

Ground tyre rubber (GTR) in thermoplastics, thermosets, and rubbers

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Abstract The disposal of worn tyres and their economic recycling mean a great challenge nowadays. Material recycling is the preferred way supported by legislative actions and economical/ecological arguments. This paper surveys the recent developments devoted to the reclamation, surface treatments, and to the use of ground tyre rubber (GTR) in thermoplastics, thermosetting resins, and rubber formulations. This review discloses also the principle underlying compatibilization to improve the adhesion of GTR to the corresponding matrix. It was concluded that value-added application of GTR can especially be expected in thermoplastic elastomers, and rubber combinations.

List of symbols

K_c	Critical stress intensity factor (MPa m ^{1/2})
M100	Modulus at 100 % elongation (MPa)
M200	Modulus at 200 % elongation (MPa)
M300	Modulus at 300 % elongation (MPa)
p	Pressure (MPa)
T	Temperature (°C)
t	Time (min)
T_g	Glass transition temperature (°C)
TM	Tensile modulus (MPa)
TS	Tensile strength (MPa)
UE	Elongation at break (%)

Abbreviations

ABS	Acrylonitrile butadiene styrene copolymer
Al	Aluminum
AN	Acrylonitrile

ANN	Artificial neural network
ATBN	Amine-terminated liquid NBR
BR	Butadiene rubber
CB	Carbon black
CNT	Carbon nanotube
CO ₂	Carbon dioxide
CPE	Chlorinated polyethylene
CR	Chloroprene rubber
CTBN	Carboxyl-terminated liquid nitrile rubber
DOE	Design of experiment
EAA	Ethylene acrylic acid
EB	Electron beam
EBA	Ethylene butyl acrylate copolymer
EGMA	Ethylene glycidyl methacrylate
ENR	Epoxidized natural rubber
EP	Epoxy resin
EPDM	Ethylene–propylene–diene rubber
EPR	Ethylene–propylene rubber
EVA	Ethylene vinyl acetate copolymer
GF	Glass fiber
GMA	Glycidyl methacrylate
GTR	Ground tyre rubber
GTR- <i>g</i> -MA	Ground tyre rubber grafted by maleic anhydride
H	Hydrogen
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulfuric acid
HClO ₄	Perchloric acid
HDPE	High density polyethylene
HDPE- <i>g</i> -MA	High density polyethylene grafted by maleic anhydride
HDT	Heat distortion temperature
HEBM	High energy ball milling
HNO ₃	Nitric acid
HPHTS	High-pressure high-temperature sintering

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IIR	Isobutylene isoprene rubber
IPN	Interpenetrating network
IR	Isoprene rubber
KMnO ₄	Potassium permanganate
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MA	Maleic anhydride
MAA	Methacrylic acid
MFI	Melt flow index
MSBR	Butadiene methylstyrene rubber
MW	Molecular weight
N	Nitrogen
NBR	Nitrile butadiene rubber
NR	Natural rubber
PA6	Polyamide 6
PBT	Polybutylene terephthalate
PE	Polyethylene
PE- <i>g</i> -MA	Polyethylene grafted by maleic anhydride
POE	Polyoctane ethylene
PP	Polypropylene
PP-GF	Glass fiber reinforced polypropylene
PP- <i>g</i> -MA	Polypropylene grafted by maleic anhydride
PP- <i>g</i> -GMA	Polypropylene grafted by glycidyl methacrylate
PS	Polystyrene
PU	Polyurethane
PVC	Polyvinyl chloride
rHDPE	Recycled high density polyethylene
rLDPE	Recycled low density polyethylene
RT	Room temperature
SBR	Styrene/butadiene rubber
SBS- <i>g</i> -MA	Styrene–butadiene–styrene block copolymer grafted by maleic anhydride
SEBS	Styrene–ethylene–butadiene–styrene
SEBS- <i>g</i> -MA	Styrene–ethylene–butadiene–styrene grafted by maleic anhydride
SGF	Short glass fiber
SSSE	Solid-state shear extrusion
SSSM	Solid-state shear milling
TDV	Thermoplastic dynamic vulcanizate
TPE	Thermoplastic elastomer
TPU	Thermoplastic polyurethane
UP	Unsaturated polyester resin
UV	Ultraviolet irradiation
XLDPE	Crosslinked low density polyethylene
ZnO	Zinc oxide

Introduction

Nowadays, plastics and rubbers are extensively used in different fields and thus the recent period is termed sometimes “Plastic Age.” Because of polymeric materials do not

decompose easily, the disposal of their wastes causes a serious environmental problem. The recycling (reutilization) of post-consumer and post-industrial polymeric wastes poses a great challenge. This note holds especially for worn (discarded, scrap) tyres. The matrix material of tyres is composed of vulcanized (crosslinked) rubbers which cannot be reprocessed owing to their crosslinked structure. It is, therefore, of paramount importance to develop technologically feasible and cost-effective methods for recycling of rubber from scrap tyres. The best way would be to devulcanize the rubber and reuse it in new rubber products. Although such processes are worked out, they often remained in preindustrial/precommercial stage, mostly due to economic reasons. Alternative solutions, following the material recycling routes “back to the feedstock”, focus on the production of oils (to be used as plasticizer, extender in rubber mixes) and carbon black (CB) [1]. The latter can be used as reinforcement and coloring additive in various polymers and rubbers.

The most straightforward option is, however, to combine (to blend) particulate rubber with a polymeric material having the ability to flow under certain conditions (supported usually by the action of heat and/or pressure), so that it can be shaped into products at acceptable cost [2]. This can be achieved using thermoplastics, thermosetting resins and rubber compounds as potential matrices.

Next, an overview will be given on how ground tyre rubber (GTR), with and without surface treatment, can be used in thermoplastic, thermoset and rubber formulations. This treatise will cover also other ground scrap rubbers when the related recycling strategy can be adapted for GTR. It is the right place to underline that GTR is termed differently in the literature. The other widely used terms are: particulate (tyre) rubber, scrap (tyre) rubber, crumb (tyre) rubber, rubber granulate, rubber powder, size-reduced rubber, pulverized rubber.

Worn tyres—quantity, composition

The world consumption of rubber (natural and synthetic) in 2010 was 24.845 kt. Most of this material (~ 65 %) is used in the tyre industry, from which, sooner or later becomes waste [3, 4].

In the 27 member states of the European Union (EU) completed with Norway and Switzerland, 3273 kt post-consumer tyres were accumulated during 2010. The ranking of states according to the quantity of the arisen used tyres is shown in Fig. 1.

Tyres have a four-phase life cycle: new, part-worn (road-worthy tyres), retreadable (casing suitable for retreading), and recyclable.

The composition of tyres for passenger cars (7.5–9 kg) and trucks/buses (50–80 kg each) is summarized in Table 1.

Fig. 1 The quantity of used tyres arisen in the EU countries completed with Norway and Switzerland in 2010 [5]

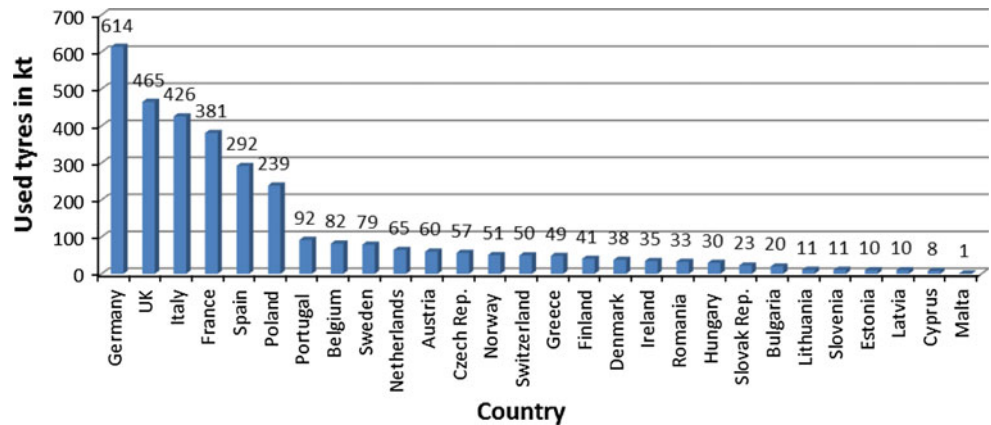


Table 1 Composition of tyres in the EU (wt%) [6]

Material	Passenger cars	Trucks/buses
Rubber/elastomers	48	43
CB	22	21
Metal	15	27
Textile	5	–
Zinc oxide	1	2
Sulfur	1	1
Additives	8	6

The major disposal routes for post-consumer tyres in the EU are depicted in Fig. 2.

The export of part-worn tyres is directed toward less developed countries. Retreaded tyres meet the same standards as new ones. Note that during retreading 2–3 kg fresh rubber is applied to rebuild a tyre, the rubber content of which is 48 % for a passenger and 43 % for a truck tyre. Energy recovery covers apart the use of tyres as non-fossil fuel (in cement kilns, paper mills, electricity generation plants) also energy recovery/material recycling (pyrolysis, production of synthesis gas, etc.) [7–9]. In the latter case, the products (oils, aromatics, gaseous products, steel, ZnO, and CB) are marketable. Land filling is no more a viable option in the EU as the Landfill Directive (1999/31/EC) forbids the disposal of entire tyres from 2003 and shredded ones (size between 50 and 300 mm) from 2006.

Material recycling is strongly favored due to several reasons

- *Legislative actions* 2000/53/EC End of Life Directive requires that from 2006 80 % and from 2015 85 % of all cars should be recyclable. This has a strong impact on rubber products built in passenger cars. Note that a compact car contains ca. 60 kg rubber; the major part (ca. 70 %) is given by tyres [9]. A further EU directive, viz. Incineration of Waste 2000/76/EC, also supports

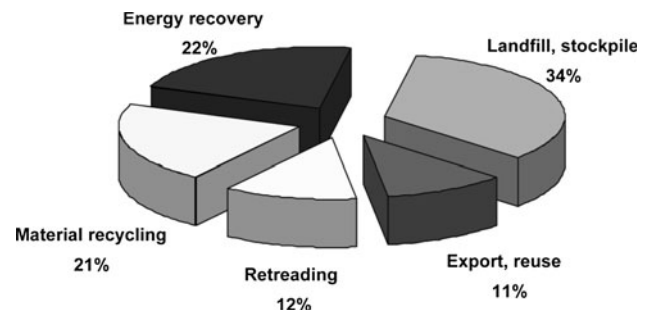


Fig. 2 Average breakdown in post-consumer tyre disposal in the EU [7]

the material recycling via lowering the emission standards of cement kilns and the like.

- *Energy balance* the energy equivalent of 1 kg of tyre is ca. 128 MJ. Its recovery by energy generation yields, however, only 30 MJ. On the other hand, ca. 6.8 MJ of additional energy is required to produce 1–1.5 kg GTR [10]. This is likely the major driving force to develop advanced grinding techniques for worn tyres.

Material recycling of post-consumer tyres goes in two directions

- Civil engineering is using greater quantity and larger pieces, such as whole tyres, shred, and chips (particle size between 10 and 50 mm) in various applications (sound deadening, insulation, artificial reefs, soil stabilization, dam/road constructions, etc.).
- Product/material manufactures are using smaller quantities (at the present) and smaller pieces (granulates lying in the range of 0.5–15 mm and powders with a particle size <0.5 mm).

Some of these applications often appear under the heading “downcycling” as the recycled product has a different application than the initial one (i.e., tyre) [9]. Nowadays under “downcycling” less demanding, inexpensive applications are

meant whose costs are controlled by the rubber granule or powder themselves. Further, the related applications have been saturated with the major exception of road paving.

Accordingly, there is a considerable demand to find new, value-added use for GTR fractions.

Worn tyres—recycling

Recycling of tyres may follow different ways such as [11]:

- retreading (truck and passenger tyres)
- use of tyres as a whole (artificial rafts, cover foil weights) or in parts (building blocks)
- grinding
- pyrolysis (to oils, monomers, CB)
- reclaiming (decrosslinking for mixing into fresh rubbers).

Note that landfill disposal is not even mentioned above being environmentally problematic (leakage of pollutants, breeding grounds for rats, mosquitoes) [12, 13] and thus in many countries banned.

Our survey deals mostly with grinding and reclaiming as they represent the major material recycling options. Moreover, they are often combined to guarantee the necessary compatibility between GTR and matrix polymer as discussed later. Rubber recycling usually concentrates on discarded tyres.

This is due to the fact that almost 70 % of all natural and synthetic rubbers are “consumed” in the tyre manufacture [11, 14]. The related recycling methods were already a topics of review articles [14–16] and book chapters [17, 18] which are, however, dated back by one decade.

In the EU, the Revised Framework Directive on Waste 2008/98/EC focuses on the EU becoming a “recycling society” whereby considering tyres as a target with specific criteria for end of waste status [5].

Ground tyre rubber (GTR)

Production, properties

As underlined before, grinding (size reduction) is the preferred recycling route for waste tyres being associated with obvious economic and social benefits [16].

To convert the whole tyre into GTR the related technology comprises the following steps: shredding, separation (steel, textile), granulation, and classification. GTRs are produced by mechanical grinding at ambient temperature, at ambient temperature under wet condition, at high temperature and at cryogenic temperature [11, 15]. Prior to grinding to higher mesh sizes, i.e., smaller particle sizes,

the tyre is cut into relatively large and then shredded into smaller pieces. Ambient grinding is usually practiced in two-roll cracker-type mill. Though termed “ambient” the temperature may rise up to 130 °C during milling [11]. The achievable particle size and particle size distribution of GTR depend on the milling sequences and mill type. By finishing mills a mean particle size of ca. 200 µm can be reached. Under wet (ambient) grinding the crumb rubber is cooled by water spraying. Afterward, water is separated from the GTR and the latter is dried [14].

High-temperature grinding ($T \sim 130$ °C), accompanied with substantial devulcanization is seldom followed. This method results in granules of 1–6 mm. This limitation is given by the viscoelastic nature of rubber along with its low heat conductivity. In order to reduce the temperature loading of the rubber during grinding water may be added. This wet process may produce GTR of <100 µm mean particle size.

Cooling the rubber below its glass transition temperature (which is type dependent and lies between –30 and –80 °C) the energy needed for grinding can be substantially reduced. At this cryogenic grinding, the “frozen” pieces pass an impact-type mill causing their shattering. The GTR is dried afterward; fibers and metals are separated and then classified into the required mesh sizes [11, 14, 15]. Unlike ambient grinding, the surface of the cryogenic GTR is not “oxidized”. The cryogenic process results in “cleaner” GTR in terms of fiber and steel residues than the ambient one. Major benefit of the ambient grinding is that the surface/mass ratio of the GTR is almost double that of the cryogenic one at equal mesh size [11]. On the other hand, the cooling via liquid nitrogen is very costly.

Figure 3 shows the differences between GTR powders produced by different grinding methods. With an ambient mechanical grinding relative high specific area can be achieved (Fig. 3a, d). At ambient temperature, water-jet process can also be applied (Fig. 3b) resulting in higher area/volume ratio. Needless to say, specific area has a great influence on the adherence of GTR to a given matrix polymer. Cryogenic GTR particles are “edgy” with flat surfaces (Fig. 3c, e) compared to the rough, irregular-shaped ambient ground powders.

