of-life-tyre (ELT) (Mangili et al., 2015). Annually, a huge volume of tyres

81 is scrapped worldwide (Wayal and Wagle, 2013; Nuzaimah et al., 2018; Shulman, 2019), that  
82 is over 17 million tons of worn-out tyres (Formela et al., 2016). In fact, more than 180  
83 million and 150 million tyres were scrapped in European Union (EU) countries and North  
84 America, respectively (Ayanoglu and Yumrutaş, 2016). Unfortunately, far less than 1% of the  
85 entire waste tyres are naturally degraded over hundreds of years as a result of the complex  
86 cross-linked structure of rubber (Adhikari et al., 2000; Gupta et al., 2012; Liu et al., 2020).  
87 There are two critical problems associated with waste tyre rubbers. The first one is the  
88 economic loss in terms of the wastage of rubber when discarded as waste, excluding an  
89 additional cost due to transportation to such disposal sites. Meanwhile, the unavailability of  
90 space has made tyre disposal by landfilling to be unrealistic with no potential in the nearest  
91 future (Thomas et al., 2016). The second one is the environmental pollution caused by the  
92 abandoned waste tyres, which is disastrous to aquatic and terrestrial organisms (Adhikari et  
93 al., 2000; Nuzaimah et al., 2018). For instance, mass dumping of tyres breeds potential  
94 dangers to the man and his environs. These landfills harbor dangerous reptiles, accumulates  
95 disease causative organisms, or creates fire hazard zones since the abandoned elastomers are  
96 combustible materials. Consequently, the EU imposed a ban on landfilling of scrapped tyres  
97 (Sadaka et al., 2012; Karger-Kocsis et al., 2013; Grammelis et al., 2021). Therefore, the  
98 attempts to recycle and re-utilize the waste tyre rubbers become necessary. Tyre recycling  
99 equally represents a source of raw material and offers a possibility of earnings for people that  
100 collect the waste tyres, thus support the economic development (De Sousa, 2016).

## 101 **2.2 Techniques of waste tyres recycling**

102 The complex composition and structure of tyres pose major restrictions to their recovery  
103 and recycling processes. Besides the 70-80% of sulphur-cured rubber component of tyres,  
104 fibre made up of polyester, nylon or cellulose, and steel cords are essential constituents used  
105 to reinforce tyres. Thus, separation of the fibres and steel components from the rubber is the

106 first difficult step during recycling of tyres (Ramarad et al., 2015). Then, the next stage of  
107 recycling of waste tyres is grinding to form GTR with different sizes and shapes (Manuel,  
108 2001).

109 Since manufactured tyres are infusible, insoluble and technically complex to be  
110 reprocessed (Zhang et al., 2009), large amount of GTR provides a source of energy. For  
111 instance, waste tyres are used as a heat source since they are made up of about 90% organic  
112 material with a heat of about 32.6 MJ/kg, far more than that of coal (18.6 - 27.9 MJ/kg (Fazli  
113 and Rodrigue, 2020)). Incineration of waste tyres is seen as an approach of eliminating a  
114 substantial amount of this post-consumer product to generate or recover energy, but this is  
115 with significant negative environmental impacts such as air pollution and global warming  
116 (Mangili et al., 2014; Cazan et al., 2019).

117 Furthermore, several efforts are made by the politicians and scientists to deal with the  
118 problem of the ever-growing waste tyres (Rincón et al., 2014; Sienkiewicz et al., 2017; Maris  
119 et al., 2018; Liang et al., 2020). The risks inherent in the scrap tyres necessitated the  
120 legislation of 1991 by United States Congress (Resource Conservation Recovery Act) and  
121 Intermodal Surface Transport Efficiency Act to mandate the use of a specified percentage of  
122 recycled tyres in any project funded by the federal government. In deviance to  
123 implementation, the funds would be withheld (Shu and Huang, 2014). European Union (EU)  
124 issued the Landfill Directive "1999/31/EC" that prohibits the disposal of whole tyres and  
125 shredded tyres (50 – 300 mm size) in 2003 and 2006, respectively (Karger-Kocsis et al.,  
126 2013). Thus, a significant use of tyres emerges in civil engineering for building and road  
127 construction, such as in insulation, sound deadening, soil stabilization, dam and road  
128 construction, artificial reefs, steel making and so on (Wang et al., 2015; Medina et al., 2018).  
129 The use of waste tyres in this field is sometimes referred to as "downcycling" since the  
130 recycled materials have entirely different applications from the original purpose (Karger-

131 Kocsis et al., 2013). However, except for road paving, most of the downcycling applications  
132 are saturated and outdated. Hence, there is a necessity for identifying innovative and value-  
133 added applications for waste tyres.

134 Reclaiming of tyres is another sophisticated technique of recycling tyres (Dubkov et al.,  
135 2012; Dobrotă and Dobrotă, 2018). Reclaiming of used tyres is the conversion and breaking  
136 down of the 3D interlinked, infusible and insoluble network of vulcanized rubber to soft, low  
137 modulus, easy processing and vulcanizable material covering properties of virgin rubber (De  
138 Sousa, 2016). Recycling of tyres can be classified into physical reclaiming and chemical  
139 reclaiming processes.

140 The physical reclaiming method involves the application of external energy on used tyres  
141 to breakdown the 3D cross-linked network of rubber. The applied energy transforms the  
142 molecular structure of rubber into fragments of smaller molecular weight availing it the  
143 miscibility with virgin matrix or blend during compounding. Applying sufficient energy,  
144 which is enough to cleave the rubber crosslink bonds, results in high quality reclaimed  
145 rubber. The physical reclaiming approach encompasses mechanical, cryo-mechanical  
146 grinding, thermo-mechanical, ultrasonic and microwave techniques (De Sousa et al., 2017).  
147 These techniques were well described in the review by Asaro et al. (2018). It should be noted  
148 that microwave technique, in particular, causes total breakdown of the polysulphide  
149 crosslinks. The remnant sulphur crosslinks exhibit largely mono-sulphide structures  
150 (Molanorouzi and Mohaved, 2016).

151 Chemical approach involves the utilization of chemical devulcanizing agents, with  
152 solvents serving as the reaction medium, and often carried out under elevated temperatures  
153 (Gumede et al., 2021). In chemical devulcanization, the main goal is the penetration of  
154 devulcanizing reagent into the rubber matrix for cleavage reaction (Liu et al., 2015). Some of



155 the recent significant solvent media used in devulcanizing GTR include ionic liquid (Seghar  
156 et al., 2015), deep eutectic solvent (Saputra et al., 2020) and periodic acid (Sadaka et al.,  
157 2012). Environmental concerns led to an innovative use of super-critical carbon dioxide as an  
158 alternative reaction medium for devulcanizing reagents like diphenyl disulphide (Mangili et  
159 al., 2014). Furthermore, thermochemical process has an extended application in pyrolysis,  
160 whereby used tyres are converted to oil, gas or char that are either deployed as a chemical  
161 feedstock or energy source (Formela et al., 2016; Guangjian and Jincheng, 2016). Oil from  
162 pyrolysis of tyre is competitive since it has fuel characteristics similar to diesel fuel  
163 (Ayanoglu and Yumrutaş, 2016; Kumaravel et al., 2016). Aside the complexity associated  
164 with control of the chemical reactions that limits its deployment in industry, this approach is  
165 expensive and does not completely eradicate toxic reagents (Sadaka et al., 2012).

