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Devulcanization Technologies for Recycling of Tire-Derived Rubber: A Review

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Abstract: In general, composite materials are difficult to recycle. Tires belong to this class of materials. On top, one of their main constitutents, vulcanized rubber, is as elastomer, which cannot be remolten and hence is particularly challenging to put to a new use. Today, the main end-of-life routes of tires and other rubber products are landfilling, incineration in e.g., cement plants, and grinding to a fine powder, generating huge quantities and indicating a lack of sustainable recycling of this valuable material. True feedstock recycling is not feasible for complex mixtures such as tires, but devulcanization can be done to reactivate the cross-linked polymer for material recycling in novel rubber products. Devulcanization, i.e., the breaking up of sulfur bonds by chemical, thermophysical, or biological means, is a promising route that has been investigated for more than 50 years. This review article presents an update on the state-of-the art in rubber devulcanization. The article addresses established devulcanization technologies and novel processes described in the scientific and patent literatures. On the one hand, tires have become high-tech products, where the simultaneous improvement of wet traction, rolling resistance, and abrasion resistance (the so-called "magic triangle") is hard to achieve. On the other hand, recycling and sustainable end-of-life uses are becoming more important. It is expected that the public discussion of environmental impacts of thermoplastics will soon spill over to thermosets and elastomers. Therefore, the industry needs to develop and market solutions proactively. Every year, approximately 40 million tons of tires are discarded. Through the devulcanization of end-of-life tires (ELT), it is possible to produce new raw materials with good mechanical properties and a superior environmental footprint over virgin products. The devulcanization process has become an interesting technology that is able to support the circular economy concept.

Keywords: rubber devulcanization; sustainability; recycling; twin screw extruder; feedstock recycling; magic triangle; elastomer

1. Introduction

With increasing global populations and welfare, consumption has been surging. Polymers—thermoplastics, thermosets, and elastomers—have shown significant growth over more than six decades from the 1950s onwards, with thermoplastics being by far the largest group. In 2018, the production volume has approached 350 million tons [1]. The steady, historic growth rate of 6% per year is expected to flatten considerably in the coming years due to a pressure toward recycling plastics materials. Plastics Europe and other associations have shifted their focus of communication from job and value creation of the industry toward recycling and littering prevention; the circular economy, sustainability, microplastics pollution, and prevention have become common concerns, which the industry is starting to address seriously. Despite the huge efforts put into the recycling of thermoplastics, the achievements have been rather disappointing, apart from selected successful recycling schemes such as PET (polyethylene terephthalate) with bottles of carbonated soft drinks.

“Thermal recycling” sounds nice; however, it should only be considered as the last step of a cascaded use, since the incineration to recapture energy is adding little value. Composite materials such as GFRP and CFRP (glass fiber-reinforced plastics and carbon fiber-reinforced plastics) make recycling extremely difficult as well as the variety of applications of plastics and various contaminations such as foodstuffs. PET bottles can be collected and recycled efficiently and effectively, because carbonated soft drinks and bottled water are put almost exclusively into PET containers. Packaging film, on the other hand, is often a multilayer material that is used particularly for perishable food, where recycling becomes virtually impossible. The low value of plastics, compared to other materials, makes recycling challenging, too. Plastics Europe, in one of their recent reports, claims that within the EU28 (Belgium, Bulgaria, Czech Republic, Denmark, Germany, Estonia, Ireland, Greece, Spain, France, Croatia, Italy, Cyprus, Latvia, Lithuania, Luxembourg, Hungary, Malta, Netherlands, Austria, Poland, Portugal, Romania, Slovenia, Slovakia, Finland, Sweden, United Kingdom), Norway, and Switzerland, in 2016, 31.1% of the 27.1 million tons of post-consumer waste collected plastics were recycled, of which 63% were inside the EU, and another 41.6% were sent to energy recovery, with 27.3% remaining for landfilling (the landfilling ban in the EU came into force in 1999) [2]. These numbers are misleading, because the total demand was in excess of 50 million tons, and the absolute recycling rates, although they are increasing from year to year driven by landfill restrictions for organic materials, are disappointingly low. Recycled thermoplastics go different routes. Production scrap is recycled most easily; typically, 10%–15% of own material (e.g., sprues in injection molding) can be shredded and added without quality issues. Post-consumer recycled plastics can go into products of lower mechanical properties. Prices of recycled polyolefins, due to consumers’ demand for “green” products, have increased sharply in the last years. Another promising route are bioplastics, which can either be based on renewable raw materials and/or be biodegradable. Currently, their market share is on the order of 1%–2% of global plastics consumption. For polymers (thermoplastics), there are typically two recycling methods: mechanical and thermal (the latter being incineration for energy recovery). Garforth et al. have defined feedstock recycling as a process that "aims to convert waste polymer into original monomers or other valuable chemicals" [3]. Synonyms for feedstock recycling are chemical recycling or tertiary recycling. According to Aguado et al. [4], one can distinguish between three main approaches in feedstock recycling: depolymerization, partial oxidation, and cracking (thermal, catalytic, and hydrocracking). Kaminsky at al. have studied the feedstock recycling of synthetic and natural rubber by pyrolysis in a fluidized bed [5]. The main issue was that the original monomers are hard to obtain and that rather a mix of different molecules results. Some authors even understand the production of low-value products such as carbon black as feedstock recycling.

