

# Green Approaches in Rubber Recycling Technologies: Present Status and Future Perspective

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## Abbreviation

<i>EPA</i>	<i>Environmental Protection Agency</i>
<i>GTR</i>	<i>Ground Tire Rubber</i>
<i>NR</i>	<i>Natural Rubber</i>
<i>TPEs</i>	<i>Thermoplastic Elastomers</i>
<i>LDPE</i>	<i>Low Density Polyethylene</i>
<i>EVA</i>	<i>Ethylene-Vinyl Acetate copolymer</i>
<i>rLDPE</i>	<i>Recycled Low Density Polyethylene</i>
<i>HDPE</i>	<i>High Density Polyethylene</i>
<i>PP</i>	<i>Polypropylene</i>
<i>LLDPE</i>	<i>Linear Low Density Polyethylene</i>
<i>EPDM</i>	<i>Ethylene-Propylene-Dien-Monomer</i>
<i>rHDPE</i>	<i>Recycled High Density Polyethylene</i>
<i>SBS</i>	<i>Styrene-Butadiene-Styrene copolymer</i>
<i>SBR</i>	<i>Styrene-Butadiene Rubber</i>
<i>NBR</i>	<i>Nitrile butadiene rubber</i>
<i>RPM</i>	<i>Revolutions Per Minute</i>
<i>DCP</i>	<i>Dicumyl Peroxide</i>
<i>ILs</i>	<i>Ionic Liquids</i>
<i>DESs</i>	<i>Deep Eutectic Solvents</i>
<i>scCO<sub>2</sub></i>	<i>Supercritical CO<sub>2</sub></i>



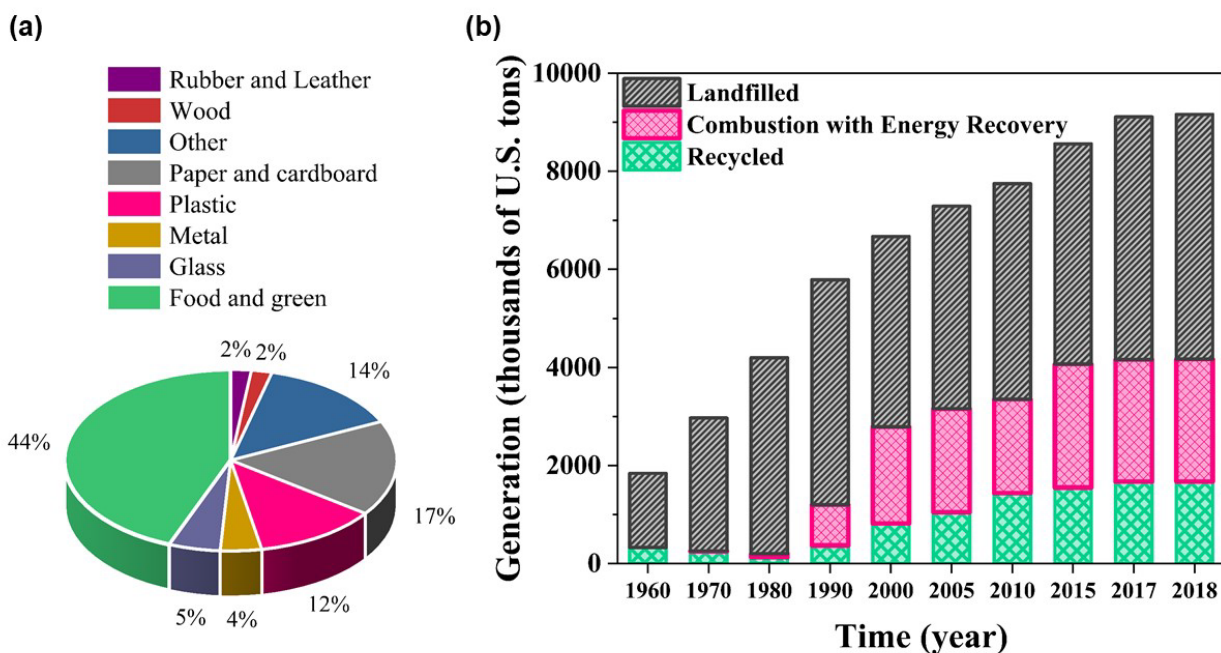
## Abstract

As a consequence of massive production and consumption of rubbers, rubber blends and composites for myriad applications, elastomeric products have enormously accumulated and become an environmental threat. The disposal and burning of rubber wastes have been banned because of the environmental and economic reasons. By contrast, a great deal of attention has been directed towards strategies enabling recycling and reuse of rubbers. Basically, conventional recycling methods suffer from several drawbacks such as the formation of dust, fumes, and toxic gases in the air, as well as contamination of underground water resources. Thus, green formulations and processing methods nowadays are of priority and importance. Taking advantages of sustainable development horizon, we review and discuss scientific and technological aspects of waste rubber management such as processing techniques, properties of the resulting products, industrial applications, and compatibilization with other materials such as thermoplastics, thermosets, and rubbers. A particular emphasis is placed on reactive extrusion. Finally, current status of green rubber recycling and future opening doors ahead of this technology are discussed.

**Keywords:** Green technologies; Waste management; Reactive extrusion; Rubber recycling; Ground tire rubber; Compatibilization

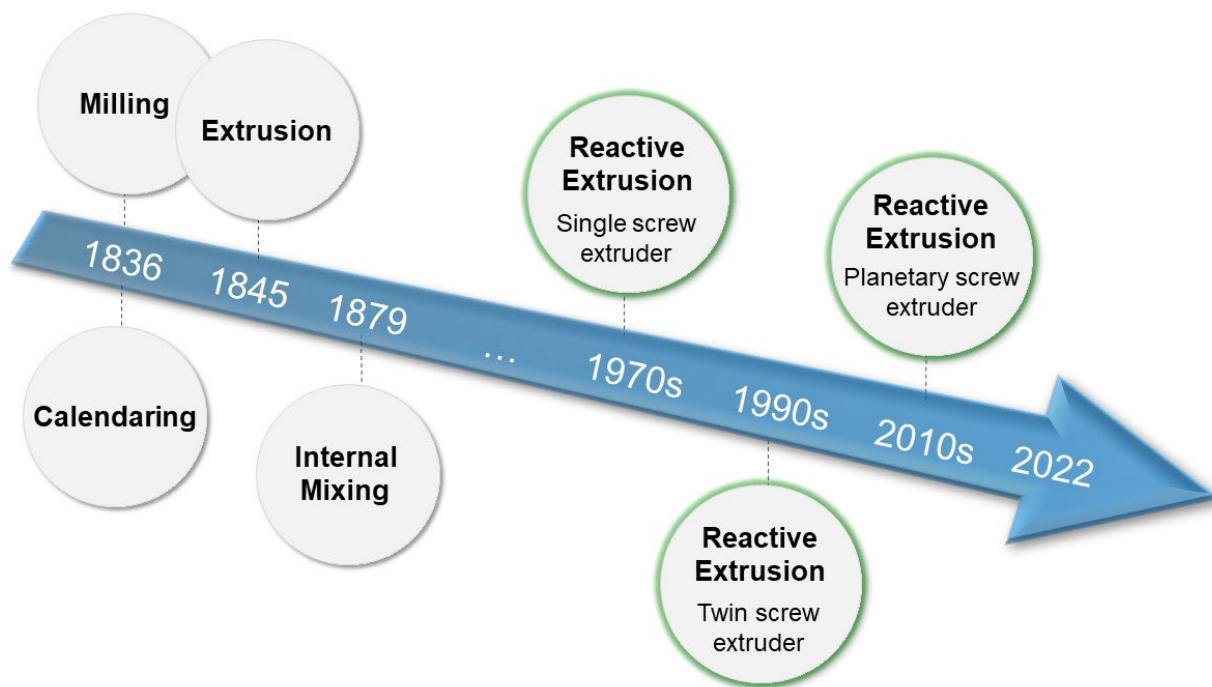
## Introduction

Over the past century, the subject of scrap rubber, particularly accounted for tire disposal and generation of reclaim rubber, has become vastly popular and discussed <sup>1-3</sup>. Depot construction, burial and incineration of tires, due to the environmental pollution such as emission of toxic gases, the presence of heavy metals and the collection of mosquitoes, have been banned by the European Union. In the meanwhile, waste management has gradually become widespread from sustainability viewpoint <sup>4-7</sup>. From the time that recycling of rubbers has become the matter of concern, researchers and engineers alike have directed much interested in reuse of rubber products as much as possible in scarcity of the virgin materials. According to **Fig. 1**, the proportion of rubber and leather was 2% in the waste material production in 2016, and its follows increasing trend. Therefore, it seems essential to find the best yet fastest solution to such a global issue, from both environmental and economic angles.



**Fig. 1. Rubber recycling statistics and proportional usage.** (a) The proportion of Rubber and Leather in the total wastes in all regions in 2016; (b) Rubber and Leather in municipal solid waste in USA 1960-2018. Increasing trend in recycling of rubber and leather is the signal of hope for environmentalists. Nevertheless, waste material management is not provided for the future analysis. (Designed by the authors of the present work based on the data reported by EPA <sup>8</sup>)

In the past, combustion (still it is common somewhere) and landfilling were the most well-known traditional strategies for rubber waste utilization, which were subject to several disadvantages such as the formation of dust, fumes, and toxic gases in the air, as well as the contamination of underground water resources<sup>9, 10</sup>. In recent years, the technology of recycling has experienced progressive growth with the manifestation of various devices and equipment. In this regard, disadvantageous features of recycling are assessed to find novel technologies more convenient with respect to the conventional solutions. The timeline of devices/processing methods used is provided in **Fig. 2**. Accordingly, the 19<sup>th</sup> century can be named “rubber technology era” when this technology solved several sorts of environmental and economic problems. However, the same as of other technologies, advantages and disadvantage of rubber recycling techniques were merged together<sup>11-13</sup>. Looking at the status of the matter in 20<sup>th</sup> century confirms that processing and management of rubber wastes have significantly advanced from the perspectives of the unit operation and machinery.



**Fig. 2. A chronology of the rubber recycling technologies over the past two centuries.** In years between 1836-1879, several papers and patents have been published, among which Milling and Calendaring<sup>14</sup>, Extrusion<sup>15</sup>, and Internal Mixing particularly in Banbury mixer<sup>16</sup> were progressively invented. In 1970s, Reactive Extrusion by Single-screw Extruder<sup>17</sup> was invented. Later in 1990w Twin-screw based Reactive Extrusion<sup>18, 19</sup>, and later in 2010s Planetary-extruder<sup>20</sup> were introduced. *(Designed by the authors of the present work)*

Typically, each technology has its own advantages and disadvantages. A comparison between reactive extrusion and other classical rubber recycling technologies witnesses some serious differences in terms of processing, quality control, and treatment efficiency <sup>21-24</sup>. Principally, reactive extrusion is an intensive mixing process accompanied by degassing, enabling facile production of high-quality multi-component mixtures. It is introduced to make it possible to chemically modify polymer materials through continuous processing. In the course of this process, chemical reactions such as grafting, cross-linking, compatibilization or polymerization take place, which allows several processes to be carried out simultaneously (e.g., functionalization). One of the advantages of reactive extrusion processing over the conventional technologies is that the reaction chamber in the former case is solvent-free, eliminating the need for removal of toxic solvents and excessive heat, which are main issues in conventional recycling techniques <sup>25-27</sup>. Moreover, reactive extrusion enables one to efficiently remove the heat generated on the surface of barrel of the extruder rather than inside the bulk of large volume reactors. Other advantages of such processing are the high flexibility in designing, modulating, and optimizing different zones of barrels and screw as well, which provide the materials with concentrated local heating and cooling - what guarantees a high recycling efficiency <sup>28</sup>. Moreover, during the convection and mixing, the materials are heated by the shear energy and allowed to circulate by the aid of screw elements, along with heating by barrel heaters assist homogenization.