166 Meanwhile, both chemical and physical approaches can lead to secondary pollution and  
167 involve huge energy consumption (Li et al., 2011). For instance, the chemical method  
168 involves high reaction temperature, complex instrumentation, and the use of reactor plants  
169 and chemicals. All these points constitute environmental and cost concerns (Choi et al.,  
170 2017). The use of microorganisms in desulphurization of vulcanized rubber (microbial  
171 desulphurization) is another alternative but it only breaks the sulphur crosslinks on the  
172 surface of powdered waste tyre rubbers. In addition, it is a slow process (Li et al., 2011; Yao  
173 et al., 2013).

174 During the last decade, one of the simple routes of tyre recycling that reduces energy  
175 consumption as well as addressing environmental challenges is incorporating GTR in  
176 thermoplastic polymers (Satapathy et al., 2010; Fazli and Rodrigue, 2020). This creates a  
177 multi-functional polymeric matrix that has the elasticity of rubber combined with the  
178 thermoplastic processability property (Fazli and Rodrigue, 2020).

### 179 **3. Recycling of waste tyre rubbers in thermoplastic matrices**

180 Mixing GTR with thermoplastics matrices or thermoplastic blends to elaborate  
181 thermoplastic elastomers (TPE) is the most promising practical approach of GTR recycling,  
182 as the thermoplastic phase in the composite makes the reprocessing or recyclability of the  
183 resulting compound feasible (Kakroodi and Rodrigue, 2013; Sripornsawat et al., 2018). Yet,  
184 thermoplastic/GTR materials show poor mechanical properties due to low compatibility. This  
185 is explained by the weak entanglement of cross-linked rubber molecules and thermoplastic  
186 molecules, causing the phase separation which limits their applications (Montagna et al.,  
187 2013). Even though the utilization of GTR in thermoplastic consumes a reasonable quantity  
188 of GTR (sometimes >50% (Kakroodi and Rodrigue, 2013)) that addresses environmental  
189 concerns, the mechanical and thermal properties of the resulted TPE needs to be improved for  
190 competitiveness. Indeed, the composition of TPE (thermoplastic-based matrix, GTR), affinity  
191 between the different phases and the GTR particle size are critical in order to achieve high-  
192 performance thermoplastic elastomer materials.

193 It is thus clear that recycling of GTR as particles in different thermoplastic matrices or  
194 thermoplastic blends is a simple and inexpensive means of removing worn-out tyres from the  
195 environment with value addition. Although polymers like polyolefins and vulcanized rubbers  
196 can be recycled via chemical techniques, this type of recycling is expensive and comes with  
197 secondary pollution (Datta and Włoch, 2015). Hence, the mechanical recycling, for which the  
198 waste materials are ground to granulated powder then mixed with the matrix, is adapted and,  
199 moreover, it supports ecological reasoning. More importantly, the resulting thermoplastic  
200 elastomer materials offer better material utilization as subsequent scraps and/or rejects can be  
201 easily recycled (Pang and Ismail, 2014). Nevertheless, several methods must be used to  
202 improve the interfacial adhesion and the degree of GTR dispersion: addition of

203 compatibilizers/coupling agents, nanofillers, energy treatment, devulcanization and  
204 revulcanization (Da Costa et al., 2010; Kakroodi and Rodrigue, 2013).

### 205 **3.1 Effect of GTR dispersion**

206 A homogenous dispersion of GTR in the matrix is an essential factor in obtaining  
207 competitive materials, because it improves, for example, the impact strength (Da Costa et al.,  
208 2010). The concentration of GTR in the matrix as well as its particle size influence the state  
209 of the GTR dispersion and the final blend properties (Datta and Włoch, 2015; Halász et al.,  
210 2020). GTR of about 1  $\mu\text{m}$  disperses more easily in the matrix (Fazli and Rodrigue, 2020),  
211 but such a particle size is not easy to produce even with cryogenic technique (Lievana and  
212 Karger-Kocsis, 2004). Equally, once the mass fraction of GTR in thermoplastic nears 10 – 20  
213 wt%, the composite mechanical performance deteriorates (Candau et al., 2021). In fact,  
214 pristine GTR aggregates within matrix, leading to a deterioration of mechanical properties.  
215 Hence, to obtain good dispersion of GTR in matrix and improve interfacial adhesion between  
216 the two phases, it is necessary to reduce the GTR particle size (Candau et al., 2021), achieve  
217 surface modification by compatibilizers or vulcanizing agents (Li et al., 2020; Zedler et al.,  
218 2020), encapsulate GTR into neat rubber phase (Lima et al., 2014) or use energy treatments  
219 of GTR (Garcia et al., 2021).

220 There are two classifications of thermoplastic/elastomer materials. Firstly, thermoplastic  
221 elastomer (TPE), which is elaborated from a mixing of rubber with a thermoplastic without  
222 any curative ingredients. Secondly, thermoplastic vulcanizate (TPV), which is prepared via  
223 dynamic vulcanization and requires additional curing agents (Cañavate et al., 2011;  
224 Sripornsawat et al., 2018). Devulcanization and/or functionalization of GTR leads to an  
225 enhancement in compatibility with the host matrix (Lievana and Karger-Kocsis, 2004), thus,  
226 improving the degree of the GTR dispersion in matrices. The dynamic vulcanization

227 treatment entails the production of thermoplastic/rubber mixture, wherein the rubber phase is  
228 selectively crosslinked (Chiang et al., 2020). The process permits high rubber content of more  
229 than 50 – 80% and produces high-performance TPV having a well-dispersed rubber phase in  
230 a low-content continuous thermoplastic phase (Li et al., 2020). TPV materials are gaining  
231 momentum in advanced applications like sport, automobile, electronics, construction and  
232 medical fields (Zheng et al., 2020). This is due to their easy processability, high elasticity,  
233 exceptional mechanical properties, and recyclability (Sripornsawat et al., 2018).

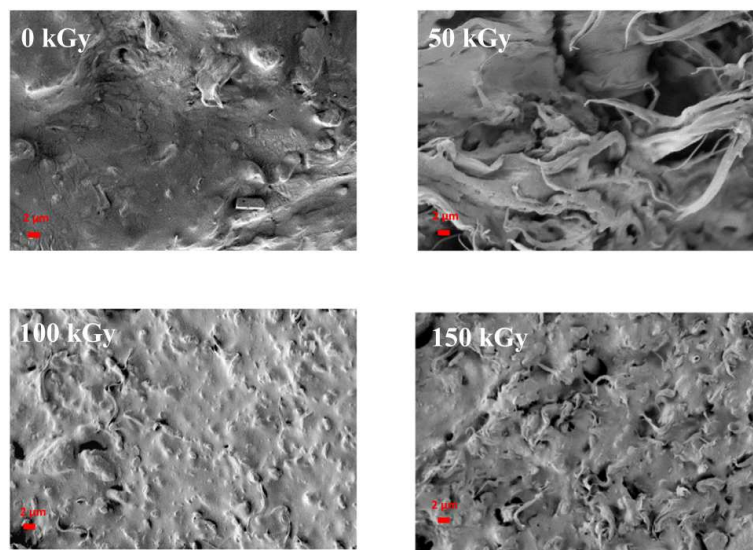
### 234 **3.2 Effect of energy treatment**

235 High-energy treatments such as gamma radiation (Hassan et al., 2014a), microwaves (De  
236 Sousa et al., 2015), plasma (Zimmermann et al., 1991) and electron beam radiations  
237 (Ramarad et al., 2017; Mohamad et al., 2021) increase the concentration of oxygen on GTR  
238 surfaces and lead to better adhesion with the host matrix (Li et al., 2003; Sonnier et al., 2007).

