Recent advances in the devulcanization technologies of industrially relevant sulfur-vulcanized elastomers

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ABSTRACT

The interesting thermomechanical properties of rubber materials have favored their widespread application in many fields, with a consequent increase in the amount of worn synthetic and natural rubber discarded every year. However, the complex three-dimensional molecular structure of rubber complicates the recycling and degradation process, and the current rubber waste management measures (i.e., landfilling, incineration, rubber grinding) are found to be unsustainable or substantially inadequate. On the other hand, devulcanization technologies, thanks to the selective cleavage of crosslinks, represent a sustainable and feasible approach to obtain a material that can be reintroduced into the rubber value chain or reused in novel eco-sustainable thermoplastic or elastomeric blends. Hence, this review provides an overview of the current rubber waste management techniques and devulcanization technologies, highlighting the underlying devulcanization mechanisms, describing the pros and cons of each method, and presenting some literature examples. Since most of the research on devulcanization has been made on waste tires, this review mainly focuses on the most widely used rubber classes for this application, i.e., natural rubber (NR) and styrene-butadiene rubber (SBR), and the most common vulcanization technique, i.e., sulfur vulcanization. Considering the importance of the application of a circular economy approach, this work also reviews the applications of rubber devulcanizates, focusing on how devulcanized rubber can be compounded with different polymeric matrices to develop eco-sustainable polymer blends with suitable physical properties.

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1. Introduction

Rubbers are elastomeric materials, characterized by their large deformability and the capability to recover the applied strain instantly and entirely once the load is removed. Industrial rubber materials are generally divided into natural rubber (NR) and synthetic rubber. NR is derived from natural rubber latex, mainly constituted by poly(*cis*-1,4-isoprene), an unsaturated hydrocarbon [1]. NR latex is produced by over 2000 plant species, belonging to the family Compositae, Moraceae, and Apocynaceae, but the commercially utilized latex is made almost entirely from Hevea brasiliensis [2]. On the other hand, synthetic rubber is synthesized as monomers from a variety of petroleum-based hydrocarbons. The most commonly produced synthetic rubbers are ethylene propylene diene monomers (EPDM) rubber [3–6], styrene-butadiene rubber (SBR) [7], chloroprene, and isobutylene [8].

The demand for rubber products has grown steadily over the last years [9,10]. Global NR production in 2018 amounted to almost 13.9 million metric tonnes, the vast majority of which (91%) has been produced by the Asia Pacific region, while the production of Europe, Middle East, and Africa (EMEA) was approx. 6.5%. NR is largely used to manufacture tires and, among other applications, also single-use gloves, the production of which has tremendously grown to meet the rising healthcare demands linked to the recent pandemic situation. On the other hand, synthetic rubbers are used primarily in the transportation industry to produce tires, the overall demand for which is estimated to reach 3.2 billion units by 2022 [11]. This conspicuous and ever-increasing rubber production demonstrates the versatility and the widespread application of this class of materials, but it also poses the challenge of how to manage the growing amount of rubber waste.

The rubber waste is a not negligible component of the total solid waste [12]. The majority of rubber waste is from the transportation industry (tires of automobiles, trucks, and motorcycles), but other sources of rubber waste include clothing, footwear, gaskets, and furniture. In 2018, the United States generate 9.2 million tonnes

List of acronyms

A/S	accelerator-to-sulfur ratio
BPO	benzoyl peroxide
CB	carbon black
CBS	N-cyclohexyl-2-benzothiazole sulfenamide
COPE	copolyester
CV	conventional vulcanization
DBU	diazobicyclo[5.4.0]undec-7-ene
DD	diphenyl disulfide
DES	deep eutectic solvents
d-GTR	devulcanized ground tire rubber
DR	devulcanized rubber
EMEA	Europe, The Middle East, and Africa
EPDM	ethylene propylene diene monomers
EV	effective vulcanization
GTR	ground tire rubber
HDA	hexadecylamine
HDPE	high-density polyethylene
HPHTS	high pressure high temperature sintering
HSM	high shear mixing
HTAD	high-temperature atmospheric devulcanization
IL	ionic liquid
LTMD	low-temperature mechano-chemical devulcanization
MBT	2-Mercaptobenzothiazole
MBTS	2-mercaptobenzothiazole disulphide
NDR	non-devulcanized rubber
NR	natural rubber
PP	polypropylene
PPh_3	triphenylphosphine
PVC	poly(vinyl chloride)
RSM	response surface methodology
SBR	styrene-butadiene rubber
$scCO_2$	supercritical carbon dioxide
SCF	supercritical fluid
SEM	scanning electron microscopy
SEV	semi-effective vulcanization
SR	synthetic rubber
TBBS	M-tert-butyl-2-benzothiazole sulfenamid
TEPA	tetraethylenepentamine
TESPT	bis(3-triethoxysily propyl) tetrasulfide
TMTD	tetramethylthiuram disulphide
VOC	volatile organic compound
WEO	waste engine oil
WTR	waste tire rubber

(mt) of rubber waste, out of which 5.0 mt were landfilled (55%), 2.5 mt were combusted for energy recovery (27%), and only 1.7 mt were recycled (18%). Recycling rubber waste is challenging, but an effort in improving the rubber recycling policies and technologies must be done in order to increase the sustainability and the circularity of the rubber industry [13].

Since most of the research on devulcanization has been made on waste tires, this review mainly focuses on the most widely used rubber classes for this application, i.e., natural rubber (NR) and styrene-butadiene rubber (SBR) and the most common vulcanization technique, i.e., sulfur vulcanization. Since there are already some comprehensive reviews in the literature on the scientific aspects of the devulcanization of rubber-based products, the present article does not aim at reviewing all the most recent findings on rubber devulcanization in a complete and detailed way.

Instead, the purpose of this work is to provide a concise and technical overview on the most important devulcanization technologies on industrially relevant sulfur-vulcanized elastomers. such as NR and SBR, and to give some practical examples of processing and applications of such materials. In fact, the target audience of this work is represented by engineers and industry professionals in the field. Considering the importance of the application of a circular economy approach, the last part of this work (Chapter 4) reviews and summarizes the applications of rubber devulcanizates, focusing on how devulcanized rubber can be compounded with different polymeric matrices to develop eco-sustainable polymer blends with suitable physical properties.

1.1. Possible disposal pathways for waste rubber

1.1.1. Landfilling

Landfilling and tire monofilling (i.e., deposit in certified sites accepting only waste tires) were among the earliest rubber and tire disposal methods due to the availability of large land areas and economic feasibility, but have severe drawbacks [14]. For example, landfilled tires can release metals and toxic chemicals such as stabilizers, plasticizers, flame retardants, and other low-molecular-weight additives, which pollute the soil and decrease its fertility

[15]. Moreover, rubber waste acts as a breeding ground for mosquitoes, rodents, and snakes, vectors for various deadly diseases. The piles of tires in open dumpsites or landfills are also highly flammable, and tire fires can burn for several weeks and are very difficult to extinguish. Most importantly, landfilling fails in recovering useful material to be reintroduced in the rubber industry as a second-generation feedstock and should therefore be used only in the very few cases in which all the other waste management technologies (reducing, reusing, recycling, energy recovery) cannot be put in place [16]. For all these reasons, landfilling of end-of-life tires was forbidden by the European Commission since 1999, which has boosted the research for alternative options for rubber waste management [17].

Therefore, many different rubber waste management technologies are being developed and constantly improved. These technologies, which are the subject of the rest of this review, not only aim at reducing the amount of waste but also to recover materials or energy that can be reintroduced into the supply chain, thereby saving primary energy resources and/or virgin material. Table 1 provides an overview of these technologies, which can be divided into thermal, mechanical, chemical, physical, and biological methods.

1.1.2. Energy recovery

Another possibility of rubber waste management is represented by the use of scrap rubber as fuel. Tires are constituted by an organic fraction higher than 90% and have a calorific value of ca. 32.6 MJ/kg, comparable with that of coal (18.6–27.9 mJ/kg) [18]. Approx. 45% and 38% of postconsumer tires and industrial wastes in the United States and in the EU, respectively, are used as supplementary non-fossil fuel in some form of energy recovery [19]. Energy recovery processes from waste tires include incineration, pyrolysis, and gasification.

Incineration is the oxidation of combustible material to give inert waste [19]. It is a highly exothermic process, initiated at controlled high temperatures (1000 °C) quickly becoming self-sustaining [20]. If the temperature is kept high enough, this process only yields H_2O, O_2, and CO_2, while too low processing

Table 1
Techniques for rubber waste management (adapted from Ref. [11]).

Thermal	Mechanical	Chemical	Physical	Biological
• Pyrolysis • Thermolysis	• Ambient • Wet • Cryogenic • Ozone cracking • Thermo-mechanical	• Radical scavengers • Chemical probes • Nucleophilic additives • Catalyst systems	• Microwave • Ultrasonic	• Bacteria • Fungi

temperatures lead to the emission of several toxic gases, such as dioxins. Incineration is often carried out by the tire industry to dispose of production waste and rejects and to produce their own energy [21]. It is also a common process in the cement industry [22], thermal power plants, pulp and paper mills, steel mills, industrial boilers, and sewage treatment installations [20]. In the case of the cement industry, the use of very high temperatures (~2000 °C) ensures the complete combustion of all the tire components, converting the steel to iron oxide and sulfur to sulfates, useful ingredients in the final cement product [19].

Pyrolysis is the process in which the organic fraction of waste tires is thermally decomposed at high temperatures (400–1200 °C) and under reducing or inert atmospheres, generating useful solid, liquid, and gaseous products [19,23]. The solid residue can be purified from steel, fiberglass, and other contaminants, and the remaining carbon-rich product is used to produce activated carbon, recovered carbon black (CB), and recovered inorganic compounds that can be used as fillers. The liquid fraction contains tar, water, aromatic hydrocarbons, and organic substances with high calorific value, which can be used as a fuel after sulfur removal. The gaseous products, rich in methane, ethane, ethylene, propylene, butylene, carbon dioxide, and carbon monoxide, can also be used as energy sources [15]. Although pyrolysis is interesting from the point of view of primary fuel saving, it is less industrially widespread than incineration, due to the non-competitive prices, the low purity of the obtained products, and the high operating and maintenance costs.

Gasification is a partial oxidation process that employs pressure, heat, and a reactive agent such as air, oxygen, hydrogen, or steam to convert tire waste into a gas mixture, the syngas, primarily composed of CO, H_2 [24], CO_2, and light hydrocarbons (CH_4). The syngas can be used as fuel in fuel cells or gas turbines to obtain a broad range of other fuels and chemicals [25]. Some of the advantages of gasification are its high conversion performance and energy efficiency (approx. 34%). Moreover, syngas contaminants (H_2S, NH_3) can be removed using well-established technologies. However, gasification involves higher temperatures than pyrolysis (1200–1500 °C).

1.1.3. Grinding

Grinding involves all those technologies that aim at reducing the size of waste rubber and producing a rubber powder of variable size, which can be used as it is for several applications but is also the starting process for rubber devulcanization [11].

1.1.3.1. Grinding technologies. The most widely used technologies to mechanically reduce the size of waste rubber components are ambient grinding, wet grinding, and cryogenic grinding.

In ambient grinding, the vulcanized rubber is broken down mechanically at room temperature. The mill type and the number of grinding steps determine the final size distribution of the rubber particles. This process is generally easy and inexpensive, but the price can become very high if a very fine mesh size is required. Moreover, the great amount of heat generated during milling can degrade the crumb rubber [17].

In cryogenic grinding, rubber is first cooled by liquid nitrogen and then crushed by an impact mill. This process produces a finer rubber crumb in a faster and cleaner way than ambient grinding, but the operating cost is higher, not only due to the costs related to the liquid nitrogen but also to the extra drying step to remove moisture from the crumb rubber [26]. Moreover, cryogenic and ambient grinding differ in the morphology and surface structure of the crumb rubber; cryogenically grounded particles are smoother and have a broader size distribution. These differences translate into different reactivity during re-vulcanization, and thus in different properties of the end product [17].

Finally, wet grinding consists of adding water as a lubricant and cooling agent before milling. This method results in a very fine (10–20 μm) and clean crumb, which must be dried after the process. Another wet grinding technique involves a water jet and is generally employed to mill large truck tires. The obtained crumb rubber has great purity and a large specific surface area, and thus it is suitable to be used as a filler in high-quality composites [10]. Water jet grinding is considered an environmentally friendly process because it is characterized by low energy consumption, low noise emission, and a closed-loop system for water recycling.

The output of any of these grinding methods can be then processed through devulcanization, using the technologies reported in the following sections. Some of these technologies can be combined, in order to obtain a higher devulcanization degree.

1.1.3.2. Applications of ground rubber. Mechanical grinding produces crumb rubber and ground rubber in different sizes, which can be used in several applications, especially in the civil engineering and manufacturing fields. Among all the rubber types that can be processed and recycled in this way, a wide variety of applications has been proposed for ground tire rubber (GTR) [22]. It can be used to produce ground covers in playgrounds, lower layers of floor coverings, walkway tiles, mulch for agricultural purposes, sports surfaces such as running tracks, crash barriers, and shock absorbers, but also as asphalt modifiers and lightweight fillers. In addition, shredded rubber, crumb rubber, and ground rubber can be employed in the replacement of gravel, sand, and filler material, respectively [27].