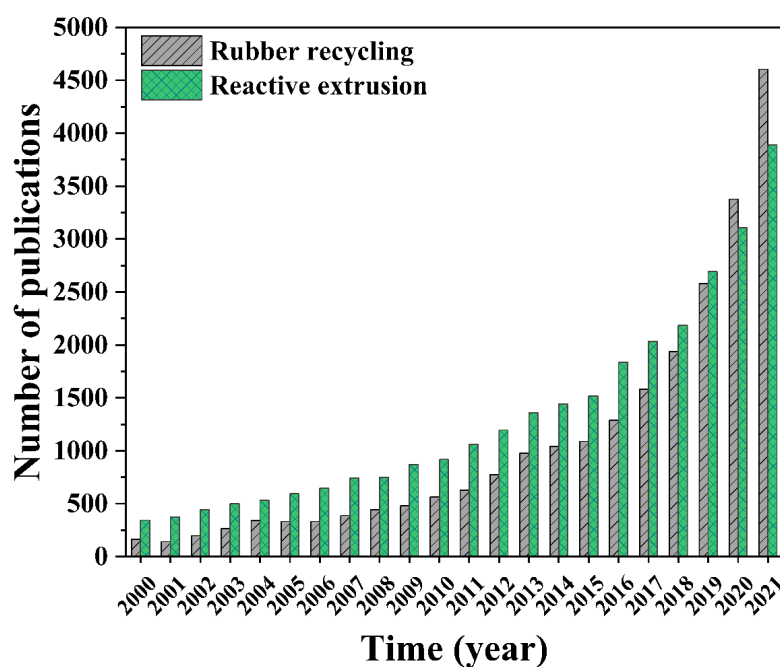
Another advantage of reactive extrusion is the ability to modulate the screw as a key in achieving effective mixing (dispersive and/or distributive mixing) with a great deal of the shear energy input. In this regard, the amount of the heat required for chemical reaction can be coincidentally provided by the combination of mechanical shear and external heating. Moreover, the addition of reactants with different states is possible at any position of the extruder, e.g., adding the heat-sensitive additives at the end of the extrusion process (somewhere in the metering zone of the screw) to minimize the residence time of the melt within the extruder <sup>29,30</sup>. Finally, the most critical section of the reactive extruder is the degassing zone, which should be placed in a proper distance along the barrel depending on the residence time, the temperature profile determining the viscosity, and the rate of diffusion of gases into the molten polymer. In this sense, sometimes more than one degassing zone would be required <sup>31</sup>. Overall, reactive extrusion makes shorter the processing of rubber recycling compared to the other conventional processes (**Table 1**) <sup>32</sup>. Correspondingly, publications on the use of reactive extrusion followed a sharp increasing trend over the last two



decades (Fig. 3). The provided statistics underlines the attention being paid to this process and flourishing feature ahead of this processing strategy for rubber recycling. Nevertheless, utilization of reactive extrusion in rubber recycling is experiencing early stage of maturity.

**Table 1.** Comparison between rubber recycling processes in terms of simplicity, economy, processing mode, and specifications/industrial uses.

Type of Process	Batch/Continues	Process Simplicity	Economical Process	Specification/Industries	Refs.
Milling	Batch	Yes	No	It allows for modeling of complex forms and trimming pieces of several materials such as metal, wood, plastic, and composites.	33
Calendaring	Continues	Yes	No	Enables manufacturing high-volume, high quality plastic films and sheets.	34
Molding	Batch	No	No	It is used in subway ticket machinery, airport security equipment and the fuel dispensing pump.	35
Internal mixing	Batch	No	No	Used for preparation of mixtures for cold pressing units.	36
Extrusion	Continues	Yes	Yes	Used in production of tubes and hollow pipes.	37
Reactive extrusion	Continues	Yes	Yes	Used for polymerization and development of new polymeric compounds.	38



**Fig. 3.** Trend in progressive interest in rubber recycling and reactive extrusion over the last two decades (2000-2021). Such a competition suggest that using reactive extrusion for rubber recycling can be a very promising approach. Two keywords of “Rubber recycling” and “Reactive extrusion” are used independently for search in Scopus (03/07/2022). (Designed by the authors of the present work)

In parallel with research activities, the market requirements on developing rubber recycling technologies have seriously been investigated over the last years. According to the results obtained by European Tire and Rubber Manufacturers Association (ETRMA) in 2019, 95% of the end-of-life tire (ELF) was managed in different European members of this association. These materials were collected and treated mainly for material recycling and energy recovery. These results are almost identical to those obtained in recent years. In Europe, 3.55 million tons of ELF are generated (4% for civil engineering, 51% for recycling and 40% for energy recovery). About 1.95 million tons of ELT were treated by material recovery, 1.36 million tons were sent to the granulation process; 476,000 tons of ELT were incorporated into cement and 112,954 tons were used in civil engineering applications. Some other minor applications in processes such as pyrolysis, steelworks and foundries, and 1.43 million tons of tires went through energy recovery. Only 165,000 tons of recycled rubber from tires outside use (NFU) are awaiting treatment. These data show that practically all the ELFs generated in Europe are used [<https://www.etrma.org>].

In conclusion, reactive extrusion has many useful features and enables many possibilities for flexible and economic production in rubber recycling technologies. Moreover, this continuous process enables one for the minimization of the residence time distribution. And additionally, it is highly flexible in terms of processing and reactive formulation. In addition, the ability of using monomers together with providing the machine with degassing zones are the key advantages of reactive extrusion. Over the past twenty years, rubber recycling using reactive extrusion units relied satisfactorily on nearly 60% of the global needs of rubber recycling market <sup>39</sup>. Furthermore, a wide range of materials with different properties and performance are experiencing processing using reactive extrusion of waste rubbers by manipulating the chemistry of ingredients as well as processing parameters, such as screw design, temperature profile along the barrel, and adjustable feeding and degassing systems. Incorporation of compatibilizers into recycled rubbers during the compounding is a key advantage adopted to improvement of the compatibility and adhesion between the rubber wastes and other ingredients, i.e., polymers, additives, monomers, and initiators basically used in this process. The compatibilizers can initiate the chemical reactions taking place during the extrusion <sup>40</sup>. Thus, reactive extrusion appears as an essential part of compounding processes, which affects the future of rubber recycling.

In the light of the above introduction, dealing with rubber recycling technology seems indispensable, while sustainability concerns and related instructions are simultaneously receiving





more attention because of regional and global policies of governments and related organizations. The latest attempts and technological advancements are taking advantage of green approaches, particularly reactive extrusion, to provide the user with an opportunity to make good use of possible reaction between the waste rubber and other ingredients, preferably green additives and polymers, to gain a reinforced rubber with value-added worth <sup>41, 42</sup>. First, we stated common composition of waste rubber compounds, mainly ground tire rubber (GTR)-based wastes resulting from waste tire grinding technologies. Second, technologies used in grinding of waste tire are summarized and classified. Third, devulcanization and compatibilization strategies used in rubber recycling are summarized and discussed based on the available reports <sup>43, 44</sup>. Fourth, reactive extrusion process and machinery are defined and their different parts and roles as well as the related functions in the processing machines are explained. In this regard, different processes comprising batch and continuous processes are reviewed, followed by summarizing their applications and progress in use of single-, twin-, and planetary-screw extruders. Fifth, we briefly reviewed green additives used in rubber recycling. Sixth, the main outcomes of studies and challenging aspects ahead of future developments in green rubber recycling techniques are discussed and some recommendations are made.

### **Waste tires composition**

Various components have already been employed in tire manufacturing, each responsible for a distinct or complementary action in processing and formulation of rubber compounds. Indeed, recycled rubbers have to be considered from the angle of composition, for it affects the economy and the efficiency of rubber recycling. Tires are mainly composed of a flexible rubber reinforced with metal and fibers. Typically, tires are composed of natural rubber (NR), a synthetic rubber as property complement to the NR, oil as processing aid, vulcanization system (mainly sulfur) for making the rubber network cross-linked, and steel cords together with filler (mainly carbon black) and fibers. Depending on the application, the composition of tires can be changed, as depicted in **Table 2** <sup>45</sup>. Accordingly, the composition of passenger/light truck tire is considerably different from that of heavy truck, each targeted at a desired function. Therefore, in addition to the need for flexibility in shredding and separation strategy, the role of processing method and formulation ingredients should be critically taken into consideration in recycling of rubber. For instance,



treatment of passenger/light truck for blending with a thermoplastic should be different from heavy truck tire, considering its 15% lower NR content, 9% lower steel, but its two-fold more synthetic rubber proportion. Although the compositions of the natural and synthetic rubbers are cumulatively almost identical ( $\approx 43\%$ ) in both formulations, from the processing point of view it appears that higher composition of synthetic rubber in the case of passenger/light truck tire should make the tire more easily recyclable. Moreover, it has been proved that selecting accelerators from zinc salts family, like thiocarbamates and dialkyl dithiophosphates, can facilitate de-crosslinking or scission of the vulcanized rubber networks<sup>46</sup>. More recently, researchers report that enzymes and bacterial strains can facilitate the degradation of polyisoprene, which is the major part of NR<sup>47</sup>.

**Table 2.** Comparison between composition of two kinds of tires, light and heavy truck tires, in a short view<sup>45</sup>.

Type of tire	NR	Synthetic Rubber	Filler	Antioxidant, antiozonant, and curing system	Steel	Textile
Passenger/ Light truck	19%	24%	26%	14%	12%	4%
Heavy truck	34%	10%	24%	10%	21%	0%

### Waste tires grinding technologies

The particle size, particle size distribution, and the chemistry of the surface of GTR are determined by the grinding or pulverization technology. In a classical or conventional grinding line, three streams are distinguished in order to collect GTR, steel cord, and textile cord. GTR, also named alternatively/interchangeably waste tire rubber (WTR) or waste tire dust (WTD) by the researchers and technologists, has been conventionally ground *via* ambient and cryogenic grinding methods. In ambient grinding method, rubber wastes experience milling at ambient temperature, but the intensity of shear is that high that may raise the temperature of compound up to 120-130 °C, which is the case of a major fire risk. On the other hand, crushing and grinding rubber wastes cryogenically at low temperatures is significantly facilitated because of the fragile character of rubber when they are cooled down well below their glass transition temperature ( $T_g$ )<sup>48</sup>. In terms of properties, however, the smoother and lower surface area of the cryogenically ground GTR is responsible for lower physical and mechanical properties compared to ambient grinding products,



as the higher surface area will possibly result in better compatibility in reactive extrusion or other recycling process <sup>49</sup>.

