

Review article

Rubber waste management: A review on methods, mechanism, and prospects

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ABSTRACT

Each year a large amount of worn synthetic and natural rubber is discarded. Due to the complex three-dimensional structure, recycling, and degradation of rubber by natural processes are proven complicated. While waste rubber disposal has become a problem globally, the current rubber waste management measures are found to be inadequate. Rubber devulcanization or degradation produces rubber with broken crosslinks or broken main chain polymer, respectively. The devulcanized or degraded rubber can be reused, recycled as a new product, or used for energy recovery in various applications. The current review addresses the problems in rubber waste management and aims to provide detailed insight into alternatives to manage rubber waste through thermal, mechanical, physical, chemical, and biological methods. The advantages, disadvantages and bottlenecks present in each method is discussed. This review also presents the circular economy establishment on rubber in current and future prospect. This review concluded that while more research on technical, economic, and environmental aspects is needed, the methods discussed in the review lead the way for a more sustainable framework in rubber waste management.

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1. Introduction

Waste generation is a product of urbanization, economic development, and population growth. An estimated 2.01 billion tonnes of municipal solid waste were generated in 2016 and are expected to reach 3.40 billion tonnes by 2050 [1]. In absolute terms, East Asia and the Pacific generated an estimated amount of 468 million tonnes. In comparison, the least amount of 129 million tonnes was generated by the Middle East and North Africa in 2016. Fig. 1 provides the amount of waste generated by regions throughout the world in percentage. The highest percentage of solid waste was contributed by Asia, accounting for a total of 60%. East Asia and Pacific as well as Europe and central Asia generated 23% and 20%, respectively, whereas South Asia alone generated 17% of the global solid waste.

The composition of the solid waste is categorized into a few types including rubber and leather waste [2–5]. The United States in the year 2018 was found to generate 9.2 million tonnes of rubber and leather waste [6]. The majority of rubber waste generated

is from tires of automobiles, trucks and motorcycles. Other sources of leather and rubber include clothing, footwear, gaskets and furniture [6].

Out of 9.2 million tonnes of rubber waste generated, only 1.7 million tonnes of rubber waste were identified as recyclable. This number amounted to only 40% of total tire waste generated, excluding its application for energy recovery and landfills. The amount of rubber waste combusted for energy recovery and dumped in landfills was 7.2% and 3.4% respectively in 2018 [6]. Besides tires and household appliances, general rubber goods like belting, hoses, tubes, and consumer products such as footwear, toys, sports and leisure goods also account to 30% of the rubber market. However, there is very little recycling effort done from the waste generated from the general rubber goods sector currently. The material recycling and reuse of general rubber goods amount to only 1.5% of the total waste generated. There are many reasons behind the lack of industrial interest in recycling general rubber goods waste. These reasons are also limiting the applications of circular economy in general rubber goods sector [7].

1.1. Rubber production

Rubbers are elastomers characterized by their ability to be reversibly deformed by external forces [8]. Rubber is generally di-

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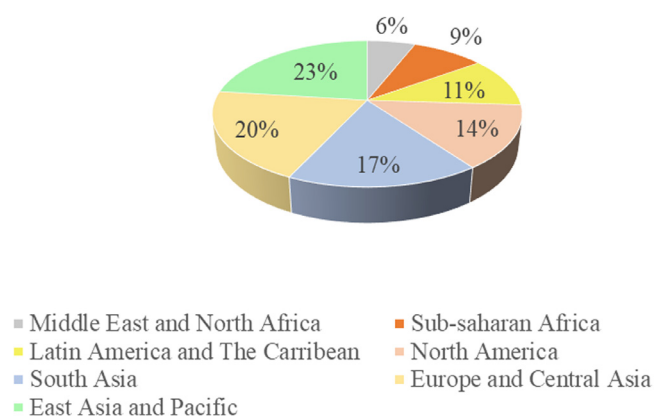


Fig. 1. Percentage of solid waste generated in the year 2016.

vided into natural rubber (NR) and synthetic rubber. Although over 2000 plant species produce natural rubber latex, the commercially utilized natural rubber latex is made from the *Hevea brasiliensis* [9]. The main constituent in natural rubber latex is poly(cis-1,4-isoprene), an unsaturated hydrocarbon [9]. The other plants producing latex belong to the family Compositae, Moraceae, and Apocynaceae [10]. In contrast, synthetic rubber is synthesized as monomers from a variety of petroleum-based hydrocarbons. The commonly produced synthetic rubbers are styrene-butadiene rubbers (SBR), butadiene, chloroprene, and isobutylene [8].

The demand for rubber products is growing drastically every year. Statistically, global natural rubber production in 2018 has amounted to almost 13.9 million metric tonnes [11]. In 2018, Asia pacific generated 91% of the world's natural rubber, whereas Europe, The Middle East, and Africa produced 6.5% of natural rubber in the world [11]. Natural rubber is primarily used in manufacturing gloves, which has tremendously grown to meet the rising healthcare demands besides their application in laboratory and food industries [12]. On the other hand, synthetic rubbers are used primarily in the transportation industry to produce tires. Overall demand for car and commercial vehicle tires is expected to have exceeded 1.6 billion units by 2018 [13] and is estimated to reach 3.2 billion units by 2022 [14]. With the increase in automobile production, the increment in the number of waste tires generated is evident. All the worn-out natural and synthetic rubber material form heaps of rubber waste which takes years to degrade naturally, thus creating a necessity to tackle the rubber waste problem.

1.2. Conventional rubber waste management methods

The conventional waste management methods mainly focus on collecting the waste, burning the waste, and disposal (open dumping, landfills). These methods have limited the growth of integrated waste management techniques such as recycling and recovery, aiming to reduce the source's waste. Rubber waste is categorized as industrial scrap and consumer scrap [15]. Successful waste management depends on the cleanliness and segregation of the generated waste, so the industrial waste scrap is easily identified for further waste management. At the same time, this is not the case with consumer waste. However, independent of the type of rubber waste generated, the most commonly used disposal methods are open dumping, landfilling, burning, and grinding the rubber waste into powder [16]. Disposed rubber waste such as tires acts as a breeding ground for various mosquitoes, vectors for various deadly diseases like malaria, dengue, and chikungunya. Waste tires are also home to disease-carrying rodents and snakes. Inherently, these methods do not allow the reduction of rubber waste, causing the piling of the rubber to form huge dumpsites. These

dumpsites are a risk for catching fire, which burns for several weeks. Moreover, extinguishing tire fires is very difficult because even if they are extinguished from the outside, they continue to burn on the inside and are prone to easy reignition.

The number of tires produced worldwide is reported to increase annually with increased vehicles on the road. Landfilling and tire mono filling (which are certified sites where the only waste tire is accepted for disposal) were among the earliest tire disposal methods [17]. Landfilling and mono-filling methods are practiced mainly due to the availability of large land areas and economic feasibility. However, eco-toxicity of the land is affected by landfills whereby the toxic chemicals like metals and additives such as stabilizers, plasticizers or flame retardants in the tires leach into the soil, harming the bacteria present in the soil, which are necessary and essential for plant growth [9,17].

With the growing demand for rubber products, developing multiple efficient waste management techniques is also essential. The present waste disposal measures are not as efficient as they cause water, land, and air pollution. Landfills used to dispose of rubber waste have become sparse as they occupy a large land area. Recycling has been adopted as another technique to manage rubber waste. However, this method is challenging due to reinforcing material added into rubber to improve its properties and applications. Several research studies and industries have established different recycling methods in the past few decades [18]. However, the continuing demand for rubber products prompts different recycling methods that are environmentally friendly and less toxic to reduce accumulation of rubber waste.

In this review, we have explored the extent of the rubber waste problem globally. The statistical data presented provides knowledge about the total rubber production and consumption around the world. Furthermore, the article briefly talks about different types of rubber, the types of cross-links formed during vulcanization, and the effect of devulcanization and degradation of rubber. The review also states the importance of the circular economy of rubber, the extent of its reach in the present scenario and how the different waste management methods can be used to alleviate the process. The main objective of the review is to provide insights into the different techniques involved in addressing the current rubber waste management problem. Different devulcanization and degradation techniques in mechanical, chemical, physical, and biological methods have been used in rubber waste management and are discussed in the present manuscript. The mechanism of the process, properties, parameters involved in each of the technique was discussed in depth. In addition, the advantages, disadvantages, and applications of devulcanizates from each method have been reviewed. Moreover, the prospects of each technique have been emphasized, giving insight into the bottlenecks present in each technique, enabling to see gaps needed to be studied in that area.

The industrial applications of different recycling measures are still limited, and this might be due to the unclear degradation pathways and mechanisms involved. The feasibility of implementing these recycling methods on a large scale is still questionable. By reviewing different methods in rubber waste management, insights can be further obtained to develop a sustainable framework in terms of technical and environmental aspects for rubber waste management.

2. Rubber waste management

Waste rubber disposal issue is being addressed as one of the significant problems globally. Improper waste management methods and lack of adequately established technologies are the primary cause of serious ecological issues that proper waste management methods must address. Also, each type of rubber waste pos-

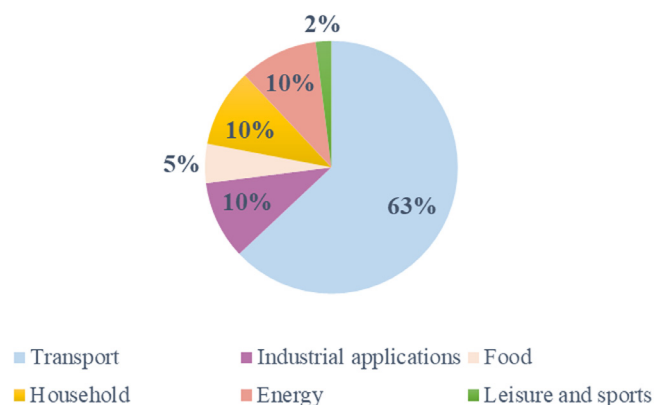


Fig. 2. Percentage of rubber used by different industrial sectors in 2016 [19].

Table 1

Composition of different scrap tires [23].

| Type of material (wt%) | Car tire | Truck tire | Off-road tire |
|------------------------|----------|------------|---------------|
| Crumb rubber | 70 | 70 | 78 |
| Steel | 17 | 27 | 15 |
| Fibres and scrap | 13 | 3 | 7 |

sesses inherent challenges that need to be managed effectively. As a result, focusing on sustainability is necessary for almost every industry, including the rubber industry. In order to understand the industrially viable rubber waste management methods, it is vital to understand the nature of rubber and rubber products.

2.1. Source of rubber waste

The primary source of rubber waste is tire rubber. The other rubber waste generated is produced during the latex rubber products manufacturing such as medical gloves, adhesives, and gaskets [19]. Fig. 2 depicts that the transport industry used 63% of the rubber produced in 2016 to produce tires. The following considerable rubber consumption is by household, industrial and energy sectors.

2.1.1. Rubber composites

Many rubber products are produced in composites form to achieve high strength to flexibility ratios intended for reinforcement purposes [20]. For instance, rubber sheets are reinforced with various materials like rayon, Nomex, Kevlar, glass cloth, steel, aramid, polyester, nylon and cotton. These substances are engineered into the rubber sheet during the manufacturing process [20]. Some industrial products categorized as composites include tires, conveyor belts, hoses, power transmission belts, inflatable boats, oil booms, and protection suits [21,22]. The tire is a major rubber composite consisting of rubber, steel, fibres and scrap. Table 1 shows the composition of different types of tires, which denotes different materials, formulations, and designs adopted in making different tires. Similarly, for conveyor belts, the rubber is then reinforced with galvanized steel, which provides good adhesion, ensuring the conveyor belts' long life [21,22]. The composition and the design are formulated depending upon the product exploitation [22]. To reclaim these products, it must first be stripped of its steel and fabric components and then undergo grinding. Due to their strong physical properties, it is a highly complicated process, as the process requires heavy machinery.

Besides composites, rubber is also widely used in many other assorted applications like medical and household appliances. In the past year alone, 65 billion gloves were consumed monthly worldwide due to the covid-19 pandemic. As a result, many used rubber gloves and PPE equipment were discarded [24]. The expand-

ing market for these products during the pandemic also adds to the rubber waste [25]. The application of rubber besides composites includes adhesive glues, erasers, balloons, tennis balls, handlebar grips, computer mouse pads, condoms, diaphragms, cosmetics, raincoats, rubber bands, nipples and pacifiers, electric cords, food handling gloves, rubber toys, scuba equipment and many more [19].

Vulcanisation of rubber by using chemicals such as sulfur, resins, peroxides is common with the purpose to form crosslinks in the rubber structure that enhances their elastic property, thermal contraction and durability. The chemicals added during the vulcanization process impact the waste management methods. Also, the crosslinks formed during the process respond differently to various waste management methods. Therefore, it is vital to understand various rubber types, structures, and crosslinks present in the rubber matrix before understanding different waste management practices, which are further discussed in this review.