GTR can also be blended with various thermoplastics, such as polyethylene (PE) [28,29], polystyrene (PS) [30], polypropylene (PP), and polyvinyl chloride (PVC) [31], and these blends can be shaped into extruded and molded products [32], whose physical-mechanical properties depend on the properties of the matrix but also on the GTR fraction [33], particle size [34], dispersion degree, and GTR-matrix interfacial interaction [35].

Moreover, GTR can be compounded with virgin rubber to produce conveyor belts, shoe soles and heels, molded and extruded profiles, car mats, tubes, sealing plates, mattresses, battery boxes, and other hard rubber goods. However, the direct incorporation of GTR in virgin rubbers usually deteriorates their mechanical and viscoelastic properties, especially the tensile strength and strain at break. This is due to the lack of reactive sites on the GTR surface, which determines a poor filler-matrix adhesion [36,37]. Moreover, the behavior of the rubber during curing may also be affected by the

GTR, as sulfur or accelerators may migrate from vulcanized GTR to the virgin matrix or vice versa [38]. Notwithstanding these issues, many authors have demonstrated the feasibility of including 10–30% of GTR into virgin NR and SBR without dramatically impairing the main mechanical properties of the final products and bringing also some advantages, such as a general increase in the damping properties [14].

The poor GTR/matrix adhesion has been addressed by increasing the GTR surface reactivity via the introduction of polar groups. This has been done with several techniques, classified as physical methods, such as plasma, ozone, high-energy gamma or ultraviolet irradiation [19], or chemical methods, such as acids, coupling agents, and chlorination treatments [7,19].

Another field of research that has been considerably developed in the last decades is the use of GTR as a cement, concrete, and asphalt modifier [39]. GTR improves the fracture resistance of concrete, decreases its density, and favors the heat, sound, and vibration absorption properties. Blending GTR with asphalt improves the performance and the longevity of roads as it reduces the noise of the vehicles, improves crack resistance, and enhances driving comfort [40]. Finally, in sludge treatment plants, a bed of GTR can absorb organic solvents, mercury (II), and other heavy metals, due to the presence of thiol and other sulfur residues able to immobilize metal ions.

1.1.4. Recycling through devulcanization

Devulcanization of post-consumer rubber is the most desirable approach to solving the problem of rubber waste management. Devulcanization, as it will be better explained in Chapter 2, is the conversion of a three-dimensionally interlinked, insoluble, and infusible thermoset polymer network to an essentially thermoplastic material, which ideally keeps the same properties of the virgin rubber and can be processed and re-vulcanized into a new product [41]. Hence, rubber devulcanization is the key technology to tackle the issue of rubber waste management and at the same time save virgin material resources [15].

The first attempts at devulcanizing scrap rubber have been performed more than a century ago [42]. Since then, many devulcanization technologies have been developed, which can be broadly classified into two groups: physical devulcanization processes and chemical devulcanization processes [43]. Physical techniques comprise mechanical, thermo-mechanical, microwave-based, and ultrasonic processes, while chemical processes include all the methods where chemical compounds or microorganisms are used to break the crosslinks [44]. The next Chapter provides a detailed analysis of the reasons behind the need for devulcanization as well as an explanation of the chemical and physical mechanisms involved in the devulcanization process of rubber.

2. Rubber vulcanization, reclaiming, and devulcanization
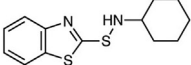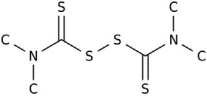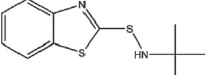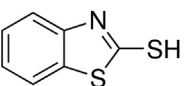
2.1. Vulcanization

The broad range of applications in which rubber materials are used depends on their interesting thermomechanical properties, especially for their high elasticity and damping. To develop these properties, elastomers must go through a complex process known as vulcanization, in which the molecular chains of rubber are joined by chemical bonds forming primary crosslinks, thereby producing a three-dimensional molecular network. This structural organization maintains or increases the elastic properties and reduces the plastic behavior of the material, makes the material insoluble, and increases its mechanical resistance [28].

Vulcanization was discovered in the mid-1800s by Charles Goodyear, who employed sulfur to form bonds between unsaturated polymer chains found in latex to yield natural rubber. Although other vulcanization techniques (e.g., the peroxidic vulcanization) have been developed in the subsequent years and are today widely employed, the most common vulcanization method is still sulfur vulcanization, and therefore this review focuses on this crosslinking technique.

Sulfur vulcanization, also used for synthetic rubber, is carried out at high temperatures and can be aided by accelerators. Common vulcanization accelerators are n-cyclohexyl-2-benzothiazole sulfenamide (CBS), tetramethylthiuram disulfide (TMTD), *m*-tert-butyl-2-benzothiazole sulfenamide (TBBS), and 2-mercaptobenzothiazole (MBT) (see Table 2 [45]).

The accelerator/sulfur ratio (A/S), generally comprised between 0.1 and 12, determines the classification of accelerated sulfur vulcanizations as conventional vulcanization (CV) for low A/S, semi-effective vulcanization (SEV) for intermediate A/S, and effective vulcanization (EV) for high A/S [46]. The chosen A/S influences the vulcanization kinetics, as a higher A/S increases the reaction rate and lowers the required curing temperature, which is positive for the resulting properties of the vulcanizate. A variable A/S also affects the mechanical properties of the resulting vulcanizate. CV, characterized by a lower A/S, leads to vulcanizates with high tensile, tear, and fatigue strength but low resistance to flexing

Table 2
Chemical structure and physical characteristics of various accelerators (adapted from Ref. [45]).

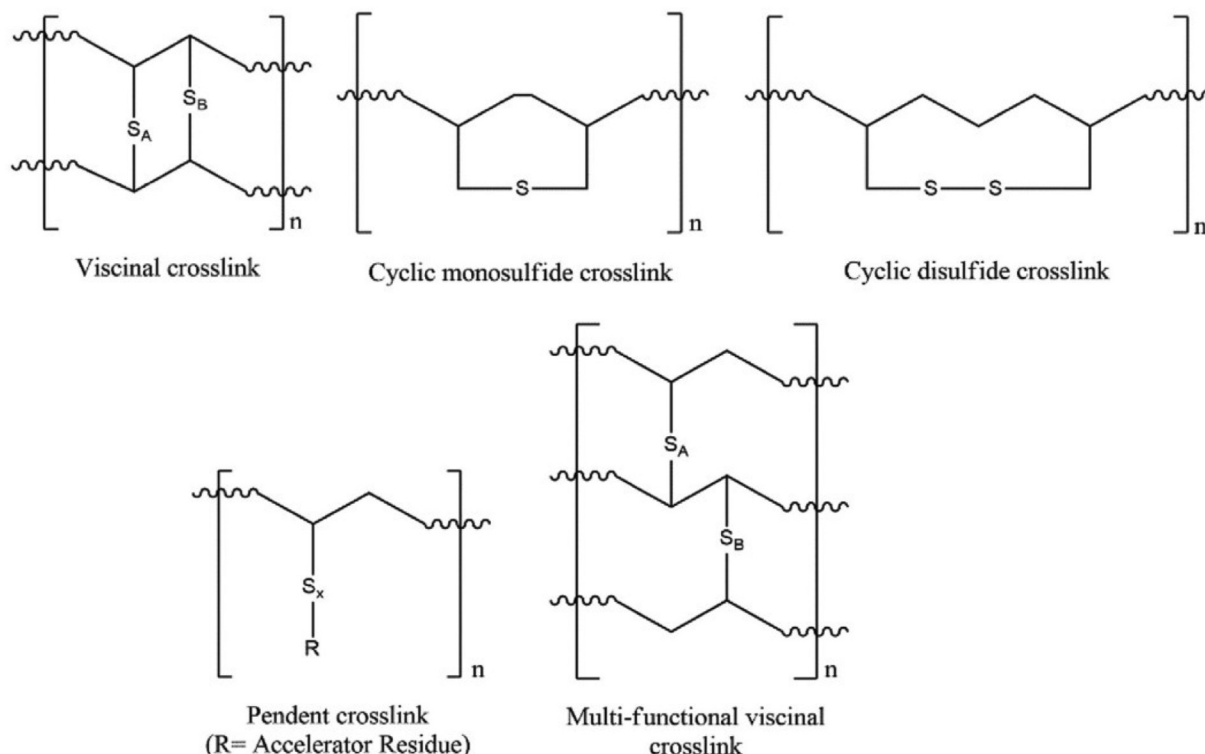| Accelerator	Chemical structure	Melting point (°C)	Vulcanization speed
N-cyclohexyl-2-benzothiazole sulfenamide (CBS)		97–105 °C	Fast delayed action
Tetramethylthiuram disulphide (TMTD)		156–158 °C	Ultra-fast
M-tert-butyl-2-benzothiazole sulfenamide (TBBS)		107–112 °C	Fast delayed action
2-Mercaptobenzothiazole (MBT)		177–181 °C	Semi ultra-fast

Fig. 1. Additional crosslinking types in rubber vulcanization (duplicated from Ref. [8]).

(reversion), which is favorable for tire applications. This owes to their chemistry, where the excess sulfur leads to the formation of mainly poly-sulfidic bonds ($-S_x-$, x > 2). On the other hand, EV provides vulcanizates with lower tensile strength but higher flexural stiffness due to a prevalence of mono-sulfidic (C–S–C) and di-sulfidic (C–S–S–C) bonds. Intermediate properties are found for SEV, characterized by intermediate A/S.

The single mono-, di- and poly-sulfidic bonds can be arranged in many complex ways, some of which are illustrated in Fig. 1. Understanding the chemical reaction mechanism leading to the formation of these crosslinking structures provides the tools to finely tune the properties of the vulcanizate. The aim of vulcanization should be to establish crosslinks within the rubber network in a certain and controlled way, to produce vulcanizates with the desired properties. However, although such a process has been employed for nearly two centuries, the details of its mechanisms and the influence of all the involved parameters have yet to be fully understood [8].

2.2. Reclaiming and devulcanization

Because of the tridimensional macromolecular network held together by strong covalent bonds and the specific composition including several additives and fillers, recycling rubber materials is a technological challenge [17]. For example, a tire is a composite made of several types of crosslinked synthetic and natural rubbers, particulate fillers (silica, carbon black, etc.), chemical additives (sulfur, oils, etc.), and textile and/or metal reinforcements [32].

Any procedure in which vulcanized rubber waste is transformed into a state in which it can be mixed with virgin rubber, processed, and vulcanized again is called reclaiming or reclamation [46]. Reclaiming has a high potential in terms of recycling rubber waste products, as it allows breaking the starting permanent

tridimensional network and decreasing the molecular weight sufficiently to achieve plasticity and reprocess the scrap rubber. However, aspecific reclaiming mostly leads to degradation, due to the cleavage of carbon-carbon (C–C) bonds on the rubber backbone that makes impossible to reobtain the initial macromolecules. Much more desirable is devulcanization, i.e., the selective cleavage of the intermolecular sulfidic bonds, such as carbon-sulfur (C–S) and/or sulfur-sulfur (S–S) bonds, which breaks down the tridimensional network without main chain scissions and degradation of the polymer (Fig. 2) [22]. However, such selectivity is difficult to achieve, since the energies needed to break the target S–S and C–S bonds (227 and 273 kJ/mol, respectively) are only slightly lower than that required to break the C–C bonds (348 kJ/mol) [47]. Moreover, synthetic rubbers are more difficult to be devulcanized than natural rubber (NR), which may be due to the different structures of the polymer chain and/or the different type, distribution, and density of the crosslink sites. For all the rubber types, the higher the selectivity of the devulcanization process, the better will be the mechanical properties of the devulcanized and revulcanized material.

The various devulcanization processes employ any of the typical methods outlined in Fig. 3, such as opening by oxidation, by heat or shear, nucleophilic reagents, rearrangement, and substitution.