Properties of GTR

It was early recognized that the quality of GTR has to be determined and guaranteed accordingly. The major quality properties of GTR are the particle size range (particle size distribution) and level of contamination (steel, textile).

The standard released on how to characterize “particulate rubber” is the ASTM D 5603 (1996). According to this standard rubber powders are classified with respect to feed stock and sieve analysis results. Accordingly, GTR should

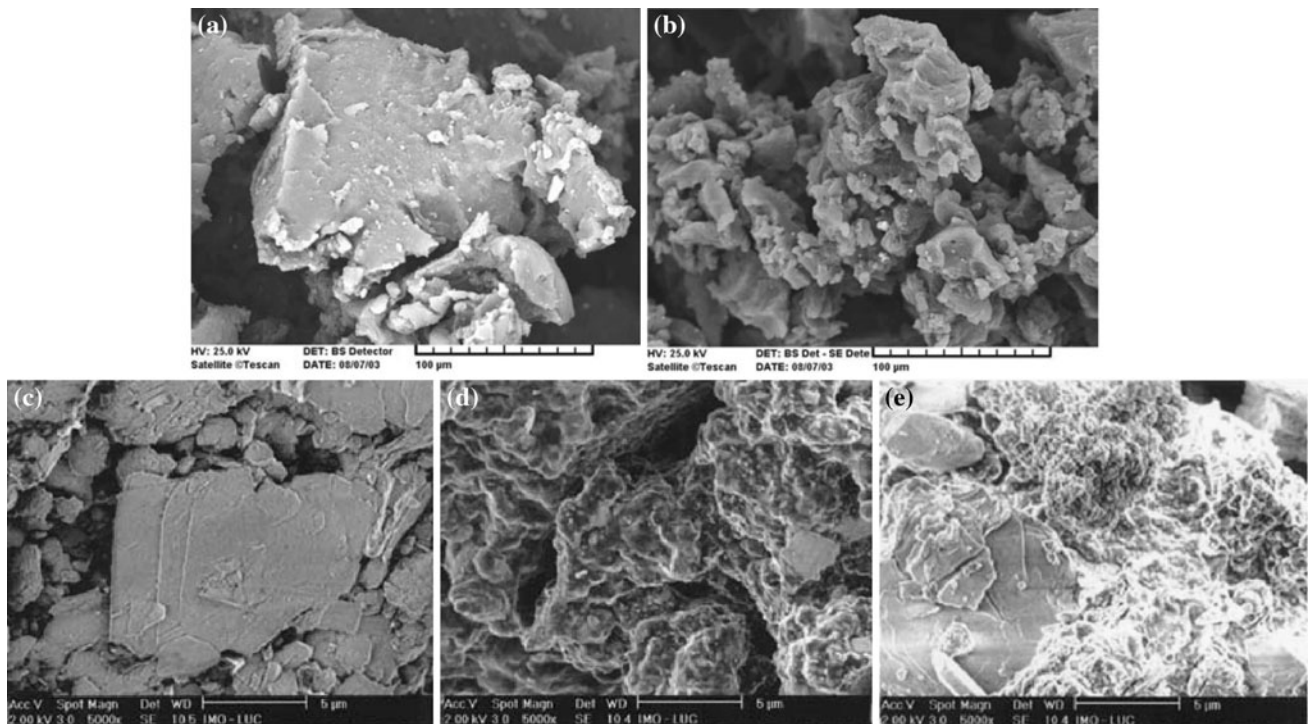


Fig. 3 SEM pictures of GTR produced in different ways: ambient (mechanically ground) (a) [19]; ambient (ground by high pressure water) (b) [19]; cryogenically ground in pin mill (c) [20]; ambient

ground in rotary mill (d) [20]; cryogenically ground in rotary mill [20] (reproduced with permission)

meet a range of chemical and physical properties including the maximum allowable concentration of fibers and metal. Manuel [11] pointed out that the ASTM D 5603 cannot be used in its current form in Europe as the raw materials and their composition in the tyres in USA differ from those in Europe.

The specifications of commercial GTR offered by Vredestein Rubber Resources contain the following characteristics: rubber origin, grinding technology, chemical composition, particle distribution, physical properties, and impurities. Recall that the ASTM D 5603 does not inform about the grinding technology, physical properties, and impurity leaching to the environment. Among the chemical composition, the acetone extract (ASTM D 297), ash content (ASTM D 297), CB content (ASTM E 1131), rubber content (ASTM E 1131), natural rubber (NR)/synthetic rubber composition (ASTM D 3452), and heat loss (ASTM D 1278) are listed. The particle size fraction is usually determined according to the ASTM D 5644 and the particle size distribution is given in millimeter (or mesh). Among the physical properties, the Vredestein specification reports about the surface appearance (rough/edgy) determined by microscopy and various densities of the rubber (specific density—ASTM D 297; pour density—ISO 1306, and compacted density—ISO 787). Among the impurities, the maximum allowable values of the steel,

textile, and others (all of them according to ASTM D 5603) are also indicated [11].

However, the determination of the above parameters is labor intensive and/or hardly reproducible. For example, the specific surface values are highly influenced by out-gassing phenomena [21, 22].

As mentioned before, the appearance of GTR strongly depends on the grinding technique. Researchers tried to describe the uniformity of the powder [23] along with its surface roughness also by other means, e.g., fractal dimensions [24]. Nonetheless, it has to be stated that the mean particle size and particle size distribution are of great practical relevance because the properties of compounds with GTR are mostly controlled by them ([24] and references therein). Unfortunately, in many scientific papers the characteristics of the GTR used were not adequately disclosed.

As in many of cited works the same GTR was used, namely fractions produced by the Genan Technology, their properties are listed in Table 2. Note that in this Genan Technology [25] the grinding to fine fractions occurs at ambient temperature in an air-gab at supersonic speeds. As GTR is made from very different tyres, only guiding values can be given on the elastomer composition of the powders. So, the rubber components are: NR—ca. 30 %, styrene/butadiene rubber (SBR)—ca. 40 %, butadiene rubber

Table 2 Characteristics of GTR produced by the Genan Technology at Scanrub (Viborg, Denmark) [25]

Properties	Test method		Unit	Specification of ASTM D 5603	Typical values of Genan GTR
	ASTM	ISO			
Specific gravity		2781	g/cm ³	NA	1.1–1.2
Ash	E 1131		%	<8	<5
Acetone extract	D 297	1407	%	8–22	11–17
CB content	E 1131		%	26–38	32–36
Rubber hydrocarbon	D 297		%	>42	>42
NR content	D 5603		%	13–35	ca. 30
Free metal content	D 5603		%	<0.1	<0.05
Free textile/fiber content			%	<0.5	0.3

(BR)—ca. 20 %, butyl and halogenated butyl rubbers—ca. 10 %.

Compatibilization strategies

The oldest technique to recycle GTR is simply to “rebond” the GTR particles using adhesive binders. These binders are usually liquid thermosetting resins, fresh (virgin) thermoplastic polymers or rubbers, as well as rubber curatives. However, this rebond approach often fails to ensure the necessary adherence of the GTR particles to the corresponding matrix. For that purpose, namely to establish a smooth stress transfer between the GTR and the matrix, the surface of GTR should be modified. This modification, termed compatibilization, makes the interfaces of the phases similar to each other or provides specific interaction sites between the phases [2]. The result is a “technologically compatible” system with useful mechanical properties. In general, compatibilization can be achieved by physico-mechanical and chemical methods. In many surface modification procedures, both physical and chemical aspects are involved. Similar to mineral-filled polymers, the introduction of dispersing aids helps to reduce the interfacial tension and to prevent agglomeration. On the other hand, this is less straightforward than chemical treatment as argued later.

Chemical compatibilization is aimed at creating good bonding between the GTR particle and the matrix polymer. This is achieved by reduction of the interfacial tension yielding improved wetting, and formation of a “thick” interphase. Good bonding can be guaranteed by both non-reactive and reactive methods. In the former case, copolymers and graft copolymers, showing compatibility toward both GTR and matrix, are preferentially used. According to the reactive route, the GTR and the matrix—mostly in presence of further additives—react with each other, thereby linking these phases chemically [2].

The efficiency of compatibilization can strongly be improved when the GTR surface is (partly) devulcanized, or its surface is activated by various treatments. Devulcanization may support the molecular entanglement with

thermoplastics and curable rubbers. In case of thermosets, a thick interphase may be formed when the resin swells the partially decrosslinked GTR particle. Surface activation by various routes, on the other hand, may trigger entanglement and/or chemical coupling with the matrix or additional polymeric compatibilizer. Therefore, next the various devulcanization and surface activation strategies will be briefly introduced.

Devulcanization, reclamation

Devulcanization and reclaiming are related but quite different processes. The outcome is practically the same: a rubber compound that can be compounded and redevulcanized similar to fresh gum. The difference between reclamation and devulcanization is given by the target of the chemical attack. Devulcanization targets the sulfuric crosslinks in the vulcanized rubber and thus C–S and S–S bonds are selectively cleaved. Note that devulcanization requires high energy to break the –C–S–C– (285 kJ/mol), –C–S–S–C– (268 kJ/mol) or –C–S_x–C– (251 kJ/mol) bonds [26]. On the other hand, reclaiming is usually accompanied with considerable scission along the polymeric chains resulting in lower molecular mass fractions. Irrespective to the above clear distinction between reclamation and devulcanization [8], the processes adapted can hardly be grouped into devulcanization or reclamation. So, in the brief survey below the processes will be classified as follows: thermomechanical, thermochemical, ultrasonic, microwave, and other processes.

Thermomechanical processes In the corresponding processes, crumb rubber is subjected to shear and/or elongational stresses on suitable equipments such as mills, twin-screw extruders, etc. Milling and extrusion are usually carried out at ambient and high temperatures. This may result in a prominent decrease in the molecular mass because even at ambient process considerable heat is generated. The characteristics of the products strongly depend on the processing equipment, its characteristics

(e.g., local shear rate), and processing parameters (e.g., residence time). Earlier, for that purpose discontinuously operating open mills were used ([26] and references therein). Nowadays, there is a clear tendency to prefer continuous operations using extruders [27–29]. To find the optimal processing parameters, various strategies of experimental design are followed, such as response surface method [29]. Moreover, the design and the construction of devulcanization extruders is a topic of ongoing research [27]. It is worth of noting that such thermomechanical processes are often performed in the presence of reclaiming agents (e.g., [25, 27, 29, 30] and references therein) and thus they belong already to the category of thermochemical decomposition processes.

Thermochemical processes To manufacture reclaim rubbers usually chemical reclaiming agents are used. There is a wide range of inorganic and organic reclaiming compounds as reviewed by Adhikari et al. [15]. Those chemical agents work exclusively at elevated temperatures and the related processes usually require mechanical mixing/kneading. Because of hazardous and costly reclaiming agents, attempts were made to avoid them, for example, using phase transfer catalyst [31].

Interestingly, one of the oldest methods, the “pan process” is a static one [15, 25]. In the “pan process”, GTR is heated in saturated steam at a high temperature (150–180 °C) in the presence of “catalysts” (peptizer) and reclaim oil. First, the mixture is allowed to swell for at least 12 h. Note that GTR is retaining its “free powder flow” characteristics when containing up to 35 parts per hundred resin (phr) paraffinic oil [25]. The material is then placed in 2–3 mm thickness in pans to allow oxygen to penetrate. The trays are autoclaved in air/steam atmosphere at ca. 190 °C for ca. 5 h. After that, the material should be strained/refined to get a homogeneous mixture from the more degraded skin (outer layer) and less degraded bulk (inner layer) [8, 15]. The related claim is plastic dough generally used in fresh rubber mixes.

The role of the reclaiming agents is to cleave the sulfuric crosslinks between the rubber chains and terminate the free radicals formed. The digester processes reclaim the rubber crumb in a steam vessels equipped with agitators, which continually stir the crumb rubber while steam applied.

It is noteworthy that the vulcanization system used strongly affects the formation of the sulfuric crosslinks. Poly- and disulfidic crosslinks are mostly formed by conventional, whereas monosulphidic ones are by efficient vulcanization systems. The grouping between conventional, semi-efficient, and efficient vulcanization systems depends on the actual accelerator/sulfur ratio [32]. The devulcanization of rubbers which were vulcanized by conventional curing system is the easiest.

Like to the pan process “softeners” (processing oil, reclaim oil) are frequently used in GTR reclaiming. The primary function is to stretch the bonds between rubber chains and thus to reduce the mechanical energy required for mixing, kneading. As softener, asphalts [33, 34] and bitumens [35, 36] can also be used. It is noteworthy that GTR is very frequently introduced in pavement mixes containing bituminous or asphaltene-rich binders. The recent research strategy is to use processing oils from renewable resources [37]. It is the right place to call the attention that repeated reclaiming is associated with some changes in the properties [38].

Partial devulcanization of GTR may occur in both batch and continuous processes. The former procedure keeps the powder appearance of GTR which can be incorporated afterward in thermoplastics and rubber mixes [39, 40]. By contrast, the output of continuous extrusion is a plastic mass which is either incorporated in fresh curable rubbers or revulcanized by adding curatives [41–43].

Devulcanization may be performed also in solid state. This was shown by Cavalieri et al. [44] making use of high energy ball milling (HEBM). It was found that HEBM led to preferential breakage of sulfur crosslinks. It was also observed that NR can be grafted onto the surface of GTR via this mechanochemical milling.

Fukumori et al. [45] pinpointed a new concept: combination of devulcanization with dynamic vulcanization to produce a thermoplastic elastomer (TPE) on line continuously. The related concept is depicted in Fig. 4.

The process is composed of pulverization, devulcanization, blending with a thermoplastic polymer (polypropylene, PP), and dynamic vulcanization. Attention was paid also to the deodorization of the final TPE compound. Thermoplastic dynamic vulcanizate (TDV) is a new member of the TPE family. TDVs are produced by dynamic curing of blends composed of a thermoplastic resin and a crosslinkable rubber. Dynamic curing means the selective curing of the rubber in the molten thermoplastic under intensive shearing. The matrix of TDV is given by the thermoplastic phase in which (sub)micron-sized crosslinked rubber particles are dispersed. Note that TDVs containing other rubbers than ethylene–propylene–diene rubber (EPDM, i.e., NR and other synthetic rubbers) can also be produced. On the other hand, differences in the devulcanization mechanisms of the related rubbers [45] should be taken into account.

