



Waste tire rubber devulcanization technologies: State-of-the-art, limitations and future perspectives

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ABSTRACT

Waste tires management is a serious and global environmental problem. Therefore, searching for low-cost and industrial-scale applicable tire recycling methods is gaining more and more attention. Waste tire rubber is valuable source of secondary raw materials for the circular economy and current trends indicate that application of waste rubbers during manufacturing value-added products should increase in near future. Sustainable development of rubber devulcanization technologies and appropriate design of cradle-to-cradle loops for rubber goods are the most promising strategies for achieving a higher level of rubber recycling.

This work presents the state-of-the-art in the patented waste tire rubber devulcanization technologies including dynamic desulfurization, reactive extrusion, microwave treatment, and also other less popular methods. Special attention was focused on the used components, rubber treatment conditions and static mechanical properties of reclaimed rubbers. Moreover, environmental aspects and limitations related to rubber devulcanization technologies implementation are also discussed.

Our findings showed that reclaimed rubbers described in patents are characterized by higher tensile strength and elongation break (depending on devulcanization technology median: 16.6–19.0 MPa and 321–443%, respectively) compared to the literature data (median: 10.3 MPa and 309%) or commercial products (median: 6.8 MPa and 250%). The significant differences observed in performance properties of reclaimed rubbers resulted mainly from devulcanization efficiency related to waste tires composition or source and rubber treatment conditions.

Considering environmental and economic aspects, reactive extrusion is the most promising method further development rubber devulcanization technologies.

1. Introduction

The constantly developing automotive industry generates more and more waste in the form of used tires, which account for as much as 80% of all rubber waste produced in the world. It is estimated that the amount of end-of-life tires is around one billion units per year (World Business Council for Sustainable Development, 2010). The lack of management of such wastes or the use of temporary and conventional

recycling strategies poses a potential threat to the environment and human health. On the other hand, proper management is a huge challenge for scientists and industry representatives. In general, recent strategies enabling economically profitable and environmentally friendly rubber recycling are constantly experiencing modifications and reconsideration for higher quality and safety reasons.

Nowadays, the most common methods of waste tires recycling includes: i) civil engineering using whole tires in safety barriers, retention

Abbreviations: BR, butadiene rubber; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DCP, dicumyl peroxide; DPDS, diphenyl disulphide; EPDM, ethylene-propylene-diene monomer rubber; EPR, ethylene-propylene rubber; EVA, ethylene-vinyl acetate copolymer; GTR, ground tire rubber; IR, isoprene rubber; LLDPE, linear low density polyethylene; MDEA, N-methyldiethanolamine; MW, microwave; NR, natural rubber; PE, polyethylene; POE, ethylene-octene copolymer; PP, polypropylene; SEBS, styrene-ethylene-butylene-styrene copolymer; SBR, styrene-butadiene rubber; TPP, triphenylphosphine.

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tanks or backfilling, ii) energy recovery, especially incineration in cement kilns, iii) pyrolysis and iv) material recycling consisting mechanical disintegration of waste tires and further use of prepared ground tire rubber (GTR).

According to statistical data published by European Tyre and Rubber Manufacturer's Association (ETRMA) (ETRMA, 2021), in 2019 an average of 95% of the used tires in the Europe were recycled by above-mentioned methods. It means that another 5% of tires has been abandoned, incinerated or illegally landfilled. Among the rubber recycling methods, material recycling is the most promising which involves reusing of waste in the production of new materials. Waste rubbers as valuable source of raw materials reduce the need for virgin polymers, which are mainly petroleum products.

The first efforts to recycle vulcanized rubber waste was through a grinding method which taken more than 150 years ago by Charles Goodyear, the inventor of vulcanization. However, further investigations on a larger scale were conducted in the late 1900s (Myhre & MacKillop, 2002). Fig. 1 gives a fast view of progress in rubber recycling over the past two decades (A) and leading countries in publishing (B) between 2000 and 2021.

The number of patents and scientific papers was estimated based on Scopus database (data available on 28/1/2022) using terms “rubber recycling”, “rubber reclaiming” or “rubber devulcanization”.

As can be seen in Fig. 1(A), the number of papers published in this field increased from 10 in 2000 to 147 in 2021 (almost 15 times), while just over the past three years (2018–2021) it experienced a very sharp rise from 48 to 147 (almost 3 times). Increasing number of published items highlights the worldwide importance of waste tires recycling technologies and serious economic investment in the field. Especially, that law regulations with current levels of waste tires recovery recycling

are still very low in many countries. For example in Poland, minimum 75% of the tires placed on the market should be recovered, but only 15% of them have to be recycled. This trend fully justify organization of more research centres all around the world aimed for commercialization of rubber recycling methods.

Although patents have also been documented each year (an average of 15 documents per year), their importance from a practical point of view has rarely been underlined. Considering legislations and environmental policies, there is no doubt that the number of patents emphasizing stabilized environmentally friendly products rich in reclaimed rubber would follow similar trend in near future. According to the data shown in Fig. 1(B), the countries with the highest share in the development of rubber recycling are China, United States, India and Poland.

Although many review works related to rubber devulcanization were published so far, most of them were focused mainly on “classic division” based on used energy source: thermal, mechanical, chemical or their combination. On the other hand, literature data indicate lack of comprehensive review of patents, which cover the innovative solutions that can be implemented for large-scale devulcanization.

This paper provides a review of state-of-the-art in rubber devulcanization technologies in terms of recent patents and published papers, including discussion about classification, analysis and interpretation of advantages and disadvantages of the most common patented rubber devulcanization methods. Furthermore, the potential limitations and future trends for rubber devulcanization technologies are also highlighted.

This work will be particularly helpful for scientists and industry representatives looking for a promising direction in rubber recycling that could inspire them to develop new technologies and the modification, functionalization or optimization of already existed solutions.

2. GTR reclaiming vs. devulcanization

Currently, ground tire rubber (GTR) is known as the main source of recycled rubber, which is available commercially. Economical aspects, easy access to GTR and increasing environmental awareness cause that a great deal of interest is currently oriented toward the modification or suitable functionalization of GTR to make it a value-added product for advanced uses, like blending with other thermoplastics (Kakroodi & Rodrigue, 2013; Mujal-Rosas et al., 2012; Wang et al., 2018; Wiśniewska et al., 2021) and rubbers (Formela & Haponiuk, 2014; Zedler et al., 2018; X. Zhang et al., 2009b; Zhao et al., 2019) or as asphalt modifier (Li et al., 2019; Liang et al., 2015; Navarro et al., 2004; Rath et al., 2019).

A “rubber devulcanization” or “rubber reclaiming” plays a crucial role in this approach. According to ASTM D 6814 “devulcanization” is defined as a process of decomposition of chemical cross-links in cured rubber. On the other hand ASTM D 1566 defined term “reclaimed rubber” as vulcanized rubber that has been thermally, mechanically, and/or chemically plasticized for use as a rubber diluent, extender, or processing aid.

