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Article

Feedstock recycling of rubber – a review on devulcanization technologies

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Abstract: Vulcanized Rubber, as elastomer, is difficult to recycle. Today, the main end of life routes of tyres and other rubber products are landfilling, incineration in e.g. cement plants, and grinding to a fine powder, with huge quantities lacking sustainable recycling of this valuable material. Devulcanization, i.e. the breaking up of sulfur bonds by chemical, thermo-physical or biological means, is a promising route that has been investigated for more than 50 years. This review article presents and update on the state-of-the art in rubber devulcanization. This review article addresses established devulcanization technologies and novel processes described in the scientific and patent literatures. 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. Tyre recycling through devulcanization has a huge lever, since approx. 30 million tons of tyres are discarded annually.

Keywords: rubber devulcanisation, rubber devulcanization, sustainability, recycling, twin screw extruder;

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1. Introduction

Polymers - thermoplastics, thermosets and elastomers – have shown significant growth over more than 6 decades from the 1950s onwards, with thermoplastics being by far the largest group. In 2018, production volume has declined to 348 million tons [1], and the historic growth rate of 6% per year is expected to flatten considerably in the coming years. Plastics Europe and other associations have shifted their focus of communication from job and value creation of the industry towards recycling and littering prevention; circular economy and microplastics pollution and prevention have become a common concern, which the industry is starting to address seriously. Despite the huge efforts put into recycling of thermoplastics, the achievements have been rather disappointing, apart from the successful PET recycling scheme with bottles of carbonated soft drinks. "Thermal recycling" sounds nice, should, however, only be considered as last step of a cascaded use. Composite materials like GFRP and CFRP (glass fibre reinforced plastics and carbon fibre reinforced plastics) make recycling extremely difficult, also the variety of applications of plastics and various contaminations such as foodstuff. PET bottles can be collected and recycled easily, 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, 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 in The EU28 + Norway + Switzerland, in 2016, 31.1% of the 27.1 mt of post-consumer waste collected plastics were recycled, thereof 63% 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 total demand was in excess of 50 million tons, and the absolute recycling rates, though increasing from year to year driven by landfill bans 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 moulding) 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. Feedstock recycling can be considered the "holy grail" of plastics recycling, in that the monomers are obtained from collected scrap, captured and reused. However, this route has not yet been developed sufficiently, and many approaches are still at a low technology readiness level. Fig. 1 shows the extent of feedstock recycling for thermoplastics packaging materials (more recent data were not given in the 2018 report).