Ultrasonic, microwave A viable alternative to decompose crosslinked rubber is the use of powerful ultrasound (low frequency range of the ultrasound defined by the interval 20 kHz to 500 MHz). The basis of the process is that the energy of sulfur–sulfur bond is on the level that can be broken up by the ultrasonic waves [14]. The chemical and

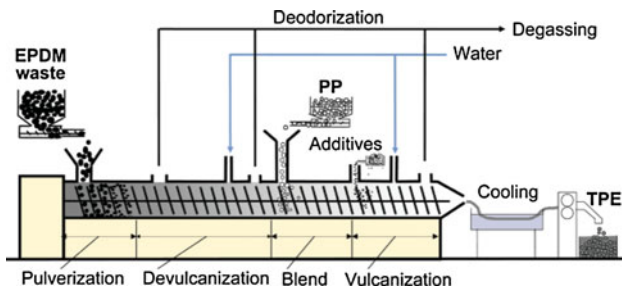


Fig. 4 Dynamic devulcanization and dynamic vulcanization processes for the product of TPE based on EPDM waste [45] (reproduced with permission)

mechanical effects of the ultrasound are caused by cavitation of bubbles (formed during the treatment) during the negative pressure period of the ultrasound. Two competing theories exist to explain the cavitation-induced chemical changes: the “hot spot” and “electrical theory.” The former postulates that the localized bubbles may have a temperature of 5000 K and a pressure of 500 bar. The electrical theory assumes that on the surface of the bubble locally generated electrical field gradient is enough to break chemical bonds [46, 47]. Ultrasonic devulcanization of rubber proved to be a useful recycling strategy. Isayev and co-workers [48, 49] studied the continuous devulcanization of various rubbers using an extruder coupled to an ultrasonic generator. In that case, the plasticized rubber was pumped through a narrow gap between the stationary die and the vibrating horn (coaxial). Another solution is possible when the horn is placed exactly after the screw and then the treated material goes through the die (barrel). Both the types of treatment are effective, the main characteristic parameters are the residence time and the ultrasound amplitude. Of course the temperature and the pressure also affect the rate of the devulcanization. After devulcanization, the mechanical properties are close to the original ones [50–52]. Ultrasonic treatment was successfully used to produce silicon rubber reclaim that was incorporated in both fresh and ultrasonically decomposed SBR to modify the surface and bulk properties of the latter [53].

The use of microwave allows the energy required for the devulcanization of the GTR to be easily obtained and controlled. The energy required for the devulcanization of rubber is around 180 Wh for 1 kg rubber [54, 55]. In the microwave technique, the waste rubber must be polar to generate the heat (>250 °C) necessary for devulcanization. The presence of CB, having high thermal conductivity and heat capacity, ensures the accumulation of internal energy and its uniform distribution in the material [54]. Softeners, when apolar, have a negative impact on the devulcanization. Nevertheless, guide lines for a highly selective and uniform devulcanization are not yet deduced. Microwaving is often coupled with extrusion and mixing. The

transformation to refined, devulcanized stock is rapid and cost-efficient. In addition, the corresponding compound may serve as raw material for the same product that has been produced from ([15] and references therein). Pistor et al. [54] used the microwave-aided devulcanization in EPDM systems. They also investigated it in the presence of paraffinic oil (apolar). They concluded that the devulcanization is best controlled when paraffinic oil is extracted from the rubber and when the samples are exposed to microwaves for short periods. Zanchet et al. [56] added microwave-devulcanized SBR waste powder up to 80 phr in a sulfur-curable SBR and studied the mechanical thermooxidative and photooxidative properties of the resulting blends. The sol content of the waste SBR increased from the initial 7 to 67 % after 3 min microwave treatment in a modified domestic-type oven with 900 W magnetron capacity.

Others There are many other methods of reclamation/devulcanization, which, however, represent some combination of the above-listed ones. The microbiological devulcanization deserves a separate entry. Encouraged by the fact that NR-latex is target of microbiological attack in the nature, researchers looked for bacteria able to scission the polysulfide linkages [57]. It has been reported that several bacteria are able to “digest” (break) the sulfide linkages and the extent of reaction can be regulated via the temperature, pH, etc. [8, 15, 57–60]. The result is a “surface modified” GTR particle, the surface layer of which is no more crosslinked. In this case, the devulcanization can be solved only partially because the bacteria can work just on the surface of the rubber. So the results also depend on the type of the grinding. Another problem could be the toxicity of rubber additives that can inhibit the function of bacteria. Microbiological devulcanization processes may become important issues in the future [3].

Quality of the reclaim/devulcanizate Recall that the major task of the rubber (material) recycling is to produce from the initial infusible, insoluble, three-dimensioning crosslinked structure (100 % gel content) a melt processable one. This means that the initial crosslinked structure should be destroyed, at least partially. As a consequence, the material becomes partially soluble (sol content >0 %) and will show a lower crosslink density than initially. It is worth of noting that the sol content of most rubbers is higher than 0 due to different low molecular mass additives, processing aids which can be removed by extraction. The (sol) gel content is exclusively determined by extraction (in Soxhlet apparatus). To determine the crosslink density, usually the Flory–Rehner [61] equation is used.

The melt processability can be characterized by the Mooney viscosity (ISO 289, ASTM D 1646), torque

(apparent viscosity) values or torque (apparent viscosity)—time curves, assessed by various torque rheometers and characterized by plasticity parameters (Defo), change in hardness, etc.

Surface activation

For the surface modification of GTR, physical and chemical methods can be used.

Physical methods For the surface modification of GTR, treatments in different environments (dry, wet) are used which result, however, in chemical changes in the GTR surface. As a consequence, the above heading, viz. “physical methods”, may be ambiguous. To modify the GTR surface reactive gas (a mixture of oxygen and chlorine [8, 62]), ozone, plasma, corona, and electron beam (EB) irradiation procedures [22] were explored. It is known that irradiation of organic systems in air leads to their oxidation which is manifested in the appearance of peroxy, hydroperoxy, hydroxyl, and carbonyl groups [63]. The presence of these groups guarantees the compatibilization of the modified GTR with polar polymers.

Chlorination is considered as an effective way to make polar the GTR surface [64, 65]. The chlorinated GTR proved to be excellent filler in polyvinylchloride (PVC) compounds. Oxidation of GTR was performed also by H_2O_2 , HNO_3 , HClO_4 , and H_2SO_4 solutions to enhance the compatibility to NR [66] and to high density polyethylene (HDPE), respectively [67].

Colom et al. [68] improved the compatibility of GTR toward HDPE by chlorination, oxidation using H_2SO_4 , and silane coupling agent. Except chlorination, the other two surface activations improved the adhesion between GTR and HDPE, which was reflected in enhanced mechanical properties. Sadaka et al. [69] explored the possibility of controlled chemical degradation of both an NR-like model compound and GTR using periodic acid (H_5IO_6). The latter is able to efficiently cleave the $-\text{C}=\text{C}-$ bonds.

As ozone is a well-known degrading agent for rubbers, it can be used for the surface modification of GTR. This was shown by Cataldo et al. [70] who functionalized GTR in a fluidized bed reactor. It was demonstrated by pyrolysis chromatography that ozonation took place exclusively at the surface of GTR.

Chemical methods These methods focus on various grafting procedures. Grafting of unsaturated monomers and oligomers on the GTR surface which may participate in the subsequent crosslinking with the fresh rubber or at least entangle with the matrix macromolecules is a very promising approach. This has been followed by several research groups making use various grafting procedures. The

monomers preferred were: styrene, glycidyl methacrylate (GMA), acrylic and methacrylic acids (MAA), and the like.

Naskar et al. [71] produced maleic anhydride (MA) grafted GTR (GTR-*g*-MA) by free radical-induced process in an internal mixer at $T = 160$ °C. It was demonstrated that the properties of GTR-*g*-MA-containing TPE were superior to the reference sample with the same amount of GTR.

Coiai et al. [72] grafted styrene onto the surface of GTR via free radical polymerization. The cited authors demonstrated that reactive double bonds are present on the GTR surface which may act as “anchoring” sites for styrene grafting. The grafting efficiency, i.e., the percentage of grafted styrene over the total weight of polymer formed reached almost 40 % when dibenzoyl-peroxide was used as initiator. Grafting was, however, negligible with azobisisobutyronitrile initiator. This was attributed to the difference in the H-abstraction capability of the radical formed from the mentioned initiators. A similar approach, namely styrene grafting onto GTR surface in dibenzoyl-peroxide-induced bulk polymerization, was followed by Zhang et al. [73].

Tolstov et al. [74] grafted MA and acrylamide by free radical-induced grafting and γ -irradiation onto GTR. The corresponding grafted GTRs were used in TPE formulations. The presence of MA groups (MA grafting at around 1 wt %) was exploited in reactions with amine ($-\text{NH}_2$) functional groups. Fuhrmann and Karger-Kocsis [75, 76] functionalized GTR with MAA, and GMA through photoinitiated grafting. GTR surface was modified by allylamine through UV-induced photografting by Shanmugaraj et al. [77–79]. The mechanical properties of PP/PP-*g*-MA/GTR blends were better when the GTR was functionalized with allylamine than without. This was attributed to the reaction between $-\text{NH}_2$ and anhydride groups of the graft and PP-*g*-MA compatibilizer, respectively [77, 78].

Du et al. [80] grafted bismaleimide by thermally and UV-induced polymerization onto cryogenic GTR. It was aimed at producing rubbers from NR/GTR blend at high GTR content. As optimum curing condition for GTR/NR/bismaleimide (85/15/5 part) system 10 min at $T = 110$ °C was found.

Abdel-Bary et al. [81] grafted waste rubber powder by various vinyl monomers (acrylamide, acrylic acid, crylonitrile) using γ -irradiation. The graft yield depended on the type of the monomer. EB irradiation was used to graft MA onto sheets produced from reclaimed rubber powder and NR with and without additional short glass fiber [82]. Yamazaki et al. [83] converted polyisoprene (IR), and vulcanized NR with and without CB into lower molecular weight (MW) compounds by subjecting them to heat treatment at 300 °C in air and N_2 , respectively. Afterward these thermally decomposed rubbers were copolymerized

with styrene in bulk via free radical initiation. Fan and Lu [84] introduced “immobile” reactive hydroperoxide groups through ozonization on the GTR surface prior to start with the grafting of methyl methacrylate. Variation in the ozone treatment and polymerization temperature resulted in a grafting degree of 20 wt %. Shahidi et al. [85, 86] developed an “impregnation” process to produce GTR particles with semi-interpenetrating network (semi-IPN) structure. This was achieved by polymerization of a reaction mixture composed of toluene (swelling agent), acrylic acid monomer, and an oil-soluble radical initiator. The final product was foreseen as carrier for wastewater purification. Amash et al. [87] pinpointed in a study which are the morphological and compositional characteristics of rubber powders which are best suited for grafting by MA or to perform other functionalizations (epoxidation, hydroxylation).

GTR in thermoplastics

The use of GTR in thermoplastics was the often preferred way of recycling besides rubbers. This was fueled by the following aspects:

- a small percentage of GTR in thermoplastics (<10 wt%) is associated with a very large consumption of GTR owing to the market share of thermoplastics [14],
- like rubbers, the thermoplastic may act as binder allowing the use of GTR as major component in the related blends,
- recycled thermoplastics are available in the market which can be modified by GTR whereby reducing the cost further,
- GTR incorporation may yield enhanced toughness in the corresponding blends. This expectation is based on the fact that the majority of toughened thermoplastics are rubber modified by whatever means achieved.

To improve the toughness, and eventual further properties, suitable compatibilization strategies should be followed. This is accompanied with increased costs impairing the production of low-cost GTR-containing compounds. Therefore, it is a straightforward to incorporate GTR in recycled, post-consumer thermoplastic wastes. One major source of the latter is the agri- and horticulture. Note that recycled PEs from agricultural films (soil and greenhouse covers) are marketed for long time. Their macromolecules are naturally “oxidized” (usually quantified by the “carbonyl index”) which supports the adherence of PE to GTR particles as mentioned before.

Next, we shall summarize the result of R&D activities devoted to thermoplastic/GTR blends in tabular form. The selected grouping is as follows: commodity thermoplastics

(Table 3), engineering thermoplastics (Table 4), and TPEs (Table 5) as this selection covers the overwhelming majority of the works done in this field.

Commodity thermoplastics

Commodity or high-volume or low-cost resins cover polyolefins (PEs and PPs), polystyrene (PS), and PVC systems—the related results are listed in Table 3. Sometimes acrylics, such as acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate and related blends are also listed here but we treat the latter among the engineering polymers.

It has to be mentioned here that some polyolefin/GTR combinations can also be treated as TPEs. However, when their rubbery characteristics were not disclosed, or failing to reach 100 % elongation at break, they were incorporated in the commodity thermoplastics heading. Besides GTR, some other powdered rubber wastes, blended with commodity thermoplastics, were also considered.

Based on the results, summarized in Table 3, the following conclusion can be drawn:

- To moderate the degradation in the mechanical properties of blends with increasing GTR content it is indispensable to perform some surface treatment of the GTR and/or use compatibilizers. Reclamation of GTR, also on its surface, seems to be cost-effective and efficient way that can be performed continuously in-line during blending. Compatibilization via surface treatments (oxidation, chlorination, corona treatment, etc.) is less efficient than using block copolymer rubbers with and without functionalization (e.g., SEBS, SEBS-*g*-MA). Unfortunately, the latter polymers are, however, expensive additives. The reactive compatibilization strategies followed so far resulted only in small property improvements.
- Because GTR incorporation is accompanied with reduction in ductility, the additional reinforcement of the corresponding blends through adding fibrous fillers (e.g., SGF) represents a promising strategy. Here, the target is the development of injection moldable granules which may compete with some engineering thermoplastics.
- The production of microcellular thermoplastics with GTR content is not only a straightforward strategy (if the adhesion between the matrix and the GTR phases can hardly be improved then why not avoid this by foaming?) but also contributes to find novel application fields that GTR badly needs.
- Until now, R&D works focused on the processability and mechanical performance of thermoplastic/GTR blends. To support the market penetration and acceptance of

Table 3 Commodity thermoplastics with GTR content—effects of GTR type and size, polymer/GTR blend ratio, compatibilization, and processing on selected properties

Thermoplastic polymer	GTR		Blend ratio polymer/GTR	Compatibilization additive strategy	Preparation		Results, comments	References
	Type	Size			Blend	Specimen		
LDPE	–	40 mesh	100/0...0/100	Thermomechanical reclaiming	Two-roll mill	Compression molding	Tensile characteristics (TM, TS) decreased with increasing GTR content. UE decreased with adding GTR	[88]
LDPE	Ambient (Genan)	0.4–0.7 mm	100/0...40/60	Oil swollen (35 wt% oil)	Twin-screw extruder	Injection molding	TM and TS decreased with increasing GTR content. Reduction with oil-containing GTR was higher than without oil	[89]
rLDPE	Ambient (Genan)	0.4–0.7 mm	LDPE/EPDM/GTR: 40/55/25	MA grafting (both LDPE and GTR) coupling agents: diamine and PA fiber, EPDM dynamically cured	Batch mixer	–	Tensile properties improved by using grafted LDPE or GTR	[74]
rLDPE	Ambient, cryogenic	0.6–0.7 mm	100/0...30/70	Oxidation (KMnO ₄ solution), γ-irradiation of GTR	Batch mixer	Injection molding	Tensile properties strongly reduced by GTR content	[90]
LDPE	Ambient	0.08–1 mm (mean 0.35 mm)	100/0...55/45	EVA (0...20 wt%)	Twin-screw extruder	Injection molding	Tensile characteristics decreased with GTR content. EVA improved the ductility (UE, perforation impact energy)	[91]
rLDPE/LDPE	Ambient	0.25–0.5 mm	30/70	EVA (0...30 wt%) EB irradiation	Twin-screw extruder	Injection molding	Tensile properties increased by the radiation. EVA improved the ductility	[92]
LDPE	Ambient	0.25–0.5 mm	30/70	EVA (20 wt%) EB irradiation	Twin-screw extruder	Injection molding	Tensile properties improved by increasing irradiation dose	[93]
LDPE	SSSM	~0.25 mm	100/40	Peroxide, foaming agent	Batch mixer	Compression molding	Co-milling of LDPE and GTR improved the mechanical properties of the foam produced	[94]
LLDPE	–	40 mesh	100/0...0/100	Thermomechanical reclaiming	Two-roll mill	Compression molding	TM and TS decreased with increasing GTR content. UE increased with adding GTR	[88]
LLDPE	Ambient, cryogenic, wet ambient	0.1–0.6 mm	LDPE/GTR: 3/2 LDPE/GTR/compatibilizer: 14/10/1	GTR treatments: plasma, corona, EB Compatibilizer: EGMA	Batch mixer	Injection molding	Ambient and wet ambient GTR yielded tougher blends than cryogenic one. Smaller GTR particles slightly improved the toughness compared to larger ones. EB markedly improved the toughness, EGMA improved the impact strength	[22]
LLDPE	Cryogenic	0.3 mm (40 mesh) 0.15 mm (80 mesh)	LDPE/GTR: 3/2 LDPE/GTR/compatibilizer: 14/10/1	GTR oxidation in air compatibilizers: EGMA, EAA, EVA, SEBS-g-MA, SEBS, PE-g-MA concentration <15 wt%	Batch mixer	Injection molding	LLDPE is more suitable matrix than HDPE. Impact energy drops with increasing GTR content and compatibilizers moderate this reduction	[95]
LLDPE	Cryogenic	0.3 mm (40 mesh)—also from tyre bladder 0.15 mm (80 mesh)	100/0...40/60	Compatibilizers: EAA (10 wt%) (GTR precoated with EAA)	Batch mixer	Injection molding	MFI decreased, tensile mechanical properties dropped with increasing GTR content. GTR precoating reduced the property deterioration. LLDPE is better matrix than HDPE for GTR blending	[96]