As can be noticed, these terms are slightly different from each other, however, due to their similar function, currently both terms are used interchangeably in many articles and patents. In fact, devulcanization and reclaiming represent a modification processes aimed at improving the interfacial interactions between GTR and other ingredients in blends, which consequently leads to the higher performance properties of the materials (Hernández et al., 2017; Sripornsawat et al., 2016; X. Zhang et al., 2009a; Zhao et al., 2019).

Rubber devulcanization can be considered as a selective scission of cross-linking bonds in order to breakdown three-dimensional structure, while rubber reclaiming is combination of main chain degradation and cross-linking bond scission. Fig. 2 shows possible reactions during thermal treatment of GTR to highlight the main differences between rubber devulcanization and reclaiming. Moreover, as can be observed GTR thermal treatment might also favours undesired secondary cross-linking resulting from free radical recombination, which should be

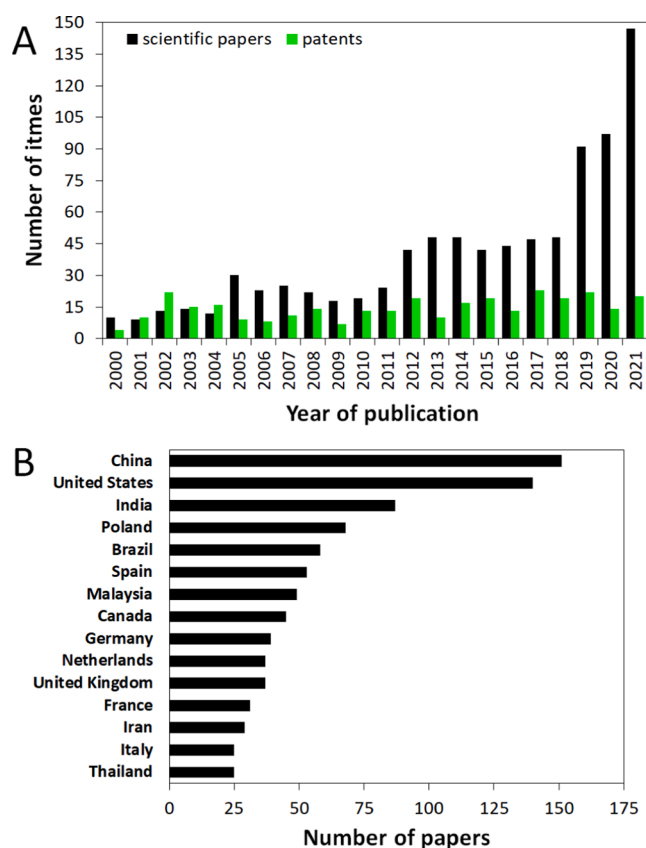


Fig. 1. (A) The recent research carried out on rubber recycling as of scientific papers and patents; (B) countries contribution to the development of rubber recycling (data according to Scopus available on 28/1/2022; keywords: “rubber recycling”, “rubber reclaiming”, “rubber devulcanization”).

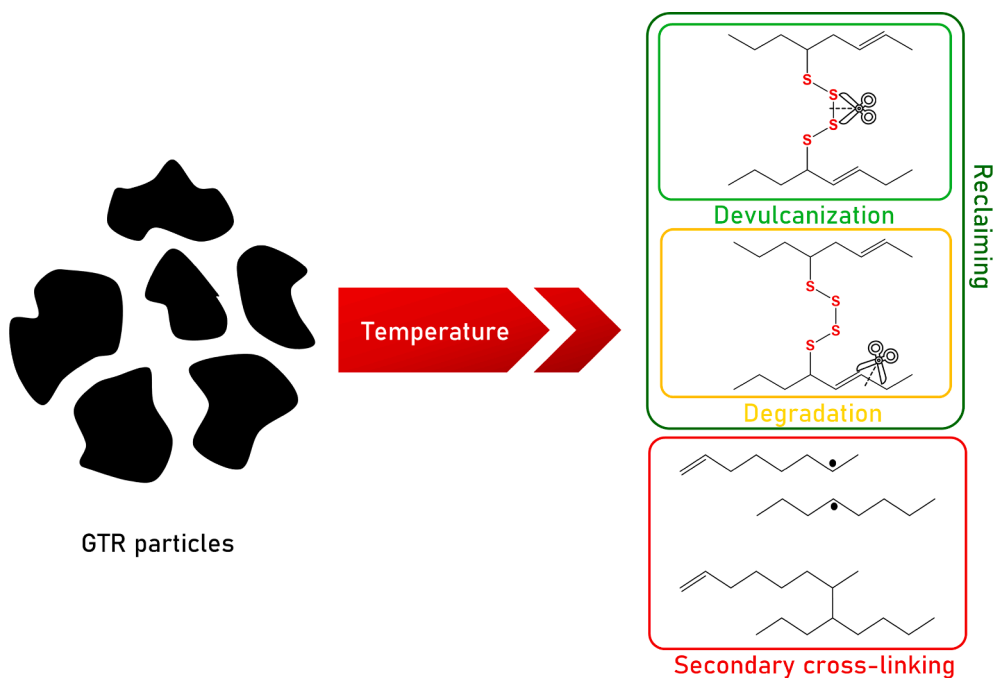


Fig. 2. Possible reactions during thermal treatment of GTR.

considered during planning of experiments in this field.

Theoretically, it is possible to breakdown the cross-linking bonds without main chain degradation, because the energy needed to break C–C bond is slightly higher compared to C–S and S–S bonds, i.e. 348, 273 and < 227 kJ/mol, respectively (Karger-Kocsis et al., 2012; Ramarad et al., 2015).

However, in practice rubber products contain higher number of the C–C bonds present in main chain of rubber, than S–S cross-link bonds. Therefore, probability of main chain degradation is much higher. Moreover, most of rubber goods contain various rubbers (or their blends) and fillers (e.g. carbon black, silica), which also restricts selective scission of cross-linking bonds uniformly in material.

Reactive sintering and vulcanization of reclaimed rubber mixed with curing system may affect the properties of the product, critically depending on the rubber particle size, purity (complete removal of steel, textile, etc. from tire), composition, devulcanization method and process conditions (Karger-Kocsis et al., 2012). For example, the tensile strength of vulcanized reclaimed rubber in the patents is usually claimed to be about 8 MPa (B. Wang et al., 2014; Wang et al., 2016a; Wang et al., 2012a; Wang et al., 2016b; Wu & Xue, 2014a; Xue, 2016; Yin et al., 2015), but in reality it hardly exceeded 5 MPa. Decreasing the size of the GTR particles, as well as adding virgin rubber or various auxiliary agents are among the most recently used strategies for improving the mechanical properties of reclaimed rubber products (Wang et al., 2016a). In many papers, devulcanization agents, which are generally organic disulfides and mercaptans are used to reclaim rubber. Based on these chemicals, many processes have been developed and subsequently patented (Bockstal et al., 2019; Wu & Xue, 2014b; Yazdani et al., 2013). This approach allows improvement of reclaimed rubber processing and/or performance properties. However, also environmental aspects should be considered, because rubber reclaiming process is required to be low-pollutant and the used components should be non-toxic.