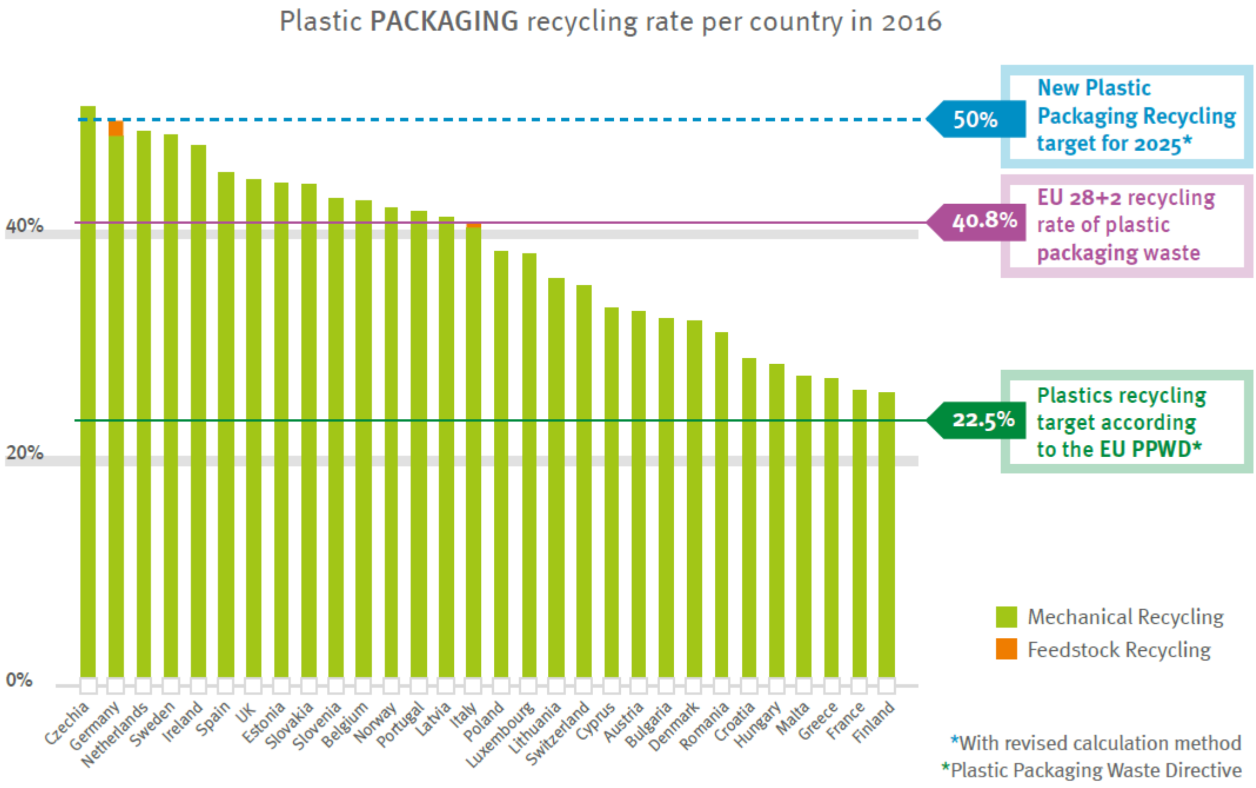


Figure 1. Feedstock recycling of thermoplastics packaging is still in its infancy. Source: [1].

Another project in this direction is OMV's ReOil project, where 100kg/h of plastics waste can be converted into a type of synthetic crude [3].

For thermosets, recycling as for thermoplastics is not feasible, because the polymer chains have been converted into a rigid network that cannot be dissolved or molten anymore. There are some attempts to e.g. burn off the polymer matrix to recycle fibers from composite materials, which in an energy efficient process can make sense for high value materials such as carbon fibers.

For elastomers, recycling options are strongly limited, too, because, the polymer is also a network. Elastomers cannot be molten nor be dissolved either. One of the huge volume applications of elastomers is tyres, where natural rubber is used next to a mix of synthetic rubbers. By vulcanization, the properties of the natural rubber are shaped (a low sulphur content on the order of 2% yields soft rubber, whereas more sulphur addition gives hard rubber). However, biodegradability of the raw materials (mostly latex) is thereby lost. Tyres are produced (and discarded) on the order of 40 million tons per year on a global basis, and they have become a huge environmental concern.

Whereas waste tyre dumps are visible to the public and are of general concern – end of life options for tyres include incineration in cement plants and grinding them to a fine powder for addition into asphalt or concrete – attrition of tyres on the roads which leads to microplastics formation is barely studied and discussed.

In the case of tyres and rubber in general, feedstock recycling would be a very beneficial approach. For more than 5 decades, devulcanization of rubber has been studied. Different technologies have been developed and some of them have already made it to the market. This review article provides an update on the state-of-the-art in rubber devulcanization with an outlook on potential future developments.

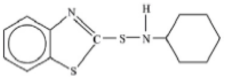
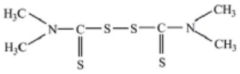
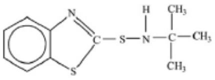
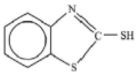
2. Materials and Methods

2.1 Rubber vulcanization

By vulcanization, as invented by Goodyear, sulphur can form bonds between unsaturated polymer chains found in latex, to yield natural rubber. The process is also used for synthetic rubber. Accelerators can be added in the process, which is carried out at elevated temperatures. Accelerated sulfur vulcanizations are classified into three different types such as conventional (CV), semi-efficient (semi-EV) and efficient vulcanization (EV) depending on accelerator/sulfur ratio (A/S) between 0.1 and 12 [4].

Common vulcanization accelerators are MBT, TBBS, TMTD, DPG and CBS, see Table1 [4].

Table 1. Chemical structure and physical characteristics of various accelerators. Source [4].

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.

2.2 Waste tyres

Tyres are used on all sorts of vehicles. After several years, they need to be replaced, because their profiles have become worn out, and/or they have become brittle.