In the case of tires, which are a complex product made from completely different raw materials such as steel, cord, natural and synthetic rubber, additives, etc., full feedstock recycling will not be feasible, i.e., obtaining the original constituents or monomers.

“Feedstock recycling” and “devulcanization” are two terms that are rather not to be used interchangeably, since the ambition is different. The expressions “depolymerization” or “molecular rearrangement” hit the meaning of devulcanization better.

True feedstock recycling can be considered the “holy grail” of plastics recycling in that the monomers are obtained from collected scrap, and then, they are captured and reused. However, this route has not yet been developed sufficiently, and many approaches are still at a low technology readiness level. Figure 1 shows the extent of feedstock recycling for thermoplastics packaging materials (more recent data were not given in the 2018 report).

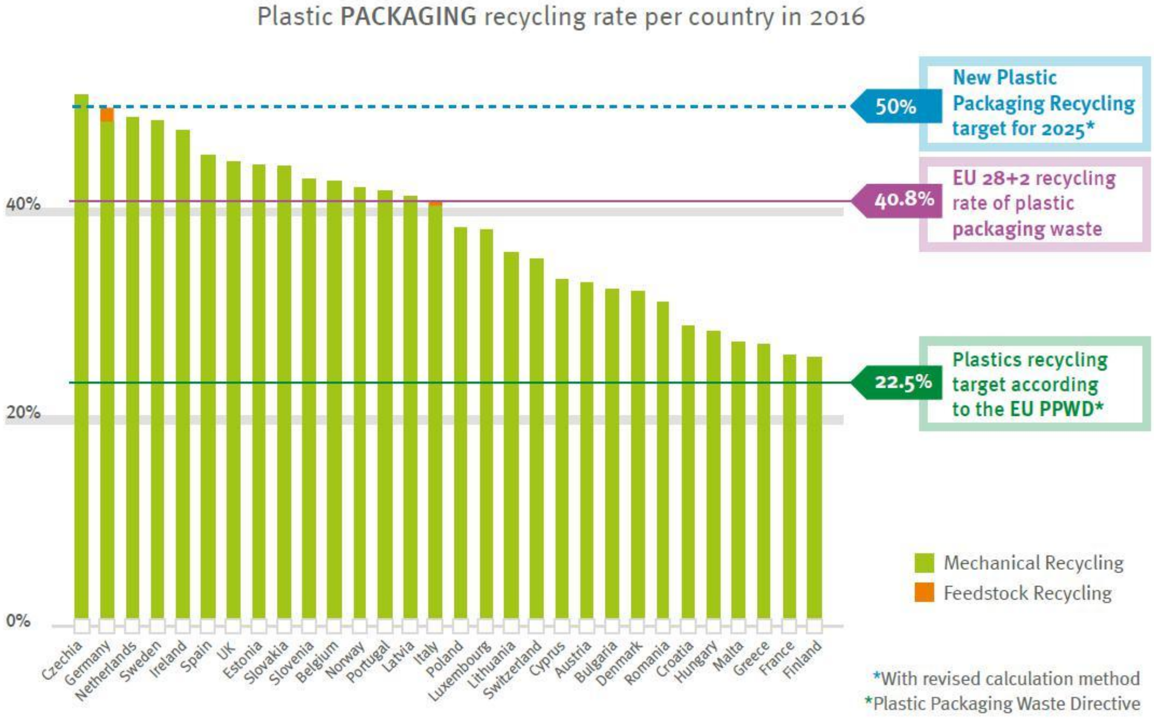

Figure 1. Feedstock recycling of thermoplastics packaging is still in its infancy. Reproduced with **Figure 1.** Feedstock recycling of thermoplastics packaging is still in its infancy. Reproduced with

2. Materials and Methods

2.1. Rubber Vulcanization

By vulcanization, as invented by Goodyear, sulfur can form bonds between unsaturated By vulcanization, as invented by Goodyear, sulfur can form bonds between unsaturated polymer chains found in latex to yield natural rubber. The process is also used for synthetic rubber. polymer chains found in latex to yield natural rubber. The process is also used for synthetic Accelerators can be added in the process, which is carried out at elevated temperatures. Accelerated rubber. Accelerators can be added in the process, which is carried out at elevated temperatures. sulfur vulcanizations are classified into three different types such as conventional (CV), semi-efficient Accelerated sulfur vulcanizations are classified into three different types such as conventional (CV), (semi-EV), and efficient vulcanization (EV) depending on accelerator/sulfur ratio (A/S) between 0.1

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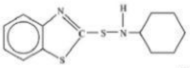
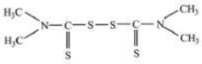
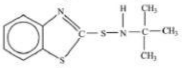
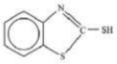