One of the most important factors affecting the waste tires recycling efficiency is the quality of GTR. Material composition varies by the intended use of tire (truck, passenger, or off-road car) and the climate region, although ingredient used for tires production remain relatively the same. The composition of the GTR is estimated to 58–60 wt% of a mix of natural rubber (NR)/isoprene rubber (IR) and synthetic rubbers, such as butadiene rubber (BR), and styrene-butadiene rubber (SBR),

27–28 wt% of carbon black and silica, 3–4 wt% of vulcanization agents and 8–11 wt% of other additives like antioxidants, antiozonants, or softeners (Bockstal et al., 2019).

Nadal Gisbert et al. (Nadal Gisbert et al., 2007) showed that GTR composition as average can be divided into: volatile compounds – 7.0 ± 0.2 wt%, rubbers (NR/IR, BR, SBR) – 56.3 ± 2.1 wt% and carbon black + ash – 36.7 ± 2.2 wt%, respectively.

Recently, Seghar and Lacroix (Seghar and Lacroix, 2021) demonstrated how the waste tires composition might affecting the quality of reclaimed GTR. Tensile strength and elongation at break of reclaimed rubber were: i) 5–8 MPa and < 200% for GTR from passenger cars tires (GTR_{car}); ii) 8–12 MPa and 200–300% for GTR from truck tires (GTR_{truck}) and iii) 14–15 MPa and 400% for GTR from truck tread (GTR_{tread}). This trend is strongly related to GTR composition (e.g. NR/synthetic rubber ratio, carbon black content, ash content, etc.) and its purity (e.g. by textile fibers).

Natural rubber (NR) and synthetic rubbers (SBR, BR) are characterized by different thermal stability and therefore different devulcanization kinetics. For example, GTR_{tread} is prepared by retreading process of truck tires, which resulted in the clean and homogeneous GTR composed mostly from NR and BR. On the other hand, basic rubbers for GTR_{car} are NR and SBR, while SBR is very difficult to reclaiming due to tendency for secondary cross-linking at higher temperature (Dierkes et al., 2019). Moreover, recipes and ingredients used by different tire manufacturers affecting the quality of GTR, especially in case of whole passenger car tires and truck tires.

Therefore, suitable GTR characterization, not limited only to simple sieve analysis, is very important for further sustainable development of waste tire recycling technologies (Formela, 2021). Research without this approach might results in the incorrect or overestimated findings and conclusions. In this field, thermogravimetric analysis based on the ASTM D6370 allows quantitative determination of: organics (oil, polymer), carbon black + ash, and seems to be the best method for GTR composition assessment. On the other hand, Mooney viscosity and tensile parameters (tensile strength, elongation at break) determined according to ISO/ASTM standards provide useful information about the processing and performance properties of reclaimed GTR. This approach allows easy comparison of standardized tests results obtained by independent research groups, which was presented in next subchapters.

3. State-of-the-art: Patented rubber devulcanization methods

Generally, works on rubber devulcanization can be classified in terms of papers and patents. In many review papers, rubber devulcanization methods are classified in classic way, which is in terms of methodologies depending on the kind of energy used for reclaiming. Overall, thermal energy (conventional heat, microwave radiation), mechanical energy (shear forces), and chemical energy (chemical substances) are the most commonly applied for rubber treatment (Asaro et al., 2018; Phiri et al., 2020). Some other approaches such as ultrasonic (Feng et al., 2004; Mangili et al., 2015; Sun & Isayev, 2008) or biological (Allan et al., 2021; Kaewpetch et al., 2019; Tatangelo et al., 2016) devulcanization are also considered. However, present technologies largely make use of the combinations of these methods, e.g. thermo-chemical (Radheshkumar & Karger-Kocsis, 2002; Yehia et al., 2004), thermo-mechanical (Formela et al. 2015; Seghar et al., 2019; Tao et al., 2013; Wiśniewska et al., 2022) and mechano-chemical (Formela et al., 2016; Hassan et al., 2013; Jana & Das, 2005; Jana, Mahaling, et al., 2005) devulcanization.

Rubber devulcanization methods developed in patents, are not classified based on energy source used, but almost limited to the description of the equipment used and the recipe. Therefore, in the present patent-based analysis, the rubber devulcanization methods are divided into: i) dynamic desulfurization, ii) reactive extrusion, iii) microwave treatment, and iv) others.

3.1. Dynamic desulfurization

At present, most patents describing the production of reclaimed rubber adopt a thermo-chemical method of dynamic desulfurization with the use of a special tank (Liang, 2017; Guan et al., 2016; Wang et al., 2014; Wu, 2012; Wu & Xue, 2014b; Yin et al., 2015). This method is commonly used in industry due to the significantly higher mechanical properties of the obtained products compared to the reclaimed rubbers prepared by other methods. It is carried out at high temperature and high pressure in the presence of water. Auxiliary agents such as activators, softeners, or others are substances that must be added during devulcanization and their selection directly affects the quality of the

obtained material. Although processing is easy to handle, additives used in this process might be highly odorous and polluting. Moreover, the main limitations of waste rubber dynamic desulfurization are related to water and energy consumption, and heavy pollution emission (Chang et al., 2021; Wu & Xue, 2014b). As far as environmental protection requirements become more and more restricted, the dynamic desulfurization should gradually be replaced by greener methods (Sheng et al., 2019).

In the recent years, many attempts have been made to develop a more ecological desulfurization process by replacing toxic compounds with additives of natural origin and recent trends in this field are summarized in Table 1.

Most commonly used additive in rubber desulfurization was found to be rosin (Liang, 2017; Wang et al., 2014; Wu, 2012; Wu & Xue, 2014b; Yin et al., 2015). It is a natural resin, a residue after turpentine distillation from the resin of coniferous trees (mainly pine), which can act as a binder, softening or reclaiming agent during rubber devulcanization. Other environmentally friendly substances that have been often chosen by inventors are tall oil and pine tar (Wang et al., 2014; Wu, 2012; Wu & Xue, 2014b; Yin et al., 2015). However, it should be noticed that the resin acids present in these components are very corrosive at the high temperatures (150–300 °C) which requires the use of special equipment made of corrosion-resistant alloys (Formela and Haponiuk, 2012).