Retreading is done for truck tyres. Passenger car tyres are single-use items. End-of-life-tires (ELTs) can be mainly recovered through two routes: The recovery of material and the recovery of energy [5]. The calorific value of ELT is close to that of coal, and they are often used in paper mills and cement works. By pyrolysis, oils can be made, as deployed e.g. in rural China on a scale of 2 million tons per year [6], leading to substantial emissions. Material recovery requires comminution. The grinding is reviewed in [7]. One can distinguish between ambient, wet and cryogenic grinding. Most technologies for tyre recycling involve the separation of metallic and textile (cord) materials and a grinding process leading to a significant reduction of the tire dimensions. During the grinding process, which typically yields granulate of a few mm or below, the temperature can be lower than the glass transition temperature (i.e. cryogenic grinding) of the polymers in the tires or close to room temperature. The resulting powder can be used as a filler e.g. in fresh tyres, and added just in a low amount. In order to increase the compatibility with the raw rubber, ELTs or their powder must be devulcanized by breaking the three-dimensional crosslink network, or they need to undergo some surface modifications [5].

2.3 Rubber devulcanization

Elastomers like rubber are cross-linked, which prevents simple recycling as it can be applied to thermoplastics [47], [48]. The devulcanization process aims at selectively cleaving the C-S bonds while leaving the C-C bonds intact. Devulcanization of waste rubber provides energy to the material in order to destroy, totally or partially, the three-dimensional network formed during vulcanization [8]. Selectivity is difficult to achieve, since the energies needed to break the S-S and C-S bonds (227 and 273 kJ/mol, respectively) are rather close to the energy required to break the C-C bonds (348 kJ/mol) [9].

The higher the selectivity of the devulcanization process, the better the mechanical properties of the material will be. Horikx [10] has developed a tool for investigating the mechanism of network breakdown in a vulcanized rubber network. According to this theory, the rate of increase of the soluble (sol) fraction of the rubber as a function of the measured crosslink density of the remaining insoluble (gel) fraction is different for cleavage of carbon-sulfur and carbon-carbon bonds. Thus, sol fraction and crosslink density measurements of devulcanised rubber samples yield an indication of the dominant mechanism of network breakdown [11].

It is estimated that 70% of global rubber production goes into tyres, and that tyres consist of up to 60% of natural and synthetic rubber [7]. Therefore, waste tyres are considered the main resource for rubber reclaiming and recycling, compare Fig. 2.

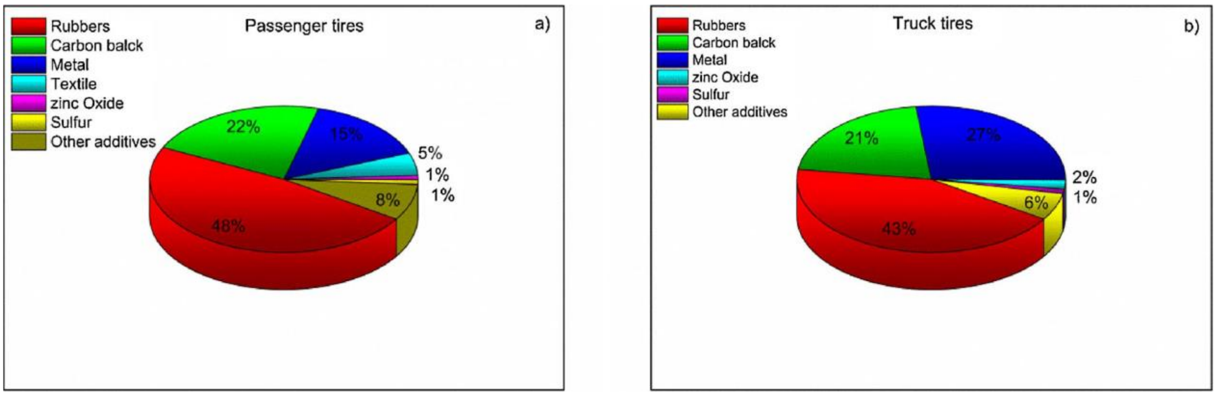


Figure 2. Tyre composition. Source: [7]

Truck tyres contain more natural rubber than tyres for personal cars, because they are subjected to more mechanical stress, which natural rubber sustains better [7].