3. Vulcanization, devulcanization and degradation of rubber

Each type of rubber material has its distinct properties besides its general elastic and malleable properties. Rubber is broadly classified into two categories in which is natural and synthetic. Fig. 3 shows the chemical structure of natural rubber and different types of synthetic rubbers available in the market. The chemical structure and properties of synthetic rubber make them attractive for engineering a variety of synthetic rubbers products. Additionally, rubber products are mostly vulcanized. After the end of life, rubber products can be recycled by subjecting them to devulcanization or controlled degradation [26]. In this section, vulcanization, devulcanization, and degradation will be discussed.

3.1. Vulcanization of rubber

The basic structure of rubber before vulcanization contains a carbon backbone with either single or double bonds. Industrial and technical applications of rubber require vulcanization to provide suitable properties to the final products [29]. Unvulcanized natural rubber is only used as crepes for shoe soles and adhesives. Rubber is subjected to vulcanization, which causes cross-linking in the elastomer molecules, bringing dimensional stability to the structure. During vulcanization, the rubber compound transforms into final vulcanizate. The most important chemical in the vulcanization process is the crosslinking agent. The most common crosslinking agent is elemental sulfur due to its abundance and low cost. Vulcanizing agents other than sulfur are peroxides, resins and metal oxides used to form cross-links in the rubber [30]. Unsaturated elastomers (C=C) can be vulcanized with sulfur, while the saturated elastomers (C-C) cannot be vulcanized with sulfur but are vulcanized by peroxides. The cross-linking reactions mainly occur at the C=C bonds.

Vulcanization is an essential process that is performed at relatively high temperature (140 to 200°C). It is a process that reduces permanent deformation by increasing the retractile force, thereby increasing elasticity and decreasing plasticity [31]. Using sulfur alone causes a slow reaction, so accelerators such as guanidines, thiazoles, sulfenamide, thiurams, dithiocarbamates, xanthates are added to increase the cure rate [31].

Different types of crosslinks can be achieved by varying the amount of sulfur to accelerator ratio in the vulcanization process [32]. Different crosslinks formed in the rubber impart different properties to the rubber, as shown in Table 2. Depending upon the rubber product's specific use, the types of crosslinks formed can be controlled through vulcanization [32]. The polysulfidic crosslink (C-S_x-C) increases the tensile and tear strength as well as compression

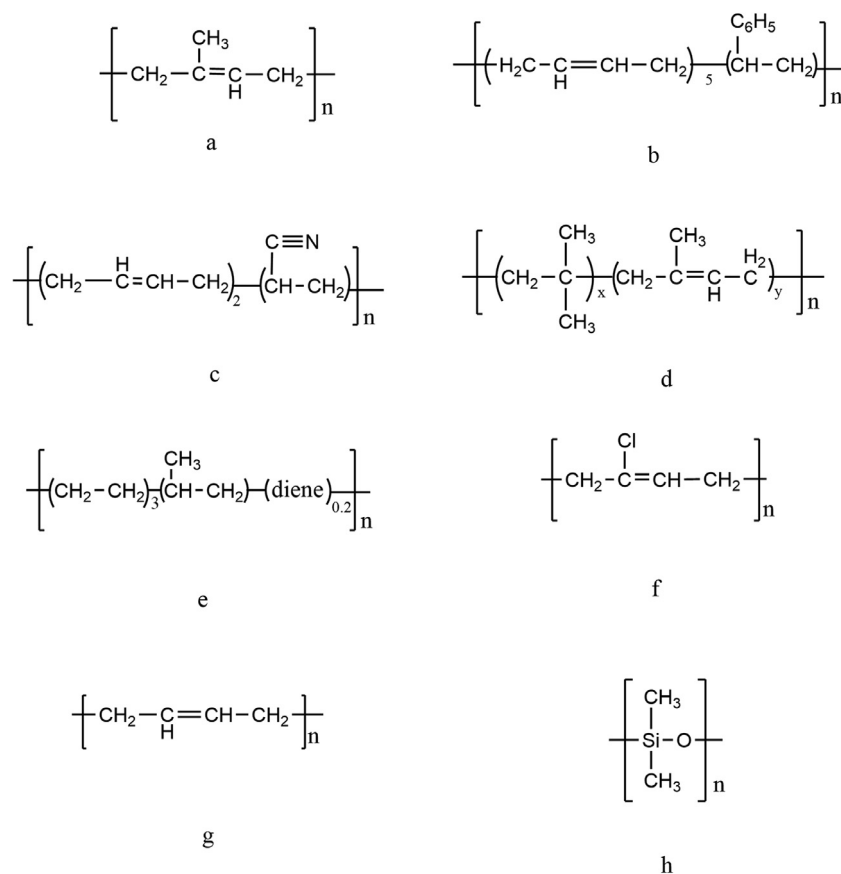


Fig. 3. a) Polyisoprene unit b) Styrene-butadiene rubber (SBR), c) Nitrile rubber (NBR), d) Butyl rubber (IIR), e) Ethylene-propylene (EPDM), f) Polychloroprene (CR), g) Polybutadiene (BR), h) Silicone [8,21,27,28]

Table 2
Types of cross-links and technological properties [34].

| Type of crosslink | Technological properties |
|--|--|
| Polysulfidic (C-S _x -C) | • Increase tensile and tear strength, high compression set, poor heat ageing |
| Monosulfidic (C-S-C) | • Excellent heat ageing, low compression set, low tensile and tear strength |
| Mixtures of mono, di- (C-S-S-C) and polysulfidic | • Compromise or balance in terms of strength and heat ageing |

set but gives poor heat ageing. However, monosulfidic crosslink (C-S-C) has excellent heat ageing and low compression set but low tensile and tear strength. A combination of monosulfidic crosslink (C-S-C) and disulfidic crosslinks (C-S-S-C) balances the heat ageing, tear, and tensile strength. Over 40,000 products are produced from vulcanized natural rubber [33].

3.2. Devulcanization of rubber

Fig. 4a shows the process of cleaving the S-S and C-S bonds while leaving the C-C bonds intact, known as devulcanization [15,18,35,36]. Devulcanization is total or partial cleaving of the monosulfide (C-S-C), disulfide (C-S-S-C), and polysulfide (C-S_n-C) bonds present in the vulcanized rubber that were initially formed during vulcanization [37]. The blue, red and green dots in Fig. 4a represent the different crosslinks present in a rubber structure before being subjected to the devulcanization process. Following which the cleaved crosslinks are shown in white dots encircled in colour. Devulcanization can be achieved via many different methods, such as mechanochemical or ultrasonication. High temperature of 180 to 300°C are required to obtain the homolytic scis-

sion during the process [18,36]. The degree of devulcanization influences other mechanical properties when recycling the devulcanized rubber material [35]. Therefore, physical parameters used for devulcanization must be carefully considered to obtain good quality final devulcanizate. Fig. 4a shows partial devulcanization, whereby only some crosslinks are cleaved during the devulcanization process. Horikx theory is often used to determine the quality and the degree of devulcanization. Fig. 4b depicts the Horikx diagram of soluble fraction of devulcanized NR against crosslink density. The solid line in the figure corresponds to selective cross-link scission (devulcanization) [38–40]. Although partial devulcanization is sufficient to study the devulcanization mechanism, almost complete devulcanization is necessary for recycling or reusing rubber in a commercial scenario [38].

3.3. Degradation of rubber

Complete degradation in rubber implies the deterioration of the material's thermal, physical and mechanical properties until they cannot be recycled further for producing new products [42]. Degradation in rubbers can be induced by light, heat, oxygen, stress,

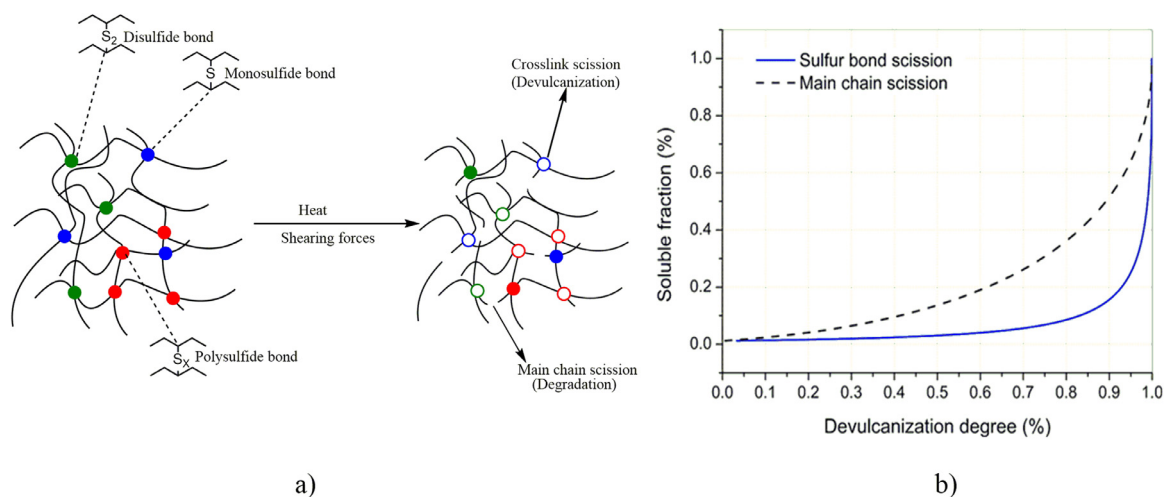


Fig. 4. a) Devulcanization and degradation effect on the rubber matrix b) Horikx diagram of devulcanized and degraded rubber [38,40,41].

Table 3
Energy required to break different bonds in vulcanized rubber structure.

| Type of bond | Energy required (kJ/mol) |
|---------------------|--------------------------|
| C-C | 348 |
| C-S-C | 273 |
| C-S-S-C | 227 |
| C-S _x -C | 251 |

and exposure to chemicals. A complete loss of elastomeric properties occurs when the rubber absorbs no more than 1-2% oxygen [42]. Thermal oxidation results in main chain scission or cross-link scission leading to the loss of mechanical properties of the rubber. In case of higher degree of degradation, the molecular weight of the rubber material is significantly reduced. The rubber material loses its elastomeric and mechanical properties. In general, degradation causes deterioration in the rubber properties, and it is non-desirable. Fig. 4a also depicts partial degradation whereby some of the main rubber chains are cleaved during the process. In Fig. 4b the dashed line corresponds to main chain scission (degradation) [39,40]. To enable recyclability and reusability of the processed rubber, it is important to limit the main chain degradation to a minimum.

3.4. Comparison between devulcanization and degradation of rubber

The primary difference between the devulcanization and degradation process is the cleavage of bonds in the rubber structure. For the context of this review, the devulcanization process denotes the cleavage of C-S and S-S bonds while keeping the C-C bonds intact [36], and the degradation process denotes major cleavage of the C-C backbone, which massively deteriorates the mechanical properties of the rubber. The process of devulcanization and degradation are both interconnected with each other. It is impossible to only cleave crosslinks or to only cleave the main polymer chain during a process. Both the devulcanization and degradation will happen concurrently during the process. It is important to limit the degradation and increase the devulcanization to enhance the chances of rubber recycling or reusing. Different amount of energy is required for cleaving each bond, as shown in Table 3, in which the main chain (C-C) cleavage requires the highest amount of energy and S-S crosslinks cleavage requires lesser energy comparatively. The primary goal of rubber recycling process is optimizing the parameters for devulcanization. Optimizing the parameters such as tem-

perature, pressure and type of chemicals used increases the degree of devulcanization while limiting the extent of degradation. The devulcanizates produced do not lose their elastomeric properties and can be further used to produce various new products. In case of higher degree of degradation, the molecular weight of the rubber material is significantly reduced. As a result, the rubber material loses its elastomeric and mechanical properties. These conditions enable the degraded rubber to act as raw material to produce many other products.

Many different rubber products are manufactured from both natural and synthetic rubber. Recycling is challenging due to the complex, crosslinked structure and the mechanical properties of the rubber. Furthermore, the chemicals used for vulcanization and additives like activators and retardants cause the release of toxic gases like sulfur oxides, carbon monoxides, and cyanides into the air during recycling process. In order to reduce the pollutants and tackle the amount of rubber waste generated, various sustainable waste management measures are imperative.

4. Rubber waste management methods

Many national and local governments have recently started to adopt the concept of circular economy as a new conduit to sustainability. The circular economy is a system that can be employed to reduce waste and raw materials scarcity through the continual use of resources [43]. The emerging challenges of depletion of raw materials and an increase in rubber demand can be met through circular economy by slowing, closing, and narrowing resource loops. In recent years increasing recycling rates or increasing the product lifetimes has become the primary goal for sustainable development.

