The author of the Ph.D. dissertation: Łukasz Zedler
Scientific discipline: Chemical sciences

DOCTORAL DISSERTATION

Title of Ph.D. dissertation: Comprehensive analysis of low-temperature methods for reclaiming of ground tire rubber

Title of Ph.D. dissertation (in Polish): Kompleksowa analiza niskotemperaturowych metod regeneracji rozdrobnionych opon samochodowych

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Gdańsk, December 2021

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The author of the Ph.D. dissertation: **Łukasz Zedler**

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DESCRIPTION OF DOCTORAL DISSERTATION

The Author of the Ph.D. dissertation: Łukasz Zedler
Title of PhD dissertation: <title of PhD dissertation>

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Keywords of PhD dissertation in Polish: odpadowa guma samochodowa, regeneracja, recykling, relacja struktura-właściwości, kompatybilizacja, modyfikacja

Keywords of PhD dissertation in English: ground tire rubber, reclaiming, recycling, structure-property relationship, compatibilization, modification

Summary of PhD dissertation in Polish: Zarządzanie zużytymi oponami stało się ważnym tematem od ostatnich dziesięcioleci. Brak efektywnej metody zagospodarowania wspomnianymi materiałami prowadzi do powstawania nielegalnych składowisk. Te problematyczne odpady można podzielić na dwie główne kategorie w zależności od stanu fizycznego odpadów: (i) częściowo zużyte opony; (ii) opony wycofane z eksploatacji. Podczas gdy pierwsza grupa może być ponownie użyta lub bieżnikowana, druga grupa wymaga specjalnych działań w celu zagospodarowania zużytych opon. Obecnie najbardziej intensywnie badaną metodą jest regeneracja miału gumowego (GTR). Według doniesień literaturowych dokonano już wielu podejść do tematu, wśród których stosowano metody mechaniczne, termiczne, chemiczne i ich kombinacje. Jednakże, znaczna większość tych publikacji nie weryfikuje wpływu przetwórstwa, jak i eksploatacji materiału na środowisko. W przedstawianej rozprawie doktorskiej przedstawiono analizę dostępnej literatury w temacie zarządzania odpadami gumowymi, jak również badania własne, których celem było (i) opracowanie technologii przetwarzania GTR, pozwalającej na uzyskanie produktu o zadowalających właściwościach użytkowych, (ii) opracowanie metodyki badań nad produktami na bazie GTR z uwzględnieniem luk w obecnym stanie wiedzy, (iii) ocena wpływu przetwarzania GTR na środowisko, (iv) ocena potencjału recyklingowego produktów na bazie GTR.

Summary of Ph.D. dissertation in English: Management of waste tires has become an important topic for decades. The lack of an effective method to manage the materials as mentioned above leads to illegal landfills. This problematic waste can be divided into two main categories depending on the physical condition of the waste: (i) partially used tires; (ii) end-of-life tires. While the first group can be reused or retreaded, the second group requires special measures to manage it. At present, the most intensively researched method is the reclaiming of ground tire rubber (GTR). According to literature reports, many approaches have already been made to the subject, among which mechanical, thermal, chemical methods and their combinations have been used. However, the vast majority of these publications do not verify the environmental impact of processing and exploitation of the material. The following dissertation presents an analysis of the available literature on the topic of rubber waste management, as well as my research aimed at (i) developing a GTR processing technology to obtain a product with satisfactory functional properties, (ii) developing a research methodology for GTR-based products considering the gaps in the current state of knowledge, (iii) assessing the environmental impact of GTR processing, and (iv) evaluating the recycling potential of GTR-based products.

*) delete where appropriate.**) applies to doctoral dissertations written in other languages than Polish or English.

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1. Introduction.

Increasing interaction between countries and interdependence (globalization processes) are the critical causes of growing consumerism [1], which reflects the unjustified acquisition of goods that are not real needs resulting from social, individual, or ecological aspects [2]. As one can imagine, this trend has a critical impact on environmental protection, affecting the increasing amount of accumulated waste and influencing the water and carbon footprint (an increase in demand equal to an increase in production). According to The World Bank, the main waste groups are food and green waste, glass, metals, waste paper, wood, plastic, rubber, and leather [3]. Although the largest one is the former (as much as 44% of the world's waste), the equally demanding challenge is polymer waste (plastic and rubber) that has been on the world's agenda for many years. According to Geyer et al. [4], who has made a detailed analysis of plastic production, use, and waste management, approx. 8300 million metric tons of plastic have been synthesized and released into the world to the publication’s date.

What is more, by 2015, approx. 6300 million metric tons of plastic waste have been generated. The worst information is that only 9 % had been recycled and 12 % was incinerated, while 79% was legally/illegally stockpiled in landfills or, worse, in the natural environment. Scholars have stated that by 2050 over 12 000 million metric tons of waste plastic will be kept this way (assuming that the production trend and current management methods will remain at this level).

So far, five main streams of plastic waste management have been presented and used in practice, which are: (i) landfilling, (ii) incineration and energy recovery, (iii) reduction, (iv) re-use, and finally (v) recycling. Depending on the commercial value of the waste product and the efficiency of the entire recycling process (including logistics, treatment, and recovery), an appropriate disposal method is selected. An equally important aspect is the degree of contamination of waste, which also influences the choice of method.

1.1. Landfilling

Landfilling of polymer waste is the primary way of managing the problem. It is the least desirable because of the high probability of causing soil and groundwater pollution, even on a well-managed landfill site [5]. Moreover, landfilling significantly reduces the likelihood of reuse or attempted recycling of these materials, leaving the waste stream in a linear process instead of being built into a closed circuit. According to The Environmental Implementation Review 2019 (POLAND), written by the staff of the Directorate-General For Environment of the European Commission, in Poland, landfilling is still the predominant way to manage waste (42% in 2016), while the EU average is much lower (24%). The report highlights the need to accelerate the transition to a circular economy in all economic sectors, significantly impacting Poland's waste management development.

1.2. Incineration

Another commonly used solution is to incinerate plastics. According to the analysis carried out by Greyer et al., this approach has gained importance over the years (1990-8.0%, 2000-15.0%, and 2015-25.5%), and with this trend, it will reach 50 % by 2050. Although there is an apparent increase in interest in this method, it also has significant disadvantages in releasing hazardous substances into the atmosphere. The best examples are polymers containing halogens, (poly(vinyl chloride) (PVC), halogenated butyl rubber, and chlorinated or brominated polystyrene), which can release furans, dioxins, or polychlorinated biphenyls [6]. If the incineration plant is adequately stocked and designed, incineration and energy recovery is an attractive solution to reduce constantly growing polymer waste; however, primarily because of this perceived risk of contamination, plastic combustion is less widespread than landfilling. There is also one crucial aspect to be addressed in terms of using this approach, which is energy recovery. This subject will be mentioned in the recycling section.

1.3. Reduction

It is also essential to minimize the number of plastics during the production process, for example, by reducing the volume of packaging, which would result in less waste. It would seem that the reduction of used raw materials is beneficial not only for the environment but also for the economic aspects of a company. However, there is a range of factors that contradict such simple thinking. For example, generating more space on a single package to place an advertisement (economic profit) or the existence of already finished technological halls for which the reduction of raw material may require significant investment. Moreover, the aesthetic aspect is also crucial from the point of view of the product recipient. In this case, without proper public awareness and reaching the basic cells of society, there won't be an effective downgauging.

1.4. Reuse

Regarding the reuse of plastics, the biggest hurdle is the issue of proper collection and logistics. In the case of local companies, such a project is feasible. Still, if the product is widely known and used on a regional/country/continent/world scale, collecting and transporting it to centralized product-filling factories becomes problematic. Moreover, the multitude of products from the same family (e.g., carbonated drinks) with packaging designed for their marketing makes it impossible to separate them properly and send them to the right producer. However, even if such a collection were possible, it is hard to imagine reusing a plastic bottle that another person has already used without proper treatment. Another issue is the use of packaging, e.g., domestic cleaning products. There are solutions for refilling waste packaging. Unilever Group, a global player in the fast-moving consumer goods industry, is campaigning to encourage consumers to use refill points [7]. However, as mentioned earlier, such actions are effective on a local scale, even though this approach can become part of the day-to-day basics of a consumer, for example, by providing refill stations in every major supermarket.

1.5. Recycling

Another essential and well-known method of plastic waste management is recycling. However, the term recycling plastics is often a complicated and confusing subject. Therefore, it is necessary to clarify the basics of the issue first. Recycling waste plastics is the sum of processes that allow to recover the waste and process it in a way that makes it useful. The recycling product does not have to be identical or even close to the starting material [8]. According to ASTM D5033-00 [9], there are four main categories: primary, secondary, tertiary, and quaternary recycling. The first one concerns all mechanical recycling methods which allow obtaining a product with properties similar to those of the starting material, while the second one concerns all mechanical recycling methods transforming the waste material into products that have less demanding performance requirements than the original application. Tertiary recycling involves all actions which transform waste materials into chemical constituents, and finally, quaternary recycling is all about energy recovery. Another standard for guidance on the recovery and recycling of plastic waste (ISO 15270 [10]) states that recycling methods should be divided into two recovery technologies: material recycling and energy recovery, however, it states that the term material recovery refers to mechanical, chemical, feedstock, biological or organic recycling. For further discussion on plastic waste management, the author of the dissertation will use terminology consistent with ISO 15270, as it is easier to address and describe the individual components of such classification.

To carry out mechanical recycling processes in such a way that the obtained product has properties similar to the initial material, it is necessary to provide an appropriate way of collecting and separating waste. What is more, already at the reprocessing stage, the variables influencing the delay of degradation should be introduced. Obviously, this is the easiest way to process waste coming directly from production lines by the producer of a particular product, e.g., overflow or waste after mechanical processing, due to the known type of recycled material. Additionally, the possibility of reprocessing plastics of the same or similar grades (e.g., poly(ethylene terephthalate)

(PET) used for bottles) facilitates the mechanical recycling process itself. However, the largest amount of plastic waste belongs to the postconsumer group. The proper collection, selection, cleaning, and transport of such materials are necessary to effectively manage it, which has already been addressed. It is also possible to use the recovered product as a partial replacement for the raw matrix. Of course, depending on the type of material, a product with unchanged properties (primary recycling – e.g., PET fibers) or with a noticeable decrease in properties (secondary recycling – e.g., production of flooring tiles from mixed polyolefins) is obtained [11].

It is also possible to carry out chemical/feedstock recycling to transform waste polymers into monomers or other equally important components by means of depolymerization, partial oxidation, or cracking. These materials are used as feedstock for various processes or as fuels [12]. In the case of depolymerization, the result of the process and its efficiency depend primarily on the type of polymer used. In the case of condensation polymers such as polyamides or polyesters, the process reverse to their synthesis can be carried out (hydrolysis, glycolysis, alcoholysis, aminolysis, or methanolysis). As products, the following can be obtained: diacids, diols, or diamines. In the case of addition polymers such as polyolefins, depolymerization processes are complicated [13] and partial oxidation, using oxygen and steam streams, is applied to convert polyolefin wastes into a mixture of hydrocarbons and synthesis gas (CO and H_2). The composition of the obtained syngas depends on the polymers used [14]. The last shortly discussed method of chemical recycling is cracking. This process involves breaking down the polymer chains into low molecular weight compounds that can be further utilized. This process is carried out in the absence of air, thus eliminating the formation of dioxins, which is crucial in terms of environmental pollution [15, 16]. There are three basic approaches to carrying it out: thermal, catalytic, and hydrocracking. Thermal cracking, which is a result of pyrolysis, is a process of heating the polymer in an inert atmosphere resulting in the thermal scission of the bond and generation of low molecular weight hydrocarbons feedstocks (liquids – olefins, paraffins, aromatics, and naphtenes; volatile fraction and solid residue) [17]. Catalytic cracking differs from thermal cracking in terms of the conduct of the process itself and has several significant advantages that the latter lacks. First of all, it significantly reduces the process temperature by lowering the activation energy. Moreover, the use of catalysts allows for better selectivity in terms of obtaining specific process products. The main disadvantages are the lifetime and the need to regenerate the catalyst beds [18].

Hydrocracking involves a transformation of polymeric waste into fuel range hydrocarbons in a hydrogen atmosphere and at elevated temperatures. Many common polymeric may be used as a feed, like polyolefins, PET, PVC, polystyrene (PS) and mixed polymer waste [19-22]. However, this method is commonly used with heavy gas oils and residues to remove nitrogen, sulfur, or metals and transform them into lighter fractions (e.g., fuel, gas, oils) [23].

The methods listed above are only the main group of processes used to manage waste plastics. Each of them has its specificity and involves different technological solutions depending on the approach of people, scientists, and entrepreneurs. However, despite this multitude of processes, the substantial amount of financial contributions from countries around the world, and the growing self-awareness of the public, we still face many problems regarding waste management. This situation is due to the quality and price of recyclates compared to their non-waste counterparts. The use of waste plastics is also associated with increased control over the material and consumer demands related to product aesthetics. And while the recycling rates for plastics such as polyethylene (PE), polypropylene (PP), low-density polypropylene (LDPE), high-density polyethylene (HDPE), PVC, and PET are at a relatively good level, there are materials whose recycling is significantly hindered by their nature, properties as well as advanced and complex physical and chemical structures.

2. Waste tire management.

The examples mentioned above and problems of recycling mainly concern plastics that are one-component materials (with the possible presence of pigments, stabilizers, or catalysts in the structure). In the case of multicomponent polymer waste, it is much more challenging to carry out appropriate activities aimed at its effective and environmentally friendly management. Even more problematic are materials with reinforcements in their physical structure, especially those belonging to other material groups (metals, ceramics, a wide range of organic and inorganic compounds). One of the most problematic materials, posing a considerable threat to the environment and human life, yet being an advanced engineering product generated by almost every household, is a tire.

2.1. Waste tires worldwide

During further discourse regarding the global generation and management of waste tires, this product will be referred to as end-of-life tires (ELT). This term refers to a tire that can no longer serve its intended purpose due to wear and tear. The data presented is based on a thorough analysis of global ELT management presented by the World Business Council for Sustainable Development (WBCSD) published in December 2019 [24]. The study presented here excludes tires that have been retreaded, reused, and exported with used cars.

For the further purpose of evaluating the generation and recovery rate of ELT, three basic methods of recycling were adopted, and these are: material recovery, energy recovery, and backfilling (e.g., in mining sites [25] or for land rehabilitation [26]) and civil engineering (e.g., water retention basins [27]). According to WBCSD data for 13 countries (United States, China, India, Japan, Indonesia, Brazil, Thailand, South Korea, Mexico, Russia, South Africa, Argentina, and Nigeria), and parts of Europe (as reported by the European Tyre and Rubber Manufacturers' Association (ETRMA)), ELT recovery is 25.7 million metric tons per year, and when include backfilling and civil engineering the number rises to 26.1 million metric tons per year, while the overall volume of ELT generated in those countries is estimated to be 29.1 million. To delve deeper into the problem of ELT management, the analysis began with ELT generation, the legal system, main recovery methods, and responsible organizations (for each of the above-mentioned world regions), which were gathered and presented in Table 1

Table 1 Summary for each region of current ELT generation, legal system, main recovery methods, and responsible organizations (data based on WBCSD report).

Country	ELT Generated	ELT Recovered (excluding Civil Engineering and backfilling)	ELT Recovered (including Civil Engineering and backfilling)	ELT recovery legal systems	Main ELT recovery methods	Main ELT management organization	Comments
	Metric kiloton				-	-	-
United States	3700.0	2668.0	2995.0	Federal waste tire management programs (depends on State)	39% - energy recovery 33.2 % - material recovery (granulation is the main approach)	The United States Tire Manufacturers Association (USTMA)	Data provided by USTMA so it is considered to be robust
China	14545.0	5650.0*	5650.0*	None	Material recovery (reclaiming and granulation)	The China Tyre Recycling Association (CTRA) and The China Rubber Industry Association (CRIA)	Data provided by CTRA and CRIA. , However,there are some uncertainties about ELT management
Russia	800.0	160.0	160.0	Extended Producer Responsibility (excluding steel and cement production. energy	19.3% - material recovery (crumb rubber or as pyrolysis) 0.7% - energy recovery	EcoTyresUnion	Data collected from a variety of reliable sources and interviews with EcoTyreUnion representatives

Table 1 Summary for each region of current ELT generation, legal system, main recovery methods, and responsible organizations (data based on WBCSD report).

