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Review article

Progress in devulcanization of waste tire rubber: Upcycling towards a circular economy

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Abstract. As a complex composite material, tire rubber has always presented significant environmental and waste management concerns due to its non-biodegradability and accumulation in landfills. The devulcanization of tire rubber has emerged as a historical challenge in the field of sustainable rubber engineering since Goodyear invented cross-linking in 1839. This review provides a comprehensive analysis of waste tire recycling processes, focusing on the sources, legislation, management strategies, and utilization across different regions. It explores the multifaceted challenges of devulcanizing rubber, with a specific focus on transitioning from ground tire rubber to the concept of multi-decrosslinking: sulfur bridge breakage, rubber chain depolymerization and micro-nano sized core-shell carbon black. Ideal devulcanization has restricted the release of reinforcing fillers, resulting in devulcanized rubber mainly containing dozens of micron particles, which hinder the wide usage of devulcanized rubber. This review comprehensively assesses the current state-of-the-art techniques for tire rubber devulcanization, including physical, chemical and biological methods. It explores the intricacies of ground tire rubber as a starting material, structural evolution of ground tire rubber during the devulcanization process and the associated challenges in achieving efficient devulcanization while retaining desirable mechanical properties. Furthermore, through an in-depth analysis of recent advancements, limitations and prospects, this paper offers a complete understanding of the challenges faced in tire rubber devulcanization. Considering the technical and environmental aspects of these processes, this work contributes to multi-decrosslinking, the ongoing discourse on sustainable materials development and circular economy initiatives, which pave the way for future innovations in the field of rubber recycling.

Keywords: *ground tire rubber, devulcanization, reclamation, compounds, carbon black*

1. Introduction

The demand for rubber manufacturing and production has remained robust over the years. According to statistics, global natural rubber (NR) production reached nearly 14.6 million metric tons in 2022 [1]. The foreseeable future anticipates a sustained demand for rubber due to its continued relevance and necessity across various niche applications [2].

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However, this surge in rubber production and consumption leads to a corresponding rise in rubber waste, posing potential environmental risks if not managed or processed properly. Statistical estimations reveal that on a global scale, around 1 billion tires become unsuitable for further usage or retreading each year [3]. According to predictions, up to 2030, the number of waste tires generated to the environment will increase to 1.2 billion tires per year [4].

Currently, the handling of discarded tires has emerged as a considerable environmental issue. Inadequate disposal practices of used tires present a hazard to both the environment and human health due to their non-degradable characteristics and the possibility of releasing toxic compounds into the soil and water. Unlike thermoplastics, rubber materials cannot be recycled through straightforward and economical reprocessing techniques such as remelting or remolding. The exceptional mechanical properties of tire rubber, encompassing its impressive elasticity during significant deformation and its capacity to absorb substantial energy, arise from the creation of a three-dimensional network of rubber chains, facilitated by sulfur bridges termed vulcanization [5]. Vulcanization is an irreversible process that takes place at temperatures ranging from 140 to 180°C and under controlled pressure conditions. The vulcanization process creates a rubber network that makes vulcanized rubber intractable and non-melting, which presents significant difficulties for recycling waste tire rubber [6, 7]. As a result, the recycling of used tires is different from thermoplastic materials [8].

Until now, the recycling of tires poses an even greater challenge due to the confidential nature of their chemical composition and the complex origins of recycled tire components. Consequently, the recycling of waste tires has become a global issue, presenting a significant challenge for researchers and industry. The primary approaches for disposing of used tires have been categorized as stockpiling, landfilling, and dumping as solid waste, secondary use through retreading, energy recovery via burning or incineration, fuel production through pyrolysis, and recycling into various products such as crash barriers, bumpers, and artificial reefs. Another method involves material recycling, where the resulting material is commonly referred to as ground tire rubber (GTR). GTR can serve as an additive in asphalt without any physical or chemical treatment and can also be bound with polyurethane. GTR can be blended with thermoset [9–12] or thermoplastic [13, 14] polymers with or without compatibilization [15, 16]. However, the volume of these applications is insufficient to meet the steadily expanding demand for rubber recycling.

Devulcanization presents a potential solution to this challenge, as it can selectively break the covalent cross-links within elastomers while preserving the integrity of the polymer structure. This results in the formation of fresh molecules capable of interacting and reacting with the surface of GTR particles, thereby improving the compatibility between devulcanized GTR (dGTR) and other polymers [17–19]. Consequently, it becomes possible to increase the proportion of recycled rubber incorporated into new rubber goods without compromising their mechanical characteristics. Traditional methods of devulcanization, such as thermo-chemical [20], microwave [21–23], thermo-mechanical [24, 25], and mechano-chemical [26] devulcanization, with decades of research in this field [27]. There are other devulcanization methods utilizing chemolithotrophic bacteria [28], supercritical carbon dioxide [29], and ultrasonics [30, 31].

This review explores the complex landscape of waste tire rubber devulcanization, emphasizing its key role in advancing toward a circular economy. By examining the solutions and challenges inherent in the process, we aim to contribute to the ongoing discourse surrounding sustainable waste tire management practices. It also aims to critically evaluate the quality and structure of rubber obtained through devulcanization processes. It will explore the mechanical, thermal, and chemical properties of devulcanized rubber, comparing them with virgin rubber and other recycled rubber materials. Overall, the purpose of this review is to serve as a comprehensive and informative resource for researchers, scientists, engineers, policymakers and industry professionals who are interested in understanding the details of tire rubber devulcanization. By addressing the challenges and opportunities within this field, the review aims to contribute to the advancement of sustainable practices and the utilization of waste tire rubber as a valuable raw material.

2. Recycling of waste tires

The use of polymeric materials has become widespread, replacing traditional materials such as wood and metal in various applications. Waste tire rubber, which contains approximately 50% rubber, is a valuable polymeric material source. The incorporation of waste tire rubber into polymer blends offers an opportunity to lower production costs and explore new market avenues. This approach is in line with the principles of the global 5R initiative (reduction, reuse, recover, replace, and recycle), aiming to minimize the use of virgin polymer, reuse waste tire rubber, and recycle discarded tires [32]. As a result, scientists and researchers worldwide are actively involved in developing and evaluating polymer blends and composites containing waste tire rubber, driven by the goal of sustainable material utilization and environmental responsibility.

2.1. Source of waste tires

An estimated large number of tires reach the end of their lifespan annually, with over 50% being disposed of in landfills or as garbage without undergoing any treatment. Over recent years, the production volume of used tires in the European Union and the United States has remained relatively consistent, totaling approximately 7 Mt annually (ETRMA) [33]. With the advancement of economic development, China's production of waste tires is steadily rising annually. In 2019 alone, the country generated a staggering 330 million waste tires, weighing over 10 Mt in total. Data indicates that the annual increase in scrapped waste tire production ranges between 6 to 8%, necessitating significant advancements in management strategies and technology development in China [34].

In 2022, Japan produced 92 million waste tires, weighing in at 1 Mt. This marked an increase of 1 million tires and 21 000 t in weight compared to 2021. Notably, in 2022, the utilization of recycling methods experienced significant growth compared to the previous year: material recycling surged by 113%, thermal recycling by 104%, and exports by 126%. The total recycling volume increased by 80 000 t from the previous year, totaling 984 000 t. The escalating prices of fossil fuels, such as coal, have led to a heightened demand for End-of-Life Tires (ELT) as an alternative fuel source [33]. Furthermore, the recent revision of the Act on Rationalizing Energy Use, set to be implemented this spring, will necessitate business operators to increasingly transition to alternatives to conventional fossil fuels, further driving the demand for ELT as a fuel [35]. The source of waste tires is mainly composed of truck tires and passenger tires; often, off-road tires and motorcycle tires are included. The truck tires mainly consist of NR, which is easily devulcanized or reclaimed. However, the passenger tires mainly consists of synthetic rubber, which is hard to reclaim and often used as fuel.

2.2. The legislation and management of waste tires in different regions

The legislation and management of waste tires are crucial for reducing environmental and public health hazards associated with tire disposal. To effectively recycle waste tire resources and minimize environmental risks, many countries around the world have established customized management systems or standards [36]. For example, in the United States, the Resource Conservation and Recovery Act (RCRA) provides guidelines for tire management, while the European Union's End-of-Life Vehicles (ELV) Directive requires the environmentally responsible treatment of tires. Extended Producer Responsibility (EPR) schemes also hold tire manufacturers accountable for managing tires throughout their life cycle. The legislation and management strategies for waste tires implemented in Europe, the USA, China, and Japan will be discussed in the following subsections.

2.2.1. Waste tires management system in Europe

Europe leads in the global recycling rate of waste tires [37]. The EU already established pertinent regulations and organizations like the European Tire and Rubber Manufacturers Association (ETRMA). As far back as 1999, the EU enacted directives such as the 'Directive on the Landfill of Waste 1000/31/EC' and the 'End-of-Life Vehicle Directive 2000/53/EC'. These directives mandate the prohibition of stockpiling waste tires, excluding bicycle tires and those exceeding an external diameter of 1.4 m, while requiring the removal of tires from end-of-life vehicles for recycling.

Continuously operational, these policies have been refined to elevate the reuse and recycling rate from 80% in 2006 to 85% starting in January 2015 and further enhance the rate of reuse and recovery from 85 to 95% [38]. Nevertheless, detailed recycling procedures for tires were not outlined within these policies. Consequently, each EU member state has formulated its regulations, leading to the emergence of three distinct systems: extended producer responsibility (EPR), tax systems, and free-market systems [39]. The producer responsibility system imposes a

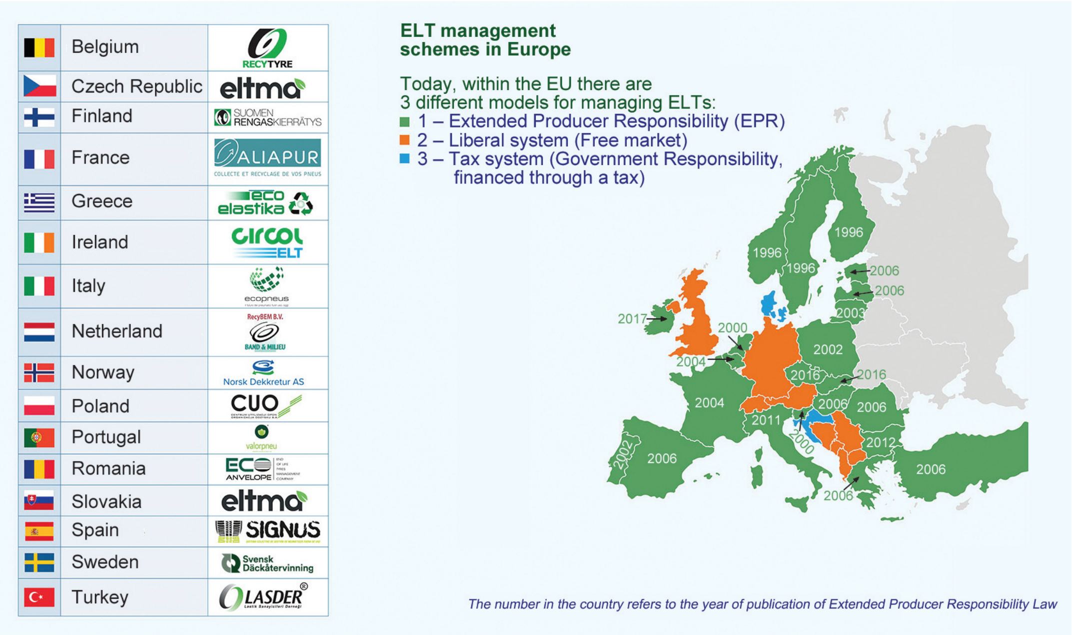


Figure 1. The ELT management scheme in Europe [43].

legal obligation on manufacturers to coordinate the industrial chain of waste tire recycling [40]. The tax management system empowers the government to utilize taxation as a tool to regulate the market [41]. The free-market system allocates resources in a Pareto-efficient manner, ensuring that no individual can benefit without causing harm to others, given specific conditions (such as the absence of externalities or informational asymmetries) [42]. Among these systems, the extended producer responsibility (EPR) system, wherein producers or importers assume responsibility for waste tire recycling, is predominantly adopted across most EU member states [38]. The ELT management schemes in the EU are illustrated in Figure 1.

2.2.2. Waste tires management system in the United States

The United States embarked on waste tire management earlier, propelled by its advanced automobile industry. In the 1990s, the federal government mandated that state-funded asphalt roads include 5% recycled tire pellets. This initiative marked a substantial improvement, considering that by 1997, 20% of waste tires were being utilized in such applications. Additionally, waste tires were included in the mandatory recycling product catalog, spurring the establishment of large-scale, comprehensive professional service companies. This initiative also initiated the process of waste tire disposal and recycling under the support of the United States government [44]. Currently, the primary responsibility for crafting environmental protection policies and regulations lies with the United States Congress. The Federal Environmental Protection Agency (EPA) is tasked with supervising the recycling of renewable resources, which encompasses used tires and other solid waste materials.

2.2.3. Waste tires management system in China

China is the world's second-largest economy and one of the most populous nations; urgently needs to draw on reference experiences in waste tire recycling and adapt them to national conditions to bolster management practices. The Chinese government acknowledges that waste tires pose a significant environmental hazard, often referred to as 'black pollution'. Presently, China is vigorously endeavoring to transform waste tires into valuable resources, termed as 'black gold', as part of initiatives aimed at fostering the sustainable growth of the industry and enhancing resource utilization efficiency. Waste tire management in mainland China seems moderately effective, with a recycling rate of approximately 30%, comparable to rates observed in countries like Japan and Poland. However, a 2020 report [45] suggested that this figure could have been higher in China. The report highlighted several factors hindering the recycling rate, including the absence of regulations, insufficient government support, and lack of relevant agencies.

Additionally, it was noted that the recycling system for car tires operated more efficiently than that for tires from bicycles and electric motorbikes. The widespread use of bicycles and motorbikes in China may have contributed to the country's lower-than-expected rubber recycling rate [45]. The Ministry of Industry and Information Technology of China has recently issued standard conditions for the comprehensive utilization of waste tires. These standards outline requirements across various domains, such as technical equipment and processes, ecological, environmental protection, product quality control, and safety management [33].

2.2.4. Waste tires management system in Japan

In Japan, the government enforces a waste tire management card system, mandating that tire sellers are responsible for recycling waste tires and preventing their illegal disposal. Additionally, the Japan Rubber Industry Association has set targets for reducing waste rubber production in factories, aiming to decrease waste rubber rates and enhance the proportion of qualified products. Since the 1980s, tire production factories have maintained a rework waste rubber index of 1%. Japan has instituted a recycling system aligned with market economy principles to facilitate organized recycling. Licensed professionals authorized by government departments are designated to purchase used tires, while unauthorized individuals and businesses are prohibited from buying or disposing of them without proper authorization. The Japanese government offers subsidies for waste tire recycling, providing incentives ranging from 10 000 to 15 000 yen/t of waste rubber disposed off.