In a recent study, Hoyer et al. <sup>50</sup> elaborated grinding of rubber wastes by using different sorts of wastes possessing identical particle sizes to compare cryogenic pulverization with different ambient grinding technologies (**Table 3**). Diversity in the values of average energy consumed in processing could be ascribed to the difference between pulverization methods. Moreover, the role of composition of waste rubber, discussed in the former section, should be taken into consideration. Overall, cryogenic grinding enjoys from being greener and also an obviously higher throughput compared to the other pulverization techniques. However, energy consumption in this method is also significant. Therefore, decision-making for choosing pulverization method depends on both the economy and safety requirements.

**Table 3.** Comparison between cryogenic pulverization of waste rubber and some other ambient grinding results <sup>50</sup>.

Pulverization (►) Parameters (▼)	Cryogenic	Solid state shear extrusion	Mill cracking	Wet grinding		Hyperboloidal mill cutting
				Truck tire	Car tire	
Waste tire source	Truck tire	Truck tire	Car tire	Truck tire	Car tire	Truck tire
Average energy demand (kW)	138	165	200	32	32	1.2
Particle size (µm)	≈400	≈400	≈400	≈400	≈400	≈400
Throughput (kg/h)	588	53	160	61	51	1.2
Energy consumption (W/h.kg)	1207	3132	1250	525	630	967

There are some other waste rubber grinding methods occasionally employed besides ambient and cryogenic conventional grinding technologies, among which are solution grinding, ozone cracking grinding, and elastic deformation grinding. These techniques are practiced to possibly make the size of particles smaller in order to enlarge that surface area provided for further processing, e.g., blending the resulting GTR particles/powders with thermoplastics or re-vulcanization. In wet or solution grinding, rubber waste is swelled in a solvent or a fatty acid followed by meshing and then positioning in the conventional lines for pulverization. By the alliance of solvents with conventional ambient or cryogenic grinding, it is possible to gain particles smaller in size <sup>51</sup>. In ozone cracking method, rubber is first exposed to high concentration of ozone to make particles smaller in size, followed by mechanical pulverization. Unfortunately, ozone cracking deteriorates the reactivity of the surface as a consequence of the oxidation of ozone during pulverization. On



the other hand, this process takes the advantage of being green. The facilitated scission of cross-links in this process provides support for cracking of polymer chains leading to an eased thermal degradation of GTR/polymer systems <sup>52</sup>. Elastic deformation grinding is also based on blends of GTR and thermoplastics under high pressure and shear force in a Banbury, followed by grinding in a single- or twin-screw extruder. Making good use of cooling and applying low temperatures rather than high temperatures for thermoplastic melting and the possibility of combining with other grinding techniques are advantageous features of elastic deformation grinding <sup>53</sup>.

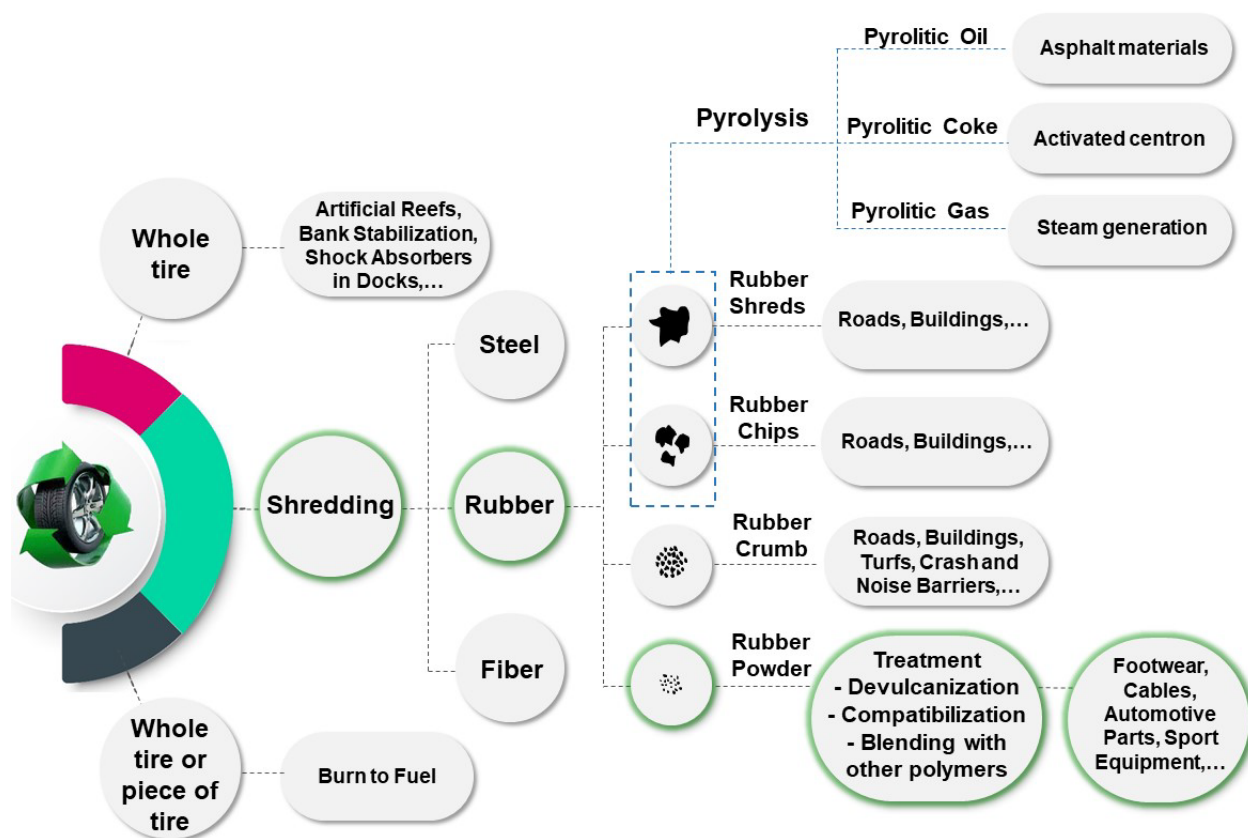
Recent trends in technological advances elucidated that attention has been centered to the use of novel methodologies, among which we can name the ultrasound <sup>54</sup>, water-jet assisted <sup>55</sup>, and superficial carbon dioxide aided pulverization <sup>56</sup> as the most frequently applied ones. Such advancements highlight the paradigm shift in using greener techniques for rubber recycling, which are noticeable aspects of modern processing methods in two ways. First, the use of multi-stage pulverization methods is nowadays more common rather than single-stage methods with lower efficiency. In line with such a school of thought on this subject, several attempts have been made to treatment and functionalization of the resulting pulverized GTR materials to gain value-added products. Second, at the present time, green processing is of prime priority, such that lower consumption of fossil-based energy, sustainability, and circular economy are centered to the technological waste management techniques. These altogether enlighten future commercialization of more sustainable products through reactive recycling technologies.

### **Fundamentals of GTR recycling**

As **Fig. 4** summarizes, conversion of tires to secondary rubber-based products takes various steps from shredding to industrial applications. In step one, tires are crushed into smaller parts with the aid of blades, followed by treatment using mechanical mills under a humid environment and ambient temperature to make rubber particles smaller in size, as explained in previous section on grinding or pulverization technologies. In step two, fibers and steels are separated to have rubbers distinguished. In the third step, the resulting rubber waste is screened and grouped based on its size into shreds, chips, crumbs, and powder. The form of waste rubber obtained determines the way of its further use. The reuse of larger sized waste rubber particles in civil engineering solutions



such as dam construction and soil stabilization, or improvement of asphalt properties are appeared very promising <sup>57</sup>.



**Fig 4. The cycle of rubber recycling in terms of steps and industrial applications of GTR.** Recycling path marked in green shows the most preferred way of managing rubber waste. Accordingly, secondary waste rubber-based products with higher properties compared to pristine GTR can be obtained. (Designed by the authors of the present work)

There has also been a growing interest in treating the used tires by pyrolysis technology to generate oil, coke and gas products. Tire pyrolysis oil is a mixture of aliphatic, aromatic and polar fractions. The gases produced from the pyrolysis of the used tires are H<sub>2</sub>, C1-C4 hydrocarbons, CO<sub>2</sub>, CO and H<sub>2</sub>S. The conversion of waste tire pyrolysis into high value products has focused on the transformation of carbon into higher quality activated carbon and to a lesser extent carbon black. The importance of catalyzed pyrolysis for the production of grey H<sub>2</sub> from waste tires should also be noted <sup>58-60</sup>. The resulting rubber powder undergoes the production of secondary products by incorporation into a polymer matrix. The GTR treatment strategy, called devulcanization, is

recommended for this purpose. It should be highlighted that materials and rubber recycling cycle altogether determine the physico-chemical properties and the quality of treated GTR. In this regard, the origin/formulation of the GTR, milling technology, particle size, the presence of additives (even trace amounts of fibers), and more critically the treatment method (devulcanization technology, compatibilization, etc.) affect the performance of final product.