Country	ELT Generated	ELT Recovered (excluding Civil Engineering and backfilling)	ELT Recovered (including Civil Engineering and backfilling)	ELT recovery legal systems	Main ELT recovery methods	Main ELT management organization	Comments
		Metric kiloton			-	-	-
Europe (EU, Norway, Serbia, Switzerland, and	3425.5	3035.5	3141.0	Extended Producer Responsibility/Free market/Taxes (depends on the country)	43% - material recovery (granulates and powder) 38%- cement kilns	ETRMA (at EU level)	Data provided by ETRMA so it is considered to be robust
Argentina	150.0	9.6	9.6	Free market system	Granulation for sport surfaces (only approx. 6% of ELT is being recovered)	The Ecological Coordination Society of The State Metropolitan Area (CEASME)	Data created by the analysis of publications and information from an organization granulating rubber
Brazil	587.9	585.2	585.2	Extended Producer Responsibility extended by the hazardous	Material and energy recovery (lack of exact numbers)	The Brazilian Institue of the Environment and Renewable Natural	Data provided by IBAMA, so it is considered to be robust

Table 1 Summary for each region of current ELT generation, legal system, main recovery methods, and responsible organizations (data based on WBCSD report).

Country	ELT Generated	ELT Recovered (excluding Civil Engineering and backfilling)	ELT Recovered (including Civil Engineering and backfilling)	ELT recovery legal systems	Main ELT recovery methods	Main ELT management organization	Comments
		Metric kiloton			-	-	-
India	2749.0	2694.8	2694.8	Lack of well-organized regulation (according to 2016 data)	75% - material recovery (crumb rubber production)	The Automotive Tyre Manufacturers' Association (ATMA)	Data provided by ATMA, so it is considered to be robust
Indonesia	684.4	513.3	513.3	No regulation	Pyrolysis (mainly TDF) 15% - material recovery	No organization focuses on the problem. Only The Indonesia Tire Manufacturer Association (ITMA) is	Data provided by ITMA. However, the presented reports mainly focused on specific regions instead of on the whole Country
Japan	849.0	780.0	781.0	Free market system	73% - energy recovery 19% - material recovery 0.1% civil engineering and backfilling	The Japan Automobile Tyre Manufacturers' Association (JATMA)	Data provided by JATMA, so it is considered to be robust
Mexico	467.5	95.0	95.0	In accordance with official standard (NOM-161-SEMARANT-2011)	14.3% - energy recovery (cement kilns), 6% - material recovery (grounded rubber)	Secretaria de Medio Ambiente y de Recursos Naturales (SEMARNAT) Manejo Responsible	Data provided by Mexican Rubber Industry Chamber (CNIH) so it is considered

Table 1 Summary for each region of current ELT generation, legal system, main recovery methods, and responsible organizations (data based on WBCSD report).

Country	ELT Generated	ELT Recovered (excluding Civil Engineering and backfilling)	ELT Recovered (including Civil Engineering and backfilling)	ELT recovery legal systems	Main ELT recovery methods	Main ELT management organization	Comments
	Metric kiloton				-	-	-
Nigeria	113.0	5.7	5.7	No regulation	tire derivated fuels (TDF) and civil engineering	No organization focuses on the problem.	Data based on domestic tire consumption
South Africa	204.0	51.0	51.0	Interim system	20% - material recovery 5% - energy recovery	Recycling and Economic Development Initiative of South Africa (REDISA)	Data provided by REDISA, so it is considered to be robust
South Korea	319.4	280.9	280.9	Extended Producer Responsibility	50.1% - energy recovery 37.9% - material recovery	Korean Tire Manufacturers' Association (KOTMA)	Data provided by KOTMA, so it is considered to be robust
Thailand	515.0	277.7	277.7	Free market system	53.9% - pyrolysis and energy recovery in cement kilns	No main organization	Data based on old analysis (2012) done by WBCSD

* According to CTRA and CRIA (authorities have claimed that 100% of the generated ELT is recovered in China)

As shown in Table 1, most ELTs are recovered by Indie, China, United States, and European Countries. However, to evaluate the efficiency of each country, the recovery rate must be taken into account. To facilitate further analysis of the global management of waste tires, the recovery rate by region is presented in Figure 1.

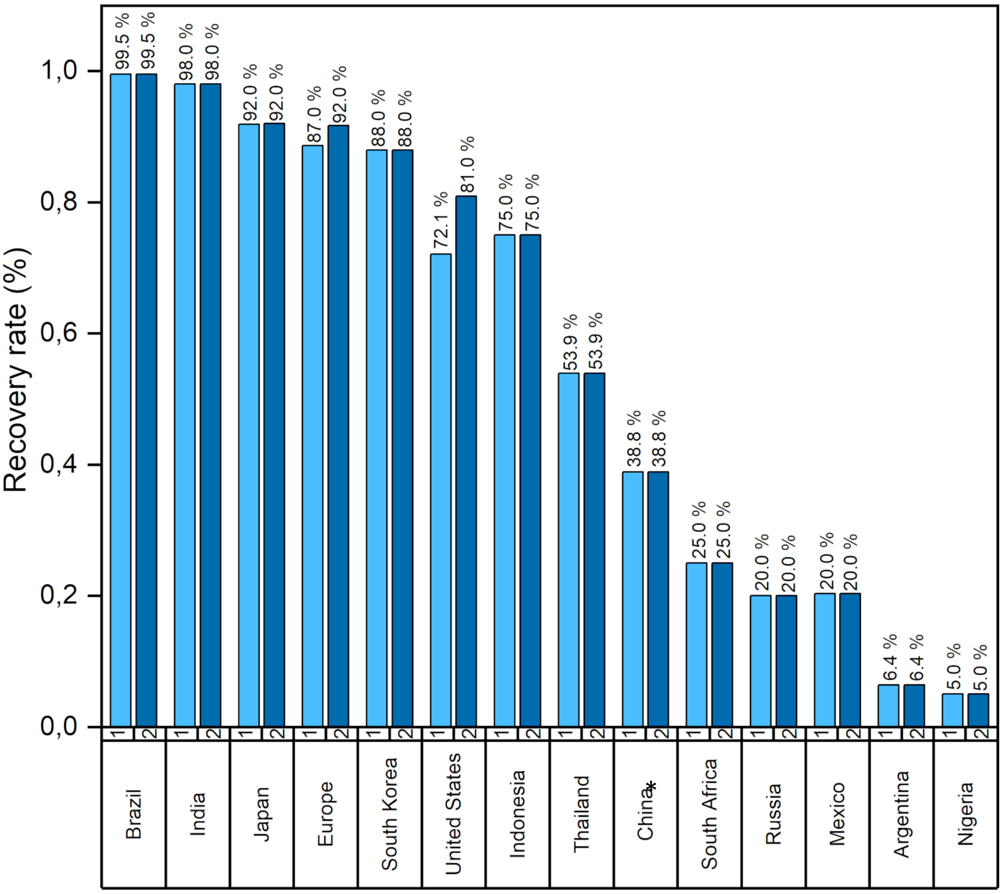


Figure 1 ELT recovery rate by region (1-excluding civil engineering and backfilling; 2- including civil engineering and backfilling) (data based on WBCSD report) * According to CTRA and CRIA (authorities have claimed it that 100% of the generated ELT is recovered in China).

The graph above indicates that Brazil, India, Japan, Europe, and South Korea have the highest recovery of generated ELT. In the case of China, the recovery depends on the data source. It is estimated at 38%, however, tires are treated as a resource in this country, so 100% of the ELT generated should be collected separately [28]. About two-thirds of the total recovery occurs in the informal arena. Taking these factors into account, one must assume that the actual data is somewhere between. In terms of managing this waste, Brazil focuses on granulation and the use of ELT in cement kilns. India, which also manages a significant portion of its waste tires in the informal arena, focuses on energy recovery as well as reclaiming of rubber waste. Japan mainly focuses on energy recovery, gasification, pyrolysis, and TDF generation and utilization. In the case of South Korea, the highest number of ELT is transformed into any form of fuel for energy production (limit set by the government up to 70%) and material recycling with reclaiming dominance. In Europe (2017), more than 1.9 million tons of ELT were sent to material recovery (through granulation and pulverization), 1.2 million tons to energy recovery (mainly in cement kilns), and 0.1 million tons to civil engineering and backfilling.

Achieving high ELT recovery rates results from many years of work on waste tire management systems. Those are based on regulations that are more or less interfered with by the government of a country or region. In some cases, the government is limited to being a stakeholder in the ELT management process, while in other cases, it may have an active and legal influence on financial management and technology development. Basic ELT management systems are presented in Table 2 with a brief explanation and examples of the countries involved.

Table 2. ELT management system and regulation principles with examples of involved countries.

System	Principles	Examples of countries involved
Extended Producer Responsibility	Tire manufacturers and importers are held responsible by national regulations for the appropriate management of end-of-life tires arising.	Belgium, Brazil, Czech Republic, Estonia, Finland, France, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Netherlands, Poland, Portugal, Russia, Slovenia, South Korea, Spain, Sweden, and Turkey
Free market system	Enterprises may invest in ELT management plans; however, every action must be following legislation/standards	Denmark, Croatia, and Slovakia
Tax system	Each country is responsible for the management of ELTs. It is financed by a tax levied on tyre producers and subsequently passed on to the consumer.	Arabia, Argentina, China, India, Indonesia, Japan, and Mexico

Despite the existence of solutions to unify the recovery systems, it is essential to emphasize that each entity focuses on different recycling methods (material, energy, etc.), characterized by different technological solutions and their degree of development. Moreover, despite the existing effective solutions, the biggest problem for the industry involved is that the resulting products are very often of average or low quality, the recycling methodology can be hazardous; hence the ELT market is most often unprofitable and not self-sufficient. Therefore, on a global scale, the ELT recovery and recycling market is still in the development phase and needs further work from governments, entrepreneurs, and research entities.

2.2. Waste tire recycling.

The whole ELT recycling cycle can be very simple (direct use in civil engineering) as well as more complex (pyrolysis or reclaiming). To better present the ELT management options, Figure 3 shows the recovery routes and their possible interrelationships.

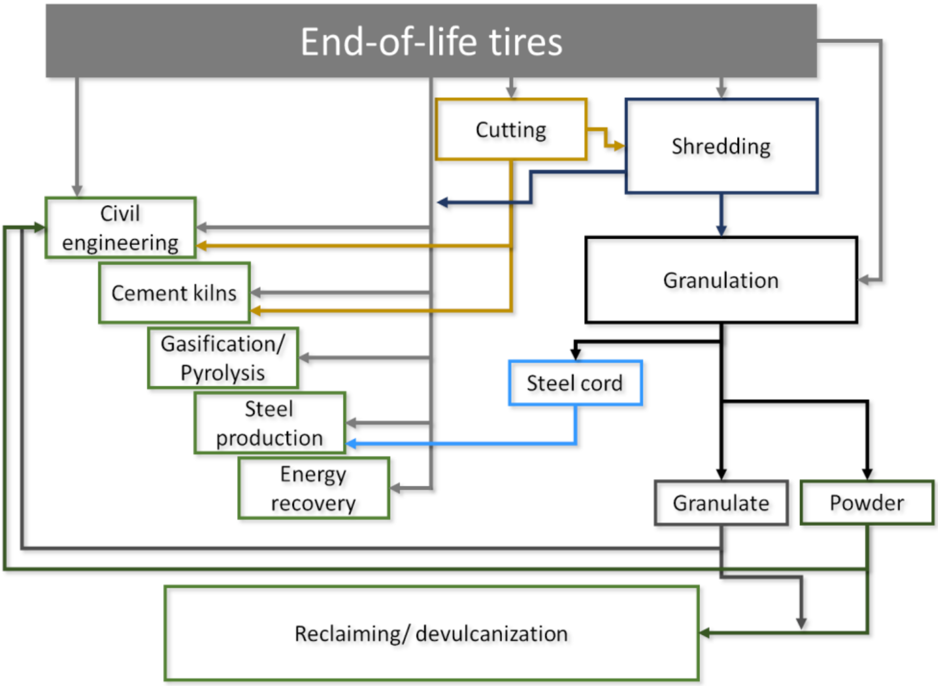


Figure 2. ELT management routs and links between steps.

The ELT recycling process begins with activities to cut, granulate, or shred them. These differ in the degree of shredding of the waste tire (cutting>granulation>shredding). Typical classification according to the European Committee for Standardization (CEN; CEN TS14243) is presented in Table 3. Two main methods can be applied to decrease the size of processed ELT: (i) grinding at ambient temperature and (ii) grinding at cryogenic conditions. It must be pointed out that the first method allows obtaining a product with a rough surface, while the second one gives a material with a smooth one. Regarding the practical use of materials, surface development is crucial (higher interaction with a raw matrix), and the ambient atmosphere grinding method is usually used, precisely because of its irregular shape and fuzzy surface [29].

Table 3. Typical classification of GTR particles according to the European Committee for Standardization.

Classification name	Fraction size (mm)
Cut tires	> 300
Shreds	20-400
Chips	10-50
Rubber granulate	0,8-20
Rubber dust	<0,8

Grinding processes are either applied to the entire ELT or a combination of them is used to gradually reduce the particle size and partial removal of steel cord and fibers from it. For example, shredded tires can be used directly in cement kilns or civil engineering, or for further shredding and then for granulation. It all depends on the needs of the product recipients (place of management or particle size). ELTs or their cut form can be used in civil engineering, cement plants, gasification, pyrolysis, energy recovery, or steel production. The granulation products, i.e., powder and granulate, are also used in civil engineering applications. However, the processed material can be subjected to other operations aimed at partial devulcanization and cross-linked waste rubber structure degradation. This process is called reclaiming.

To understand how to recycle waste tires, one needs to delve a little deeper into each option.

2.2.1. Waste tires in Civil Engineering

Regarding developing ELT in various forms, the discussion should start with civil engineering. As a raw material, it is characterized by low density, high elasticity, low stiffness, and high thermal insulation, and it can innovatively get a second life. Typical applications are noise barriers and sound insulation panels [30], vibration-damping layers beneath rail lines [31], rubberized asphalts [32-34], fills for highway barriers [35, 36], or insulation against frost penetration in roadways [37]. Not only can scraped tires be used in civil engineering; for example, a waste fiber obtained during granulation and separation can also be applied as a filler enhancing concrete properties [38].

2.2.2. Waste tires in Cement Kilns.

Another pathway briefly discussed will be the use of ELT in the cement kilns. This solution is separated from energy recovery due to the sophistication and prevalence of this technology. In the case discussed, waste tires are used as fuel for cement production. The important fact is that cement production is very energy-consuming (3.3 GJ/tonne), and energy generation costs are about 40% of the total production amount [39]. However, what distinguishes this technology from others is that the whole process works in a closed system, and the generated ash is introduced into the cement composition. Thanks to that, the ash generated is not treated as waste and does not generate further problems with its disposal. Due to the complex chemical and physical structure, this solution allows for oxidation of all components, so the ash generated consists of 100% of the ELT used [40].

2.2.3. Waste tires for steelmaking

Similar assumptions are used when using waste tires for steelmaking. The production of "green steel" uses Polymer Injection Technology, which allows ground waste tires to be fed straight into the furnace. In this process, ELT is used as a partial or complete substitute for coke, which has been proven to lead to a more stable slag [41]. Furthermore, the introduction of ELT significantly increases the reduction and carburization of the metal produced, compared to coke alone. The researchers conclude that the hydrogen introduced by the rubber-based waste, and thus the reactions in which this element participates, promote faster coal gasification (more rapid reduction of iron oxide in coke) [42].