Common vulcanization accelerators are MBT, TBBS, TMTD, DPG, and CBS; for definitions, see Common vulcanization accelerators are MBT, TBBS, TMTD, DPG, and CBS; for definitions, Table 1 [8]. see Table 1 [8].

Table 1. Chemical structure and physical characteristics of various accelerators. Reproduced with permission from [8].

Accelerator	Chemical structure	Melting point (°C)	Accelerator type	Vulcanization speed
N-Cyclohexyl-2-benzothiazole sulfenamide (CBS)		97 – 105°C	Sulfenamide accelerator	Fast delayed action
Tetramethylthiuram Disulfide (TMTD)		156 – 158°C	Thiuram accelerator	Ultra fast
N-tert-butyl-2-benzothiazole sulfenamide (TBBS)		107 – 112°C	Sulfenamide accelerator	Fast delayed action
2-Mercaptobenzothiazole (MBT)		177 – 181°C	Thiazole accelerator	Semi ultra fast

Vulcanization gives the properties to natural or synthetic rubber; it renders the material into an Elastomer Vulcanization. gives the properties to natural or synthetic rubber; it renders the material into an elastomer. Regarding the useful life, there are two types of tires: the reusable tires and the non-reusable tires. The reusable tires are sent to tire retreading companies, providing them a new tread and run into service again. The non-reusable are tires that cannot be retreaded due to an advanced damage, structural deformation, or high degradation. These tires are the starting materials for recycling, according to Asaro et al. [14].

For devulanization, waste rubber tire (WRT) material is typically first processed into ground tire rubber (GTR). While waste tires are often just landfilled or burnt in an ill-controlled manner, GTR can be processed into rubberized asphalt [23,24], bitumen [25], cement [26], concrete, tiles, thermal and acoustic isolation [14], and other products. However, simply mixing untreated GTR into an (elastomeric) matrix greatly decreases its mechanical properties, because the cross-linked rubber particles will show poor interfacial adhesion and dispersion.To improve these, devulcanization has been researched for more than five decades [27]. In the process, monosulfidic, (C-S), di-sulfidic (S-S), and polysulfidic (–S_X-) bonds in the rubber matrix are cleaved.

It was shown by de Sousa et al. that the final temperature reached by the rubber mixture is the main factor responsible for the success of the process [28]. Too high temperatures are to be avoided to prevent degradation of the main chains.