Regarding properties, tensile strength and elongation at break of reclaimed rubber vary in the range of: 10–23.2 MPa (median: 16.6 MPa) and 335–550% (median: 443%), respectively, depending on formulation. Although this method is questionable environmentally, it is worth mentioning that mechanical properties of the products are very high, bearing in mind the use of recycled rubber. This unexpected properties might result from GTR composition or source rather than devulcanization method. It can be suspected that high quality of reclaimed rubber could have been achieved by selecting some parts of tire rich in natural rubber (e.g. tread) or using post-production tires residues.

On the other hand, it can be concluded from detailed analysis of the related patents that a relatively common problem with dynamic desulfurization is the low stability of Mooney viscosity of the reclaimed rubber prepared by this method. During the storage period, the Mooney viscosity value may increase by 3 to 4 by day (Wang et al., 2014). It

Table 1
Examples of patents related to dynamic desulfurization of waste tire rubber.

Used components	Rubber treatment conditions	Mechanical properties of reclaimed rubber		References
		Tensile strength (MPa)	Elongation at break (%)	
GTR + tap water + auxiliary additives (e.g. pine oil-based tall oil, rosin, activator)	GTR and additives are added to desulfurization tank and treated for 1–2.5 h at 170–380 °C, subsequently air cooling of obtained reclaimed rubber for 6 h	10.0–14.6 (median: 12.3)	340–400 (median: 370)	(Wu, 2012)
GTR + auxiliary additives (e.g. softener pine tar or rosin, activator, stabilizer)	Process is performed in the pipeline type desulfurization tank, where GTR and additives are treated at 80–130 °C for 5–15 min and 130–230 °C for 10–40 min. Next, obtained reclaimed rubber is cooled and refined.	min. 15	min. 430	(Wang et al., 2014)
GTR + auxiliary additives (e.g. aromatic oil, rosin, activator, tall oil, pentachlorothiophenol, calcium carbonate, clay, titanate coupling agent)	GTR and additives are treated by continuous dynamic high-temperature atmospheric desulfurization to achieve a plasticized compound, which usually takes 25–35 min. Processing temperature is around 340–350 °C, and at the end of process decreased to around 60 °C. Subsequently, reclaimed rubber is cooled and refined.	13.2–18.6 (median: 15.9)	335–485 (median: 410)	(Yin et al., 2015)
GTR + auxiliary additives (e.g. rosin, activator, tall oil, pentachlorothiophenol, ferric chloride, diethylene glycol diethylether, liquid phosphite ester, linoleic acid, 4-methoxyphenethylamine, titanate coupling agent)	Preliminary mixing of GTR and additives at 30–50 °C. In next step, desulfurization of the obtained composition in the tank at 125–140 °C for 30 min (under pressure of 0.7–1.2 MPa) and at 190–220 °C for 40–70 min (under pressure of 2.5–3.2 MPa). In the final step, reclaimed rubber is cooled and refined.	14.5–23.2 (median: 18.9)	373–550 (median: 462)	(Wu & Xue, 2014b)
Summary		10–23.2 (median: 16.6)	335–550 (median: 443)	–

results in significant processing difficulties and fall in the quality of the final products. Therefore, further development of research focused on reclaimed rubber with stabilized Mooney viscosity should be considered.

3.2. Reactive extrusion

Reactive extrusion is a greener rubber devulcanization method compared to dynamic desulfurization. Thermo-mechanical and/or mechano-chemical rubber devulcanization with the use of extruders with a special configuration of the plasticizing unit, enables the generation of considerable shear forces. For the waste rubber reclaiming, a co-rotating twin-screw extruders are most often used, which provide effective plasticization and homogenization with acceptable efficiency of the process. The degree of devulcanization is largely dependent on the barrel temperature and screw speed (Formela, Cysewska & Haponiuk, 2014; Tao et al., 2013; Yazdani et al., 2011). It was found that the product performance can be also improved by using suitable screw configuration (Formela, Cysewska & Haponiuk, 2014; Yazdani et al., 2013).

The great potential of this method results from the fact that under specific conditions rubber devulcanization can be effectively carried out without using of any additives. Another advantages of extruder are appropriate heat transfer, low oxidation of GTR and easy removal/degassing of volatile organic compounds emitted during rubber devulcanization. Moreover, unlike to other methods, the rubber devulcanization via extrusion is continuous, short-time and high-efficient process. On the other hand, main disadvantages of this technology are high initial cost related to purchase of extruder and supporting equipment, and the limited length of the plasticizing unit that may result in an insufficient degree of devulcanization (Chen et al., 2018). The durability and suitable maintenance of the extruder is also a challenge because of the solid and elastic characteristic of GTR. The presence of sulfur in the rubber might present the corrosive problem for the long time operation at higher temperature.

Table 2 summarizes information about reactive extrusion conditions for GTR treatment and tensile properties of reclaimed GTR described in the selected patents.

It has been found that in many patents the common strategy for obtaining high quality rubber product is GTR treatment with addition of auxiliary agents, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and triphenylphosphine (TPP) mixture (Vorobyev & Bosnik, 2018), a substance containing the chemical group $-\text{SO}_2-\text{NH}-$ (Kubainek et al., 2008), a mixture of rosin and bitumen (Gavrilenko et al., 1999), catalyst based on powdered cement (Teixeira, 2020), a mixture of aromatic hydrocarbon disulfide and various tars or oils (L. Zhang et al., 2020), polyalkylphenol disulfide (Wang et al., 2016a), tall oil and pine tar (Zhang et al., 2012). Another interesting approach to enhance reactive extrusion of GTR is addition of thermoplastics (Y. Zhang et al., 2009). However, the final properties of the obtained materials are highly dependent on the type and content of the thermoplastics used as modifier. Inventors indicate that the tensile strength and elongation at break of the proposed materials are in the range of: 7–31 MPa (median: 19 MPa) and 82–560% (median: 321%), respectively. However, it should be mentioned that in some cases 50 %wt. of thermoplastics was used, which indicated that some of obtained materials were rather thermoplastics/GTR blends than “standard” reclaimed rubber.

Several inventors have focused on increasing the degree of devulcanization of waste rubber by multiple extrusion (Maris, 2021; Sheng et al., 2019; Zhang et al., 2012; L. Zhang et al., 2020). Sheng et al. (2019) claim that it is possible to obtain reclaimed rubber with satisfactory mechanical properties (tensile strength above 9 MPa) in a simple way without adding any auxiliary agent. Moreover, the proposed technology can be to high extent automatic. It is estimated that the production line can achieve the efficiency even 16,000 tons per year.