2.3. Evaluating and monitoring the devulcanization process

During devulcanization, it is fundamental to investigate the specificity of the process and the mechanisms of network breakdown. According to a theory developed by Horikx [49], the rate of increase of the soluble (sol) fraction of the rubber as a function of the cross-link density of the remaining insoluble (gel) fraction is different for cleavage of C–S and C–C bonds. Thus, measuring the sol fraction and crosslinking density yields an indication of the dominant mechanism of network breakdown [46].
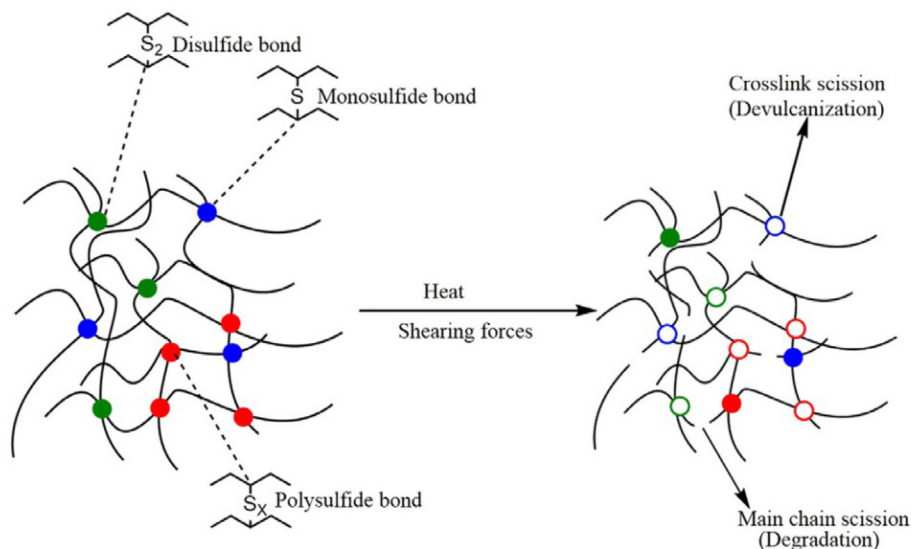
Fig. 2. Schematic representation of degradation and devulcanization processes in a crosslinked rubbery material (duplicated from Ref. [11]).
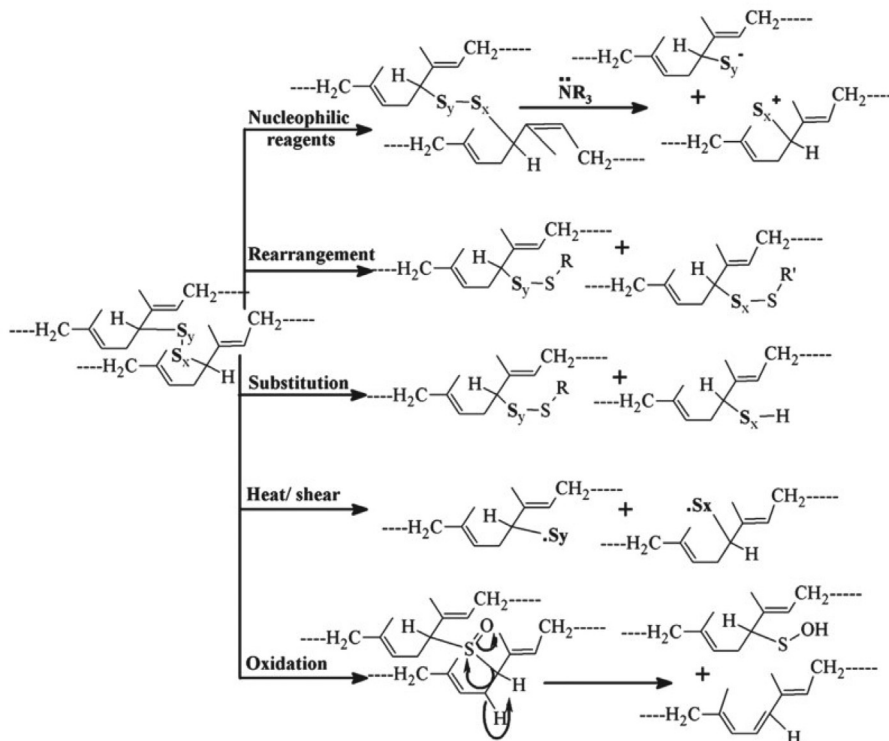

Fig. 3. General principles employed for crosslink scission in devulcanization processes (duplicated from Ref. [48]).

According to ASTM D 6814 [50] the sol fraction can be determined by extracting the soluble part via swelling methods, while the remaining insoluble part can be considered as the gel content. This method must be carried out after pre-removal of the low-molecular-weight substances such as processing oil, which can be done via a Soxhlet apparatus with acetone as the extraction solvent for at least 12 h. After Soxhlet extraction, the obtained sample can be dried to a constant weight (m_1). A small amount of sample can be then immersed in toluene for 72 h at room temperature. After swelling, the sample is taken out and weighed instantly after blotting the solvent out of the surface. Finally, the sample can be placed in an oven at 80 °C to reach a constant weight (m_2). The sol fraction $S(\%)$, proportional to the extension of network breakdown [51,52], is then calculated via Equation (1):

$$S(\%) = \frac{m_1 - m_2}{m_1} \cdot 100 \tag{1}$$

The crosslink density (V_e) of the gel part of the samples can be determined using the Flory-Rehner approach as described in Equation (2):

$$V_e = \frac{-\left[\ln(1 - V_r) + V_r + XV_r^2 \right]}{\left[V_1 \left(V_r^{1/3} - V_r / 2 \right) \right]} \tag{2}$$

where X is the interaction parameter between the solvent and the rubber (e.g., for the toluene-NR system, $X = 0.393$) and V_r and V_1 are the rubber volume fraction in the swollen sample and molar volume of the solvent, respectively. The degree of devulcanization ($D\%$) can be calculated using Equation (3):

$$D\% = \frac{V_{e2} - V_{e1}}{V_{e1}} \cdot 100 \tag{3}$$

where V_{e1} and V_{e2} are the crosslink densities before and after devulcanization, respectively.

Horikx's theory can be used to determine the relationship between sol fraction after degradation of the network structure of the rubber and the relative decrease in crosslink density [49]. Horikx investigated two extreme cases: when main chain scission occurs (cleavage of C–C bonds), the decrease in crosslink density is calculated with Equation (4):

$$1 - \frac{V_{e2}}{V_{e1}} = 1 - \frac{(1 - S_2)^2}{(1 - S_1)^2} \tag{4}$$

where S_1 and S_2 are the sol fractions before and after the devulcanization, respectively. On the other hand, when crosslink scission occurs (cleavage of C–S or S–S bonds), the relative decrease in crosslink density is calculated using Equation (5):

$$1 - \frac{V_{e2}}{V_{e1}} = 1 - \frac{\gamma_2 (1 - S_2)^2}{\gamma_1 (1 - S_1)^2} \tag{5}$$

where the parameters γ_2 and γ_1 are the crosslink index and refer to the average number of crosslinks per chain in the residual gel before and after the devulcanization, respectively. Horikx's theory is restricted in the two mentioned cases and cannot explain the intermediate situations. An example of application of the Horikx's theory is found in the work of Sabzekar et al., in which chemical devulcanization of sulfur-cured NR was performed with benzoyl peroxide (BPO) as a devulcanizing agent [50]. By plotting the experimental sol fractions of the devulcanized rubber as a function of the decrease in crosslink density and comparing them with Horikx's theoretical trends (Fig. 4), it is evident that the experimental points are located on the dashed curve, indicating a selective crosslink scission.

However, some of the main polymer backbones are always broken during devulcanization and, thus, the properties of the devulcanized material are always different from those of the virgin rubber [9]. Hence, reclaimed/devulcanized rubber can only be used for less demanding functions and, according to the application, it can be used either as obtained or mixed in different amounts with virgin rubber or other polymers, where it can significantly reduce the cost of the final products (see Chapter 4).

2.4. Introduction to devulcanization methods

The history of devulcanization has seen the rise and development of several methods, but only few of them succeeded in being robust and credible enough for the industrial scale up. Most of them are mostly dry processes, quickly implementable on normal rubber processing equipment [48].

Devulcanization can be carried out by different means, such as chemical [50], mechano-chemical [53], ultrasonic [54], microwave
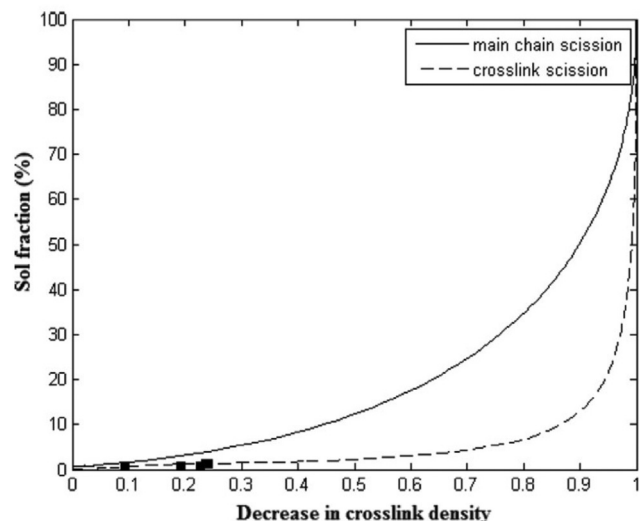

Fig. 4. Sol fraction of chemically devulcanized NR (process time = 2 h, temperature = 80 °C) as a function of the relative decrease in crosslink density (duplicated from Ref. [50]).

[51,55], biological [56], thermo-mechanical [57], and supercritical CO_2 [58]. The most promising are microwave and ultrasonic devulcanization, because they are dry and eco-friendly techniques that can be easily implemented, allow for high productivity, and yield devulcanized products with good properties. However, the process conditions must be carefully chosen to achieve selective bond breaking and avoid degradation [17]. The various devulcanization processes are discussed in Chapter 3.

3. Devulcanization technologies for rubber-based products

As reported in Chapter 2, many existing and novel devulcanization methods have been explored that can be grouped into 3 major categories: physical, chemical, and biological devulcanization, as illustrated in Fig. 5. For all the devulcanization technologies, understanding the resulting degree of devulcanization, the soluble content, and the crosslinking density is crucial [8].

Table 3 reports a representative list with some examples of the most important rubber devulcanization methods, indicating the devulcanizing agent, the rubber type, the processing parameters, and the properties of the re-vulcanizate in terms of the tensile strength (T_s) and strain at break (ε_b) [59].

3.1. Thermal devulcanization

Thermal devulcanization, which is the oldest devulcanization technique invented nearly 150 years ago [26], refers to a method to devulcanize rubber by providing energy in the form of heat [8]. Thus, it is important to know the type and energy of the chemical bonds in the sample, to provide the right amount of energy to break just the desired bonds. For instance, the energies required to cleave C=C, C–C, C–S, and S–S bonds are 614, 347, 273, and 227 kJ/mol, respectively [52]. For effective devulcanization, only C–S and S–S bonds are to be cleaved, but, as mentioned in the previous sections, the energy required to break C–S and S–S bonds is very similar to that needed to break the C–C bond, which poses a challenge to the selectivity of the devulcanization process.

For example, the thermal devulcanization of waste tire rubber (WTR) starts with the removal of fibers and steel. Then, the rubber compound is milled to obtain ground tire rubber (GTR), autoclaved
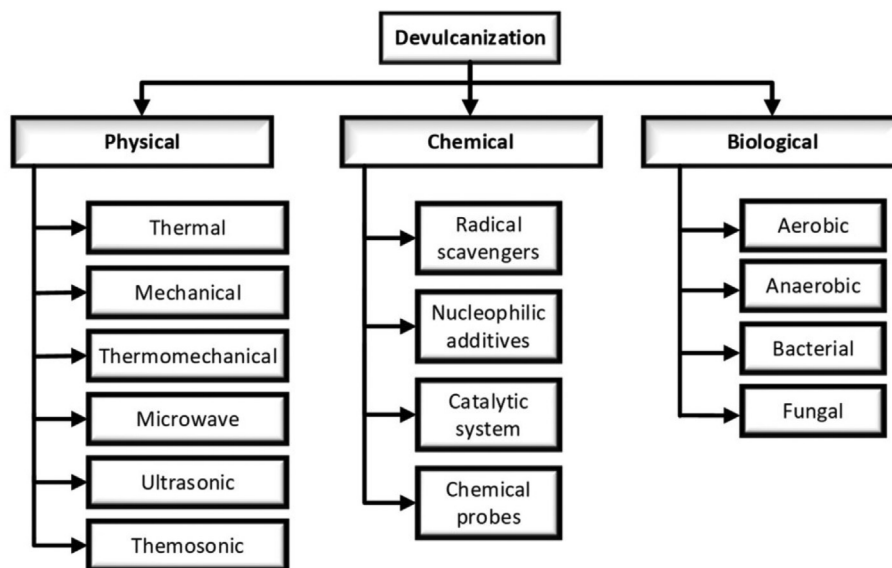
Fig. 5. Overview of the devulcanization technologies for rubber (duplicated from Ref. [8]).