Table 3 continued

Thermoplastic polymer	GTR Type	Size	Blend ratio polymer/GTR	Compatibilization additive strategy	Preparation		Results, comments	References
					Blend	Specimen		
LLDPE	–	0.3 mm (40 mesh)	LLDPE/EPDM/GTR: 100–50/0–45/0–30 Partial replacement of EPDM by GTR	–	Single screw extrusion	–	Thermal and rheological properties studied [97]	
LLDPE	–	100–180 mesh	100/200	Compatibilizers: EBA, EVA, SBS (10 wt%) Dynamic curing with peroxide	Batch mixer	Compression molding	SBS was the best compatibilizer [98]	
rPE (LDPE + LLDPE + EVA)	Ambient (Genan)	0.4–0.7 mm	75/25...25/75	–	Batch mixer and twin screw extruder	Compression and injection molding	Effects of processing conditions studied and optimum compounding temperature concluded. Injection molded samples showed better performance than compression molded ones [99]	
HDPE	–	40 mesh	100/0...0/100	Thermomechanical reclaiming	Two-roll mill	Compression molding	Strong drop in the tensile properties with increasing GTR amount [88]	
rHDPE	Ambient (Genan)	0.4–0.7 mm	LDPE/EPDM/GTR: 40/35/25	GTR grafted by acrylamide, EPDM dynamically cured. Compatibilizer: HDPE-g-MA Coupling agents: diamine and PA fiber, EPDM dynamically cured	Batch mixer	–	Best compatibility and mechanical performance achieved by γ -induced functionalization of HDPE and GTR, respectively [74]	
rHDPE	Ambient, cryogenic	0.6–0.7 mm	100/0...30/70	Oxidation (KMnO ₄ solution), γ -irradiation of GTR	Batch mixer	Injection molding	Tensile properties strongly reduced by GTR content. Effect of GTR oxidation is negligible [90]	
HDPE	Cryogenic	0.3 mm (40 mesh) 0.15 mm (80 mesh)	LDPE/GTR: 3/2 LDPE/GTR/compatibilizer: 14/10/1	GTR oxidation in air Compatibilizers: EGMA, EAA, EVA, SBS-g-MA, SEBS, PE-g-MA concentration 15 wt%	Batch mixer	Injection molding	Relative toughness improvement using compatibilizers is less for HDPE than for LLDPE. Small but significant increase in the impact energy by decreasing GTR particle size [95]	
HDPE	Cryogenic	0.3 mm (40 mesh)—also from tyre bladder 0.15 mm (80 mesh)	100/0...40/60	Compatibilizers: EAA (10 wt%)	Batch mixer (GTR precoated with EAA)	Injection molding	Poor mechanical properties with GTR especially at large particle size fractions [96]	
HDPE	–	10 mesh originally	20/80...80/20	GTR ultrasonically devulcanized. Blend dynamically vulcanized (sulfur). Compatibilizers: PP-g-MA, chlorinated PE (CPE) 10 phr	Batch mixer, twin-screw extruder	Compression molding	Effects of GTR devulcanization and sulfuric dynamic devulcanization. Compatibilizers showed small effect. Blends mixed in twin-screw extruder prior to devulcanization and dynamic devulcanization in batch mixer showed the best performance [100]	

Table 3 continued

Thermoplastic polymer	GTR Type	Blend ratio polymer/GTR	Size	Compatibility additive strategy	Preparation Blend	Specimen	Results, comments	References
HDPE	-	70/30...30/70	0.5–0.6 mm (reclaimed)	Dynamic curing (peroxide, sulfur and mixed system) Compatibilizer: PE-g-MA (10 phr)	Two-roll mill	Compression molding	Izod impact strength went through a maximum at 50/50 composition. Tensile property reduced with increasing GTR content; its loss was the smallest after sulfuric dynamic curing. Compatibilizer is as efficient as dynamic curing	[101]
HDPE	-	100/0...60/40	0.4–0.6 mm	GTR treatment by sulfuric acid, chlorination and silane coupling	Two-roll mill	Compression molding	Best mechanical performance by sulfuric acid (surface roughing) and silane	[68]
HDPE	-	100/0...60/40	0.4–0.6 mm	GTR treatment with sulfuric, nitric and perchloric acids	Two-roll mill	Compression molding	TM, UE and toughness (tensile area) were reduced above 10 wt% GTR content. sulfuric acid treatment had the best effect	[67]
rHDPE	-	100/0...30/70	0–0.5 mm (mean 0.38 mm)	Compatibilization by γ -irradiation in air of the granulated blend	Twin-screw extruder	Injection molding	UE and Charpy impact strength strongly enhanced after 25–50 kGy irradiation doses. High dose lowered the mechanical performance	[102]
HDPE (+PP-GF) composite	Ambient	HDPE/PP-GF/GTR: (87.5–62.5)/(12.5–37.5)/(0–25)	<0.4 mm	-	Twin-screw extruder	Injection molding	With increasing GTR content the TM, yield stress and impact strength decreased	[103]
rHDPE	-	50/50	0.4–0.5 mm	Compatibilization via peroxidic dynamic curing and γ -irradiation	Batch mixer, twin-screw extruder	Injection molding	Interfacial co-crosslinking triggered by peroxide coating of the GTR particles prior to blending. The effect of compatibilization was merely traced to delayed debonding	[104]
rHDPE	-	100/0...60/40	<0.2; 0.2–0.5, and >0.5 mm	Acid pretreatment of GTR (sulfuric, nitric and sulfuric/nitric solutions)	Two-roll mill	Compression molding	Acidic pretreatment is beneficial. Blends of smaller GTR particles show better TM and TS than larger ones (>0.5 mm). The latter drastically reduces the mechanical performance with increasing GTR content	[105]
rPE	-	PE/GTR/talc: 60/40/0–20	0.15 mm (80 mesh)	Adding MA (2 wt%) followed by γ -irradiation	Batch mixer	Compression molding	TS increases and UE decreases with talc content. Irradiation up to 50 kGy improved the mechanical properties	[106]
HDPE	-	100/0...60/40	0.4–0.6 mm	As compatibilizers wetting agents and waxes used	Two-roll mill	Compression molding	Waxes enhanced the TM and TS due to co-crystallization with HDPE. Some wetting agents reduced the property drop as a function of GTR content	[107]
EVA	Wet ambient	EVA/LDPE/PU/GTR: (25–72)/(9–27)/(5–25)/(0–15)	0.2–0.6 mm	-	Batch mixer	Compression molding	Flame retardancy studied	[108]
EVA	-	100/0...25/75	0.2 mm	Peroxidic crosslinking	Two-roll mill	Compression molding	Crosslinking kinetics studied through rheological and thermal methods	[109]
PP	-	100/0...0/100	40 mesh	Thermomechanical reclaiming	Two-roll mill	Compression molding	TM, TS and heat distortion temperature decreased, while UE increased with increasing GTR content	[88]

Table 3 continued

Thermoplastic polymer	GTR Type	Size	Blend ratio polymer/GTR	Compatibilization additive strategy	Preparation		Results, comments	References
					Blend	Specimen		
PP	Ambient (Genan)	0.4–0.7 mm	100/0...40/60	Oil swollen (35 wt% oil)	Twin-screw extruder	Injection molding	TM and TS decreased with increasing GTR, especially when it was oil modified. Increasing GTR amount enhanced the notched Charpy impact strength at room temperature (RT)	[89]
PP	Recycled rubber powder	0.25–0.5 mm	PP/NR/rubber powder: 70/(0–30)/(0–30)	Replacement of NR by rubber powder	Batch mixer	Compression molding	TM and TS enhanced, UE reduced with increasing rubber powder content	[110]
PP	Recycled rubber powder	0.25–0.5 mm	PP/NR/rubber powder: (100–40)/(20–60)/(20–60)	Replacement of NR by rubber powder	Batch mixer	Compression molding	TM and TS enhanced, UE reduced with increasing rubber powder content	[111]
PP	–	Shoe sole scrap powder 0.01 mm	75/25	Compatibilizers: SBS, SEBS, SEBS- <i>g</i> -MA, PP- <i>g</i> -MA, PE- <i>g</i> -MA, PP- <i>g</i> -GMA (≤ 10 phr)	Single-screw extruder	Injection molding	SEBS and an SEBS- <i>g</i> -MA proved to be the best compatibilizers	[112]
PP	–	GTR and GTR reclaim 8 mesh (~ 2.4 mm) 16 mesh (~ 1.2 mm) 40 mesh (~ 0.4 mm) 30 mesh	80/20...60/40	Compatibilization with sulfur curatives and peroxide/MA combination	Two-roll mill + twin-screw extruder	Injection molding	Notched Izod impact strength was markedly improved by sulfuric vulcanization for reclaimed GTR by contrast to the reference GTR. The highest toughness was reached by PP/reclaimed GTR/MA/peroxide formulation	[113]
PP	–	–	40/60	Ultrasonic treatment of the blend before and after dynamic revulcanization (sulfuric type)	Twin-screw extruder + ultrasonic reactor + batch mixer	Compression molding	Rheology and mechanical properties of the blends as a function of processing (ultrasonication, de- and revulcanization) studied	[114]
PP	–	Recycled rubber powder 0.25–0.5 mm	PP/NR/recycled rubber powder/fillers: 70/15/15/(0–30)	CB, silica and calcium carbonate were used as fillers	Batch mixer	Compression molding	CB and silica improved the TS and TM opposed to calcium carbonate	[115]
PP	Ambient	0.2–0.63 mm	100/0...10/90	–	Batch mixer + single screw extruder	Compression molding	Reduction in TM and TS was assessed and described mathematically	[116]
PP	–	–	PP/PP- <i>g</i> -MA/GTR (unmodified): 100/(0–15)/(0–30)	UV-induced grafting of GTR. Compatibilizer: PP- <i>g</i> -MA	Batch mixer	Compression molding	Surface-grafted GTR in presence of PP- <i>g</i> -MA resulted in better mechanical properties, especially in term of ductility	[78]
PP	–	40 mesh (~ 0.3 mm)	PP/EPDM/GTR (100–50)/(0–45)/(0–45)	Compatibilizer: EPDM	Single-screw extruder	Injection molding	Notched Izod impact strength of the PP/GTR blends was enhanced by adding EPDM	[117]

Table 3 continued

Thermoplastic polymer	GTR Type	Size	Blend ratio polymer/GTR	Compatibility additive strategy	Preparation Blend	Specimen	Results, comments	References
PP	-	Recycled rubber powder ≤ 0.5 mm	PP/recycled rubber powder: (100–40)/(0–60)	-	Batch mixer	Compression molding	TPE-like material produced	[118]
PP, PP-g-MA	Wet ambient	-	PP or PP-g-MA/GTR: 35/65	Compatibilizers: SEBS and SEBS-g-MA (≤ 10 phr)	Twin-screw extruder	Injection molding	Morphology development studied. Best mechanical properties achieved by PP-g-MA/GTR/SEBS-g-MA blends. Reprocessing did not affect the tensile mechanical behavior	[119]
PP-g-MA	-	0.03–0.05 mm	35/65 (55–25)/(45–75)	Compatibilizer: SEBS-g-MA (≤ 10 phr)	Twin-screw extruder	Injection molding	Effects of screw configuration studied. TM and TS decreased with increasing GTR content. The blend PP/GTR = 35/65 combines both melt processability and rubberlike elasticity	[120]
PP	-	-	PP/PP-g-MA/GTR: 100/(0–25)/(0, 40)	GTR grafted by allylamine via UV-irradiation Compatibilizer: PP-g-MA	Batch mixer	Compression molding	TS and UE improved by GTR grafting. These properties were improved with increasing amount of PP-g-MA	[77]
PP	-	0.075–0.8 mm (mean 0.3 mm)	PP/PP-g-MA/GTR: 100/(10–50)/(0–80)	Allylamine grafting onto GTR by free radical mechanism (peroxide)	Batch mixer	Compression molding	Grafting and compatibilization reactions studied. Tensile and rheological behavior of the blends as a function of allylamine, peroxide and GTR concentration investigated	[121]
PP	Wet ambient	0.03–0.04 mm	100/0...60/40	Foaming with supercritical CO ₂	Batch mixer	Compression molding	Processing conditions studied by design of experiments (DOE)	[122]
PP (virgin, waste, recycled)	-	Rubber dust (PVC/NBR)	100/0...50/50	-	Batch mixer	Compression molding	Tensile, flexural and impact (Charpy, Izod) properties studied. Static mechanical properties reduced while the impact strength improved with increasing rubber dust amount. Good damping was noticed	[58]
PP	Wet ambient	~0.09 mm	90/10...20/80	Reactive blending (peroxide, phenolic resin)	Batch mixer	Compression molding	TS reduced, UE enhanced with increasing amount of GTR. Reactive blending yielded better results than traditional melt blending. Considerable effect of MW of PP	[123]
PP	Wet ambient	0.03–0.05 mm	PP/PP-g-MA/EPDM/GTR Large composition variation	Compatibilizers: PP-g-MA and EPDM	Twin-screw extruder	Injection molding	Tensile properties assessed and optimized in function of composition using the artificial neural network (ANN) algorithm. TPE produced	[124]
PP	Wet ambient	50 mesh	100/0...50/50	Chemical foaming	Twin-screw extruder	Injection molding	The foam cell size decreased with increasing GTR content. Similar change in the specific (density related) TM and TS	[125]
PP	Wet ambient	50 mesh	100/0...60/40	Chemical foaming Compatibilizer: SEBS-g-MA (≤ 10 phr)	Twin-screw extruder	Single-screw extruder for foaming	Closed cell foam with mean cell size of <0.1 mm was produced continuously. With increasing GTR content irregular cells developed. SEBS-g-MA reduced the mean cell size. Processing effects also deduced	[126]