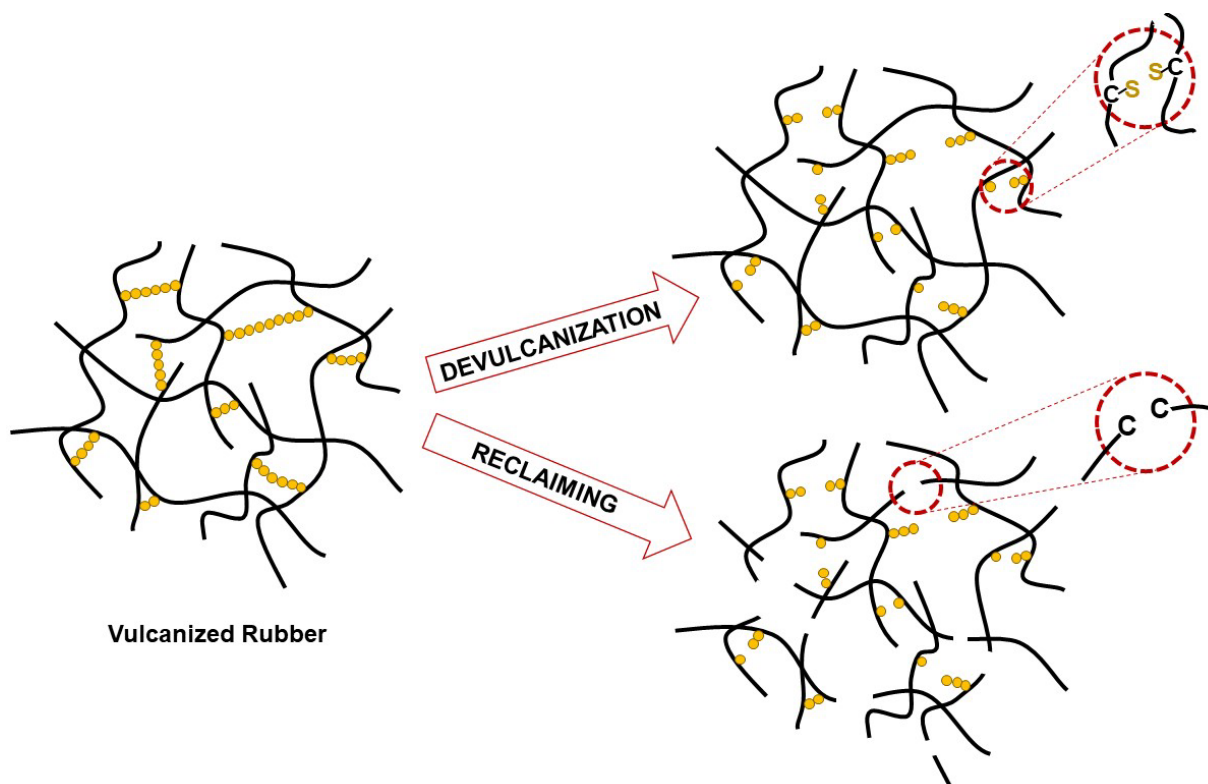
### *GTR devulcanization*

The most common ways of GTR recycling are grounded on blending GTR with bitumen, polymers or concretes. Typically, poor mechanical properties are the consequence of phase separation, since the cross-linked GTR suffers from inadequate interfacial adhesion when processed with other components. Such a lack of compatibility considerably confines the GTR to processing. Since GTR itself suffers from poor chemical reactivity, modification of GTR is necessary. The most cost-effective and environmentally-friendly way to recycling of tires is to convert rubber wastes into devulcanized GTR through a devulcanization or reclaiming process, which is possible through physical, chemical, or physicochemical methods. Devulcanization and reclaiming are two possible methods enabling breakage of sulfur bonds. They are best known as the most widely used chemical and physical techniques for GTR modification, respectively. These methods enable rubber chain scission in a 3D network already formed through vulcanization by sulphur, peroxide or other cross-linking agents. It is disappointing that some researchers mistakenly used devulcanization and reclaiming interchangeably. Reclaiming means random scission of the polymer chains, while devulcanization means selective scission of the covalent cross-links, which are physically and chemically, respectively.

Taking the physical reclaiming process as a reference with moderate efficiency of rubber chain scission, one would be able to break down cross-linked GTR networks through the scission of C-S and S-S bonds. However, chemical devulcanization can additionally enable one to break down C-C bonds through a more aggressive destruction way, which ends in having chains with much lower molecular weights compared to ones reclaiming could afford. Basically, cross-linking (vulcanization) process in any elastomer compound consists of generation of S-S bridges with which the macromolecular chains connect together, which induces the elastic behavior. The devulcanization process is referred to breakage of the S-S bonds solely in an elastomeric material. On the other hand, as illustrated and compared in **Fig. 5**, reclaiming affects all the bonds that make



up the elastomer, i.e., both C-C in the main chain and S-S as interchain bonds. Thus, reclaiming suffers from much lower possibility of selective/controlled debonding in a recycling process. Once the elastomer is devulcanized (depending on the devulcanization process used and the effects of curing additives), instaurations are generated in the main chain, which allow the subsequent revulcanization of the elastomer. It is also known that the revulcanization process will never be complete <sup>61-63</sup>.



**Fig. 5. Overview of devulcanization of GTR as a chemical treatment in comparison with reclaiming process of GTR.** Reclaiming is considered as the most known physical (or here a reference process here for comparison) to explain possibility of chain (C-C) and crosslink (S-S) scission of bonds. *(Designed by the authors of the present work)*

Physical reclaiming the rubber chains are broken as a result of applying an external force. Physical treatment includes processes such as mechanical, ultrasonic and microwave, crumbles 3D network and cross-connections to form products with a low-molecular weight. The use of microwave seems to be the best option due to the very short time of this method (5-7 min), its green nature because of its solvent-free mode, the ability to accurately control the energy applied, as well as improving



the matrix-GTR compatibility. On the other hand, some problems such as hot spots and emission of the volatile degradation products into the atmosphere are among its disadvantages <sup>64</sup>. The cost of the reactor is also considerable, as a serious challenge of this technology.

Thermo-mechanical treatment is another physical treatment process, which makes use of devices such as mill, milling and/or twin-screw extruder to apply mechanical stress on rubber particles <sup>65</sup>. However, temperature rise up to 200°C makes this process highly flammable and energetically less profitable. A number of solvents such as hexane and supercritical liquids or oils are served to accelerate heat transfer and swelling of rubber particles. Accordingly, an internal stress accumulation and consequently breakdown of cross-links are possible. This process can be implemented in both batch or continuous processes, but when using an extruder it becomes more industrial and economic, such that the process condition can be controlled by optimization of the screw speed and temperature <sup>32</sup>.

Another method of recycling of vulcanized rubber wastes through physical treatment is the ultrasonic treatment. This method leads to production of a considerable amount of sols through softening of crosslinked rubber domains, which is grounded on the basis of bubbles resulting from combination of mechanical waves and shaking to reduce the size of particle *via* cross-joints' density reduction. Such a process can be performed under continuous (with flow) or static (no flow) conditions <sup>66</sup>. It is common that the ultrasonic treatment is combined with reactive extrusion to make the process continuous and efficient.

Chemical devulcanization makes use of chemical agents for breakdown of cross-links. Unlike physical treatments, chemical treatment is often performed at high temperatures, where solvents such as alcohols and supercritical liquids provide the reaction medium and mixing is comprehended by a kneader. Since molecular structure is completely collapsed by chemical treatment of GTR, mechanical properties are significantly decreased. Finally, it should be noted that physical and chemical treatments are very costly and polluting. Due to the proximity of the failure energy of the cross-joints that triggers the main chains, the chain breakdown consumes a great deal of energy. Therefore, attention was turned to the use of microorganisms capable of desulfurizing rubber network by controlling factors such as pH and temperature <sup>67</sup>.

It is experimentally hard to quantify the contribution of the breakage of all types of bonds (C-C, C-S, and S-S) in a rubber network. In other words, selective breakage or scission of S-S or C-S bonds without main chain scission (C-C bonds breakage) is near-to-impossible. Horikx' analysis



is a commonly accepted method to establish a mathematical relationship between the sol fraction and the degree of devulcanization. It can rather successfully indicate whether or not the main phenomenon during devulcanization is random scission of the polymer chains (reclaiming) or selective scission of the covalent cross-links (devulcanization). Practically, however, selective scission of sulphur (S-S) or main chain (C-C) bonds in a crosslinked (vulcanized) rubber network is far from perfect. It is well-accepted that the devulcanization of crosslinked rubber leads to heterogeneous products, which are a mixer of partially devulcanized rubber and degraded rubber fractions. Accordingly, experimental points lie in between two theoretical curves of Horikx, where the main chain scission (C-C bond scission) and crosslink scission (S-S bond scission) are upper and lower limits of theoretical curves of soluble fraction of rubber, respectively <sup>68</sup>. For instance, Simon et al. applied Horikx's analysis on thermomechanically devulcanized GTR as a reference and mixtures containing vulcanizing agents and different amounts of paraffin oil as well as NR-based mixture with different amounts of devulcanized GTR, where a moderate chain scission was estimated by Horikx' analysis <sup>69</sup>.

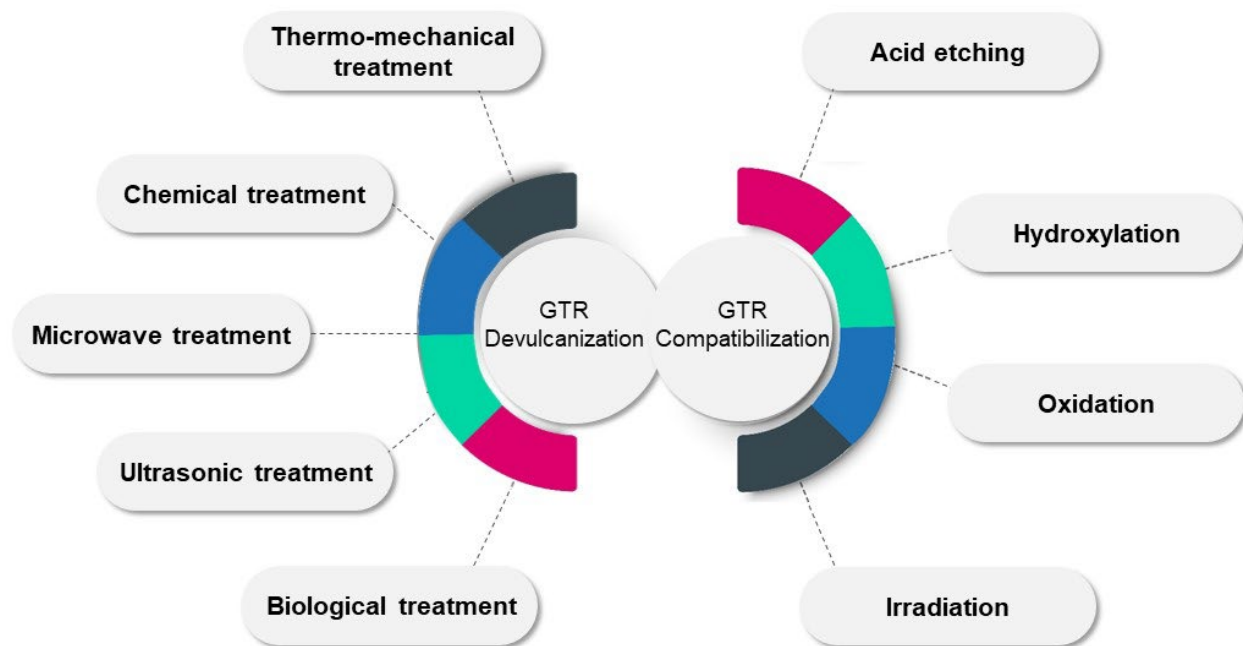
There are several single- and multi-stage GTR treatment methods to be underlined. Among different strategies used for GTR devulcanization is thermomechanical treatments. Formela et al. have studied different thermomechanical processes to reclaim GTR by means of a twin-screw extruder <sup>70</sup>. They considered the effects of machine variables on the efficiency of reclaiming varying the speed of screw, plasticizing zone design optimization and the role of rotation direction (used both co-rotating and counter-rotating configurations). They also re-vulcanized the obtained products with styrene-butadiene rubber (SBR) varying the time and temperature of blending, and concluded that reclaiming intensively affects ultimate properties of recycled compound. Later, they have reclaimed GTR at ambient temperature mechano-chemically, in order to reduce the energy costs, using a two-roll mill <sup>71</sup> or by means of a mechano-chemical method using road bitumen 160/220, which was used as reactive plasticizer, combined with microwave radiation <sup>72</sup>, <sup>73</sup>. A wide range of bitumen (2.5–20 phr) used from road bitumen and styrene-butadiene-styrene (SBS)-modified bitumen enabled evaluation of the role of bitumen. The enhancement of processing and ultimate properties was the result of combination of mechanical and thermal reclaiming processes occurring simultaneously, which accelerated C-C chain scission, as per gel fraction measurements. Several more methods have been proposed in order to reclaim/devulcanize

GTR and other industrial elastomers, which are occasionally reported. A combination of thermomechanical and microwave treatments<sup>74,75</sup>, thermomechanical methods with the aid of dual function disulfide chemicals<sup>76</sup>, thermomechanical treatment utilizing silane-based tetrasulfides as devulcanizing agents<sup>77,78</sup>, ultrasound processes<sup>79,80</sup>, supercritical CO<sub>2</sub><sup>81</sup>, or microbial<sup>82,83</sup> or chemolithotrophic bacteria<sup>84</sup>. However, sustainability concerns should pinpoint exactly which technique would be reliable.