2.2.4. Waste tires in pyrolysis/gasification

Pyrolysis/gasification is another option for ELT development. These are thermal methods to convert waste tires into valuable products, the difference being that the gasification process is carried out in an atmosphere of air, oxygen, hydrogen, or steam, while pyrolysis is an endothermic process done without access to air or oxygen (sometimes hydrogen or steam is used to suppress oxidation processes resulting from the presence of elemental oxygen in the feedstock) [43]. Due to the presence of reactive gases, the obvious conclusion is that gasification is more efficient than pyrolysis and has a much narrower range of temperatures at which it is carried out (700 – 800 °C – gasification; 400 - 800°C – pyrolysis) [44]. By controlling the temperature and the heating and cooling rate, it is possible to control the quality and quantity of products. In pyrolysis, running processes at low temperatures promote liquid products, while high temperatures promote gas production. When the process is run slowly, char production is increased [45]. When the process is cooled rapidly, the production of liquid products is favored due to the condensation of the formed gases. For gasification, the type of gases used has a crucial impact on the quality of the products obtained. Conducting the reaction at this stage offers many possibilities, including introducing additional variables into the process to obtain a specific product (for example, the synthesis of specific gaseous or liquid fuels), while for the pyrolysis products further processing further is needed. Of course, this does not mean that all gasification products are already finished, products that do not require additional treatment. The resulting products from both processes can be used to produce syngas, synthetic oils, and char. For better visualization, Table 4 presents the compounds detected in the highest amounts as components of ELT pyrolysis products.

Table 4. ELT pyrolysis products and their main composition.

Detected components	References
Pyrolysis oils	
polyaromatic hydrocarbons	[46]
polyaromatic nitrogen hydrocarbon	
polymeric sulfur hydrocarbons	
benzene	[47]
toluene	
xylenes	
styrene	
limonene	
indene	
Gaseous products	
hydrogen	[47]
methane	
ethane	
ethene	
propane	
propene	
butane	
butene	
butadiene	
carbon dioxide	
carbon monoxide	
hydrogen sulfide	
Solid residue	
Char containing inorganics used in tire manufacture such as: zinc, calcium or silicon	[47]

2.2.5. Waste tires in energy recovery

Due to their high calorific value (33-35 MJ/kg), ELTs are used directly or after size reduction to generate energy by simply incineration or co-combustion with other fuels like coal. Shredded waste tires used for incineration are commonly called tire-derivated fuel (TDF). These solutions are often used in the pulp and paper industry, electric utilities, or industrial boilers and give tangible benefits like lower air pollution, reduced energy generation costs, and efficient heat recovery. However, despite its advantages and the aspects related to the management of waste tires, this solution has a few problems. First of all, to design and build a proper plant, high capital investment is needed. The whole process requires a flue-gas cleaning and well-trained staff.

2.2.6. Waste tires reclaiming/devulcanization

The ELT management methods listed above mainly focus on high-temperature processes. Although these methods are already widely used worldwide and can partially cover the demand for waste tire management, two important things must be considered before using ELT as fuel. The first is possible environmental pollution through the generation of substances that negatively affect human health and life. When a tire burns, there is a high probability of generating harmful substances such as dioxins and furans. These substances are produced by the combustion of halogen derivatives in the presence of hydrocarbons and oxygen. ELT used as a fuel itself contains great amounts of hydrocarbons and the process itself is carried out in the presence of air. The chlorine can be found in the chlorinated butyl rubber liner, which slows down air leak. Justice Energy Network [48] reported that the application of ELT as a fuel in cement kilns and paper mills increases the amount of dioxins/furans generated during incineration (depending on the quantity and the measurement location, an increase of 4.1 - 247 % was observed). In addition to data shown in Table 4 not only dioxins can be generated during thermal treatment of ELTs. Among mentioned substances, some are generally considered carcinogenic (e.g., butadiene and styrene). The potential risk of generation and release of hazardous chemicals into the atmosphere is an important aspect to consider when using TDFs. However, analysis of the ELT development market indicates that treatments of this type are continuing. This is due to advanced technologies to capture these compounds and thus reduce the number of toxic substances below the permitted levels. However, the potential risk of toxin leakage is not the essential factor in using ELT as a TDF. As mentioned earlier, when TDF is burned, we get an energy yield of about 32-35 MJ/kg. At this point, it is vital to consider the energy generated during compound production used for tire manufacturing, tire production itself, and the processes applied for ELT cutting/shredding/granulation. A detailed analysis,made by Amari T. et al. [49], indicates that the energy recovered during the combustion of TDF represents about 37% of the energy needed to produce a tire (including the production of raw materials and the tire itself, as well as the grinding of tires to the required size for use as fuel). At this point, an important question arises, would it not be better to perform material recovery of the tire and use it as a matrix for a new product, a partial substitute, or as a hybrid filler/filler? It overcomes the energy loss problem resulting from the difference between the energy input in the tire production and the energy recovered from its combustion. However, appropriate processes must be carried out to modify the rubber waste for this approach to be applicable on a large scale. Such possibilities are provided by the reclaiming of waste rubber. In this case, the most commonly used raw material is ELT after the granulation or powdering process. Generally speaking, the basis of reclaiming processes is the phenomenon of devulcanization, i.e., breaking crosslinking bonds (most often mono-, di- and polysulfide bridges but also in the form of C-C bonds) occurring in the structure of cross-linked rubber. If such selective degradation of these bonds was possible, one would obtain a product that could be re-crosslinked, significantly eliminating the problem of waste rubber recycling. However, the selective devulcanization process is still not feasible because of the ratio of S-Sx-S bonds to C-C bonds present in the elastomer chain. Therefore, all processes aiming to partially restore the non-crosslinked structure of waste rubber are supposed to be called reclaiming. An essential difference between reclaiming and devulcanization is that partial devulcanization and degradation of elastomer chains occur during reclaiming. Moreover, the phenomena used in this process often lead to new reactions or cyclic crosslinking and de-crosslinking, dramatically changing the physical and chemical structure of the material. Figure 3 illustrates the difference between the discussed processes

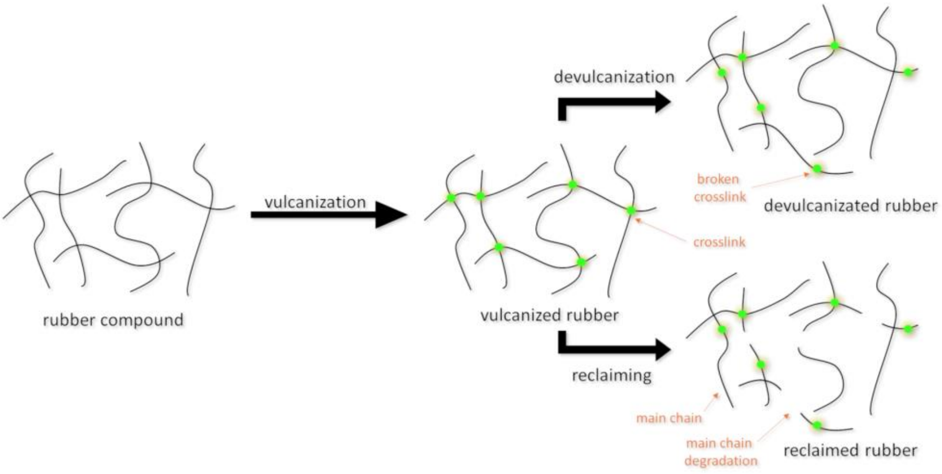


Figure 3. The difference between the molecular structure of rubber compounds, vulcanized, devulcanized, and reclaimed rubber.

The presented above possible structural changes are induced by supplying the system with an appropriate amount of energy, an appropriate chemical compound, or even living organisms. The existing terminology of reclaiming depends on the source initiating the discussed process. Therefore, there are thermal, chemical, physical, biological, mechanical, and combined methods.

An essential problem in classifying and describing the methods mentioned above is that combined methods are most often used, and the line between the different methods is heavily blurred. This is due to the lack of standardization of the process and the fact that literature reports deal with one method. Therefore, this chapter will discuss examples of reclaiming methods used in aggregate form, emphasizing the type of method used and potential inaccuracies.

To highlight the multitude of ongoing research towards the remanufacturing of rubber waste from tires, only works published since 2014 will be cited. Moreover, the analysis of increasing interest in rubber recycling will be presented. The exception is the biological method, which is little developed, and there are few relevant literature reports. This is also why it will be treated a little differently in this chapter than the other methods, which are much more commonly combined.

2.2.6.1. Biological methods.

The discussion will begin with the least obvious choice, which is the biological method. In the literature, a new trend is being observed. Scientists take the effort to reclaim rubber waste with enzymes [51] and sulfur-assimilating microorganisms.

Yao et al. [51] tested the ability to desulfurize waste latex rubber with Alicyclobacillus sp. selected from the soil of an iron mine. It was shown that adding 5% weight per volume of waste latex rubber into microbe medium does not hinder the growth of Alicyclobacillus sp. Moreover, due to the lipophilic character of latex and the hydrophilic character of microbes, the surfactant was applied to increase the contact probability. It was noticed that surfactant has a toxic effect on Alicyclobacillus sp.; however, the effect was limited via proper technique. Longer desulfurization time resulted in increased swelling degree values and decreased cross-link density, and after 8-10 days, a good desulfurization effect was achieved. Mechanical properties show significant improvement of desulfurized waste latex rubber/natural rubber blends over waste latex rubber/natural rubber blends. XPS and FTIR analysis revealed that the applied microbes break sulfur bonds and oxidize them to sulfone groups.

In the next study, [52] authors carried out desulfurization of waste latex rubber with Sphingomonas sp.; however, a new half-submerged cultivation method has been applied. Compared to the traditional submerged cultivation method, the new one allows for the addition of much more waste latex rubber and is carried out without stirring. Due to the limited space and absence of mechanical agitation in the half-submerged method, microorganisms grew on the surface of waste latex rubber instead of creating colonies without contact with rubber. In Figure 4, the states of Sphingomonas sp. in desulfurization by the submerged and half-submerged cultivation methods are compared. The results showed that the process was the most efficient when 40 weights per volume of waste latex rubber were added into the medium without surfactant. The desulfurization lasted for 10 days. The XPS and FTIR analysis showed that the content decreases of S-C and S-S bonds were greater when compared to the traditional method. For better contrast, the mechanical properties of styrene-butadiene rubber blends with waste latex rubber, submerged waste latex rubber, and half-submerged waste latex rubber were tested. It was concluded that the new method enhanced the mechanical properties. Moreover, increased compatibility was confirmed via scanning electron microscopy.

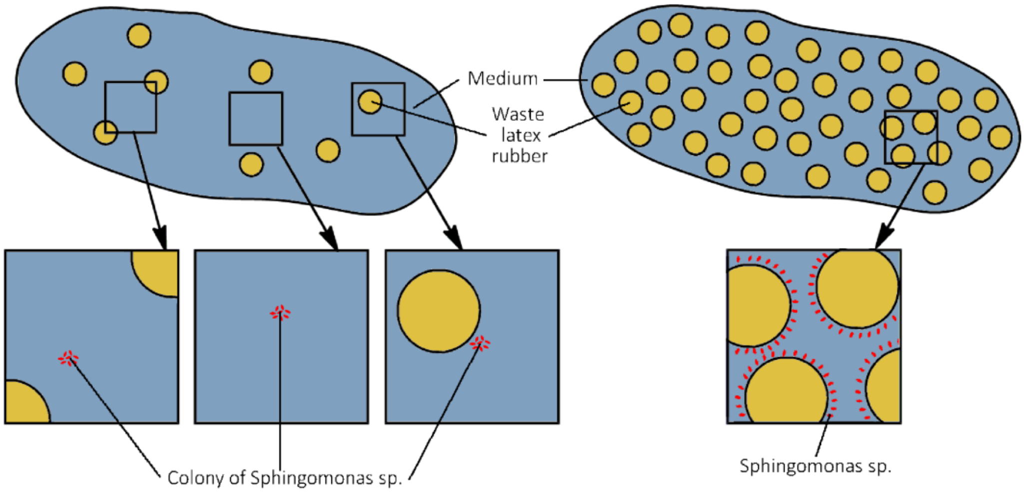


Figure 4. Comparison of states of Sphingomonas species in desulfurization by submerged and half-submerged cultivation methods.

Hu et al. [53] investigated the influence of three types of surfactants (Tween 20, Tween 60, and Tween 80) on the affinity between ground tire rubber (lipophilic character) and Sphingomonas sp. (hydrophilic character). The toxic effect of Tween was reduced by premixing ground tire rubber with surfactants before desulfurization. The process was most efficient when Tween 20 was applied. Scanning electron microscopy conjugated with energy-dispersive X-ray spectroscopy has shown that the amount of sulfur on the rubber surface was reduced by 67%. As it could be expected, XPS analysis revealed the reduction of S-S and S-C bonds and an increase of S-O bonds. For better understanding, desulfurized ground tire rubber was blended with styrene-butadiene rubber and a curing system. The results proved that the addition of Tween 20 significantly enhanced the mechanical properties compared to the desulfurized blend without surfactant.

Cui et al. [54] carried out desulfurization of ground tire rubber using Sphingomonas sp., Gorodnia sp., and their mixed consortium. The results presented in this study demonstrated that the mixed bacteria biomass value was higher during the desulfurization process than the biomass value of any single bacteria. This fact indicates that those two kinds of bacteria support each other and can grow together. The mixed bacteria desulfurization caused a decrease in the cross-link density of ground tire rubber and a reduction in sulfur content on the sample's surface. Moreover, desulfurized ground tire rubber treated by mixed bacteria and blended with styrene-butadiene rubber showed better mechanical properties than the same type of blends, in which ground tire rubber part was desulfurized with single bacteria species. This result indicates that the combination of bacteria types caused better compatibility between ground tire rubber and styrene-butadiene rubber.

A significant disadvantage of using biological methods is the time required to finish the process, which is related to the nature of the processed waste. Sulfur assimilating microorganisms live in an aqueous environment, while rubber is hydrophobic, which significantly slows the growth of the microbes down. Moreover important is the fact that reclaiming occurs with this method, but only on the surface of the structure, which is also related to the water-resistance of GTR.

2.2.6.2. Combined methods.

The first of the cited publications dealing with the management of rubber waste is the work of Molanorouzi et al. [55]. In this work, the authors perform devulcanization/reclaiming of waste rubber using microwave radiation (200-240°C) and chemical modifiers in the form of hexadecylamine (HDA), Diphenyl disulfide (DPDS), N-cyclohexyl-2-benzothiozyl sulfenamide (CBS) 2-mercaptobenzothiazole disulfide (MBTS) and two types of the oils, aromatic and paraffinic with various contents (all samples were mixed with 30 phr of oils). The authors confirmed with the TGA technique that the raw material used was in fact from passenger car/truck tires. The authors determined the degree of devulcanization, sol fraction, and degree of crosslinking of their samples depending on the modifier used. After determining which compound was the most effective (highest sol fraction), the effect of temperature was investigated. According to the authors, the most suitable compound for devulcanization is DPDS. However, several important concerns arise after analyzing the demonstrated method. The use of microwave methods to reclaim rubber waste containing carbon black in its structure is risky and often challenging to control. As I indicated in one of my papers [56] for the power of 800W and a time of more than 120 seconds, a GTR ignition occurs, related to the Maxwell-Wagner polarization effect [57]. In the case of the cited research, the process lasts 180 seconds (900W). However, the addition of 30 phr of aromatic oils may have slowed the ignition of the sample, hence the absence of this phenomenon. Additionally, note how the degree of devulcanization of the sample was determined. GTR is an already cross-linked material (after reclaiming processes, it often also exhibits a high degree of cross-linking) with many components in its structure, including carbon black to a large extent. The method used to determine the degree of crosslinking does not consider the interaction between the elastomer matrix with the filler, which gives unreliable results. The Kraus correction must be included to calculate the degree of crosslinking correctly [58]. The authors mention in their paper the lack of proper correction and explain that these are illustrative results to evaluate the degree of crosslinking of the samples. However, since carbon black is an active filler, it has a significant effect on the measurements. Furthermore, the calculation did not consider the added oil, which affected the sol fraction content, and thus calculated the degree of crosslinking and devulcanization.