Truck tyres typically contain natural rubber (NR) and synthetic rubber (Butadiene Rubber, BR and Styrene-Butadiene Rubber, SBR) [5].

"Regarding the useful life, there are two types of tyres: the reusable tires and the non-reusable tires. The first ones are tires which are sent to retreading companies providing them a second life. The second ones are tyres which cannot be retreaded due to an advanced damage, structural deformation or high degradation. These tyres are starting materials for recycling [7].

For devulanization, **waste rubber tyre** (**WRT**) material is typically first processed into ground tyre rubber (GTR). While waste tyres are often just landfilled or burnt in ill-controlled manner, GTR can be processed into rubberized asphalt [12] or cement [13], concrete, tiles, thermal and acoustic isolation [14] and other products. However, simply mixing untreated GTR into an (elastomeric) matrix greatly decreases mechanical properties, because the crosslinked particles will show bad interfacial adhesion and dispersion.

To improve these, devulcanization has been researched for more than 5 decades.

In the process, monosulfidic, (C-S), di-sulfidic (S-S) and polysulfidic (–Sx-) bonds in the rubber matrix are cleaved.

It was shown that the final temperature reached by the rubber mixture is the chief factor responsible for the success of the process [15]. Too high temperatures are to be avoided to prevent degradation of the main chains.

(Thermo) Mechanical [9], chemical [16], [17], [18], ultrasonic-based [19], microwave-assisted [20], [15], [21] and biological devulcanization methods [22] have been studied extensively. A twin screw extruder for thermo-mechanical devulcanization is considered most practical [9], because that type of machinery is commonly used in the industry. Also, scalability to an industrial scale is seen best for extrusion [7].

Fig. 3 shows a typical co-rotating twin screw extruder setup (a) and a screw configuration for devulcanization (b).

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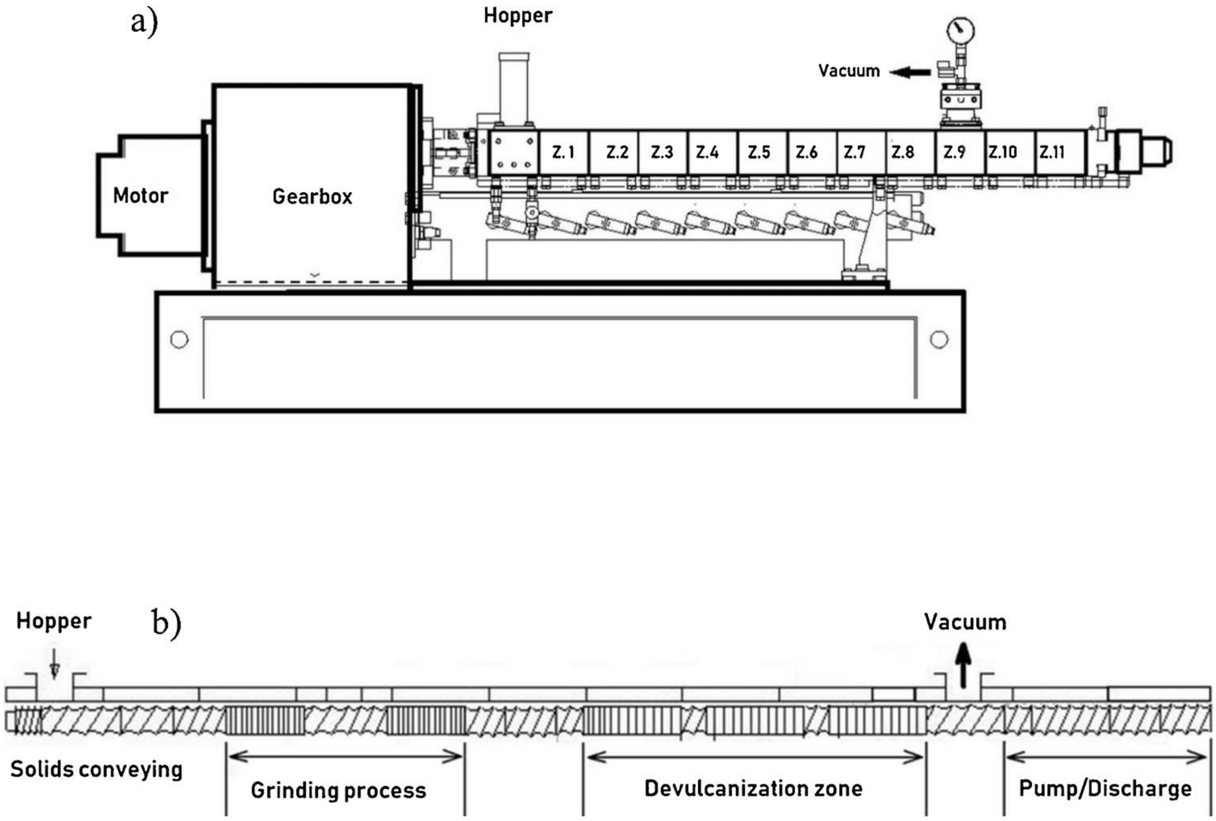