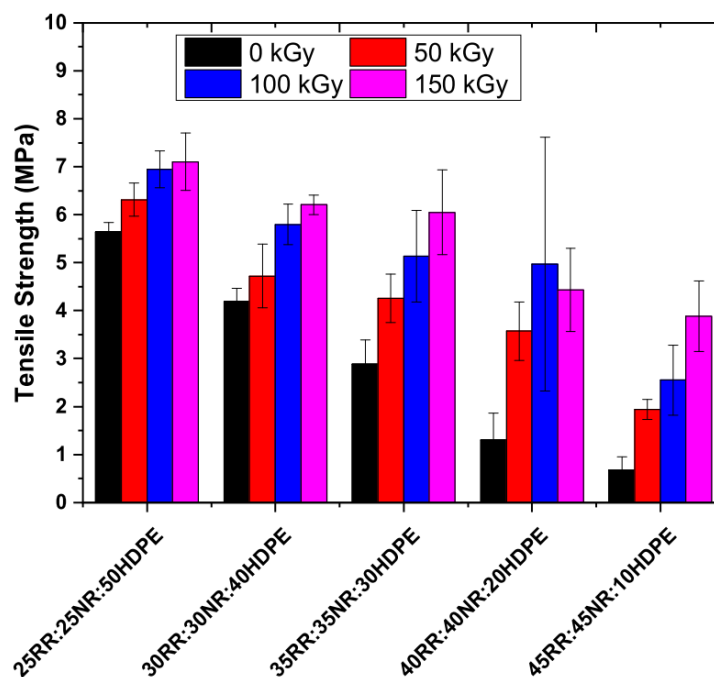
239 Ramarad et al. (2017) mixed GTR with EVA and thereafter treated the composite with  
240 different doses of electron beam irradiation. The EVA/GTR material has lower processing  
241 torque compared to neat EVA, suggesting easier processability of the product due to the GTR  
242 rubbery feature. Irradiation improved the dispersion of GTR entities within EVA matrix, by  
243 reducing their size. It was also reported that the irradiation induced formation of crosslink,  
244 leading to an increase of storage and loss moduli of EVA/GTR composite. In another work,  
245 Mohamad et al. (2021) prepared TPE by mixing different ratio of natural rubber (NR), HDPE  
246 and GTR to form NR/HDPE/GTR composite. They studied the influence of irradiation on the  
247 properties of different TPE blends and reported that irradiation enhanced the bond between  
248 the rubbery phases and HDPE matrix, as highlighted in Fig. 1. Increasing the irradiation  
249 dosage seems to lead to higher adhesion force and uniform surface interaction of the  
250 constituents. This resulted in improved mechanical strength of the composites, as shown in

251 Fig. 2. Similarly, Hassan et al. (2014a) reported that gamma irradiation improved the  
252 adhesion between PE and GTR, leading to an improvement in thermal and mechanical  
253 performances of the composite, in particular its hardness. Moreover, De Sousa et al. (2015)  
254 reported a less coarse morphology in the HDPE/GTR composite when it was exposed to  
255 microwaves for some period, which resulted in better mechanical properties of the composite.

256 Therefore, the importance of energy treatments in aiding the crosslinking of GTR,  
257 lowering the interfacial energy between GTR and matrices, and creating a finer structure of  
258 GTR is sometimes essential. This can create an improvement in the physical properties in  
259 thermoplastic/GTR composites.



260  
261 Fig. 1 SEM of NR/HDPE/GTR composite irradiated at 0, 50, 100, and 150 kilograys (kGy)  
262 absorption doses (Mohamad et al., 2021).



263

264 Fig. 2 Tensile strength of NR/HDPE/GTR composites irradiated at 0, 50, 100, and 150 kGy

265

absorption doses: RR stands for GTR (Mohamad et al., 2021).

266

### 3.3 Effect of additives

267

A third component incorporated into thermoplastic/GTR system may be used to improve the processability and end-use properties. For instance, it can help in the preparation of a thermoplastic blend as a matrix and/or increase the affinity between phases by playing the role of a coupling agent.

270

271

Datta and Włoch (2015) utilized recycled polyethylene (rPE), GTR and thermoplastic poly(ester urethane) (TPU) to prepare rPE/GTR/TPU system by melt mixing. Increasing the concentration of neat TPU, while the rPE/GTR composition ratio was kept constant, improved the processability, due to the high melt flow index of TPU compared to rPE. Unfortunately, while hardness property was unaffected, both tensile strength and elastic modulus decreased with an increase of the TPU concentration. In the same way, rebounding resilience, that is the ability of a material to absorb high impact energy, was also decreased. They related the behavior to stronger interactions between GTR and rPE than between GTR

278

279 and TPU. However, the decrease of TPU content, while increasing rPE content, resulted in  
280 more permanent plastic deformation (typical of polyolefins) but improved abrasion resistance  
281 due to the best rPE/GTR interfacial interaction. This study shows the difficulty in obtaining  
282 an efficient balance between processability and mechanical performance.

283 Montagna et al. (2013) mixed 10 wt% of GTR in polypropylene (PP), high impact  
284 polystyrene (HIPS), and blend PP/HIPS via injection moulding, under an injection pressure  
285 of 60 bar and a temperature of 220°C. Firstly, the study established that the decrease of GTR  
286 particle size leads to improved performances of such materials. For PP/GTR blend, the  
287 morphology study revealed voids created as a result of the pullout of GTR particles, and the  
288 void size increased with GTR particle size, confirming poor interfacial adhesion between PP  
289 and GTR. Consequently, both tensile and flexural moduli of PP/GTR blend are reduced  
290 compared to neat PP. However, good interfacial interaction was observed between HIPS and  
291 GTR, which was associated to the presence of polybutadiene in HIPS, resulting in increased  
292 tensile and flexural moduli. On other hand, PP/GTR absorbed the highest impact energy of 23  
293 kJ/m<sup>2</sup> compared to HIPS/GTR (6.3 kJ/m<sup>2</sup>) or ternary composite PP/HIPS/GTR (13.1 kJ/m<sup>2</sup>).  
294 Low impact energy observed for HIPS/GTR was related to high rigidity of the material.

295 The efficient role played by polybutadiene is also highlighted by Wang et al. (2012). High  
296 impact polystyrene (HIPS), ethylene-vinyl acetate copolymer (EVA) and GTR were mixed  
297 and the effect of styrene-butadiene-styrene copolymer (SBS) as a compatibilizer was studied.  
298 The addition of SBS increased the tensile strength by 145% and elongation at break by  
299 1280%. Sample HIPS/EVA/GTR revealed highly stiff behavior, while those of  
300 HIPS/EVA/GTR/SBS indicate soft and tough profound behavior due to the presence of SBS  
301 inclusion. They explained that the GTR toughened the HIPS plastic phase while the SBS  
302 improved the interfacial adhesion of GTR and HIPS. Thus, the presence of a high

303 concentration of GTR (55 - 70 wt%) increased elongation at break and decreased initial  
304 modulus of HIPS/EVA/GTR/SBS.