Another relatively new work worth discussing is the article by Zhang et al. [59]. In the paper, the authors emphasize that they use a chemo-thermomechanical devulcanization method, which is important in standardizing the terminology used during research in the field discussed. The process was carried out in an internal mixer with a speed of 45 rpm at 180°C and 200°C using as a devulcanizing agent a self-synthesized thiobisphenol (4,4'-dithiobis(2,6-di-t-butylphenol) in different ratios (0, 0.1, 0.3, 0.5, 1.0 and 3.0 grams). The origin of GTR was confirmed by TGA analysis.

Furthermore, the authors conducted the revulcanization process to evaluate the effectiveness of the process in terms of the potential use of the resulting regenerate as a raw material for new products. This approach is essential since the main objective of the research on the reclaiming of rubber waste is to create a technology allowing for the management of a large number of waste tires, as well as waste rubber products in general. In the conclusions, the authors raised an important issue related to the process efficiency versus the properties of the regenerates. The study shows that the increasing addition of devulcanizing agent and process temperature decreases the degree of crosslinking and Mooney viscosity. However, at the same time, a too high reclaiming degree negatively influences the parameters of regenerates. Clearly, this is important when using rubber regenerates to manufacture flexible products. However, for use, for example, as an asphalt filler, a higher degree of devulcanization has a positive effect. This fact means that the design of the GTR recovery method should start at the stage where the final product is planned. Moreover, these authors analyzed the degree of crosslinking of their samples without running Kraus corrections.

Another of the analyzed publications that bring an important aspect to the question of practical methods of reclaiming of rubber waste is the work of Guo et al.[60]. In this case, the starting material is a natural rubber-based vulcanizate specially prepared for publication; however, the article is analyzed here due to the importance of the study in terms of the development of tire management technology. The authors performed mechano-chemical reclaiming, with emphasis on the fact that it is a low-temperature process. The results were compared with a traditional high-temperature reclaiming. As a reclaiming agent, the authors used a composition of vegetable oil, vegetable esters, and anti-recrosslinking additives (the authors do not specify the exact composition). The highest temperature used for the high-temperature process was 290°C, while the highest temperature of 120°C characterized the low-temperature process. The only significant difference is the order used during the reclaiming process. Instead of one variable being temperature, the type, amount, and order of ingredient dosing also change. This results in too many variables being introduced into the system that can affect the final result, making the comparison of those two technologies difficult. In addition to the well-known techniques for evaluating the efficiency of waste rubber reclaiming (sol fraction, degree of devulcanization), the aging of the material, as well as the application potential of products based on the obtained regenerate, were also investigated. The results indicated that low-temperature regenerates have superior properties to high-temperature ones.

Conducting these processes at low temperatures is crucial for emissions of volatile organic compounds (VOCs), which are hazardous to the environment and those operating the technology (example Chapter 2.2.4.). Previous research works have also addressed the aspect of running processes at low temperatures [61-63] highlighting the essence of this approach. Generally speaking, few publications indicate the harmfulness of high-temperature GTR reclaiming. However, the problem should be underlined in every study regarding reclaiming, as well as the impact of the designed technology on the environment should be quantified.

Another publication that raises an important issue is the work presented by Shi et al. [64] and deals with continuous methods. In this study, thermo-chemo-mechanical reclaiming of waste rubber, allegedly from used truck tires, was performed using a co-rotating twin-screw extruder. Two sets of screw configurations, two temperatures 260°C and 300°C (exact zones temperatures given), several screw speeds, and three different reclaiming recipes were used as variables for the research. The authors also attempted to evaluate their material's application potential as a reactive polymeric plasticizer by preparing samples based on the obtained regenerates and natural rubber. It was shown that a regenerate with a sol fraction of 73.5% was achieved. As mentioned earlier, too high sol fraction negatively affects the mechanical properties of the regenerate, while the authors clearly understand that what matters is the target market and customization of regenerate parameters and the search for new markets. What is more, a continuous method has been applied, which is the most effective method of processing the discussed waste due to its economic aspect. This fact is due to two important reasons. (i) The extrusion process is one of the most widely used methods in the plastics industry, which facilitates the implementation of the new technology. (ii) GTR is a waste material whose purchase cost is in the range of 600-1200 PLN/tonne (approx.. 130-220 euro – calculated by the exchange rate on 28.06.2021). Therefore, the equipment used to design the rubber waste reclaiming technology should be economically viable. Of course, suppose technology is developed to effectively manage rubber waste on a national/continental/worldwide scale, thus essentially eliminating the problem of landfilling and incineration of rubber waste. In that case, the ratio of raw material prices to technology will not be as significant. However, current knowledge in the field allows obtaining products with average properties at best. This is why the potential implementation of the solution should be taken into account when designing a new solution.

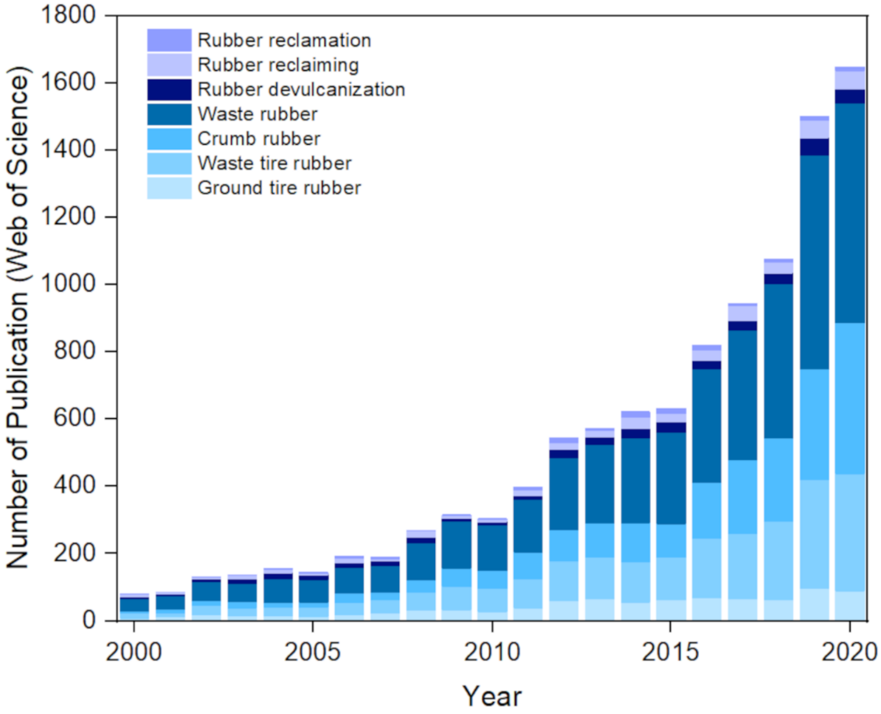
The article, while not direct, also raises another important issue in the characterization of the GTR. The author indicates that the GTR used is from the tread part of heavy truck tires and the composition is approximately 70% NR and 30% synthetic rubber (SBR and/or BR). However, the thermogravimetric analysis performed by the authors and the description included in the publication indicate the presence of one type of rubber (NR – peak at 375°C, which is in agreement with the literature data) while there should be the second one from the synthetic rubber [65-68]. It is true that when analyzing the derivative course of the TG curve, one can see a small peak in the range of 400-450 °C; however, this issue is not addressed by the authors, and the intensity of the peak itself may not indicate the presence of about 30% of synthetic rubber. The dTG curve presented in the study is similar to NR-based materials thermogravimetric characteristics [69, 70]. There is a reliable chance that the raw material used is not GTR, but rubber waste coming from a different source. For this reason, before starting research on GTR, additional tests confirming the origin of the raw material should be carried out (for example, dTG).

An interesting approach was also presented by Dobrota et al. [71]. A thorough analysis of the composition of waste rubber based on conveyor belts has been made, however, the authors in their publication do not simply say whether the described material is the starting raw material or whether another one was used. However, regardless, the described method is suitable for conducting GTR recovery processes. The reclaiming method belongs to the thermo-chemical methods. Its main element is the autoclave. Two methods were compared. For both, di-xylene di-sulphide and mineral oil (plasticizer) were used. The working pressure was approx. 30 bar. After reaching the set point, the pressure was raised to 40 bar and the temperature was set to 225°C. The waste rubber with chemical components was kept in those conditions for 2.5 h. After the process, the autoclave was depressurized, and the system was cooled down. The second method was identical to the first, except that the pressure was lowered to about 1.3 bar after the entire process, and a vacuum generating system was installed. This made it possible to achieve a pressure of 0.1-0.2 bar, which, according to the authors, has a positive effect on the efficiency of the process. Thanks to this low pressure, the resulting gases were transported to a condenser, where they were turned into wastewater and purified in a wastewater treatment plant. The resultant regenerate was subjected to homogenization, plasticization, refining, and baling regardless of the process. The efficiency of the processes was evaluated by analyzing the degree of cross-linking of the samples, showing the superiority of the latter. However, the addition of oil was not considered (the waste-to-oil ratio is 90:7). It should be mentioned at the outset that the publication takes seriously the development of rubber waste reclaiming technology, taking into account aspects such as (i) environmental protection, (ii) energy consumption, (iii) conducting processes under near-real conditions, (iv) evaluation of the potential of the obtained product, (v) cooperation with companies that produce materials based on rubber waste, (vi) designing a technology that does not require the selective collection of rubber waste, and (vii) an influence of waste rubber particle size on the physico-mechanical and chemical properties.

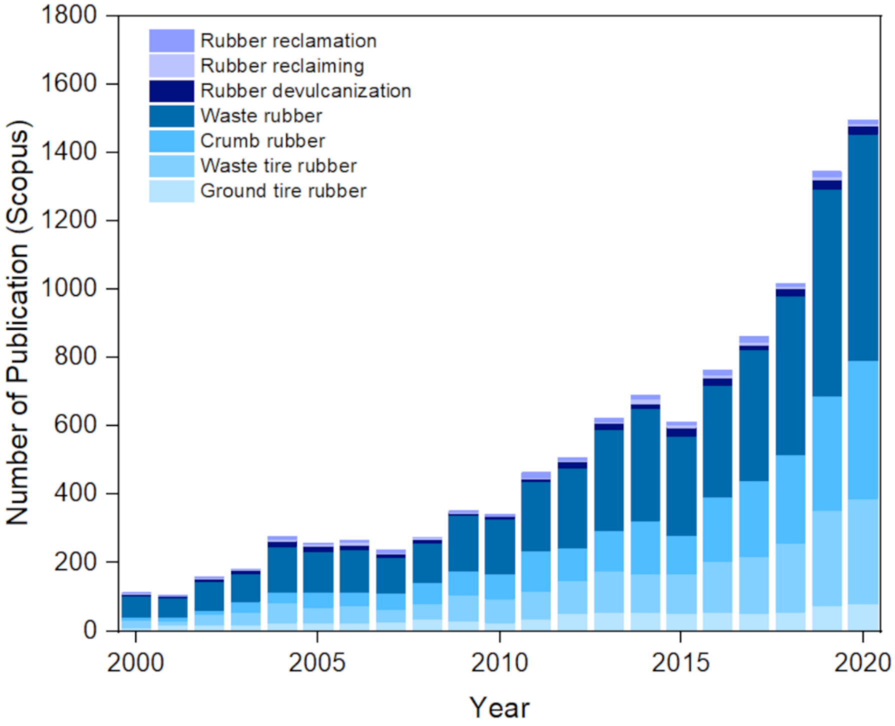
2.3. Publication trend analysis

The examples cited above illustrate in significant part the methods and problems associated with the reclaiming of rubber waste. However, a careful analysis of the number of publications from 2000 to 2020 was done to demonstrate the multiplicity of publications in this area.

It should be noted at this point that the data presented are subject to several rules chosen by the author. The data collection was based on regional vocabulary (tire - U.S.; tyre - English speaking countries outside North America), databases (Scopus and Web of Science), and several commonly used phrases in terms of waste tire management such as rubber reclamation, rubber reclaiming, rubber devulcanization, waste rubber, crumb rubber, waste tire rubber, and ground tire rubber. Please also note that the databases used, in the case of affiliation analysis, assign a publication to as many units as shown in a paper.



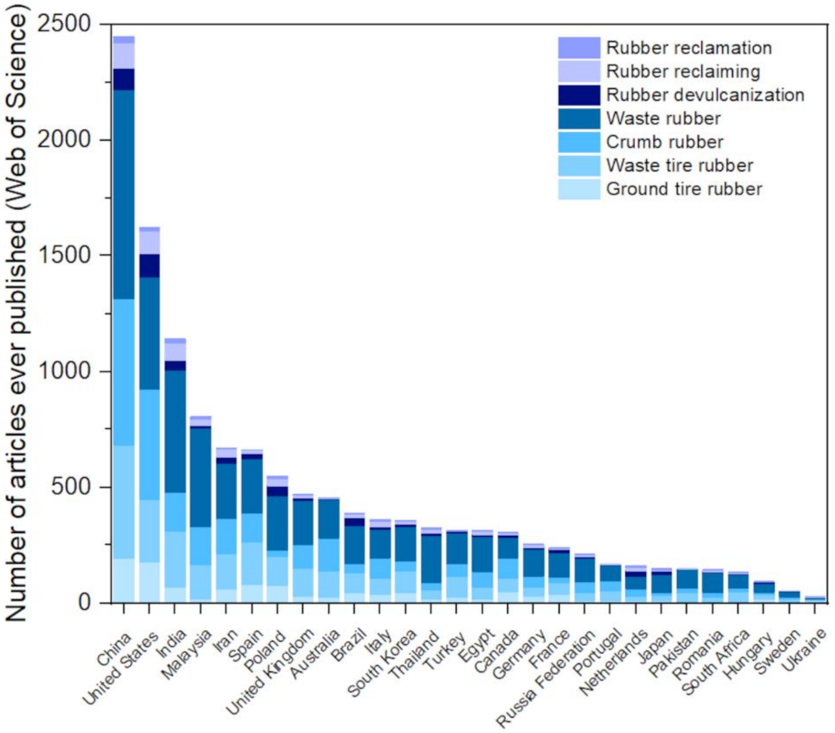
Rubber reclamation
Rubber reclaiming
Rubber devulcanization
Waste rubber
Crumb rubber
Waste tire rubber
Ground tire rubber
Number of Publication (Web of Science)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2005
2010
2015
2020
Year



Rubber reclamation
Rubber reclaiming
Rubber devulcanization
Waste rubber
Crumb rubber
Waste tire rubber
Ground tire rubber
Number of Publication (Scopus)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2005
2010
2015
2020
Year

Figure 5. Number of published articles on the subject of waste rubber management according to Scopus and Web of Science databases (2000-2020).

Analyzing the graphs shown in Figure 5, one can see clearly the growing interest in the topic of my work. Regardless of the terminology used, there is a positive average increase in publications given the entire analysis period in each case. For the Scopus database it is 4.05, 16.7, 22.2, 30.9, 1.8, 2.4, and 0.45, respectively for ground tire rubber, waste tire rubber, crumb rubber, waste rubber, rubber devulcanization, rubber reclaiming, and rubber reclamation. In the case of Web of Science, the rise is as follows: 3.5, 14.3, 19.7, 30.1, 0.95, 0.1, and 0.45 for "ground tire rubber", "waste tire rubber", "crumb rubber", "waste rubber", "rubber devulcanization", "rubber reclaiming", and "rubber reclamation" respectively. As one can see, the highest growth as well as the highest number of publications are related to the terms waste rubber, crumb rubber, and waste tire rubber. This is due to the fact that these terms can be assigned to any method using the discussed material, be it devulcanization, energy recovery, use as a filler in new matrix or asphalts, etc. On the other hand, rubber reclaiming, rubber reclamation, and rubber devulcanization refer to a much narrower subject of rubber waste management. Now that we know the basic trend of publishing in the work topic as a function of time, it is important to look at the distribution as a function of countries/regions.