Figure 3. *A twin screw extruder for continuous devulcanization. Source: [9]*

In [23], the effect of screw configuration is studied.

It was found that up to 65 wt% of virgin natural rubber (NR) can be replaced by rubber recycled with devulcanized material [9]. In general, lower temperatures than for vulcanization are deployed to avoid the formation of harmful volatile organic compound (VOC) and destructive polymer degradation (cleavage of C-C bonds). H2S and mercaptanes are toxic compounds, and the resulting fumes need to captured and controlled. 180-300 °C are often recommended. [9] has used 80-220°C. Fig. 4 takes a look at the postulated devulvanization mechanism.

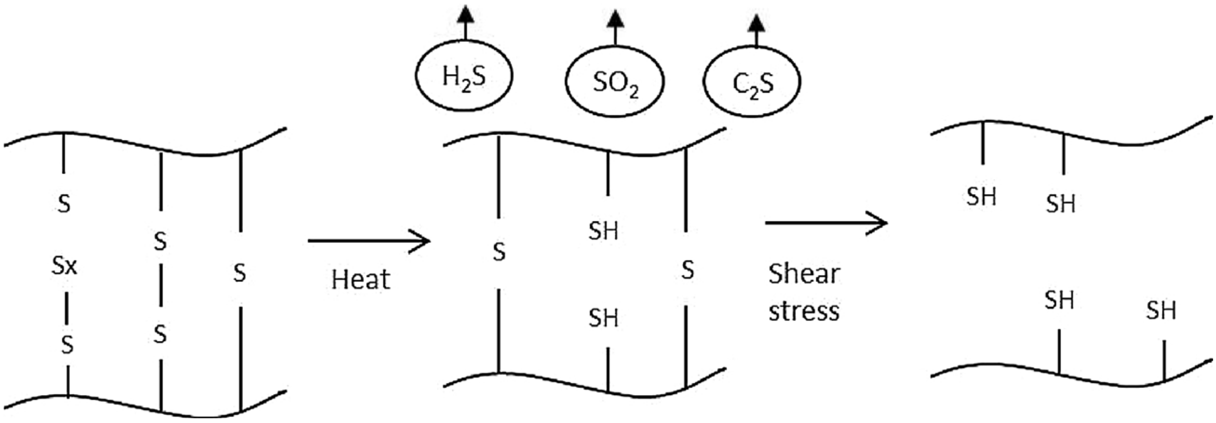

Figure 4. *Mechanism for the crosslinking breakage in thermomechanical devulcanization process. Source: [7]*

For the thermochemical approach in an extruder, the use of supercritical CO2 has been suggested [7], [24]. CO2 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 chemical methods, oxidation of sulfur bonds using nitric acid (HNO3) and benzoyl-peroxide (C14H10O4) was studied [17], [18], [25]. Fig. 5 takes a look at the mechanism using that agent.