Besides tires, 50% of the world's rubber production is used for the consumption of general rubber goods (GRG). Reliable industrial technology and processes are needed to reuse and recycle the waste produced from GRG. The processed waste can be transformed into cheaper and more sustainable material to feed their production. This cycle of producing tires and GRG from their used, worn-out materials increases sustainability. The use of worn-out tires and scrap GRG granulates in new products can significantly reduce the carbon footprint up to one-third compared to the products produced without recycled material [43]. Thus, the circular economy of rubber can alleviate the global waste rubber problem.

To date, among the many different rubber products produced, circular economy has only been established for tires which is a complex rubber composite. This serves as a reminder that, given



Fig. 5. Tire circular economy [43].

time and resources, it is possible to establish circular economy to many other rubber goods similar to tires. According to ETRMA (European tyre and rubber manufacturers' association), data collected from 32 countries (EU28, Norway, Serbia, Switzerland and Turkey) showed that 91% of end-of-life tires (ELT) were collected and treated for material recycling and energy recovery in 2018 [43]. Fig. 5 shows the circular economy of the tire industry in which 48% of the used and ELT collected are used for energy recovery, whereas 52% is used for material recovery. The cement industry utilizes 42% of the energy recovery, while the power industry utilizes only 6%. Retreading is the oldest method employed to reuse ELT. Retreading extends the lifespan of rubber, consumes less energy, and is cost effective. The improper waste management methods and limitation of current existing measures prompt the need to establish a circular economy to manage the rubber waste. One of the practices involved in the circular economy is "extended producer responsibility (EPR)," which involves focus on designing and delivering products using sustainable methods. The manufacturers are urged to design the products so that the entire life cycle of the product can be made optimal from an environmental protection point of view. However, EPR alone cannot tackle the waste management challenge due to the ever-increasing demand for rubber goods. Different initiatives are directly required to tackle the waste management threat posed by used rubber materials.

In the current scenario, the circular economy for GRG is lacking. Due to the increased production to meet the demand, various sustainable methods for managing the rubber waste are needed. Research studies are currently ongoing to establish efficient ways to manage and reuse rubber waste effectively. Fig. 6 shows several waste management methods that have been gaining interest in the past few decades. Primarily rubber waste management processes are classified into thermal, mechanical, physical, chemical, and biological. Each method involves different processes that employ different parameters and chemicals to either devulcanize or degrade

the rubber. The mechanism, advantages, disadvantages, and recent advancements of these methods are discussed in section 4. Depending on the use of the end product, different methods are utilized to dispose of waste rubber.

4.1. Thermal methods

The thermal method has been among the most commonly used and studied methods for rubber devulcanization and degradation. For energy recovery from rubber, thermolysis and pyrolysis are the two methods used. In general, thermolysis is the process of breaking down the rubber under the action of heat, while pyrolysis is breaking down in the absence of oxygen. Studies have shown that scrap tires, NR and SBR were subjected to thermolysis under sub-critical or supercritical water [44]. The products formed at the end of the process were oil and methane (CH_4), ethyne (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), and propane (C_3H_8) gases. The results indicated that with increased pressure and temperature, oil yield increased and reached maximum when the state of water reached the critical point. At 420°C , a pressure of 18 MPa maximum oil yield of 21.21% was achieved within a reaction period of 40 min, which could be improved further. The molecular weights of the chemicals in the oil yield were in the range of 70–140 g/mol. Although thermolysis is favoured for energy and material recovery in circular economy perspective, the drawback associated with this technique is the release of toxic gases [44]. The high temperature, high cost of kilns and gas generation are the main limitation for thermolysis.

Pyrolysis of waste rubber is one of the most prominent thermal techniques in terms of recycling and recovery. The lab-scaled thermo-gravimetric, differential thermal, and pyrolysis-gas chromatography analysis are commonly used to evaluate the thermal efficiency of rubber material devulcanization and degradation [45]. The thermo-gravimetric analysis of rubber showed that the degra-

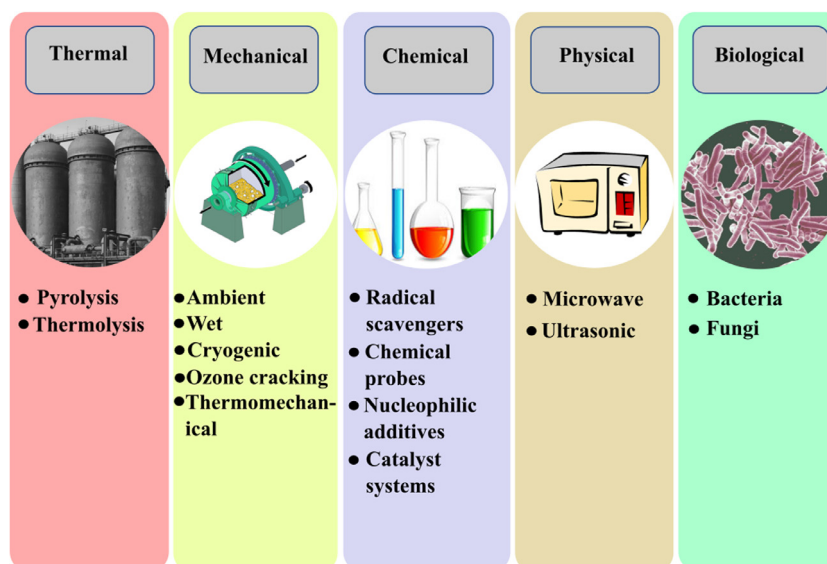


Fig. 6. Waste Management techniques for degradation and devulcanization of rubber.

degradation of different rubbers occurs at different temperatures. It was observed that the main chain degradation of NR and BR happens at 380°C and 460°C, respectively [45]. At a temperature range of 350°C to 450°C, the liquid fraction obtained are alkanes, alkenes, and aromatic compounds. The xylene and benzene present in the aromatic compounds are toxic [46]. Thermal degradation of NR was an exothermic reaction caused by several other internal reactions. However, the heating rate of pyrolysis does not increase the rate of thermal degradation. The by-products formed during the thermal degradation of rubber caused temperature suppression, thereby reducing its thermal stability [47].

The rubber is prone to degradation when subjected to a very high temperature in the range of 350°C to 600°C. Also, the degraded rubber products have extremely low thermal stability and loss most of the mechanical properties. From a circular economy perspective, the thermal degradation method of rubber contributes to the energy recovery pathway. Therefore, the use of rubber could potentially replace the use of crude oil in energy platforms.

Devulcanization of rubber through the thermal method also requires high temperature to break down the crosslinks present. However, the higher the temperature applied, the greater the chances of rubber degradation. Temperature plays a pivotal role in all rubber waste management methods. For example, rubber grinding generates a high amount of localised heat, causing high temperature (130°C), resulting in an undesirable reduction of the molecular weight and oxidization of crumb rubber. Alternatively, mechanical grinding could be operated at a very low (-196°C) temperature involving liquid nitrogen to limit rubber degradation. In the chemical treatment of the rubber waste, moderate temperature enhance the feasibility of chemical agents cleaving the crosslinks present in the rubber material. Using microwaves or ultrasound also involves high temperature, reaching up to 200°C or 250°C [48]. These high temperatures coupled with energy from the radiation are one reason for producing a more significant amount of devulcanized rubber in shorter exposure times. The devulcanizates produced by microwave and ultrasonic methods retain much of the molecular weight and mechanical properties due to the scission of mono, di and polysulfide crosslinks and limited main chain scission of the rubber structure. For biological methods, temperature need to be controlled between 30°C to 40°C for optimal rubber degradation by bacteria. The use of higher temperature will cause denaturation of the enzymes in the microorganisms responsible for the degradation process.

The temperature range varies in devulcanization and degradation processes. In degradation, as the C-C main chain scission occurs, higher energy and higher temperature are required. Conversely, in devulcanization, less energy and lower temperature are required to break the mono, di, and poly sulfidic crosslinks. Temperature and other parameters involved in the rubber waste management techniques are further discussed in the next section.

4.2. Mechanical grinding

The mechanical process destroys the rubber structure by simple mechanisms that destroy the physical characteristics like shape, rigidity, and weight-bearing capacity. The processes involved in mechanical grinding, the advantages and disadvantages are shown in Table 4. Mechanical grinding includes ambient grinding, wet grinding, cryogenic grinding, and grinding by ozone cracking. The different sizes of crumb rubber and ground rubber produced through mechanical grinding are used in several civil engineering projects, such as modifiers to asphalt paving mixtures, playgrounds, lightweight fillers, the crash barrier, shock and vibration absorbers [49]. In addition, shredded rubber, crumb rubber, and ground rubber are used to replace gravel, sand and filler material, respectively [49].

Downsizing of the rubber materials can only be achieved by grinding the rubber waste. The obtained crumb rubber can be used to blend with other polymers. The compatibility of the obtained crumb rubber with other polymers in a blend can be enhanced by breaking the cross-links, which can be achieved by the devulcanization of the crumb rubber. Therefore, mechanical grinding is always conducted, followed by a devulcanization process.

Though the ground rubber loses its mechanical and elastic properties, it is still feasible to be classified as material recovery or reuse under the circular economy concept. Crumb rubber produced from the grinding methods can be used for several applications like level crossings, extruded pipes, gardening hoses, car pedal pads, floor coverings, shoe soles, mudflaps, automotive gaskets and seals, sheet roof and levelling roof components [50]. Another promising application for powdered rubber is its use as fillers in various thermoplastics. The thermoplastic elastomers can be used in several applications like conveyor belts, drive belts, flooring, window seals, gaskets, geomembranes, car bumpers, car-pet backing, etc.

Table 4
Types of Mechanical grinding, advantages and disadvantages.

| Type of Mechanical grinding | Description | Advantages | Disadvantages |
|-----------------------------|--|---|---|
| Ambient grinding | <ul style="list-style-type: none"> • Rubber is passed through two-roll mills, shredders, granulators. | <ul style="list-style-type: none"> • A particle size of 200 µm can be achieved. • High surface area. | <ul style="list-style-type: none"> • Temperature can reach up to 130°C. • Oxidation of crumb rubber due to heat. • Requires excess water for cooling |
| Wet grinding | <ul style="list-style-type: none"> • Grinding by mixing water with the crumbs, producing a slurry. • Water cools the granulates and produces cleaner crumbs. | <ul style="list-style-type: none"> • Particle size 60 mesh can be achieved. • High surface area. | <ul style="list-style-type: none"> • High energy consumption. • The extra step of drying makes the process costlier. |
| Cryogenic grinding | <ul style="list-style-type: none"> • Rubber is cooled in liquid nitrogen and then crushed with hammer mills | <ul style="list-style-type: none"> • Particle size 40- 60 mesh can be achieved. • No oxidation of crumb rubber. • Clean crumb rubber is obtained. • High production rate and low energy cost. | <ul style="list-style-type: none"> • High cost of Liquid nitrogen. • Smoother surface area resulting in poor binding ability. • Pre-grinding and drying steps add to the cost. |
| Ozone cracking | <ul style="list-style-type: none"> • Exposed to higher ozone concentrations and ground into crumb rubber using ambient grinding | <ul style="list-style-type: none"> • Consumes less energy. • Physical properties of the rubber are not altered | <ul style="list-style-type: none"> • Rubber has low surface activity |

4.2.1. Thermomechanical devulcanization

The focus in thermomechanical devulcanization is that the bond energies of cross-links are lower than that of the C-C bonds building the rubber backbone. The main bonds present are C-C, C-S and S-S bonds. The thermomechanical process primarily aims to break the C-S and the S-S bonds [15,17]. In the thermomechanical devulcanization process, the rubber is subjected to high shear and extensional stressing levels that provide an efficient way of selectively breaking the bonds. This process is carried out by using equipment such as mills and extruders, which is generally carried out at ambient or high temperature. The characteristics of the end products (shear rate) depend upon the processing parameters like time and pressure [51].

The most practical machinery used for thermomechanical devulcanization by the polymer industry is a twin-screw extruder. A study was conducted with three different barrel temperatures (60, 120 and 180°C), and the screw rotation speed was set at 500 rpm. It was found that an increase in barrel temperature resulted in decreased screw torque, Mooney viscosity and degree of cross-linking. The rubber obtained from 60°C process had the best mechanical properties such as high tensile strength, resilience, elongation at break and abrasion resistance and high cross-link density [52]. The reclaimed rubber obtained was used in different SBR blends. Vulcanizates containing reclaimed rubber that was obtained at higher temperature had the best mechanical properties. The process at lower temperature requires high torque; however, lesser amounts of toxic gases and by-products are produced. A considerable increase in the mechanical properties of the reclaimed rubber was seen at a lower temperature. However, the processability characteristics (behaviour and interactions of the different additives) were worse than the rubber obtained at high barrel temperature. The schematic representation and the different screw sections of the twin-screw extruder are shown in Fig. 7. This shows the importance of designing an effective mechanical system to optimize devulcanization while limiting rubber degradation.