Number of articles ever published (Web of Science)
2500
2000
1500
1000
500
0
Rubber reclamation
Rubber reclaiming
Rubber devulcanization
Waste rubber
Crumb rubber
Waste tire rubber
Ground tire rubber
China
United States
India
Malaysia
Iran
Spain
Poland
United Kingdom
Australia
Brazil
Italy
South Korea
Thailand
Turkey
Egypt
Canada
Germany
France
Russia Federation
Portugal
Netherlands
Japan
Pakistan
Romania
South Africa
Hungary
Sweden
Ukraine

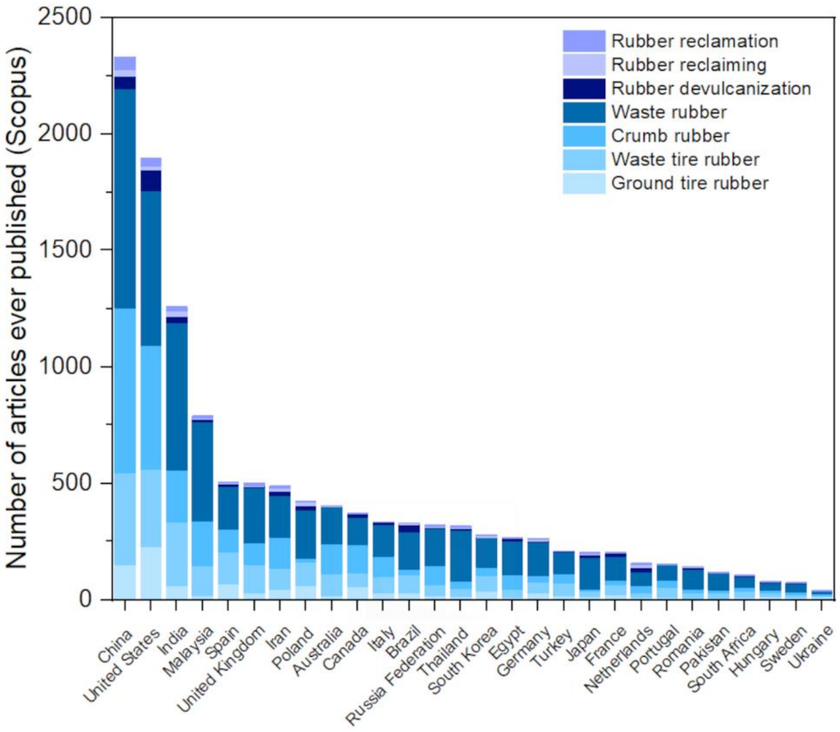
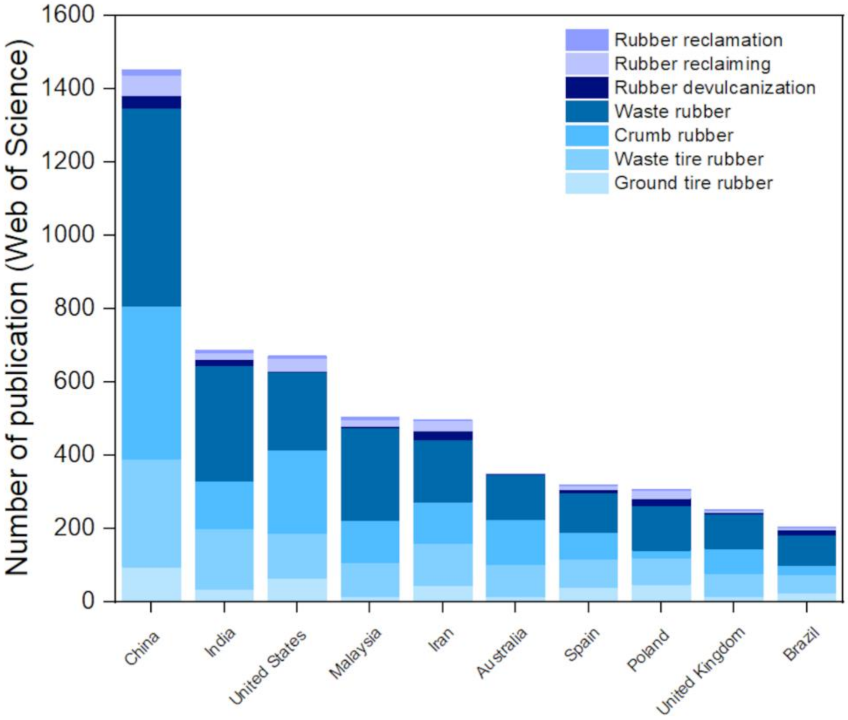
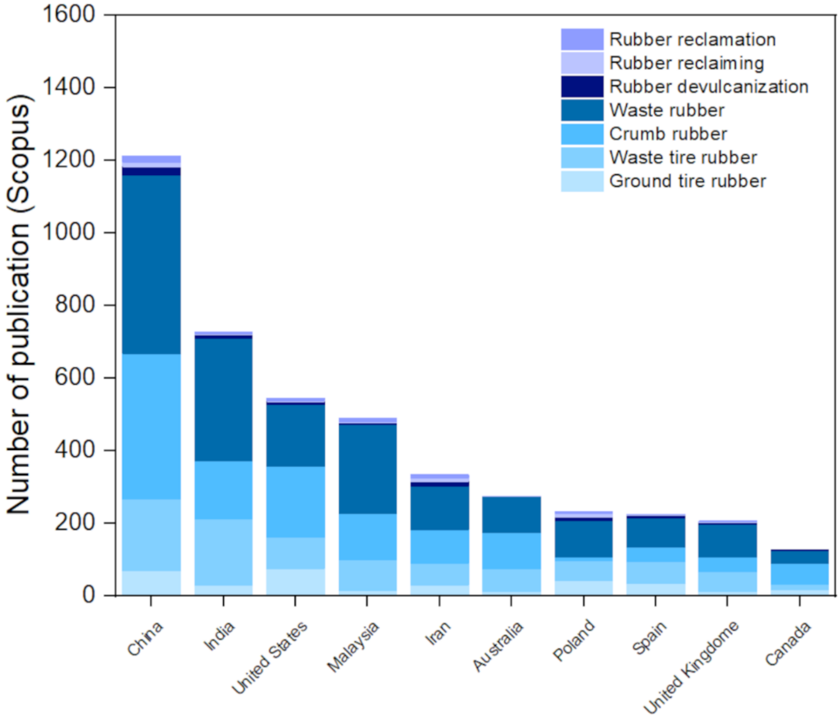

Number of articles ever published (Scopus)
2500
2000
1500
1000
500
0
Rubber reclamation
Rubber reclaiming
Rubber devulcanization
Waste rubber
Crumb rubber
Waste tire rubber
Ground tire rubber
China
United States
India
Malaysia
Spain
United Kingdom
Iran
Poland
Australia
Canada
Italy
Brazil
Russia Federation
Thailand
South Korea
Egypt
Germany
Turkey
Japan
France
Netherlands
Portugal
Romania
Pakistan
South Africa
Hungary
Sweden
Ukraine

Figure 6. Number of published articles on the subject of waste rubber management according to Scopus and Web of Science databases as a function of countries/regions (no period restiction).

Figure 6 shows the number of publications on tire management as a function of countries/regions. The resulting data for the two databases show significant discrepancies in the number of publications attributed to specific keywords. The number of publications for the phrases used to create the graphs is 1003, 2531, 2464, 5135, 476, 540, and 159 (Web of Science) and (1009, 2634, 2834, 6360, 375, 162, and 314 (Scopus) for “ground tire rubber”, “waste tire rubber”, “crumb rubber”, “waste rubber”, “rubber devulcanization”, “rubber reclaiming”, and “rubber reclamation” respectively. The data indicate that the number of publications attributed to given keywords varies significantly depending on the database used. Moreover, the sum of publications varies and is 12 308 (Web of Science) and 13 688 (Scopus). This state of affairs results from the methods used by specific databases when searching for requested phrases, double attribution of publications to the same affiliation (several authors with the same affiliation), and treating one publication as several when several affiliations are shown. However, these are minor errors that any user can easily verify. Nevertheless, the data obtained is important and gives a general idea of the interest in the topic. Moreover, these data are important from the application point of view of the developed technologies. Knowing in which countries there is the greatest demand, you can try to implement the developed solutions in the territory/cooperation of a given country with a higher degree of probability, or if you want to implement the solution in your home country, supporting your regional economy, it can be used for basic market analysis to establish cooperation or identify potential competitors. Further analysis will follow on a narrower group of countries.



Number of publication (Web of Science)
1600
1400
1200
1000
800
600
400
200
0
Rubber reclamation
Rubber reclaiming
Rubber devulcanization
Waste rubber
Crumb rubber
Waste tire rubber
Ground tire rubber
China
India
United States
Malaysia
Iran
Australia
Spain
Poland
United Kingdom
Brazil



Number of publication (Scopus)
1600
1400
1200
1000
800
600
400
200
0
Rubber reclamation
Rubber reclaiming
Rubber devulcanization
Waste rubber
Crumb rubber
Waste tire rubber
Ground tire rubber
China
India
United States
Malaysia
Iran
Australia
Poland
Spain
United Kingdome
Canada

Figure 7. Number of published articles on the subject of waste rubber management according to Scopus and Web of Science databases as a function of top countries/regions (no period restiction).

Figure 7 presents data for the countries with the highest interest in the topic since the last 5 years, which are China, India, the United States, Malaysia, Iran, Australia, Poland, Spain, the United Kingdom, Canada, and Brazil. Depending on the database, there are several differences (swapping places between Poland and Spain and Canada or Brazil on the list). The data presented partly agrees with the data on the amount of ELT generated in each country (Table 1). In the case of China, the United States, Brazil, and India, it is clear that the size of the problem in terms of the amount of waste tires generated coincides with the number of publications with the affiliation of these countries. In this comparison, Poland and Spain are part of the European Union, and specific numbers are not listed. Nevertheless, according to ETRMA report regarding ELT collection and treatment in 2019, both countries are at a similar level of ELT generation [72]. In the graphs presented above, Russia does not appear either, while the number of ELTs generated, according to Table 1, is relatively high. This is due to the fact that Russia significantly restricts access to research results by scientists from outside the country. Therefore, also in the databases used, they are not taken into account. An important aspect is that regardless of the database, Poland is in the top 10. That being said, it's also worth looking at which country's units are making the most significant impact on such an excellent global performance.

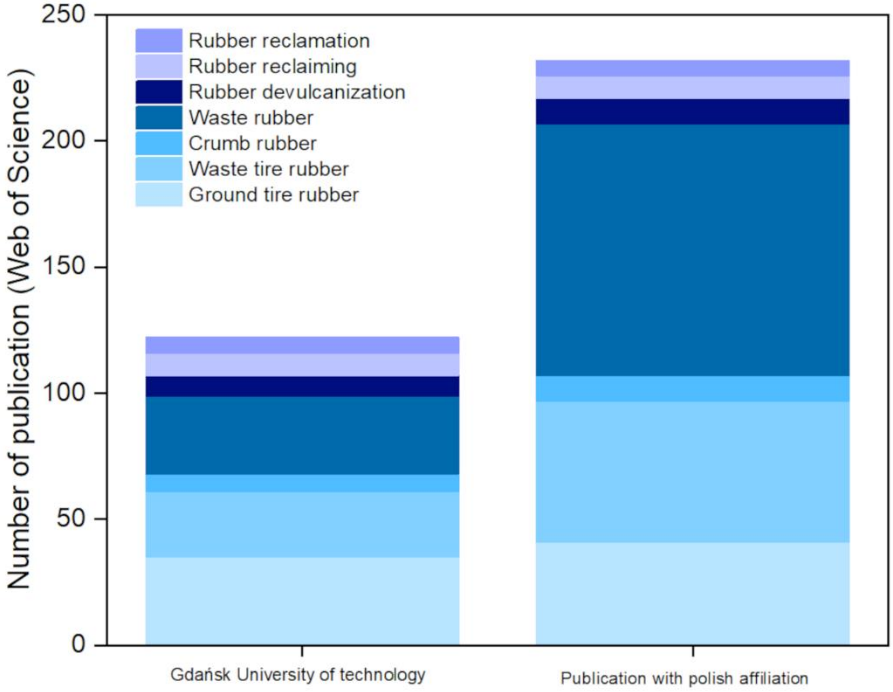


Figure 8. Contribution of the Gdańsk University of Technology to publications on rubber waste management.

Figure 8 shows the contribution of Gdańsk University of Technology to publications on rubber waste management, and it is approx. 52%. These data indicate that the Gdańsk University of Technology is a national leader in research on the management of waste tires, which is also confirmed by numerous projects carried out in this area.

2.4 Summary

An analysis of the available literature and reports on the subject, as well as publication trends, revealed:

- Existing waste tire management methods worldwide are heterogeneous and mainly focus on energy recovery, which does not fit into the ideology of sustainable development.

- Due to their cross-linked structure and complex composition, ELTs are challenging to recycle, and products based on them are of average or low quality, and the recycling process itself can be highly hazardous to human life.

- Management methods are mostly based on high temperature processes. This involves the risk of harmful compounds, including potentially carcinogenic ones, entering the atmosphere during the processing of ELT and the use of products based on this material.

- Existing scientific publications are mainly based on rubber waste management methods. However, many of them do not include such important information as: the impact of the process on the operators/work environment, the analysis of the starting raw material, or the cost-effectiveness of the process. Basic data are presented without highlighting the application potential. In the case of such materials, given the existing body of work, describing only basic parameters such as strength properties, hardness, sol fraction, degree of swelling is insufficient. The most important aspects in the reclaiming of waste rubber such as the influence of the reclaiming degree on the final properties of the product, the formation of blends and the influence of GTR on their characteristics, or the mechanism of the reclaiming process have already been understood. And despite so many works, there is still no ideal solution, significantly reducing the problem of ELT management. According to the author of the dissertation, this is due to: the lack of attempts to commercialize the results by many research groups (write a publication and leave the topic), the lack of reproducibility of the results, the inability to reproduce the process following the experimental description, and the lack of research that is relevant from the point of view of the entrepreneur and the recipient of the product.

The data and statements presented above are based on an extensive analysis of available literature in the form of scientific publications, statistical reports, my trend analysis, and professional experience (gained during research projects and commissioned studies). They are presented to provide the reader with the most relevant information on rubber waste management. They show that despite intensive work on improving the state of affairs, there are still a lot of inaccuracies related to the subject, and effective management of rubber waste, especially that coming from car tires, still requires a lot of work.

3. Aim of the research work

Objectives of the research work, conducted during the doctoral studies, include (i) development of GTR processing technology, allowing to obtain a product with satisfactory utility properties, (ii) development of research methodology on GTR-based products taking into account gaps in the current state of knowledge, (iii) evaluation of the impact of GTR processing on the environment, (iv) assessing the recycling potential of GTR-based products.

Due to the broad spectrum of research work, the following section will present published works on the issues mentioned above.

The following is a list of publications that were included as relevant to the dissertation. The contributions of specific authors are shown in each of the included publications.