Table 3
Examples of some devulcanization techniques with common processing parameters and typical thermo-mechanical properties of the resulting revulcanizates (adapted from Ref. [59]).

| Process and devulcanizing agent	Treated rubber	Treatment parameters	Properties of reclaimed rubber vulcanizate	References
Thermo-mechanical	Tire waste NR/SBR	220 °C/30 rpm	—	[60]
Thermo-mechanical	Tire waste	180 °C/120 rpm	T_s = 12.9 MPa ε_b = 351%	[61]
Thermo-mechanical	Tire waste NR/SBR	180 °C/250 rpm	T_s = 4.2 MPa ε_b = 140%	[62]
Mechano-chemical Pentachlorothiophenol Hydrazine Zinc chloride	Tire waste NR/SBR	150 °C/30 rpm	T_s = 3.1 MPa ε_b = 100%	[36]
Mechano-chemical Diallyl disulphide	NR	110 °C/10 min	T_s = 12.3 MPa ε_b = 1007%	[63]
Mechano-chemical bis(3-triethoxysilyl propyl) tetrasulfide (TESPT)	NR	23 °C/40 min	T_s = 7.8 MPa ε_b = 387%	[53]
Mechano-chemical bis(3-triethoxysilyl propyl) tetrasulfide (TESPT)	SBR	23 °C/40 min	T_s = 9.6 MPa ε_b = 121%	[64]
Mechano-chemical tetramethyl thiuram disulphide (TMTD)	SBR	23 °C/40 min	—	[65]
Mechano-chemical Thiobisphenols	Tire waste	200 °C	T_s = 5.9 MPa ε_b = 325%	[66]
Mechano-chemical Thiosalicylic acid	NR	140 °C/30 min	—	[67]
Mechano-chemical Benzoyl peroxide	NR	80 °C/30 min	—	[68]
Mechano-chemical 1,8-diazabicycloundecene (DBU)	Tire waste	30 rpm	T_s = 13.6 MPa ε_b = 390%	[69]
Mechano-chemical 2-butanol	Tire waste	30 °C/40 min 10 MPa	—	[70]
Ultrasonic	SBR	120 °C/20 rpm 3000 W/20 kHz	T_s = 1.6 MPa ε_b = 198%	[71]
Ultrasonic	Tire waste	120 °C/20 rpm 3000 W/20 kHz	T_s = 10.5 MPa ε_b = 250%	[72]
Ultrasonic	Tire waste NR/SBR/BR	120 °C/20 rpm 3000 W/20 kHz	T_s = 8.7 MPa ε_b = 217%	[73]
Microwave	SBR	900 W/3 min	T_s = 2.5 MPa ε_b = 86%	[74]
Microwave Diphenyl disulphide	Tire waste	900 W/3 min 240 °C/2000 MHz	T_s = 10.0 MPa ε_b = 226%	[75]
Mechanical Supercritical CO_2	SBR	240–260 °C 50 rpm	T_s = 3.3 MPa	[76]
Mechano-chemical Supercritical CO_2 2-butanol	SBR	270 °C/6.2 MPa 20 min 50% CO_2	—	[77]
Mechano-chemical Subcritical water Peroxide Alkylphenol polysulfide	Tire waste SBR	200 °C/1.6 MPa 1000 rpm	—	[78]
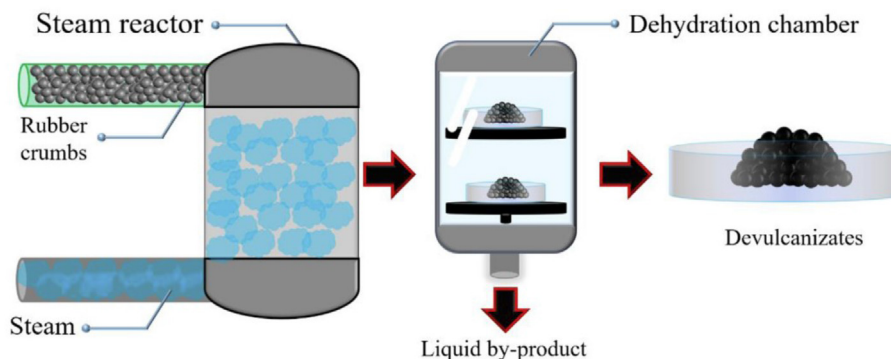
Fig. 6. A representative scheme of thermal devulcanization process (duplicated from Ref. [8]).

using steam at 180–260 °C and 15 bar for 12 h, and dried, as shown in Fig. 6. Although this process is effective in cleaving bonds, it is not selective over crosslink breakage, which leads to devulcanized rubber of low quality [79].

Moreover, as noticed by De et al. [26], this process impacts almost exclusively NR, while SBR, one of the main types of rubber incorporated in tires, is left unaffected, which could be due to its higher thermal stability. Additionally, this treatment increases the material's hardness, thus hindering the overall treatment and ultimately resulting in a low devulcanization. These drawbacks are overcome by coupling thermal devulcanization and other devulcanization methods, where heat is used as an aiding factor for bond scission. One of these combined techniques is thermo-mechanical devulcanization.

3.2. Mechanical and thermo-mechanical devulcanization

Thermo-mechanical methods are the most widely used in industrial applications. In these systems, the rubber crumb is subjected to mechanical shearing and high temperature, approx. 200 °C, brought by internal friction as well as an external heat source. In some cases, solvents such as water, oils, hexane, or supercritical fluids can be added before or during the grinding to facilitate the process, solubilize the small chains and obtain swollen rubber [59].

Thermo-mechanical devulcanization has been largely studied during the last decades because it generally yields high devulcanization degrees [59].

A mechanism of thermo-mechanical devulcanization was proposed by Mouri et al. [80] and is illustrated in Fig. 7. First, the application of heat is sufficient to break the weaker poly-sulfidic

links but not the stronger mono-sulfidic bonds, which are then cleaved by applying shear stresses. This mechanism also leads to the breakage of some main chains, which may result in the formation of carbon disulfide (CS_2), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S).

The majority of devulcanization methods in this field involves the simultaneous application of heat and mechanical stress. However, in principle, it is possible to devulcanize rubber only by applying stress, without increasing the temperature [48]. An example is represented by the patented "High Shear Mixing" (HSM) devulcanization technology, aimed at devulcanizing rubber production scrap through a fully mechanical process. In fact, since, in some conditions, sulfur bonds are weaker than carbon-carbon bonds, the sulfur crosslink points should break preferentially, if stress is correctly applied. This process, claimed to apply to any kind of rubber production waste, involves the use of ad-hoc designed equipment that moves the material through a series of high-stress and relaxation zones, whilst the integrated cooling system ensures that the material remains at controlled temperatures (max 80 °C) during the mixing cycle [81].

The most common mechanical and thermomechanical devulcanization technologies can be divided into batch mixers (open or internal) or continuous extruders, but other equipment has also been presented. These technologies are described in the following subsections.

3.2.1. Batch mixers

Devulcanization based on batch mixers is relatively simple, low-cost, and environmentally friendly, generally performed without external heating or any chemicals [48]. Batch mixers are divided into (i) open, two-roll mills or Brabender mixers, and (ii) close,
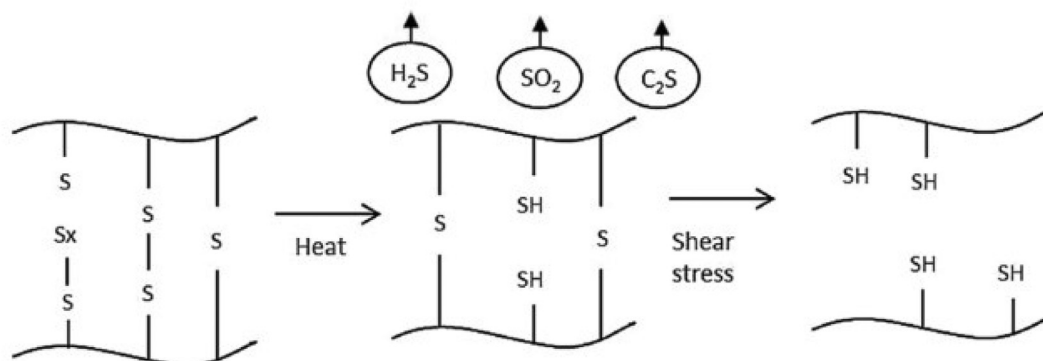

Fig. 7. Mechanism for the crosslinking breakage in a thermo-mechanical devulcanization process (duplicated from Ref. [80]).
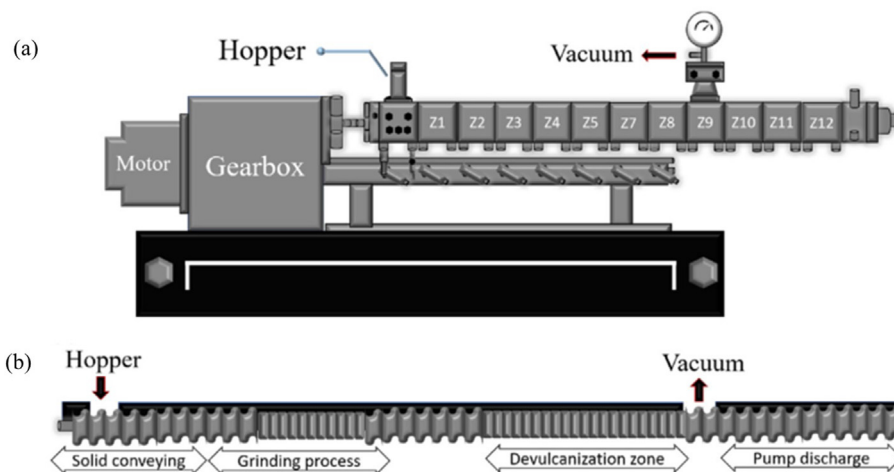
Fig. 8. Representative twin screw extruder for rubber devulcanization. (a) Main scheme of the whole extruder, (b) screw configuration (duplicated from Ref. [47]).

Lancaster-Banbury or the internal batch mixers. In both cases, crumb rubber is devulcanized through intense mechanical shearing for some minutes, in which the temperature can reach 250 °C [82]. To prevent excessive heating and degradation of the polymer chains, a technique has recently been proposed that involves a water-cooled two-roll mixing mill, which was used to devulcanize carbon black (CB)-filled NR [83]. However, the resultant degree of devulcanization was quite low, between 20 and 37.8%.

3.2.2. Extruders

The most common mechanical devulcanization technique is represented by the Ficker's or single/twin-screw extruder method. This technology is widely used because extruders are commonly and readily available in rubber manufacturing industries and allow for a continuous and high-yield devulcanization process. Fig. 8(a and b) illustrates the schematics of a twin-screw extruder. The most important parameters affecting the devulcanization outcome are the barrel temperature, the screw configuration, and the screw speed. The internal temperature must be kept above 50 °C, below which the devulcanization rate is too low, and 400 °C, above which the degradation and polymer scission are not negligible [84].

The fundamental importance of optimizing the screw speed and the barrel temperature for proper devulcanization is highlighted in many research works, which correlate these two processing parameters with the devulcanization quality and yield also with response surface methodology (RSM) optimization [85—88]. It has generally been observed that the selectivity of crosslink scission decreased as temperature increased, with a consequent increase in the C—C bond cleavage and a reduction in the mechanical performance of the revulcanizate [52], as also shown in the exemplificative Horikx diagram reported in Fig. 9 [47]. This indicates that the quality of the devulcanization increases at moderate operating conditions; for example, for the devulcanization of GTR in a twin-screw extruder with an L/D ratio of 40, the optimal parameters were 220 °C and 120 rpm [60].

Moreover, it was shown that a plasticizing system that induces high shear stresses is preferable, as it allows the use of a lower devulcanization temperature [57,62]. Also, the degree of sulfidic selectivity was seen increasing with the addition of suitable devulcanizing agents or processing aids [87]. For example, Li et al. thermo-mechanically devulcanized GTR with the help of waste engine oil (WEO) in a 150 rpm and 3 kg/h twin-screw extruder. The temperature of the barrel varied between 150 and 280 °C. Treated
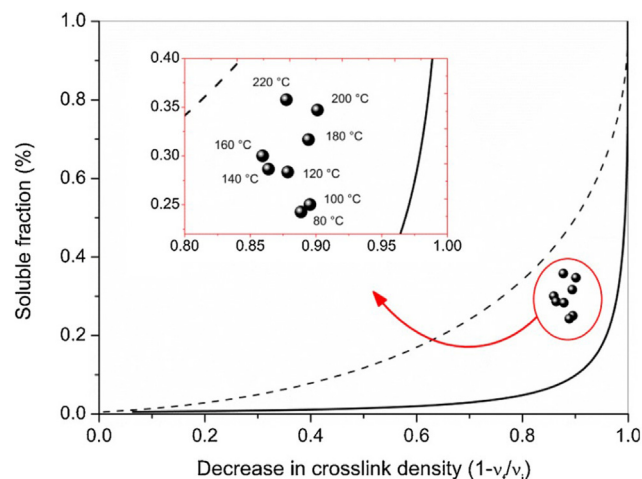

Fig. 9. Horikx diagram for the thermo-mechanical devulcanization in an extrusion process on NR at different barrel temperatures (duplicated from Ref. [47]).

GTR resulted in a decrement of gel fraction as WEO content increased, which could be related to the increasing degree of devulcanization and decrease in crosslink density. Even in this case, the authors concluded that low-bound barrel temperatures between 180 and 210 °C were preferred as it gives better rheological properties (e.g., dynamic viscosity, tensile, storage modulus [89]). On the other hand, de Sousa et al. indicate that there should not be a too high degree of soluble fraction during devulcanization, as it will significantly shift the data point within the Horikx curve upwards, indicating greater polymeric scission and reducing the degree and quality of devulcanization [90].

3.2.3. Other approaches

In a different approach from those presented so far, Diaz et al. [44] devulcanized GTR in a unique metallic-cone-like high shear mixer. In this setup, one cone was static, while the other rotated and pressurized the system, which was cooled by a stream of cold water. The authors fed the instrument with large chunks of GTR, which experienced size reduction and decreased crosslink density at the same time. However, such reactions mainly occurred at the rubber particle surface, which classifies this technique as a surface activation phenomenon rather than a proper bulk devulcanization.