2.3. Waste tire utilization

Recovered waste tires are considered valuable materials due to their composition and properties, making them a source of useful raw materials [46]. The efficiency of waste tire recovery models has enabled the effective conversion of waste tires into energy or other materials. These valuable waste tires can be utilized to manufacture new goods with practical or utilitarian significance. Various utilization methods and the typical composition of waste tires are illustrated in Figure 2.

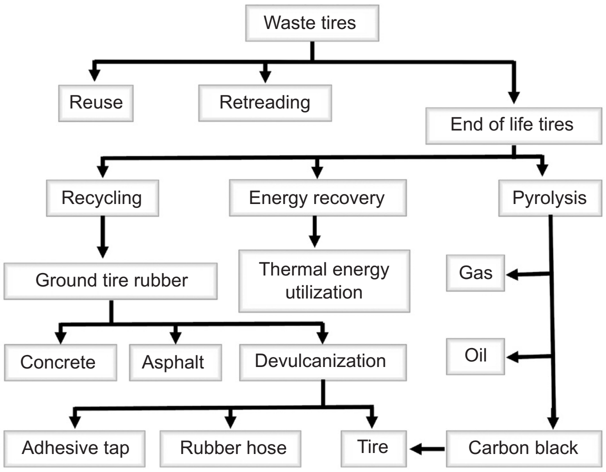


Figure 2. Utilization methods and their common applications of waste tires.

The waste tires are typically generated through either the replacement of old tires with new ones or the removal of tires from vehicles before scrapping. These waste tires can be categorized into part-worn tires, which are still suitable for on-road use, and ELT, which cannot be reused for their original purpose. Various methods have been explored to utilize waste tires, including energy recovery [47, 48], pyrolysis [49, 50], high-pressure and high-temperature sintering [51, 52], reclamation [53, 54], devulcanization [55, 56], and others. Table 1 presents the utilization and distribution of waste tire recycling across the EU, USA, China, and Japan. The primary methods of recycling include utilizing heat energy (or producing tire-derived fuel) from waste tires and using crumb rubber or rubber powder. Energy recovery is predominantly employed in industries such as paper manufacturing, chemical factories, cement factories, and steel manufacturing. Numerous new processing technologies have been extensively documented in

Table 1. Utilization and proportion of waste tire recycling in EU, USA, China and Japan (ETRMA, 2021 [60]; USTMA, 2019 [33], CTRA 2019 [61], JATMA, 2019 [33]).

Recycling form	Proportion in EU [%]	Proportion in USA [%]	Proportion in China [%]	Proportion in Japan [%]
Energy recovery	40.0	44.0	13.8	63.0
Recycling	53.0	26.0	50.0	17.0
Civil engineering	2.0	8.0	0	0
Land disposed and stockpiling	0	16.0	36.2	7.0
Export	0	3.0	0	13.0
Unknown	5.0	3.0	0	0

the literature [57–59]. However, these statistics may not fully reflect market shares as market data tends to be macro-level with limited details. As a result, the scale of implementation of new processing methods remains relatively small. Retreated tires, crumb rubber, or rubber powder comprise a significant portion of the tire recycling market.

2.3.1. Reuse and retreading

Reuse and retreading are essential practices for extending the lifespan and maximizing the value of waste tires. Reuse involves repurposing used tires for various applications without significantly altering the original tire tread. On the other hand, retreading involves refurbishing worn-out tire casings with a new tread layer, effectively extending the tire's life and performance [62]. This process includes thorough inspection, buffing, application of a new tread layer, and curing. Retreading is particularly popular in the commercial trucking industry, where it offers significant cost savings and environmental benefits. Retreaded tires provide comparable performance to new tires when properly maintained and operated, making them a reliable option for commercial vehicles. Both the markets for reusable and retreaded tires face challenges due to the competitive pricing of new tires and consumer expectations regarding safety and reliability [59].

2.3.2. Recycling

Recycling stands as one of the prevalent methods for managing waste tires. Sienkiewicz *et al*. [63] define recycling as a process that excludes any form of treatment, whether physical or chemical, focusing solely on disintegration. Additionally, the characteristics of tires, including their shape, initial dimensions, durability, elasticity, vibration absorption, and high damping properties, render them highly valuable and versatile materials suitable for various applications. The recycled tires find usage in numerous applications, yielding diverse end products such as manufacturing new tires, athletic tracks, insulation materials for buildings, matting surfaces, playground surfaces, marine non-slip surfaces, and more [64].

2.3.3. Energy recovery

Many industrial processes are dependent on non-renewable energy sources like coal, which are readily available and utilized to meet demand. One method to utilize waste tires from other rubber products is by incorporating them as energy sources, such as fuel, contributing to the recovery of energy resources. Waste tires consist of organic materials, constituting over 90% of their composition, with a notable heat value of 32.6 MJ/kg [63]. In comparison, coal typically ranges from 18.6 to 27.9 MJ/kg [65]. The waste tires can serve as an alternative fuel source in various industries such as cement kilns, paper mills, and electricity generation. Utilizing waste tires as fuel in processes operating at temperatures exceeding 1200 °C offers a cost-effective solution to meet the high-temperature demands of cement industries. However, the combustion and burning of waste tires pose environmental pollution concerns. In terms of air pollution levels, it is comparatively minor when contrasted with the emissions resulting from coal combustion [63].

2.3.4. Pyrolysis

Pyrolysis is a thermolysis process involving the breakdown of organic compounds which results in a change in the chemical composition and phase [66]. The thermo-chemical decomposition occurs in the absence of oxygen, and it is an irreversible process. During GTR pyrolysis, three phases are obtained: solid residue (carbon black,CB and impurities), liquid oil, and gas byproducts. The key products of pyrolysis gas include H_2, CO, CO_2, and CH_4; the liquid phase primarily comprises CH_3OH, CH_3COOH, and H_2O, and the remaining solid products typically consist of carbon and ash [67, 68]. The stages of the waste tire pyrolysis process are illustrated in Figure 3. Martínez *et al*. [69] and Lewandowski *et al*. [70] extensively studied the pyrolysis process. The pyrolysis process is influenced by variables such as temperature, material size, residence time, and more [71, 72].

Figure 3. Waste tire pyrolysis process.

Various types of pyrolysis reactors have been developed and studied in recent years to produce oil, char, and gas from waste tires. The yields of pyrolysis production are contingent upon factors such as feedstock preparation, reactor types, and pyrolysis reaction conditions [73, 74]. However, the high operating costs of pyrolysis plants pose a significant challenge to this endeavor. Slow pyrolysis, also known as light pyrolysis, refers to a process that operates at lower temperatures, making it cost-effective and suitable for certain applications, as discussed in the following section.

2.3.5. Light pyrolysis

Light pyrolysis generally refers to a pyrolysis process that operates at relatively lower temperatures compared to conventional pyrolysis methods. Light pyrolysis typically involves heating the feedstock, such as biomass or waste materials, at temperatures ranging from 300 to 500 °C in the absence of oxygen. Light pyrolysis can also be defined as the process of breaking down cross-linked rubber into liquid rubber with molecular weights of approximately 10 000 g/mol, which can be used as a reactive plasticizer. Additionally, light pyrolysis is regarded as a chemical devulcanization process, given the chemical decomposition that takes place, even in the absence of specific added compounds [66]. The pyrolysis does not align with the criteria for recycling as outlined in the directive 2008/98/EC, as this process primarily results in energy recovery. However, light pyrolysis has been considered a devulcanization technique. Light pyrolysis can be used for the separation of rubber from reinforcing fillers, which is a multifaceted process that plays a crucial role in creating high-performance rubber compounds. Undri *et al*. [75] used microwave pyrolysis of GTR and got a relatively small ash content of 5.9 to 9.5 wt%. The light pyrolysis at lower temperatures could potentially reduce energy costs, but the properties of the resulting recovered carbon black (rCB) were found to have less reinforcing efficiency compared to commercial CB [76]. Yamazaki *et al*. [77] utilized a process to convert waste tire rubber into polymers with a lower molecular weight ($M_n = 10\,000$ g/mol) at 300 °C under a controlled air and nitrogen atmosphere. These lower molecular weight polymers could subsequently undergo copolymerization with various vinyl monomers to produce grafted copolymers based on NR.

2.4. Ground tire rubber (GTR) production

Ground tire rubber (GTR) refers to recycled rubber derived from waste tires through a mechanical grinding process. This process involves shredding whole tires into particles ranging from 20 to 80 mesh (177 to 840 µm) for further compounding process. The GTR possesses properties like traditional rubber but offers several advantages, including cost-effectiveness, sustainability, and resource conservation. It is used in various industries, including automotive, construction, sports, and manufacturing, where it is used to produce a wide range of products such as tires, asphalt, rubber mats, and footwear [78]. The GTR plays a crucial role in promoting environmentally friendly practices by reducing waste from discarded tires and contributing to the circular economy.

The production of GTR primarily consists of the removal of steel and fabric from the tires followed by the utilization of a granulator or mill to reduce the size of tire rubber particles, as illustrated in Figure 4. The size reduction can be achieved through different methods, such as ambient shredding, water jetting, or cryogenic grinding, as shown in Table 2 [79]. The size reduction is the initial step in GTR recycling, which leads to an increase in the specific surface area and enhances surface activity [80]. The larger GTR particles with a diameter (6.3–9.5 mm) are commonly blended with polyurethane resins to create surfaces of athletic tracks or game floors and walkway tiles. Medium-size GTR particles with a diameter (0.41–0.62 mm) are used in various applications such as rubber-modified asphalt for road constructions, sound insulation materials, and as a component in rubberized asphalt for pavement. The smaller size GTR particles with diameter (0.15–0.4 mm) are typically used as fillers in polymer composites [81].

The addition of GTR into a polymer blend can enhance the mechanical properties up to a specific load level, depending on particle size and distribution [82]. Kiss *et al*. [83] compared the properties of low-density polyethylene (LDPE) blends with different amounts of ultrafine GTR (30 µm) produced by water jet milling and conventional fine GTR (400 µm). The results showed that ultrafine GTR significantly improved all mechanical properties compared to conventional fine GTR, which is attributed to the smaller particle size.

Figure 4. Preparation of GTR from waste tires.

Table 2.: Types of mechanical grinding, advantages and disadvantages [84].

Methods	Description	Advantages	Disadvantages
Ambient grinding	• Rubber is passed through two-roll mills, shredders, and granulators.	• A particle size of 70 mesh (200 µm) can be achieved. • High surface area.	• Temperature can reach up to 130 °C. • Oxidation of crumb rubber due to heat. • Requires excess water for cooling
Wet grinding	• Grinding by mixing water with the crumbs, producing a slurry • Water cools the granulates and produces cleaner crumbs.	• Particle size 60 mesh (250 µm) can be achieved. • High surface area.	• High energy consumption. • The extra step of drying makes the process costlier.
Cryogenic grinding	• Rubber is cooled in liquid nitrogen and then crushed with hammer mills	• Particle size 40–60 mesh (250–425 µm) can be achieved. • No oxidation of crumb rubber. • Clean crumb rubber is obtained. • High production rate and low energy cost.	• High cost of liquid nitrogen. • Smoother surface area resulting in poor binding ability. • Pre-grinding and drying steps add to the cost.
Ozone cracking	• Exposed to higher ozone concentrations and ground into crumb rubber using ambient grinding	• Consumes less energy. • Physical properties of the rubber are not altered	• Rubber has low surface activity

2.5. Modification of GTR

Incorporating GTR into virgin rubber as a semi-active filler is feasible; however, ensuring compatibility with the matrix poses a significant challenge. Factors such as the type curing system, rubber cross-link density, and the presence of additional ingredients like fillers, accelerators, and plasticizers play an important role in the rubber recycling. Therefore, directly incorporating GTR into rubber composites leads to a notable deterioration in their physical and viscoelastic properties, particularly tensile strength, when compared to virgin rubber. This is attributed to inadequate adhesion between the GTR and the rubber matrix, as well as the absence of reactive sites on the GTR surface.

Additionally, the presence of GTR affects curing behavior by influencing the migration of sulfur or accelerators between GTR and the virgin matrix. To overcome this challenge, various methods have been employed to modify the surface of GTR, including surface and chemical modifications, blending with polymers, and devulcanization or reclamation processes. Among the various modification methods, devulcanization has been extensively discussed in the following section, along with the different challenges associated with the devulcanization of GTR.

3. Rubber devulcanization vs reclamation

Reclamation is the oldest method used for the modification of GTR [65, 85]. Reclaimed GTR is the most used form of waste tire rubber in polymer blends. By definition, reclamation is the process of breaking down carbon-carbon (C–C) bonds within the rubber backbone with the objective of decreasing molecular weight to achieve increased plasticity. Devulcanization is a process aimed at breaking down the cross-linked network, *i.e.*, sulfur-sulfur (S–S) and carbon-sulfur (C–S) bonds of vulcanized rubber, allowing for increased plasticity [47, 86].

Despite their shared objective of obtaining a rubber compound suitable for processing and vulcanization comparable to fresh/virgin rubber, it is challenging to precisely target bond cleavage as per the definition. Both devulcanization and reclamation occur concurrently at any given moment, as shown in Figure 5 [42]. Currently, techniques for dismantling a vulcanized rubber framework focus on breaking down mono-, di-, and poly-sulfidic bonds, while endeavoring to limit the cleavage of C–C bonds, which may still occur to some degree [43]. Therefore, it allows the term devulcanization and reclamation to be used interchangeably. The reaction mechanisms involved in this process are intricate and have not been thoroughly investigated. The mechanism may proceed by breaking the existing cross-links in vulcanized rubber (cross-link scission) or by facilitating the scission of the polymer main chain (main-chain scission), or by a combination of both processes. Each of these possibilities is described separately in this section.