A similar study was conducted on recycling natural rubber, with different barrel temperatures ranging from 80°C to 220°C [38]. The devulcanization extent was determined through crosslink density, sol fraction, Mooney viscosity and Horikx diagram. It was found that selective sulfur bonds scission occurred at samples treated at 80°C and 100°C. The self-heating of the rubber explained this selective scission during the devulcanization process. It was also noted that higher temperature input did not necessarily enhance the devulcanization. A high level of devulcanization, approximately 90%, was achieved in the process at temperature of 80°C and 100°C. However, the higher temperature promoted the rubber degradation without increasing the devulcanization degree or any improvement in the properties in the devulcanized material.

In a recent study, the recycling of EPDM rubber was carried out through thermomechanical devulcanization. A two-step devulcanization method involving a two-roll mill, and an internal mixer was developed. Devulcanization was carried out on two EPDM mixtures, one with a sulfur base and a peroxide base [53]. Blends of EPDM and high-density polyethylene (HDPE) were prepared to study the compatibility between cured, uncured and devulcanized EPDM rubbers with HDPE. The rubber was first cryogenically ground and processed in a two-roll mill at 230°C for 25 mins. The devulcanization process is then carried out at 200°C in an internal mixture. The results showed an 85% decrease in crosslinking density in both sulfur and peroxide cured samples. However, there was an increase in sol fraction in the peroxide cured sample, which indicated degradation was taking place, whereas the sulfur cured samples showed higher crosslink scission. The devulcanization degree in the sulfur cured samples was determined to be 83%. The mixture's elasticity was severely affected, showing the elongation at break between 10% and 20% [53]. There was no clear trend ob-

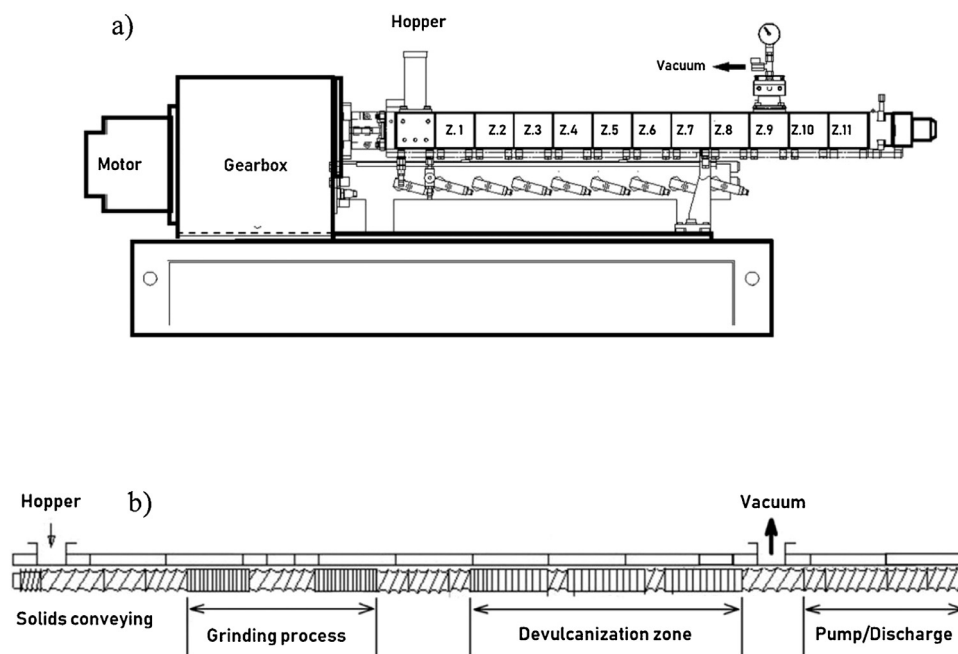


Fig. 7. (a) Schematic of a twin-screw extruder. (b) screw configuration with different process sections [18].

served how the cured, uncured and devulcanized rubber affects the tensile properties.

From the above studies, devulcanization occurs in the lower temperature range between 60°C to 100°C. EPDM mixtures required higher temperature like 200°C for devulcanization. Generally, rubber undergoes degradation beyond these temperatures. Further studies in the area should focus on optimizing the parameters such as oxygen-free, low shear force and lower temperature to achieve desired devulcanizates. Some novel and environment-friendly methods could be developed based on such optimization requirements. The major downside of this devulcanization is the release of H_2S , SO_2 and C_2S gases into the atmosphere, which are toxic. It was determined that there was a decrease in mechanical properties indicating degradation does occur. Although devulcanization did take place, it was limited to less than 50% in studies with NR and SBR. It is important to enhance the thermomechanical process further to augment the feasibility of industrial-scale rubber devulcanization or degradation adaptation. The devulcanizates produced through the thermomechanical process are suited for feedstock or raw materials to produce new rubber products. Hence, it is possibly an important method from the perspective of circular economy establishment for rubber products.

4.3. Chemical methods

The purpose of chemical devulcanization or degradation is to use chemicals to break down the cross-links present in the rubber. The process is conducted to retain most of the elastomeric properties so that the devulcanized product can be reused further to produce new rubber products [26,54]. The process involves chemical reclaiming agents like organic disulfides, mercaptans, and inorganic compounds [23].

4.3.1. Organic solvents

Devulcanization was conducted by using organic solvents such as xylene, toluene, or benzene to cause swelling in the rubber [54]. The organic solvents concentration is generally in the range of 0.5 to 10 wt% [55,56]. The chemical reaction that occurs during devulcanization is complex and is not entirely understood. Diphenyl

disulfide (DD) is one of the widely used chemicals for devulcanization. There were few mechanisms proposed for devulcanization with DD [55,56]. Some by-products, such as hydrogen sulfide and thiols, were released during the reaction [18,57].

The mechanism involves the thermal devulcanization of DD producing two reactive radicals, shown in Fig. 8. The radicals then react with the cross-linked sites and break the sulfur bond, which can be achieved by temperature, stress, or nucleophilic agents. A hydrogen atom from the main polymeric chain is taken up by another sulfide radical, opening a new active cross-linking site. The devulcanized rubber can then be used for re-vulcanization or combined with a polymer matrix for the proposed use [18].

A similar chemical devulcanization method involving DD was proposed by I. Mangili et al. [58], in which initial reaction with DD produces sulfide radicals. The sulfides can deduct the allylic hydrogen of the rubber to form benzenethiol or react to form a double bond, followed by polymer degradation, as shown in Fig. 9. However, the devulcanized rubber produced by the process above exhibits poor mechanical properties due to the scission of the main rubber chains.

Thiosalicylic acid was used as a devulcanizing agent in devulcanizing natural rubber in a mechanochemical process. In this process, the rubber was first ground and then treated with thiosalicylic acid. Thiosalicylic acid is advantageous due to the thiols and carboxyl functional group of thiophenol and benzoic acids. Thiosalicylic acid is expected to function as a bifunctional devulcanizing agent due to the devulcanizing property of thiophenol and the retardant (less susceptible to fire) property of the benzoic acid [60]. In the study, NR was ground to a size of 20 mesh and was mixed with the thiosalicylic acid at a temperature of 140°C for 30 minutes [60]. The results showed that the sol fraction of the devulcanizates obtained is significantly less when compared with the NR vulcanizates. Better mechanical properties comparable to the rubber devulcanized by DD were reported in thiosalicylic acid devulcanized rubber subjected to re-vulcanization. The chemical methods, though effective, are limited by their use of harmful ecotoxicology properties, as shown in Table 5.

A study using the twin-screw extruder was carried out at different barrel temperatures of 200, 220 and 240°C. The reclaiming agent used was DD in the presence of supercritical CO_2 ($ScCO_2$).

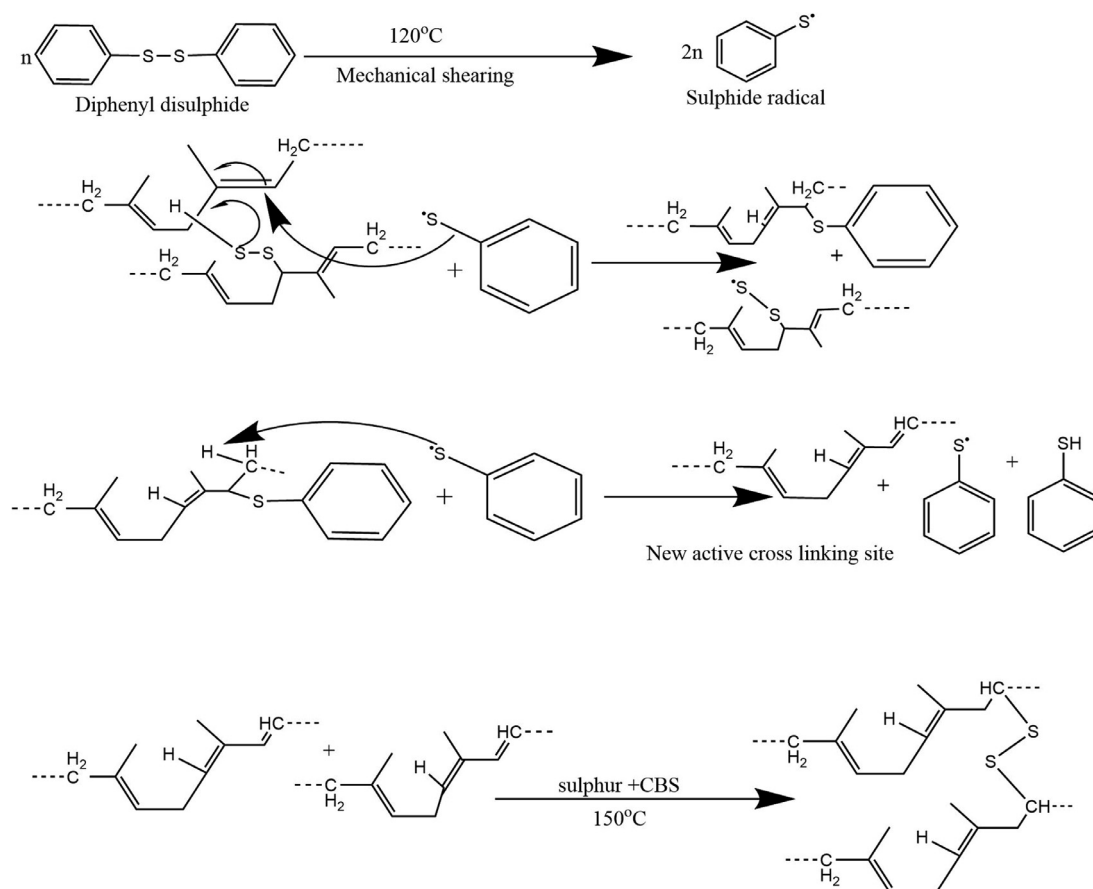


Fig. 8. Mechanism of DD in chemical devulcanization [18].

Table 5
Effects of different devulcanizing agents.

| Devulcanizing agent | Effect | References |
|--|---|---------------|
| Dibenzyl disulfide | <ul style="list-style-type: none"> • Toxic and carcinogenic | [61] |
| DES | <ul style="list-style-type: none"> • Biodegradable, green | [62,63] |
| HDA | <ul style="list-style-type: none"> • Biodegradable, expensive | [64] |
| IL | <ul style="list-style-type: none"> • Non-Biodegradable | [65] |
| $\text{ScCO}_2 + \text{DD}$ | <ul style="list-style-type: none"> • Toxic, carcinogenic | [58,59,66,67] |
| Supercritical fluids | <ul style="list-style-type: none"> • Economical, safe but VOC emission | [68] |
| Tetrabutylammonium bis(4-methylphenylsulfonyl dithiocarbamate) zincate(II) | <ul style="list-style-type: none"> • Green and safe | [69] |

The results showed that important reclaiming parameters such as temperature, shear force, time, reclaiming agent could effectively devulcanize the rubber. However, it also showed higher sol fraction, indicating more severe main chain scission. Oxygen concentration, high temperature and high shear force were found to have adverse effects as they cause the scission of the main chain. The study reported approximately 78% of devulcanization through

the thermomechanical method in the presence of ScCO_2 . The recommended method to maximize devulcanization while limiting degradation would be oxygen-free medium, low shear force and low temperature [68]. Thermomechanical devulcanization of GTR and EPDM was carried out by a twin-screw extruder with ScCO_2 [70]. It was reported that feed rate and screw speed influence the sol fraction and crosslink density. As the feed rate increases,