Table 3 continued

Thermoplastic polymer	GTR Type	Size	Blend ratio polymer/GTR	Compatibilization additive strategy	Preparation		Results, comments	References
					Blend	Specimen		
PP	Wet ambient	50 mesh	100/0...60/40	Chemical foaming. Compatibilizer: SEBS- <i>g</i> -MA (5 wt% with respect to GTR content)	Twin-screw extruder	Single-screw extruder for foaming	DOE used (response surface type) to study the effects of processing conditions on foam characteristics (cell size, cell density)	[127]
PP	Wet ambient	0.03–0.05 mm	100/0...50/50	Physical foaming by supercritical CO ₂ . Compatibilizer: SEBS- <i>g</i> -MA (5 wt% with respect to GTR content)	Twin-screw extruder	Single-screw extruder for foaming	DOE used (response surface type) to study the effects of processing conditions on foam characteristics (cell size, cell density)	[128]
PP	–	–	–	UV-induced grafting of GTR with allylamine. Compatibilizers: PP- <i>g</i> -MA, SEBS- <i>g</i> -MA	Twin-screw extruder	Injection molding	The effect of GTR grafting was most pronounced when using SEBS- <i>g</i> -MA—tensile strength (TS) enhanced slightly, ductility markedly	[129]
PP	Wet ambient	50 mesh	60/40	Chemical foaming. Compatibilizer: SEBS- <i>g</i> -MA (10 wt%)	Twin-screw extruder	Injection molding	DOE by the Taguchi method. Foam characteristics of PP/GTR may be similar to those of PP	[130]
PP (waste)	–	50 mesh	PP/bitumen/GTR/SEBS- <i>g</i> -MA (varied)	GTR devulcanized by extrusion then blended with bitumen in a further extrusion step	Single-screw extruder + twin-screw extruder	Injection molding	ANN algorithm used for DOE. Optimum formulation deduced with respect to tensile characteristics	[131, 132]
PP composite	–	0.25–0.50 mm	PP/GTR/SGF/silane: 70/30/(0–20)/(0–1.5)	Property improvement by reinforcement	Batch mixer	Compression molding	SGF incorporation enhanced the TM, slightly decreased the TS and UE. Use of silane coupling beneficial	[133]
PP	–	0.18 mm (80 mesh)	PP/GTR/rubber: 40/50/10	Hydrosilated degraded PP was grafted onto SBR. Dynamic sulfuric curing adapted	Batch mixer	Compression molding	Interfacial effects studied. UE remained under 100 %	[134]
PP	Ambient (Genan)	<0.4 mm 0.4–0.7 mm	100/0...50/50	–	Twin-screw extruder	Compression molding	The tensile properties decreased with increasing GTR content. Smaller GTR particles resulted slightly better results	[135]
PP	–	30 mesh	80/20...20/80	GTR ultrasonically devulcanized. MA-containing compatibilizers, sulfuric dynamic vulcanization	Batch mixer and twin-screw extruder	Compression molding	Large differences observed in UE, but the related data remained under 40 %. Strong effect on mixing techniques. Beneficial effect of dynamical curing	[136]
PS	–	0.3 mm 0.3–0.5 mm 0.5–1.0 mm	100/0...80/20	GTR grafted by styrene (free radical mechanism)	Batch mixer	Compression molding	TS and energy to break strongly decreased, UE slightly increased with increasing GTR content. Styrene grafting of GTR significantly enhanced UE and energy to break values	[137]

Table 3 continued

Thermoplastic polymer	GTR		Blend ratio polymer/GTR	Compatibility additive strategy	Preparation		Results, comments	References
	Type	Size			Blend	Specimen		
PS	–	5 mm (SBR)	PS/SBR(SBS): 90/10...70/30	SBR ultrasonically devulcanized and then homogenized in two roll mill.	Batch mixer	Compression molding	Rheological properties and change in the mean particle size of the ground SBR studied [138]	
PS (high impact)	–	40 mesh	100/0...0/100	Compatibilizer: SBS Thermomechanical reclaiming	Two-roll mill	Compression molding	TM, TS, and UE decreased with increasing GTR content [88]	
PS (high impact)	Ambient (Genan)	0.4–0.7 mm	100/0...40/60	Oil swollen (35 wt% oil)	Twin-screw extruder	Injection molding	TM and TS decreased with whereas notched Charpy impact strength maintained with increasing GTR content. Oil treatment of GTR reduced the tensile properties [89]	
PVC (plasticized)	Cryogenic	0.16–0.21 mm	100/40	GTR chlorinated (wet method)	Batch mixer	Compression molding	Dynamic mechanical and dielectrical properties studied [139]	
PVC (plasticized)	Cryogenic	0.16–0.21 mm	100/0...100/80	GTR chlorinated (wet method)	Batch mixer	Compression molding	Plasticized PVC can be filled with chlorinated GTR up to 40 phr, beyond which the mechanical properties are adversely affected. Stress relaxation proved improved adhesion between PVC and chlorinated GTR [64]	
PVC (plasticized)	–	0.1–0.3 mm (waste NBR)	100/0...10/90	–	Batch mixer	Compression molding	TS decreased, UE and impact energy increased with increased ground NBR [140]	
PVC (plasticized)	Cryogenic	0.16–0.21 mm	100/40	GTR chlorinated (wet method)	Batch mixer	Compression molding	Chlorination studied. Chlorinated GTR is a better filler than untreated GTR [65]	
PVC	–	<0.2 mm 0.2–0.5 mm >0.5 mm	100/0...30/70	–	Batch mixer	Compression molding	TM, TS, UE and toughness decreased with increasing GTR content. Properties deterioration was the smallest for the finest GTR fraction [141]	
PVC (plasticized), PVC waste	–	0.1–0.3 mm (ground NBR)	100/0...35/65	–	Dry blending + twin-screw extruder	Compression molding	TS decreased and UE mostly increased with increasing waste NBR. Flexural crack resistance and impact strength also improved [142]	

Designation: not disclosed or measured

GTR other properties, such as mechanical and acoustic damping, should also be considered next.

Engineering thermoplastics

Engineering thermoplastics are qualified for continuous use at temperatures above 100 °C, and showing tensile strength higher than 40 MPa [143]. Table 4 lists those works in which engineering polymers were combined with GTR.

Data in Table 4 suggest that modification of engineering thermoplastics with GTR is possibly not the right way even if waste thermoplastic materials are used. Recall that the property level of the virgin material can only be reached by sophisticated compatibilization methods if the GTR amount is 20 wt% or less in the corresponding blend.

Thermoplastic elastomers

TPEs are thermoplastic polymers which can be melt-processed at elevated temperatures while possessing elastomeric behavior at their service temperature. TPEs thus contain a thermoreversible network (also called physical network) structure. This is formed by phase separation in all cases. In segmented (multi)block copolymers, the “knots” of the physical network are given either by glassy or by crystalline domains. They are referred as “hard phase.” The hard phase domains are dispersed in the “soft” rubbery phase. The latter forms the matrix in block copolymers with the flexible segments.

Upon cooling from the melt, the glassy and the crystalline domains (knots) are reformed by phase segregation and crystallization processes, respectively. A physical network can be generated also by ionic interaction. In the so-called ionomers the clusters, acting as “knots”, are held together by ionic bonds. This is usually achieved by saponification of acidic groups in copolymers.

TPE character can be received by blending of thermoplastics and elastomers whose final morphology is co-continuous, i.e., the related phases are intermingled. Blending of polyolefins with rubbers (NR, EPDM, etc.) to produce TPEs has a long history [150]. A further impetus to the related R&D activities was given by adaption of the dynamic vulcanization ([151–153] and references therein).

TDVs are new members of the family of TPEs. TDVs are produced by dynamic curing of blends composed of thermoplastics and crosslinkable rubbers. The term “dynamic curing” means the selective curing of the rubber and its fine dispersion in the molten thermoplastic via intensive mixing/kneading [151, 153–155]. The microstructure of TDV fundamentally differs from the physical networks formed by phase segregation. Note that matrix phase here is given by the “hard” thermoplastic which accounts per se the melt

processability. The rubbery properties (recovery) are guaranteed by the matrix ligaments (between the crosslinked rubber particles) undergoing inhomogeneous deformation but not yielding, upon loading ([152, 156] and references therein). It is important to emphasize that the rubber particle dispersion in the thermoplastic matrix of the TDV is very fine, i.e., few microns and below.

It is most likely that the TDV technology was the driving force to develop TPE compounds with GTR content. Recall that TDV involves some kind of reactive compatibilization. Though the mean particle size requirement for rubber inclusions in TDV can hardly be reached with GTR particles (not even by cryogenic milling), nevertheless, the GTR-containing blends possess rubbery behavior, albeit with some limitation in the stress–strain behavior [152]. That is the reason why we define TPEs as such compounds whose tensile strain under the usual testing conditions is at least 100 %. The other important parameters are the set properties. The requirement for TPEs that their compression set should be lower than 50 %.

One of the first reports on TPE composed of PP or PP/LDPE blend and GTR was published in 1989 [157]. Al-Malaika and Amir [157] reported that reclaimed tyre rubber should be used together with fresh NR to improve the properties of the corresponding blend. Dynamic vulcanization of the latter by peroxide yielded further property improvements. Many recent works target the development of TPEs which represents an “upcycling” strategy for GTR use. Upcycling is related to fact that TPEs are “costly” products. Considering the large body of works devoted to polyolefin/GTR combinations (cf. Table 3) and the fact that TDVs are usually of polyolefinic nature, the development of GTR-containing TPEs focused on systems containing polyolefins as matrices. In order to improve the adhesion between the phases various compatibilization methods have been followed (swelling, reclamation, reactive and non-reactive compatibilization, etc.). Nonetheless, additional use of rubber (fresh, devulcanized, reclaimed) in the thermoplastic/GTR blend to produce TPE is inevitable. Table 5 lists the activities performed on GTR-containing TPEs.

Results listed in Table 5 clearly suggest that the development of GTR-containing TPEs is a very promising research strategy. The related products may have comparable properties with competing TPEs, however, at lower costs. The key issue is to improve the interfacial adhesion between GTR particles and matrix polymer. As matrix polymers, polyolefins are most suited being inexpensive, and even available as wastes without problematic contaminants. To increase the interphase bonding, different strategies were followed which can be grouped into: in situ, ex situ, and compatibilizing methods. They differ from one another whether the interphase is created during blending

Table 4 Engineering thermoplastics with GTR content—effects of GTR type and size, polymer/GTR blend ratio, compatibilization, and processing on selected properties

Thermoplastic polymer	GTR		Blend ratio polymer/GTR	Compatibilization additive strategy		Preparation		Results, comments	References
	Type	Size		Blend	Specimen				
ABS	–	40 mesh	100/0...0/100	Thermomechanical reclaiming	Two-roll mill	Compression molding	TM and TS decrease and UE increased with increasing amount of GTR reclaimed	[88]	
ABS	Ambient	0.25; 0.44 mm	100/0 (60–40)/(40–60)	Surface treatments: chlorination, grafting onto chlorinated surface (amine-terminated liquid NBR (ATBN), amine containing chelate) in situ compatibilization via catalyst	Single screw extruder	Compression molding	Melt mixing of ABS with untreated GTR leads to significantly lower tensile properties than those of ABS. They can be partially recovered by the treatments used. Best results achieved by grafting the GTR with ATBN	[144]	
PA6	–	150 nm (ultrafine acrylate powder)	PA6/acrylate powder: 100/0...100/10	–	Twin-screw extruder	–	TS reduced, UE passed a maximum, notched impact strength monotonously increased with increasing amount of rubber powder	[145]	
PA6	Ambient (Genan)	0.4–0.7 mm	100/0...40/60	Oil swollen (35 wt% oil)	Twin-screw extruder	Injection molding	TS, TM and notched Charpy impact strength all reduced with increasing GTR content	[89]	
PA6	Ambient	Mean ~0.3 mm	100/0...80/20	GTR functionalized by UV-induced surface grafting of GMA	Twin-screw extruder	Injection molding	Only slight improvement in the tensile and impact characteristics compared to non-grafted GTR	[146]	
rPA (waste PA6/PA66)	–	0.15 mm (80 mesh)	100/0...40/60	Compatibilization by γ -irradiation of final sheets (≤ 200 kGy)	Batch mixer	Compression molding	Negligible effect of γ -irradiation	[147]	
rPA (waste PA6/PA66)	–	0.15 mm (80 mesh)	50/50	Compatibilization by γ -irradiation of final sheets (< 200 kGy) Adding CB up to 24 wt%	Batch mixer	Compression molding	Small improvement in TS at 50 kGy irradiation dose. TS, TM, UE and hardness increased with increasing CB content	[148]	
PBT	Ambient (Genan)	0.4–0.7 mm	100/0...40/60	Oil swollen (35 wt% oil)	Twin-screw extruder	Injection molding	TS, TM and notched Charpy impact strength—all reduced with increasing GTR content. Oil modified GTR yielded even poorer properties than untreated GTR	[89]	
PBT	Ambient	Mean ~0.3 mm	100/0...80/20	GTR functionalized by UV-induced surface grafting of MAA	Twin-screw extruder	Injection molding	Slight improvement in tensile and impact characteristics using grafted GTR compared to the non-grafted one	[146]	
PC (virgin/recycled)	Cryogenic	<0.14 mm 0.14–0.32 mm	100/0...75/25	Surface treatments: oxidation by flaming; oil removal by “washing” Compatibilizers: ethylene-ethyl acrylate–methyl acrylate–GMA (3 wt%)	Batch mixer	Compression molding	Property deterioration with smaller GTR size is markedly less than with larger one. All treatments enhanced the TS and UE but decreased the TM	[149]	

Designation: not disclosed or measured

Table 5 TPEs with GTR content—effects of GTR type and size, additional rubber, composition, compatibilization, and processing on selected properties