Main chain scission of vulcanized rubber refers to the breaking of chemical bonds within the primary

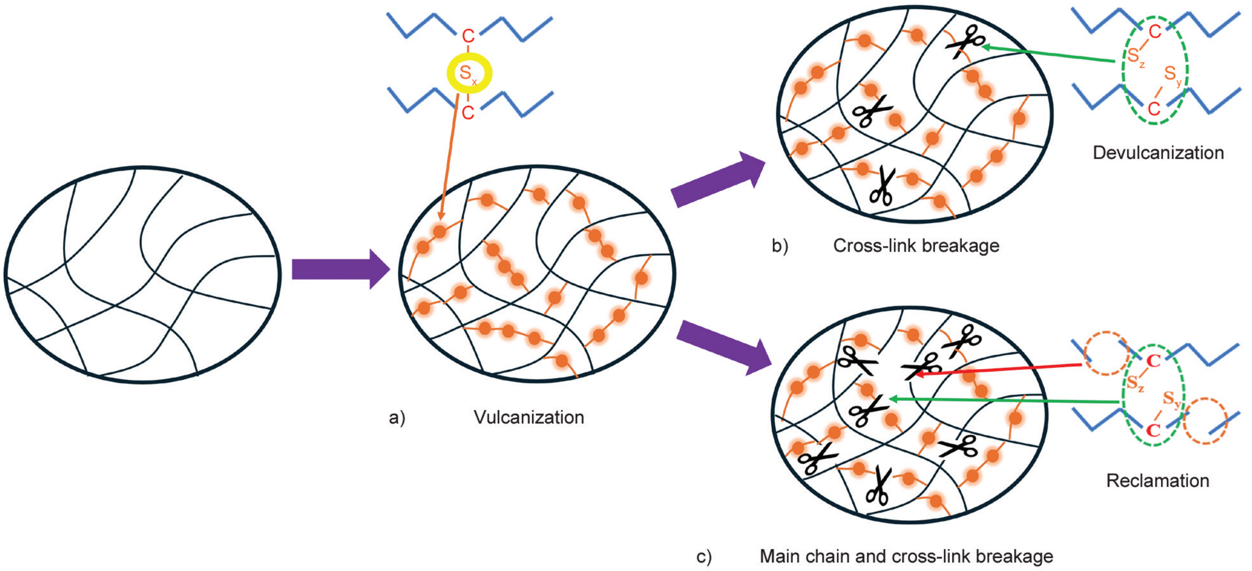


Figure 5. Schematic representation of devulcanization and reclamation. a) Vulcanization (sulfur cross-linking), b) devulcanization and c) reclamation.

backbone structure of the rubber material that has undergone vulcanization. This process involves the cleavage of C–C bonds in the polymer chains, leading to a reduction in molecular weight and increased plasticity. The main chain scission can occur due to various factors such as heat, mechanical stress, or chemical reactions, and it can influence the overall performance and characteristics of the rubber material.

As an example of this process, consider the phenyl hydrazine–iron (II) chloride system (PH–$FeCl_2$), which exhibits notable efficacy in oxidatively breaking down rubber molecules at 50 °C. In this reaction, involving NR and PH–$FeCl_2$ in the presence of oxygen, phenyl hydrazine serves as the primary reagent while $FeCl_2$ functions as a catalyst. The pace of rubber reclamation hinges on the concentration of phenylhydrazine. Furthermore, phenyl hydrazine itself readily decomposes upon exposure to oxygen, resulting in the release of nitrogen gas [87]. The rate of main chain scission occurs at a significantly accelerated pace when a metal salt is present. Figure 6 illustrates the initial oxidative breakdown of rubber molecules with the PH–$FeCl_2$ system. In the presence of oxygen, the radicals generated by this reaction proceed to break down the rubber chains, as depicted in Figure 7. Additionally, Figure 8 demonstrates the decomposition of hydroperoxide in the presence of transition metals.

Cross-link scission refers to the breaking of chemical bonds between cross-linked polymer chains in a material. In vulcanized rubber, which is a cross-linked polymer network formed through the vulcanization process, cross-link scission involves the rupture of bonds that connect the polymer chains. This process can occur due to various factors such as heat, mechanical stress, or exposure to certain chemicals. The cross-link scission can lead to a decrease in the degree of cross-linking and alter the mechanical properties of the material, such as reducing its strength and elasticity. For example, triphenylphosphine (TPP) is recognized for its ability to initiate a nucleophilic reaction, thereby opening the sulfur cross-links, as depicted in Figure 9. While radicals may recombine, there is also potential for interaction with a double bond, ultimately resulting in the disruption of the cross-linking network.

Main chain and cross-links scission usually occurs in the presence of devulcanizing agents such as thiols and disulfides. The thiols and disulfides interact with radicals produced during the rubber devulcanization. It is postulated that they trigger oxidative

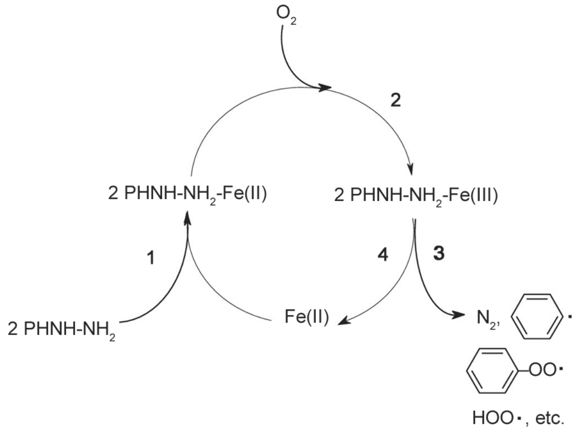


Figure 6. Oxidation mechanism for the PH–$FeCl_2$ system [88].

ROO• + RH → R• 6 ROOH
ROOH → RO• + HO•
ROOH + RH → ROH + R• + HO•
RO• + RH → ROH + R•
HO•+ RH → HOH + R•

ROO• + R• → ROOH
RO• + R• → ROR
R• + R• → RR

Figure 7. Bolland oxidation mechanism (RH = rubber hydrocarbon) [88].

ROOH + Fe^{2+} → RO• + Fe^{3+} + OH^-
ROOH + Fe^{3+} → ROO• + Fe^{2+} + OH^+

Figure 8. Decomposition of peroxides by ions of metals (redox mechanism) [88].

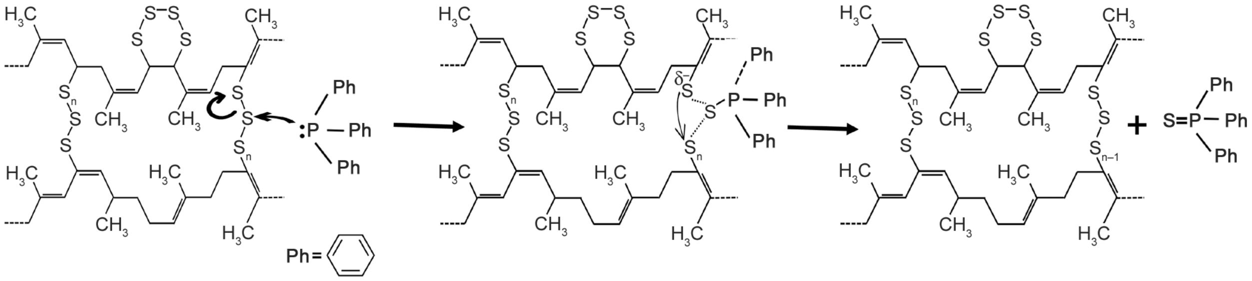


Figure 9. Desulfuration of cross-links by triphenylphosphine.

degradation of both the sulfur cross-links and the main chain of vulcanized rubber [89], simultaneously impeding gel formation by forming combinations with the radicals. When a vulcanizate undergoes recycling with thiols and disulfides, a more extensive network breakdown is observed.

In thermo-mechanical processes, disulfides and thiols exhibit comparable reactivity [90]. Aliphatic thiols (ethanethiol (C_2H_5SH)) demonstrate lower activity compared to aromatic thiols (thiophenol (C_6H_5SH)). The effectiveness of aromatic compounds appears to escalate upon the substitution of alkyl groups or halogens on the benzene ring. A commonly suggested mechanism for the interaction between disulfides and sulfur vulcanizates involves the opening of cross-links or the cleavage of chains due to heat and shearing forces. These broken bonds then react with disulfides, impeding recombination. Atmospheric oxygen is purported to further hinder recombination by stabilizing radical sites. Additionally, antioxidants and other compounds with stabilizing effects play a role [91]. Consequently, the outcome is a reduction in the molecular weight of the devulcanized rubber.

3.1. Devulcanization methods

Elastomers are cross-linked, which prevents their simple recycling, as they can be applied to thermoplastics [92]. The devulcanization process aims at selectively breaking the C–S bonds while leaving the C–C bonds intact. The devulcanization applies specific energy to the GTR to break up the three-dimensional network formed during vulcanization. It is difficult to achieve the selectivity because the specific energies required to break S–S and C–S bonds (268 and 285 kJ/mol, respectively) are rather close to the energy required to break the C–C bonds (348 kJ/mol) [93]. The higher the selectivity of the devulcanization, the better the mechanical properties. The devulcanization of GTR has been researched for more than five decades using various devulcanization methods [92].

Generally, devulcanization methods depend on the kind of energy used for the cross-linking bonds scission. Overall, mechanical energy (shear forces), thermal energy (conventional heat, microwave radiation) and chemical energy (chemical compounds) are commonly used for the devulcanization of GTR [80, 94]. Some other techniques such as ultrasonic [31, 95, 96] and biological [97–99] devulcanization are also used. However, current technologies largely use combinations of these methods, e.g. thermo-mechanical [100, 101], thermo-chemical [102, 103] and mechano-chemical [25, 104] devulcanization.

3.1.1. Chemical devulcanization techniques

Among rubber devulcanization methods, chemical methods are the preferred choice for industries *i.e.* mechano-chemical and thermo-chemical. Rubber devulcanization uses a variety of organic and inorganic chemicals. Sulfides and mercaptan compounds are frequently used in chemical methods. However, non-sulfur-containing compounds are presently under investigation due to their more environmentally friendly and cost-effective nature. The chemical devulcanization method has been in use since the 1960s and involves the application of various organic and inorganic chemical compounds. These compounds are strategically chosen to selectively break the C–S and/or S–S bonds [105]. In this process, the monosulfide, disulfide, and polysulfide cross-links are specifically targeted, making it a method where devulcanizing agents are utilized to break only the S–S and C–S bonds in a rubber vulcanizate [106]. The ability to selectively cleavage S–S and C–S bonds with devulcanizing agents is made possible by the fact that compared to the C–C bonds of the rubber main chain, the S–S bonds require relatively lower energy for cleavage.

Generally, chemical devulcanization is facilitated by the provision of thermal and mechanical energy to expedite the treatment process [80]. The majority of chemical devulcanization methods operate as batch processes, involving the mixing of GTR with chemical agents under controlled temperature and pressure conditions, as illustrated in Figure 10. Various chemical compounds can be employed for this purpose, including sulfides, mercaptans, amine-based compounds, inorganic solvents like propane thiol/piperidine, triphenylphosphine (TPP), trialkyl phosphites, lithium aluminum hydride and methyl iodide, as well as organic solvents such as alcohols and ketones and ionic liquids (ILs).

Organic disulfides and mercaptans

Organic disulfides and mercaptans play a pivotal role in the process of devulcanization, a vital aspect of GTR recycling and sustainable material management. The organic disulfides containing two sulfur atoms and mercaptans containing a thiol group (–SH) act as powerful reagents in this process. By cleaving

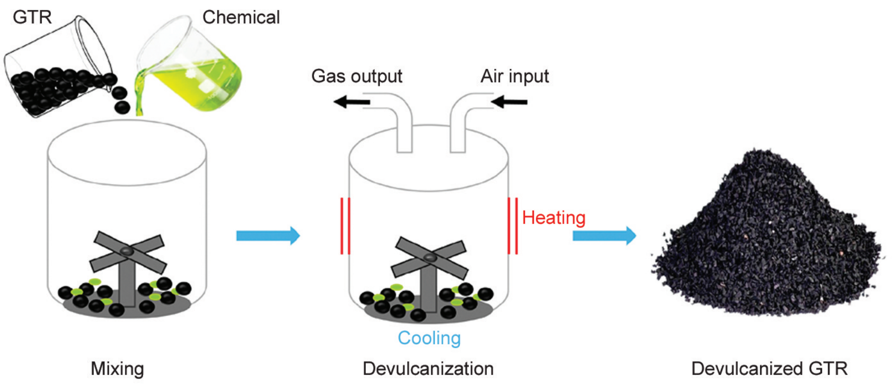


Figure 10. Chemical-based devulcanization system.

S–S bonds in the rubber matrix, these chemicals help to reverse the vulcanization process, leading to the restoration of rubber's desirable properties. Through the controlled application of heat, pressure, and these devulcanizing agents, GTR can be transformed into a more malleable state, facilitating its reprocessing into new rubber products.

Over the past century, numerous disulfides and mercaptans (Figure 11), had been formulated and assessed with the aim of devulcanizing rubber from waste tires. The devulcanization procedures using these organic disulfides and mercaptans encompass multiple sequential reaction stages, which can be summarized in a generalized manner as illustrated in Figure 12 [106]. This process required heat to initiate the homolytic breakdown of the sulfur cross-links. Consequently, produces free radicals of polysulfide cross-links and devulcanizing agents, enabling them to couple with each other and leading to the devulcanization of rubber. However, there is also the possibility of homolytic scission occurring within the primary polymer chain, along with coupling with the devulcanizing agent, which could result in polymer degradation.

Ghorai *et al*. [107] explored simultaneous devulcanization using silane, specifically bis(3-triethoxysilyl propyl) tetrasulfide (TESPT), as a devulcanization agent along with silica reinforcement for GTR based on NR. The devulcanizate not only eliminated the need for fresh NR but also facilitated the dispersion of silica. The presence of the pendant ethoxy group in the devulcanizate was identified as a factor contributing to the homogeneous distribution of silica in the blend or composite system. A devulcanizate blend comprising 50% (w/w) with the virgin compound exhibited a tensile strength of 16.7 MPa and an elongation at break of 882%. In comparison, a 60% (w/w) devulcanizate blend demonstrated a tensile strength of 17.9 MPa and an elongation at break of 863%. The study also reported enhancements in abrasion loss, tear strength, aging resistance, and rolling resistance. The proposed mechanism is shown in Figure 13.

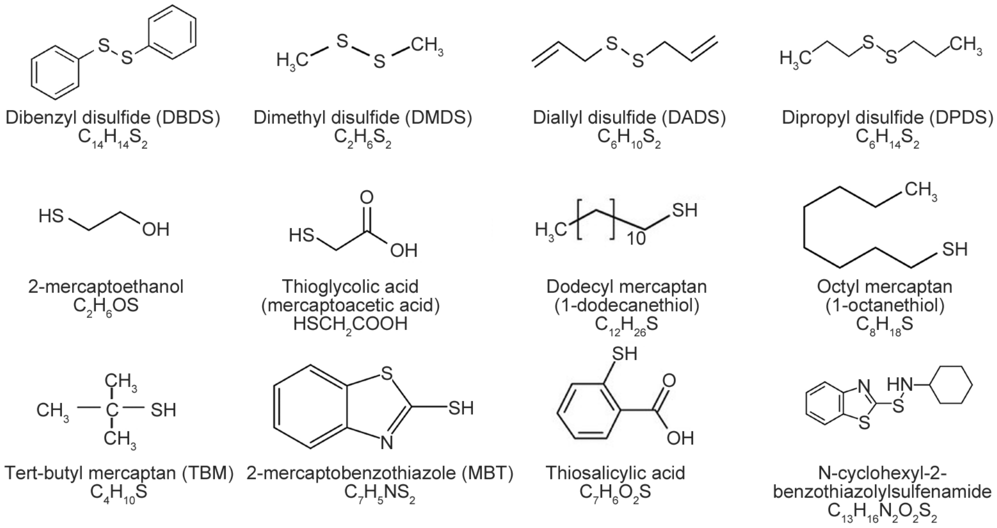


Figure 11. Organic sulfides and mercaptans used in waste tire devulcanization.