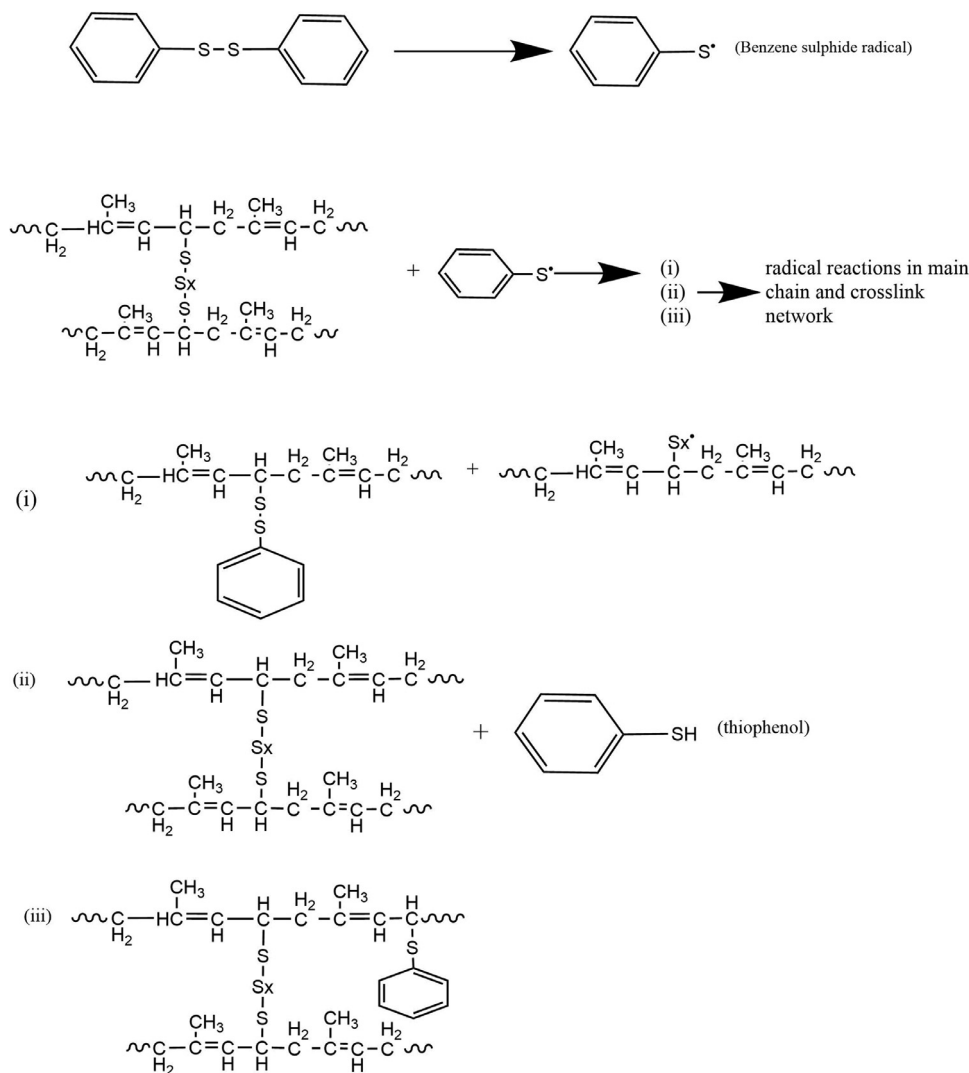


Fig. 9. Alternative devulcanization mechanism by the use of DD in rubber [18,59].

the sol fraction and crosslink density decrease and increases respectively. Upon analysis on the quality of the devulcanization, it was found that samples with a higher degree of devulcanization were obtained by a selective crosslink cleavage mechanism, whereas the other samples were randomly cleaved [70]. Devulcanization with ScCO_2 is a relatively new process as it is harmless and less toxic. The mechanism induced by ScCO_2 has yet to be fully understood. Further attempts to understand the mechanism will help to achieve a higher devulcanization rate through this relatively environmentally friendly and non-toxic approach.

The types of chemicals used, the operating conditions, percentage of devulcanization, bonds cleaved, and end products formed in the few other reported organic chemicals process are illustrated in Table 6. The most common chemical used for devulcanization is DD operated at 180°C and 24 MPa. The highest degree of devulcanization achieved by using DD was 78.4%. The common by-product gained from the chemical reactions are thiophenols followed by sulfur dioxide. Sulfur bonds are mainly cleaved selectively by DD in the devulcanization process.

4.3.2. Peroxides (PO)

Peroxides are chemical compounds where a single covalent bond links two oxygen atoms. Treatment of waste rubber was studied by using two types of peroxide compounds, hydrogen per-

oxide and benzoyl peroxide. Degradation of isoprene units of NR using hydrogen peroxide is another extensively used approach [73]. The process is conducted in the presence of formic acid and is called epoxidation. It is reported that epoxide is formed as an intermediate by using periodic acid, followed by cleavage into a telechelic carbonyl oligomer [74]. The epoxidation is usually carried out in formic acid with a carefully controlled pH of the reactive media. It is considered that the epoxidized isoprene units undergo an oxidative cleavage reaction by periodic acid [23,73]. A one-step oxidative process has successfully achieved the controlled degradation of natural rubber-based low molecular weight polyisoprene with periodic acid [74].

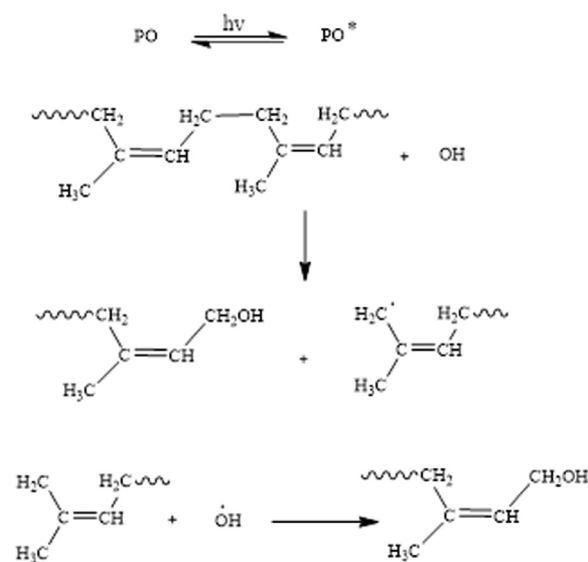
Another degradation process involving UV light and hydrogen peroxide was studied. Fig. 10 shows the basic photooxidation mechanism involved, in which the polymer chain is cleaved in the presence of oxygen and UV light. The mechanism involves the decomposition of hydrogen peroxide to form hydroxyl radicals in UV light which act as scavengers to the rubber chain [75].

Chemical devulcanization was also studied using benzoyl peroxide (BPO) as the devulcanizing agent in xylene as a solvent, which breaks down the C-S or S-S bonds [23] [54]. Xylene is generally used due to its higher boiling point. The study investigated the different benzoyl peroxide concentrations (0, 2, 4, 6, 8 phr) for 2hrs at 80°C. It was observed that at lower concentrations and at 2

Table 6 Different chemicals and types of rubber, operating conditions, bonds cleaved, and the end products produced during devulcanization.

| Type of rubber | Chemical used | Loading sample | Operating temperature (°C) | Operating pressure (MPa) | Operating time (min) | Devulcanization (%) | Types of bonds cleaved | By-products | References |
|----------------------|--|----------------|----------------------------|--------------------------|----------------------|---------------------|--|--------------------------|------------|
| Waste Tire rubber | Nitric acid | 10g | 110 | NA | 600 | NA | Selectively attack weakest or C-S bonds. | Sulfur dioxide | [71] |
| Waste Tire rubber | Benzoyl peroxide (BPO) | 2 phr | 80 | NA | 10 | 13.5 | Selectively attack weakest or C-S bonds | Sulfur dioxide | [72] |
| | | | | | 20 | 29.6 | | | |
| | | | | | 30 | 45.2 | | | |
| Natural Rubber | Diphenyl disulfide (DD) | 1g | 80 | NA | 10 | 16.7 | Sulfur bonds | Thiophenol and a radical | [67] |
| | | | | | 20 | 35.9 | | | |
| | | | | | 30 | 48.3 | | | |
| Waste tire rubber | Thiophenol (PhSH), n-butylamine (n-BuNH ₂) | 1g | 180 | 10 | 60 | 25 | Sulfur bonds | Thiophenol and a radical | [66] |
| Waste tire rubber | Diphenyl disulfide (DD) | 50 g | 180 | NA | 120 | 72.7 | Sulfur bonds | Thiophenol and a radical | [68] |
| Waste natural rubber | Diphenyl disulphide (DD) | 1g | 180 | 24 | 60 | 75.5 | Sulfur bonds | Benzenethiols | [58] |
| | | | | | 150 | NA | | | |
| | | | | | 180 | NA | | | |
| Ground tire rubber | Supercritical CO ₂ in the presence of DD | 10g | 180 | 15 | 60 | 52±3 | Cross-link network | Thiols | [59] |

Note: NA- not available, phr-per hundred rubber

**Fig. 10.** Degradation of rubber chain by hydroxyl radical [75].

hours, the selective devulcanization of the cross-links can be observed. However, as the BPO's concentration and reaction time increases, nonselective scission of cross-link and backbone was observed with decrease in mechanical properties indicating degradation [54].

In another study, a chemical and mechanochemical process was carried out to study the devulcanization of NR by benzoyl peroxide. The devulcanization in the chemical process was conducted by using 2 g of BPO as a devulcanizing agent in xylene at 80°C. In the mechano-chemical process, rubber sheets were devulcanized in a sigma mixer with different concentrations (2 and 4 phr) of BPO at 80°C and a rotor speed of 60 rpm [72]. It was shown that in chemically treated rubber, 10.5% of devulcanization was seen after 2 hours of treatment with BPO, 43.5% and 46.8% of devulcanization was seen after 4 and 6 hours respectively. Through the mechanochemical, at 2 phr concentration 13.5%, 29.6% and 45.2% of devulcanization was seen after 10, 20 and 30 minutes respectively. At 4 phr concentration 16.7%, 35.9% and 48.3% of devulcanization was seen after 10, 20 and 30 minutes of treatment respectively [76]. From the above results it is evident that treatment time and concentration of BPO played a significant role in achieving higher amount of devulcanization. Although both processes successfully devulcanized rubber, it was found that the mechanochemical process was more efficient than the chemical method. When the devulcanizates were blended with virgin NR, there was an increase in tensile strength compared to the original vulcanized NR. This showed that mechano-chemically devulcanized rubber could be used as fillers.

Similarly, another study used BPO as devulcanizing agent and cyclohexane as a solvent on thermoplastic vulcanizates [76]. The process was carried out between 80 to 190°C using a mixer at a rotor speed of 25 rpm. It was found that at 1 phr of BPO, the crosslink density decreased to 29.37% compared to the original thermoplastic vulcanizate. Furthermore, at 5phr concentration of BPO, the crosslink density of the devulcanizates decreased to 64% and gradually decreased to 69% as the temperature increased to 10°C [76]. Thus, the above-conducted study shows that the devulcanization percentage of NR is higher at 80°C when treated mechanochemically with BPO.

It is observed that almost 50% of devulcanization can be achieved at 4 to 6 phr of BPO [76]. However, at higher concentrations of BPO and increased reaction time, random scission of

crosslinks and main chain was observed which indicated increasing degradation rate. BPO can be used for devulcanization of rubber at optimum concentration of PO, time and lower temperature. The devulcanized rubber obtained through these methods can be used as fillers.

4.3.3. Green solvents

Solvents developed as a more environmentally friendly alternative to petrochemical solvents are known as “green solvents.” The toxicity of the chemicals used in the chemical treatment of rubber waste causes severe environmental issues. Therefore, the interest in using ionic liquids (IL) to replace the volatile organic solvents for the devulcanization of NR has been increasing [77]. IL's are composed primarily of an anion and a cation. They have unique characteristics such as low vapour pressure and high thermal stability, which offers advantages such as ease of containment, product recovery and easy recycling. In addition, they have good thermal stability and do not decompose over higher temperature [77]. A study reported the use of ILs for controlled depolymerization of NR for the single-step synthesis of acetoxy telechelic polyisoprenic oligomers. Trihexyl-(tetradecyl)phosphonium chloride (Cyphos101) and N,N-dioctylimidazolium bromide (C_8C_8ImBr) were used in the process through which low-dispersity telechelic polymers were produced [78]. The process was carried out by adding 350 mg of NR 45°C under nitrogen, low IL quantity (1 ml) for 3 hours. C_8C_8ImBr was used in a controlled degradation process for five consecutive cycles resulting in the formation of acetoxy telechelic polyisoprenic polymers. This degradation was applied successfully on waste tires to provide telechelic oligomers. They are key intermediates for the innovation and production of new materials like block copolymers, thermoplastic elastomers, compatibilizers, etc. Although there are certain advantages to IL's, they are non-biodegradable, expensive and difficult to synthesize on an industrial scale [79].