Patents proposed by Chen et al. (2018) and Y. Zhang et al. (2014)

present an unconventional method of devulcanization by extrusion in the presence of carbon dioxide or alcohol under critical pressure, respectively. Y. Zhang et al. (2014) conclude that such a method improves the selectivity to break cross-links and; thus, the efficiency of devulcanization.

In recent years, low-temperature extrusion (Gavrilenko et al., 1999; Kubainek et al., 2008; Vorobyev, & Bosnik, 2018) is attracting growing attention due to the decrease in energy consumption and the significant reduction in toxic gas emissions. This rubber reclaiming method is more environmentally-friendly and should develop in the future.

3.3. Microwave treatment

Among patents, another method used in the production of reclaimed rubber is microwave treatment. This method is characterized by the possibility of precisely controlling the amount of energy delivered to the waste rubber (microwave irradiation) by selecting the appropriate processing parameters (e.g., magnetron power, treatment time). Accordingly, high selectivity of the sulfur bonds scission versus main chain degradation can be achieved. This approach allows for highly efficient devulcanization in a very short time (a few minutes on average) (Formela et al., 2019). It is claimed that compared to other methods, microwave devulcanization is at least five times more efficient (Xue, 2016). The process itself is environmentally-friendly (solvent-free and energy efficient), however emission of the volatile degradation products into the atmosphere is a serious concern (Formela et al., 2019).

Selected examples of patents related to microwave devulcanization are presented in Table 3. As can be noticed, using microwave irradiation is not so commonly patented method of reclaimed rubber production compared to the previously-mentioned methods. Microwave irradiation and magnetron power are crucial parameters affecting mechanical properties of the reclaimed rubber. It can be concluded that carrying the devulcanization process with a microwave irradiation power of 800 W for 100 s may bring promising results (tensile strength above 23.7 MPa and elongation at break above 450%).

However, microwave treatment of waste rubber efficiency depends from rubber composition, especially carbon black content. Sousa and Scuracchio (2015) studied the role of carbon black on microwave devulcanization of NR vulcanizates. Waste rubber was modified in microwave oven adopted with motorized stirring system set at 40 rpm. The treatment time was 5 min, while magnetron power was 700 W. It was found that temperature of cross-linked rubber after microwave (MW) treatment and sol fraction in reclaimed rubber increasing proportionally to carbon black content. As can be noticed, MW treatment of NR with 60 phr of carbon black can reach temperature above 300 °C and sol fraction ~ 55%, while for sample with 20 phr the values of these parameters were only 138 °C and ~ 22%. Moreover, in some works also ignition of rubber after short-time (up to 5 min) microwave treatment is also described (Pistor et al., 2011).

This observation confirms importance of waste rubber characteristics before use, otherwise unexpected results related to MW treatment of ground rubber can be interpreted (Landini et al., 2007; Ateeq Al-Shamma'a, 2017), which should be verified and explained.

3.4. Other methods of rubber devulcanization

Despite the fact that rubber devulcanization based on above-mentioned methods is to some extent well-implemented, the research in this field still developing. Therefore, some other attempts have been made mainly by using different processes/machines to increase the efficiency of rubber devulcanization from both quality and quantity viewpoints.

Based on patents, which are characterized by an individual approach to devulcanize rubber, it is worth mentioning that apparatus already used in rubber industry can be successfully adopted rubber devulcanization. For example, Chang et al. (Chang et al., 2021; Wang et al.,

Table 2
Examples of patents related to reactive extrusion of waste tire rubber.

Used components	Rubber treatment conditions	Mechanical properties of reclaimed rubber		References
		Tensile strength (MPa)	Elongation at break (%)	
GTR + devulcanizing agents (e.g. DBU, TPP and product of petroleum distillation).	GTR and devulcanizing agents are blended in the Ross mixer at speed 30 rpm and for 20 min, next the extrusion at 45–65 °C of prepared composition is performed.	12.4–13.6 (median: 13.0) (4.8 MPa for reclaimed GTR without the devulcanizing agents)	350–390 (median: 370) (225% for reclaimed GTR without the devulcanizing agents)	(Vorobyev, & Bosnik, 2018)
GTR + thermoplastic polymer (e.g. PE, PP, LLDPE, EVA, POE, EPDM, SEBS, uncured rubbers)+ stabilizing agent (organic phenol and metal stearate)	Devulcanization is performed using a co-rotating twin screw extruder at 150–320 °C and a screw speed of 300–1600 rpm.	8.4–31.0 (median: 19.7)	82–434 (median: 258)	(Y. Zhang et al., 2009)
GTR + softener (e.g. coal tar, aromatic hydrocarbon oil, pine tar, tall oil, dipentene, paraffin oil, oleic acid, cottonseed oil, rosin) + devulcanizing agent (e.g. aromatic hydrocarbon disulfide, multi alkyl phenol sulfide, phenylmercaptan, amine compounds)	Pre-mixing GTR and softener in a mixer for 5 to 25 min at 60–120 °C, and then feeding the mixture into a twin screw extruder, where the residence time is 1–6 min at 100–340 °C and next cooling material to 40–80 °C. In next step, partially reclaimed rubber and additives are added to multi screw extruder, mixed at 20–110 °C for 1–6 min and cooled to 25–60 °C. In last step, reclaimed rubber is fed to a third multi screw extruder at –5–50 °C and refined for 1–10 min under shear condition	15.0–16.3 (median: 15.7)	480–535 (median: 508)	(L. Zhang et al., 2020)
GTR + auxiliary additives (e.g. calcium carbide, silica, resin and oil and catalysts)	Premix of GTR and auxiliary additives is added into into a closed loop reactor extruder. The process is carried out at a temperature of 120–500 °C and under the pressure of 80–100 bar. Reclaimed rubber is cooled by water to 20–30 °C.	8–18 (median: 13)	300–350 (median: 325)	(Teixeira, 2020)
GTR + rosin + bitumen + activator (e.g. thiazoles, polysulfides)	Pre-mixing of GTR and additives at a room temperature and then devulcanization in a cam extruder at 70–100 °C. Subsequently, material is cooled to 30–60 °C, homogenized and refined.	7.0–9.2 (median: 8.1)	187–325 (median: 256)	(Gavrilenko et al., 1999)
GTR + polyalkylphenol disulfide + stearic acid	GTR treatment is performed using one of the following devices: twin-screw extruder or rotary magnetic drive reactor. During extrusion the screw rotation speed is in the range of: 75–100 rpm and temperature of 260–300 °C. In rotary reactor, the rotor speed is 40–350 rpm, the desulfurization time is controlled at 45–60 min, and the temperature is 300–320 °C. Obtained reclaimed rubber is refined for 10 min.	18–26 (median: 22)	400–560 (median: 480)	(Wang et al., 2016a)
GTR (without additives)	GTR extrusion using a single-screw extruder at a screw speed of 90–125 rpm. Subsequently, cooling the material to 50–60 °C and extrusion using a twin-screw extruder at a screw speed of 55–70 rpm	9.1–9.7 (median: 9.4)	286–308 (median: 297)	(Sheng et al., 2019)
GTR + supercritical CO ₂	GTR extrusion using the twin-screw extruder at a screw rotation speed of 140 rpm. During extrusion supercritical CO ₂ (T: min. 32 °C, p: min. 8 MPa) is injected directly to extruder barrel.	min. 10.4	min. 312	(Chen et al., 2018)
GTR + tall oil + pine tar	Pre-mixing of GTR and additives at 90 °C using a high-speed mixer with a speed of 1000 rpm. In next step, composition is transfer to a co-rotating twin-screw extruder at the screw speed of 250 rpm at 10–100 °C and single-screw extruder at the screw speed of 60 rpm at 10–100 °C	15.2–17.5 (median: 16.4)	480–540 (median: 510)	(Zhang et al., 2012)
GTR + linear polymer (e.g. PE, PP, POE, uncured rubbers)+ desulfurization aid (e.g. di- and polysulfides used with an subcritical alcohol or an subcritical alcohol/water mixture)	GTR, linear polymer and desulfurization aid (subcritical alcohol injected directly to barrel) are added to a co-rotating twin-screw extruder at temperature of 150–300 °C; the pressure of 0.48–8.6 MPa and the screw speed of 100–1000 rpm. Reclaimed rubber is cooled by water and dried.	Tensile properties of reclaimed rubber/SBR in ratio 30/70% reached 99.6% and 209% of the reference SBR compound with tensile strength and elongation at break, 24.0 MPa and 356%, respectively		(Zhang et al., 2014)
GTR + devulcanizing agent (substance containing the chemical group -SO ₂ -NH-)	GTR + devulcanizing agent mixing at temperatures of 40–100 °C for 10–60 min using a kneader, calender or an extruder.	Prepared reclaimed rubber has properties (tensile strength, flexibility, hardness and abrasion) similar to products prepared from standard vulcanization mixture.		(Kubainek et al., 2008)
Summary		7–31 (median: 19)	82–560 (median: 321)	–