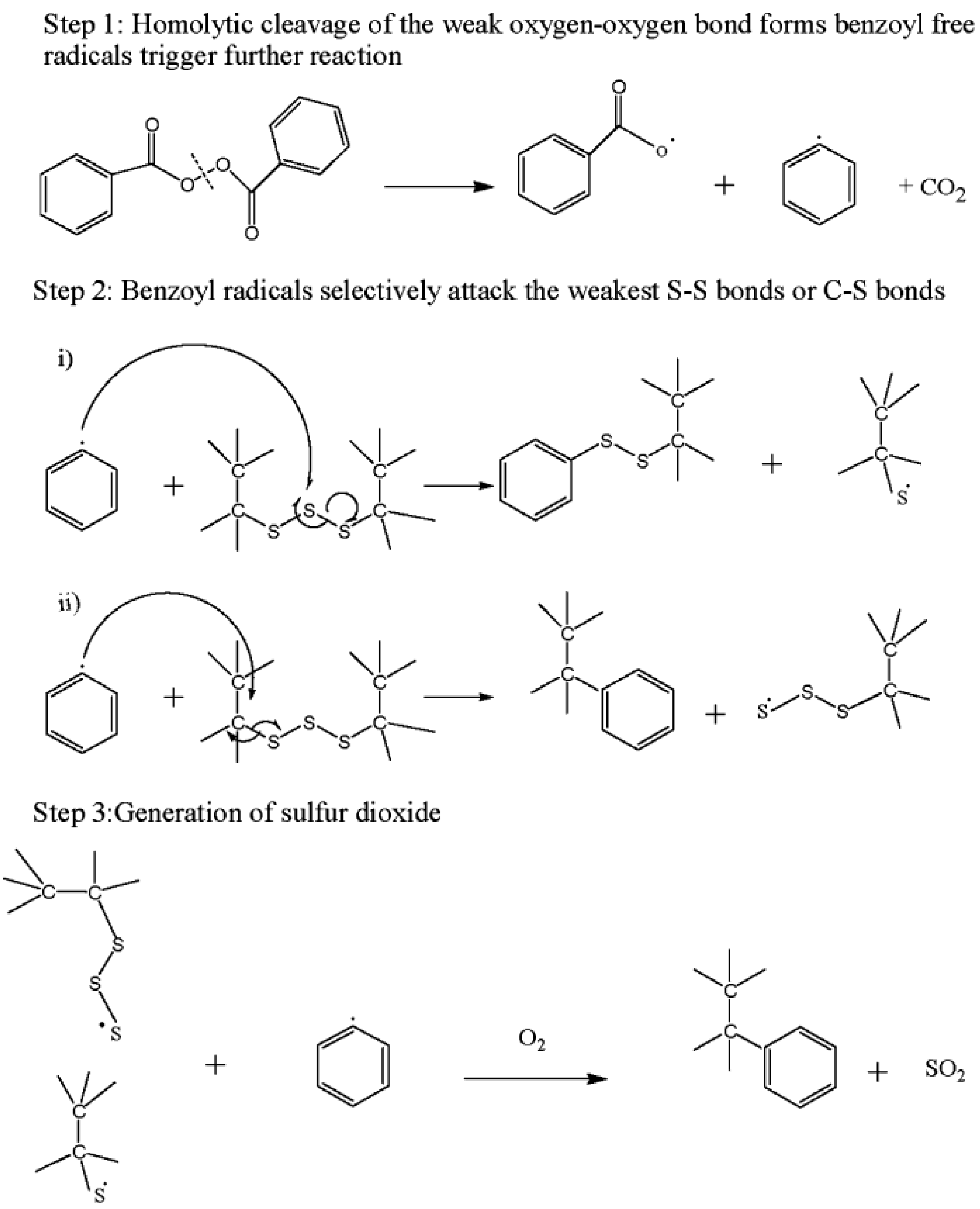

Figure 5. *Plausible reaction mechanism of devulcanization: [25]*

[7] has suggested Diphenyl disulfide (DD) as effective devulcanizing agent. DD was also proposed by [26], [27], [28], [29], [30], [31] and [32].

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[5] used ground truck-tire rubber (GTR) for devulcanization in supercritical CO2 (scCO2) in the presence of Diphenyl Disulfide (DD) as devulcanizing agent.

Temperature and pressure were 180 °C and 15 MPa, and the ratio between rubber and DD was 10 wt %.

ScCO2 was found to be a good swelling agent, and it exhibits a good distribution coefficient for DD [5].

The most limiting factor for this devulcanization process is the amount of unreacted DD in the treated GTR [5].

For ultrasound, 20-50 kHz were proposed [33].