### *GTR compatibilization*

A highly recommended rubber recycling method encourages the use of GTR as sustainable low-cost filler/modifier in various composites. This direction is preferred due to the large share of polymers, especially thermoplastics and thermoplastic elastomers (TPEs) in the global market. Therefore, even the use of small proportion of rubber waste ( $\approx 10$  wt.%) could considerably reduce its accumulation in the environment. Additionally, polymers can act as a binder for the GTR particles. However, due to the non-reactive surface, GTR is incompatible with most polymer matrices, which consequently leads to deterioration of the properties and performance of the resulting products. As a result, it requires pre-modification of the rubber powder to improve interfacial bonding at the rubber-matrix interface<sup>85</sup>. As discussed above, devulcanization is essential to promote interfacial adhesion between GTR and other components. However, it may not be sufficient in the case of advanced materials with multi-functional missions. Therefore, recently various modification strategies promoting the compatibility of rubber waste with other polymers combined with suitable reclaiming/devulcanization have been in the core of attention. Although much emphasis has been placed on chemical etching methods (e.g., irradiation, acid etching, and oxidation), other modifications like *in situ* grafting are also considered. Nevertheless, the use of chemical compatibilization is the best way and it is believed to be able to pave the way for more industrial applications of GTR<sup>86</sup>. **Fig. 6** presents technologies available for improving interfacial adhesion of GTR with other polymers and additives by devulcanization and/or compatibilization.





**Fig. 6. Different technologies used in GTR properties enhancement through interfacial interaction modification.** Sometimes GTR devulcanization and functionalization of devulcanized GTR are interchangeably used, which should be noticed. (*Designed by the authors of the present work*)

In a recent study, GTR was added at loadings up to 75 wt.% to various kinds of thermoplastics<sup>87</sup>. The influence of interfacial interactions on processing and physico-mechanical properties of materials was analyzed. It was found that linear polymers show the lowest affinity to GTR, but better fluidity of the blends. Nevertheless, regardless of the thermoplastic type, the resulting materials suffered from poor compatibility, highlighting the need for compatibilizers. Therefore, **Table 4** broadly summarizes the main compatibilization strategies of GTR when blending with thermoplastic, and thermoset polymers, as well as, elastomers. All presented works confirmed an improved interfacial adhesion between the recycled rubber and other polymers, which resulted in an enhancement in other physico-mechanical properties<sup>88,89</sup>.

Incorporation of GTR into thermoplastics and TPEs is receiving much attention compared to the thermoset polymers. Incorporating GTR into thermoplastics is particularly worthwhile when waste materials (e.g., agricultural films and discarded shipping boxes) are used as the matrix, but even then, new markets should open up. On the other hand, with thermosets, GTR can be used to improve some properties, but researchers are still working to optimize such strategies, mainly through improving the mechanical strength<sup>90</sup>. The research and development sectors propose



combination of thermosets with GTR, such that the role of thermoset (especially polyurethane) as a GTR particle binder has been discussed for civil engineering applications. A new trend can also be seen in GTR recycling, such that the focus is on properties other than mechanical properties<sup>91</sup>. In this context, the acoustic and vibration damping applications can be named. Rubbers and rubber-like materials with a highly heterogeneous cross-linked structure are known to be excellent absorbers. GTR particles are predestined to create such structures in different matrices.

**Table 4.** A comprehensive overview of the effects of compatibilization method on the main properties of GTR blends/composites from application standpoint.

Polymer family ▼	Matrix	GTR particle size and source	Mixing Technique	Compatibilization method	Main Achievements	Refs.
Thermoplastics	LDPE	Passenger and light truck tires ~250 µm	Batch mixer/ Compression molding	Co-milling of GTR and LDPE in a pan-mill	Co-milling of LDPE and GTR improved the interfacial adhesion between these components and consequently the mechanical properties of the foam produced.	92
	LDPE LDPE/EVA	Automobile tires 250-500 µm (ambient)	Twin-screw extruder/Injection molding	Electron beam irradiation	Tensile properties improved by increasing irradiation dose.	93
	rLDPE/LDPE	Tire rubber 250-500 µm (ambient)	Twin-screw extruder/Injection molding	Electron beam irradiation	Tensile properties increased by the radiation. EVA improved the ductility.	94
	EVA	Tire rubber	Batch mixer/ Compression molding	Silane agent/Electron beam irradiation	Both treatments method increased mechanical strength, but reduced the ductility.	95
	HDPE	Tire rubber 400–600 µm	Two-roll mill/ Compression molding	Acid etching	The tensile strength of GTR increased with H <sub>2</sub> SO <sub>4</sub> treatment contrary to HNO <sub>3</sub> and HClO <sub>4</sub> .	96
	PP	Rubber 3–5 mm	Batch mixer/ Compression molding	Acid etching	Compressive yield strength of the H <sub>2</sub> SO <sub>4</sub> -treated GTR composites was superior to untreated	97

					ones for the similar GTR content.	
	LLDPE	Tire rubber 400 $\mu\text{m}$	Twin-screw extruder/ Compression molding	Grafting with maleic anhydride (MAH),	The tensile properties increased significantly.	98
	HDPE	Car and truck tires 400–500 $\mu\text{m}$	Batch mixer/ Injection molding	Incorporation of DCP (through blending or by immersing the GTR in cyclohexane/DCP solution)	The optimum DCP content for GTR modification was 2 wt%. Elongation at break and impact energy increased. The lower and higher DCP contents gave partially cured and over-cured composites, respectively. Immersing the GTR in cyclohexane/DCP solution enhance properties more considerably compared to easy incorporation.	99
	HDPE	Car and truck tires 400–500 $\mu\text{m}$	Twin-screw extruder/ Injection molding	Gamma irradiation	Compatibilization by gamma irradiation increased elongation at break and impact energy.	99
<b>Thermoplastic Elastomers (TPEs)/ Elastomers</b>	rLDPE/EPDM rHDPE/EPDM	Tire rubber 400-700 $\mu\text{m}$	Batch mixer/ Compression molding	Chemical or $\gamma$ -induced grafting with MAH, acrylamide (AAm), and DCP	Used of grafted GTR strongly improved the tensile strength and elongation at break of the resulting compositions, regardless of the grafting technique.	100
	EPDM/HDPE	Tire rubber 150 $\mu\text{m}$	Two-roll mill/ Compression molding	Gamma irradiation	Tensile strength went through a maximum in function of irradiation dose (150 kGy). Modulus, hardness monotonously increased, elongation at break monotonously decreased with increasing irradiation dose.	101
	EPDM/HDPE	Tire rubber 150 $\mu\text{m}$	Batch mixer/ Compression molding	Gamma/UV irradiation	Tensile strength went through a maximum in function of gamma irradiation dose (150 kGy). Modulus,	102

					hardness monotonously increased, elongation at break monotonously decreased with increasing $\gamma$ -irradiation. Slight improvement in tensile strength and modulus after UV-irradiation.	
	rHDPE/SBS	Passenger car and truck tires 800 $\mu\text{m}$ (ambient)	Two-roll mill/ Batch mixer /Compression molding	Incorporation of peroxides	Increased cross-link density, tensile strength, and thermal stability of composites. The highest improvement was observed for DCP.	103
	SBR	Tire rubber 180 $\mu\text{m}$	Two-roll mill/ Batch mixer/Compression molding	Gamma radiation	The tensile properties increased with an increase in radiation dosage.	104
	NBR	Passenger car and truck tires 800 $\mu\text{m}$ (ambient)	Two-roll mill/Compression molding	Curing system	Incorporation of peroxides improved mechanical properties of the studied materials compared to sulfur-based systems, although they provide more efficient cross-linking.	105
<b>Thermosets</b>	Epoxy resin	Tire rubber 120 $\mu\text{m}$	Batch mixer/Compression molding	Grafting with hyperbranched poly(amidoamine)	The grafted GTR was foreseen for both curing (demonstrated) and toughening (not shown) roles.	106
	Polyester resin	Rubber 0.85–1.70 mm (cryogenic)	Compression molding	Hydroxylation/oxidation	The treatment with NaOH improved the tensile strength of the composite, but $\text{H}_2\text{SO}_4$ and $\text{KMnO}_4$ treatments led to the reduction of this parameter.	107
	Epoxy resin	Tire rubber 0.35–0.50 mm (cryogenic)	Compression molding	Plasma methods	Slight improvement in the fracture toughness due to the compatibilization.	108
	Epoxy resin	Tire rubber 180 $\mu\text{m}$ (cryogenic)	Batch mixer/Compression molding	Silane coupling agents	GTR treated with some of the studied silane coupling agents increased the tensile strength of	109

					composites, but slight reduction in toughness was observed.	
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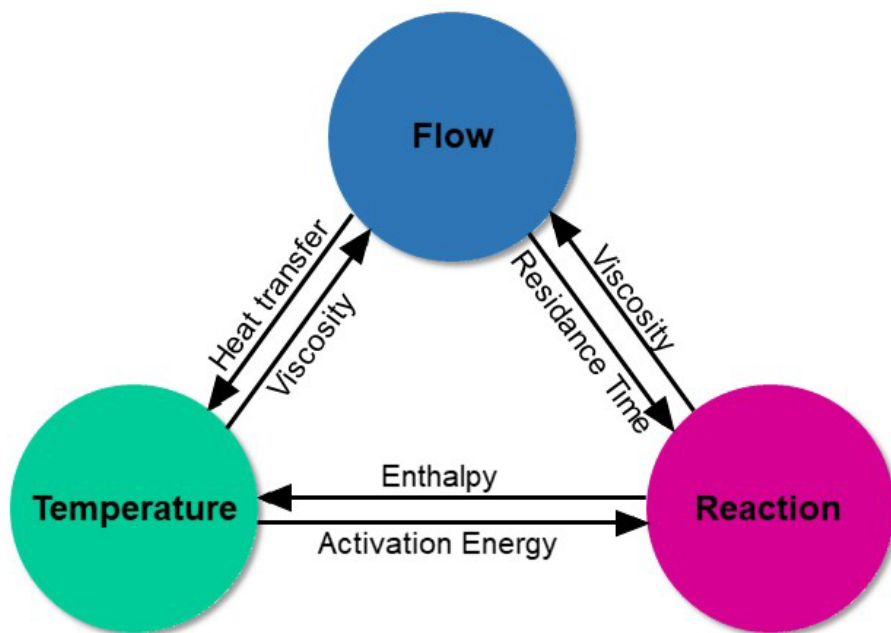
In order to improve the quality of the devulcanized rubber and to obtain properties similar to those of the original rubber, several proposals have been published in recent years. These methods make use of different types of additives in both thermochemical and mechanical-chemical processes <sup>63, 77, 110, 111</sup>. In view of sustainability, attention should be paid to utilize greener devulcanization and compatibilization methods by the aid of advanced reactive extrusion processes preserving mechanical properties of thermoplastics/GTR blends <sup>112</sup>. In this regard, assessment of Volatile Organic Compounds (VOC) emission has been taken into account most recently by the researchers <sup>113, 114</sup>. Application of reactive extrusion makes it possible to tailor-make GTR-based blends with thermoplastics and TPE applying various additives, antioxidants and other functional monomers as well as varying extrusion parameters such as screw speed and temperature profile. Partial reclaiming or devulcanization of GTR is also possible during reactive extrusion, which enables one to consider this technique as a tool for interfacial adhesion manipulation of the compound.