Fig. 10. General representation of the process of high-pressure high-temperature devulcanization (duplicated from Ref. [48]).

Another technology is the so-called High-Pressure High-Temperature Sintering (HPHTS), represented in Fig. 10, which allows the recycling of vulcanized rubber powder by applying heat and pressure [48]. The applied pressure (0.5 MPa–26 MPa) compresses the particles and increases the interparticle contact, while the temperature (80 °C to 240 °C) promotes the cleavage of cross-link bonds and likely also some main chain bonds. This in turn allows the formation of new covalent bonds at the particle interface, thereby sintering the particles into a single piece. The authors found that the mechanical properties of the sintered rubber were comparable with those of conventionally manufactured rubbers.

Thermo-mechanical devulcanization can be implemented with the aid of different devulcanizing agents, to promote the further scission of sulfidic bonds. In these cases, the process is called mechano-chemical devulcanization [17], which will be described in Section 3.6.

3.3. Ultrasonic devulcanization

Ultrasonic devulcanization is one of the most interesting and convenient devulcanization processes, as it allows a high degree of devulcanization and precise control of the properties of the devulcanizates. This type of devulcanization is fast and does not involve chemical solvents, but it requires specialized technological equipment, which still hinders its large-scale application [17].

Ultrasonic methods exploit mechanical waves at high frequencies to produce extension-compression stresses and cavitation bubbles in the medium, which provide enough energy to break C–S and S–S bonds [59]. However, under pressure and temperature, the ultrasonic waves could also break the carbon backbone chains, which is why the test conditions must be carefully selected. Fig. 11 shows the typical ultrasonic treatment setup, i.e., an ultrasonic extruder, which can be located at the end, as in this case (end-extruder), or in the middle (mid-extruder). Different setups are also available (e.g., ultrasonic probe and water bath) [8].

The first patent on rubber ultrasonic devulcanization was filed by Pelofsky et al., in 1973 [91]. In the following years, Isayev et al. [72] and Yu Levin et al. [71] investigated the continuous ultrasonic devulcanization of GTR and SBR in an extruder. In this process, an ultrasoni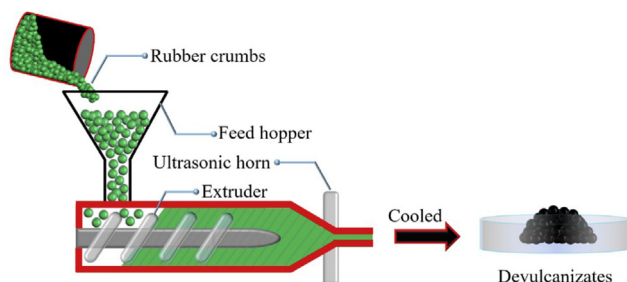c horn was added to one of the extruder zones, allowing a continuous devulcanization treatment. The process led to partial devulcanization but also partial degradation of the polymer chains. Therefore, the authors concluded that the ultrasonic devulcanization required local energy concentration, which would have allowed increasing the energy density of the ultrasonic field in the vicinity of the collapsing cavity, thereby breaking chemical bonds according to their energy level. Such energy concentration was proposed to be the most suitable to initiate devulcanization, due to the lower bond energy of the crosslinks compared to that of the C–C bonds [48]. After the devulcanization treatment, the rubbers were revulcanized and the mechanical properties of the resulted materials were comparable to those of the virgin rubber. This was found also by other authors for other rubber systems. For example, Fig. 12 [92] shows the mechanical properties of ultrasonically devulcanized unfilled NR after revulcanization, as a function of the barrel temperatures and ultrasound amplitude. The tensile strength decreased with increasing ultrasound amplitude, whereas the elongation at break was comparable with that of the original sample [92].

In 2004, Yun et al. focused on the recycling of carbon black (CB)-filled EPDM rubber in a grooved barrel reactor. A small devulcanization proportion was obtained because a part of the ultrasonic energy was used to break CB-EPDM links, but this problem was solved by increasing the ultrasound amplitude [54]. Other authors also demonstrated that the initial molecular weight distribution [93], the initial size of rubber particles [94], and the ultrasonic amplitude [95] strongly affected the final devulcanization degree. Yun et al. also performed a comparative study between two types of ultrasonic reactors, i.e., a coaxial and a barrel reactor, to evaluate

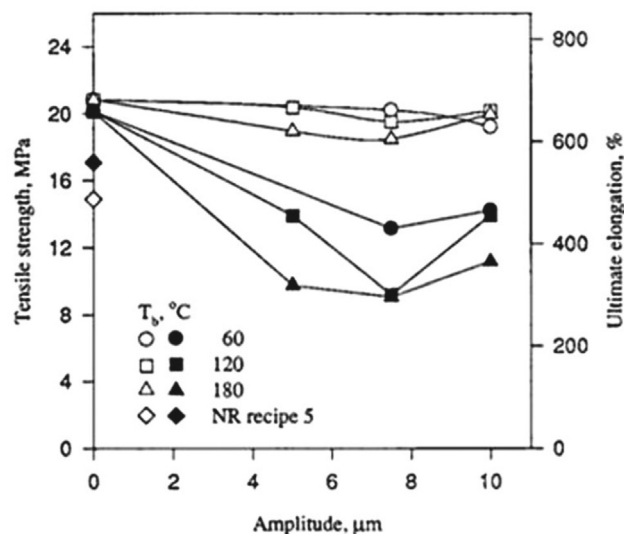**Fig. 11.** Typical ultrasonic extruder devulcanization setup (duplicated from Ref. [8]).

Fig. 12. Tensile strength (closed symbols) and strain at break (open symbols) of revulcanized NR vulcanizates after ultrasound devulcanization performed at different ultrasound amplitudes and barrel temperatures (T_b) (duplicated from Ref. [92]).
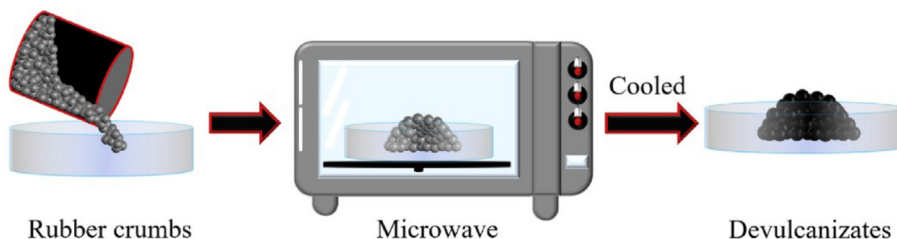
Fig. 13. Devulcanization by microwave irradiation technique (duplicated from Ref. [8]).

the role of additional shear stresses induced by the barrel reactor. The barrel reactor allowed obtaining a devulcanized GTR rubber with good mechanical properties (tensile strength of 8.7 MPa, elongation at break of 217%, and modulus at 100% elongation of 2.6 MPa) and limited degradation, and these mechanical properties were evaluated as unreachable by coaxial ultrasonic devulcanization at the same flow rate [73].

Similar conclusions were made by Si et al., who demonstrated that additional shear stresses induced more crosslink breakage and decreases the gel content and Mooney viscosity on a GTR/thermoplastic elastomers blend [96]. They also pointed out that a GTR made mainly of NR was more easily degraded than a GTR rich in SBR due to the abundance of allylic structures, and that the process could be accelerated and improved by alkyl-phenol polysulfide, which prevented crosslinking reactions and improved the mechanical properties.

3.4. Microwave devulcanization

Microwave devulcanization uses microwave irradiations to cause molecular motion, thereby raising the temperature and inducing the crosslink breakage [97,98]. Unlike ultrasound devulcanization, microwave processes cannot be implemented in line with the production process (are a batch treatment). Nevertheless, they are among the most widely investigated devulcanization techniques.

Fig. 13 shows the typical microwave devulcanization treatment. The material absorbs the microwave radiation through the interaction of the oscillating electric field of microwaves with the molecular dipoles and/or charged ions present in the sample, thereby raising the temperature of the material rapidly to approx. 250–350 °C [48]. Therefore, microwave devulcanization works better with polar rubbers, or with rubbers containing polar fillers or fillers able to absorb microwaves, such as CB. As for the other devulcanization treatments, the involved energy should be carefully controlled to break only the S–S and C–S bonds [17]. The rubber reclaimed by this technique is not depolymerized and can be revulcanized, reaching properties very close to the original vulcanizate. The radiation's wavelength and frequency range from 1 to 1000 mm and 300 MHz to 300 GHz, respectively [99].

Microwave devulcanization was presented first in a patent by the Goodyear Tire & Rubber Co., who employed a frequency of 915 or 2450 MHz and energy between 325 and 1404 kJ/kg and claimed the obtainment of a material that could be revulcanized without a significant decrease in the physical-mechanical properties [100]. In fact, in this range of frequency, the energy is sufficient to cleave crosslinks but not to cleave C–C bonds. Therefore, the authors presented this process as an efficient devulcanization treatment with reduced processing time.

Further studies on microwave devulcanization of GTR demonstrated the importance of controlling the processing parameters and the reached temperature to promote the selectivity of bond cleaving and achieve a high-quality devulcanizate. Scuracchio et al.

[101] and Garcia et al. [102] highlighted that microwave treatment increased the sensitivity of GTR to thermo-oxidation, and therefore it is crucial to control the microwave exposure time and polymeric degradation in order to obtain a reclaimed material with suitable properties. De Sousa et al. [55] highlighted that the ultimate temperature reached by the material was the main responsible for the success of GTR devulcanization, as reported in Fig. 14(a). In fact, depending on the final temperature, different types of sulfur bonds can be broken. Since the GTR used in this work was made of NR and SBR, the authors could observe the effect of temperature on the two different rubber types. As shown in the Horikx diagram reported in Fig. 14(b), in the samples more exposed to the microwaves (GTR5 and GTR5.5), the NR phase underwent random scission, with the concurrent cleavage of both the crosslinks and the C–C bonds. On the other hand, the SBR phase was only subjected to the cleavage of the crosslinks, for all the investigated microwave treatments.
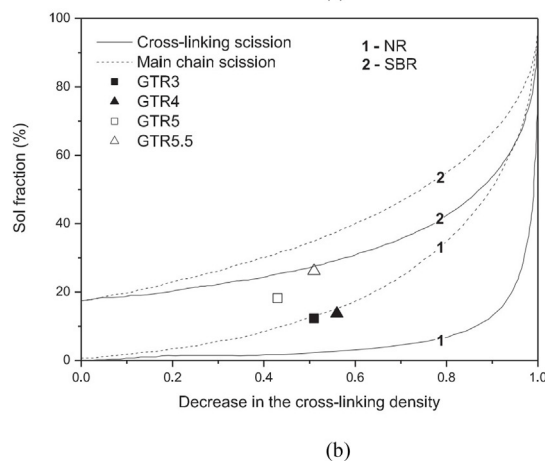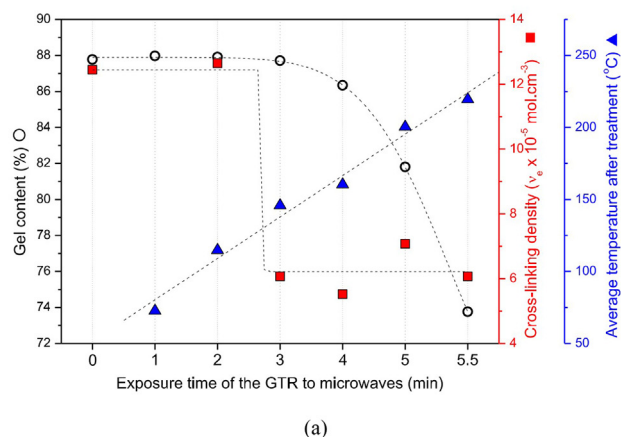

(a)

(b)

Fig. 14. (a) Gel content, cross-linking density, and average temperature after treatment as a function of the exposure time to microwaves; (b) Horikx diagrams for the different microwave treatments for the NR and SBR phases (duplicated from Ref. [55]).
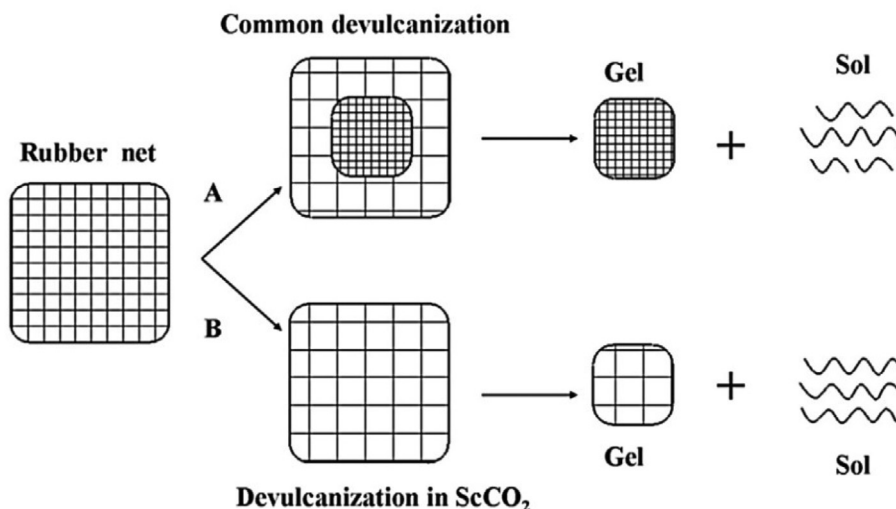
Fig. 15. Schematic representation of the differences between common and $ScCO_2$ devulcanization process (duplicated from Ref. [115]).