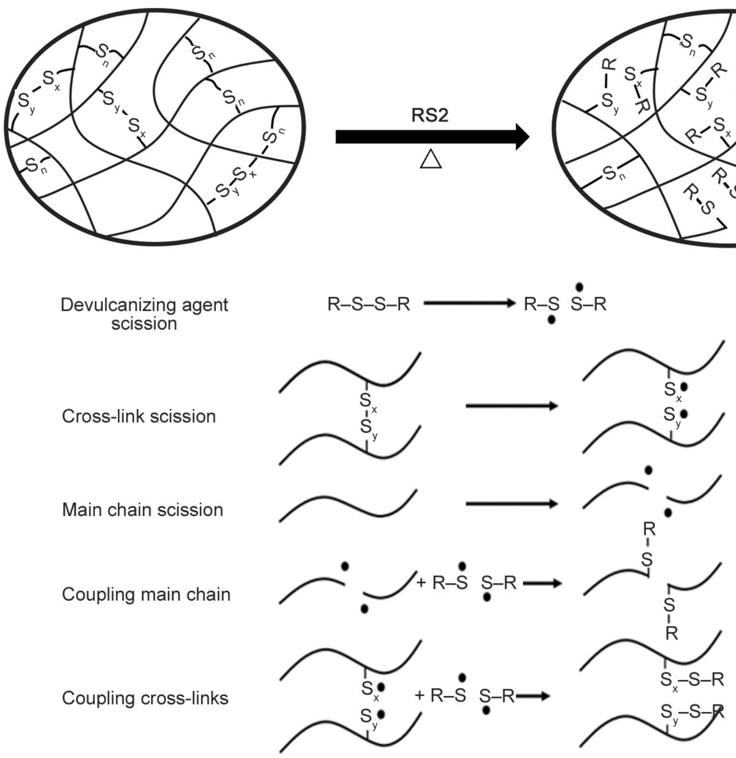


Figure 12. The radical devulcanization mechanism with sulfide devulcanizing agent [106].

Valentini, *et al*. [108] used urea with mono-, di- and tri-substituted derivatives and dicarboxylic acids containing 2–8 carbon atoms in the main chain for the devulcanization of GTR. The resulting dGTR was then incorporated into ethylene propylene diene monomer rubber (EPDM), which improved interfacial adhesion and enhanced impact properties, particularly in energy absorption and elongation at break. Additionally, it provided benefits such as reduced density and increased porosity, making it suitable for lightweight applications. In another study, they blended dGTR with polystyrene (PS), which significantly improved the blend's ductility and impact resistance, supporting its use as a toughening agent for brittle thermoplastics.

Mondal *et al*. [109] conducted a study to evaluate the efficacy of TESPT as a devulcanizing agent for 40 mesh GTR particles. The mechano-chemical devulcanization process was conducted using an open two-roll mill at room temperature for 20, 40 and 60 min. The most effective devulcanizate obtained showcased a sol content of 25% and a degree of network breakdown amounting to 32%. A 40 wt% devulcanizate, when blended with 60 wt% virgin compound, exhibited a tensile strength of 7.2 MPa and maintained a processable Mooney viscosity.

Inorganic and sulfur-free organic compounds

The sulfur-free organic compounds have been developed to selectively cleave the cross-links (C–S) and (S–S) bonds while leaving the polymer chain (C–C) bonds untreated: triphenylphosphine (TPP), trialkyl phosphites [110, 111], propane thiol/piperidine [112], methyl iodide [113] and lithium aluminum hydride [114]. Some inorganic compounds are also investigated for GTR devulcanization. By cross-metathesis, Smith *et al*. [115] reported a catalytic breakdown of polybutadiene and styrene-butadiene rubber (SBR). The soluble polymer was obtained from the treatment of polybutadiene. During reclamation, the first and second-generation Grubb catalysts were conducted with and without the addition of diester. The second-generation Grubb catalyst exhibited higher activity even without diester under specific conditions. Depolymerization was conducted with minimum degradation at room temperature for two to three hours.

Moore and Trego [110, 111] explored using triphenylphosphine (TPP) and sodium di-n-butyl phosphite as chemical probes to analyze sulfur cross-link structures in NR vulcanizates cured with sulfur. Their work included cis-1,4-polyisoprene with tetramethylthiuram disulfide (TMTD)-zinc oxide

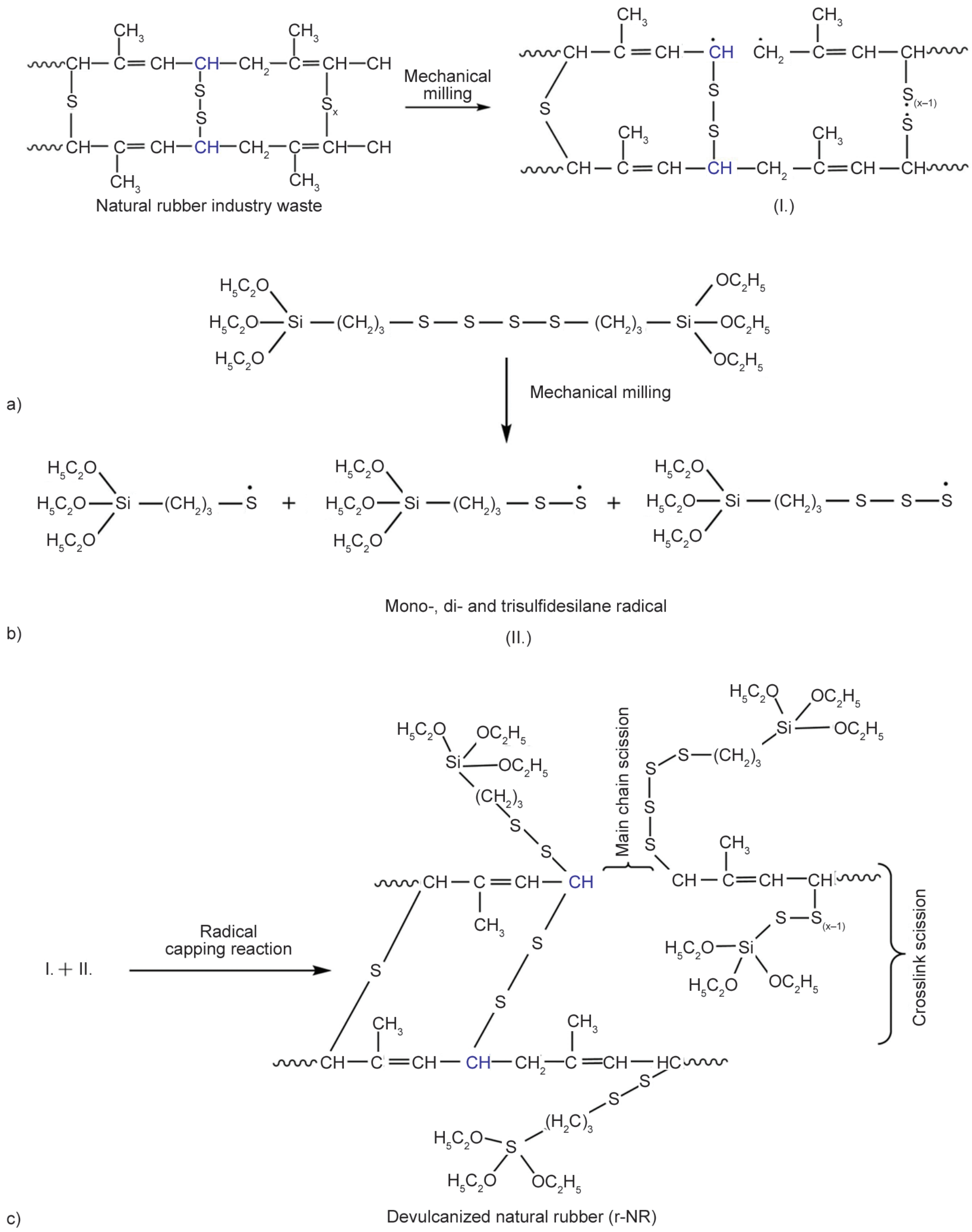


Figure 13. Mechanism of NR devulcanization by tetrasulfide silane a) breaking of NR chains, b) breaking of tetrasulfide silane and c) formation of devulcanized NR (r-NR) through radical capping reaction [107].

and NR-EPDM crosslinked with dicumyl peroxide and sulfur. The TPP converts polysulfide cross-links into monosulfide and disulfide bonds, depending on reaction time, molecular structure, and temperature. This transformation process can be seen in Figure 9. The sodium di-n-butyl phosphite cleaves di- and polysulfide cross-links without affecting monosulfide or carbon-carbon bonds. While TPP can be used as a devulcanizing agent, the properties of the vulcanizate cannot closely match those of virgin rubber.

Bockstal *et al*. [106] reviewed the use of TPP and 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) blends as devulcanizing agents. The DBU on its own could be capable of devulcanization and significantly impact the retention of mechanical properties after being blended with TPP. However, the small amount ranging from 0.03 to 0.3% weight of blended devulcanizing agents obtained good mechanical properties. Some other chemical compounds were employed for reclamation, but they reduced the molecular weight of rubber without devulcanization.

Dubkov *et al*. [54] employed nitrous oxide for rubber degradation through the ketonization of the unvulcanized carbon double bonds. This method produced a homogeneous rubber and enabled the separation of rubber from steel wires and fabric. Sadaka *et al*. [116] used periodic acid to conduct the oxidative cleaving of the leading polymer chains. They successfully achieved the reclamation of GTR through a controlled reaction that begins with the epoxidation of the double bond, followed by the cleavage of oxirane units. This oxidative process has the potential to reclaim GTR effectively using only periodic acid, which is an inexpensive oxidant and readily available.

Overall, using inorganic and sulfur-free organic compounds represents a promising approach for recycling vulcanized rubber, offering a sustainable solution for using waste rubber materials and contributing to the circular economy. However, further research is needed to optimize devulcanization processes and develop environmentally friendly and cost-effective devulcanizing agents.

3.1.2. Physical devulcanization approaches

Physical devulcanization approaches involve different physical and mechanical methods to cleave the cross-links in GTR, making it recyclable and restoring its original properties. These techniques are essential for recycling and reusing GTR. Some physical devulcanization approaches are described in this section.

Thermo-mechanical devulcanization

The thermo-mechanical devulcanization process employs a combination of both shear and elongational stresses to cleave the sulfur cross-links in vulcanized rubber. Extruders (single, twin screws, and multi-screws) and open mills are commonly used in the thermo-mechanical devulcanization of GTR. The thermo-mechanical process utilizes heat to enhance the breakdown process of cross-link sulfur bonds. However, the combination of high temperature, shear, and elongational stresses can lead to cleavage of the main polymer chains, resulting in a substantial reduction in molecular weight and other physical properties. Therefore, the characteristics of the equipment and the processing parameters are very important to achieve selectivity in breaking down the cross-link bonds [117].

Rigotti *et al*. [118] conducted mechanical devulcanization of GTR using a custom-made two-roll mill. By systematically varying parameters such as rolling speed and the number of rolling cycles, they examined the impact on the devulcanization level and chemical structure of the materials obtained. Subsequently, they incorporated different proportions of GTR and dGTR into EPDM through melt compounding. The dGTR demonstrated a stronger interface with the EPDM matrix compared to untreated GTR, attributed to revulcanization, which enabled restored cross-link sites to form chemical bonds with EPDM, resulting in increased energy absorption and strain at break.

Mouri *et al*. [119] presented a research study on the thermo-mechanical devulcanization of waste EPDM rubber. They employed a continuous process to utilize controlled shear flow reaction technology to cleave the sulfur cross-links selectively. The expected mechanism of this approach is shown in Figure 14. When the heat is applied to the rubber within the extruder, the initial bond to break is the polysulfide

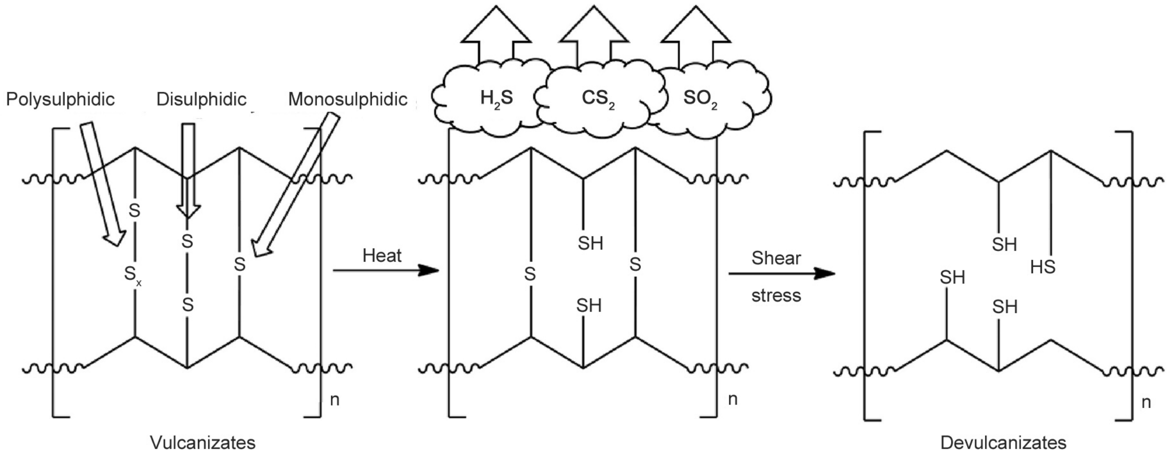


Figure 14. Thermo-mechanical devulcanization mechanism [120].

($–S_x–$) bond due to its low bond energy. Consequently, the C–S bond percentage increases in the vulcanized rubber, which can be broken by applying high shearing stress. During the thermo-mechanical process, some percentages of gaseous compounds such as SO_2, H_2S, and CS_2 are produced.

The extruder with twin screws was used in this process and the effects of different parameters, like screw configuration, screw speed, screw geometry, controls, reactor fill factor, time, rubber residence, mixing force, shearing force, processing temperature and internal pressure were investigated. The high hydrostatic pressure and high shearing deformation resulted in better devulcanization. Through optimum screw designing, they were able to produce a continuous sticky strand of devulcanized rubber. They also inspected the devulcanization process within the twin screw extruder. The twin screw extruder is considered the most practical option for thermo-mechanical devulcanization and is commonly used in the polymer industry [93]. Furthermore, when it comes to comparing with industrial volume the extrusion process is the best choice [80]. Figure 15a shows a typical co-rotating twin-screw extruder setup and Figure 15b a screw configuration for devulcanization.

The key advantage of thermo-mechanical devulcanization is its ability to produce reclaimed rubber with desirable properties, such as improved processability, flexibility, and compatibility with other materials. This method offers the possibility of achieving high levels of devulcanization without the need for chemical additives or processing aids, making it an environmentally friendly and cost-effective solution for rubber recycling.

Overall, thermo-mechanical devulcanization represents a promising approach for recycling vulcanized rubber, offering a sustainable solution for using waste tire rubber and contributing to the circular economy.