- P1 - Zedler Ł., Przybysz-Romatowska, M., Haponiuk, J., Wang, S., Formela, K. (2020). Modification of Ground Tire Rubber—Promising Approach for Development of Green Composites. Journal of Composites Science, 4, 1-11. https://doi.org/10.3390/jcs4010002

Journal: Journal of Composites Science (IF: N/C, 20 points)

- P2 - Zedler Ł., Klein, M., Saeb, M., Colom, X., Cañavate, J., Formela, K. (2018). Synergistic Effects of Bitumen Plasticization and Microwave Treatment on Short-Term Devulcanization of Ground Tire Rubber. Polymers, 10(11), 1-17. https://doi.org/10.3390/polym10111265

Journal: Polymers (IF: 3.164 (publication year), 100 points)

- P3 - Zedler Ł., Kowalkowska-Zedler, D., Colom, X., Cañavate, J., Reza Saeb, M., Formela, K. (2020). Reactive Sintering of Ground Tire Rubber (GTR) Modified by a Trans-

Polyoctenamer Rubber and Curing Additives. Polymers, 12, 3018. https://doi.org/10.3390/polym12123018

Journal: Polymers (IF: 4.329 (publication year), 100 points)

- P4 - Zedler Ł., Kowalkowska-Zedler, D., Vahabi, H., Saeb, M., Colom, X., Cañavate, J., Wang, S., Formela, K. (2019). Preliminary Investigation on Auto-Thermal Extrusion of Ground Tire Rubber. Materials, 12, 1-16. https://doi.org/10.3390/ma12132090

Journal: Polymers (IF: 3.057 (publication year), 140 points)

- P5 - Zedler Ł., Burger, P., Wang, S., Formela, K. (2020). Ground Tire Rubber Modified by Ethylene-Vinyl Acetate Copolymer: Processing, Physico-Mechanical Properties, Volatile Organic Compounds Emission and Recycling Possibility. Materials, 13, 4669. https://doi.org/10.3390/ma13204669

Journal: Materials (IF: 3.623, 140 points)

Publication 1: Modification of Ground Tire Rubber—Promising Approach for Development of Green Composites

Article Summary

The objective of the research presented in this article was to improve the processability of GTR by adding bitumen, and to attempt reclamation and revulcanization with organic peroxides, taking advantage of their property to form free radicals.

Materials preparation

The samples were mechano-chemically modified at ambient temperature, within 10 min, using two-roll mills. During the process, GTR was modified with 10 phr of bitumen as a reactive plasticizer as well as two types of organic peroxides (0.5 and 2.0 phr). The type of bitumen was 100/150, and two commercialy available peroxides dicumyl peroxide (DCP), and di-(2-tert-butyl-peroxyisopropyl)-benzene (BIB) were used with two diffrent amounts (0.5, and 2.0 phr). As a reference sample pure GTR and GTR modified with bitumen were prepared and treated with the same manner. The obtained samples were compression-molded into 2-mm thick samples at 180 ◦C and 4.9 MPa according to the determined optimal cure time or (if not determined) for 5 min. For a better understanding of the obtained data, the reference sample of the unmodified GTR was prepared in the same conditions as the other samples

Methodology

- Curing Characteristics
- Physico-Mechanical Properties

Journal of
Composites Science

Article

Modification of Ground Tire Rubber—Promising Approach for Development of Green Composites

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Abstract: Ground tire rubber (GTR) was mechano-chemically modified using a road bitumen 100/150 and two types of organic peroxides: di-(2-tert-butyl-peroxyisopropyl)-benzene (BIB) and dicumyl peroxide (DCP). The impact of used additives on reactive sintering efficiency and physico-mechanical properties of modified GTR was investigated using oscillating disc rheometer measurements, followed by tensile tests and swelling behavior studies. It was found that the application of bitumen and both used peroxides (DCP/BIB) improves processing and reactive sintering efficiency better than untreated GTR. However, the results indicate that BIB is more prone to blooming on the surface of modified GTR, thus limiting (especially at higher content) its application as a modifier and promotor of GTR reactive sintering.

Keywords: waste tires; recycling; modification; reactive sintering

1. Introduction

The management and environmentally friendly recycling of waste rubbers has been a huge challenge for industry and scientists since the vulcanization process was invented [1–7]. One of the most problematic waste rubber to the environment is used tires, which constitute ~80% of total waste rubbers generated each year. Tires are high-quality products which must meet all safety requirements in order to be put into service. However, the outstanding properties of tires become problematic after the end of their service life. The reason behind this is the chemical and physical structure of vulcanized rubber, which does not decompose easily [8]. The cross-linked structure and the presence of unreacted curatives, additives and plasticizers make the waste rubber a serious threat to the environment, leading to the pollution of local surface and groundwater and fires [9], and their design is perfect for breeding sites for mosquitoes spreading diseases [10].

Without meaningful and industrially applied recycling methods, end-of-life tires (ELTs) are still commonly disposed of in landfills, which has been illegal in Europe since 2003 [11].

Among many existing recycling technologies of ELTs, energy recovery is still the most used method, which utilizes waste tires as an alternative fuel in cement kilns and power plants [12]. Even though this approach is extremely non-environmentally friendly, it is still acceptable to industries and governments due to the lack of a better solution to the rising problem. Under those circumstances, many attempts have been made to find an appropriate recycling method of ELTs.

Over the years, scientists have focused their efforts on reclaiming and modifying ground tire rubber (GTR) in order to obtain new products with unique properties or to apply the GTR as a filler

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or modifier in different polymer composites [13,14]. One of the industrially applicable solutions is the reactive sintering of GTR by applying high pressure and temperature [15]. The process can be done without additives and with the use of curing systems or adhesive binders. However, it should be noted that this method is limited to the production of low-cost products with simple shapes and low-quality requirements. In order to improve reactive sintering efficiency and further application of GTR, an interesting and promising approach seems to be modification or functionalization of GTR.

GTR reclaiming usually requires a high temperature, high shear forces and other specific conditions necessary for the essence of the process, which is the scission of cross-linking bonds. The control of the process parameters is essential to find a balance between selective scission of cross-linking bonds and the unwanted degradation of main polymeric chains, which affect the final properties of the obtained reclaimed rubber [16,17]. On the other hand, there are solutions to improve reclaiming efficiency, such as the application of reclaiming agents facilitating the process [18,19]. It must be pointed out that some of the commonly used agents are used as curing additives [20,21]. Following this logic, it is possible to apply peroxides as a source of free radicals. Those would allow the formation of new bonds between polymer chains, while perhaps simultaneously degrading the main polymeric chains.

Despite the application of a reclaiming agent, the processing of GTR may be still difficult. One of the solutions to enhance GTR processability during reclaiming is the application of low-cost plasticizers, such as heavy oils from pyrolysis of tires [22], disulfide oil [23] or bitumens [24]. The obtained results indicate that the plasticization of GTR allows the selective scission of cross-linked bonds, which has a beneficial influence on the mechano-chemical reclaiming efficiency as well as enhancing the processing of GTR.

However, to the best of our knowledge, there are no published data about the combined impact of plasticizer and curing additive on the efficiency of reactive sintering of GTR. In this work, GTR was mechano-chemically modified in the presence of bitumen and two types of organic peroxides. The effect of the applied treatment procedure on the reactive sintering of treated GTR was evaluated by curing characteristics and physico-mechanical properties.

2. Materials and Methods

2.1. Materials

GTR was kindly provided by Grupa Recykl S.A. (Śrem, Poland). The material was obtained by grinding used tires in ambient atmosphere (mix of passenger car tires and truck tires). The particle size distribution of the used GTR was determined by the sieve analysis. Seven sieves with different mesh sizes were chosen: 1.5 mm, 1.0 mm, 0.8 mm, 0.5 mm, 0.355 mm and 0.212 mm. The initial mass of the tested GTR was 100 g. The obtained results are presented in Figure 1. Road bitumen 100/150 with penetration at 25 °C: 100–150 (1/10 mm) and softening point: 39–47 °C was received from Lotos Asfalt Sp. z o.o. (Gdańsk, Poland). BIB and DCP were obtained from the Pergan Peroxides Company (Bocholt, Germany). The chemical structures and selected properties of used peroxides are presented in Figures 2 and 3 and Table 1.

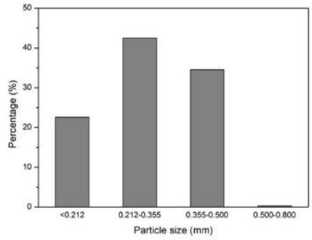

Figure 1. Particle size distribution of ground tire rubber (GTR).

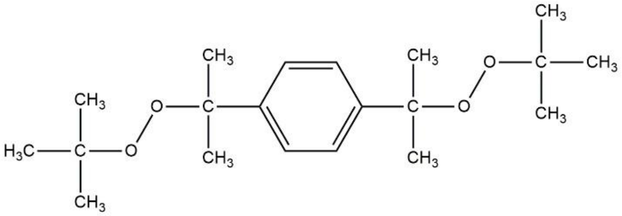

Figure 2. Chemical structure of di-(2-tert-butyl-peroxyisopropyl)-benzene (BIB).

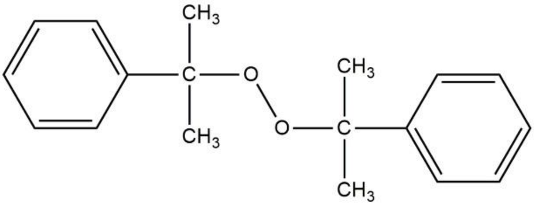

Figure 3. Chemical structure of dicumyl peroxide (DCP).

Table 1. Characteristics of used organic peroxides.

Name	Abbreviation	Active Oxygen (%) *	The Half-Life Temperature (°C) *
Di-(2-tert-butyl-peroxyisopropyl)-benzene	BIB	8.98	169
Dicumyl peroxide	DCP	5.80	162

* Datasheet from Pergan GmbH.

2.2. Sample Preparation

The compositions of the prepared samples is presented in Table 2. The samples were mechano-chemically modified at ambient temperature, within 10 min, using two-roll mills model 14201/P2 from Buzuluk (Komárov, Czech Republic). During the process, GTR was modified with 10 phr of bitumen as a reactive plasticizer as well as two types of organic peroxides, which are a source of free radicals allowing the formation of new bonds between polymer chains, while simultaneously possibly causing main chain degradation. The obtained samples were compression-molded into 2-mm thick samples at 180 °C and 4.9 MPa according to the determined optimal cure time or (if not determined) for 5 min. For a better understanding of the obtained data, the reference sample of the unmodified GTR was prepared in the same conditions as the other samples.

Table 2. The compositions and codings of the studied samples.

Components (phr)	Sample Code					
	GTR	GTR/B [a]	GTR/B$_{BIB0.5}$ [b]	GTR/B$_{BIB2.0}$ [b]	GTR/B$_{DCP0.5}$ [c]	GTR/B$_{DCP2.0}$ [c]
GTR	100	100	100	100	100	100
Bitumen 100/150	-	10	10	10	10	10
BIB	-	-	0.5	2.0	-	-
DCP	-	-	-	-	0.5	2.0

[a] B—10 phr of road bitumen 100/150; [b] BIBx—0.5 or 2.0 phr of BIB; [c] DCPx—0.5 or 2.0 phr of DCP.

2.3. Measurements

The vulcanization process of the prepared samples was investigated using a Monsanto R100S rheometer with an oscillating rotor (USA) in accordance with ISO 3417. In order to determinate the cross-linking rate, the cure rate index (CRI) was calculated according to the Formula (1):

$$CRI = \frac{100}{t_{90} - t_1} \tag{1}$$

where t_{90}—optimum vulcanization time (equal to 90% of maximal torque), min; t_1—scorch time (time equal to 1 dNm rise above minimal torque), min.

Determination of R_{300} parameter allowed to investigate the aging resistance of prepared samples at raised up temperature. R_{300} is calculated from the time at which torque reaches the maximum value (M_H) and it describes the percentage of reversion degree after period of 300 s [25]. It was calculated according to Formula (2):

$$R_{300} = \frac{M_H - M_{300s}}{M_H} \times 100\% \tag{2}$$

where M_H—maximum torque, dNm; M_{300s}—torque 300 s after maximum torque, dNm.

The tensile strength, elongation at break and modulus at 100% of elongation (M_{100}) were estimated in accordance with ISO 37. Tensile tests were carried out on the Zwick Z020 machine (Germany) at a constant speed of 500 mm/min. Direct extension measurements were conducted periodically using an extensometer with sensor arms. The reported results stem from at least five measurements for each sample. Shore hardness type A was assessed using a Zwick 3130 durometer (Germany) according to ISO 7619-1.

The density of the samples was measured based on the Archimedes method, as described in ISO 1183. Accordingly, all measurements were carried out at room temperature in methanol medium.

The swelling degree of sintered GTR samples (0.2 g) was estimated via a swelling test carried out in toluene at room temperature. The swelling degree was calculated according to Equation (3):

$$Q = \frac{m_t - m_o}{m_o} \times 100\% \tag{3}$$

where Q—swelling degree, %; m_t—mass of the sample swollen after time t, g; m_o—initial mass of sample, g.

Sol fraction was determined as the mass difference of sintered GTR before swelling (W_1) and after extraction (W_2), according to Equation (4):

$$\text{Sol fraction} = \frac{W_1 - W_2}{W_1} \times 100\% \tag{4}$$

3. Result and Discussion

3.1. Curing Characteristics

The effect of the road bitumen 100/150 and two types of peroxides (DCP/BIB) on curing characteristics of modified GTR samples is presented in Figure 4 and summarized in Table 3. According to the presented data, the reference sample and GTR modified with bitumen 100/150 do not show typical curing curves for the vulcanization process. This is due to the lack of any additional curing systems inside the composition, however, the addition of road bitumen shifts the curve to the lower torque values. This indicates that applied bitumen significantly influences processing properties, which is a critical aspect of GTR recycling and the quality of the product [26]. The lack of a typical curing curve is noticeable for GTR/$B_{DCP0.5}$, even though, for the same amount of BIB in GR/$B_{BIB0.5}$, the vulcanization process occurs. This is due to the structure of applied peroxides (Figures 2 and 3). BIB possesses the higher capability to creates free radicals (higher active oxygen content) causing the formulation of additional covalent bonds during reactive sintering, and the process itself can be detected even at a low concentration of the peroxide.

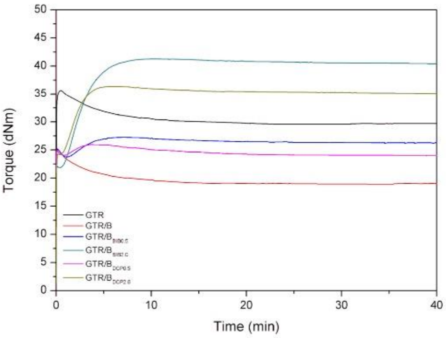

Figure 4. Curing curves of the studied samples (curing at 180 °C).

Table 3. Curing characteristics of modified GTR performed at 180 °C.

Properties	Sample Code					
	GTR	**GTR/B**	**GTR/B$_{BIB0.5}$**	**GTR/B$_{BIB2.0}$**	**GTR/B$_{DCP0.5}$**	**GTR/B$_{DCP2.0}$**
Minimal torque (dNm)	-	-	23.7	21.9	-	24.3
Maximal torque (dNm)	-	-	27.3	41.3	-	36.4
ΔM (dNm)	-	-	3.6	19.4	-	12.1
Scorch time (t_1, min)	-	-	3.0	1.2	-	1.2
Optimum cure time (t_{90}, min)	5	5	4.9	5.3	5	3.5
Cure rate index (CRI, min^{-1})	-	-	52.9	24.0	-	42.2
Thermal aging resistance (R_{300}, %)	-	-	1.5	0.6	-	1.6

It was observed that the increase of BIB caused a drop in minimal torque (ML) values (23.7 dNm to 21.9 dNm for GTR/B$_{BIB0.5}$ and GTR/B$_{BIB2.0}$, respectively). During the modification process, the peroxide was added to the GTR. High shear forces acting on the mixing sample could result in the formulation of free radicals, which enhance reclaiming and modification of GTR. A higher reclaiming degree results in a higher amount of low molecular compounds and a more disintegrated polymeric network, which translates into lower resistance (better processing) during the early stage of curing characteristics. Due to this, the minimal torque value decreased.