The very important role of the process temperature was also underlined by Simon et al. [103], who found that the repeatability and quality of devulcanized GTR are improved when the microwave process is performed in a temperature-controlled oven.

The literature also reports on the important role of nanofillers such as CB and silica in the microwave devulcanization process. Hirayama and Saron [104] showed that the microwave devulcanization of SBR can only be performed with high CB loadings, starting from 60 phr, due to the high dielectric constant of CB that absorbs electromagnetic radiation. In fact, neat SBR lacks the intrinsic dipole required for microwave absorption, while the addition of CB allows the blend to undergo microwave heating. Colom et al. [105] showed that a high SiO_2 content also favors the devulcanization of GTR.

Among the drawbacks of microwave devulcanization are the high equipment cost, the high thermal runaway possibility, hot spot issues, inefficient mixing, and high volatile organic compound (VOC) emissions and the consequent need to operate in vacuum conditions, thereby further raising the equipment cost. These drawbacks strongly hinder the wide industrial application of this devulcanization method. To improve devulcanization efficiency and reduce treatment energy, promising new approaches are being developed that combine microwave irradiation with devulcanizing agents and ionic solvents [106]. Molanorouzi et al. [75] highlighted the positive contribution of diphenyl disulfide (DD) to the microwave devulcanization of GTR, while Movahed et al. proved the efficacy of aromatic oil mixed with six different devulcanizing agents in the devulcanization of EPDM rubber. They found the highest degree of devulcanization with n-cyclohexyl-2-benzothiazole sulfenamide (CBS), hexadecylamine (HDA), and mercaptobenzothiazole (MBT) and the best tensile properties upon revulcanization with 2-mercaptobenzothiazole disulphide (MBTS) [107].

3.5. Supercritical solvents

The supercritical state is a particular state of aggregation in which there is no separation between the gas and liquid phases. Because of the absence of liquid/gas phase boundary, supercritical fluids (SCF) have no surface tension, show solvent properties similar to those of liquids, and transport properties similar to those of gases. Thus, they can dissolve solutes, are miscible with ordinary gases, and can penetrate the pores of the solids. SCFs show liquid-like density, but their viscosity and diffusivity are intermediate between those of gases and liquids [108,109].

Supercritical carbon dioxide ($scCO_2$) has been recently presented as an innovative and green devulcanization medium [58], due to its chemical inactivity, non-toxicity, non-flammability, and low cost. Its low-temperature and low-pressure critical point ($\sim$31.1 °C; $\sim$7.4 MPa) allows the use of simple equipment, and excess $scCO_2$ can be easily removed by releasing pressure. The role of $scCO_2$ is not yet completely understood, but it is probably related to the fact that $scCO_2$ can swell vulcanized rubber. In this way, $scCO_2$ stretches the sulfide links, making them easier to break, and favors the penetration of devulcanizing agents, allowing devulcanization to take place in the bulk material [17].

Most of the literature on this topic deals with the devulcanization with $scCO_2$ in autoclaves and reactors. The $scCO_2$-assisted devulcanization has been studied for various rubber systems, such as unfilled polyisoprene rubber [110], unfilled and CB-filled NR [111,112], butyl rubber [113], and GTR [114,115], mainly using diphenyl disulfide (DD) as a devulcanization reagent. These works proved that devulcanization was faster and more effective in presence of $scCO_2$ given the same amount of DD, since DD can be dissolved in $scCO_2$ and reaches the bulk rubber more easily. Therefore, the DD-promoted devulcanization reaction occurs not only on the surface but also inside the material, which results in lower chain scission, higher molecular weight, and lower polydispersity index of the sol, as exemplified in Fig. 15 [115].

These studies also evidenced that the beneficial effects of $scCO_2$ were not affected by the presence of fillers such as CB [111], while the amount of DD was proven not only to affect the devulcanization process, but also the quality of the devulcanizate and the mechanical properties of the subsequent revulcanizate. Higher DD concentrations were associated with revulcanizates with higher strain at break and lower Young's modulus [114].

Other works have investigated a combined devulcanization method that includes $scCO_2$ in the mechanical devulcanization in an extruder [116,117]. These authors found that the presence of $scCO_2$ positively contributed to the continuous extrusion devulcanization of various rubbers such as EPDM and GTR, but a high sol fraction and a high crosslink cleavage are reached only after optimization of the extrusion process parameters, the most important of which are the $scCO_2$ flow rate, temperature, screw speed, and feed rate.

Other subcritical, near-supercritical, and supercritical solvents have also been investigated, such as water, ethanol, and toluene, which have been applied alone or together with devulcanization
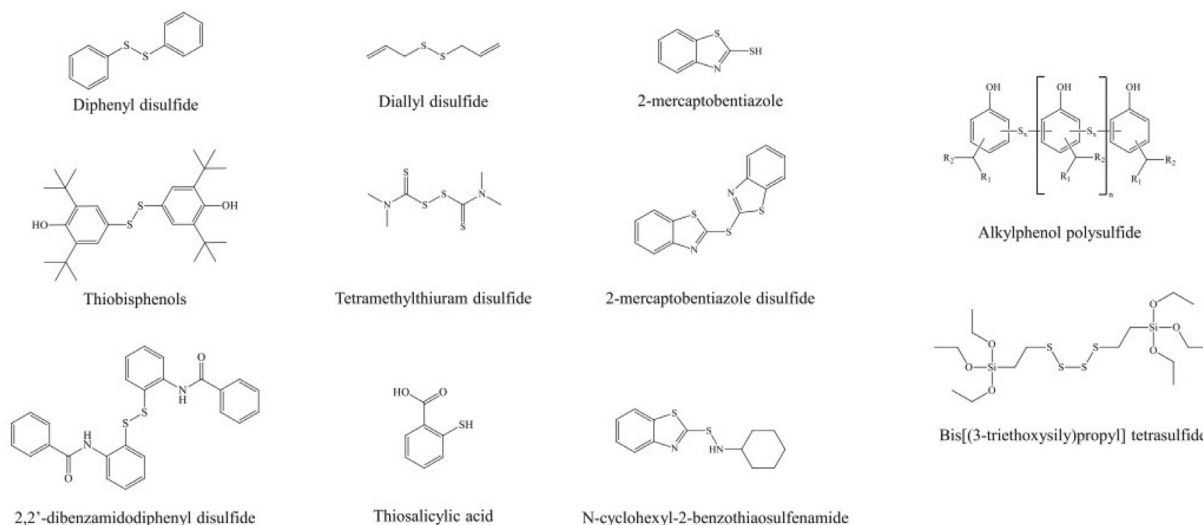
Fig. 16. Some of the most important sulfides and mercaptans used in the chemical devulcanization of rubber (duplicated from Ref. [59]).

agents such as DD [118–121]. For example, subcritical water was employed as a swelling agent during the mechano-chemical devulcanization of SBR-based ground tire in a twin-screw extruder. Subcritical water successfully promoted devulcanization preventing oxidative degradation, which improved the mechanical properties of the final products. Although the devulcanization level using solely subcritical water allowed reaching satisfying mechanical properties of the revulcanizates, better results were obtained with the addition of chemical devulcanization agents, which enabled to reach tensile strength and elongation at break retention of 85.4% (20.5 MPa) and 201% (715.6%) respectively.

3.6. Chemical devulcanization

Chemical devulcanization, applied since 1960s and nowadays among the most diffused devulcanization techniques, employs various organic and inorganic chemical compounds that selectively break the carbon-sulfur and/or sulfur-sulfur bonds. Generally, chemical devulcanization is aided by a supply of thermal and mechanical energy to accelerate the treatment [48]. Most chemical devulcanization methods are batch processes, in which the ground waste rubber is mixed with the chemical agents, at a controlled temperature and pressure. Many types of chemical compounds can be used, such as sulfides, mercaptans, amine-based compounds, inorganic solvents such as propane thiol/piperidine, triphenyl-phosphine (PPh$_3$), trialkyl phosphites, lithium aluminum hydride, and methyl iodide, organic solvents as alcohols and ketones, and ionic liquids (ILs).

The drawback is related to the toxicity of the chemicals This problem could be partially mitigated by employing less toxic, more environmentally friendly non-sulfured compounds, which are currently being investigated but are not yet very widely diffused. The chemical reaction of chemical devulcanization is complex and it is not fully understood for all the involved solvents [17]. A comprehensive explanation of the mechanisms involved in the chemical devulcanization of rubber is reported in the review of Joseph et al. [48].

3.6.1. Sulfides and mercaptans

The most widely used chemicals in devulcanization processes are sulfides and mercaptans such as disulfides (such as DD, thio-phenols, and their zinc salts), thiol-amine reagents, hydroxide or chlorinated hydrocarbons, added typically in concentrations of 0.5–10 wt%. Some of the most important sulfides and mercaptans used in tire reclaiming are reported in Fig. 16.

Although all the chemical reactions involved in chemical devulcanization are not yet well understood, some mechanisms have been proposed for the devulcanization with DD, one of the most used devulcanization agents. As reported in Fig. 17, at high temperature DD initiates an oxidative breakdown of the sulfur crosslinks and reacts with the radicals, while it may also degrade the rubber by breaking some C–C bonds. This reaction releases some by-products, such as hydrogen sulfide (H$_2$S) and thiols (R–SH) [122]. Because of the thermal stability of monosulfide bonds, such bonds are not affected in these conditions, but a further temperature increase would lead to increased degradation of the main chain, implying poor mechanical properties of the resulting product [59].

Very often, chemical devulcanization is combined with other devulcanization techniques. For example, Jana et al. worked on a mechano-chemical process of NR devulcanization, assisted by diallyl disulfide and process oils. The mechanical properties of the revul-canizate were retained, but only at higher concentrations of diallyl disulfide, which was proven to limit the main chain degradation during devulcanization [63]. Diallyl disulfide was used by De et al. [123], who performed a mechanochemical devulcanization on NR optimized at 60 °C for 35 min. Other chemical reagents employed in mechano-chemical treatments were bis(3-triethoxysily propyl) tet-rasulfide (TESPT), which was also proven effective as a nanosilica dispersing agent [53], tetramethylthiuram disulfide (TMTD) [124], 2,2-dibenzamidodiphenyldisulphide [125], mercaptobenzothiazole [126], thiobisphenols [66], and thiosalicylic acid [67].

Sulfide chemicals were also used in combination with other treatments, such as microwave treatments and supercritical fluids. For example, Molanorouzi and Mohaved experimented with several sulfide-containing chemicals with aromatic oils and a microwave process to reclaim waste tire rubber. The optimal parameters were 6 phr of diphenyl disulfide and 30 phr of aromatic oils at 240 °C for 3 min. The process yielded a sol content of 15% and a final crosslink density of 81 mol/m^3 [75]. As mentioned in Section 3.6, diphenyl disulfide has also been used in combination with scCO$_2$. For example, NR was devulcanized with diphenyl disulfide and scCO$_2$ at 180 °C under a 10 MPa pressure for 60 min. With such a treatment, the crosslink density decreased of one order of magnitude, from $1.93 \cdot 10^7$ mol/L to $0.85 \cdot 10^6$ mol/L [111].
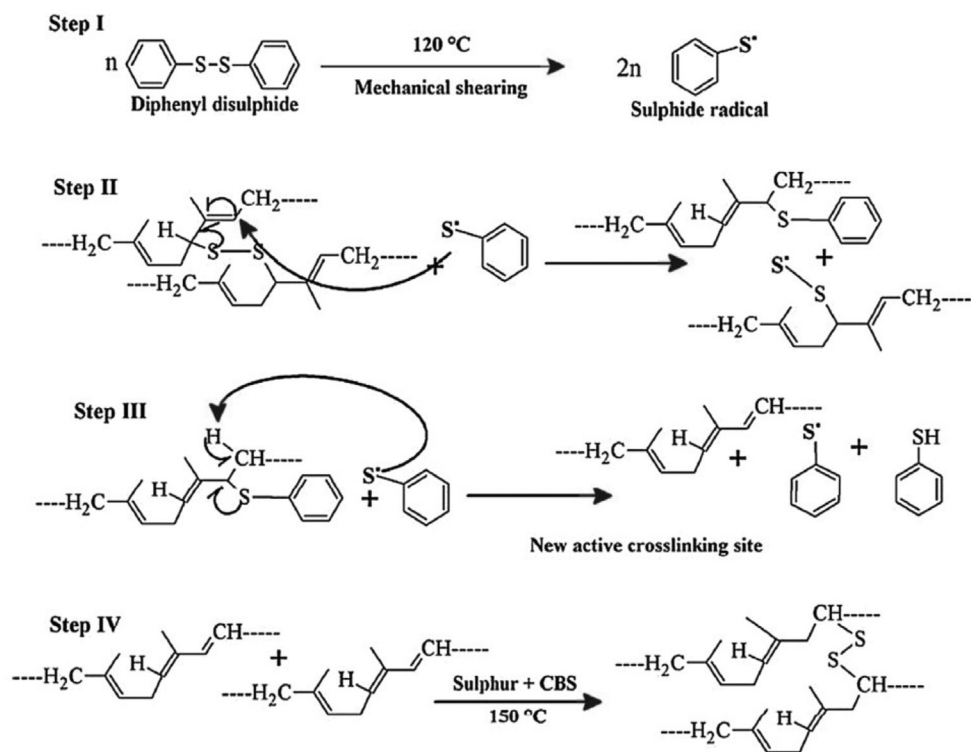
Fig. 17. Mechanism of actions of diphenyl disulfide during devulcanization (duplicated from Ref. [122]).