Thermoplastic polymer	GTR		Additional rubber	Composition	Compatibilization additive strategy	Preparation		Results, comments	References
	Type	Size				Blend	Specimen		
LDPE	Ambient (Genan)	0.4–0.7 mm	EPDM NR SBR	LDPE/GTR/rubber: 50/25/25	GTR thermochemically devulcanized in presence of paraffin oil. Dynamic curing: sulfuric, peroxidic	Batch mixer (master batch)	Compression molding	Thermomechanical devulcanization and dynamic curing with sulfur improved the tensile mechanical properties compared to untreated and peroxidic cured blends. The efficiency of fresh rubber followed the ranking EPDM > NR > SBR. EPDM acted as dual phase compatibilizer. Limited UE found	[158]
LDPE	Ambient (Genan)	0.4–0.7 mm	EPDM NR SBR	LDPE/GTR/rubber: 50/25/25	GTR thermochemically devulcanized. Dynamic curing: sulfuric, phenolic peroxidic	Batch mixer (master batch)	Compression molding	Thermomechanical devulcanization of GTR and dynamic curing (sulfuric, phenolic) are beneficial. EPDM is the most suited fresh rubber. UE 100 % was not reached	[159]
rLDPE	Ambient (Genan)	0.4–0.7 mm	EPDM	LDPE/GTR/rubber: 40/35/25	Both GTR and LDPE grafted by MA and γ -irradiation). Coupling agents: diamine and PA fiber (1 phr)	Batch mixer	Compression molding	Used of grafted GTR (γ -irradiated) and coupling agent (PA fiber) strongly improved the TS and UE of the resulting TPE	[160]
rLDPE (LDPE + LLDPE + EVA)	Ambient (Genan)	0.4–0.7 mm <0.4 mm	EPDM	LDPE/GTR with bitumen (1/1)/ rubber: (40–50)/(45–15)/(15–35)	GTR reclaiming by bitumen in batch and extrusion blending	Batch mixer	Compression molding	Bituminous reclaimation of GTR (various methods) strongly enhanced the UE of TPE (reaching 1000 %)	[161]
LDPE	Ambient	0.4 mm	EPDM NR	LDPE/GTR/rubber: (25–50)/ (25–37.5)/ (25–37.5) but mostly 50/25/25	Dynamic curing with peroxide and sulfuric (various) curatives. GTR also masticated on two-roll mill	Batch mixer	Compression molding	Mastication of GTR and incorporation of EPDM lead to optimal properties of TPE (TS = 8.8 MPa, UE = 310 %). Peroxidic and sulfuric curing failed	[162]
XLPE (waste)	–	0.04–0.5 mm (mean 0.34 mm)	–	XLPE/GTR 50/50	Decrosslinking of both XDLPE and GTR in solid state using high shear pan-mill. Blends dynamically vulcanized (peroxide, sulfuric)	Batch mixer	Compression molding	Dynamic vulcanization strongly improved TS and UE. These parameters were affected by the melt blending temperature. Sulfuric dynamic vulcanization proved to be better than peroxidic	[163]
LLDPE	Cryogenic	Different particle sizes (<0.84 mm)	ENR (epoxidization 50 %)	LLDPE/ GTR + ENR: 70/30	LLDPE grafted with MA, methyl methacrylate and butyl acrylate	Two-roll mill	Compression molding	ENR + LLDPE grafted vinyl monomers worked as dual compatibilizer. TS reached 9 MPa, and UE 300 %	[164]
LLDPE	–	<0.4 mm	NR	LLDPE/ GTR + rubber: 60/40	Reactive blending with MA in presence of peroxide. NR replaced by GTR	Batch mixer	Compression molding	The negative effect of GTR incorporation was compensated by the reactive blending	[165]
LLDPE	–	50 mesh	SEBS-g-MA	LLDPE/GTR/ rubber: 40/60/ (0,10)	Dynamic curing by peroxide	Batch mixer	Compression molding	SEBS-g-MA compatibilizer and dynamic curing improved the TS and UE (two- and threefold, respectively) compared to the LLDPE/GTR blend	[166]

Table 5 continued

Thermoplastic polymer	GTR		Additional rubber	Composition	Compatibilization additive strategy	Preparation		Results, comments	References
	Type	Size				Blend	Specimen		
LLDPE	–	–	Reclaimed rubber	LLDPE/reclaimed rubber: 90/10...50/50	Compatibilizer: PE-g-MA (≤ 21 phr) Dynamic vulcanization (sulfuric). Additional use of organoclay (≤ 7 phr)	Batch mixer	Compression molding	Increasing organoclay content enhanced TM, but reduced TS and UE for a given composition	[167]
rHDPE	Ambient (Genam)	0.4–0.7 mm	EPDM	LDPE/GTR/rubber: 40/35/25	Both GTR and LDPE grafted by MA and acrylamide (peroxide, γ -irradiation). Coupling agents: diamine and PA fiber (1 phr)	Batch mixer	Compression molding	Best compatibility in terms of the mechanical properties was achieved by γ -induced grafting of monomers	[160]
HDPE (acrylic modified)	Cryogenic	0.16–0.21 mm	EPDM	HDPE/GTR/rubber: 40/68/30 (100–0)/(0–50)/(0–50)	Dynamic curing by peroxide	Batch mixer	Compression molding	Dynamic curing improved TS, modulus at 100 % elongation and UE. Strong compositional dependence of the properties	[168, 169]
HDPE	Cryogenic	60 mesh	EPDM	HDPE/GTR/rubber: (100)/(0–60)/(0,10)	Dynamic curing by peroxide in presence of silicon oil (4 phr)	Batch mixer	Compression molding	Both TS and UE decreased with increasing GTR content. Dynamic curing reduced the related drop	[170]
HDPE	Ambient	80 mesh	EPR EPDM	HDPE/GTR/rubber: (25.50)/50/(0,25)	Dynamic curing by peroxide	Batch mixer	Compression molding	Dynamic curing strongly enhanced the TS and UE. The efficiency ranking of rubbers: POE > EPR > EPDM	[171]
HDPE	Ambient	80 mesh	POE EVA POE	HDPE/ GTR + rubber: 60/40	–	Batch mixer	Compression molding	Polarity of the fresh rubber affects the mechanical properties. POE is better additive than EVA	[172]
rHDPE	Ambient (Genam)	0.4–0.7 mm	EPDM	HDPE/GTR/rubber: (40–50)/(25–35)/(25–35)	GTR reclaimed in bitumen by various methods. GTR/bitumen ratio: 1/1	Batch mixer, single-screw extruder	–	Bitumen was a reclaiming agent for GTR and curing one for EPDM. TPE properties depend on GTR reclamation. TPEs with GTR pretreated in bitumen showed outstanding mechanical properties and good reprocessability	[173]
HDPE	–	0.15 mm (80 mesh)	EPDM	HDPE/GTR/rubber: 50/(25–50)/(50–75)	EPDM dynamically cured. γ -irradiation of the ready-to-test samples	Two-roll mill	Compression molding	TS went through a maximum in function of irradiation dose (150 kGy). Modulus, hardness monotonously increased, UE monotonously decreased with increasing γ -irradiation	[174]
HDPE	–	0.15 mm (80 mesh)	EPDM	HDPE/GTR/rubber: 50/(25–50)/(50–75)	GTR thermomechanically devulcanized. Ready-to-test samples γ -irradiated	Batch mixer + two-roll mill	Compression molding	TS went through a maximum in function of irradiation dose (150 kGy). Modulus, hardness monotonously increased, UE monotonously decreased with increasing γ -irradiation. UV-irradiation also studied	[175]
HDPE	–	0.4–0.6 mm	EPDM	HDPE/GTR/rubber: (10–100)/(0–45)/(0–45)	Samples statically cured by peroxide	Two-roll mill	Compression molding with curing	Best properties found for HDPE/GTR/EPDM = 40/30/30 statically cured using two peroxides. GTR encapsulated by EPDM	[176]

Table 5 continued

Thermoplastic polymer	GTR		Additional rubber	Composition	Compatibilization additive strategy	Preparation		Results, comments	References
	Type	Size				Blend	Specimen		
HDPE (acrylic modified)	Cryogenic	0.16–0.21 mm	EPDM	HDPE/GTR + rubber: 40/60	GTR-g-MA also used. Dynamic curing (peroxide) applied	Batch mixer + two-roll mill	Compression molding	GTR grafting beneficial. GTR can replace up to half of EPDM	[71]
PP	–	0.25 mm (60 mesh)	–	PP/GTR: 50/50	Mixing together with reclaiming and crosslinking agents	Batch mixer + pelletizer	Injection molding	Co-vulcanization in phase boundary layer claimed. Four-fold increase in UE compared to simple PP/GTR blend. TPE called elastic alloy	[38]
PP	–	Ground EPDM waste	–	PP/EPDM: 30/70	Replacement of fresh by waste EPDM. Dynamic curing by peroxide	Batch mixer + two-roll mill	Compression molding	EPDM can be replaced up to 45 % by ground waste EPDM	[177]
PP	Ambient	0.25 mm (60 mesh)	–	PP/GTR: (20–50)/(50–80)	Melt mixing with reclaiming and crosslinking agents including dynamic curing with peroxide	Batch mixer + pelletizer	Injection molding	Elastomeric alloys with TPE characteristics produced. Efficient phase coupling between PP (matrix) and GTR (dispersed)	[178]
PP	High temperature	≤0.4 mm	–	PP/GTR: (20–50)/(50–80)	Reactive systems composed of radical donors and acceptors	Batch mixer, two-roll mill + pelletizer	Injection molding	Elastomeric alloys with various hardness values and with UE ≥200 % produced	[179]
PP	High temperature	Waste EPDM	–	PP/EPDM: 20/80	Reactive systems EPDM devulcanization followed by dynamic vulcanization	Twin-screw extruder	Extrusion or injection molding	Continuous process to produce “recycled rubber based thermoplastic elastomer”, see Fig. 4. Properties similar to thermoplastic olefin elastomers	[180]
PP	Ambient	Mean 0.4 mm	–	PP/GTR: (30–70)/(30–70)	Reactive melt mixing with peroxide	Batch mixer, two-roll mill + pelletizer	Injection molding	Highly improved UE composed to reference blends. Compatibilization via interfacial reaction quoted	[181]
PP	Ambient (Genam), cryogenic	<0.1 mm <0.4 mm 0.4–0.7 mm 0.4–0.63 mm	EPDM (various, also with extender oil)	PP/GTR/rubber: (30,50)/(12.5,17.5)/(37.5,52.5) PP/(GTR + rubber): 50/50, 30/70	Dynamic curing—sulfuric	Batch mixer	Compression molding	Below GTR particle size ≤0.1 mm no effect of dynamic curing. At higher GTR particle size larger increase in UE compared to reference blends. GTR incorporation improved the melt flow of PP/EPDM blends	[182]
PP	–	Uncured GTR-like model rubber	SEBS SEBS-g-MA	PP/GTR/rubber: 35/65/10	PP also replaced by PP-g-MA	Twin-screw extruder	Injection molding	Reaction mechanism and morphology of the blends studied. PP-g-MA is a better suited matrix than PP	[183]
PP waste	Wet ambient	–	SEBS SEBS-g-MA	PP/GTR/rubber: 50/50/(0–20)	PP also together with PP-g-MA	Twin-screw extruder	Injection molding	Combined use of PP-g-MA and compatibilizing rubber yields TPE with balanced properties	[184]
PP	Wet ambient	50 mesh	SEBS, SEBS-g-MA EPDM-g-MA	PP/GTR/rubber: (40–60)/(40–60)/(0,20)	GTR thermomechanically reclaimed in presence and absence of bitumen	Twin-screw extruder	Injection molding	Bitumen worked as devulcanizing and plasticizing agent. Bitumen treatment of GTR resulted in improvements in UE, thermal stability and flowability. Additional use of rubber compatibilizer was beneficial	[185]

Table 5 continued

Thermoplastic polymer	GTR Type	Size	Additional rubber	Composition	Compatibilization additive strategy	Preparation		Results, comments	References
						Blend	Specimen		
PP	–	0.45 mm (35 mesh)	SBR	PP/GTR: 30/70 PP/GTR/rubber: 30/30/40	Dynamic vulcanization with peroxide and co-agent (bismaleimide)	Batch mixer	Injection molding	PP/GTR and PP/GTR/SBR systems with TPE-like characteristics (high TS and UE) produced. Bismaleimide acted as compatibilizer [186]	
PP	–	0.3 mm (40 mesh)	EPDM	PP/GTR/rubber (various composition)	–	Twin-screw extruder	Injection molding	Response surface methodology as DOE used. Optimization with respect to tensile and impact strength. Highest impact strength reached by the composition PP/GTR/EPDM = 50/25/25 [187]	
PP	–	50 mesh	SEBS- <i>g</i> -MA	PP/GTR/rubber: (35–65)/(21.5–55.5)/(0–20)	GTR first thermomechanically and afterward with bitumen devulcanized	Twin-screw extruder	Injection molding	ANN used for DOE to study the major factors: PP, bitumen and SEBS- <i>g</i> -MA concentration. Predicted optimal formulation agreed with that of the experimental one. [131]	
PP	Ambient (Genam)	<0.4 mm 0.4–0.7 mm	MSBR	PP/GTR/rubber: 30/(0–35)/(35–70)	Dynamic curing by sulfuric systems	Twin-screw extruder	Compression molding	TS, TM increased, UE decreased with increasing GTR content [155]	
PS (high impact)	–	120 mesh	EVA SBS	PS/GTR/rubber: (25–40)/(55–70)/(5–25)	–	Twin-screw extruder, two-roll mill	Compression molding	SBS proved to be a good compatibilizer. TS, UE and tear strength strongly improved at 12 phr SBS content	
TPU	Ambient	Mean ~0.3 mm	–	TPU/GTR: (85–100)/(0–15)	GTR also grafted with MAA	–	Curing in closed Al molds	Slight decrease in UE with increasing GTR content. GTR grafting is beneficial with respect to TS and compression set [146]	

Designation: not disclosed or measured

or partial destruction of the initial crosslinked structure takes place in a separate process. They cover different chemical (decrosslinking, grafting) and physical reactions (molecular entanglement). In this respect, the role of dynamic curing should be emphasized. The goal of compatibilization strategies is to encapsulate the GTR particles. This is usually achieved by additional compatibilizers which are mostly rubbers. The reason behind the selection of fresh rubbers is that rubbers, being amorphous, can highly be filled. Moreover, many of them are well compatible with polyolefins, such as ethylene–propylene rubber (EPR), EPDM, polyoctane ethylene (POE). The encapsulation strategy is most straightforward when a co-continuous phase structure can be set. Note that this is thermodynamically less stable in blends whose structure turns generally into a dispersed one. On the other hand, GTR particles may promote the preservation of the co-continuity of the phases. This aspect is not always articulated (except [2]) though the composition range thermoplastic/GTR = 30/70...70/30 already suggests the possible formation of dual-phase continuity. Large body of R&D works addressed the improvement of UE. According to our feeling, the best way to reach it that besides encapsulating phase (not necessarily rubber), a dynamically cured rubber phase should also be present. The corresponding morphology is outlined in Fig. 5.

In case of TPE with high GTR content the creation of a finely dispersed crosslinked rubber phase is not necessary when the GTR surface is well reclaimed. It has to be underlined that the surface reclamation of GTR, by whatever method achieved, is very beneficial with respect to the final properties of the TPE. Here, the bitumen treatment,

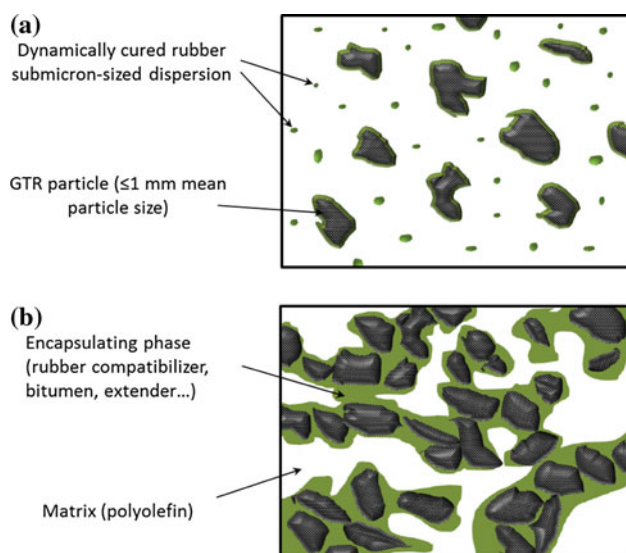


Fig. 5 Morphology of thermoplastic/GTR blends: dispersed (a) and co-continuous (b)

proposed by Lievana and Karger-Kocsis [6, 161] may be the right way, however, for some limited applications (dilatation parts in building/construction). The development to produce GTR-containing TPEs requires the adaptation of novel experimental design techniques (already emphasized in the notes of Tables 3, 4), as well as modeling studies [188] considering the optimal morphology. For GTR reclaiming, thermomechanical methods will be favored instead of thermochemical ones. Nevertheless, thermochemical reclamation will further be explored [45]. This is predicted based on the fact that cost-efficiency triggers the set-up of on-line compounding lines performing the reclamation of GTR and its reactive compounding with polyolefins.