## Green rubber recycling technologies

### *Reactive extrusion: General features*

Development of novel polymers with tailored microstructure and properties would necessitate development of polymerization plants, which itself may take several years from the scratch to commercialization of products. In addition, undesirable side reactions inevitably taking place in the reactor in parallel with the main polymerization reaction lowers the rate of production. Another concern would be the lack of green ingredients in production chain. To rely on the need for high-performance materials, developers suggest advanced processing methods, particularly reactive extrusion. Reactive extrusion is a fast, solvent-free (almost green), cost-effective pro-ecologic alternative for ‘conventional’ polymer processing methods. It is a continuous process in which polymerization, chemical bonding, and physical changes are all performed simultaneously during

a processing time shorter than that of a batch process <sup>115</sup>. This technique may be utilized for modification, compatibilization, *in situ* grafting or blending as well. Facilitated heat and mass transfer during the extrusion are also accompanied by using this processing method. Materials having a wide range of viscosities from monomers to polymers can be processed by well mixing of ingredients. In general, the production efficiency with this machine is controlled by several factors such as the feeding rate, screw speed, temperature, and screw configuration <sup>116</sup>. **Fig. 7** shows reactive extrusion in terms of processing and phenomena involved. Reactive extrusion has been widely used in recent years for modification and functionalization of natural fillers and fibers, as well as production of composites, particularly composed of waste materials. Particularly, it can be easily adapted to industrial applications, making the process less complex, more efficient, and economically reasonable.



**Fig. 7. Reactive extrusion setup, operation, and parameters in a brief view.** In general, thermal changes in the system together with ingredients and design of machinery determine the quality of the resulting products. (*Designed by the authors of the present work*)

Reactive extrusion is a flexible process that includes several parts, each of which pursues a specific function. Different types of polymers can be processed by reactive extrusion filled with different kinds of additives varying the loading level under a controlled processing <sup>117, 118</sup>. A reactive extrusion setup starts with a feeding zone providing the screw with ingredients needed for reactive compounding. The efficiency of the process is not solely dependent on the speed of the screw, but



also on the feeding rate, which itself determines the production quality and speed. Unlike the common extruders, reactive extruders are multi-feeding, such that the main components are fed through the first feeder, while some other ingredients such as additives, initiators or cross-linkers can be incorporated subsequently into the system along the barrel; depending on the materials specifications and formulation <sup>118</sup>. For liquid feed stocks, a positive displacement or metering pump is used to achieve a proper flowability required for size reduction and preventing from composition drift <sup>118</sup>.

The energy required for chemical reactions and physical changes in reactive extrusion process is supplied by two sources, i.e. mechanical shear/stress and thermal energy provided by the heating elements <sup>25</sup>. The mechanical stress generated by the screw plays a key role in the quality of mixing, where two kinds of mixing including dispersive mixing (responsible for particle breakup) and distributive mixing (responsible for distribution of particles in the matrix) control the whole mixing process. The protocol/kind of mixing has a tremendous effect on the quality of the final product. Notably, the mechanical or shear stress transfer and distribution supplied by the screw prevent the thermal degradation of polymers <sup>118</sup>. Mechanical shear in counter-rotating twin-screw extruders provides the melt with more energy during the reactive processing, including the chemical reactions and melting. Moreover, there is an optimized screw length at which the highest possible conversion is achieved such that the bulk temperature reaches the maximum level. Thus, screw design and configuration (the rotation direction (co- or counter-rotating), the length of kneading section, the length of screw, and the diameter of screw) are keys for successful processing <sup>119</sup>. The existence of kneading zone, the speed of screw rotation and the power of the extruder motor all determine the mechanical force/shear applied to the polymer melt <sup>118</sup>. The humidity of the feedstock passing through the feeding screw also affects processing and the quality of the final product. Once the moisture inside the extruder evaporates, it generates excess gasses leading to blistering on the surface of extrudate, which can be minimized by degassing zones <sup>120</sup>.

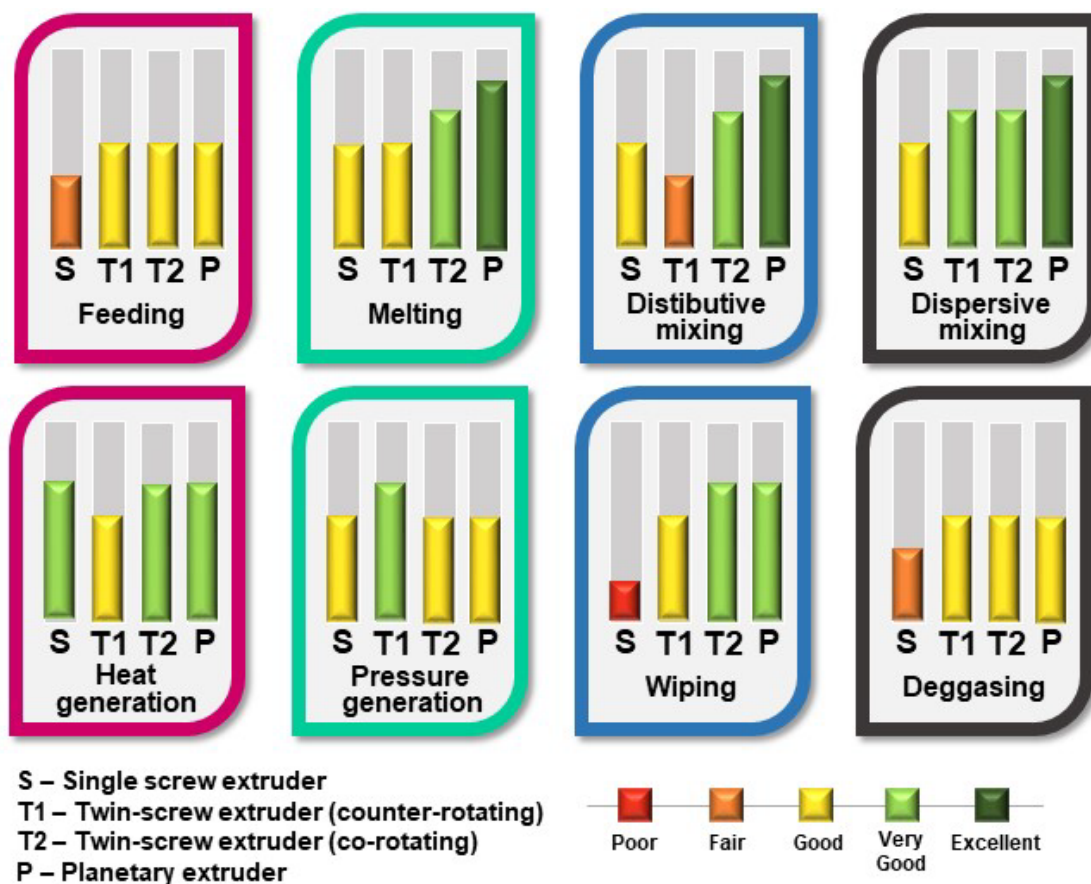
There are different machines for reactive extrusion, which are classified based on the type and the number of screws. Overall, the main difference between the extruders is based on the transport mechanism <sup>121</sup>. A single-screw extruder typically consists of an empty hollow cylinder, heaters and a screw that is the heart of the extruder <sup>122</sup>. In these extruders, the polymer is the raw material conveying through the cylinder and getting melted by screw reciprocal movement with the aid of thermal energy supplied by the heaters <sup>123</sup>. However, from twin-screw extruders, two main tasks

of supplying the mechanical shear and melt mixing are expected. Therefore, the screw design plays the key role in processing efficiency. Moreover, the presence of pins prevents the material from rotating within the screw channels and thereby improves the efficiency<sup>30</sup>. According to the process needs, the direction of screw rotation (co- or counter-rotating) and the configuration and the fitness of the screw (intermeshing and non-intermeshing) can be selectively prefixed<sup>124</sup>. For liquid monomers it is better to have the screw partially starving to gain a higher throughput efficiency<sup>125</sup>. Counter-rotating twin-screw extruders are less frequent for reactive extrusion mainly because of the inability to modularity, especially for high-viscosity melts or highly-loaded polymer compounds. Instead, they are frequently used for the synthesis of copolymers with different blocky nature, which enable shuffling of polymer segments<sup>126, 127</sup>. Unlike counter-rotating machines, melting in a co-rotating twin-screw extruder normally happens in the first kneading disc block, ending in highly efficient reactive blending<sup>128</sup>. More importantly, co-rotating machines are modular, which gives the user a wider processing window. Thus, direction of rotation plays a key role in reactive extrusion of polymer compounds.

In recent years, planetary-screw extruders consisting of several mesh areas and a central area have been introduced for the processing of polymers. This type of extruder has received a great deal of attention due to its high contact surface, high efficiency, modular design and precise control over the cooling and heating. Reactive planetary extruders has a high mixing, masticating and dispersing ability, with a contact surface five-ten times higher than the single- and twin-screw machines. They have also the ability to separately apply thermal or mechanical forces to the molten polymer. Economically, they are good alternatives to traditional polymer processing methods. Other unique features of this type of extruder include a wide operating window, high transfer speed and homogenization power, which brings good operational safety, as well as the ability to work with 10% capacity in a very wide processing temperature range<sup>129</sup>. All of the above, along with the possibility of custom production to design different sequences for selective chemical and physical reactions, have made this invention one of the best polymer processing machines. Although the performance of this device can be predicted with the help of mathematical simulations, the lack of experimental knowledge is strongly felt for its widespread use and further developments<sup>130</sup>.