305 Wang et al. (2018) reported a clear phase separation in the morphology of  
306 uncompatibilized PE/GTR blend, which resulted in poor mechanical properties. So, two  
307 different compatibilizers were selected and their individual effects were studied on the  
308 properties of the blend: Ethylene-octene copolymer (Engage 8180) and Trans-polyoctenamer  
309 (Vestenamer 8012). Addition of Engage 8180 created a homogenous morphology wherein the  
310 embedded GTR particles were difficult to be identified. This is the signature of a very good  
311 PE-GTR interaction that led to improved properties. The use of Vestenamer 8012 also created  
312 a homogenous morphology, but some GTR particles were observed in the blend, and weaker  
313 mechanical properties were obtained for the prepared composite. In fact, the "ethylene"  
314 component in Engage 8180 is compatible with PE, while the other component "octene" has a  
315 weak affinity with PE and mainly interacts with styrene butadiene rubber (SBR) contained in  
316 GTR. Hence, the good interaction between PE and GTR was obtained in the presence of  
317 Engage 8180, which facilitates better stress transfer. Thus, it is critical to select the right  
318 compatibilizer for each blend formulation.

319 Different coupling agents were also used, and their efficiency is attested. Kakroodi and  
320 Rodrigue (2013) prepared maleated polyethylene (MAPE)/GTR thermoplastic elastomer  
321 using high concentration of GTR (50 - 90 wt%). The blend MAPE/GTR displayed more than  
322 200% elongation at break and, thus, qualified it as a competitive material. Normally, a TPE is  
323 expected to display at least 100% elongation for it to be classified as a high-performance  
324 material. For comparison, GTR was incorporated in neat HDPE, but only 64% elongation at  
325 break was achieved in the HDPE/GTR composite. This was attributed to poor homogeneity  
326 of the morphology of the blend, which was improved with the incorporation of 5 wt% MAPE



327 coupling agent to form the ternary HDPE/MAPE/GTR system. Similarly, the presence of  
328 MAPE improved the elastic properties.

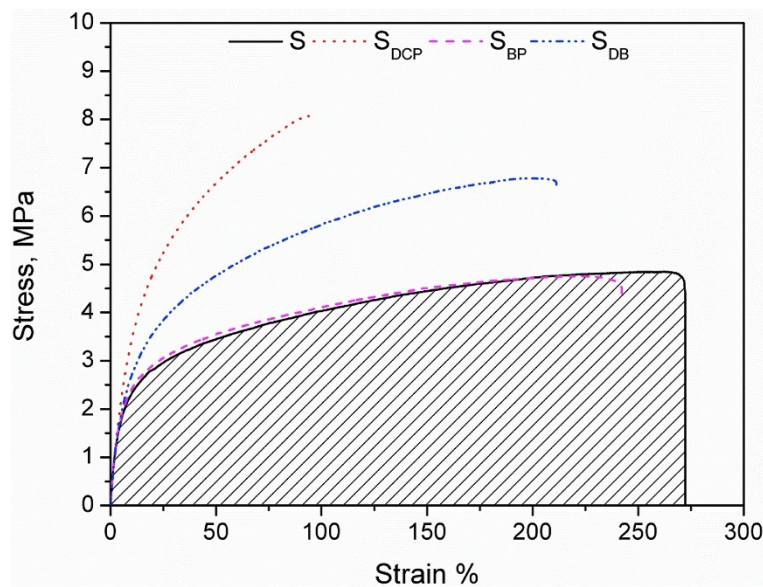
329 Hamim et al. (2014) examined the effect of polyethylene grafted maleic anhydride (PE-g-  
330 MAH) on the mechanical and swelling behavior of HDPE/ethylene-vinyl acetate (EVA)  
331 copolymer/GTR blend. The tensile strength of HDPE/EVA/GTR material reduced with  
332 increasing GTR concentration because of incompatibility of HDPE/EVA and GTR, leading to  
333 fracture. A similar trend of property reduction with increasing GTR content was observed for  
334 HDPE/EVA/GTR/PE-g-MAH. But, at the same GTR fraction, the enhanced adhesion created  
335 by PE-g-MAH leads to strongly higher tensile strength of HDPE/EVA/GTR/PE-g-MAH  
336 material compared to HDPE/EVA/GTR one. On the other hand, the mass swell of both  
337 HDPE/EVA/GTR and HDPE/EVA/GTR/PE-g-MAH increased with GTR due to increase in  
338 elastomer content that absorbed the swelling liquid (toluene). However, for a given  
339 concentration of elastomeric phase, the mass of swollen HDPE/EVA/GTR was greater than  
340 that of HDPE/EVA/GTR/PE-g-MAH. The chemical bond created by the reaction of the PE-  
341 g-MAH acrylic anhydride group and EVA functional group established a good interaction  
342 with HDPE, thus, limited the swelling property of the compatibilized sample.

343 Da Costa et al. (2010) used the response surface methodology (RSM) to formulate a  
344 ternary PP/EPDM/GTR system. A strong deterioration in mechanical strength, elongation and  
345 toughness with increasing GTR content was reported, owing to the poor interfacial adhesion  
346 between PP matrix and GTR. Indeed, the GTR without strong adhesion with the matrix could  
347 not play the role of transferring energy in material, hence, creating microvoids at blend  
348 interface, causing crack propagation under tensile loading. However, whenever the EPDM  
349 content is superior or equal to that of GTR in PP/EPDM/GTR, the elongation at break  
350 increased because EPDM plays a compatibilizing role between PP and GTR phases. Thus,  
351 EPDM served the role of compatibilizer, ensuring homogeneous morphology of the

352 composite. However, since EPDM and GTR are softer materials compared to PP, an increase  
353 in their concentration resulted in a reduction of PP/EPDM/GTR stiffness.

### 354 3.4 Effect of cross-linking and vulcanization

355 Hejna et al. (2019) investigated the influence of three radical initiators (benzoyl peroxide  
356 (BP), dicumyl peroxide (DCP) and di-tert-butyl peroxide (DP)) on the crosslink density of  
357 HDPE/SBS/GTR blends. Irrespective of the peroxide kind, the measured sol fraction from the  
358 swelling test showed an increase in crosslink densities, compared to the untreated blend, in  
359 the following order: DCP > DB > BP. As shown in Fig. 3, this resulted in an increase in the  
360 mechanical strength of 80%, 50% and 0% for blends crosslinked with DCP, DB and BP,  
361 respectively. This was related to the fact that the use of DCP initiator in the HDPE/SBS/GTR  
362 blend caused the least change in melt flow index, which ensured good crosslinking at the  
363 GTR-SBS interface.



364

365 Fig. 3 Stress-strain curves of HDPE/SBS/GTR (S) blends mixed with different peroxides

366

(Hejna et al., 2019).

367 Cañavate et al. (2011) formulated a thermoplastic vulcanizate from HDPE, EPDM and  
368 GTR by a combination of melt-mixing and dynamic vulcanization in the presence of  
369 peroxides. HDPE/GTR samples, without EPDM, displayed weak performance due to  
370 incompatibility of HDPE and GTR that resulted in poor adhesion. On adding EPDM to the  
371 HDPE/GTR composite, toughness and elongation at break increased, but tensile strength and  
372 modulus reduced. It was showed that peroxide only vulcanized EPDM, but not GTR. As  
373 peroxide content increased, HDPE/EPDM/GTR mechanical properties increased due to  
374 greater crosslinking effect of peroxide on EPDM, creating a network of co-continuous phase  
375 that encapsulated the GTR particles. Authors reported a reduction in swelling degree with  
376 increasing peroxide content, which confirmed the increased crosslinking reaction. When  
377 peroxide concentration is sufficiently high, the elongation at break drops, which could be  
378 explained by the possible peroxide reaction with the thermoplastic HDPE. These results show  
379 the importance of the peroxide vulcanization.