Recently, deep eutectic solvents (DES) were studied as a chemical agent intended for rubber devulcanization. DESs are formed by combining a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). DESs are considered a new class of green solvents due to their unique properties such as low cost, environmentally friendly, less volatile, highly biodegradable, and easy synthesis. Saputra et al. (2019) has investigated the use of Choline chloride: urea (ChCl: urea), Choline chloride: Zinc chloride (ChCl: $ZnCl_2$), $ZnCl_2$: urea for ground tire rubber (GTR) devulcanization [63]. The ratios of GTR: DES were 1:20, 1:30, and 1:40, with the total loading fixed at 50 g. The mixture of rubber and DES was heated using a hotplate stirrer at 180°C and 300 rpm with varying 5, 15, and 30 min. [63]. The FTIR and Horikx analysis further identified that the devulcanization was confined to sulfidic bondages keeping polymeric chains intact. An increase in the devulcanization percentage (approx. 96%) was observed in the 1:30 mass ratio at 5 min and then decreased in ChCl: urea. The decrease in the percentage can be attributed to the scission of main chains ChCl: urea (approx. 96%) was found to have the most rapid and highest extent of devulcanization, followed by $ZnCl_2$: urea (approx..94%) and ChCl: $ZnCl_2$ (approx..92%) [66]. DESs are considered as an alternative to ILs to overcome their non-biodegradability and cost. Though their high viscosity and solid state at room temperature could be disadvantageous, they can be tailored by properly selecting HBA and HBD and their molar ratio [79].

In another study, EPDM rubber compounds were reclaimed by using hexadecylamine (HDA) as a devulcanizing agent [64]. HDA is a green solvent as they are less toxic and biodegradable. During the process, a significant reduction in the crosslink density of more than 50% was observed at the temperature range of 225 to 275°C. The HDA was able to cleave the poly and disulfidic bonds, which are transformed into monosulfidic bonds. HDA was also ca-

pable of cleaving the monosulfide crosslinks to a certain extent. It was found that when only thermal treatment without HDA was applied, random main-chain scission of the rubber network caused the production of oligomeric fragments. The temperature set for the devulcanization had the largest influence on the extent of devulcanization within the test parameters that were investigated. More than 50% of decrease in crosslink density was observed at temperature between 225°C to 275°C. The 50% reclaimed rubber showed good mechanical properties compared to the original rubber compound [64]. Using HDA for devulcanization is advantageous as it is biodegradable but is limited due to the high cost.

The chemical devulcanization techniques are more favourable in the industrial setting to achieve a controlled devulcanization without degrading the rubber backbone and losing the mechanical properties. Although chemicals like disulfides and peroxides have proven to yield better devulcanizates, these chemicals are toxic and hazardous. The alternatives to these chemicals can be replaced by green solvents like ILs, DES and HDA. They have been reported to have similar devulcanization levels as the disulfides and peroxides. Due to the advantage of controlled devulcanization of the discussed chemicals, the higher quantity and quality of devulcanizates produced can be reused. From the discussion on green solvents, with further studies on various other DESs, they could be potentially used at an industrial level for devulcanization. The devulcanizates produced can be used as cost-effective raw material to produce new rubber goods.

4.4. Physical methods

Physical methods focus on using external energy to devulcanize rubber in contrast to chemical or mechanical methods. Microwave and ultrasonic devulcanization are the most explored physical methods due to the absence of toxic agents in the process.

4.4.1. Microwave treatment

Microwave methods is said to be one of the most promising techniques for devulcanization due to the promising properties of the resulting devulcanized rubber. Microwave devulcanized rubber exhibits increased fluidity and enhanced reusability of the rubber. These properties allow the devulcanizates to be easily remolded and revulcanised. The microwave method involves volumetric heating, heating by generating internal energy throughout the volume of the material using microwaves, promoting uniform heating compared to other traditional methods [65,80–82]. As the process energy focused and does not use chemicals, it is considered a physical process.

De Sousa et al. have investigated microwave degradation on GTR with 1 to 5.5 minutes of exposure to microwave energy. The structural modification of the GTR after the exposure was characterized by solvent extraction, swelling, and ATR-FTIR [80]. Due to the radiation from the microwaves, the crosslinks were cleaved, and free radicals were formed. The radicals formed can also undergo rearrangement through linking to the broken crosslinks. The possible mechanism of the microwave devulcanization of NR and SBR is shown in Figs. 11 and 12. An S-S bond is adopted between the two main chains to depict the changes in the structure as a result of devulcanization. Due to radiation, the C-S and S-S bonds can be broken and rearranged by linking radicals formed and X, where “X” is S or $\frac{1}{2} O_2$. The formation of cyclic structures during the process is a possibility due to the devulcanization process. The results indicated that increased exposure time intensified the amount of energy absorbed by GTR and converted to heat. The converted heat is the key factor responsible for decreasing crosslinking, resulting in devulcanization [80]. Prolonged exposure to microwaves resulted in many structural changes such as decreased

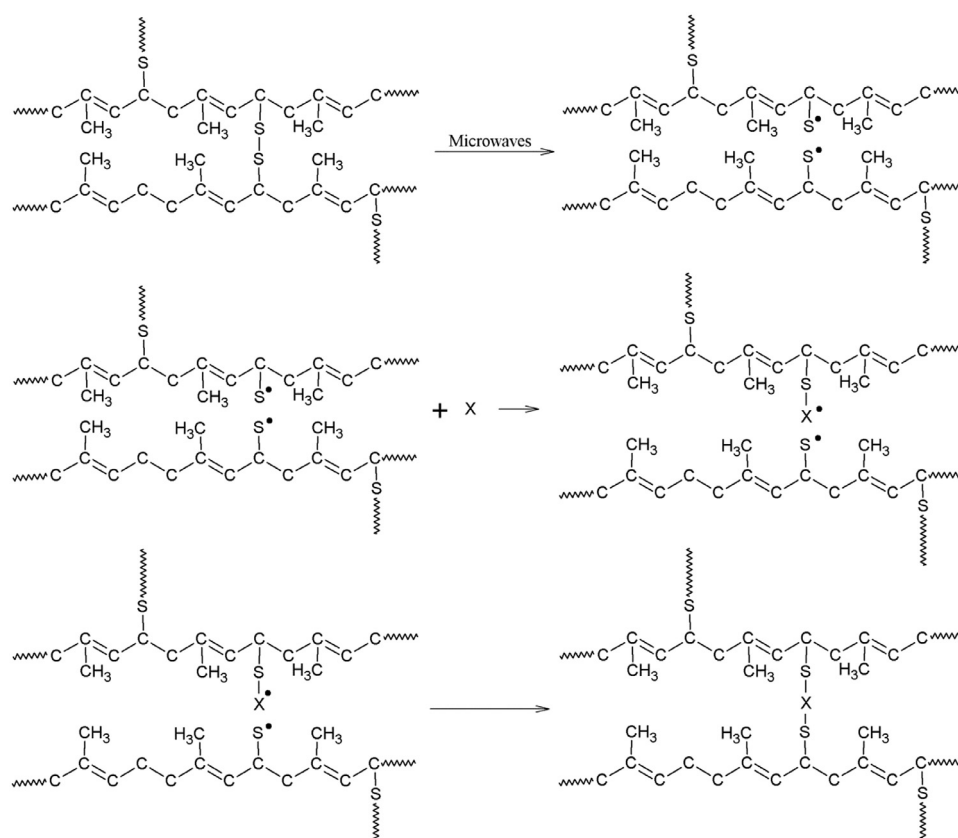


Fig. 11. Proposed microwave devulcanization mechanism of NR [80].

gel fraction and cross-linking density of the sample and increased sol-fraction, indicating devulcanization. However, the scission of the rubber main chain was also found with longer exposure times, which suggests the dominance of degradation compared to devulcanization.

In another study, devulcanization of styrene-butadiene rubber (SBR) using microwave method in the presence of an ionic liquid, pyrrolidinium hydrogen sulfate [Pyr][H₂SO₄], was reported. It was observed that the heat produced when exposed to the microwave irradiation was favoured by IL. This mechanism reduced the energy required for devulcanization and is called ionic conduction [64]. The performance was measured in terms of cross-link scission, which was well fitted with Horikx's curve suggesting the occurrence of devulcanization by selective breakage of cross-links [64]. Cleavage of more C-S bonds than S-S bonds was observed with an increase in temperature. The energy required for breaking C-S, S-S bonds was 285 and 268 kJ/mol, respectively. Whereas 346 kJ/mol are required for C-C bonds breaking, suggesting that C-S bonds are more likely to be cleaved than S-S bonds [81,82]. FTIR analysis combined with swelling measurements showed that the devulcanized ground tire rubber (DGTR) underwent a regeneration phenomenon, a combination of devulcanization and degradation. The qualitative analysis of regeneration level was achieved by studying the swelling values in toluene.

It has been reported that the microwave method produces superior devulcanized rubber, which exhibits properties very close to the original rubber-like properties. In addition, the devulcanized rubber regained its fluidity, the capability of being remolded and re-vulcanized [23,64]. However, it was found that the devulcanized rubber through this process emits volatile organic compounds (VOC), which are toxic, and optimization is necessary to assess the amount of energy required for the process.

4.4.2. Ultrasonic frequency treatment

Another well-known physical approach is the ultrasonic method, as it does not change the chemical makeup of the polymer and reduces the molecular weight by cleaving the most susceptible chemical bonds [58,83]. It was first studied on rubber and reported by Sathiskumar et al. [84]. The recycling of carbon black filled EPDM was conducted by using a continuous ultrasonic grooved barrel reactor. They have reported an increase in devulcanizates output twice the amount in comparison with the coaxial reactor. The crosslinked density and sol fraction analysis indicated higher devulcanization degree was achieved at higher amplitudes. However, comparatively fewer devulcanizates of carbon black filled rubber were obtained due to energy consumption for cleaving the bonds between carbon black and EPDM rubber. Viscoelastic properties studies indicated that EPDM devulcanizates had higher elasticity and re-vulcanized EPDM rubber had lesser elasticity than equivalent virgin rubber [84].

Utara and Moonart studied ultrasonic degradation on natural rubber latex [83]. The natural rubber was subjected to 20 kHz and 25 kHz for 240 minutes, and the changes in molecular weights were observed. Lower molecular weights were observed after 10 min. However, after 30 minutes of exposure, fluctuations in molecular weight distributions were observed in both samples, which can be possibly explained by chain scissions and cross-linking of the polymer chain by radical. The study suggested that determining the optimal frequency for ultrasonic degradation is essential for yielding the desired molecular weight. FTIR results suggested that the polyisoprene structure remained unaltered at the above-studied frequencies [83].

In another study, the effect of ultrasound intensity on NR/SBR blends was investigated. The ground vulcanizates were devulcanized in an extruder barrel with a temperature set at 120°C. The

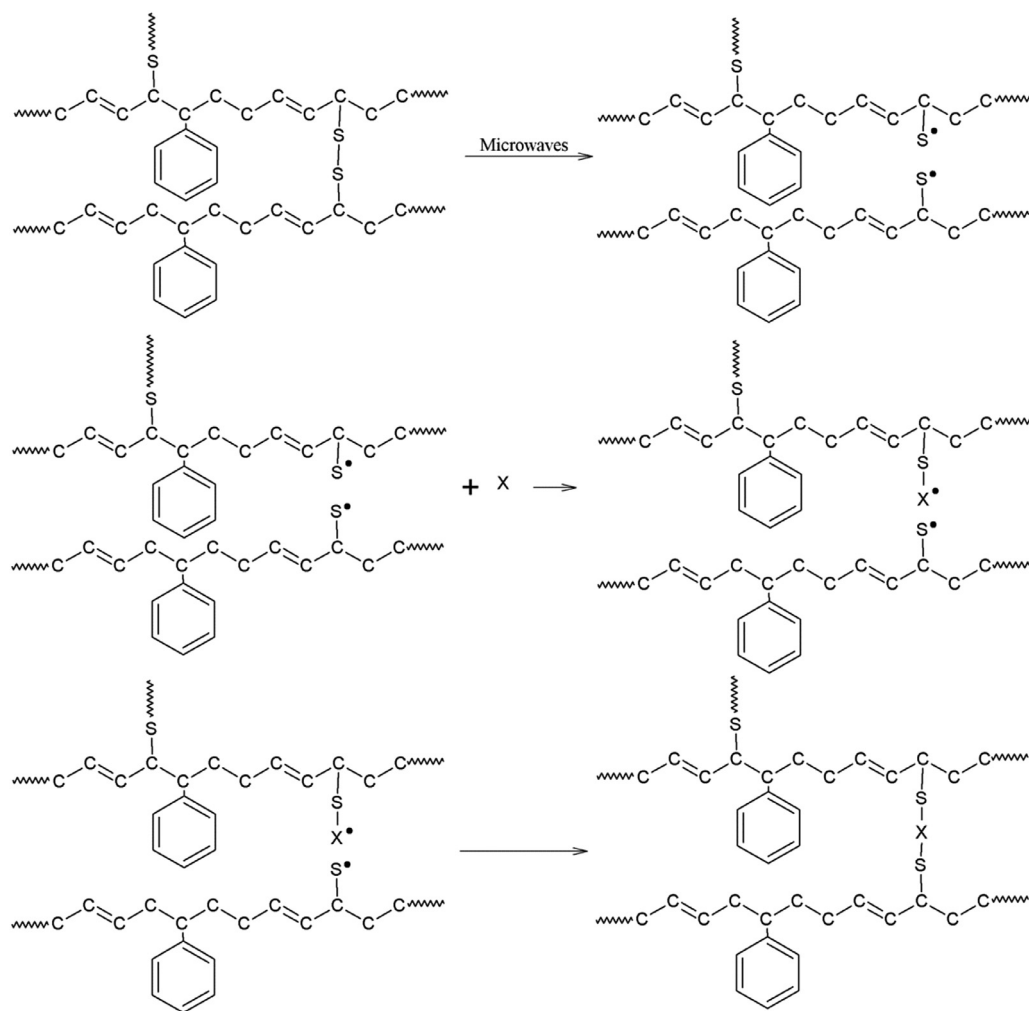


Fig. 12. Proposed mechanism of microwave devulcanization of SBR [80].

devulcanization was carried out at 20 kHz and 5, 7.5 and 10 μm amplitudes [85]. During devulcanization, the ultrasonic power consumption for 75/25 and 50/50 (w/w) NR/SBR blends, and pure NR were found to be 7.5 μm . For pure SBR and 75/25 NR/SBR blends, the power consumption increased with ultrasonic amplitude. It was also reported that the power consumption for devulcanization of NR was higher when compared to SBR. On the other hand, the power consumption for NR/SBR blends decreased with increasing SBR content at 5 μm . Higher power consumption led to a higher degree of devulcanization, which concluded that NR devulcanization is easier than SBR [85].