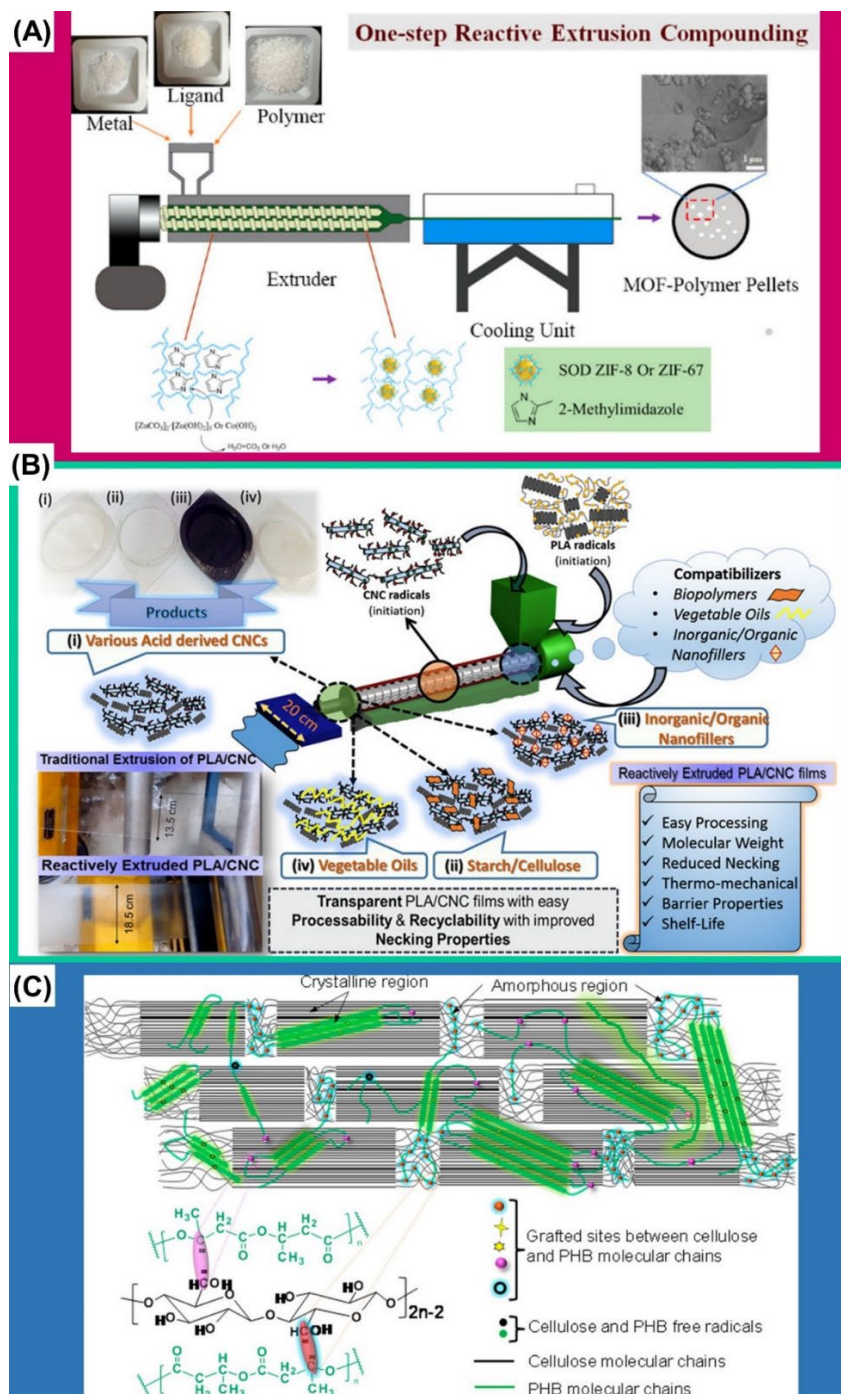
From a comparative viewpoint, twin-screw extruders offer higher melting, mixing and devolatilization potentials with respect to the single-screw machines, reason for their more

frequent use in reactive processing. It is also known that co-rotating intermeshing twin-screw extruders, working at much higher screw speed, can generate higher shear forces compared to the counter-rotating ones<sup>131</sup>. Planetary extruders, compared to single- and twin-screw configurations, show superior capability of blending and dispersing additives in polymers because of huge difference in flow field. This provides the compound with prolonged residence time required for intensive mixing and plasticizing<sup>132</sup>, regardless of the viscosity of compound and additive content<sup>133</sup>. From power consumption standpoint, however, planetary extruders consume an energy 1.5 times, on average, higher than the co-rotating twin-screw extruders despite their is 1.3 times higher productivity<sup>134</sup>. **Fig. 8** compares reactive extrusion efficiency for the aforementioned configurations in terms of eight key characteristics, including the feeding, melting, distributive mixing, dispersive mixing, heat and pressure generation capability, wiping and degassing.



**Fig. 8.** A qualitative comparison between the efficiency of single-, twin- and planetary extruders used in reactive processing of polymers. The performance of each extruder (processing machine) in each zone is simply visualized by the qualitative assessment. (Designed by the authors of the present work)

To sum up, according to the statistics, reactive extrusion has become a route for the chemical modification or functionalization of polymers, fillers, fibers and recycled polymers <sup>135</sup>. By changing the temperature along the zones of heating as well as the speed of screw and screw configuration, it is possible to change the residence time, the capacity of production, and the amount of shear force applied to the materials in a reactive processing for the optimized functionalization of polymers, polymer blends, and polymer composites. Such a wide processing and optimization window together with the green or solvent-free basis (no need for cleaning and environmental concerns) are reasons why reactive extrusion is in the core of attention nowadays <sup>136</sup>. **Fig. 9** illustrates possible polymer processing technologies with reactive extrusion emphasizing both chemistry and engineering aspects. In the case of rubber recycling, reactive extrusion revolutionized the modification of TPEs through improvement of filler-polymer interaction, e.g. foamed polyurethane rubber composites <sup>137</sup>. Therefore, reactive extrusion has allowed for tailoring the microstructure and properties by functionalization or in-situ modification of compounds <sup>138</sup>. Obviously, the wide application of reactive extrusion from research to industry put this technology on the popularity and maturity road.



**Fig. 9. Different approaches of using reactive extrusion with a focus on chemistry and engineering. (A)** Sustainable and efficient way of manufacturing metal-organic framework (MOF)-based polymer nanocomposites by reactive extrusion. As visualized, MOF was produced in a one-step process from solid components. It give hopes for industrial commercialization of MOFs, because of the environmentally-friendly (solvent-free) technology and high efficiency ( $1.2 \times 10^5 \text{ kg/m}^3/\text{day}$ )<sup>139</sup>. **(B)** Single-step industrially scalable reactive extrusion of polylactic acid (PLA)/cellulose nanocrystal (CNC)-based films for food packaging applications. The utilization of reactive extrusion leads to the improved processability, rheological behavior and reduced necking<sup>140</sup>, **(C)** Grafting of bacterial polyhydroxybutyrate (PHB) onto cellulose via *in situ* reactive extrusion with dicumyl peroxide. Figure shows chemical reactions between components, which occurs during reactive extrusion process<sup>141</sup>.

### *Reactive extrusion for GTR treatment*

Based on recent literature and patents <sup>142</sup>, both the present and future perspectives over GTR treatment are focused on reactive extrusion with thermoplastics. Accordingly, it is worth disseminating and developing this green and economically viable technology. GTR processing combined with reactive extrusion technology, which has a high ability to control, can primarily assist in improvement of properties towards optimal usage of rubber wastes, which seems to be beneficial both economically and environmentally. Reactive extrusion, contrary to other rubber recycling methods, allows for simultaneous reclaiming/devulcanization, compatibilization, as well as, blending with other polymers. Addition of cross-linking agents, additives, and other ingredients at any stage of reactive extrusion is also possible. Although highly loaded GTR compounds are characterized by the lack of flow, they are still able to be processed via reactive extrusion as the shear forces present in the barrel restore some plasticity to the vulcanized rubber. Besides, the modification of the GTR surface for making it chemically active also prevents agglomeration of GTR particles. Therefore, the longstanding thermal and mechanical stability of the resulting GTR-based compound depends on the interfacial adhesion achieved in the course of reactive processing. For example, Tao et al. in the comprehensive study <sup>143</sup> revealed that the temperature and screw speed highly affects the devulcanization degree of extruded GTR and its post-revulcanization properties. Fourier transform infrared spectroscopy and elemental analyzer studies showed that the chemical structure of GTR changed and many complex reactions occurred after devulcanization. In addition, they prepared a contour plot of gel content, cross-link density, tensile strength and elongation at break as a function of reactive extrusion parameters. The results indicated that GTR extrusion at 180°C with a screw speed of 100 rpm is the most optimal as it leads to the largest decrease in gel content (77%) and the highest value of tensile strength (12.9 MPa) and elongation at break (360%). Furthermore, some researchers reported about devulcanization reaction in GTR/TPE systems <sup>144</sup>. They declared that by increasing screw speed less gel content in GTR/TPE blend was observed, characteristic of network degradation. At 1000 rpm of screw rotation speed, the mechanical properties of dynamically vulcanized elastomers were significantly improved. In reactive extrusion, high intensive shear stress applied to extrudate was the case at 1000–3000 rpm, efficient for industrial applications.

Moreover, the inclusion of cross-linking agents has also been found to promote compatibility and improve the re-vulcanization efficiency in the systems. In our recent study <sup>113</sup> we performed



reactive extrusion of GTR enriched with 10 phr of ethylene-vinyl acetate copolymer (EVA, 18% vinyl acetate content). Although the devulcanization process occurred, the properties of resulting materials were relatively poor. However, more recently <sup>145</sup>, we prepared similar composition, but GTR was pre-mixed with 2.5 phr dicumyl peroxide (DCP) prior to extrusion. Extracting some data from both works, it can be seen that cross-link density of premixed GTR after re-vulcanization was higher, and thus the tensile strength (8.3 MPa compared to 3.2 MPa) and elongation at break (174% compared to 146-151%). It can therefore be concluded that by selecting the appropriate cross-linking agent and manipulating the reactive processing parameters, it is possible to obtain products of higher quality without using an additional compatibilization technique. Similar findings were provided by Kościuszko et al. <sup>146</sup> who compared GTR/polypropylene (PP) systems with and without 1.5 wt.% 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane. Except for the enhancement of mechanical properties, a significant improvement in the volume-flow rate (MVR) as a measure of processability was observed after the addition of the peroxide.

It should be noted that reactive extrusion of GTR modified by small amounts of thermoplastics seems to be a promising trend in rubber recycling. Thermoplastics not only increase the processability and tensile properties of GTR-based compounds, but also was found to reduce the amount of volatile organic compounds emitted from the surface of devulcanized rubbers. Interestingly, the presence of thermoplastics facilitates the self-heating phenomenon of GTR, limiting the energy consumption for heating the barrels <sup>113</sup>.

Despite the aforementioned reports, still data on treatment and modification of GTR using reactive extrusion are limited, which makes it impossible to draw a conclusion over the effect of materials and processing parameters on the efficiency of reactive extrusion.

### **Green additives in rubber recycling**

There are some newly born terms in polymer science and technology, which highlight the importance of developing greener materials rather than synthetically abundant polymers. In this regard, *green polymer blends*, *green polymer composites*, and *green polymer nanocomposites* can be named, which are receiving more attention by the academia and industry alike. On the other hand, the terms *biodegradable polymer blends* and *biodegradable polymer composites* are representative of polymer materials aimed at biomedical applications <sup>147</sup>. In the case of green composites, the idea which comes to mind is that both the matrix and filler should be green.