GTR in thermosets

The use of GTR particles in thermoset resins usually targeted their toughness improvement. It is well known that rubber particles when dispersed in micron-scale range may improve the fracture toughness and energy of the corresponding thermoset matrix. These particles are created in situ via phase separation or mixed in particle form into the resin [189]. The latter approach can be adapted for GTR which was followed, in fact. Next, we shall list those works which were devoted to the toughening of thermosets by adding GTR. It is the right place to mention that the R&D works addressing thermoset/GTR combinations in which the role of thermoset (especially polyurethane) just a binder of GTR particle will not be covered. Interested reader in this field is directed to Refs. [190–192].

Most of the works performed on GTR/thermoset combinations addressed the modification of epoxy resins (EPs)—cf. Table 6. The GTR particles were introduced in the corresponding resin by mixing.

The results summarized in Table 6 clearly suggest that the modification of thermosets with GTR is less promising because the desired toughening cannot be achieved. This note holds also for using surface-modified GTRs. The scenario may change when ultrafine GTR particles (≤ 10 μm) are incorporated. It is interesting to note that researchers did not consider other effects which may be of interest, such as changes in the residual stress state and shrinkage, when incorporating GTR in thermosets.

GTR in curable rubbers

Earlier, it was accepted that GTR could be extensively recycled into traditional rubber products. However, the incorporation of GTR in rubber mixes in appreciable amounts alters the processability and it is associated with

Table 6 GTR-containing thermosets—effects of GTR (type, size and amount), and compatibilizers/additives on selected properties

Matrix	GTR		GTR content	Compatibilization additive strategy	Results, comments	References
	Type	Size				
EP (amine hardener)	–	0.075–0.425 mm	≤6 wt%	GTR surface modified. GTR used together with carboxyl-terminated liquid nitrile rubber (CTBN)	Fracture toughness (K_c) the higher the larger the GTR particle size. Combined use of GTR and CTBN is beneficial for toughness improvement	[193]
EP (amine hardener)	–	0.075 mm (200 mesh)	≤10 phr	GTR surface modified. GTR used together with CTBN	Synergetic toughening with 7.5 phr CTBN and 2.5 phr GTR	[194]
EP (-)	Ambient (Genan)	0.4–0.7 mm	10 wt%	GTR with and without grafting	E modulus decreased, Charpy impact strength increased with GTR incorporation. GTR- <i>g</i> -MA yielded high impact strength than unmodified GTR	[75]
EP (anhydride)	Cryogenic	0.35–0.5 mm	≤25 vol%	GTR plasma treated (oxygen, nitrogen), grafted by acrylic acid. GTR also treated by silanes	No improvement in the mechanical properties by adding GTR. Slight improvement due to treatment in the properties compared to untreated GTR	[195, 196]
EP (anhydride)	Cryogenic	0.18 mm	5 vol%	GTR silane (various) treated	Untreated GTR reduced the TM, TS and UE. Similar trend for K_c and Charpy impact strength. Silane treatment had no effect	[197]
EP (anhydride)	Cryogenic	0.18 mm	5 vol%	Combination with epoxy functionalized liquid silicone rubber (2 vol%)	Untreated GTR reduced the TM, TS and UE. Similarly, K_c and Charpy impact strength decreased. The combined use of GTR and silicon rubber improved only the Charpy impact strength which still remained below the reference EP	[198]
EP (amine hardener)	–	~0.15 mm	≤10 phr	GTR together with amine-terminated liquid nitrile (ATBN) rubber	K_c obeys the rule of mixture in the composition range except GTR/ATBN = 2.5/7.5 phr where synergism was observed. Beneficial effect of GTR disappears at high deformation rate	[199, 200]
EP	–	60 mesh	10 wt%	Hyperbranched polyamidoamine was grafted on the GTR surface and used as amine type hardener for EP	The grafted GTR was foreseen for both curing (demonstrated) and toughening (not shown) roles	[201]
PU (-)	Ambient (Genan)	0.4–0.7 mm	10 wt%	GTR with and without grafting	Unmodified GTR strongly decreased the TS and UE of PU. These parameters were not influenced when adding GTR- <i>g</i> -MA	[75]
UP (free radical)	Cryogenic	Mean 0.15 mm, 0.25 mm	≤40 wt%	GTR treated with silanes	GTR presence delayed the curing of UP. Surface treatment of GTR improved the tensile properties compared to the reference GTR-containing resin. Particle size too large for toughening	[202]

Designation: not disclosed or measured

some reduction in the mechanical properties, such as tensile and tear strength. Nonetheless, there has been always considerable interest to recycle GTR in rubber stocks [7–9, 203–213]. From the earlier studies, the following rule of

thumb was deduced: incorporation of 1 wt% of GTR result in 1 % deterioration in the mechanical properties. Accordingly, the GTR content of vulcanizable rubbers generally did not surpass the 10-wt% threshold [214].

Table 7 Revulcanization of GTR—effects of GTR type and size, crosslinking, additives, and processing on selected properties

GTR		Crosslinking method	Research strategy, variables	Processing conditions	Results, comments	References
Type	Size					
Cryogenic	0.3–0.9 mm	Sulfuric	Cure parameters (vulcanization agent percentage, time, pressure, temperature) varied. Molding also without vulcanization agent	$T = 160\text{--}220\text{ }^{\circ}\text{C}$ $t = 3\text{--}30\text{ min}$ $p = 1\text{--}30\text{ MPa}$	TS mostly depended on the vulcanization agent (type, amount) and curing time	[215]
Cryogenic	0.3–1.0 mm	Sulfur	Plasticizer (phthalate) also used	Optimum: $T = 180\text{ }^{\circ}\text{C}$ $t = 10\text{ min}$ $p = 10\text{ MPa}$	Sulfur amount should be 2 wt%. Plasticizer did not affect UE. Mechanical damping and effect of UV radiation studied	[216]
Cryogenic	0.3–0.9 mm	Sulfur	Plasticizer (phthalate) also used. Effect of sulfur concentration studied (0–5 wt%)	$T = 160\text{--}200\text{ }^{\circ}\text{C}$ $t = 10\text{ min}$ $p = 10\text{ MPa}$	Mechanical and acoustic damping in function of T and sulfur concentration studied	[217]
–	20–140 mesh various rubbers (and crosslinked thermoplastics, thermosets)	Without and with sulfur	High-pressure high-temperature sintering (HPHTS)	Sintering at $T = 80\text{--}240\text{ }^{\circ}\text{C}$ $t = 1\text{--}1440\text{ min}$ $p = 0.5\text{--}26\text{ MPa}$	Mechanism of consolidation/particle adhesion concluded. Additional sulfur accelerates this process. Mechanical properties as a function of processing condition studied	[218]
Cryogenic	~0.3 mm only NR	Without and with sulfuric curatives and reclaiming agents	HPHTS	Sintering at $T = 200\text{ }^{\circ}\text{C}$ $t = 60\text{ min}$ $p = 8.5\text{ MPa}$	Pronounced effect of reclaiming agents. De- and revulcanization mechanisms studied and concluded	[213]
SSSE	0.09–1.4 mm (NR-based scrap)	Without and with sulfur	Effects of particle size and processing conditions studied.	$T = 115\text{--}207\text{ }^{\circ}\text{C}$ $t = 15\text{--}120\text{ min}$ $p = 3.1\text{--}6.1\text{ MPa}$	Powder characteristics and molding condition affected the crosslink density and failure behavior. High temperature and pressure generally improve the particle bonding	[219]
–	0.32 mm	No curative	Use of sisal fiber as reinforcement (different length) up to 10 wt%. Sisal also surface treated.	$T = 200\text{ }^{\circ}\text{C}$ $t = 180\text{ min}$ $p = 40\text{ MPa}$	Mercerization, acetylation of sisal improved the stiffness (modulus) of the sintered GTR. Highest modulus and TS got at 10 mm fiber length	[220]
–	30 mesh	Ultrasonic devulcanization of GTR	Revulcanization of the devulcanized GTR with sulfuric system	–	Revulcanization process studied	[221]
Cryogenic	60 mesh	Devulcanization of GTR in pan-mill	Waste short fiber as reinforcement used ($\leq 15\text{ phr}$). Sulfuric revulcanization.	$T = 150\text{ }^{\circ}\text{C}$ $t = 15\text{ min}$ $p = 10\text{ MPa}$	Co-milling of GTR with fiber yielded the best mechanical performance. Effect of fiber alignment noticed	[222]
–	Waste tyre rubber	Thermomechanical devulcanization	Sulfuric revulcanization, reinforcement with carbon nanotube (CNT, $\leq 5\text{ phr}$)	$T = 150\text{ }^{\circ}\text{C}$ $t = 30\text{ min}$ $p = 4\text{ MPa}$	Strongly improvement in the stiffness with increasing amount of CNT. The latter influence the hysteresis and electric conductivity, as well	[223]

Table 7 continued

GTR		Crosslinking method	Research strategy, variables	Processing conditions	Results, comments	References
Type	Size					
Ambient (Genan)	<0.4 mm 0.4–0.7 mm	–	Without and with sulfuric curing	$T = 160\text{--}220\text{ }^{\circ}\text{C}$ $t = 3\text{--}30\text{ min}$ $p = 10\text{--}30\text{ MPa}$	Without curative, increasing T , t and p all increased the TS. Curative improved the stress–strain behavior. Smaller GTR particle size improved the TS and UE by contrast to the modulus compared to compaction with larger GTR	[135]
–	–	Thermochemical shear extrusion	Sulfuric	–	Mechanical properties as a function of extrusion temperature determined	[27]
Ambient	$\leq 0.2\text{ mm}$	Microbial desulfurization	Sulfuric	$T = 150\text{ }^{\circ}\text{C}$ $t = 20\text{ min}$ $p = 15\text{ MPa}$	TS improved from 2.5 to 4.9 MPa, UE from 153 to 178 % and M100 from 1.8 to 2.6 MPa after microbial desulfurization	[224]

Designation: not disclosed or measured

Further, learning from these studies was that the smaller the property degradation, the finer the used GTR fraction is. The reports are mostly in harmony about the reason of the property (ultimate tensile and tear properties) drop. They locate it in the missing interfacial bonding between the GTR and the rubber matrix. This argument is supported by the fact that the mechanical properties of GTR-containing rubbers are less affected when GTR particles are smaller. Klüppel et al. [209] considered the GTR-containing rubber as a rubber with locally varying network density and filler (CB) content. This may be beneficial with respect to some properties (oil-resistance, compression set, acoustic damping), whereas detrimental for others (fatigue, tensile, and tear characteristics).

The R&D activities in this field have been running in two directions: (a) to use GTR without adding fresh rubber and (b) to incorporate GTR as filler in curable rubber stocks. Needless to say that partial reclamation/devulcanization of GTR, by whatever method achieved, is preferred in both the above-mentioned recycling strategies.

On the other hand, devulcanization is exactly that mechanism, which allows us to produce rubber products from 100 % GTR. Employing heat and pressure, the different sulfide linkages (mono-, di-, polysulfide) can be cleaved in situ during molding. Recall that the sulfide-, sulfur-bonds are the weakest with respect to the bond energies among the chemical crosslinks. Nowadays, considerable efforts are devoted to shed light on the decrosslinking reactions upon heating and in the presence of reclaiming agent [213].

Next, we shall split the works done on this field whether GTR was used alone (cf. Table 7) or in combination with other rubber(s)—cf. Table 8.

GTR particle bonding (without fresh rubber)

A recent work was devoted to the “direct powder molding” or direct molding of GTR particles. Gugliemotti et al. [225] studied the effects of particle size, particle size distribution, and processing conditions on the mechanical performance of the related products made only from GTR without any additives. Major advantage of the strategy of “GTR particle bonding” is that a high amount of GTR can be recycled by this way. On the other hand, mostly “non-critical” rubber items (mats, pads, carpet underlays, walkway tiles, sport field surface, etc.) can be manufactured, whose market is limited. Incorporation of fibrous reinforcements of different origins, including waste products, is a straightforward approach. Further investigations are needed to find devulcanization/reclaiming additives, which “activate” the surface of GTR prior to the “sintering” (bonding) process.

GTR with fresh rubber

GTR with and without reclaiming have been introduced in virgin rubber recipes to reduce material costs. This was accompanied with sacrificing some properties and had a negative impact on the processability, as well. A large body of works was dedicated to clarify what is that GTR amount

Table 8 GTR in virgin rubbers—effects of GTR (type, size and treatment), composition, crosslinking, and processing on selected properties

Fresh rubber mix	GTR		Size	Treatment	Rubber/GTR or GTR content	Crosslinking/vulcanization system	Mixing	Results, comments	References
	Type	Size							
BR, IR, SBR BR/IR/ SBR(40/20/ 40)	Ambient (Genan)	0.4–0.7 mm	Devulcanization in oil, resin, “mineral rubber”, anhydride, indene-coumarone resin	100/0...20/80	Sulfur sulfur-donor peroxide	Two-roll mill	Reclaimed GTR up to 20 wt% slightly improved the mechanical performance of BR/GTR and SBR/GTR. Tensile properties decreased with GTR content for IR/GTR. Most effective curative for IR and SBR was a sulfur donor system, whereas sulfur for BR. The properties of model tyre compound (BR/IR/SBR) were maintained up to ≤ 20 wt% GTR content	[39]	
BR, EPDM, IR, MSBR	Ambient (Genan)	<0.4 mm 0.4–0.7 mm	–	75/25...50/50	Sulfuric (two versions)	Batch mixer	No effect of GTR particle size on the tensile properties for IR and EPDM. Pronounced improvement with lower GTR particle size for BR and MSBR	[135]	
CR	Wet ambient, high temperature	~ 0.035 mm ~ 0.035 mm	–	15–80 phr	Sulfuric + metal oxide	Batch mixer two-roll mill	Small effect of GTR production method. TS markedly reduced, UE not affected, tear strength slightly and compression set markedly improved at 60 phr GTR content	[209]	
EPDM	–	40 mesh	Thermomechanical reclaiming	100/0...0/100	–	Two-roll mill	TM increased, UE decreased, TS went through minimum in function of GTR content	[88]	
EPDM	Ambient	EPDM rubber waste <0.06 mm	–	EPDM particle ≤ 100 phr	Sulfuric	Two-roll mill	All tensile properties improved with increasing ground rubber content. Rheological behavior, processability also studied	[226, 227]	
EPDM	Ambient (Genan)	<0.4 mm 0.4–0.7 mm	Reclaimed in bitumen (GTR/bitumen: 1/1)	90/10...50/50	Sulfuric	Batch mixer	TS and UE decreased for the uncured EPDM/GTR blends with increasing GTR content. Similar trend for the cured EPDM/GTR containing the coarse GTR fraction. Synergetic TS improvement in case of the fine GTR fraction. Bituminous reclamation of GTR was beneficial	[228]	
EPDM	Ambient	Ground EPDM ~ 0.03 mm	–	Ground EPDM ≤ 200 phr	Sulfuric (high amount of extender oil)	Batch mixer two-roll mill	TS, UE maintained; moduli at various elongations and tear strength decreased with increasing ground EPDM content. Vulcanization kinetics and rheology also studied	[229]	
EPDM, SBR	–	Ground waste EPDM 0.2–0.4 mm	–	Ground rubber EPDM ≤ 450 phr SBR ≤ 140 phr	Sulfuric	Two-roll mill	M100 decreased with increasing ground rubber content. Tear strength decreased for SBR but increased for EPDM with ground rubber content. Vulcanization kinetics also studied	[230]	