3.6.2. Amine based devulcanization

Amine-based devulcanization was first patented in 2003 by Van Duin et al. [127]. Their work showed that amines might help the high temperature devulcanization, which is mainly radical. They also evidenced that the treatment is preferably done with 0.1–15 wt% of amine compounds and works only with the amines with at least an α-H atom, which reduced the crosslink density mainly by crosslink scission [128]. As for sulfides and mercaptans, also amine-based chemicals are often used in combination with other devulcanization treatments.

Dijkhuis et al. employed hexadecylamine (HDA) as a devulcanizing agent for EPDM in thermal devulcanization and reported a reduction of crosslink density of 50% in the temperature range 225–275 °C, even though mainly di- and poly-sulfide bonds were cleaved. Devulcanizates were then blended with virgin EPDM and the revulcanized showed good mechanical properties compared to the neat virgin vulcanizate [129]. HDA and other amine compounds such as tetraethylenepentamine (TEPA) have also been combined with ultrasonic or mechanical devulcanization, where they allowed the treatment to be performed at lower temperatures [84,130].

3.6.3. Other organic and inorganic compounds

Other kinds of catalysts, inorganic, and sulfur-free organic compounds were developed in the past decades. Among them are propane thiol/piperidine, Grubbs catalysts, PPh₃, trialkyl phosphites, lithium aluminum hydride, methyl iodide, 1,8-diazobicyclo [5.4.0]undec-7-ene (DBU), and benzoyl peroxide (BPO) [68,69].

For example, Grubbs catalysts were employed in a catalytic rubber breakdown by cross-metathesis on polybutadiene and SBR. The process was performed at room temperature for 3 h, with minimum degradation [131]. Myers et al. report on the devulcanisation of crumb rubber using sodium desulfurization agent in organic solvents. The molten sodium at high temperature in anaerobic conditions was able to cleave mono-, di- and poly-sulfide bonds of the swelled vulcanizate with high selectivity, as the reclaimed rubber showed a similar molecular weight to the virgin polymer. However, this process has to overcome the non-economical and non-ecological use of organic solvents as swelling agents [132]. Another widely used organic solvent is 2-butanol [59], employed between 200 °C and 350 °C. To decrease the process temperature and increase the eco-sustainability of the process, 2-butanol can be partly substituted with turpentine liquids, and more particularly α-terpineol, derivable from renewable resources. 1:1 blends of turpentine liquids, employed below 150 °C, resulted in devulcanization levels of 75%–100% [133].

Deep eutectic solvents (DES), such as mixtures of choline chloride (ChCl) or ZnCl₂ with urea, p-toluene sulfonic acid, or glycerol, were also proposed as devulcanization agents, especially in combination with ultrasonic devulcanization [134]. DESs are interesting as they are widely tunable, non-flammable, and have low volatility and low toxicity. For example, ZnCl₂:urea blends were proven effective as devulcanizing agents at 130 °C in an ultrasonic bath, already after 15 min [59].

3.6.4. Ionic liquids

Ionic liquids (ILs), such as phosphonium, imidazolium, and pyrrolidinium salts, are also employed in addition to other physical and chemical devulcanization processes due to their interesting properties, such as their high conductivity, high thermal stability, low flammability, and low volatility. Not only are ILs safer and less toxic than other types of solvents, but they can also solubilize a large variety of compounds and their properties are tunable according to the selected cations and anions [135].

ILs have been used alone or in combination with other treatments. For example, pyrrolidinium hydrogen sulfate was used to swell SBR before microwave treatment [51]. The IL favored the ionic conduction mechanism of microwave heating, thereby facilitating the conversion of microwave energy into heat. ILs also improved

the heat distribution and temperature homogenization during microwaving, increased the soluble fraction, and significantly decreased the crosslink density above the energy threshold.

Other ILs proved to be effective as devulcanizing agents on NR are trihexyl(tetradecyl)phosphonium chloride or N,N-dioctylimidao-lium bromide in combination with Grubbs catalyst [136,137], which led to the production of telechelic oligomers such as acetoxy telechelic polyisoprene with high yield (between 95% and 99%).

3.7. Biological devulcanization

Although vulcanized materials are generally resistant to microbial attack, in some cases it is possible to promote biological devulcanization, i.e., a type of devulcanization in which microorganisms such as bacteria and fungi selectively break the sulfur bonds. However, biotechnological devulcanization processes are still far from being applied industrially, due to some persistent limitations such as the low devulcanization ratio, the risk of bacteriological contamination, and the fact that the process is limited to the surface of the components, thus resulting very slow (several weeks) [17].

The scientific literature contains various examples of bacterial devulcanization on different rubber substrates, such as GTR, NR, and latex rubber. The process, performed in aerobic or anaerobic environments, has been proved feasible with several strands of bacteria, such as Sphingomonas sp. [138], Alicyclobacillus sp. [139], Gordonia desulfuricans [140], Nocardia [141], Rhodococcus [142], and Bacillus cerus [143]. In the case of anaerobic bacterial devulcanization, researchers made use of sulfur-reducing bacteria, while in aerobic devulcanization sulfur is oxidized to produce sulfone groups on the rubber surface. Generally, the authors reported a reaction time of 1—30 days, a reaction temperature of 30 °C, a decrease in sulfur content in the sample of 8—30%, and the obtainment of a partly devulcanized product that can be revulcanized yielding a material with similar or improved mechanical properties compared to those of the virgin rubber.

For example, Tatangelo et al. reported on the devulcanization of ground NR by using Gordonia desulfuricans DSM44462 and Rhodococcus sp. AF21875. The treatment was performed in two bioreactors of 1.5 L on 150 g of GTR with a mineral salt medium at 30 °C for 1 day. The strand DSM44462 was more effective than AF21875, as it resulted in a higher sol content (see Table 4). The obtained biodevulcanized GTR was then compounded with NR at 10 phr and revulcanized, and the mechanical properties of the resulting revulcanized compound were comparable with those of virgin NR [140,144].

Another example is that reported by Kaewpetch et al. [143], who investigated the biological devulcanization of NR by Bacillus cereus TISTR 2651. It was found that this bacterium can selectively cleave sulfide bonds, but only in the first days of exposure. The mechanism of bacterial devulcanization was investigated via the Horikx analysis (Fig. 18), which evidences that the high selectivity of this devulcanization method is limited to the first 10 days of exposure.

Another type of biological devulcanization is that making use of fungi. Fungal devulcanization was studied by Bredberg et al., who employed three white-rot fungi (i.e., Pleurotus sajor-caju, Trametes
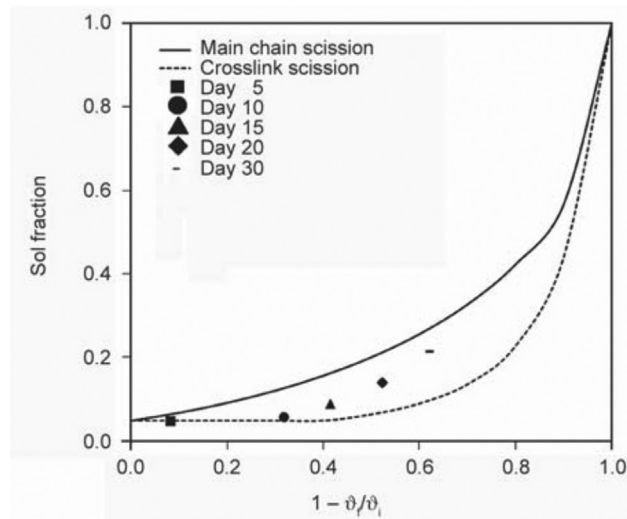

Fig. 18. Horikx diagram for the devulcanization of NR by Bacillus cereus TISTR 2651 (duplicated from Ref. [143]).

Versicolor, and Recinicum bicolor) to degrade a specific polymer called Poly-R478. The study showed that R. bicolor showed the highest efficiency as its growth rate was proportional to the sulfur oxidation rate in the rubber matrix [145]. In another study, a white rot basidiomycete, Ceriporiopsis subvermispora, was proven to degrade vulcanized NR sheets on a wood medium. The fungus promoted the cleavage of sulfide bonds and decreased the sulfur content of the rubber by 29% in 200 days, which demonstrated the potential of ligninolytic basidiomycetes for rubber biological devulcanization [146].

Despite the increasing number of research papers on the biological devulcanization of rubber, the commercial exploitation of this technology is currently performed by few companies on a small to medium scale. For example, the Recircle group applies a bacterial devulcanization process on various types of natural and synthetic ground rubber, and this process yields an intermediate that can be revulcanized [48].

4. Applications of devulcanized rubber

As mentioned in Sections 2 and 3, the most established way of utilizing re-vulcanized or devulcanized elastomers is through the production of polymeric blends, that is, physically mixing the devulcanizated rubber with one or more other polymers. When producing polymer blends, the general aim is to improve the properties compared to neat polymers, i.e., to obtain materials with additional or improved physical-mechanical properties, or to minimize the loss of the original properties while achieving other benefits, such as a decreased cost or improved processability. Hence, polymer blending is a way to obtain additional properties without the need, and the cost, of creating a new molecule [147].

Virgin and devulcanized rubbers can become part of many different blends. These elastomer-based blends can be divided into two types, i.e., (i) the blends composed of two or more types of elastomers (elastomeric blends) and (ii) the blends made of a thermoplastic and an elastomeric phase. The latter are called thermoplastic elastomers (TPEs) when the main phase is elastomeric and toughened plastics when the main phase is thermoplastic.

When producing a blend using devulcanized rubber, one must keep in mind that the revulcanization is more complex than the vulcanization of virgin rubber, because the devulcanization might

Table 4
Sol and gel fraction of GTR and G/R-GTR samples, G = DSM 44462 and R = AF21875 (adapted from Ref. [144]).

Sample	Gel fraction (wt%)	Sol fraction (wt%)	Standard error
GTR	97.7	2.3	0.1
G-GTR	96.7	3.3	0.1
R-GTR	97.1	2.9	0.6
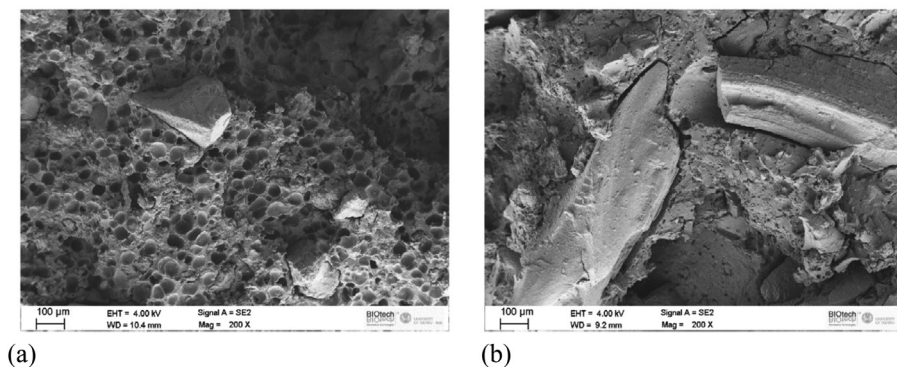
Fig. 19. SEM micrographs of tensile fracture surfaces from quasi-static tensile tests of (a) EPDM/DR and (b) EPDM/NDR foamed samples, rubber content 30 wt% (duplicated from Ref. [152]).

have chemically changed the nature of the rubber in ways not always predictable, and all these changes can affect the revulcanization [28]. The following sections report some representative examples of the most important physical properties of polymeric blends containing devulcanized rubber.

4.1. Blends based on NR

For as concerns elastomeric blends with devulcanized rubber, the greatest attention was devoted to NR-based blends and composites. For example, Joseph et al. [148] mechanically devulcanized CB-filled NR by shearing in a two-roll mill. To simulate the recycling of end-of-life rubber products, the authors also devulcanized samples aged at 70 °C and 100 °C for some days. The devulcanized rubber was then incorporated in virgin NR in different proportions, i.e., 85/15, 75/25, and 60/40), and various amounts of fillers were added during blending. It was shown that the properties of the blends can be adjusted by tuning the amount of added filler, which demonstrated that mechanical devulcanization and the optimization of the compounding composition are viable and effective strategies to recycle NR. Other authors prepared blends by incorporating up to 50 phr of mechanically devulcanized and non-devulcanized GTR virgin NR and evidenced the importance of devulcanization on the mechanical properties of the final material [149,150].