Mechano-chemical processes

The mechano-chemical devulcanization process combines mechanical and chemical methods, like temperature, shearing forces, and chemical compounds [121]. Yehia *et al*. [122] studied the comparison of thermo-mechanical and mechano-chemical processes. The obtained results were similar for both

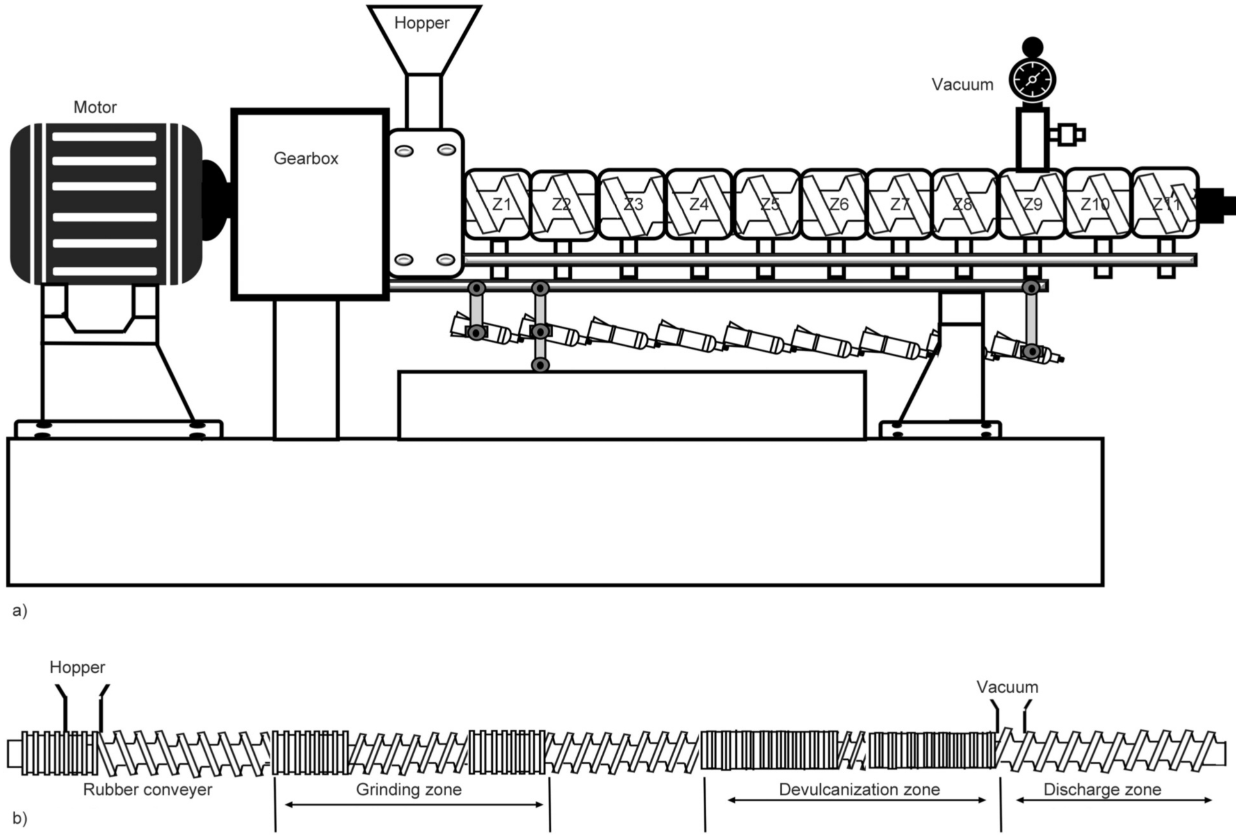


Figure 15. A twin-screw extruder for continuous devulcanization. a) Scheme of the extruder, b) typical screw configuration with the different process sections.

methods. They used a mechanical process by adding oil and chemical agents such as pentachlorothiophenol or zinc chloride to devulcanize GTR. This process is commonly known as mechano-chemical devulcanization. They mixed 10–30% of the devulcanized GTR with virgin rubber and observed no effect on basic properties. However, the higher amount of devulcanized GTR has no significant effect on the mechanical properties. For instance, the abrasion resistance, modulus, hardness and compression set increased while tensile strength, elongation at break, resilience and tear strength decreased [122].

Microwave devulcanization

Microwave devulcanization utilizes microwave energy with a specific frequency to scission the cross-link bonds of vulcanized rubber. The microwave contains radiations with frequency and wavelength ranging from 300 MHz to 300 GHz and 1 to 1000 mm, respectively [19, 120].

The microwave technique utilizes volumetric heating by microwaves, enabling more uniform heating than traditional methods, which rely on conduction and/or convection [8, 123]. Different materials respond uniquely to the electromagnetic field generated by microwaves. In polar materials, molecules or free ions create a dipole moment, resulting in volumetric heating. Elastomers like NR, EPDM, and SBR exhibit low microwave absorption capacity. However, this limitation can be addressed by adding conductive fillers like carbon black (CB) and silica [47, 124], which induce a phenomenon called Maxwell-Wagner polarization [125, 126]. This process is purely physical, involving no chemicals, making it an eco-friendly alternative [127].

The existence of polar groups in the GTR and CB absorbs the microwave energy and produces enough heat required to cleave the targeted bond. Hirayama and Saron [128] reported an interesting study regarding chemical changes in SBR after microwave treatment. The fresh SBR was initially compounded with varying amounts of CB (0–49.1%), then vulcanized and shredded to 20-mesh of particle size for devulcanization at 0.7 kW for 120 s. The result showed that polysulfidic ($–S_x–$) bonds were broken, as well as other sulfur-containing groups, whereas monosulfidic bonds remained intact. However, these findings were only observed in compounds having high CB contents due to the high polarity of CB, which results in better microwave treatment.

The microwave devulcanization is one of the most effective devulcanization methods, offering several advantages such as (i) more uniform heating promotes selective scission of cross-links [8] (ii) chemicals free method [127] (iii) the process parameters are easy to and (iv) can achieve higher productivity [21, 129]. The very first microwave devulcanization method was used and patented by Goodyear Tire & Rubber Co. [130]. In this process, the GTR with particle size 6–10 mm was devulcanized by a microwave system operated in a range of 0.915–2.45 GHz. It was observed that the temperature of GTR was rapidly increased from 260 to 350 °C. Adhikari *et al*. [65] published a review and proposed that microwave devulcanization techniques can reduce and control environmental pollution. The devulcanized rubber obtained from the microwave method can be used as a compounding material to be blended with virgin rubber. Landini *et al*. [131] studied the impact of microwave devulcanization techniques on bromo-butyl rubber (BIIR) and chloroprene rubber. The microwave irradiation time was 9–25 min, and the power supply was about 1000 W. The results indicated that the degree of devulcanization increased proportionally with increasing time and power. In both studies, the devulcanized rubbers were revulcanized and tested for their hardness and ash content. The results revealed that the revulcanized rubber lost hardness without a significant loss in molecular weight. These observations suggested the retention of the polymer networks. Seghar *et al*. [132] studied microwave devulcanization of SBR with the energy level of 110–440 W·h/kg and time 0–100 s. The higher degree of devulcanization was achieved at about 60%, at 440 W·h/kg, with an exposure time of 100 s. Microwave devulcanization is considered an environmentally friendly method and a contributor to green chemistry. It offers several benefits, including reduced CO_2 emissions, decreased reliance on primary raw materials, and lower energy requirements, which can lead to cost reductions [127] . However, the process has some disadvantages in terms of economic benefits because of expensive equipment. It is not feasible for industrial applications due to high thermal runaway possibility under specific operational conditions [105].

3.1.3. Biological and enzymatic devulcanization

In biological devulcanization, the sulfur cross-links in vulcanized rubber are broken down through biological degradation. Certain species of bacteria and archaea can selectively break the sulfur bonds on the surface of vulcanized rubber. Among these, sulfur-oxidizing species, such as *Thiobacillus* genus and thermoacidophiles of the *Sulfolobales* order, have been extensively studied [133]. Some research has also explored using bacteria from the *Thiobacillios* and *Nacardia genera* to achieve devulcanization of SBR and NR [117]. It is important to note that the biological process can only occur on the surface of the rubber, resulting in a relatively low degree of devulcanization.

Kaewpetch *et al*. [98] found that *Bacillus cereus* (*TISTR 2651*) effectively devulcanized NR vulcanizates. The bacteria demonstrated the capacity to oxidize sulfide cross-links and partially cleave the primary carbon chain in the rubber. Horikx-Verbruggen analysis indicated that the primary mechanism involved the early-stage cleavage of sulfur cross-links by the bacteria. After 20 days of devulcanization, the cross-link density and gel fraction analyses showed a substantial reduction compared to the control sample before bacterial treatment. The enzymes within the microorganism are believed to catalyze the oxidation reaction, and the proposed desulfurization pathway of *B. cereus TISTR 2651* resembles the 4S pathway illustrated in Figure 16. Therefore, all these findings suggest that *Bacillus cereus* holds the potential for recovering virgin rubber and recycling end-of-life rubber.

The first isolated strain of *Rhodococcus, IGTS8*, which can desulfurize dibenzothiophene (DBT), has been studied for its desulfurization capabilities [134]. The DBT desulfurization pathways are known as the 'Kodama' and the '4S' pathways. Only the 4S pathway involves the sequential oxidation of the sulfur component and the cleavage of C–S bonds while preserving the C–C bonds. Three enzymes DszC, DszA, and DszB have been identified as catalyzing the stepwise reactions that convert DBT to DBT-5-oxide (DBTO), DBT-5,5′-oxide (DBTO2), 2′-hydroxybiphenyl-2-sulfinate (HPBSi), and 2′-hydroxybiphenyl (HBP) without degrading either aromatic ring [135]. Despite their structural similarities, most DBT-desulfurizing bacteria cannot desulfurize benzothiophene (BTH), another major sulfur constituent

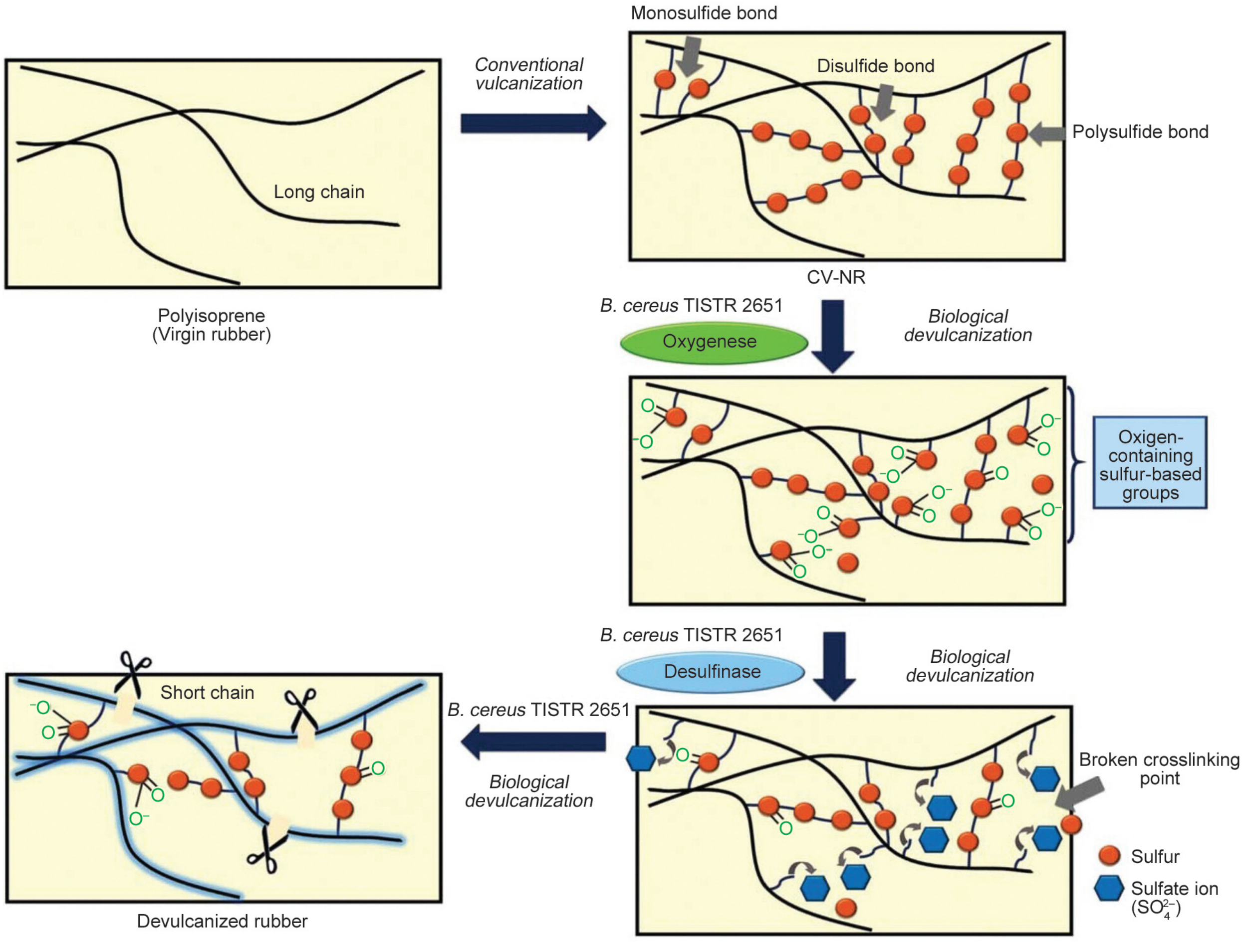


Figure 16. Oxygenase and desulfinase mechanism in microbial (TISTR 2651) devulcanization of NR [98].