Thermomechanical [7,18], chemical [29–31], ultrasonic-based [32], microwave-assisted [28,33], and biological devulcanization methods [34] have been studied extensively.

Molanorouzi and Mohaved have proposed an irradiation technique for rubber devulcanization [35]. Chen et al. [36] describe supercritical solvent-based devulcanization.

A twin-screw extruder for thermomechanical devulcanization is considered most practical [18], because that type of machinery is commonly used in the polymer industry. In addition, scalability to industrial volume is seen best for extrusion [14]. Figure 3 shows a typical co-rotating twin-screw extruder setup (a) and a screw configuration for devulcanization (b). Chen et al. [36] describe supercritical solvent-based devulcanization.

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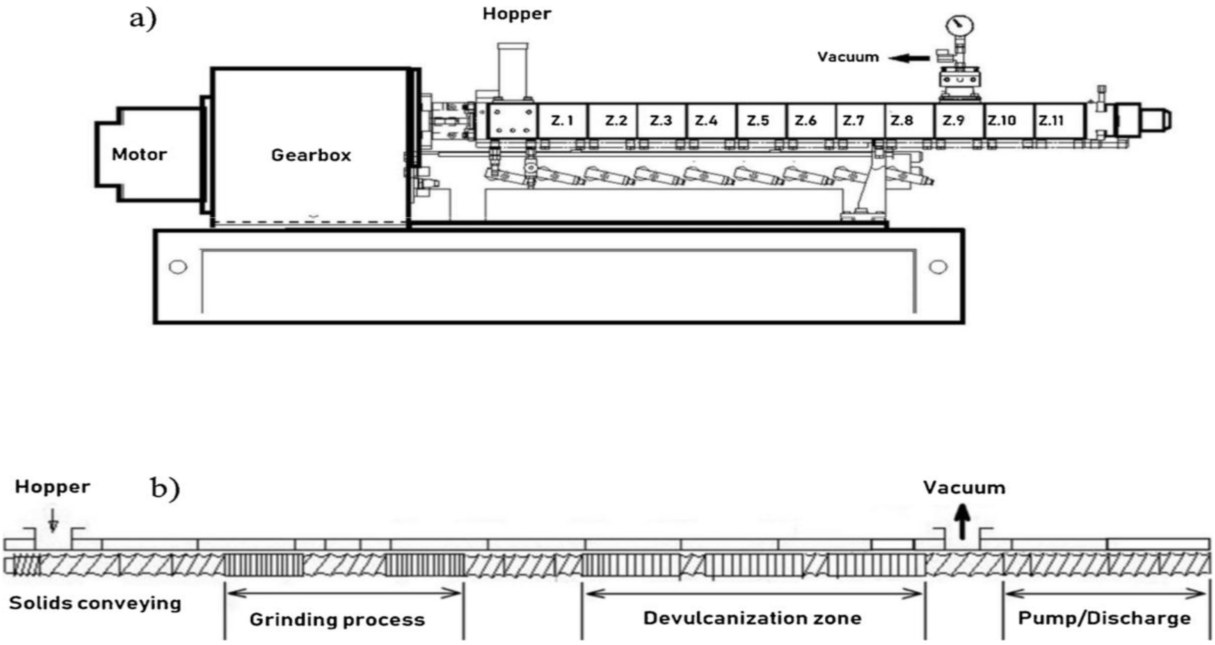
MaterialsFigure2020,133, shows1246 a typical co-rotating twin-screw extruder setup (a) and a screw configuration7of 16for devulcanization (b).



For the thermochemical approach in an extruder, the use of supercritical CO_2 ($scCO_2$) has been suggested [14,38]. CO_2 is chemically inactive, non-toxic, non-flammable, and inexpensive. Its critical point can be reached easily (31.1 C, 7.38 MPa), and residual $scCO_2$ in the devulcanized rubber is removed easily.