380 Lu et al. (2014) prepared thermoplastic vulcanizate (TPV) from PP/EPDM, with different  
381 particle sizes and fractions of GTR, by using a two-roll mill. They observed that tear strength,  
382 tensile strength and elongation at break improved with GTR particle size reduction, while the  
383 same properties reduced with increase in GTR content. The incorporation of polypropylene  
384 grafted maleic anhydride (PP-g-MAH) compatibilizer increased significantly PP/EPDM-GTR  
385 interfacial adhesion, hence the enhancement of above-mentioned properties. Moreover, the  
386 rheological study indicated a lower apparent viscosity of compatibilized TPV compared to  
387 uncompatibilized TPV, which depicted that PP-g-MAH improved the processing  
388 performance.

389 Zhang et al. (2011) mixed crosslinked polyethylene (XLPE) and GTR in a high-shear  
390 mechanical mill to de-crosslink the constituents in solid-state before melt-mixing them. After  
391 20 cycles of milling, the strength of XLPE/GTR increased from 5.5 to 6.0 MPa, with an

392 elongation at break of 185%. Moreover, after dynamic vulcanization in the presence of  
393 sulphur, the strength and elongation at break increased to 9.1 MPa and 201%, respectively.

394 Li et al. (2003) cryogenically mixed GTR with HDPE and reported significant  
395 deterioration of impact strength and elongation at break of the obtained HDPE/GTR material,  
396 compared to HDPE matrix. Stress maxima occurring at the HDPE-GTR interface, due to  
397 incompatibility of the components, produced cracks and propagated, which resulted in the  
398 material break. By against, the impact strength and elongation at break of HDPE/GTR  
399 increased by 160% and 150%, respectively, when EPDM, peroxide and silicone oil additives  
400 were added. Meanwhile, HDPE/GTR and HDPE/EPDM binary materials present a reduced  
401 storage modulus, signifying the influence of the dynamic vulcanizates.

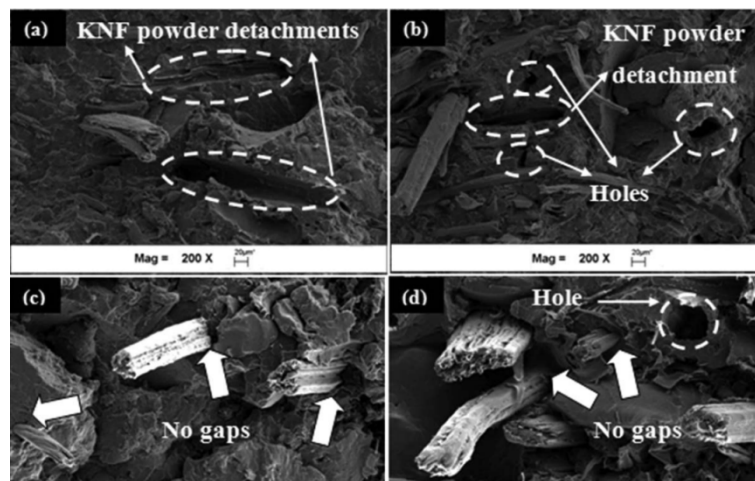
### 402 **3.5 Effect of added fillers**

403 Generally, the primary objectives of the use of GTR to fabricate TPE are to recycle  
404 rubbers, and to obtain materials with competitive properties and cost. To extend applications  
405 of TPE/TPV and considering the clean environment, without compromising the targeted  
406 properties, the incorporation of different fillers is currently practiced in the development of  
407 composites (Noriman and Ismail, 2012; Naderi et al., 2016; Irez et al., 2017; Sripornsawat et  
408 al., 2018; Deriszadeh et al., 2019; Favakeh et al., 2020). Incorporated fillers sometimes  
409 perform a dual role of compatibilizer and reinforcement. Fillers can reduce the GTR sizes and  
410 facilitate their homogeneous distribution in the host matrix. This may therefore allow  
411 microstructural synergy between the composite constituents, which consequently improve the  
412 physical properties of the final product (Vahidifar et al., 2019; Papadopoulos et al., 2021;  
413 Sanusi et al., 2021b).

#### 414 **3.5.1 Micrometric fillers**

415 To obtain durable and more eco-friendly materials, natural cellulose fibres, such as kenaf  
416 (Pang and Ismail, 2013), hemp, flax and wood flours (Cosnita et al., 2017), are now being  
417 incorporated in thermoplastics/GTR to create high-property recyclable composites (Mohanty  
418 et al., 2018).

419 Pang and Ismail (2014) studied the dependence of kenaf particle fibres (KNFs) and kenaf  
420 particle powders (KNFp) on the processing and properties of PP/GTR blends. The  
421 stabilization torque is higher during the mixing of PP/GTR/KNFs system. This is attributed to  
422 the higher viscosity of PP/GTR/KNFs system, which allows a better dispersion of KNFs  
423 within the blend, compared to that of KNFp. The morphology of both systems, observed by  
424 scanning electron microscopy (Fig. 4), confirms this claim, as the KNF powder was  
425 completely pulled out of the PP/GTR/KNFp composite, leaving voids. The increase of  
426 dispersion degree leads to a higher mechanical performance of PP/GTR/KNFs composite  
427 compared to PP/GTR/KNFp.



428  
429 Fig. 4 SEM images of fractured surface of PP/WTP/KNF composites filled with (a) 10 phr  
430 KNFp; (b) 20 phr KNFp; (c) 10 phr KNFs; (d) 20 phr KNFs composites (Pang and Ismail,  
431 2014).

432 Kakroodi et al. (2012) incorporated lignocellulosic flax fibre in HDPE/GTR in the  
433 presence of coupling agent (SEBS) to improve matrix-rubber-fibre surface adhesion.  
434 Substantial physical properties improvement was reported. Then, Kakroodi et al. (2013)  
435 prepared a ternary composite of maleic anhydride grafted polyethylene/GTR/hemp.  
436 Significantly, the addition of hemp fibres increased the mechanical and thermal properties of  
437 the system, which were sustained even after ageing in water. More recently, wood-plastic  
438 composites based on HDPE and GTR were prepared using either red pine wood flours (RPF)  
439 (Başboğa et al., 2020) or sugarcane bagasse (SB) (Rodríguez-Anda et al., 2020). In the later  
440 study, it was found that the best mechanical properties were achieved with the sample having  
441 50/20/30 wt% (HDPE/GTR/SB) concentrations.

442 Aside the natural cellulose fibres discussed above, other fillers like natural mineral (e.g.,  
443 feldspar), industrial wastes (fly ash from coal thermal plants, brewer spent grain) and glass  
444 fibre are among the fillers incorporated in thermoplastic/GTR blends to achieve high-  
445 performance composites (Sridhar et al., 2009; Hassan et al., 2014b; Bukit et al., 2018;  
446 Allouch et al., 2020). However, careful material design, selection and treatment process must  
447 be ensured to avoid properties degradation. For instance, Sridhar et al. (2009) incorporated  
448 GTR in PP thermoplastic and studied the effect of fly ash on performances of the resulting  
449 composite. The fly ash showed more affinity towards the rubbery GTR phase than PP, which  
450 created widespread debonding of fly ash particles. The weak interaction between the PP and  
451 fly ash particles leads to a reduction of strength by ~3% for 10 wt% added fly ash. The  
452 authors assumed that the trend could be reversed by treatment of fly ash with coupling agents.  
453 Formela et al. (2017) prepared a composite foam composed of a polyurethane (PU) filled  
454 with GTR and brewer spent grain (BSG). Incorporation of GTR into PU/BSG composite  
455 raised its strength higher by 50% and accelerated its foaming reaction. In the same way,  
456 dynamic mechanical properties and thermal stability were increased with increasing GTR in

457 ternary composite PU/GTR/BSG composite. The authors suggest that BSG fillers hinder the  
458 polymer chains movement, thus increasing the stiffness of the composite. Zainal and Ismail  
459 (2011) put short glass fibre (SGF) in PP/GTR blends. With the use of silane-coupling agent  $\gamma$ -  
460 aminopropyltrimethoxysilane ( $\gamma$ -APS), the thermal, tensile and swelling resistance properties  
461 of PP/GTR/SGF composite were significantly increased due to improved PP/GTR-SGF  
462 interaction.