The ML value for GTR/B$_{DCP2.0}$ (24.3 dNm) is 2.4 dNm higher than GTR/B$_{BIB2.0}$. As mentioned previously, DCP has a lower capability to create free radicals than BIB, and as a result, the modification process was less efficient. M_H values correspond with stiffness and shear modulus of cross-linked samples, while the torque increment (ΔM) is correlated with their cross-link density [27]. It was observed that with an increasing amount of BIB, the M_H value increased (from 27.3 to 41.3 dNm, for GTR/B$_{BIB0.5}$ and GTR/B$_{BIB2.0}$, respectively) which was caused by the higher amount of used peroxide. The GTR/B$_{DCP2.0}$ was characterized with an M_H value lower than GTR/B$_{BIB2.0}$ (36.4 and 41.3 dNm, respectively) and ΔM (12.1 and 19.4 dNm, respectively), that only proves the lower efficiency of GTR modification and further reactive sintering in the presence of DCP than BIB.

The GTR/B$_{BIB0.5}$ and GTR/B$_{BIB2.0}$ were characterized by scorch time (t_1) (3.0 and 1.2 min, respectively) and optimum curing time (t_{90}) (4.9 and 5.3 min, respectively), the same as GTR/B$_{DCP2.0}$ (t_1—1.2 min and t_{90}—3.5 min). Interestingly, regardless of the curing additive applied, the scorch time (when 2.0 phr applied) was the same; however, due to the higher amount of active oxygen, the vulcanization process ends later (t_{90}) for GTR/B$_{BIB2.0}$.

All samples were also analyzed in terms of cure rate index (CRI) and thermal aging resistance (R_{300}). CRI shows how fast the studied sample was cured and the higher the value, the faster the process; however, this does not translate to the quality of the product and the efficiency of the process. In this case, CRI values for GTR/$B_{BIB0.5}$ and GTR/$B_{BIB2.0}$ were 52.9 and 24.0 min^{-1}, respectively. The process is shorter for GTR/$B_{BIB0.5}$, only due to the small amount of curing agent, which resulted in the later start of the process (t_1). In fact, the processes end at similar times (t_{90}) so the CRI values should always be analyzed with a critical view. The CRI value for GTR/$B_{DCP2.0}$ was 42.2 min^{-1} which is significantly higher than for GTR/$B_{BIB2.0}$. This is simply caused by the shorter vulcanization process influenced by the lower amount of created free radicals by DCP than BIB during the process. R_{300} is the lowest for GTR/$B_{BIB2.0}$ (0.6%), while for GTR/$B_{BIB0.5}$ and GTR/$B_{DCP2.0}$, the values are similar (1.5% and 1.6%, respectively). It is well known [28] that polymers with a higher cross-linked structure offer a higher thermal stability as it is harder to reduce the molecular weight due to the higher amount of bonds to break. While 2.0 phr BIB shows the best results in cross-linking than any of the studied samples (ΔM and swelling degree—chapter 3.2), the R_{300} parameter has the best value for GTR/$B_{BIB2.0}$.

3.2. Physico-Mechanical Properties

The physico-mechanical properties of the studied samples are summarized in Table 4. At first, it can be noticed that the application of road bitumen decreased the tensile strength (from 3.2 ± 0.1 to 2.6 ± 0.1 MPa for GTR and GTR/B, respectively), increases elongation at break (from 176 ± 6 to 206 ± 12% for GTR and GTR/B, respectively), decreased modulus at 100% of elongation (M100) (from 1.8 to 1.3 MPa for GTR and GTR/B, respectively) as well as decreasing hardness (from 58 ± 1 to 49 ± 1Sh A for GTR and GTR/B, respectively). Those changes are caused by the fact that the bitumen used acts as a plasticizer. In our previous studies [29], it was highlighted that in GTR, unreacted accelerators or other curing additives are present. During processing, those components can migrate within a sample, which facilitates the sintering process of GTR, resulting in a higher quality of the obtained revulcanizates. However, bitumen may capture migrating components as well as encapsulate GTR particles, decreasing cross-linking capability. Thus, as the amount of obtained cross-links is lower for GTR/B than GTR, the tensile strength, modulus at 100% and hardness decreases and at the same time, elongation at break increases.

Table 4. Physico-mechanical properties of modified GTR sintered at 180 °C.

Properties	Sample Code					
	GTR	**GTR/B**	**GTR/$B_{BIB0.5}$**	**GTR/$B_{BIB2.0}$**	**GTR/$B_{DCP0.5}$**	**GTR/$B_{DCP2.0}$**
Tensile strength (MPa)	3.2 ± 0.1	2.6 ± 0.1	3.1 ± 0.1	3.8 ± 0.2	3.0 ± 0.2	3.7 ± 0.1
Elongation at break (%)	176 ± 6	206 ± 12	170 ± 7	103 ± 6	206 ± 12	159 ± 15
M100 (MPa)	1.8	1.3	1.5	3.6	1.4	2.4
Hardness (Sh A)	58 ± 1	49 ± 1	55 ± 1	65 ± 1	57 ± 1	62 ± 1
Density at 25 °C (g/cm^3)	1.162 ± 0.010	1.142 ± 0.011	1.149 ± 0.012	1.18 ± 0.011	1.144 ± 0.010	1.149 ± 0.013
Swelling degree (%)	158 ± 5	175 ± 4	143 ± 4	107 ± 4	159 ± 3	130 ± 2
Sol fraction (%)	9 ± 1	17 ± 2	16 ± 1	14 ± 1	17 ± 1	15 ± 1

The analysis of physico-mechanical properties of GTR modified with the addition of peroxides shows that the tensile strength of the obtained sample is similar regardless of the chemical modifier applied (3.1 ± 0.1, 3.8 ± 0.2, 3.0 ± 0.3 and 3.7 ± 0.1 MPa for GTR/$B_{BIB0.5}$, GTR/$B_{BIB2.0}$, GTR/$B_{DCP0.5}$, and GTR/$B_{DCP2.0}$, respectively). However, the type of peroxide has a significant influence on elongation at break values (170 ± 7, 103 ± 6, 206 ± 12 and 159 ± 15% for GTR/$B_{BIB0.5}$, GTR/$B_{BIB2.0}$, GTR/$B_{DCP0.5}$, and GTR/$B_{DCP2.0}$, respectively). As curing characteristics indicated, samples cured with BIB were characterized by a more cross-linked structure, nevertheless, this phenomenon is not always desired. Creating too many cross-links might simply deteriorate the mechanical properties of a sample. An overly cross-linked structure is also confirmed by M100 values, as well as hardness. GTR/$B_{BIB2.0}$ shows a significantly higher M100 value than GTR/$B_{DCP2.0}$ (3.6 and 2.4 MPa, respectively) and hardness value

(65 ± 1 and 62 ± 1 ShA, respectively). For better visualization of the obtained results, strain–stress curves are presented in Figure 5. The density values do change significantly, only when the reference sample is compared to the rest of the test set (1.162 ± 0.01 to approx. 1.142–1.149 ± 0.01 g/cm^3). This is caused by the presence of 10 phr of the bitumen. It is worth mentioning that even though the curing curves were not recorded for GTR, GTR/B and GTR/B$_{DCP0.5}$ the properties of the samples are similar to those with curing curves (GTR and GTR/B$_{BIB0.5}$) or even better (GTR/B$_{DCP0.5}$ and GTR/B$_{BIB0.5}$). This is due to the processing parameters. The sintering process of GTR is based on high temperature and high pressure. Those conditions are enough to initiate the reclaiming process, followed by revulcanization [30]. With that, it is possible to obtain a product with satisfactory parameters using no or a low amount of curing additives. However, the revulcanization process without any curatives may be at such a low level that it is not recorded by the rheometer.

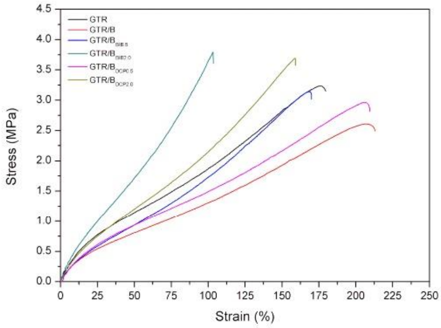

Figure 5. Stress–strain curves of modified GTR sintered at 180 °C.

In order to better understand the changes occurring inside the studied samples during reclaiming and reactive sintering processes, four chosen physico-mechanical properties were compared with the swelling degree and presented in Figure 6. The degree of swelling allows the estimation of the structural changes of sintered GTR caused by curing reactions. The simple comparison of swelling degree with other properties allows an easier understanding of factors affecting the obtained results. Figure 6A presents the relationship between swelling degree and tensile strength of the studied samples. The lower the swelling degree values, the higher the tensile strength values. Tensile strength is strictly connected with the amount of obtained cross-links during the curing process (more cross-links result in higher tensile strength) [31]. On the other hand, with more cross-links, it is more difficult to penetrate the structure of the sintered GTR with solvent, resulting in a lower swelling degree. In the case of elongation at break (Figure 6B), values rise with the increasing swelling degree. The strain of tested materials is connected with the type of matrix, the applied reinforcement and the possibility of polymer chains rotating and moving, which is partially dependent on the number of cross-links. Hardness, as well as tensile strength, are higher when the swelling degree decreases (Figure 6C), and it is also connected with the increase of the cross-linking degree. The sol fraction represents the loose macromolecules in the sample [32]. In the case of GTR, the sol fraction depends on the reclaiming degree, the number of unreacted additives and plasticizers. As can be noticed, the sol fraction of GTR (9 ± 1%) is visibly lower than the rest of the tested samples (17 ± 2, 16 ± 1, 14 ± 1, 17 ± 1 and 15 ± 1% for GTR/B, GTR/B$_{BIB0.5}$, GTR/B$_{BIB2.0}$, GTR/B$_{DCP0.5}$ and GTR/B$_{DCP2.0}$, respectively), which was caused by the presence of bitumen plasticizer extracted by the solvent during the measurement. In Figure 6D, the dependence of the swelling degree on the sol fraction is presented. Excluding the reference sample, the sol fraction is similar for every sample and the influence of peroxides on reclaiming degree and consequently, further sintering of GTR is interrupted by the presence of bitumen.

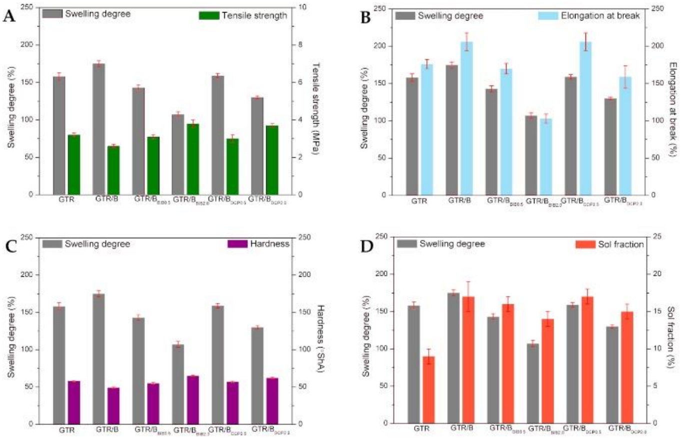

Figure 6. Comparison of swelling degree with: (**A**) tensile strength, (**B**) elongation at break, (**C**) hardness and (**D**) sol fraction of studied samples.

During the studies, in the case of GTR treated with 2.0 BIB, it can be noticed that 24 h after the revulcanization process, the blooming occurred, leaving yellowish powder on the surface. The FTIR analysis showed that the bloomed compound is BIB or BIB derivative (FTIR analysis not included in the article). The quality of the surfaces in terms of the type and amount of peroxides is presented in Figure 7. It must be highlighted that the application of any modifier, which results in blooming, must be studied further in order to find a proper replacement for the component or to establish new composition, preventing from blooming. The presence of easily removable powder on the surface comes with environmental risk (uncontrolled release to the environment) and may influence the health of workers dealing with that kind of material.

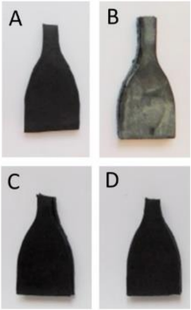

Figure 7. Appearance of the sample 24 h after reactive sintering: (**A**) GTR/$B_{BIB0.5}$, (**B**) GTR/$B_{BIB2.0}$, (**C**) GTR/$B_{DCP0.5}$, (**D**) GTR/$B_{DCP2.0}$.

4. Conclusions

In this study, GTR was reclaimed at low temperatures by applying mechano-chemical treatment via milling in the presence of road bitumen 100/150 and two types of peroxides: (i) di-(2-tert-butyl-peroxyisopropyl)-benzene and (ii) dicumyl peroxide. The influence of the amount and type of peroxides on the curing characteristics and physico-mechanical properties was evaluated. The results indicate that the application of bitumen as a plasticizer significantly improves the processing of GTR, which is one of the critical parameters for GTR recycling. Decreasing the amount of energy put into the process (lower forces on the motor due to the presence of bitumen) may result in a significant decrease in the processing cost. The type and amount of added peroxides have a notable influence on curing characteristics, as well as physico-mechanical properties; however, it is possible to obtain a product with satisfactory properties even though the curing curve was not recorded (GTR and GTR/$B_{DCP0.5}$). It was found out that the structure of peroxides plays an important role in cross-link creation, which is reflected in the physico-mechanical properties. As BIB poses a higher amount of active oxygen, creating more cross-links, the GTR modified with the peroxide was characterized by a similar tensile strength, lower elongation at break, higher modulus at 100%, a similar hardness, a lower swelling degree and slightly lower sol fraction compared to samples cured with DCP. Moreover, it was noticed that in sample GTR/$B_{BIB2.0}$, surface blooming occurred. The aforementioned characteristics of the obtained revulcanized GTR samples indicate that dicumyl peroxide is a better curative in terms of physico-mechanical properties as well as health and environmental issues (blooming).

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Conflicts of Interest: The authors declare no conflict of interest.

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Publication 2: Synergistic Effects of Bitumen Plasticization and Microwave Treatment on Short-Term Devulcanization of Ground Tire Rubber

Article Summary

In the study, GTR was mechano-chemically modified with road bitumen 160/220 and subsequently treated using microwave radiation. The course of the process and their effect on the test material were examined using the following methods

Materials preparation

GTR was processed at ambient temperature by means of two-roll mill. In order to improve the GTR processing during mechano-chemical devulcanization, GTR was modified with a variable content of bitumen (in the range of: 0–2.5 phr) as a reactive plasticizer. Low-temperature mechano-chemical treatment of GTR was performed using a high shear forces (small gap) for 10 min. The following two-roll mill settings were used: ambient temperature, friction equaled 1.08 and the gap width varied between 0.2 and 3 mm. The mechano-chemical treatment of GTR allows the formation of sheets with constant thickness (3 mm). The obtained sheets were cut into circular samples with constant weight (65 g), which were put directly on turn-table and subsequently treated by microwave radiation. The power of the magnetron oven was set up to 800 W.

Methodology

- Infrared Thermal Imaging Camera And Weight Loss
- Wavelength Dispersive X-Ray Fluorescence Spectrometry
- Static Headspace And Gas Chromatography-Mass Spectrometry
- Thermogravimetric Analysis Conjugated With Fourier-Transform Infrared Spectroscopy
- Curing Characteristics and Aging Resistance
- Static Mechanical Properties

polymers

MDPI

Article

Synergistic Effects of Bitumen Plasticization and Microwave Treatment on Short-Term Devulcanization of Ground Tire Rubber

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Abstract: Ground tire rubber (GTR) was mechano-chemically modified with road bitumen 160/220 and subsequently treated using a microwave radiation. The combined impact of bitumen 160/220 content and microwave treatment on short-term devulcanization of GTR was studied by thermal camera, wavelength dispersive X-ray fluorescence spectrometry (WD-XRF), static headspace, and gas chromatography-mass spectrometry (SHS-GC-MS), thermogravimetric analysis combined with Fourier transform infrared spectroscopy (TGA-FTIR), oscillating disc rheometer and static mechanical properties measurements. The obtained results showed that bitumen plasticizer prevents oxidation of GTR during microwave treatment and simultaneously improves processing and thermal stability of obtained reclaimed rubber.