As a chemical method, the oxidation of sulfur bonds using nitric acid (HNO_3) and benzoyl-peroxide

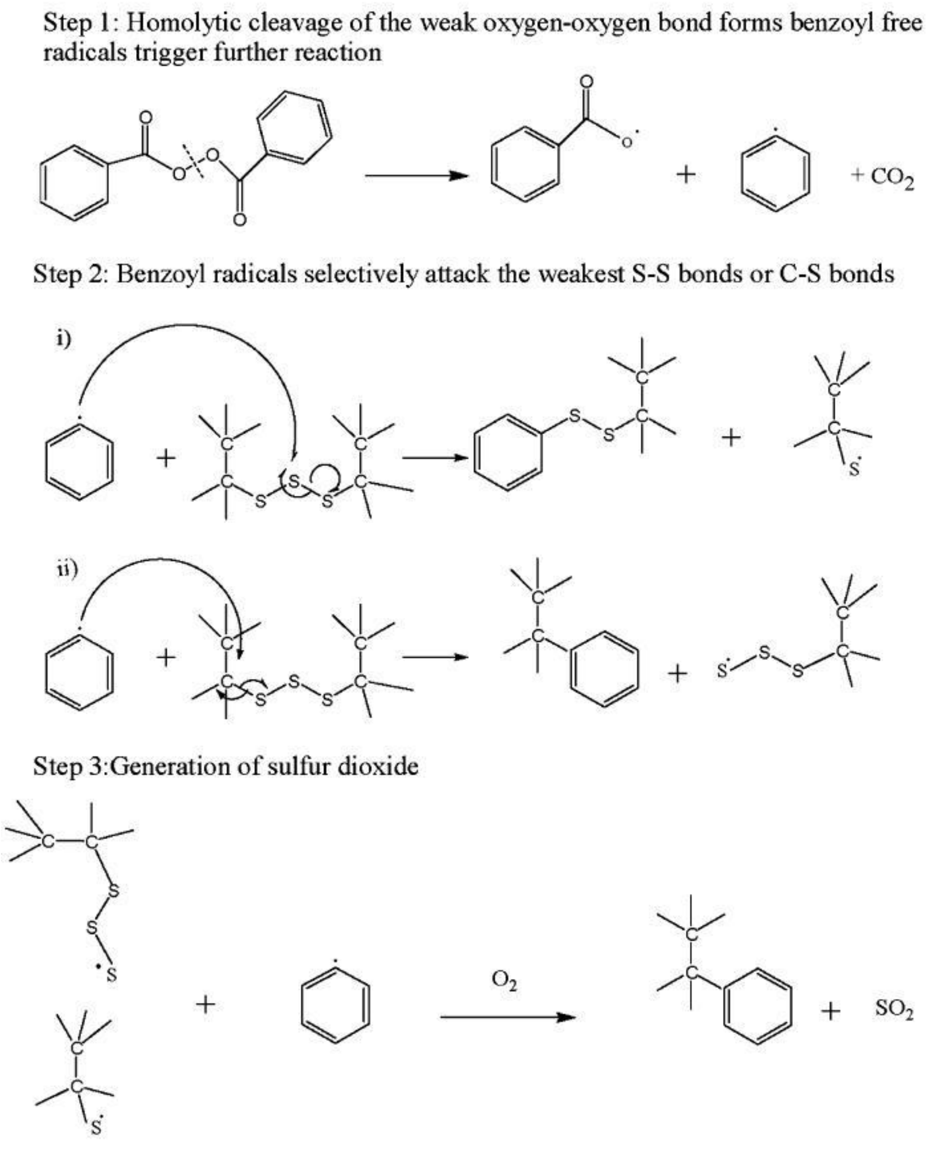


Figure 5. Plausible reaction mechanism of devulcanization. Reproduced with permission from [39].

Asaro et al. [14] have suggested diphenyl disulfide (DD) as effective devulcanizing agent. DD was also proposed by other authors such as Kojima et al. [40–43], Jiang et al. [44], Shi et al. [45], and Mangili et al. [46].

Mangili et al. [9] used ground truck-tire rubber (GTR) for devulcanization in supercritical CO_2 in the presence of diphenyl disulfide as the devulcanizing agent.

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$ScCO_2$ was found to be a good swelling agent, and it exhibits a favorable distribution coefficient for DD [9]. The most limiting factor for this devulcanization process is the amount of unreacted DD in the treated GTR [9].

For ultrasound, 20–50 kHz were proposed by Liang et al. [47].