From the studies conducted, microwave and ultrasonic methods were reported as the most promising techniques at present due to their high productivity in shorter operating time and are environmentally safe [18,23,80,83]. However, the operation cost of the reactors is hindering its industrial applications.

Although the microwave method produces higher quantity and better devulcanizates in a shorter time and uses lesser energy, it is important to note that it does not guarantee even irradiation due to the hot spots. Precise control of temperature and power is essential during microwave treatment to achieve the desired vulcanizates. Though industrial microwave reactors can solve this problem, the setup cost is too high which limits its applications. Similarly, ultrasonication of waste rubber has proven effective with up to 90% of devulcanization [86]. However, the downside of ultrasonic treatment is also the high cost for industrial setup.

4.5. Biological methods

The biological process of rubber degradation involves microorganisms growing on the rubber surface to mediate devulcanization and degradation. The microorganisms act by either adhering to the rubber surface or secreting enzymes that aid in rubber devulcanization and degradation. Soil contains various types of microbes, including bacteria and fungi, that can degrade the rubber. Several bacteria and fungi were isolated, and their cultures were tested for their biodegrading ability. These studies have shown that the actinomycetes are the major bacteria capable of degrading the rubber in considerable amounts [9]. *Nocardia* sp 835A and *Nocardia* sp. 835A strains have been reported to degrade about >90% and 80% of the rubber material [87]. Various bacteria belonging to the actinomycetes such as *Streptomyces coelicolor* CH13 [88], *Streptomyces* sp. K30, *corynebacterium*, *Nocardia*, *Gordonia* sp. *Mycobacterium* group [89], *Alicyclobacillus* sp. [90] were identified as rubber biodegrading bacteria. Biodegradation of natural rubber was first studied in 1914 by using solution cast films of natural rubber as a carbon source [91].

4.5.1. Bacteria cultivation

Rubber degradation through the biological method is a slow process. Therefore, incubation periods can extend over weeks, months or years for significant degradation to take place. There are two kinds of rubber degrading bacteria, the ones which se-

crete enzymes that degrade rubber and the ones which degrade the rubber by adhesive action. The bacteria releasing rubber degrading enzymes form a clear zone on latex agar plates as latex is the sole energy and carbon source. Bacteria such as *Xanthomonas* sp, *Streptomyces griseus* 1D, *Streptomyces coelicolor* 1A, *Streptomyces* sp. K30, *Streptomyces* sp. S1G, S3D, S4C, S4E, S4F, S4G has an incubation period of 6-12 weeks [10] except for *Xanthomonas* sp. 35Y, which was reported to have one week incubation period [92].

The most popular rubber degrading bacteria belong to mycolic acid-containing bacteria and actinobacteria belonging to the genera of *Gordonia*, *Nocardia*, and *Mycobacterium*. *Nocardia* sp. 835A strain Rc, *Gordonia* sp. VH2, *Nocardia* sp. 835A, *Actinobacter calcoaceticus* is reported to have incubation periods ranging from 4 – 10 weeks and do not produce enzymes or form clear zones but degrade the rubber by adhesive action on the rubber surface [87,93,94]. The direct contact of the bacteria with the rubber enables it to degrade the polyisoprene chains in the rubber structure.

Table 7 contains types of rubber degraded by different bacterial strains, operating conditions, and percentage of rubber weight reduced by the biodegradation. Most of the bacteria are gram-positive except *Xanthomonas* sp, which is gram-negative. The optimum temperature for effective degradation was 30 °C. The maximum degradation of more than 90% was achieved by adhesive action of *Nocardia* sp. 835A within three weeks of incubation. In comparison, minimum degradation of 10% was achieved via enzyme degradation within six weeks of incubation by *Streptomyces* sp. [95].

Two novel strains of *G. polyisoprenevorans*, VH2, and Y2K, were identified by Arenskötter et al., (2001) [96] as rubber degrading bacteria. *G. polyisoprenevorans* Y2K was accidentally identified during the cultivation of *P. aeruginosa* when it was found to be infected. However, the growth was inhibited by an unknown strain that was later identified as *G. polyisoprenevorans* Y2K. It was reported that *G. polyisoprenevorans* Y2K could utilize rubber as a carbon source and degrade the rubber, whereas *P. aeruginosa* could not. *Gordonia westfalica* sp. and *Gordonia amicalisa* are two other rubber degrading actinomycetes identified and reported [97]. In addition, *G. amicalisa* was reported to produce a desulfurizing enzyme when vulcanized SBR and vulcanized IR were used, and dibenzothioephene was used as an enzyme-substrate [98].

Rubber degrading bacterial strain, *Bacillus* sp. SBS was identified and isolated from soil. The bacteria could grow between the temperature range of 15 to 42°C and a pH range from 5 to 9. The biodegraded products were analyzed for carbon dioxide evolution and were subjected to thin-layer chromatography (TLC). Analysis by TLC showed sodium bicarbonate's presence with the liberation of CO₂ and the presence of lipids, which indicated that the bacteria have utilized and mineralized the rubber [101]. Similarly, *Bacillus* sp. AF-666 was isolated and identified to degrade natural rubber gloves. The bacteria were identified to grow on both latex overlay agar plates and in a liquid medium. Gravimetric analysis of carbon dioxide evolution by strums test resulted in 4.43 g/l in the plates containing the bacteria, whereas 1.57 g/l of CO₂ was reported in the case of control [102]. *Bacillus* sp. Strain S10 was isolated from sewage sludge and was reported to degrade tire rubber [103]. The growth conditions of *Bacillus* sp. S10 was studied at a temperature range of 25 to 40°C and at a pH range of 5 to 10. The maximum degradation of tire rubber by the bacteria *Bacillus* sp. S10 was found to occur at the temperature range of 30 to 35°C and pH 7 [103,104]. Fig. 13 shows the SEM photographs of tire rubber degraded by the bacteria *Bacillus* sp. S10 cultured in MSM medium for 28 days at 35°C [103]. The micrographs show the formation of pits and cracks when treated with the bacteria.

Another bacteria belonging to the same genera, *Bacillus cereus* TISTR 2651, was reported to devulcanize the NR vulcanizates. The bacteria could oxidize the sulfide crosslinks and could partially

Table 7
Operating conditions for rubber degradation by different bacterial strains.

| Type of rubber | Microorganism | Temperature (°C) | Rotation per minute (rpm) | Incubation time (weeks) | Degradation method | Rubber weight reduction (%) | References |
|----------------|--|------------------|-----------------------------------|-------------------------|--------------------|-----------------------------|------------|
| Tire rubber | <i>Nocardia</i> sp. 835A strain Rc | 30 | 0-300 | 8 | Adhesive action | 80 | [87] |
| Glove | <i>Nocardia</i> sp. 835A | 30 | 0-300 | 3 | Adhesive action | > 90 | [87] |
| rubber | <i>Gordonia</i> sp. VH2 | 30 | 180 | 4 | Adhesive action | > 50 | [93] |
| | <i>Pseudomonas citromellolis</i> | 30 | Incubated with occasional shaking | 10 | Adhesive action | 13 | [94] |
| | <i>Actinobacter calcoaceticus</i> | 30 | Incubated with occasional shaking | 10 | Adhesive action | 12 | [10] |
| | <i>Pseudomonas</i> sp. | 30 | 220 | 6 | Adhesive action | 10.38 and 43.11 | [99] |
| | <i>Xanthomonas</i> sp. 35Y | 30 | Incubated without shaking | 1 | Enzyme production | NA | [92] |
| | <i>Xanthomonas</i> sp. | 30 | Incubated with occasional shaking | 10 | Enzyme production | 60 | [10] |
| | <i>Streptomyces griseus</i> 1D | 30 | Incubated with occasional shaking | 10 | Enzyme production | 12 | [10] |
| | <i>Streptomyces coelicolor</i> 1A | 30 | Incubated with occasional shaking | 6 | Enzyme production | 18 | [10] |
| | <i>Streptomyces</i> sp. K30 | NA | NA | 12 | Enzyme production | 10-18 | [100] |
| | <i>Streptomyces</i> sp. S1G, S3D, S4C, S4E, S4F, S4G | NA | NA | 6 | Enzyme production | 13.4 > 10 | [100] |

Note: NA- not available.

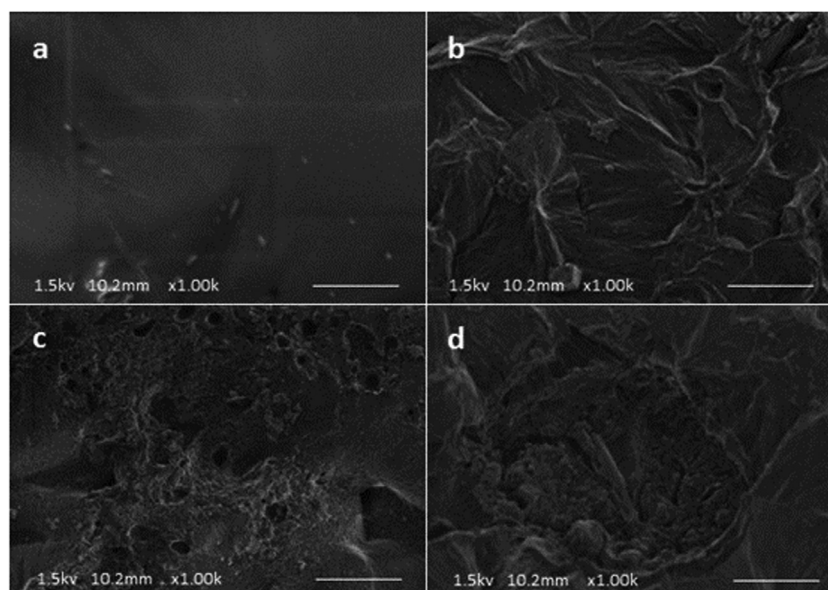


Fig. 13. SEM photographs of (a) Control (b-d) different tire pieces treated with *Bacillus* sp.S10. The bar represents 10µm [103].

cleave the main carbon chain present in the rubber. It was found from Horikx analysis that the primary mechanism of the bacteria was to cleave the sulfur crosslinks, which took place very early on during the process [105]. After 20 days of devulcanization, the crosslink density and gel fraction analysis revealed that the physical properties were significantly reduced compared to the control sample before bacterial treatment. The FTIR spectra showed characteristic peaks at S=O stretching (1088 cm^{-1}) and C=O stretching (1730 cm^{-1}). These results supported the oxidation of sulfide crosslinks to form carbonyl groups and oxygen-containing sulfur-based groups. X-ray photoelectron spectroscopy results confirmed the decrease in C-S bond S-S bonds after the treatment [105]. A decrease in C-C intensity was also observed. This signifies that *B. cereus* TISTR 2651 cultivation can be applied to recover the virgin rubber and recycle waste rubber. The devulcanizates can be used as feedstock for raw materials in the industry.