Concerning devulcanization by microwaves, it was found that the natural rubber phase of tyres, which contains most of the carbon black as opposed to the synthetic rubber phase, can be degraded more by microwaves [15].

An alternative approach has been the use of ionic liquids [34]. To improve devulcanization efficiency, [35] has tested deep eutectic solvents (DES) in thermochemical-ultrasonic devulcanization of GTR. As DES, ChCl:urea, ChCl:ZnCl2 and ZnCl2:urea were used.

Thiobisphenols, 4,40-dithiobis(2,6-di-t-butylphenol), were also studied for thermo-chemical devulcanization [36]. 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 °C and 200 °C for 10 min [36].

[37] proposed to use bis(3-triethoxysilyl propyl) tetrasulfide (TESPT) for chemical devulcanization. [38] used N2O in organic solvents.

[39] deployed benzoyl peroxide (BPO) as a devulcanizing agent. In [4], bis(3-triethoxysilyl propyl) tetrasulfide (TESPT) was used. Also, N-cyclohexyl-benzothiazyl-sulphenamide (CBS), tetramethylthiuram disulfide (TMTD), 2-mercaptobenzothiazol (MBT) and N-tert-butyl-2-benzothiazyl-sulphonamide (TBBS) could be deployed successfully for devulcanization of cured rubber. Amines are another class of devulcanizing agents [40].

In [41], different devulcanization methods were compared. The scCO2 (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 towards sulfur; It requires a low amount of energy and chemicals [41]. However, this process does not have high yields [41].

To study devulcanization, researchers have used ground tryes, or they have prepared fresh ground natural rubber (GNR). For instance, in [4], GNR is prepared from vulcanized natural rubber through compounding of 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. The compounded NR was then cured at 150°C for 3.5min 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 analyse 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 [35].

Also, solvent extraction and swelling, as well as attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were applied [15], plus crosslink density, soluble fraction and

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Mooney viscosity, and by using the Horikx diagram [9]. [32] used crosslink density, sol fraction, gel fraction and sulfur content.

In order to reduce the processing costs of "full devulcanization", dynamic vulcanization of GTR/plastic blends was proposed. This is a cross-linking process between GTR and a plastic matrix initiated by sulphur [42], [43] or peroxides [44], [45], [46] during melt blending. The resulting cross-linking will improve interfacial adhesion [6].

Another approach is to limit devulcanization to the surface of ground rubber tyre powder. Thereby, particles can be reactivated to incorporate them into a new polymer matrix. This was investigated for PE in [6] 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 [6]. In that paper, GTR was masticated in a two-roll mill with minimum roller distance (for maximum mechanical shear forces) for 20 times. Then, 5 wt% TEPA as chemically devulcanizing agent were added into the GTR, and the mixture was kneaded on the two-roll mill for 10 times to obtain surface-devulcanized GTR. The process was followed by in-situ grafting, see Fig. 6 below.