Table 8 continued

Fresh rubber mix	GTR		Size	Treatment	Rubber/GTR or GTR content	Crosslinking/vulcanization system	Mixing	Results, comments	References
	Type	Size							
EPDM	Ambient	Ground EPDM ≤ 0.05 mm (mean ~ 0.01 mm)	Ground EPDM ≤ 500 phr	–	Sulfuric	Two-roll mill	M100, M300 and tear strength monotonously increased, TS and UE went through maximum as a function of ground EPDM content. Vulcanization kinetics, sulfur migration, rheology also studied	[231]	
EPDM	Ambient (Genan), cryogenic	< 0.1 mm < 0.4 mm $0.4-0.7$ mm $0.4-0.63$ mm	75/25	GTR also thermomechanically activated	Sulfuric	Batch mixer	Stress-strain behavior significantly affected by the GTR particle size (the smaller the better). Additional thermomechanical reclaiming reduced the reduced the tensile properties	[182]	
IIR	–	5 mm	100/0...0/100	Ultrasonic devulcanization of ground tyre-curing bladder	Sulfuric	Batch mixer	Hardness monotonously increased, TS decreased while M100 and tear strength did not change with increasing devulcanized rubber content	[232]	
IIR (chlorobutyl)	–	40 mesh	100/0...0/100	Thermomechanical reclaiming	–	Two-roll mill	TM monotonously increased, UE monotonously decreased and TS went through a maximum in function of GTR content	[88]	
NBR	Wet ambient, high temperature	~ 0.035 mm ~ 0.035 mm	15–80 phr	–	Sulfuric	Batch mixer two-roll mill	Strong influence of the acrylonitrile content of NBR and production method of GTR. TS reduced and compression set deteriorated at 60 phr GTR content compared to the reference without GTR	[209]	
NR	Wet ambient, high temperature	~ 0.035 mm ~ 0.035 mm	15–80 phr	–	Sulfuric	Batch mixer two-roll mill	Strong effect of GTR production method. TS decreased, UE slightly decreased, tear strength maintained, compression set markedly deteriorated at 60 phr GTR content compared to the reference without GTR	[209]	
NR, SBR	Ambient	Ultrafine ≤ 0.02 mm also from NR	≤ 210 phr	–	Sulfuric	Batch mixer	Tensile and fatigue properties in function of GTR and sulfur concentration studied. Vulcanization kinetics, rheology (extrudability) also considered. Tyre tread compound containing 100 phr ultrafine GTR developed	[233]	
NR	–	Waste rubber powder	NR only “binder” —6 phr with respect to the rubber powder (100 phr)	Thermochemical devulcanization	Sulfuric	Batch mixer	Optimum devulcanizing agent content considering the mechanical properties determined.	[40]	

Table 8 continued

Fresh rubber mix	GTR		Rubber/GTR or GTR content	Crosslinking/vulcanization system	Mixing	Results, comments	References
	Type	Size					
NR	Ambient	Waste rubber powder 0.25–0.5 mm	≤50 phr	Sulfuric	Two-roll mill	Effects of rubber powder, CB and calcium carbonate compared. M100 and M200 did not change, while TS and UE reduced with increasing rubber powder content	[234]
NR, SBR	Ambient	0.08–0.09 mm (170–200 mesh) 0.13–0.15 mm (100–120 mesh) 0.18–0.25 mm (60–80 mesh) 0.42–0.6 mm (30–40 mesh)	≤50 phr	Sulfuric	Batch mixer	Strong effect of the GTR particle size on the mechanical and rheological behavior. TM, TS and fatigue life time decreased with increasing GTR particle size at a given GTR content. The flex crack growth delayed with increasing GTR content and decreasing GTR particle size. This behavior was more prominent for SBR than NR. Abrasion was more dependent on the characteristics of the abrading surface than on the loading level and particle size of GTR	[203]
NR	Ambient	Waste rubber powder 0.25–0.5 mm	≤50 phr	Sulfuric	Two-roll mill	M100 and M300 slightly increased, TS and UE decreased with increasing rubber powder content	[235]
NR	Ambient	Waste rubber powder 0.25–0.5 mm	70/30...40/60	Sulfuric (conventional, semi-efficient, efficient)	–	M100, M300 and hardness increased, resilience, TS and UE decreased with increasing rubber powder content. The latter characteristics were highest with efficient, whereas the moduli and hardness with conventional vulcanization system	[236]
NR	No	Reclaimed tyre tread	100/0...20/80	Sulfuric	Two-roll mill	Dynamic mechanical and swelling properties studied	[237]
NR	No	Reclaimed tyre tread	100/0...0/100	Sulfuric	Two-roll mill	M100 increased; TS and UE decreased with increasing reclaim content. Rheological and vulcanization properties also studied	[212]
NR	GTR converted into plastic plug	Thermochemical shear extrusion	≤40 phr	Sulfuric	Twin-screw extruder, two-roll mill	TS and UE decreased, whereas M300 increased with increasing amount of GTR reclaim	[27]
NR	–	0.2–0.4 mm initially Devulcanization by HEBM in presence of reclaiming agents	15 phr	Sulfuric	Two-roll mill	Up to 15 phr GTR no compromise in TS and UE and improved resistance to crack growth	[44]

Table 8 continued

Fresh rubber mix	GTR		Rubber/GTR or GTR content	Crosslinking/vulcanization system	Mixing	Results, comments	References
	Type	Size					
NR	Ambient	Waste rubber powder 0.25–0.5 mm	ENR and EAA (<5 wt%) as compatibilizers	Sulfuric	–	Incorporation of silica (up to 50 phr) and polymeric compatibilizers improved the mechanical properties compared to unfilled, uncompatibilized reference samples	[238]
NR	–	Scrap rubber 0.05–0.5 mm	Mechanochemical reclaiming, surface treatment (HNO ₃ , H ₂ O ₂ , H ₂ SO ₄)	Sulfuric	Two-roll mill	TS and UE decreased, M200 increased with reclaim content. Virgin rubber can be replaced up to 30 wt% without sacrificing the basic properties. Surface treated rubber can replace CB	[239]
NR	Ambient (Genan)	<0.2 mm 0.71–1.0 mm 4 mm	–	Sulfuric	Batch mixer Two-roll mill	Good property retention with respect to TS and abrasion resistance, especially with smaller particles, below 10 phr loading	[240]
NR, SBR	–	Waste rubber powder	Mechanochemical reclaiming presence of oil softener	Sulfuric	Two-roll mill	Effects of reclaiming agents and process parameters studied. TS and UE decreased and M200 increased with increasing reclaim content. Reclaim can replace 10–30 wt% of virgin rubber without sacrificing the essential properties	[43]
NR	–	Waste NR 40 mesh Initially	Thermomechanical reclaiming in twin-screw extruder	Sulfuric	Two-roll mill	Response surface methodology used to determine the optimal processing parameters for devulcanization of cured processing waste of NR	[41, 42]
NR	–	0.125–0.5 mm	Surface oxidation by HNO ₃ and H ₂ O ₂	Sulfuric	Two-roll mill	GTR as filler to replace CB checked. 10–20 phr CB can be replaced by surface treated GTR thereby maintaining the basic mechanical properties. Thermal aging slightly impaired	[66]
NR	Ambient (Genan)	4 mm initially	Devulcanization in “continuous shear-flow reaction treatment” (extruder)	Sulfuric	Batch mixer two-roll mill	TS, UE decreased, tear strength increased with increasing GTR loading. Reclaiming was beneficial in respect to the above properties. Abrasion resistance was negatively affected by reclaiming. Revulcanization characteristics also determined	[241, 242]

Table 8 continued

Fresh rubber mix	GTR		Treatment	Rubber/GTR or GTR content	Crosslinking/vulcanization system	Mixing	Results, comments	References
	Type	Size						
NR	Cryogenic	0.2 mm	UV-induced surface grafting with bismaleimide compound	1.5/85	Sulfuric	Two-roll mill	Hardness and tensile/tear properties determined in function of bismaleimide content acting as antireversion agent. Using bismaleimide-grafted GTR excellent mechanical properties obtained at NR/GTR = 15/85 ratio	[80]
NR	–	40 mesh	–	≤600 phr + waste leather fiber (100 phr) as additional reinforcement	Sulfuric	Two-roll mill	TS, UE and tear strength were all enhanced with increasing GTR content. Incorporation of waste leather proved to be beneficial especially at lower GTR loading	[243]
NR	–	40 mesh initially	Devulcanization in a twin-screw extruder	30/70	Sulfuric (sulfur/accelerator ratio varied)	–	Additional incorporation of CB (≤25 phr) markedly enhanced the moduli (M100, M300), slightly the TS and tear strength and reduced the UE. Optimum properties obtained at 15 phr CB	[244]
NR	–	Reclaimed tyre tread	–	100/0...40/60	Sulfuric (microwave, thermal)	Two-roll mill	TS, UE, tear strength decreased, while M100 and hardness increased monotonously with increasing reclaim content. Traditional (thermal) curing is more efficient than microwave	[245]
NR	–	4 mm	Devulcanization in “continuous shear-flow treatment” (extruder)	≤50 phr	Sulfuric	Batch mixer two-roll mill	Curative amount adjusted whether the reclaim considered as filler or rubber. In case of filler TS, UE, hardness and abrasion resistance deteriorated with increasing reclaim loading. When considered as rubber the TS and UE were improved at 10 phr reclaim content compared to the reference NR	[246]
NR	Cold but not cryogenic	≤0.85 mm	–	≤50 phr GTR model material produce by different sulfuric and peroxide curing	Sulfuric (conventional, semi-efficient, peroxide)	–	Effects of GTR content on the cure behavior and physical properties of differently cured NR studied. TS, tear strength and UE abruptly dropped with a small amount of GTR, but the UE increased with increasing GTR content. Largest decrease in the physical properties observed for vulcanizates containing peroxide-cured GTR	[247]
NR	Ambient	≤0.2 mm	Microbial desulfurization	≤40 phr	Sulfuric	Two-roll mill	GTR filled NR exhibited better mechanical properties of the same loading when the GTR particles were desulfurized by “thiobacillus ferrooxidans”	[224]

Table 8 continued

Fresh rubber mix	GTR		Rubber/GTR or GTR content	Crosslinking/vulcanization system	Mixing	Results, comments	References
	Type	Size					
NR	–	0.15–0.25 mm	–	Sulfuric	Two-roll mill	Effect of CB replacement by GTR on the curing behavior and mechanical properties studied	[248]
ENR	Ambient	NR-based latex waste 0.3–0.5 mm 0.6–0.9 mm 1.7–2.5 mm 9–11 mm	–	Sulfuric	Two-roll mill	Rubber powder proved to be active filler. Its particle size had a great impact on the curing and the properties	[249]
SBR	–	0.2 mm 0.15 mm	–	Sulfuric	Two-roll mill	Swelling behavior as a function of crosslink density studied	[250]
SBR	Cryogenic high-temperature (different)	<0.16 mm <0.6 mm (different)	GTR grafted by MA and also hydroxylated GTR involved	Sulfuric	Batch mixer two-roll mill	SBR also replaced by SBR- <i>g</i> -MA. Change in the TS and UE in a function of GTR treatment (MA grafting, hydroxylation) and SBR modifications studied	[87]
SBR	–	SBR scrap 28–35 mesh	–	Sulfuric	Two-roll mill	Property retention (TS, UE, tear strength, hardness, compression set, and abrasion loss) after accelerated aging studied	[251]
SBR	Ambient	≤0.4 mm	Microbial desulfurization	Sulfuric	Two-roll mill	TS, UE enhanced; tear strength did not change; M100 and M300 decreased after GTR desulfurization at the same GTR loading	[252]

Designation: not disclosed or measured

which does not influence the requested property profile markedly, and how the GTR content of the rubber stocks can be increased. Next, we shall review the related works to conclude the related achievements and to forecast future developments. To provide the reader with a broad overview, the use of pulverized rubbers (processing or post-consumer waste), other than GTR, will also be considered (cf. Table 8). This is due to our belief that the related recycling technique can be adapted, or serve as example for GTR recycling.

The results summarized in Table 8 suggest that incorporation of GTR in fresh rubber stocks remains a promising recycling route for GTR. In order to enhance the GTR loading in the recipes without sacrificing the basic property requirements, it is inevitable to subject the GTR to devulcanization/reclaiming. Otherwise, the GTR amount, that can be incorporated, remains below 10 phr. For devulcanization/reclaiming continuous processes should be preferred. This suggestion is based on two basic aspects. First, continuously operating devulcanizing lines do not require finely powdered GTR which contributes to cost saving. On the other hand, for that purpose most probably special extruders should be developed. Second, during breakage of crosslinks (devulcanization) and molecular chains (reclaiming) macroradicals develop and their recombination, when not associated with reduction in the crosslink density, should be avoided. This can be efficiently done during extrusion by introducing suitable reclaiming additives, diluting with fresh rubber, etc. Accordingly, the macroradicals generated during devulcanization/reclaiming should be involved in co-reactions with suitable “diluting additives.” By this way, even an accelerator-containing, ready-to-incorporate mix can be produced. Accordingly, preparation of rubber mixes in traditional batch mixers can be circumvented.

Conclusion and outlook

Many arguments support the material recycling of worn tyres via production/use of GTR. The use of GTR in thermosets to improve some properties of the latter is practically not feasible though researchers still follow this route. Thermosets (especially PU based) will play further on, however, a role as binders for GTR in construction and civil engineering applications. Incorporation of GTR in thermoplastics is also not rewarding unless waste materials (e.g., agricultural films, discarded transportation crates) are used as matrices. However, even in that case new markets should be found. The above survey clearly articulates that GTR recycling should target the production of TPEs, and its (re)use in the rubber industry. The yearly consumption of TPEs is increasing. So, the development of

GTR-containing TPEs with useful characteristics would contribute to the recycling of a large amount of GTR. The same note holds for the GTR use in rubber industry provided that GTR devulcanization/reclaiming is economically solved. According to the authors’ feeling, it may happen by preferring thermomechanical, eventual (thermo) mechanochemical, decomposition routes than others.

One can also recognize a new trend in GTR recycling: instead of the mechanical other properties become under spot of interest. In this respect, acoustic and vibration damping should be mentioned. It is well known that rubbers and rubber-like materials with very inhomogeneous crosslinked structure are excellent sound absorbers. GTR particles are predestinated to generate such a structure in different matrices [253–255].

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