2012b) showed that reclaimed rubber with satisfactory quality can be produced using an internal mixer alone.

Wang et al. (2012b) mixed GTR with softeners, coupling and

reclaiming agents and treated all components in internal mixer at 170°C for 3.5 h. Authors claim that tensile strength and elongation at break of the reclaimed rubber can reach even 19.5 MPa and 500%, respectively.

Table 3
Examples of patents related to microwave treatment of waste tire rubber.

Used components	Rubber treatment conditions	Mechanical properties of reclaimed rubber		References
		Tensile strength (MPa)	Elongation at break (%)	
GTR + softener (naphthenic oil or pine tar) + activator + coupling agent	Pre-mixing of GTR and additives at 40 °C using open mill for 10 min. In next step, microwave treatment of obtained composition for 100–150 s, magnetron power 800–1200 W. In the final step, cooling and refining of reclaimed rubber.	23.7–25.6 (median: 24.7)	450–480 (median: 465)	(Wang et al., 2016b)
GTR + stearic acid + palm oil + rosin + MDEA + calcium bicarbonate + natural resources reclaiming agent (lemon, orange or grapefruit peel) + activator	Pre-mixing of GTR and calcium bicarbonate supported by ultrasonic treatment (frequency of 200–300 Hz) for 1–3 min. Subsequently, obtained composition is blended in mixer at 80–100 °C for 5–10 min, speed of rotor: 500–1000 rpm. In next step, microwave treatment of GTR and additives for 3–10 min is performed. At the end of procedure, reclaimed rubber is refined.	10.9–12.1 (median: 11.5)	347–364 (median: 356)	(Zhou et al., 2021)
GTR + rosin + dipentene	Pre-mixing of all the components and next microwave treatment of modified rubber powder for 100 s with magnetron power of 800 W. Prepared reclaimed GTR is cooled to below 45 °C and refined at 35–50 °C for 20 min.	min. 18	min. 400	(Wang et al., 2012a)
Summary		10.9–25.6 (median:18.3)	347–480 (median:414)	–

Table 4
Methods and reclaimed rubbers described in the literature.

GTR particle size	Rubber treatment conditions	Mechanical properties of reclaimed rubber		References
		Tensile strength (MPa)	Elongation at break (%)	
GTR – 0.595 mm	GTR extrusion using a co-rotating twin-screw extruder at 160–240°C and screw speed of 80–160 rpm	5.6–12.9 (median: 9.2)	337–360 (median: 349)	(Tao et al., 2013)
GTR – 1.5 mm	GTR extrusion using a co-rotating twin-screw extruder at 180°C and screw speed of 200–600 rpm	5.3–7.2 (median: 6.3)	144–177 (median: 161)	(Formela et al., 2013)
GTR – 0.4 mm	GTR extrusion by a counter-rotating twin-screw extruder at 170°C and screw speed of 30 rpm	7.8	160	(Balasubramanian, 2009)
GTR – 0.6 mm	GTR/DCP premix with 0–15 phr EVA extrusion using a co-rotating twin-screw extruder at 130°C and screw speed of 150 rpm	2.6–9.3 (median: 6.0)	78–225 (median: 152)	(Wiśniewska et al., 2021)
GTR – 0.6 mm	GTR/DCP premix with 2.5–15 phr elastomers extrusion using a co-rotating at 60°C and screw speed of 150 rpm	5.2–8.1 (median: 6.7)	113–136 (median: 125)	(Wiśniewska et al., 2022)
GTR – 0.8 mm	GTR with addition of 0–20 phr bitumen was treated using two-roll mills at ambient temperature for 30 min	3.3–5.5 (median: 4.4)	162–194 (median: 178)	(Formela et al., 2016)
GTR – 2 mm	GTR extrusion at 120°C combined with ultrasounds treatment	1.5–10.5 (median: 6.0)	130–250 (median: 190)	(Tukachinsky et al., 1996)
GTR – 0.319 mm	Pre-mixing of GTR with 30 phr aromatic oil an 0–5 phr DPDS in glass beaker and heating at 80°C for 12 h. GTR microwave treatment at 240°C with a magnetron power of 900 W for 3 min	10–19 (median:14.5)	226–540 (median: 383)	(Molanorouzi & Mohaved, 2016)
GTR – 0.3 mm	GTR treatment in pan-mill reactor for 25 cycles at a rotation speed of 30 rpm	10.9	290	(X. Zhang et al., 2009a)
GTR – 0.841 mm	GTR extrusion at 100–180°C and screw speed of 300–600 rpm in the presence of supercritical CO ₂	9.4–11.4 (median: 10.4)	209–225 (median: 217)	(Meysami et al., 2017)
GTR – 0.2–0.4 mm	GTR extrusion using a co-rotating twin-screw extruder at 140–240°C at a screw speed of 60–180 rpm	No information about tensile parameters of reclaimed GTR. NR/reclaimed GTR composites: TS _b ~ 15 MPa* and E _b ~ 340%*		(Simon & Bárányi, 2021)
Summary		1.5–19 (median: 10.3)	78–540 (median: 309)	–

* - data estimated from the graphs.