463 At last, Moghaddamzadeh and Rodrigue (2018) utilized two waste components derived  
464 from worn-out tyres, i.e. GTR and recycled tyre fibre (RTF), and incorporated them in linear  
465 low-density polyethylene (LLDPE). In the presence of the RTF particles and compatibilizer  
466 MA-g-SEBS, GTR were well dispersed in the LLDPE matrix, resulting in an increase in the  
467 impact resistance of the LLDPE/GTR/RTF composite.

468 Thus, it is clear that the incorporation of natural fibres and other micro-sized fillers can  
469 enhance the properties of thermoplastic/GTR blends. Ecologically, renewable composites are  
470 created by using natural fibres as reinforcements in blends. Nevertheless, optimal attention  
471 should be paid to the size, shape and mass fraction of the fillers as an inappropriate filler  
472 choice can deteriorate material performances. Further process treatments or agents  
473 incorporation may also be required to enhance the targeted properties. Table 1 details the  
474 summary of thermoplastic/GTR blends incorporated with different types of micrometric  
475 fillers as earlier discussed.

476 **Table 1**

477 Thermoplastic/GTR blends incorporated with different types of micrometric fillers

Blend	GTR particle size	GTR concentration range	Filler type	Filler concentration range	Additional treatment/ agent	Processing method	Properties analyzed	Reference
PP/GTR	-	65 phr	Fly ash	10-50 phr	SEBS-g-MAH	Extrusion	Morphology, Tensile, DMA, Thermal, Rheology, Magnetic property	(Sridhar et al., 2009)
PP/GTR	0.2-150 $\mu$ m	30 phr	Kenaf	5-20 phr	-	Melt mixing	Morphology, Tensile, Thermal, Water uptake test	(Pang and Ismail, 2014)
HDPE/GTR	250 $\mu$ m	7.5-30 wt%	Flax	7.5-30 wt%	SEBS-g-MAH	Melt mixing	Morphology, Tensile, Flexural, Density	(Kakroodi et al., 2012)
MAPE/GTR	50-850 $\mu$ m	5-26 wt%	Hemp	10-60 wt%	-	Extrusion	Morphology, Tensile, Impact test, Water uptake and ageing, Hardness, Thermal, Density	(Kakroodi et al., 2013)
PU/GTR	1 mm	5-20 wt%	Brewers' spent grain	5-20 wt%	Flame retardant, Foaming agents	Mechanical stirring	Foaming parameter, Morphology, Tensile, Structure, DMA, Thermal stability	(Formela et al., 2017)



HDPE/GTR	0.5-2 mm	10-30 wt%	Sugarcane bagasse	20-50 wt%	MAPE, sulphur	Thermo-compression	Flexural, Shear resistance, Swelling test, Morphology, Machining test	(Rodríguez-Anda et al., 2020)
LLDPE/GTR	90 <sup>±10</sup> μm	5-25 wt%	RTF	5-25 wt%	SEBS-g-MA	Injection molding	Density, Thermal, Morphology	(Moghaddamzadeh and Rodrigue, 2018)
PP/GTR	250-500 μm		Short glass fibre	5-20 php	γ-APS	Melt mixing	Tensile, Thermal, Swelling resistance, Morphology	(Zainal and Ismail, 2011)
HDPE/GTR	≤4 mm	7.5, 15, 22.5 wt%.	Red pine wood flours (RPF)	15, 30 wt%	PE-g-MA, wax	Screw extruder Injection molding	Density, Swelling, Flexural, Tensile, Impact test, Thermal, Morphology	(Başboğa et al., 2020)

### 478 3.5.2 Nanometric fillers

479 The addition of nanofillers in polymeric blends leads to high-performance material, as  
480 there is the advantage of combining blends and nanocomposites properties (Yeetsorn et al.,  
481 2020; Sanusi et al., 2021a, 2021c). It seems that the nanoparticles act as compatibilizer,  
482 which reduces interfacial tension and promote reduction of GTR particle size during  
483 processing (De Sousa et al., 2015). Thus, the particles coalescence is reduced, and increase in  
484 morphology refinement is achieved. Besides, dynamic vulcanization is adopted to  
485 significantly improve the interaction of matrix, GTR and nanoparticles (Razmjooei et al.,  
486 2012; Paran et al., 2018). Meanwhile, when nanoparticles such as carbon black (CB) are  
487 added in the matrix, carbon crystallites form, leading to particles aggregation, which causes  
488 reduction in the specific surface area of the nanofillers (Huang, 2002). Therefore, appropriate  
489 preparation techniques, like surface treatment of the particles, should be achieved to facilitate  
490 agglomerate-free dispersion of nanoparticles in matrix.

491 Cazan et al. (2019) mixed polyethylene terephthalate (PET), HDPE and GTR. It was  
492 shown that the incorporation of different oxides ( $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{ZnO}$  and  $\text{SiO}_2$ ) in the ternary  
493 PET/HDPE/GTR material influences the interface performance towards improving  
494 mechanical properties at different temperatures, as summarized in Table 2. Remarkably,  $\text{SiO}_2$   
495 gives the superior properties at negative temperature, while  $\text{CaO}$  supports high-temperature  
496 condition. The behaviors of the composites were correlated to specific ionic character of each  
497 oxide.