Other work compared different devulcanization strategies on the properties of the final blend, since each devulcanization process uniquely affects the structure of the rubber and therefore the properties of the final blends. For example, Mangili et al. [151] compared scCO₂, ultrasonic, and biological devulcanization of GTR, and the resulting devulcanizates were then blended into neat NR at a concentration of 10 phr. The ultrasonic and scCO₂ methods yielded a higher devulcanization fraction, while the biological treatment, although more selective, was limited to the particle surface. These differences affected the mechanical properties of the final blends, as the mechanical properties of the blends containing biologically devulcanized GTR were comparable with those containing non-devulcanized GTR, while the GTR from ultrasonic treatment showed the greatest improvement in mechanical properties, but only up to a certain ultrasonic amplitude.

4.2. Blends based on synthetic rubbers

Devulcanized rubber has also been blended with different kinds of synthetic rubber. For example, in a recent paper by Valentini et al. [152], various amounts of both devulcanized (DR) and non-devulcanized (NDR) recycled rubber coming from truck tires were compounded with a virgin EPDM rubber, and the resulting

compounds were expanded with azodicarbonamide. DR particles were better encapsulated within the EPDM matrix and showed a better interfacial adhesion, probably due to the re-vulcanization process in which the free crosslinking sites that typically characterize DR could form linkages with the EPDM matrix (see Fig. 19(a and b)). Tensile impact behavior of expanded EPDM/recycled rubber blends highlighted a strong improvement of the normalized total absorbed energy, the normalized impact strength, and the elongation at break compared to the neat expanded EPDM for all the investigated compositions, and especially with a DR content of 20 wt%. The preparation of expanded EPDM containing considerable amounts of devulcanized rubber was, therefore, demonstrated to be a practical route to reduce the costs and improve the properties and the environmental sustainability of rubber products.

Other authors reported the devulcanization of GTR and SBR crumbs via microwave devulcanization and their reintroduction in virgin SBR [74,153]. All these works generally report that devulcanization significantly increases the properties of the blends, which always show improved properties compared to the blends with non-devulcanized rubber powder. For example, Karabork et al. [153] measured a strain at break of 445% of the composites containing devulcanized GTR and only 217% for the composites with untreated GTR. This was due to an improved interfacial interaction between treated GTR and the surrounding matrix, as evidenced by scanning electron microscopy (SEM).

Other authors compared low-temperature mechano-chemical devulcanization (LTMD) and the traditional high-temperature atmospheric devulcanization (HTAD) to reclaim waste rubber powders, mixed them with different amounts of additives, and then revulcanized the reclaimed rubber after blending with all-terrain vehicle (ATV) tread rubbers. It was noticed that not only LTMD yielded a higher devulcanization fraction, but the blends devulcanized via this method also reached higher mechanical properties even without additional additives [154].

4.3. Blends with thermoplastics

Devulcanized rubber is an interesting blend component not only for full-elastomeric blends but also for rubber/thermoplastic compounds. Devulcanized rubber powder have been blended with several thermoplastic materials, including polypropylene (PP) [155], high-density polyethylene (HDPE) [156], copolyester (COPE) [157], and polystyrene (PS) [158,159].

For example, mechano-chemically devulcanized WTR powder was mixed with PP in different proportions, and the thermo-mechanical properties were investigated as a function of the DR content and the dose of gamma irradiation [155]. As observable in
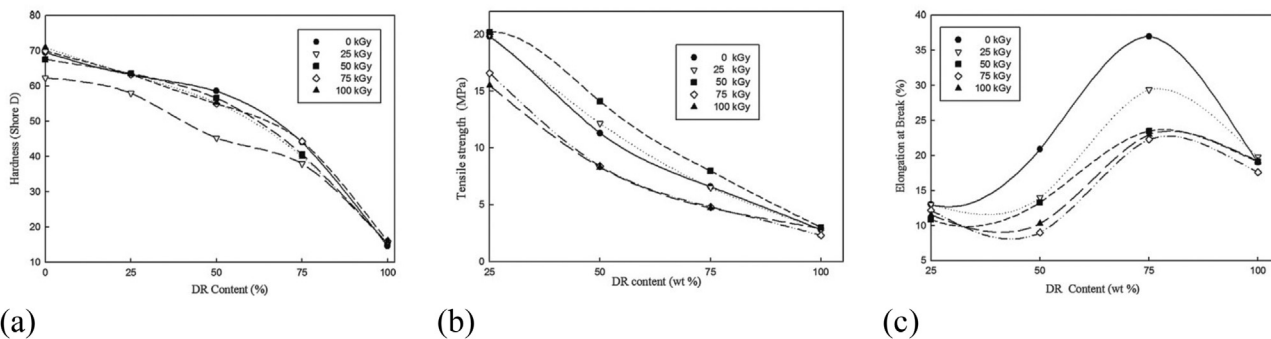
Fig. 20. Mechanical properties of DR/PP blends of different compositions irradiated with various gamma radiation doses. (a) Shore hardness, (b) tensile strength, (c) elongation at break (taken from Ref. [155]).
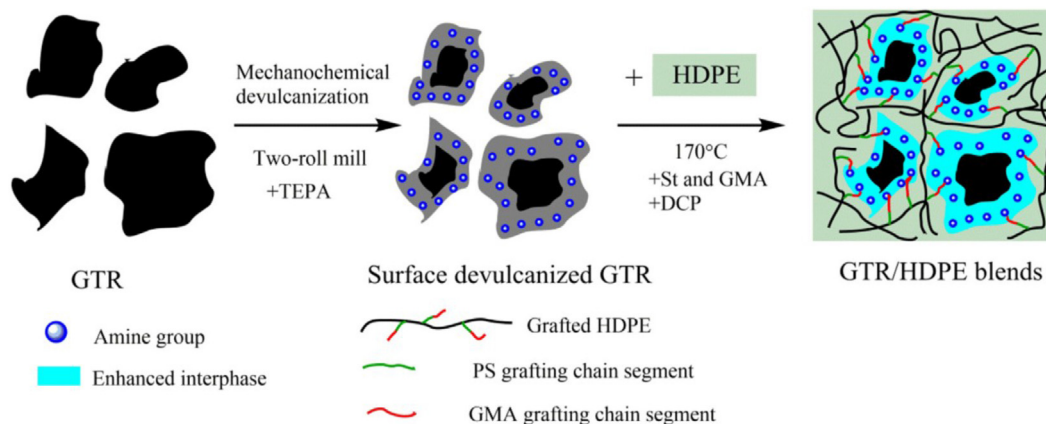

Fig. 21. Preparation of GTR/HDPE blend by combining surface devulcanization and in-situ grafting technology (duplicated from Ref. [156]).

Fig. 20(a–c), the hardness of the blends decreased with the DR fraction and increased with the radiation dose up to 50 kGy, especially at higher DR fractions. A similar trend can be observed for the tensile strength, which increases with the radiation dose but is strongly impaired by the incorporation of DR, probably because of the DR aggregation. On the other hand, the strain at break increased with the DR loading up to 75 wt% but decrease with the radiation dose. Therefore, DR was proven an interesting filler to tune the mechanical properties of PP.

Jang et al. prepared GTR/HDPE blends by combining chemical surface devulcanization of GTR with tetraethylenepentamine (TEPA) and in-situ grafting of HDPE by styrene and glycidyl methacrylate (see Fig. 21). This combined technique was proven to

strongly improve the compatibility and mechanical properties of the blends, and these properties could be tailored by adjusting the initiator/grafting monomers ratio. Moreover, the d-GTR/HDPE blends possessed a stable processing and reprocessing ability.

Other authors studied the incorporation of DR in a brittle matrix such as PS. For example, in a recent work by Valentini et al. [158], devulcanized (DR) and non-devulcanized rubber (NDR) coming from waste truck tires were melt-compounded and compression molded with PS.

Also in this case, DR domains were smaller and better dispersed in the surrounding matrix, and also exhibited an improved interfacial interaction compared to NDR. This was at the basis of the higher mechanical properties of the blends containing DR (see Fig. 22(a–c)).
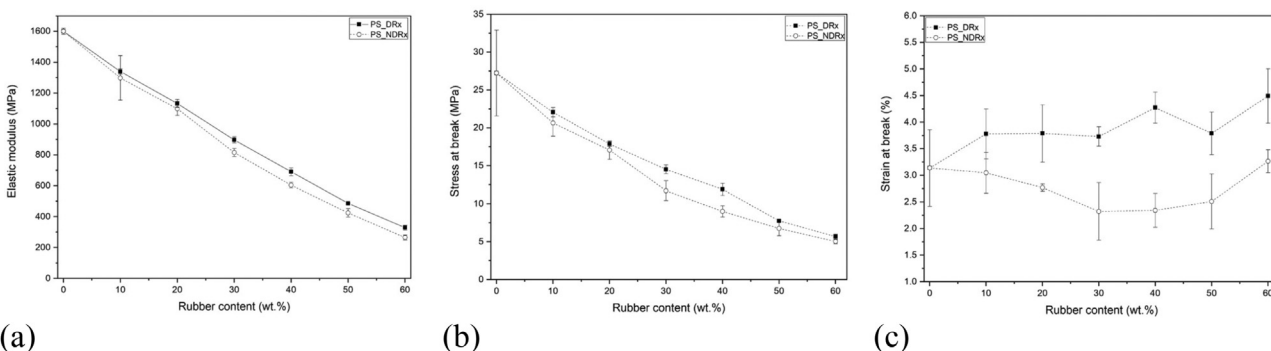

Fig. 22. Results of quasi-static tensile tests on PS/rubber blends as a function of the rubber content. (a) Elastic modulus, (b) stress at break, (c) strain at break (duplicated from Ref. [158]).

However, the surface hardness, tensile modulus, and stress at break were negatively affected by both DR and NDR, because of the still limited compatibility between PS and rubber particles and the relatively large size of the rubber domains. On the other hand, high rubber fractions determined an increase in ductility, with an enhancement of the tensile strain at break and of the impact resistance.

Hittini et al. [159] investigated the use of DR powder coming from waste tires as a filler for thermoplastic thermal insulators based on PS. DR was added in different proportions (0–50 wt%) to PS using a melt extruder, and the resulting materials were then hot pressed. Composites with less than 40 wt% DR exhibited superior properties, with thermal conductivity ranging from 0.050 to 0.071 W/m·K, density from 463 to 482 kg/m^3, compressive strength from 11.7 to 7.5 MPa, and flexural strength from 40.4 to 19.3 MPa. Moreover, these mechanical properties further increased after alkaline treatment of the DR, which increased the interfacial adhesion between DR and PS.

5. Conclusions and future perspectives

Considering the ever-increasing production, consumption, and disposal rates of rubber-based products, proper valorization of rubber waste is one of the most critical challenges that need to be globally addressed. However, the sustainable disposal of waste rubber is not an easy goal. Most of the rubber-based products are vulcanized, and if the resulting three-dimensional molecular network endows rubbers with interesting thermo-mechanical properties such as high elasticity and damping, it also poses severe challenges for their reprocessing and recycling.

The analysis presented in this work leads to the following conclusions:

1. Given that landfilling and open burning are unsustainable and polluting, the approach of downsizing waste rubber to GTR or other rubber-based pellets and powder can be useful and is still vastly used. The resulting materials can be added to various cementitious and rubber-based blends to produce rubberized asphalt and concrete, playground mats, running floors, and many more items. However, this approach is insufficient to valorize all the rubber waste globally generated every year, and the scarce adhesion between the rubber particles and the surrounding polymer matrix strongly limits the amount of rubber waste that can be incorporated into virgin polymers in this way.

2. The approach that most suits the need for sustainable recycling of rubber products is devulcanization, intended as the process able to selectively break the crosslink bonds (S–S and C–S bonds) in the material leaving the main chains intact, in order to recover a material very similar to virgin rubber, which can be reprocessed and turned into high added-value products.

3. Devulcanization can be performed through several techniques, making use of mechanical, thermal, thermomechanical, chemical, microwave, ultrasonic, or biological agents that can be applied alone or combined. All these methods present advantages and limitations, and therefore a proper combination of these techniques is required to enhance the degree of devulcanization, limit the main chain degradation, and further optimize the properties of the devulcanizates. To this aim, one must also properly select the devulcanizing agents and the operational conditions, such as temperature, pressure, time, and shear rate.

4. The so-obtained devulcanized rubbers can be used to partially replace virgin materials, thereby saving primary feedstock and reducing the cost. Devulcanized rubber can also be blended with different elastomeric and thermoplastic matrices, thus obtaining a blend with interesting physical properties. However, when using devulcanized products, particular attention should be paid to re-vulcanization conditions and the role of additives and fillers in the revulcanization process.

Hence, the main challenges in this field remain the correct implementation of sustainable and effective devulcanization techniques and the development of a consolidated market for devulcanizated and revulcanized material. This cannot be achieved without a more in-depth understanding of the precise correlation among the physical-chemical properties of the initial vulcanizate, the devulcanization technique and parameters, and the properties of the resulting devulcanizates.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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