Mixed culture was also applied to improve the efficiency of rubber degradation. A mixed culture by using *Sphingomonas* sp. and *Gordonia* sp. has been found to be more effective for the devulcanization of GTR [106]. Both bacteria were co-cultured in MSM medium with pH 6.5 at 30°C. The mixed culture treatment obtained a 9.5% decrease in cross-linking density and a 32.4% decrease in surface sulfur content. This indicates that both bacteria could significantly reduce the sulfur content, and the devulcanization rate increased to a certain extent compared to the single bacteria. The results from the water contact angle showed that the angle was about 100° and 92.7° after being treated with a single bacterial culture and mixed culture, respectively. This was noted as a desirable finding as it showed an increase in hydrophilicity of GTR [106].

4.5.2. Fungi cultivation

Besides bacteria, natural rubber degradation by fungi was first reported by cultivating various strains of *Penicillium* and *Aspergillus* in two different mediums containing NR and 10% (w/v) NaCl. A 6% increase in the biomass and a decrease in the weight of the rubber material in the range of 15.5% to 30.9% was documented after incubating them for a period of 19 months to 5 years [89]. Fungi attack materials with rough or cracked surfaces, allowing them to be attached to and penetrating the materials. Rough surfaces on rubber may contain nutrients and retain water enabling fungal growth.

Enzyme laccase and manganese peroxidase were produced by the fungi *Penicillium chrysogenum* and the bacteria *Bacillus subtilis* and *Bacillus pumilus* [107–109]. The activity of the enzymes was reported to be maximum at 00138 IU for laccase and 0.0155 IU for manganese peroxidase in the seventh week of cultivation of *Bacillus subtilis*. In contrast, laccase and manganese peroxidase activity in *Penicillium chrysogenum* was highest in the tenth week, which were 0.0247 IU and 0.0262 IU, respectively [107,109].

Another study utilised three types of filamentous fungi belonging to *Alternaria alternata* (ANR and BNR strains) and *Penicillium chrysogenum* [110]. NR discs of 2 mm thickness and 150mm diameter were introduced into flasks containing the fungi. The growth rate of the fungi was determined at two different temperatures, 25°C and 30°C. The results showed that the BNR strain has a higher growth rate of 0.042 cm/h at 25°C, whereas ANR showed 0.032 cm/h in the Czapek (CZ) medium. On the other hand, *P. chrysogenum* showed the highest growth rate at 0.042 cm/h on CZ medium at 30°C, whereas it only showed 0.036 cm/h at 25°C on MEA medium. The biodegradation was carried out for 65 days. After considering the production of enzymes and biomass, BNR strain at 25°C is concluded to have the highest biodegradation potential. At 41 days, 0.242 IU/L of manganese peroxidase activity was observed, and at the end of 65 days, 4.3% of biodegradation rate was reported.

4.5.3. Enzymatic degradation

To date, five types of enzymes, namely rubber oxygenase A (roxA), rubber oxygenase B (roxB), latex clearing protein (lcp), laccase, and manganese peroxidase, are produced by bacteria that is forming a clear zone on the latex overlay agar plate for rubber degradation [111]. The clear zone formation indicates latex (polyisoprene) breaking into smaller products consumed by the bacteria as the sole carbon and energy source [111]. Two essential proteins, rubber oxygenase A and Latex clearing protein (lcp), were identified in gram-positive *Streptomyces* sp. strain K30 and rubber oxygenase A (roxA) from the Gram-negative *Xanthomonas* sp. strain 35Y [95]. Products with aldehyde ($-\text{CH}_2-\text{CHO}$) and keto ($\text{CH}_3-\text{CO}-\text{CH}_2$) groups were produced when roxA and lcp enzymes attack the double bond oxidatively [111–114]. However, the biochemical mechanism by which lcp catalyzes the reaction remains inconclusive [112,113].

Table 8
Advantages and disadvantages of biological degradation.

| Method | Advantages | Disadvantages |
|-------------------------------|---|---|
| Bacteria and fungi Enzymes | <ul style="list-style-type: none"> • Environment friendly • Less energy consumption. • No release of toxic gases. • Microorganisms are available in nature. • Environment friendly • Less energy consumption. • No release of toxic gases. | <ul style="list-style-type: none"> • The process can take up to several weeks or months. • Degradation is only limited to the rubber surface. • Additives present in the rubber hinder their activity. |

Recently, another rubber oxygenase namely roxB with some similarities to roxA genes was discovered in *S. cummioxidans* 35Y and *Rhizobacter gummiphilus* NS21 [115]. It was reported that roxB cleaved polyisoprene randomly to yield 20 carbon units and higher oligoisoprenoids with terminal aldehyde and keto functional groups [111,113,115]. 12-oxo-4,8-dimethyltrideca-4,8-diene-1-al (ODTD), the final cleavage product of roxA, was only formed in minor quantities by roxB [111].

Laccase is a versatile, oxidoreductase and ligninolytic enzyme with the capability to oxidize a wide range of phenolic and non-phenolic compounds by converting oxygen molecule to water [116]. Laccases are glycoproteins found in various fungi to higher plants and has been significantly exploited for its application in the industrial processes like in degradation of dyes, degradation of textiles, as pollutant degradation and rubber degradation [117]. Laccases were reported to be produced by the bacteria *Bacillus pumilus* and *Bacillus subtilis* and by the fungi *Penicillium chrysogenum*, which were reported to degrade rubber [107–109]. Although the type of bonds broken in natural rubber by the enzymes is not reported, FTIR analysis of the natural rubber discs showed peaks between wavelengths 2725.89 cm^{-1} and 1662.34 cm^{-1} corresponding to H-C=O: C-H stretch and C=O stretch indicating aldehyde and ketone groups are being released as a result of biodegradation [111].

Similarly, manganese peroxidase (MnP) is a ligninolytic enzyme that is ubiquitous [118]. MnP oxidizes the phenolic and non-phenolic compounds by converting Mn (II) to Mn (III). MnP has many applications in various sectors such as degradation of phenolic and non-phenolic compounds, degradation of lignin to CO₂ and H₂O, wastewater treatment, biofuel production, biosensors, dye decolorization, bioremediation, and rubber degradation [118]. MnP was reported to be produced by the fungi *Penicillium chrysogenum* and bacteria *Bacillus pumilus*, *Paenibacillus* sp., and *Bacillus subtilis* which degrade rubber. Though the exact bond scission is not identified, FTIR analysis of the degraded rubber showed the formation of aldehyde and keto groups. Peaks were observed at wavelengths 2725.89 cm^{-1} and 1662.34 cm^{-1} indicating the presence of aldehydes and ketones, respectively.

The biodegradation process is limited to the surface of the rubber because of the structural complexity and water-insoluble nature [111]. In addition, many rubber products contain additives like accelerators, antioxidants, and stabilizers, limiting the biodegradation ability of the enzymes. Therefore, the limitations shown in Table 8 can be potentially resolved by appropriate treatment of rubber to remove the stabilizers and break the sulfur bridges [118].

The use of the biological method for rubber devulcanization or degradation is in the infancy stage. Although advantages outweigh the disadvantages compared to the other methods with respect to low toxicity, milder operating conditions, and no emission of toxic gases, they are yet to be industrially viable. This is due to the vast and diversified nature of microorganisms. Furthermore, controlled devulcanization is challenging as microorganisms cannot be con-

trolled to selectively cleave the crosslinks present in the rubber. Moreover, the devulcanization or degradation by the microorganisms are only effective on the rubber surface and effective methodology to penetrate the entire rubber depth is debatable. Despite this, research and development on biological methods are essential for environmentally sustainable methods of handling rubber waste.

5. Prospects of rubber waste management

Natural rubber and synthetic elastomers are likely to continue playing an essential role in industrial and domestic applications, turning into waste at the end of the product lifetime. Over the past few decades, rubber degradation by various methods has been vastly studied and developed. The advantages of devulcanized rubber are that the rubber obtained has reduced carbon footprint. It can be introduced repeatedly into the production of new products, improving the circular economy, cost effectiveness, sustainability, and environmental footprints [119]. In the current scenario, the circular economy of the tire, one of the major rubber products, is being rapidly established in developed countries but has yet to be established in other countries around the globe. On the other hand, the circular economy for general rubber goods is almost non-existent. Better segregation, collection and initiatives for the non-tire and general rubber goods are direly needed for a wholesome rubber waste management and establishment of the circular economy.

Judging by the current environmental situation, discarded tires or other rubber products should not be treated as waste or pollutants but rather should be treated as an inexpensive raw material for producing other innovative products. The tires and other rubber products can be downsized to obtain ground rubber through various grinding techniques available. Due to their cost effectiveness grinding is the most widely used method for downsizing. The ground rubber obtained can be used as fillers in new tires, playground mats, rubberized asphalt, shock absorbers and many other products. In near future, waste rubber recycling will attract more research and development as a promising approach to improving rubber's sustainability and circular economy.

The grinding of the rubber should be followed by the devulcanization techniques in which the crosslinks present in the rubber are partially or entirely cleaved. The heavily documented methods such as thermal, mechanical, chemical and physical have been presented in this paper. It is essential to understand the limiting parameters to ensure the dominance of devulcanization over degradation. Additionally, there is a growing interest in combining two or more methods to enhance the quality of the resulting rubber. It is vital to continue enhancing many different methods to determine the best methods suited for the thousands of different rubber products turning into waste. Diversity in terms of methods is already present; however, the types of rubber subjected to these methods are very limited. Focus has always been on waste tires and gloves, which indeed should also be diversified.

Table 9
Application of devulcanized and degraded rubber in different fields.

| Recycle | Reference | Reuse | Reference | Energy recovery | Reference |
|--|-----------|--|--------------|-------------------------------|-------------|
| Additives in Portland cement concrete | [49] | Crash barriers, bumpers, artificial reefs | [25,49] | Alternative fuel | [121] |
| Modifiers in asphalt paving mixtures | [25,49] | Ion-exchanger for heavy metals in industrial water | [25,120,122] | Energy source for electricity | [25,46,123] |
| Replacement for virgin rubber | [120,122] | Automotive floor mats | [25,124] | | |
| Semi-pneumatic tires | [25,124] | Shock and vibration absorbers | [25,124] | | |
| fillers for flooring, playgrounds and parking lots | [25,49] | | | | |
| Inner lining of tubeless tires | [25,124] | | | | |

Ultrasound and microwave methods are proven to be the most promising methods over other methods due to the highly effective devulcanization of rubber waste and production of good quality devulcanizates. In addition, the microwave devulcanization process resulted in the production of new rubber products with unique properties that can be used for various applications. However, the adoption of microwave devulcanization in the industry is limited due to the cost of microwave reactors, hot spots, and problems with VOC emissions. Similarly, ultrasonic devulcanization is proven efficient in producing rubber devulcanizates in the laboratory; the high cost of scaling up limits its commercialization.

Rubber degradation methods should also be developed as it enables completion of circular economy establishment of rubber. Waste rubber with inferior properties should be subjected to degradation that enables the circular economy's material and energy recovery pathways. All the methods discussed in this manuscript can be effectively used for degradation by tweaking the parameters. One most environmentally friendly method for degradation could be the biological method. However, the method is still at an infancy stage and has recorded a prolonged rate of degradation. At present, studies have successfully identified microorganisms capable of rubber degradation and parameters influencing the degradation rate. Future research should be focused more on the different types of by-products of biological degradation and determine the feasibility of closing the loops of the rubber product cycle. Commercialization and industrialization of rubber degradation using biological methods would require time, legislation, and technology readiness.

The rubber obtained from the methods mentioned above can have a plethora of applications in several fields, as shown in Table 9. The devulcanizates can be formed into different products, and this can be classified as reuse. The devulcanized rubber obtained can replace 30% of the virgin rubber without altering the basic properties, and as a result cost of new rubber, production can be reduced [120]. These applications are classified as recycling. On the other hand, the degraded rubber can be used as an energy source elsewhere and classified as energy recovery. Thus, each of the application specifications can form a pathway in establishing a circular economy.

6. Conclusion

The synthetic and natural rubber products market increases remarkably, prompting better and sustainable rubber waste management measures. Thermal, mechanical, and chemical degradation methods are the most examined and present the potential of scaling up. Physical methods, microwave and ultrasonic degradation are arguably the most promising method of processing waste rubber. Although the biological method is proven successful and environmentally friendly, large-scale applications are yet to be employed, due to multiple limitations. This review concluded that rubber devulcanization and degradation methods are essential and should be developed further to establish the circular economy of rubber products. The technical and economic aspects of the different methods should be investigated for industrial development. The focus should be emphasized on a sustainable framework for rubber waste management. The waste management methods discussed in this manuscript are promising to establish a sustainable and circular economy for rubber products.

Declaration of Competing Interest

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

CRediT authorship contribution statement

Harika Chittella: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Li Wan Yoon:** Supervision, Conceptualization, Writing – review & editing, Methodology, Project administration, Funding acquisition. **Suganti Ramarad:** Supervision, Project administration, Writing – review & editing, Funding acquisition. **Zee-Wei Lai:** Supervision, Project administration.

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