Concerning devulcanization by microwaves, it was found out by de Sousa et al. that the natural rubber phase of tires, which contains most of the carbon black as opposed to the synthetic rubber

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Concerning devulcanization by microwaves, it was found out by de Sousa et al. that the natural rubber phase of tires, which contains most of the carbon black as opposed to the synthetic rubber phase, can be degraded more by microwaves [28].

An alternative approach has been the use of ionic liquids as studied by Seghar et al. [48]. To improve the devulcanization efficiency, Saputra et al. [49] have tested deep eutectic solvents (DES) in thermochemical–ultrasonic devulcanization of GTR. As DES, ChCl:urea, ChCl:ZnCl$_2$, and ZnCl$_2$:urea were used, with ChCl being choline chloride.

Thiobisphenols, e.g., 4,40-dithiobis(2,6-di-t-butylphenol), were also studied for thermochemical devulcanization by Zhang et al. [50]. In that study, 100 parts of GTR were mixed with 10 parts of aromatic oil with different contents of thiobisphenols of up to 3 g by a blender at room temperature. Subsequently, the devulcanization process was carried out using an internal mixer at 45 rpm between 180 and 200 C for 10 min [50].

Ghorai et al. [8,51] proposed using bis(3-triethoxysilyl propyl) tetrasulfide (TESPT) for chemical devulcanization. Dubkov et al. [52] used N$_2$O in organic solvents.

Sabzekar et al. [53] deployed benzoyl peroxide (BPO) as a devulcanizing agent. In addition, N-cyclohexyl-benzothiazyl-sulphenamide (CBS), tetramethylthiuram disulfide (TMTD), 2-mercaptobenzothiazol (MBT), and N-tert-butyl-2-benzothiazyl-sulphonamide (TBBS) could be deployed successfully for the devulcanization of cured rubber. Amines are another class of devulcanizing agents according to Sutanto et al. [54], e.g., hexadecylamine (HDA) [35].

Mangili et al. have compared different devulcanization methods [55]. The scCO$_2$ (with DD) and ultrasonic methods as bulk treatments involve a high amount of energy and chemicals; however, they are quite selective processes. On the other hand, the biological process (using e.g., the bacterium G. desulfuricans 213E) is limited to the surface and is highly selective toward sulfur; it requires a low amount of energy and chemicals [55]. However, this process does not have high yields [55].

To study devulcanization, researchers have used ground tires, or they have prepared fresh ground natural rubber (GNR). For instance, in [8], Ghorai et al. prepared GNR from vulcanized natural rubber through compounding NR (100 phr = per hundred resin) with ZnO: 5 phr, stearic acid: 2 phr, CBS: 1.2 phr, and sulfur: 1.8 phr in a two-roll mixing mill at a friction ratio 1:1.25. Then, the compounded NR was cured at 150 C for 3.5 min, followed by aging at 70 C for 96 h. The vulcanized and aged rubber sheets were ground in a two-roll mixing mill to obtain GNR.

To analyze the quality of devulcanization, energy-dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscope (FESEM) and thermogravimetric analysis (TGA) were used by Saputra et al. [49].

In addition, solvent extraction and swelling, as well as attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, were applied by de Sousa at al. [28], alongside cross-link density, soluble fraction, and Mooney viscosity, and by using the Horikx diagram by Seghar et al. [18]. Mangili et al. used cross-link density, sol fraction, gel fraction, and sulfur content [46].

In order to reduce the processing costs of “full devulcanization”, the dynamic vulcanization of GTR/plastic blends was proposed. This is a cross-linking process between GTR and a plastic matrix initiated by sulfur [56,57] or peroxides [58–60] during melt blending. According to Jiang et al., the resulting cross-linking will improve interfacial adhesion [11].

Another approach is to limit devulcanization to the surface of ground rubber tire powder. Thereby, particles can be reactivated to incorporate them into a new polymer matrix. This was investigated for PE by Jiang et al. [11] to prepare ground tire rubber/high-density polyethylene (GTR/HDPE) blends.