On the other hand, although the mechanical properties reported by Chang et al. (2021) are lower than in the previously mentioned case (tensile strength of 7.8–9.5 MPa and elongation at break of 356–391%), the authors declare that the formulation developed by them is completely environmentally friendly. The reclaiming agent dedicated to the process is odorless, non-toxic and low-polluting, but at the same time it fulfils its function well. J. Zhang et al. (2020) proposed a method to produce low Mooney viscosity reclaimed rubber without any additives, using an internal mixer and kneader. Inventors claim that the obtained reclaimed rubber can be successfully applied as an additive to asphalt in the amount range of 5–50% of weight of the asphalt to improve its quality and extends its service life.

Thiruganasambandam (2015) developed economically viable rubber devulcanization method, carried out by refiner at ambient temperature

and using low cost materials such as maltenes or bitumen. Tensile strength of reclaimed GTR was above 8.1 MPa, while elongation at break ranged from 240 to 260%.

Michel (2013) disclosed an idea to devulcanize waste rubber by using alternating electric field. Similar to microwave devulcanization, this method provides appropriate energy to rubber particles by selecting specific parameters. Another unconventional technology, rubber devulcanization in the presence of 2-butanol and carbon dioxide, was described by Benko et al. (2004). According to the inventors, the obtained reclaimed rubber can be applied with virgin rubbers in quantities of up to 40 phr in the same types of rubber articles, as the original rubber (for example tires, hoses, or belts). The inventors also claim that there is no deterioration in processing and mechanical properties.

4. Reclaimed rubbers properties: patents, literature vs. Commercial products

Generally, patents cover the innovative solutions that can be implemented at industrial scale. Therefore, for a better, more critical overview, in this subchapter, finding from patent based analysis in field of rubber devulcanization were compared with scientific papers reported so far and also with technical information provided for commercially available reclaimed rubbers.

The most useful information in this regard was collected and presented in Tables 4 and 5, which summarized achievements in manufacturing of reclaimed rubbers described in the literature (Table 4) and at industrial scale (Table 5), respectively.

As can be seen in Tables 4 and 5, the most widespread rubber reclaiming method among scientific papers is thermo-mechanical devulcanization via extruder, while both thermo-mechanical and thermo-chemical devulcanization are dominant among industrial

methods. The most commonly methods described in the literature based on reactive extrusion of GTR, while it is very difficult to find published research articles about dynamic desulfurization. For reclaimed rubbers described in the literature tensile strength and elongation at break are in the range: 1.5–19 MPa (median: 10.3 MPa) and 78–540% (median: 309%), which are values lower comparing to described in the patents.

The examples of companies working in the field of rubber reclaiming or devulcanization are summarized in Table 5. One of the oldest companies working in this field is Rubber Resources B.V. from the Netherlands, which produce the reclaimed rubber from 1956. As can be observed, many companies are located in India, e.g. GRP Reclaim Rubber, Star Polymers Inc. or Rolex Reclaim Pvt. Ltd., however, the quality of produced reclaimed rubbers are rather very similar.

It should be pointed out, that more than 50% of companies presented in Table 5, started production reclaimed rubber within less than 15 years ago. This is related to implementation of green devulcanization technologies and opening of start-ups in this field, especially in China,

Table 5
Technology and tensile properties of commercially available reclaimed rubbers.

Country and year of establishment	Devulcanization technology	Mechanical properties of reclaimed rubber		Website
		Tensile strength (MPa)	Elongation at break (%)	
United Kingdom, 1824 (from 1984 starts activity related to rubber recycling)	Thermo-chemical process in presence of plasticizers performed in autoclave. Next, the product is refined by using extruder sieving and/or a refining mill.	2.5–7.4 (median: 5.0)	150–250 (median: 200)	J. Allcock & Sons Ltd. www.allcocks.co.uk (available on 04 March 2022)
Netherlands, 1956 founded by Vredestein (tire producer), from 2011 part of Elgi Rubber Company Ltd.	Mechanically devulcanized (lack of information about the process or used additives). Subsequently extrusion process of reclaimed rubber	4–7 (median: 5.5)	160–240 (median: 200)	Rubber Resources B.V. www.rubber-resources.com (available on 04 March 2022)
India, 1974	No published data. Probably thermo-chemical batch method (autoclave) is used.	3.4–3.9 (median: 3.7)	150–200 (median: 175)	GRP Reclaim Rubber www.grpweb.com (available on 04 March 2022)
India, 1985	No published data. Probably thermo-chemical treatment by using a two-roll mills.	6–10 (median: 8)	250–290 (median: 270)	Star Polymers Inc. www.starpolyrubber.com (available on 04 March 2022)
Poland, 1991	No published data. Probably thermo-chemical batch method (autoclave) is used.	~11	~420	Geyer & Hosaja www.geyer-hosaja.com.pl (available on 04 March 2022)
India, 1995	No published data. Probably thermo-chemical batch method (autoclave) is used.	3.4–7.4 (median: 5.4)	200–250 (median: 225)	Rolex Reclaim Pvt. Ltd. www.rolexreclaim.com (available on 04 March 2022)
Vietnam, 2007	No published data. Probably thermo-chemical treatment by using a two-roll mills.	8–10 (median: 9)	300–350 (median: 325)	Long Long Rubber Recycling Co., Ltd. https://longlongrubber.com (available on 04 March 2022)
Canada, 2008	Plasticizer swelling combined with thermo-kinetic mixing	No published data about properties of reclaimed rubber. The studied samples showed the application of 20% of reclaimed rubber into rubber compound dedicated on tire tread resulted in increase of Mooney viscosity by ~ 15% and decrease of tensile strength by ~ 20%		Phoenix Innovation Technologies Inc. www.phoenixregeneration.com (available on 04 March 2022)
Canada, 2009	Thermo-mechanical extrusion supported with supercritical CO ₂	6–8 (median: 7)	–	Tyromer Inc. www.tyromer.com (available on 04 March 2022)
India, 2012	No published data. Probably thermo-chemical treatment by using a two-roll mills or chemical batch method (autoclave).	min. 7.5	min. 250	Lead Reclaim & Rubber Products Ltd. http://www.leadrubber.com/ (available on 04 March 2022)
France, 2013	Extrusion supported with supercritical CO ₂ (first Tyromer's license in EU)	~11	~220	Phenix Technologies www.phenix-technologies.eu (available on 04 March 2022)
China, 2015	Thermo-mechanical extrusion (lack of information about used additives)	9.0	350	Jiangsu Zhonghong Environmental Protection Technology Co., Ltd. www.r4rubber.com (available on 04 March 2022)
Summary		2.5–11 (median: 6.8)	150–350 (median: 250)	–