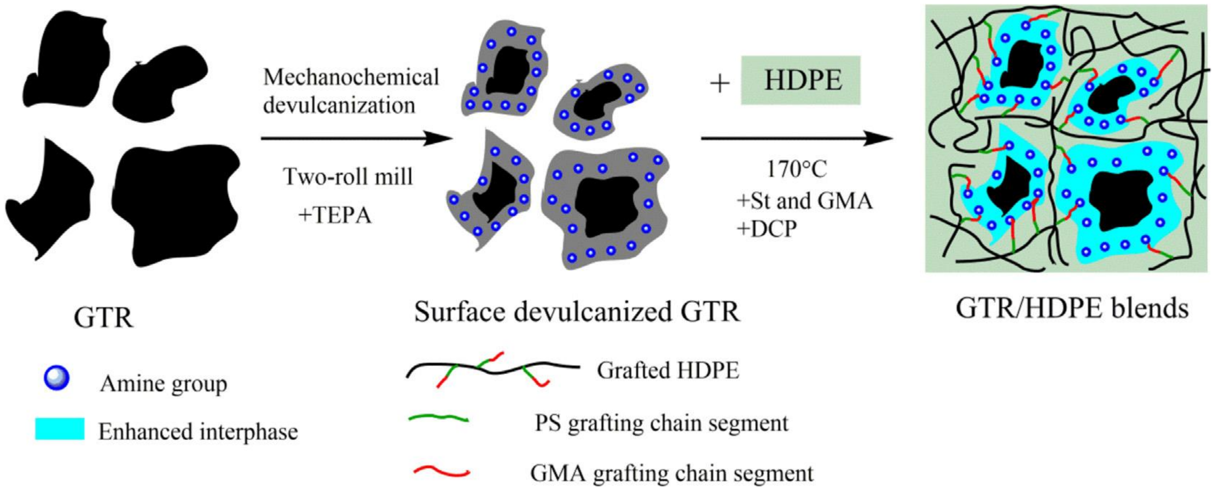

Figure 6. This is a figure *Fig. 6. Schematic illustration of the preparation of GTR/HDPE blend by combining surface devulcanization and in-situ grafting technology. Source: [47].*
Styrene (St), glycidyl methacrylate (GMA) and dicumyl peroxide (DCP) were used.

2.4 Revulcanization

For revulcanizing the devulcanized rubber, the following recipe has been suggested:

On 100 parts of devulcanized rubber 2 part of stearic acid, 4 parts of ZnO, 1.5 parts of CBS (N-Cyclohexyl-2-benzothiazole sulfonamide) and 1.5 parts of S were used [48].

In [36], 100 parts of devulcanized rubber were mixed with 2.5 g of zinc oxide, 0.3 g of stearic acid, 0.8 g of accelerator NS (N-tert-butyl-2-benzothiazylsulfonamide) and 1.2 g of sulfur. Curing was done at 145 °C and 15 MPa.

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2.5 Potential advantages of rubber recycling

Reclaiming rubber from end of life products such as tyres bears several advantages.

*Conservation of natural resources (less natural rubber is needed)

*Conservation of energy (less transportation, less energy in manufacturing)

*Avoidance of uncontrolled or high-emission end of life scenarios such as dumping or burning.

*Cost savings for goods producers, since the devulcanized material is cheaper than its replacement, natural rubber.

3. Results

In [39], 40% of reclaimed (devulcanized) rubber could be added to natural rubber without significant decrease in mechanical properties.

It was found that up to 65 wt% of virgin natural rubber (NR) can be replaced by rubber recycled with devulcanized material [9].

Several studies confirm that devulcanized rubber can be reprocessed into rubber products such as tyres without adverse effects.

Some of the studies have used laboratory equipment, such as roller mixers, while others have utilized industrial equipment such as co-rotating twin screw extruders.

4. Conclusions

The literature bears a wealth of information on rubber devulcanization, which can be achieved by thermal, thermo-chemical, mechanical and biological means. The process as such has a good environmental performance, and it can bring about significant cost savings.

Apart from addressing recycling of large volume rubber product streams such as tyres, solutions need to be found to

a) Make raw material manufacturing (i.e. latex/natural rubber) more sustainable

b) Make attrition to microplastics particles from tyres less harmful, i.e. biodegradable. This might be achieved through suitable bioplastics materials.

Natural rubber today is mainly produced from latex, the sap of the rubber tree. The rubber tree is grown in tropical areas, where plantations have often been established on previous rain forest land. Due to its nature to partially crystalize, natural rubber is harder than synthetic one, and it will give a longer lifetime to tyres. This is also the reason while truck tyres, which can run for well over 100,000km, contain a larger fraction of natural rubber than do passenger car tyres. Tyre 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 feedstock recycling of rubber; On the one hand, this route provides a meaningful end-of-life exit for waste tyres, and on the other hand, it conserves resources by reducing fresh natural and synthetic rubber demand. The circular economy concept is to be extended to elastomers, where tyres will play a crucial role.

5. Summary

This review article has provided an update on the state-of-the-art in rubber devulcanization, as a promising alternative to tyre landfilling, grinding to powder and incineration in cement plants.

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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 sole carbon source. This offers the potential for biodegradable tyres, where attrition would be significantly less harmful due to is shortened life time. Also, microbial production would not require arable and avoid competition with feed and food production, an issue often raised against biofuels and bioplastics. It is expected that the world fleet of cars will continue to grow, and that tyres 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 devulcanization technology is a promising route with a realistic potential for large scale implementation in the near future.

6. About the authors

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