Surface devulcanization was achieved using intense shear and tetraethylenepentamine (TEPA), and then amine groups were grafted to the surface of devulcanized GTR by Jiang et al. [11]. In that paper, GTR was masticated in a two-roll mill with minimum roller distance (for maximum mechanical shear forces) 20 times. Then, 5 wt % TEPA as the chemically devulcanizing agent was added into the GTR, and the mixture was kneaded on the two-roll mill for 10 times to obtain surface-devulcanized GTR*Materials*.The2020process,*13*,xFORwasPEERfollowedREVIEWby in situ grafting; see Figure 6 below. 10 of 16

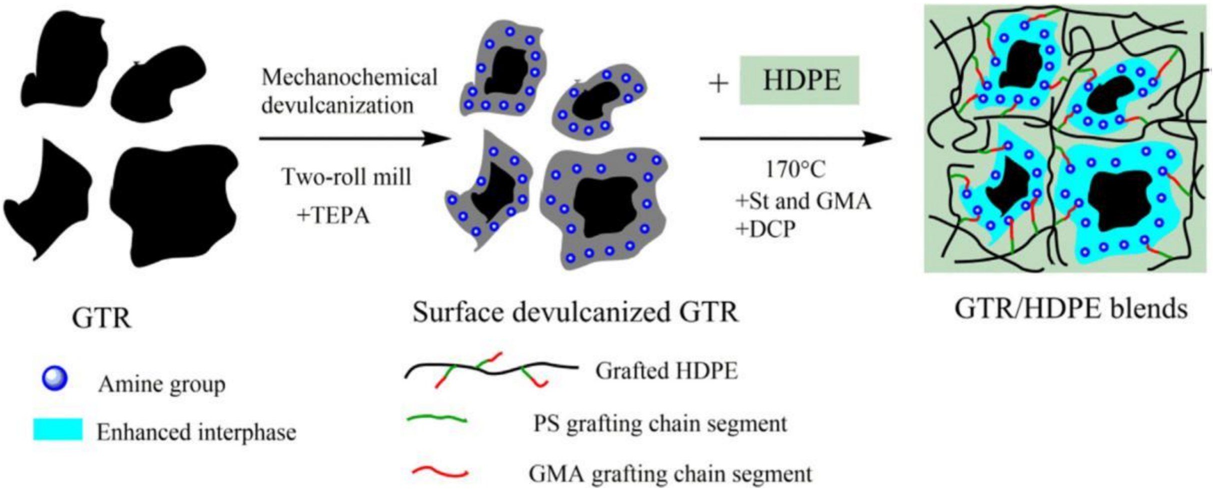

Figure 6. Schematic illustration of the preparation of ground truck-tire rubber/high-density polyethylene **Figure 6.** Schematic illustration of the preparation of ground truck-tire rubber/high-density (GTR/HDPE) blend by combining surface devulcanization and in situ grafting technology (styrene (St), polyethylene (GTR/HDPE) blend by combining surface devulcanization and in situ grafting glycidyl methacrylate (GMA), and dicumyl peroxide (DCP) were used). Reproduced with permission technology (styrene (St), glycidyl methacrylate (GMA), and dicumyl peroxide (DCP) were used). from [15].