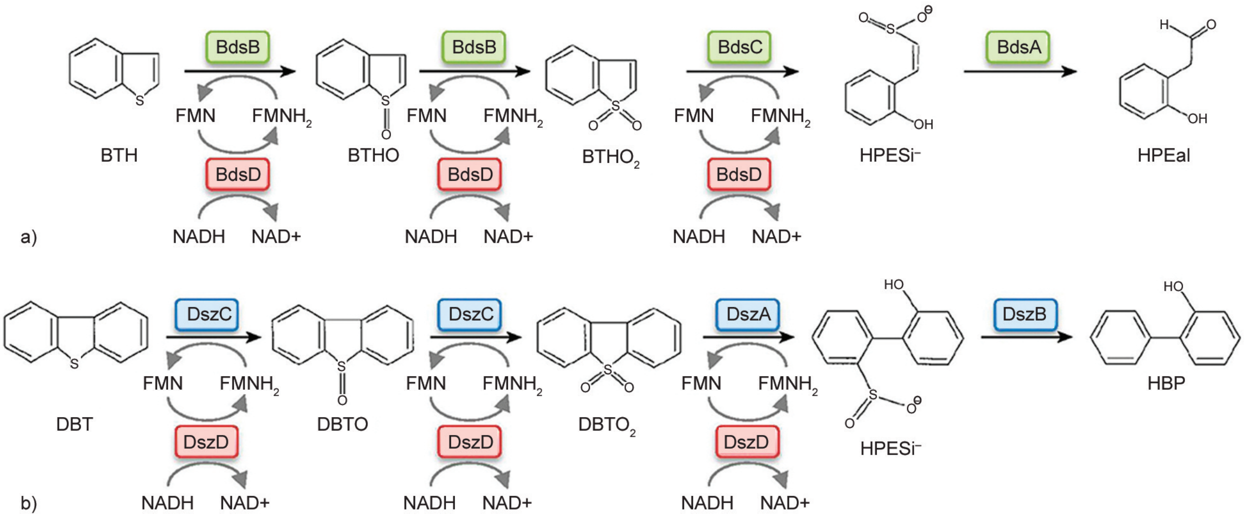


Figure 17. Comparison of the proposed '4S' BTH desulfurization pathway for *Gordonia desulfuricans* (a) with the DBT desulfurization pathway of *Rhodococcus* sp. strain IGTS8 (b). BTH, benzothiophene; BTHO, benzothiophene S-oxide; $BTHO_2$, benzothiophene S,S dioxide; $HPESi^-$, (Z)-2-(2H-hydroxyphenyl)-ethen 1-sulphinate; HBPEal, 2-(2H-hydroxyphenyl)-ethan 1-al [133].

of fossil fuels. However, *Gordonia* desulfuricans is one of the few microorganisms identified that can selectively cleave sulfur from BTH without breaking the C–C bonds [136]. The 4S pathway for BTH and DBT desulfurization is shown in Figure 17 [133]. Haroune *et al*. [137] reported some detoxification through *Rhodococcus* bacteria and degraded mercapto-benzo thiazole (MBT) that exists in rubber structures and road dust. The MBT is a hazardous chemical that causes bladder cancer and dermatoses [138, 139]. This bacterium metabolized MBT in the rubber structure, rendering tire disposal safer for the environment. Although research on the biological method of devulcanization is currently limited and demanding, it has several limitations that need to be addressed. One of these limitations is the long processing time, which takes approximately 40 days [65]. As a result, the biotechnological devulcanization method still has a long way to go before it can be practically applied in industrial settings.

3.2. Comparison of devulcanization methods

A comparison of different devulcanization methods can help to understand their advantages and limitations and their use for specific applications. Table 3 shows the comparison of some commonly used devulcanization methods. Each devulcanization technique has advantages and disadvantages, and its choice depends on the required degree of devulcanization, such as the type of rubber, application of the devulcanized rubber, and economic viability. It is necessary to balance different methods to achieve efficient devulcanization and maintain good rubber properties for the required application. Current research and development initiatives are focused on improving the capability of these techniques and enhancing their applications in GTR recycling.

3.3. Structural evolution of GTR during devulcanization

The structural evolution of GTR during devulcanization plays an important role in understanding the purpose of application. Structural evolution is a multifaceted process influenced by various factors such as temperature, pressure, chemical agents, and mechanical forces. Initially, GTR consists of a highly cross-linked network of polymer chains due to the vulcanization process, which imparts strength and durability to rubber products. The structure of cross-linked networks involves three primary types of cross-links: rubber-rubber chain cross-links, rubber chain-filler interactions (also known as bound rubber), and filler-filler interactions, as shown in Figure 18. During devulcanization, these cross-links are broken down, leading to the fragmentation of the rubber network and the release of sulfur and sulfur derivatives compounds from the cross-linked bonds. This process can be facilitated by factors such as heat, which increases the mobility of polymer chains, and chemical agents or reactive species, which react with the sulfur cross-links to cleave them.

Table 3. Comparison of different devulcanization methods.

Method	Characteristics	Pros	Cons
Chemical devulcanization	In chemical devulcanization, chemical compounds *i.e.* organic sulfides and mercaptans are used to cleave the sulfur cross-links in GTR.	The chemical devulcanization method can achieve highly efficient and selective devulcanization, resulting in mechanical properties of devulcanized rubber closer to virgin rubber and can be used for different rubber blends.	The chemical devulcanization method requires careful control of chemical reactions and it can generate chemical waste. Some chemical agents are hazardous and require special handling. Chemical devulcanization required additional purification of some products that were obtained.
Extrusion	In the extrusion method, heat and pressure can be used to devulcanize GTR.	The extrusion method is widely used in rubber recycling industries. This method is relatively simple and cost-effective. The extrusion method can achieve partial devulcanization and reclamation.	The extrusion method has some limitations, such as partial devulcanization and reclamation of rubber, so the properties of devulcanized rubber do not completely match those of virgin rubber.
Mechanical milling	In mechanical milling, different mechanical forces, like ball mills and hammer mills, are used to break down the cross-links in GTR.	The mechanical milling method can be used for GTR, and it can control the particle size. This method is useful to produce GTR for filler applications in different rubber blends.	The mechanical milling method cannot achieve complete devulcanization of GTR. The mechanical milling method leads to a reduction in the mechanical properties of GTR.
Microwave devulcanization	The microwave devulcanization used microwave radiations to break down the cross-links in GTR and promote devulcanization.	The microwave devulcanization method can produce precise heating and reduce energy consumption. This method is environmentally friendly and produces low CO_2.	The microwave method faces challenges when applied to large-scale industrial settings. Achieving uniform heating in large volumes of rubber can be difficult, and the high equipment cost may limit its widespread adoption.
Biological devulcanization	Biological devulcanization methods use microorganisms or enzymes to break down the sulfur cross-links in GTR.	The biological devulcanization method is an energy-efficient, cost-effective and environmentally friendly method to devulcanize GTR.	The biological devulcanization method is a less efficient, complex and time-consuming method.

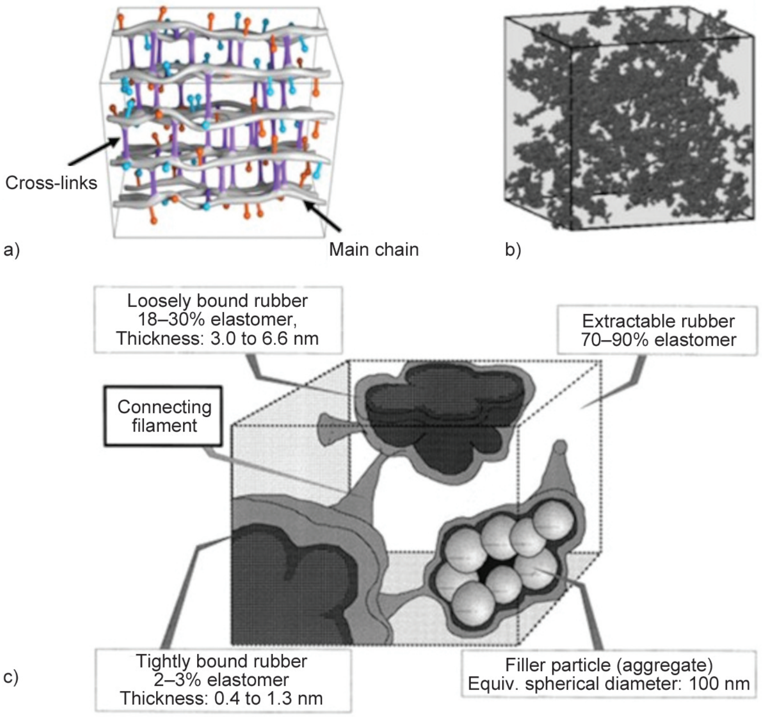
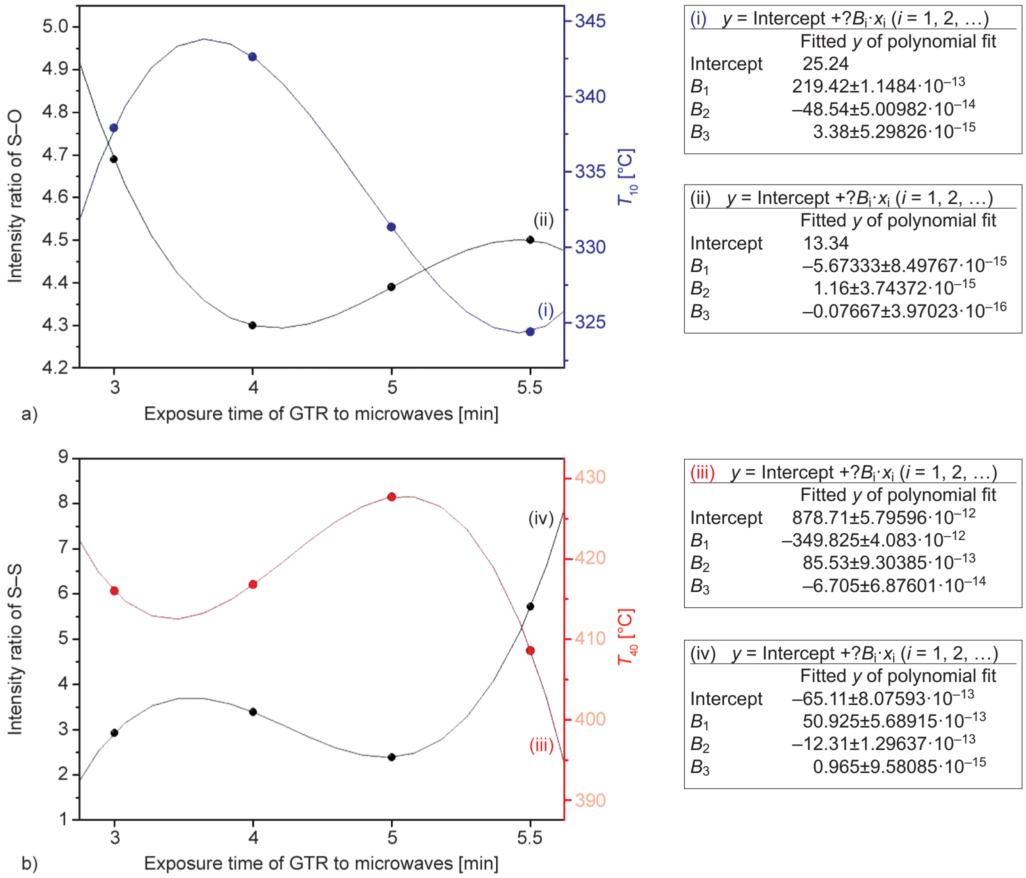


Figure 18. Multi cross-linking of GTR: a) rubber chains cross-link, b) rubber chain and filler (bound rubber), c) filler and filler (aggregates) [140].

As devulcanization progresses, the molecular weight distribution of the rubber shifts towards lower molecular weights, indicating the breakdown of polymer chains. During the devulcanization process, the simultaneous and random breakage and formation of new chemical bonds occur, resulting in a modified



(i) y = Intercept +?$B_i \cdot x_i$ (i = 1, 2, …)	Fitted y of polynomial fit
Intercept	25.24
B_1	$219.42 \pm 1.1484 \cdot 10^{-13}$
B_2	$-48.54 \pm 5.00982 \cdot 10^{-14}$
B_3	$3.38 \pm 5.29826 \cdot 10^{-15}$

(ii) y = Intercept +?$B_i \cdot x_i$ (i = 1, 2, …)	Fitted y of polynomial fit
Intercept	13.34
B_1	$-5.67333 \pm 8.49767 \cdot 10^{-15}$
B_2	$1.16 \pm 3.74372 \cdot 10^{-15}$
B_3	$-0.07667 \pm 3.97023 \cdot 10^{-16}$

(iii) y = Intercept +?$B_i \cdot x_i$ (i = 1, 2, …)	Fitted y of polynomial fit
Intercept	$878.71 \pm 5.79596 \cdot 10^{-12}$
B_1	$-349.825 \pm 4.083 \cdot 10^{-12}$
B_2	$85.53 \pm 9.30385 \cdot 10^{-13}$
B_3	$-6.705 \pm 6.87601 \cdot 10^{-14}$

(iv) y = Intercept +?$B_i \cdot x_i$ (i = 1, 2, …)	Fitted y of polynomial fit
Intercept	$-65.11 \pm 8.07593 \cdot 10^{-13}$
B_1	$50.925 \pm 5.68915 \cdot 10^{-13}$
B_2	$-12.31 \pm 1.29637 \cdot 10^{-13}$
B_3	$0.965 \pm 9.58085 \cdot 10^{-15}$

Figure 19. Comparison of thermal stability and intensity ratios of the S–O and S–S bonds in FTIR analysis: a) Correlations between the intensity ratio of S–O bonds and T10; and b) intensity ratio of S–S bonds and T40. The circles are the experimental results, while the lines are the fits [141].

chemical structure of the devulcanized rubber. Research indicates that sulfidic bonds, in particular, are broken [128], transforming into other bonds through a recombination process of sulfur present in the samples. This recombination involves the rearrangement of sulfur-free radicals due to the cleavage of crosslinks [19]. This alteration in the chemical structure of devulcanized rubber has implications for its thermal stability, which is crucial to assess when considering using GTR as a raw material in producing new consumer goods. De Sousa and Ornaghi Júnior [141] compared the thermal stability and peak intensity ratios of the S–O and S–S bonds of FTIR analysis during microwave devulcanization of GTR, as shown in Figure 19.

The results indicated the correlation between the chemical composition of the devulcanized GTR and its thermal stability. It appeared that S–O type bonds, likely formed through the rearrangement of sulfur-free radicals during the devulcanization of GTR in the presence of oxygen, were more closely associated with the stability of the NR phase. Conversely, S–S bonds appeared to have a stronger correlation with the stability of the SBR phase. The devulcanization process, particularly under microwave irradiation, exhibited a more pronounced devulcanization of the NR phase [19], likely due to the presence of S–O bonds indicative of oxidation [142]. In contrast, the SBR phase remained relatively stable, potentially fostering the formation of polysulfidic cross-linkages through the rearrangement of sulfur-free radicals resulting from the breakdown of sulfidic bonds [19]. Additionally, using a third polynomial order facilitated predicting the behavior or intensity of S–S and S–O bonds at the two temperatures investigated. The general mechanism for forming S–O and S–S bonds, applicable to both NR and SBR, is illustrated in Figure 20.