Although this looks environmentally brilliant, serious challenges are associated with strengthening the mechanical properties because of poor interfacial adhesion in fully green compounds <sup>148</sup>. In other word, having a fully green polymer composite with acceptable properties still seems far from access, but some steps have been taken until now. **Table 5** summarizes mostly used green plasticizers, activators, reinforcing additives/processing aids, and curing agents used in development of sustainable recycled elastomers and elastomer composites. According to the table, there are some promising examples which imposed positive effects on properties, but still a long way should be paved towards development of fully green and sustainable elastomers.

**Table 5.** Some green ingredients used in development of sustainable elastomers and elastomer composites with their content in the compound and main effects.

Kind of additive	Examples	Amount	Main Effect	Refs.
Plasticizer	Waste soybean oil	20 -150 phr	<ul style="list-style-type: none"> <li>- an increase in the sol fraction resulting from higher degradation level</li> <li>- an increase in the intensity of C=O peak (based on FTIR analysis), indicating the enhancement in controlled oxidation efficiency</li> <li>- improvement of tensile strength and elongation at break in SSBR blends due to better dispersion</li> </ul>	149
Plasticizer	Waste engine oil	25-45 wt.%	<ul style="list-style-type: none"> <li>- an increase in the sol fraction resulting from higher degradation level</li> <li>- improvement of rheological properties and storage stability of modified asphalt</li> </ul>	150
Plasticizer	Waste oil	20-40 phr	<ul style="list-style-type: none"> <li>- improvement of interfacial adhesion</li> <li>- an increase in compressive and tensile strength, as well as, elongation at break of GTR/PU composite foams</li> <li>- a decrease in average cell size and increase in closed cells content in foams</li> </ul>	65
Activator/antioxidant	Bahera gum	1-10 phr	<ul style="list-style-type: none"> <li>- similar activating and antioxidating effect to commonly used additives</li> <li>- improvement of tack strength</li> </ul>	151
Reinforcing filler /processing aid	Microcrystalline cellulose	2.75-11 phr	<ul style="list-style-type: none"> <li>- reduction in power consumption</li> <li>- decrease in viscosity</li> <li>- reduction in the amount of aromatic process oil in the formulation</li> </ul>	152
Curing agents	Sorbic acid/ferulic acid	2-25 phr	<ul style="list-style-type: none"> <li>- similar effect to sulfur curing</li> <li>- increase in abrasion resistance</li> </ul>	153

In recent years, the use of green solvents, more frequently the ionic liquids (ILs), deep eutectic solvents (DESs), and sup- and supercritical CO<sub>2</sub> with exceptional chemical tunability, higher



thermal resistance, and lower evaporation to the environment, has become welcomed worldwide<sup>154</sup>. Supercritical treatment makes use of the state of fluid at which there is no interphase between the liquid and gas phases, which occurs above the critical pressure and temperature of the substance, which makes possible conversion of materials into smaller molecules<sup>155</sup>. A great deal of attempts were made by Kojima and coworkers, later by Jiang et al., Mangili et al., Shi et al., and Meysami and coworkers for GTR devulcanization by using supercritical CO<sub>2</sub>, individually or in combination with other methods like thermomechanical reclaiming<sup>37</sup>. Besides the green nature of this recycling strategy, it is cost-effective in view of using less energy compared to conventional approaches. By the use of supercritical CO<sub>2</sub>, a very high degree of devulcanization, even up to ≈78%, can be reached. Of note, working at lower temperatures and shear forces in an oxygen-free medium appears as a greener treatment method. Another green rubber recycling approach is DES-assisted devulcanization of rubber wastes. For instance, Saputra et al. used three DESs (ChCl:Urea, ZnCl<sub>2</sub>:Urea, and ChCl:ZnCl<sub>2</sub>) for the thermo-sonic devulcanization of GTR (sonication frequency: 37-80 kHz; sonication time: 26-60 min; heating time: 0-60 min; heating temperature: 25-200 °C) with a high degree of selectivity towards breakdown of sulfur bridges<sup>156</sup>. They optimized the process by experimental design approach and achieved a significant DES-assisted devulcanization efficiency of 75%, characteristic of a very high degree of sulfur debonding without scission of rubber chains.

Nowadays, there is a strong tendency in rubber recycling towards the maximal use of GTR, which necessitates compatibilization of GTR to overcome the poor interface between the surface of GTR and the secondary polymer or additive phase. Green technologies are targeted at development of environmentally friendly GTR blends and composites, where reactive extrusion plays a key role. Due to the aforementioned advantages of reactive extrusion in terms of solvent-free basis, highly loaded GTR/thermoplastic blends and composites can be good candidates to practice development of fully sustainable elastomers from waste rubbers. Surface chemical etching treatment of GTR by the aid of acid etching, hydroxylation, oxidation, and radiation is also useful for the development of sustainable GTR-based products<sup>157</sup>. In such systems, it would be of priority to consider devulcanization as well as the possibility of re-vulcanization of the compound as TPEs, which may rely on both properties and environmental requirements. Nevertheless, available knowledge and data on such systems are inadequate for drawing a perspective for future developments.

## Concluding remarks, current challenges and future direction

Rubber reclaiming, which contains downsizing and devulcanization (de-crosslinking) of rubbers provided a strong support for waste rubber treatment, particularly GTR that accounts for  $\approx 80\%$  of rubber wastes. The resulting reclaimed rubber can be shaped into useful materials by blending with a thermoplastic or re-vulcanization in a fully elastomeric formulation to be useful for practical applications. The degree of success in achieving a product worthy of consideration depends on several parameters, including materials, processing, economic, and sustainability variables, each posing individual or combinatorial effects on the industrial worth of the resulting products. The time, temperature, and composition of GTR-based together with the type of solvent, processing machine, and secondary phase (thermoplastics, rubbers, additives, etc.) are also of significant importance. Legislations are against incineration of GTR because of environmental threats; moreover, GTR is not processable because of lack of flowability. Thus, incorporation of a secondary polymer along with optimization of processing conditions should be carefully considered for a safe and economically viable treatment. Over the past decade, attention has been paid to obtain value-added products by possible incorporation of GTR up to 80-90 wt.% from one side (economic needs) and development of sustainable blends and processing from the other side (environmental needs). Thus, using green additives, curing agents, plasticizers, and antioxidants were proposed and practiced, along with reactive extrusion technology was taken into account for green and economically reasonable production of GTR-based blends and composites. The ability to control and improve the properties of compounds based on waste rubber was increased by using reactive processing strategies. Since reactive extrusion is a continuously rapid and solvent-free processing method, it is possible to develop GTR-based blends with thermoplastics and thermosetting polymers as complements to rubber waste for the sake of higher properties and more particularly to compensate for the poor fluidity *via* rheological manipulation. Moreover, high-performance nanocomposites privileged for exceptional electrical conductivity, flame retardancy, anti-aging, reduced necking, and other engineering features could be developed through reactive extrusion of GTR/thermoplastic blends as a result of the incorporation of surface active fillers possessing very high surface area, e.g., MOF, graphene oxide (GO), and carbon nanotubes (CNTs). This approach enables commercialization of products based on rubber wastes.



Besides such promising angles and attempts done, there are some challenging features ahead of future development of GTR-based blends and composites through green approaches. First, development of fully green and highly-loaded GTR compounds necessitates a long way to be paved. So far, practices in using green ingredients in GTR treatment have been mainly limited to the use of green/waste additives, but a few examples of using green accelerators and curing agents or plasticizers are available. Second, behavior of GTR-based blends during reactive extrusion is dependent to several individual and simultaneously interrelated parameters among materials (composition), processing (temperature, screw design, type of extruder, etc.) which needs a large pool of data for a reliable optimization. Third, highly-loaded GTR systems need to be compatibilized, which itself brings about some more difficulties in terms of fluidity of compound and stability of process and properties. In the case of reactive extrusion, the multiplicity of parameters to be involved and optimized (materials, processing, and economic parameters) from one side and the diversity of works done with limited information about process conditions, apparatus, and materials used from the other side make it difficult to reach a general picture about future research. Thus, future research in this field should focus on finding, examining, screening, and processing of many green ingredients in single-, twin- and planetary-screw extruders considering their particular advantageous and implicated features. Circular economy approach has already been used in a few cases of waste rubber recycling, but to have a comprehensive model it is necessary to collect more data and experience. Green processing methods make use of fully green ingredients, which still seems to be far from reach. Analysis of in-process consumption of energy, as well as VOC generated and released in the course of reactive processing accompanied by the use of greener crosslinking agents, plasticizers, and processing aids are highly recommended.

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**Paulina Wiśniewska:** Writing—original draft preparation, formal analysis; **Józef T. Haponiuk:** Methodology, supervision; **Xavier Colom:** Validation, formal analysis, writing—review and editing; **Mohammad Reza Saeb:** Conceptualization, funding acquisition, supervision, writing—review and editing.

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## Photographs and biographies



**Paulina Wiśniewska** is a PhD student at the Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology, Poland. Her research is mainly focused on rubber recycling-science and technology- as well as development of advanced sustainable materials from rubber wastes and other bio-based polymers. She is now focused on developing highly ground tire rubber (GTR) loaded polymer composites with flame retardancy and electrical conductivity performance features. Formulation, optimization of properties and processing variables of polymer blends, composites and nanocomposites are among her latest scientific activities.



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**Prof. Xavier Colom** is the Director of the POLQUITEX Research group. He has been part of 8 Ministry Projects, four as IP. He has published 104 research articles (42% within Q1), among which 5 articles have been cited more than 200 times. According to Scopus, his *h*-index is 28 and the total number of citations is 3450. He has presented more than 110 papers in Congresses and has participated as a speaker (20 as invited speaker) in more than 50 Congresses, also published 7 book chapters. Prof. Colom has been advisor of 5 PhD, advised 65 PFG and 25 PFM both to UPC students and to Erasmus students. He is a member of the Editorial Board of the Polymers and Frontiers in Materials, and referee of multiple journals both on materials and polymers.



**Prof. Mohammad Reza Saeb** works at the Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology, Poland. He is actively working at the juncture of Materials, Chemistry, and Engineering. He authored/coauthored more than 450 papers in high-ranked/indexed journals, mainly on exploration and mechanistic interpretation of interrelationships between processing, microstructure, properties, and performance of polymers, including bio-based polymers, polymer blends, and polymer nanocomposites. He conceptualized two dimensionless indices, namely *Cure Index* and *Flame Retardancy Index*, for classification of polymer composites in terms of cross-linking and flame retardancy performance, respectively. He is currently focused on management of polymer wastes, particularly rubber wastes. He obtained as PI  $\approx 1.1$  M€ in 2022 from Gdańsk University of Technology, namely PLATINUM, to develop 3D printable flame-retardant electrically-conductive products from ground tire rubber (GTR) wastes.





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Reactive extrusion as an authoritative technology for green rubber recycling, enabling production of sustainable value-added secondary waste rubber-based products.