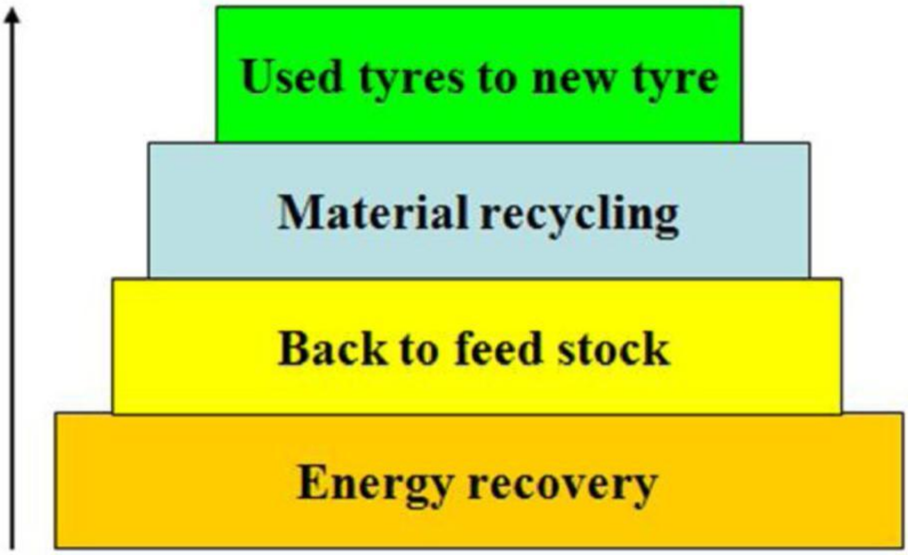

Figure 7. Proper waste management hierarchy. Reproduced with permission from [21].

tree is grown in tropical areas, where plantations have often been established on previous rainforest land. Due to its nature to partially crystalize, natural rubber is harder than synthetic rubber, and it will give a longer lifetime to tires. This is also the reason while truck tires, which can run for well over 100,000 km [66], contain a larger fraction of natural rubber than do passenger car tires. Tire collection needs to be improved, and less environmentally friendly end-of-life options should be land. Due to its nature to partially crystalize, natural rubber is harder than synthetic rubber, and it will give a longer lifetime to tires. This is also the reason while truck tires, which can run for well over 100,000 km [66], contain a larger fraction of natural rubber than do passenger car tires. Tire collection needs to be improved, and less environmentally friendly end-of-life options should be discontinued. There is a very strong, scientifically rooted interest in the feedstock recycling of rubber. On the one hand, this route provides a meaningful end-of-life exit for waste tires, and on the other hand, it conserves resources by reducing fresh natural and synthetic rubber demand. The circular economy concept [67] is to be extended to elastomers, in which tires will play a crucial role.

Other approaches to make tires more sustainable can be found in the use of alternative raw materials. For instance, Midhun et al. have suggested replacing carbon black (CB) by rice husk derived nanocellulose (RHNC) [68]; see also Fan et al. [69] for a carbon black outlook. Jiang [70] suggested using waste lignin to obtain a CB replacement material. Other novel fillers under discussion are functionalized starch (Li et al. [71]) and carbon nanotubes (Gumede et al. [72]).

Summary

Feedstock recycling can be considered the ultimate goal for polymers in that the original monomers are recovered. It seems feasible for some pure polymers. For complex product mixtures such as tires, feedstock recycling back to isoprene and the other constituents seems not feasible today. However, a process to reverse vulcanization, and hence make the elastomeric material meltable and processable again, is devulcanization. Devulcanization offers a route to recycling end-of-life tires back into high value-added products, so that virgin natural and synthetic rubber can be partly replaced and saved with economical and environmental benefits.

This review article has provided an update on the state-of-the-art in rubber devulcanization, as a promising alternative to tire landfilling, grinding to powder and incineration in cement plants. Previous reviews are e.g., [73] by Manzano-Agugliaro et al., [74] by A. I. Isaye, [75] by Bockstal et al. [21], Forrest [15], De, Isayev, and Khait [16], Karger-Kocsis et al. [76], Simon et al. [77], and Garcia et al. [78].

Another area in need of more technology development is the natural rubber feedstock base. Today, it is dominated by latex from rubber trees. Alternative isoprene sources such as fig tree milk offer the potential to be more sustainable in terms of land usage, transportation, and cultivation requirements. Medium chain-length polyhydroxyalkanoates (mcl PHA) are biodegradable, and they can either be made from carbohydrates or through photoautotrophic microorganisms using CO_2 as the sole carbon source. This offers the potential for biodegradable tires, where attrition would be significantly less harmful due to is shortened lifetime. In addition, microbial production would not require arable land and avoid competition with feed—and food—production, which is an issue often raised against biofuels and bioplastics. It is expected that the world fleet of cars will continue to grow, and that tires will be needed in future in large quantities. Therefore, sustainable end-of-life options are necessary, and more sustainable raw materials need to be sought. The circular economy concept needs to be extended to elastomers such as rubber and products made out of rubber. The devulcanization technology is a promising route with a realistic potential for large-scale implementation in the near future. Therefore, governments and the EU must introduce new laws for the circular economy and support companies to develop even more efficient recycling technologies.

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