Shi *et al*. [143] observed a similar phenomenon in the sol fraction of reclaimed rubber processed using a twin-screw extruder at various shearing times (5, 10, 20, 30, and 40 min) at 180 °C. The sol fractions recorded were 30.3, 64.0, 41.1, 33.8, and 26.8%, respectively. Initially, the sol fraction increased, reaching a peak, but subsequently decreased due to

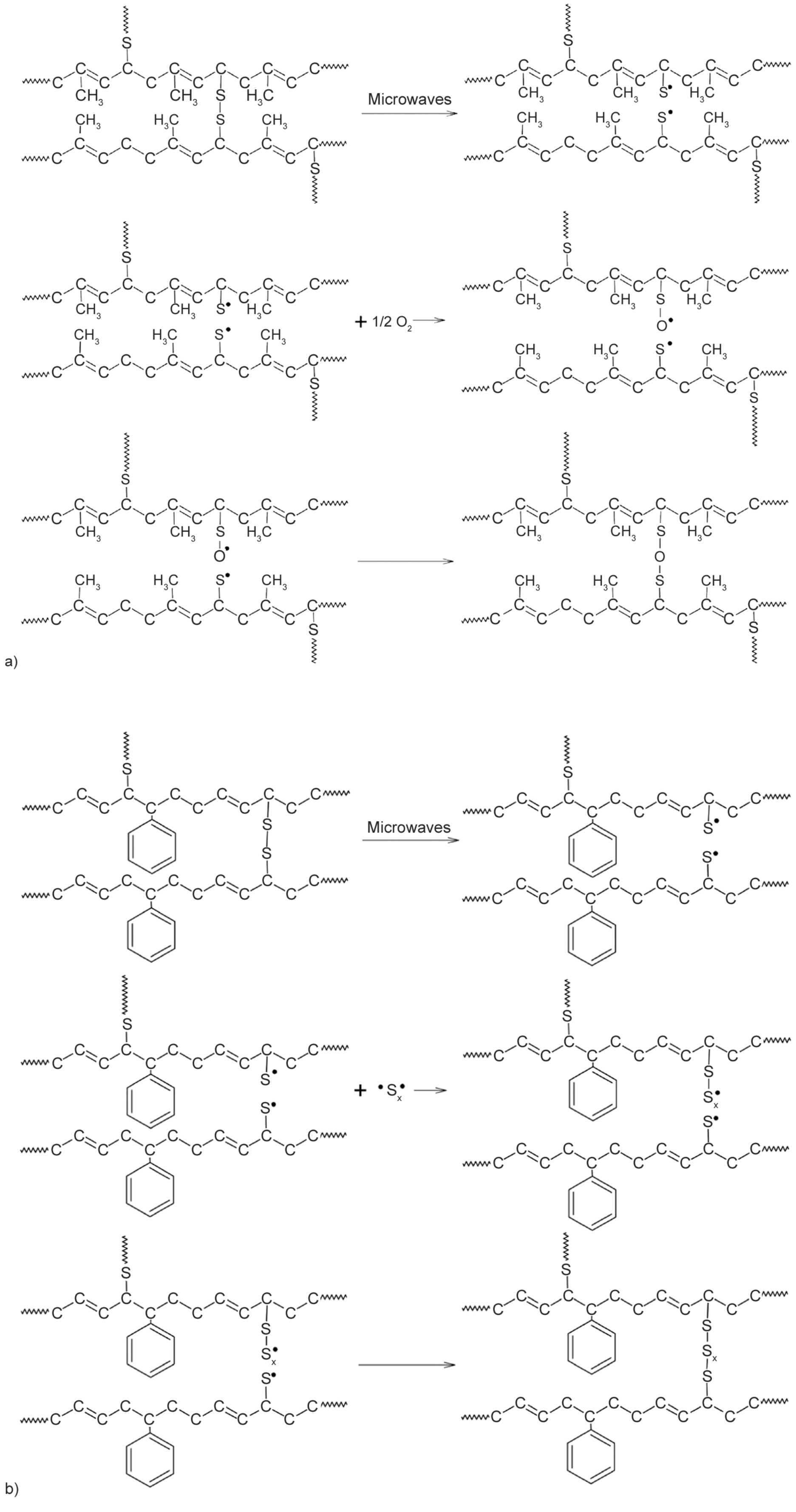


Figure 20. Simplified mechanism proposed for the formation of a) S–O bonds during devulcanization of NR and b) S–S bonds during devulcanization of SBR by microwaves [141].

chemical transformations occurring during the process. These transformations involved the breakdown of the main chain and cross-links, including polysulfidic, disulfidic, and monosulfidic bonds, as well as the conversion of sulfidic cross-links into cyclic sulfidic structures along the elastomer backbone. Additionally, polysulfidic cross-links transformed into disulfidic and monosulfidic cross-links [144]. Prolonged devulcanization led to the formation of new intermolecular and intramolecular bonds, which ultimately reduced the sol fraction beyond a specific shearing time. They concluded that GTR can be effectively devulcanized by shear force in the presence of oxygen, particularly at elevated temperatures. However, the high-temperature presence of oxygen also has side effects, such as causing main-chain scission.

Zhang *et al*. [4] employed a thermo-oxidative method to reclaim GTR using adjustable pulse air input at 200 °C for 5, 10, 15, and 20 min of oxidative durations. The sol fraction of reclaimed ground tire rubber (RGTR-1, RGTR-2, RGTR-3, and RGTR-4) as a function of stirring time (5, 10, 15, and 20 min), respectively, during thermal-oxidative reclamation is shown in Figure 21. The sol fraction increases significantly over time, reaching approximately 66.5% after 20 min at 200 °C. This trend highlights the progressive breakdown of the cross-linked rubber network facilitated by oxygen in the air atmosphere at elevated temperatures. The rising sol fraction demonstrates this dynamic thermal-oxidative process's efficacy in promoting cross-link scission and main-chain fragmentation. In the initial stages, oxidation primarily targets the weaker cross-link bonds. At the same time, extended stirring time leads to more extensive polymer chain fragmentation, releasing smaller, soluble rubber fragments.

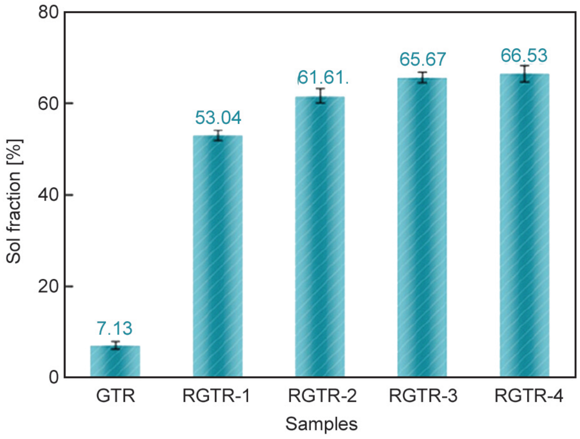


Figure 21. The sol content of GTR and RGTR-1, RGTR-2, RGTR-3 and RGTR-4 [4].

During devulcanization, the structure of rubber undergoes substantial changes influenced by its chemical composition. Unsaturated rubbers, such as NR and SBR, with double bonds in their polymer backbones, experience significant main-chain scission, particularly at high temperatures [145]. The main chain scission occurred at cross-linked sites on the secondary carbon atom adjacent to the cross-link moiety [146]. In contrast, saturated rubbers like EPDM, lacking double bonds in their main chains, exhibit greater resistance to chain scission. Fillers and additives further influence the process, impacting the extent of structural breakdown. Li *et al*. [147] conducted transmission electron microscope (TEM) analysis to investigate the structural changes that occur during the reclamation of GTR using a twin screw extruder at temperatures 280 and 300 °C, as shown in Figure 22. The study revealed that CB released during decrosslinking exhibited a core-shell structure, with the core consisting of aggregated CB particles and a rough surface layer of colloidal substance, indicating the presence of bound rubber on the CB surface. As decrosslinking progressed, the bound rubber became more uniformly distributed with a thickness of more than 2 nm (Figure 22a). Research suggested that bound rubber consisted of loosely bound rubber and tightly bound rubber, with the tightly bound rubber having a thickness of 0.4 to 2 nm [148]. This indicated that the secondary network breakage mainly occurred in the loosely bound rubber. Ultimately, the bound rubber thickness decreased with deep decrosslinking, showing the complete removal of the loosely bound rubber while tightly bound rubber remained (Figure 22b). There is no obvious rubber shell on the surface of H-CB$_{lp}$, which was heated in a furnace at 500 °C (Figure 22c). The decrosslinked gel can function both as an elastic filler and exhibit binder potential through the remaining bound rubber. The bound rubber forms a complex and stable layer around CB particles and agglomerates, arising from covalent and physical bonding interactions, including van der Waals forces, between polymer chains and CB during the compounding process. It consists of two layers: a primary layer of tightly bound rubber and a secondary layer of connected filaments as shown in Figure 23. This structural composition impacts the separation of CB and rubber during devulcanization. However,

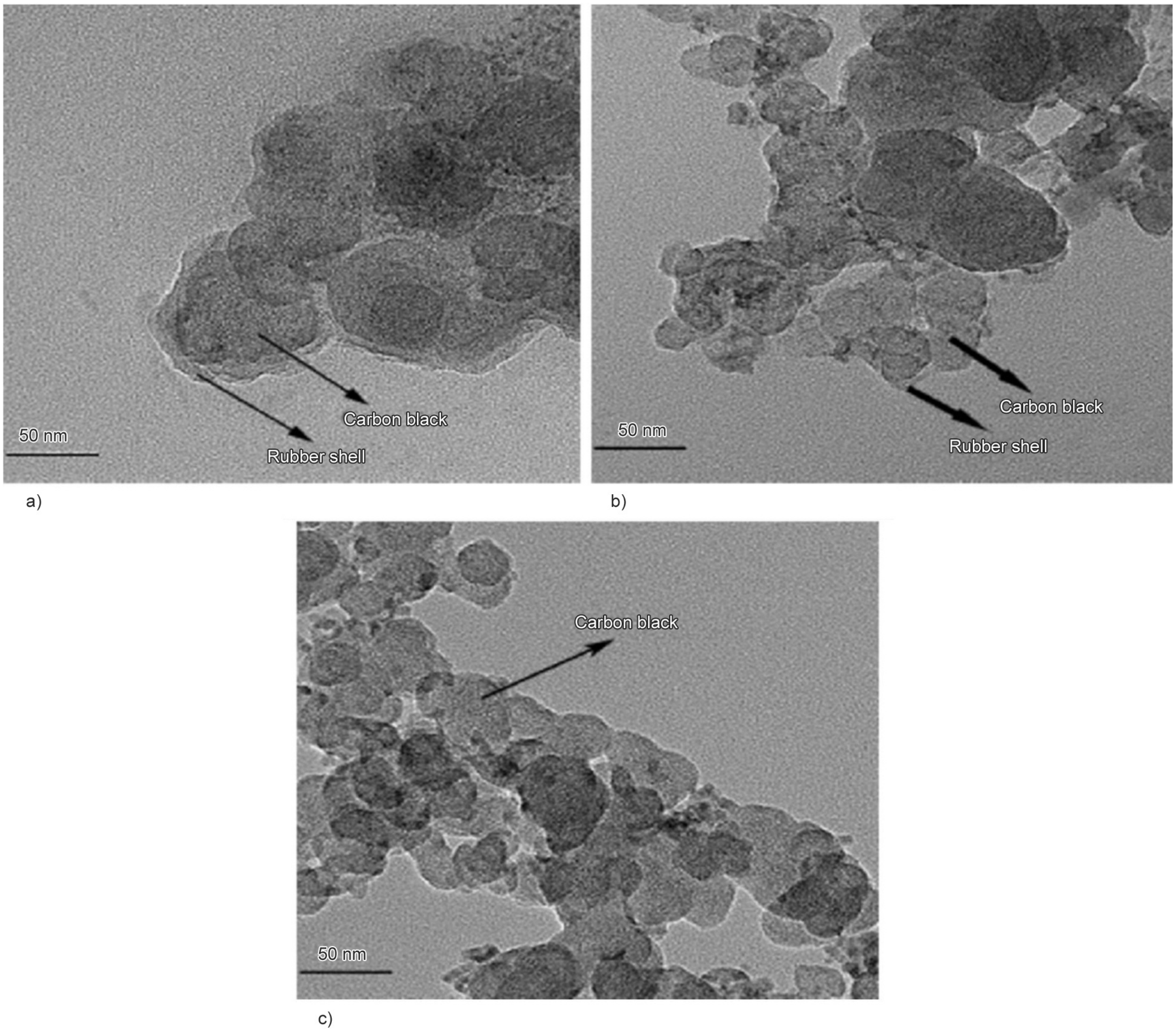


Figure 22. TEM micrographs of core-shell structured carbon black (CBlp) nanoparticles a) CB$_{\text{lp}}$-280, b) CB$_{\text{lp}}$-300, c) H-CB$_{\text{lp}}$ [147].

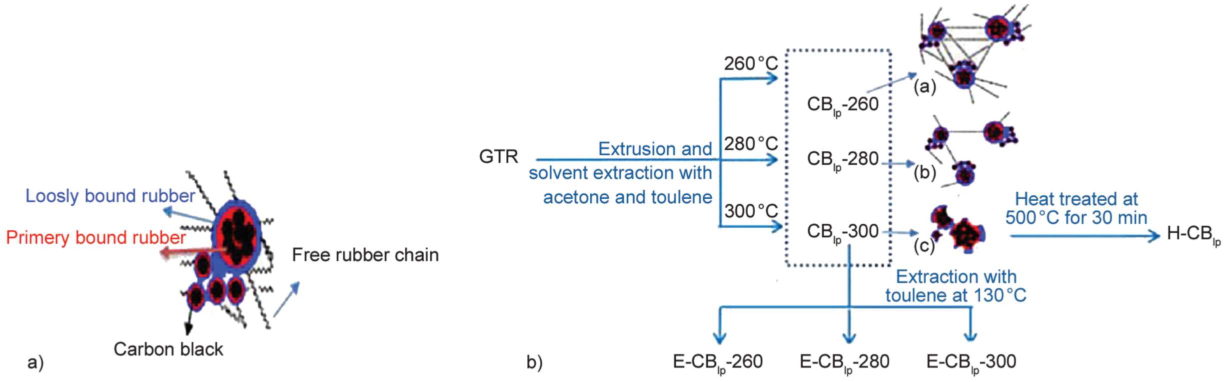


Figure 23. Procedure and schematic illustration of a primary layer of tightly bound rubber and a secondary layer of loosely bound rubber [147]. a) Schematic of original tire rubber, b) processing procedure of light pyrolysis and separation.

understanding the structural changes occurring during devulcanization is crucial for optimizing the process and tailoring the properties of the resulting devulcanized rubber for specific applications.

3.4. The application of reclaimed rubber

Reclaimed rubber can be used in many different applications. The reclaimed rubber serves as a vital component across a wide spectrum of industries due to its cost-effectiveness, sustainability, and versatility. In the automotive sector, it is extensively utilized in tire manufacturing, where it contributes to the carcass, sidewall, and under-tread sections of passenger, light truck, and off-the-road tires, enhancing their elasticity, durability, and overall performance.

Additionally, reclaimed rubber is used in the production of tubeless passenger-tire inner liners and inner tubes, providing enhanced air retention and puncture resistance. Semi-pneumatic tires also benefit from incorporating reclaimed rubber, improving their shock absorption and resilience. Beyond tire manufacturing, reclaimed rubber finds application in automotive floor mats, where its abrasion resistance and flexibility are valued. In the realm of mechanical goods, it contributes to the production of various products requiring elasticity and impact resistance. Reclaimed rubber is an essential ingredient in adhesive, sealing, and tape compounds, where its adhesive properties and flexibility are leveraged.