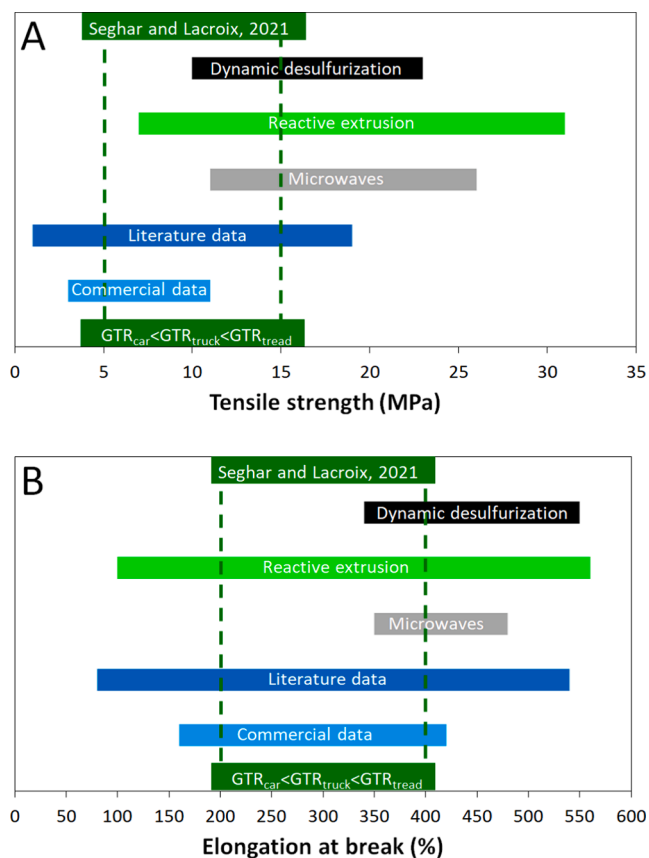


Fig. 3. Comparison of mechanical properties (A – tensile strength and B – elongation at break) determined for reclaimed GTR described in patents, literature and commercial data.

France or Canada, which seems to develop in near future also in other countries.

As can be observed in Table 5, regardless of the used methodology, mechanical properties of reclaimed rubbers declared by producers are surprisingly significantly lower compared to those presented in patents, however mostly consistent with those described in the literature. Tensile strength and elongation at break of commercially available reclaimed rubbers is in the range of: 2.5–11 MPa (median: 6.8 MPa) and 150–350% (median: 250%).

For better understanding the correlation between devulcanization technology and final performance properties of obtained reclaimed rubber, Fig. 3 shows the summary of mechanical properties ranges determined for reclaimed rubber described in the patents, literature, and commercial data.

Tensile strength and elongation at break ranges of reclaimed GTR based on waste tire source/composition ($GTR_{car} < GTR_{truck} < GTR_{tread}$) according to Seghar and Lacroix (2021) findings, were used as reference. As can be observed, regardless of used devulcanization technology (described in patents, literature or commercial data), selected reclaimed rubbers fits well to ranges defined by Seghar and Lacroix (2021). However, it is clear that mechanical properties ranges of reclaimed rubbers presented in most patents are higher than those described in the literature or for commercial products. This trend can be related to GTR composition or waste rubber source (post-production or post-consumer waste) used in patents. Other explanation is high content of fresh matrix (e.g. thermoplastics, elastomers, thermoplastic elastomers), which might improves tensile properties of reclaimed rubbers.

5. Conclusions, limitations and future trends

Waste tires, if not properly managed, poses a serious threat to the environment and human health. Therefore, sustainable development of waste tires recycling technologies is gaining more and more attention. As consequence, rubber recycling is becoming a value-added processing rather than previously used general tactic for reuse of waste rubber material. This approach can be divided to: i) using whole tires in civil engineering, ii) energy recovery, iii) pyrolysis, or iv) material recycling. In field of material recycling of rubber, devulcanization is one of the most promising approaches. This work summarized literatures, especially recently patented rubber devulcanization methods in terms of used components, treatment conditions and mechanical properties of obtained reclaimed rubbers. Moreover, a special attention was focused on the ecological aspects related to rubber devulcanization technologies.

It was found that a majority of patents use a dynamic desulfurization method (especially in China) or reactive extrusion, while rarely microwave devulcanization, which is related to expensive apparatus necessary for this method. Moreover, it was found that the tensile properties of reclaimed rubbers described in patents are usually higher than in the literature or commercial data.

In the studied patents, mechanical properties (median value of tensile strength and elongation at break) of reclaimed rubbers were: 16.6 MPa and 443% for dynamic desulfurization; 19.0 MPa and 321% for reactive extrusion and 18.3 MPa and 414% for microwave devulcanization. On the other hand, for reclaimed rubbers described in the literature the median values of tensile parameters were: 10.3 MPa and 309%, while for commercial products: 6.8 MPa and 250%, respectively. Significant difference might be related to obvious difference in GTR treatment conditions depending of used devulcanization technology, however more important factor seems to be the GTR composition (car, truck, tread) or source post-production/post-consumer.

Current research trends indicates that green devulcanization of waste tires and production of GTR-based materials dedicated for high-value end-use markets will develop in the near future, which fits to the strategies of circular economy. Therefore, suitable classification and full characterization of waste rubber prior to use is strongly recommended during further research in this field. This approach significantly improves process repeatability and performance properties of obtained rubber recycling products.

From environmental point of view, dynamic desulfurization is the most polluting method due to the presence of water, very high processing temperature and the toxicity of used components. Reactive extrusion seems to be the most pro-ecological rubber devulcanization method provided that it is carried out at moderately high temperature and without using hazardous additives. Moreover, reactive extrusion of GTR seems to be the most suitable for industrial scale application due to its efficiency and versatility. Performance properties of reclaimed rubber prepared via reactive extrusion can be easily tailored or modified by various parameters, e.g. processing temperature, screw speed, plastifying unit configuration or suitable additives.

In conclusion, future investigations in this field should concentrate on: i) optimization of the devulcanization condition (e.g. lowering temperature, reduce the energy or water consumption, etc.) and elimination/reduction of toxic-gas emission level during rubber decomposition; ii) application of renewable and non-toxic additives; iii) combination of devulcanization with suitable functionalization or modification of GTR (method related to rubber upcycling strategies); iv) devulcanization technologies upscaling (implementation of laboratory results to large-scale production).

6. Disclosure statement

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

Declaration of Competing Interest

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