#### 498 **Table 2**

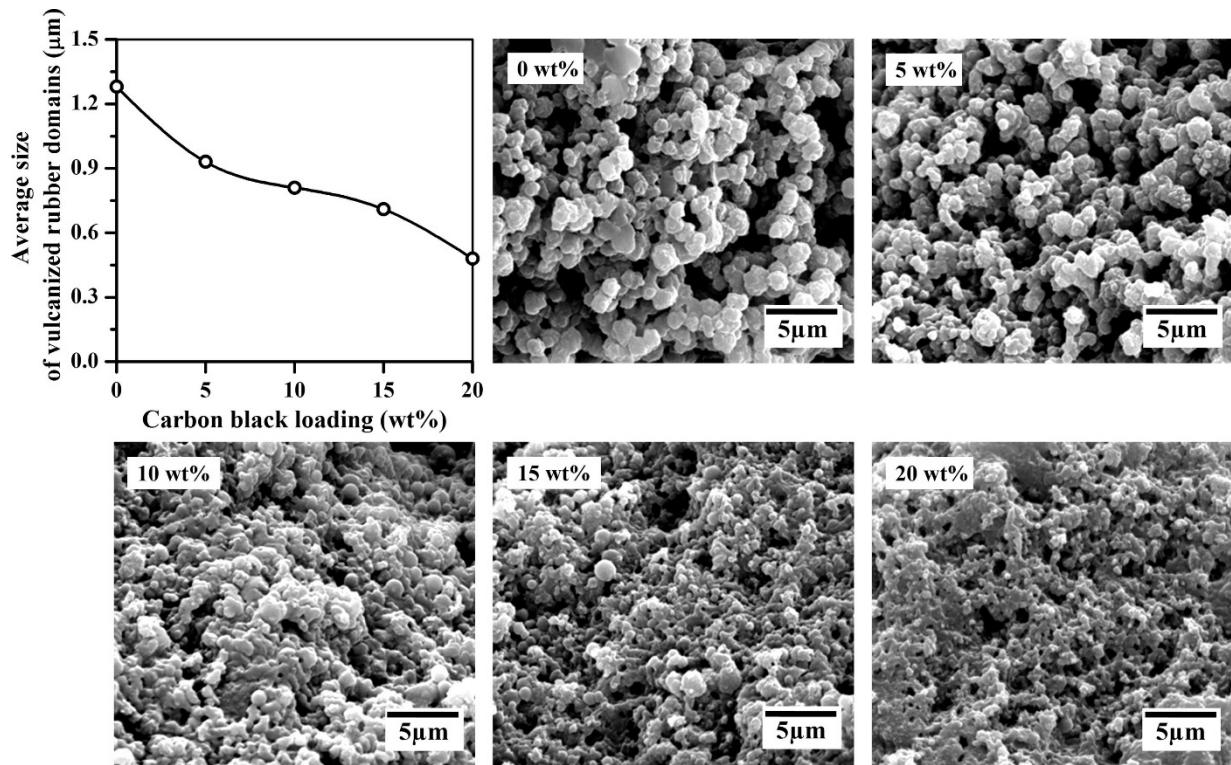
499 Mechanical properties of polymer blends composites subjected to different temperature  
500 conditions (Cazan et al., 2019).

Blend composition	Nanofillers	$\sigma_T$	$E$	$\sigma_C$	$E_{\text{impact}}$
-------------------	-------------	------------	-----	------------	---------------------

	(oxides)	(MPa)	(MPa)	(MPa)	(kJ/m <sup>2</sup> )
PET/HDPE/GTR (35:5:60)	0	1.57	2.56	69.7	7.12
PET/HDPE/GTR/Oxide	TiO <sub>2</sub>	1.10	17.9	72.1	8.70
(No-aged samples)	CaO	1.12	11.7	70.4	11.4
	ZnO	0.92	20.9	82.4	10.6
	SiO <sub>2</sub>	1.29	25.3	82.7	12.1
PET/HDPE/GTR/Oxide	TiO <sub>2</sub>	1.25	14.1	43.7	10.5
(Samples kept at high temperature: +10 to +50 °C)	CaO	1.35	21.6	71.9	11.0
	ZnO	0.82	3.15	35.2	10.1
	SiO <sub>2</sub>	0.96	6.23	68.8	10.9
PET/HDPE/GTR/Oxide	TiO <sub>2</sub>	1.38	8.56	74.6	9.78
(Samples kept at low temperature: -40 to -10 °C)	CaO	1.04	4.03	70.2	9.51
	ZnO	1.08	7.59	86.5	12.3
	SiO <sub>2</sub>	1.70	9.77	80.2	9.92

501 NB:  $\sigma_T$  - tensile strength,  $E$ - Young's modulus,  $\sigma_C$  - compressive strength, and  $E_{impact}$  -  
502 impact energy.

503 Sripornsawat et al. (2018) mixed thermo-chemical devulcanized GTR and copolyester  
504 (COPE) and examined the effect of carbon black (CB) on the microstructure and mechanical  
505 behavior of COPE/GTR composite. They found that an increase in CB content facilitated the  
506 transformation towards the co-continuous structure of COPE/GTR and favored a uniform  
507 dispersion of smaller vulcanized GTR domains in the COPE matrix (Fig. 5). The  
508 incorporated CB particles, which facilitated the rubber-filler interaction, significantly  
509 increased the viscosity of the COPE/GTR blend. The resulting shear effects during mixing  
510 were enhanced, leading to better CB dispersion and hence strengthening of the composite.  
511 Thus, the composite COPE/GTR/CB exhibits increased stress relaxation, tensile strength and  
512 hardness compared to COPE/GTR, however with little a reduction in elongation at break. The  
513 authors also found that CB inclusion improved the damping property of composite.



514

515 Fig. 5. SEM images showing the average size of GTR domain in COPE/GTR/CB at different  
 516 concentration of CB: {0, 5, 10, 15, 20} (wt%) (Sripornsawat et al., 2018)

517 Vahidifar et al. (2019) incorporated multi-walled carbon nanotubes (MWCNT) in PE/GTR  
 518 blend, with the presence of a PE-g-MAH as a compatibilizer. The rubber phase was  
 519 dynamically vulcanized using curing agents including sulphur. Though the GTR entities were  
 520 well-dispersed within the PE matrix, the MWCNT further reduced the GTR sizes and  
 521 improved the homogeneity of PE/GTR/MWCNT morphology. MWCNT also served as a  
 522 crystallization-nucleating agent in the PE matrix and restricted the mobility of the PE/GTR  
 523 blend chains, thus increasing the tensile and viscoelastic properties of the nanocomposite.  
 524 Moreover, percolation threshold was identified at a low concentration of 1 wt% MWCNT. In  
 525 fact, at this concentration, the nanofillers formed a network structure along blend to achieve  
 526 high electrical conductivity property.

527 Kazemi et al. (2018) developed MA-g-PE/GTR/MWCNT nanocomposite for an electrical  
 528 application. They observed that the Fourier transform infrared spectroscopy (FTIR)

529 characteristic peaks of maleic anhydride (1714 and 1791  $\text{cm}^{-1}$ ) in neat MA-g-PE are  
530 significantly reduced in MA-g-PE/GTR. This suggests that the maleic anhydride groups  
531 grafted on PE formed a chemical link with the C=C bonds of GTR particles, which favors the  
532 interfacial adhesion. Moreover, the incorporation of MWCNT facilitates the dispersion of  
533 GTR in MA-g-PE. So, the MA-g-PE/GTR/MWCNT nanocomposite exhibited good  
534 mechanical performance. In fact, the strong compatibility achieved with the help of MWCNT  
535 prevents crack propagation through the interface. If MWCNT facilitates the dispersion of  
536 GTR in MA-g-PE, GTR in return lowers the amount of MWCNT required to obtain  
537 significant electrical conductivity. This is partially explained by the fact that MWCNT cannot  
538 penetrate into the complex 3D-structure of GTR and is localized in the MA-g-PE phase of the  
539 ternary system, easily creating 3D networks of MWCNT. Thus, the electrical conductivity of  
540 the material is enhanced, while the required concentration of the MWCNT is reduced.

541 As far as nanoplatelets are concerned, Deriszadeh et al. (2019) reinforced the PET/GTR  
542 blend with graphene oxide (GO) particles in presence of maleic-anhydride grafted styrene-  
543 ethylene-butylene styrene (SEBS-g-MAH) compatibilizer, aiming at developing epoxy/metal  
544 joining adhesive. The high stiffness of GO resulted in PET/GTR/GO nanocomposite  
545 exhibiting more than 33, 248 and 551% increases in tensile modulus, strength and toughness,  
546 respectively. De Sousa et al. (2015) devulcanized GTR by microwaves method and mixed it  
547 with vulcanization additives in a two-roll mill, before melt mixing the treated devulcanized  
548 GTR with the HDPE matrix and with the HDPE/nanoclay nanocomposite. Contrary to  
549 mechanical properties deterioration attributed to poor adhesion in HDPE/GTR blend, the  
550 addition of nanoclay improved the stiffness, rheological and thermal properties. It is  
551 interesting to emphasize that the authors utilized up to 80 wt% of GTR in HDPE/GTR blend.