Another significant application lies in rubber-modified asphalt. The incorporation of reclaimed rubber improves the elasticity, flexibility, and durability of asphalt pavements, resulting in reduced cracking, rutting, and deformation over time. The rubberized asphalt also exhibits superior resistance to temperature variations and aging, resulting in long-lasting road surfaces and reduced maintenance costs. When GTR or crumb rubber is mixed and heated with bitumen, the rubber particles swell in a time and temperature-dependent manner during the interaction process, which results in a reduction in the interparticle distance, thereby increasing viscosity, as shown in Figure 24. The prolonged exposure to high temperatures or extended duration can result in ongoing swelling of the crumb rubber. However, beyond a certain threshold, this swelling transitions into reclamation due to prolonged heat exposure. This transition leads to the dispersion of rubber into the bitumen. The reclamation initiates the release of rubber components back into the liquid phase, thereby causing a decrease in the complex modulus (G^*), which signifies material stiffness. Meanwhile, the phase angle (δ), indicating elastic properties [149]. The increase in bitumen's viscosity causes several problems, *i.e.*, adhesion, cohesion, temperature sensitivity, durability, performance grading, and rutting resistance. Therefore, using reclaimed rubber saves more energy and time in rubber-modified asphalt. These diverse applications underscore the importance and utility of reclaimed rubber in modern industries, playing a crucial role in enhancing product performance, reducing costs, and promoting environmental sustainability.

4. Challenges in the devulcanization process and promise in multi-decrosslinking

Devulcanization faces several significant challenges that impact its efficiency, scalability, and environmental sustainability. A major issue lies in achieving selective breaking of sulfur-sulfur (S–S) and carbon-sulfur (C–S) cross-links without damaging the carbon-carbon (C–C) backbone of the rubber matrix. The existing technologies achieved this to some extent but also break the carbon chain bonds, reducing the recycled rubber's physical properties, limiting its potential applications and limiting its use to low-value rubber products [133].

Many devulcanization methods are energy-intensive, requiring high temperatures, mechanical forces, or specialized equipment, which increases operational

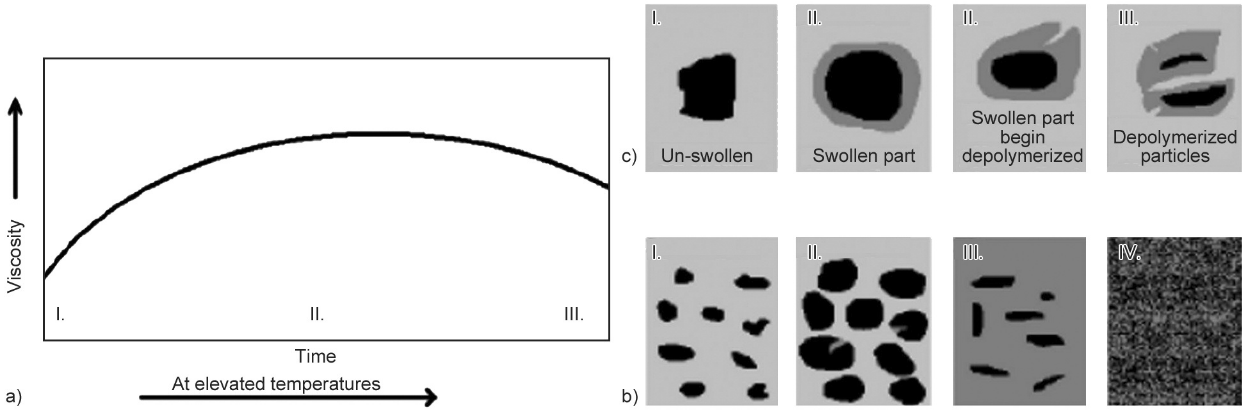


Figure 24. Bitumen-GTR interaction phenomenon at elevated temperatures: change of properties over time [150]. a) Binder viscosity, b) binder matrix, c) particles size.

costs and environmental impact. Chemical reclamation methods pose additional challenges due to using sulfur-containing or toxic agents, which can lead to environmental hazards, such as chemical residues or harmful emissions in the final product [65]. Similarly, microbial devulcanization methods face challenges related to material homogeneity and particle size, as larger particles hinder mixing and smaller ones may experience shear tension issues during processing. Knowledge gaps in biotechnological approaches, such as understanding enzyme pathways and overcoming feedback inhibition like sulfate repression, limit their potential as a proper devulcanization solution [133].

The GTR contains contaminants and additives, such as oils, fillers, and processing aids, that complicate the devulcanization process [151]. These materials may hinder the cleavage of sulfur cross-links or remain in the devulcanized rubber, adversely affecting its mechanical properties. Developing special techniques for the devulcanization process that are suitable for industrial production is essential. Many techniques are still confined to the laboratory level and may not be applicable to large-scale industrial applications.

Scaling these processes to industrial levels presents additional hurdles, particularly for biotechnological methods, where maintaining sterility, ensuring adequate oxygen levels, and achieving uniform mixing in large-scale systems is challenging. Furthermore, the absence of comprehensive life cycle assessments (LCA) for most methods hinders the evaluation of their environmental and economic feasibility. Ensuring the quality and efficiency of devulcanized rubber through standardized and quality-controlled testing remains a significant challenge for acceptance in various industries [152].

Extensive research and development in the devulcanization process and optimization of the properties of devulcanized rubber are ongoing, but it will take time before these methods can be widely adopted at the commercial level. These challenges highlight the need for innovative solutions to improve devulcanization technologies and ensure their scalability, efficiency, and environmental sustainability.

4.1. Complex rubber materials, reinforcing fillers, and vulcanization cross-links

Tire rubber composites are made of a complex mixture of different materials, *i.e.*, NR, synthetic rubbers, CB, silica, antioxidants, accelerators, cross-linking agents, steel cord, and fiber [36]. Table 4 compiles data demonstrating the material composition for different types of vehicles. The good mechanical properties of tire rubber, such as high energy absorption capacity and good elastic behavior at large deformations are achieved through the vulcanization process, which creates three-dimensional cross-links between

Table 4. Material composition of tires depending on their intended use.

Type of tire Authors	Rubber		Carbon black [wt%]	Silica [wt%]	Metals [wt%]	Textile [wt%]	Others [wt%]	Reference
	Natural [wt%]	Synthetic [wt%]						
Car tires								
Hita *et al.*	14.0	27.0	28.0	–	14.0–15.0	–	–	[154]
Czajczyńska *et al.*	22.0	23.0	28.0	–	13.0	–	14.0	[155]
Siddika *et al.*	21.0–42.0	40.0–55.0	30.0–38.0	–	–	–	3.0–7.0	[156]
Siddika *et al.*	41.0–48.0	–	22.0–28.0	–	13.0–16.0	–	4.0–6.0	[156]
Valentini and Pegoretti	21.2	24.5	18.9	7.7	10.8	3.7	13.1	[157]
Xiao *et al.*	47		22.5		14.0	5.5	11.1	[158]
Truck tires								
Thomas and Gupta	27.0	14.0	28.0	–	14.0–15.0	–	16.0–17.0	[159]
Czajczyńska *et al.*	30.0	15.0	20.0	–	25.0	–	10.0	[155]
Siddika *et al.*	41.0–45.0		20.0–28.0	–	20.0–27.0	–	0.0–10.0	[156]
Valentini and Pegoretti	37.1	10.0	22.3	1.3	21.1	0.2	8.0	[157]
Xiao *et al.*	45		21.0		23.5	1.0	9.5	[158]
Other tires								
Thomas and Gupta	47.0		22.0		12.0	10.0	9.0	[159]
Torretta *et al.*	48.0		22.0		15.0	5.0	10.0	[160]
Roychand *et al.*	51.0		25.0		–	–	4.5	[161]

rubber chains through sulfur bridges [153]. Consequently, vulcanized rubber cannot be reprocessed and recycled like thermoplastics because the cross-linked network renders vulcanized rubber non-melting and insoluble, leading to significant challenges in recycling GTR [6, 8]. Another problem is that different types of rubber, such as natural rubber and synthetic rubbers like nitrile rubber, SBR and EPDM, have different cross-linking patterns, resulting in in varied levels of stability, degradation resistance, and devulcanization complexity. These differences make it challenging to apply a single devulcanization temperature across different rubber types, as each requires tailored conditions. Therefore, current research aims to develop efficient devulcanization methods to selectively and efficiently break down the cross-links, making the recycling process of GTR more sustainable and eco-friendlier. A deep understanding of the complex nature of cross-link networks is important for both vulcanization and devulcanization processes. This idea can facilitate advancements in rubber technology and promote the recycling of rubber waste in pursuit of a circular economy.

4.2. Balancing devulcanization purpose, efficiency and quality

Balancing the purpose, efficiency, and quality of devulcanization is a multifaceted challenge that requires careful consideration and optimization of several key factors. The primary purpose of devulcanization is to selectively break down the sulfur cross-links in vulcanized rubber [120], thereby reverting it to a more malleable state that can be reused in the production of new rubber products. The devulcanization process not only helps to recycle waste rubber, thereby reducing the volume of rubber waste that ends up in landfills, but also contributes to resource conservation by decreasing the demand for raw materials. Efficiency and quality in the devulcanization process are interdependent factors critical to its viability and scalability. Efficiency emphasizes optimal use of energy, chemicals, and time to minimize environmental impact while ensuring the process remains cost-effective [133]. Concurrently, quality focuses on the precise control of sulfur cross-link breaking without degrading the rubber matrix. This balance ensures the integrity of polymer chains, maintaining the mechanical and chemical properties of the devulcanized rubber. Achieving a delicate balance between efficiency and quality requires a comprehensive understanding of how different factors, such as temperature, pressure, chemical agents, and mechanical forces, interact during devulcanization. Each of these factors can significantly influence the effectiveness of devulcanization and the properties of the resulting devulcanized rubber. This often involves advanced techniques such as chemical, microwave, and biological methods, which offer controlled and uniform devulcanization but face challenges such as high energy demands, operational complexities, and environmental concerns. Several studies have explored innovative approaches to devulcanization, contributing to the advancement of sustainable rubber recycling.

Saiwari *et al*. [162] transformed the batch devulcanization process for GTR into a continuous process using a twin-screw extruder setup. The optimization of process parameters, such as temperature, screw speed, and devulcanization aid concentration, was essential for effectively reclaiming rubber while minimizing polymer degradation, thus retaining essential properties for reuse in tire applications. This research offers a pathway for scaling up devulcanization processes for sustainable material reuse in the tire industry. Ramezani *et al*. [163] developed a novel, sustainable approach for devulcanizing GTR using a choline chloride–urea deep eutectic solvent (DES). By combining chemical, ultrasonic, and thermal techniques, they selectively broke sulfur cross-links, achieving a 58% devulcanization rate. This method significantly reduces energy and time requirements, while promoting environmental compatibility and recyclability in line with sustainable practices.

Sutanto *et al*. [164] pointed out that the selective breaking of sulfide bonds is feasible when the quantity of C–C bonds closely matches or equals the number of C–S and S–S bonds. In practice, rubber industry products tend to have a higher abundance of C–C bonds originating from the main elastomer chains rather than the cross-linking sulfide bonds. This imbalance increases the potential for greater degradation of the main chain. Hence, devulcanization faces a significantly low possibility of achieving selective or controlled decrosslinking in recycling processes.

Although some of the technologies mentioned above claim to achieve decrosslinking rates close to 100% and complete devulcanization, but their impact on the circular economy and the global rubber market is limited. This is due to the simultaneous degradation of the rubber polymer and the resulting decline in the mechanical properties of the reclaimed rubber. Therefore, balancing the purpose, efficiency, and quality of devulcanization is needed to optimize the recycling process towards a circular economy.

4.3. The challenges in the application of reclaimed rubber

Using reclaimed rubber in rubber products faces several significant challenges that affect performance, processing, and broader market adoption. One major issue is the degraded mechanical properties of reclaimed rubber compared to those of virgin rubber. The devulcanization process often results in the partial breaking of sulfur cross-links and can damage the polymer backbone, reducing tensile strength, elasticity, and durability. The GTR composed of NR and SBR is more prone to main-chain scission than saturated rubbers like EPDM [145]. Tamura *et al*. [146] observed that degradation tends to occur at cross-linked sites, particularly at secondary carbon atoms adjacent to cross-link moieties, when cis-polyisoprene is heated above 200 °C, especially if cross-links are broken. Furthermore, Tripathy *et al*. [165] explained that the main-chain scission results in the formation of conjugated double bonds, leading to a deterioration of properties. This degradation confines using reclaimed rubber to the low-value applications, such as mats or flooring, rather than in tires or other high-performance products [143].

Additionally, regulatory compliance and concerns about the long-term durability and aging characteristics of reclaimed rubber products require attention. Addressing these challenges necessitates advancements in devulcanization technologies, quality control measures, and regulatory standards to enhance the performance and sustainability of reclaimed rubber across various industries.

5. Conclusions and recommendations

In conclusion, this review paper provides a comprehensive exploration of waste tire recycling, focusing on the production of GTR and its subsequent devulcanization, marking a crucial step toward achieving a circular economy. The study highlights the significant potential of these practices for sustainable waste tire utilization. Through in-depth analysis, various methods of devulcanization, including chemical, physical, and biological approaches, have been examined, revealing their respective advantages and challenges. The structural evolution of GTR during devulcanization emerges as a critical factor influencing the properties of the devulcanized rubber and its suitability for diverse applications. The deep decrosslinking process results in the production of core-shell carbon black, which can be utilized as a reinforcing filler.

Despite the effective progress made in this field, several challenges persist in the devulcanization process, such as the complex tire rubber composition and the need to balance devulcanization efficiency and quality. The application of devulcanized or reclaimed rubber faces hurdles related to compatibility, performance and regulatory requirements. Addressing these challenges will necessitate further research and innovation in devulcanization technologies to drive the widespread recycling of waste tire rubber.

It is imperative to focus on developing standardized testing methods, improving process efficiency, and enhancing the performance of devulcanized rubber in various applications, including tire manufacturing, rubber-modified asphalt, and other rubber products. By embracing devulcanization technologies, we can contribute to resource conservation, environmental sustainability, and the circular economy by transforming waste tires into valuable raw materials for new products and applications. This holistic approach aligns with the principles of sustainable development and underscores the importance of integrating innovative solutions into waste tire management practices.

Recommendations for future research in GTR devulcanization are diverse. Firstly, this field needs some collaborative efforts across academia, government bodies and industries, and it should be promoted to speed up the advancement of GTR devulcanization technology. This collaborative effort can facilitate the exchange of knowledge and the sharing of resources, and regulatory support is needed to drive innovations.

Secondly, a deep understanding of the complex nature of cross-link networks is important for both vulcanization and devulcanization processes. This idea can facilitate the advancement in rubber technology and promote rubber waste recycling in the goals of a circular economy.

Thirdly, GTR, as a complicated material for stable and value-added applications, is always a challenge for large-scale applications and standard commercialization; much work is always needed to make a breakthrough from cradle to cradle instead of cradle to grave.

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