552 Bee et al. (2018) analyzed the effect of montmorillonite (MMT) nanoparticles and electron  
553 beam irradiation on the properties of EVA/GTR blend. They found that the nanoclay, at low

554 mass fractions, in EVA/GTR exhibited an intercalated structure that favored its dispersion  
555 and resulted in high mechanical strength, whereas an increase in the MMT concentration led  
556 to clay agglomeration that resulted in strength reduction. On the further treatment of  
557 EVA/GTR/MMT nanocomposite with irradiation, the interaction between the blend and the  
558 MMT nanoparticles was improved. Hassan (2015) studied the combined effect of MMT  
559 nanoparticles and gamma irradiation on the thermal and mechanical properties of the blend  
560 constituted with polyamide (PA) and GTR. It was reported that the gamma radiation  
561 remarkably increased in the tensile strength and thermal stability of the PA/GTR/MMT  
562 nanocomposite compared to untreated nanocomposite. The gamma radiation treatment  
563 facilitated the release of free radicals on GTR surfaces that attacked the thermoplastic PA to  
564 form covalent bonds within the two phases. In addition, the radiation induced the cross-  
565 linking that created interatomic interaction by hydrogen bond, while the MMT nanoparticles  
566 were homogeneously dispersed, leading to improved properties.

567 On a notably ecological importance, Cosnita et al. (2017) mainly used GTR, recycled PET  
568 and little amount of HDPE (5 wt%) to prepare a PET/HDPE/GTR blend for outdoor  
569 applications. The ternary blend was filled with wood dust and rigid calcium oxide (CaO)  
570 nanofillers, aiming at achieving low density, high mechanical properties and dimensional  
571 stability of the final composite. Two significant roles of the CaO nanoparticles were  
572 identified: First, they ensure dimensional stability of PET/HDPE/GTR/wood composite by  
573 absorbing water molecules. Second, the absorbed water molecules make the CaO ordering  
574 degree increased, which promotes its interactions with the other composite constituents  
575 (GTR, PET and wood). The wood dust plays the role of a coupling agent at PET-HDPE-GTR  
576 interface, whereas the dispersed CaO absorbs the wood dust moisture (and acidity) to achieve  
577 outstanding water resistance material.

578 Therefore, the role of nanofillers in facilitating GTR particle size reduction and dispersion in  
579 matrices is an asset for creating high performance materials. Nanofillers can act as a barrier,  
580 coupling agent as well as a conductive material depending on the intended application. Table  
581 3 summarizes various thermoplastic/GTR/nanofillers materials as previously discussed  
582 above.

583 **Table 3**

584 Thermoplastic/GTR nanocomposites filled with different types of rigid nanofillers.

Blend	GTR particle size	GTR concentration range	Filler type	Filler concentration range	Additional treatment/ agent	Processing method	Properties analyzed	Reference
COPE/GTR	40 mesh	50 wt%	CB	0-40 phr	Dynamic vulcanization	Melt mixing	Mechanical, DMA, Rheology, Morphology	(Sripornsawat et al., 2018)
EVA/GTR	-	20 phr	MMT	2-10 phr	Electron beam irradiation	Extrusion and compression molding	Structure, Gel content test, Tensile, Thermal, Morphology	(Bee et al., 2018)
HDPE/GTR	-	80 wt%	MMT	5 wt%	Dynamic vulcanization	Melt mixing	Tensile, Rheology, Morphology, DMA	(De Sousa et al., 2015)
LLDPE/GTR	11-14 $\mu\text{m}$	30-50 wt%	MWCNT	1-3 wt%	PE-g-MA, Dynamic vulcanization	3-step melt mixing	Morphology, Tensile, Hardness, Thermal, Rheology	(Vahidifar et al., 2019)
MAPE/GTR	<50 $\mu\text{m}$	50 wt%	MWCNT	0.5-1.0 wt%	PE-g-MA	Solution, melt casting	Structure, Morphology, Calometric, Tensile, Electrical	(Kazemi et al., 2018)
PET/HDPE/GTR	1 mm	60 wt%	TiO <sub>2</sub> , CaO, ZnO, SiO <sub>2</sub>	0.25-2 wt%	-	Melt mixing	Tensile, Thermal, Contact angle, Structure, Morphology	(Cazan et al., 2019)
PET/HDPE/GTR	1 mm	78-80 wt%	CaO	0.5-2 wt%	-Wood sawdust	Melt mixing	Physicochemical	(Cosnita et al., 2017)



							structure, Contact angle, Morphology, Mechanical	
PET/GTR	-	20-80 wt%	GO	0.1-0.5 phr	SEBS-g-MAH	Extrusion	Tensile, Single-lap shear test	(Deriszadeh et al., 2019)

#### 585 **4. Conclusion**

586 The mixing of waste tyre particles (GTR) with thermoplastic matrices to fabricate  
587 thermoplastic elastomers (TPE) is an efficient, promising, and practical means of recycling  
588 large amount of the worn-out tyres. The development of recyclable composites is further  
589 possible with the incorporation of renewable reinforcements. Although the incorporation of  
590 GTR in thermoplastic consumes reasonable quantity that addresses environmental concerns,  
591 the properties of the final TPE composites need to be improved for competitive advantage,  
592 especially if higher percent of GTR (>50%) is to be used. Several methods have been  
593 highlighted to improve the interfacial adhesion: addition of compatibilizers/coupling agents,  
594 application of dynamic vulcanization techniques, high-energy irradiation treatments and so  
595 on. These approaches, individual or coupled, improve the compatibility of crosslinked rubber  
596 (GTR) molecules making them entangle with thermoplastic molecules and favoring their  
597 dispersion to form high-performance composites. More particularly and more recently,  
598 adding nanoparticles in thermoplastic/GTR blends improves the GTR dispersion in  
599 thermoplastic phases and facilitates the reduction of GTR size in the TPE, leading to better  
600 nanocomposite performance. The recyclability and renewability of thermoplastic/GTR can  
601 also be achieved by using natural cellulose fibres as reinforcing phase without altering the  
602 mechanical properties of the composites.

603 The developed thermoplastic/GTR composites have been applied in various engineering  
604 fields. For instance, these materials have been used in high-thermal foam (Formela et al.,  
605 2017), ferromagnetic (Sridhar et al., 2009), impact resistance (Başboğa et al., 2020), electric  
606 conductive (Kazemi et al., 2018) and adhesive (Deriszadeh et al., 2019) applications. Aside  
607 other conventional applications of thermoplastic/GTR composites in the construction and  
608 sports sectors, their relevance in defence and security technology may be another interesting  
609 application area. Specifically, in the field of armour and ballistic engineering,

610 thermoplastic/GTR nanocomposites could be a potential alternative due to their reported  
611 impact resistance, thermal and mechanical properties. Thermoplastic/GTR nanocomposites  
612 could also be relevant in acoustic and sound applications. In the meantime, more strict  
613 regulations against indiscriminate disposal of waste tyres need to be considered worldwide.  
614 Aggressive awareness creation and research support for more innovative research  
615 development around waste tyre recycling and management should be pushed across all  
616 nations.

### 617 **Acknowledgement**

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