Keywords: waste tire recycling; bitumen plasticization; microwave treatment; synergistic effects; structure-property relationships

1. Introduction

Dynamic development of the automotive industry is responsible for the continuous increase of post-production and post-costumer waste rubber. For example, a compact car contains around 60 kg of rubber, the tires constitute about 70% of the total rubber weight [1]. According to European Tyre Rubber Manufacturers Association statistics, in 2016, the production of tires in the European Union increased to 494 million tons (~25% of global production) with an approximate growth of 1% annually [2]. On the other hand, estimated data indicate that around 1000 million waste tires are discarded worldwide each year, more than 50% of them are directly discarded, landfilled or burned [3]. This presents a serious threat to the natural environment. Therefore, searching for new and pro-ecological reutilization methods of used tires and other waste rubbers is one of the biggest challenges of the 21st century waste management [4].

As mentioned above, nowadays, energy recovery is the most used method, which utilizes waste tires as alternative fuel in cement kilns and power plants [5]. The common acceptance to this solution is related mostly to economic factors because alternative industrial technologies are still in a low degree

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of development in order to provide competitive environmental-friendly utilization or "up-cycling" of waste tires.

In this context, during the last two decades, many attempts have been focused on laboratory applications of GTR. An option is to include GTR as a filler or modifier in different polymer composites, which were comprehensively reviewed in works of Karger-Kocsis et al. [6], Ramarad et al. [7], and Sienkiewicz et al. [8]. Another interesting approach is the valorization of waste rubber by reclaiming. This process, sometimes called in the literature as devulcanization, is related to the transformation of waste rubber using thermal, mechanical or chemical energy, in order to destroy the three-dimensional network of a cross-linked rubber. Compared to untreated waste rubber, the obtained reclaimed rubber can be easily processed, shaped, and vulcanized [9,10].

Waste rubber reclaiming is usually performed at high temperature, high shear forces, and specific conditions, which are necessary for the scission of cross-linking bonds present in rubber. The reclaiming conditions strongly affect the course of chemical degradation reactions, having an influence on the balance between pursued selective scission of cross-linking bonds and the undesired degradation of main polymeric chains, consequently determining the final properties of obtained reclaimed rubber [11–13].

According to recent literature, "green" reclaiming/devulcanization methods applied to GTR constitute a very promising approach to provide alternative utilization of waste rubber. Research studies in this field are usually focused on combining low temperatures and short time of processing. These conditions allow to reduce energy consumption and production costs while simultaneously prevent the emission of hazardous volatile organic compounds during GTR reclaiming [14–16]. Moreover, published data also indicates that lower temperature during GTR reclaiming allows the selective scission of cross-linking bonds. Additionally, limited degradation of the main polymeric chains enhances the mechanical properties of the resulting material [17,18]. Under these conditions, the possibility to meet the strict requirements of sustainable development for currently used reclaiming/devulcanization technologies is open, therefore, further research on this area is fully justified.

The main disadvantage of low-temperature reclaiming might be the technological problems related to the processing of GTR [19]. In order to overcome this limitation, the application of plasticizers suitable to increase flexibility or workability of GTR during low-temperature reclaiming has been proposed [20,21]. Another solution is applying a microwave treatment to GTR [22–24], which allows devulcanization of GTR in a short-time, affecting its structure, morphology, processing, and consequently its final performance properties. However, according to the our best knowledge, the studies regarding the combined effects of GTR bitumen plasticization and microwave treatment were not published so far.

In this work, GTR was mechano-chemically modified with road bitumen 160/220, which was used as reactive plasticizer. The modification was performed at ambient temperature using a two-roll mill, which allowed the generation of suitable shear forces on GTR and reduce energy consumption during the process. The obtained products were subsequently treated by microwave radiation. For better understanding of synergistic effects of bitumen plasticization and microwave treatment on short-term devulcanization of ground tire rubber (GTR), the impact of bitumen content (in the range of: 0–2.5 phr) on structure-properties of resulting materials was determined.

2. Materials and Methods

2.1. Materials

GTR with particles size below 0.5 mm was received from Grupa Recykl S.A. (Śrem, Poland). GTR was obtained by ambient grinding of used tires (mix of passenger car tires and truck tires). The particle size distribution of used GTR is presented in Figure 1. Road bitumen 160/220 with penetration at 25 °C: 170–210 (1/10 mm) and softening point: 35–43 °C was received from Lotos Asfalt Sp. z o.o. (Gdańsk, Poland).

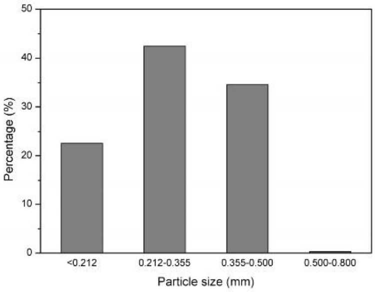

Figure 1. Particle size distribution of GTR.

2.2. Sample Preparation

2.2.1. GTR Modification and Microwave Treatment

GTR was processed at ambient temperature by means of two-roll mill model 14201/P2 from Buzuluk (Czech Republic). In order to improve the GTR processing during mechano-chemical devulcanization, GTR was modified with a variable content of bitumen (in the range of: 0–2.5 phr) as a reactive plasticizer. Low-temperature mechano-chemical treatment of GTR was performed using a high shear forces (small gap) for 10 min according to the procedure described in our patent application [25]. The following two-roll mill settings were used: ambient temperature, friction equaled 1.08 and the gap width varied between 0.2 and 3 mm. The mechano-chemical treatment of GTR allows the formation of sheets with constant thickness (3 mm). The obtained sheets were cut into circular samples with constant weight (65 g), which were put directly on turn-table and subsequently treated by microwave radiation using a domestic microwave R270W from Sharp (Osaka, Japan). The power of the magnetron oven was set up to 800 W. Preliminary investigations showed that reference sample (GTR without bitumen) cannot be treated with microwaves under these conditions for a period longer than 120 s, otherwise the material burnt. The ignition can be related to the evaporation of low molecular compounds and their inflammation. The microwave specific energy E (Wh/kg) during microwave treatment can be estimated by Equation (1):

$$E = \frac{P \times t}{m} \quad (1)$$

where: P—microwave power (W), t—radiation time (h), and m—weight of sample (kg).

Based on preliminary investigation results, for all studied samples microwave power (P = 800 W) and radiation time (t = 120 s) were assumed to be constant. These settings resulted in a received microwave specific energy equal to 410 Wh/kg. This value corresponds with data published by Seghar et al. [26], who used 440 Wh/kg as maximal microwave energy to perform controlled devulcanization of GTR.

The samples were coded as GTR+YB-MW, where Y means bitumen 160/220 (B) content. For example, GTR+2.5B-MW is a sample of GTR modified with 2.5 phr of bitumen 160/220, which was subsequently microwave-treated. GTR without prior bitumen modification and processed in the same conditions was used as a reference sample and coded as GTR-MW.

These samples were studied by the thermal camera, wavelength dispersive X-ray fluorescence spectrometry (WD-XRF), static headspace and gas chromatography-mass spectrometry (SHS-GC-MS) and thermogravimetric analysis combined with Fourier transform infrared spectroscopy (TGA-FTIR).

In order to evaluate the mechanical properties of the final product, the vulcanization process was carried out.

2.2.2. Vulcanization of Reclaimed GTR

In order to determine the combined impact of bitumen plasticization and microwave treatment on the curing behavior and performance properties of GTR after short-term microwave-induced devulcanization, the obtained samples were mixed with a sulfur curing system using two-roll mill from Buzuluk (Komárov, Czech Republic).

For all samples the same curing system was used. The composition in parts per hundred of rubber (phr) was: stearic acid 1.0; zinc oxide 2.5; TBBS (*N-tert*-butyl-2-benzothiazole sulfenamide) 0.35; sulfur 1.5.

The samples were shaped in sheets with 2 mm thickness and then cured in a electric heated press at 150 °C under a pressure of 4.9 MPa for the optimum vulcanization time (t_{90}) determined by an oscillating disc rheometer according to the ISO 3417 standard.

2.3. *Measurements*

Temperature distribution into reclaimed GTR after microwaves treatment was measured using a infrared thermal imaging camera model InfRec R300SR from NEC Avio Infrared Technologies (Tokyo, Japan). The characteristics of InfRec R300SR is presented in Table 1.

Table 1. Characteristics of InfRec R300SR infrared thermal imaging camera.

Item	Specification
Detector	Uncooled focal plane array (microbolometer)
Number of pixels	320 (H) × 240 (V) (Three edge lines of the screen is out of the specs)
Measuring range	0 to 500 °C
Spectral range	8 to 14 μ
Noise equivalent temperature difference (NETD)	0.3 °C (at 30 °C)
Temperature indicating accuracy	At ambient temperature over −15 to 50 °C: ±2 °C or ±2% of readings, whichever is greater
Instantaneous field of view	1.21 mrad
Field of view	22° (horizontal) × 17° (vertical), accuracy: ±10%
Frame time	60 Hz
A/D resolution	14 bit

Weight loss after microwave treatment of GTR was determined as the mass difference of samples before (W_1) and after treatment (W_2), according to Equation (2):

$$\text{Weight loss after microwave treatment} = \frac{W_1 - W_2}{W_1} \times 100\% \tag{2}$$

Temperature and weight loss after MW treatment of GTR were measured at least three times per sample and the obtained results are presented as median values.

The content of the elements in microwave treated GTR was determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) using a spectrometer S8 Tiger 1KW from Bruker (Billerica, MA, USA). Examined samples were put into dishes for powder studies on Prolen® foil with thickness 4 μm. Measurements were performed in a helium atmosphere.

Volatile organic compounds (VOCs) emitted from reclaimed GTR were determined using static headspace and gas chromatography-mass spectrometry (SHS-GC-MS). Measurements were performed using a Shimadzu GC2010 PLUS GC-MS (Shimadzu Corporation, Kioto, Japan) equipped with a split/splitless inlet. The GC-MS system was equipped with an AOC5000 Headspace Auto-Sampler. During analysis, the vial was transported by the injection unit from the tray to the agitator; when the sample achieved the equilibrium, the headspace sample of 2.5 mL volume was drawn from the vial and injected into the GC injector. The sampled vial was then returned by the injection unit to the tray. Conditions and parameters of SHS-GC-MS analysis are summarized in Table 2.

Table 2. The conditions and parameters of SHS-GC-MS analysis of reclaimed GTR.

Instrumental GC Analysis Parameters				
	Carrier Gas		Helium	
Inlet	Injector mode Split Ratio Flow Temperature		Split 10 2.0 mL/min 220 °C	
Oven	Column		DB-624 60m	
	Temp. (°C)	Rate (°C/min)	Final temp. (°C)	Hold (min)
	35	0	35	4.5
	35	10	200	-
	200	30	290	5
Mass Spectrometer	Solvent cut time Ion source temp. Interface temp. Scan range		5 min 220 °C 245 °C 35–350 *m/z*	
Headspace Parameters				
	Incubator temp Syringe temp Incubation time Injected volume		150 °C 160 °C 20 min 2.5 µL	

The thermal analysis of GTR after microwaves treatment was performed using the simultaneous TGA/DSC model Q600 from TA Instruments (New Castle, DE, USA). Samples of reclaimed GTR weighing approx. 10 mg were placed in a corundum dish. The study was conducted in an inert gas atmosphere—nitrogen (flow rate 100 mL/min) in the range from 25 to 800 °C with a temperature increase rate of 20 °C/min. Volatile products from thermal degradation of studied samples were also evaluated using a Fourier transform infrared spectroscopy (FTIR). During TGA/DSC measurements volatile degradation products were directed (using heated transfer line with temperature 220 °C) to Nicolet iS10 spectrometer from Thermo Scientific (Waltham, MA, USA). The presented solution allows "on-line" characteristics of volatile products during TGA/DSC measurements. The timing offset of FTIR spectra comparing to TGA curves is related with a volume of thermogravimetric apparatus chamber.

The curing process of reclaimed GTR samples was investigated at 150 °C, using a Monsanto R100S (Monsanto Company, St. Louis, MO, USA) rheometer with an oscillating rotor according to ISO 3417. Oscillation angle was 3° and torque range 0–100 dNm. Cure rate index values were calculated in accordance with the Equation (3):

$$\mathrm{CRI} = \frac{100}{t_{90} - t_2} \tag{3}$$

where: t_{90}—optimum vulcanization time, min; t_2—scorch time, min.

In order to determine the aging resistance of studied vulcanizates at elevated temperatures, R_{300} parameter was determined. R_{300} defines the percentage reversion degree after a period of 300 s calculated from the time of reaching maximum torque (M_H). R_{300} was calculated in accordance with Equation (4):

$$R_{300} = \frac{M_H - M_{300s}}{M_H} \times 100\% \quad (4)$$

where: M_H—maximum torque; M_{300s}—torque 300 s after maximum torque.

The tensile strength, elongation at break and modulus at 100% of elongation (M_{100}) were estimated in accordance with ISO 37. Tensile tests were performed on the Zwick Z020 machine (Zwick Roell Group, Ulm, Germany) at a constant speed of 500 mm/min. Direct extension measurements were conducted periodically using an extensometer with sensor arms. The reported results stem from five measurements for each sample. Shore hardness type A was estimated using Zwick 3130 durometer (Zwick Roell Group, Ulm, Germany) in accordance with ISO 7619-1.

3. Results and Discussion

3.1. Temperature Distribution and Weight Loss of GTR after MW Treatment

Figure 2 presents the temperature distribution into GTR after microwave treatment as a function of bitumen 160/220 content. The results determined by using an InfRec R300SR infrared thermal camera and weight loss of samples after MW treatment are summarized in Table 3. It was observed that maximal and average temperatures of reclaimed GTR gradually decreasing with higher bitumen content. Comparing to sample GTR-MW, application of 2.5 phr of bitumen 160/220 in sample GTR+2.5B-MW caused a decrease of maximal temperature and the average temperature by 89.6 °C and 35.1 °C, respectively. This phenomenon is related to lower carbon black content in studied materials due to partial substitution of GTR by bitumen, which affects the efficiency of Maxwell-Wagner polarization effect. The results of temperature distribution also indicate that during MW treatment bitumen acts as an insulator and protect GTR from uncontrolled oxidation and ignition, which resulted in lower values of weight loss after MW treatment (for about 62%) than GTR-MW sample (the exception was the sample with the smallest amount of bitumen). Additionally, it was found that using bitumen as a plasticizer has a beneficial impact on temperature distribution into reclaimed GTR compared to the reference sample (GTR-MW).

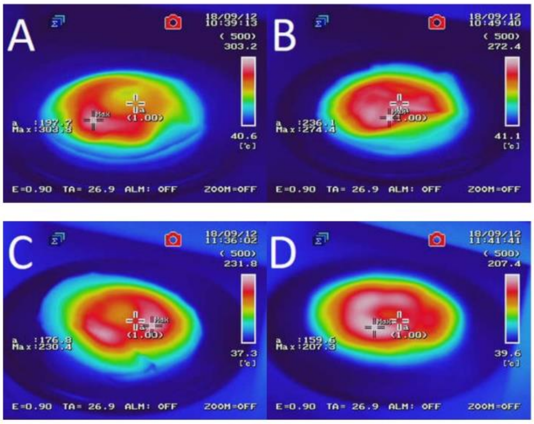

Figure 2. *Cont.*

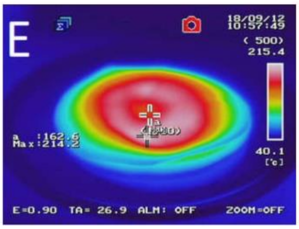

Figure 2. Temperature distribution measured with a thermal camera for sample: (**A**) GTR-MW; (**B**) GTR+0.25B-MW; (**C**) GTR+0.5B-MW; (**D**) GTR+1.0B-MW; and (**E**) GTR+2.5B-MW.

Table 3. Characterization of studied samples after MW treatment.

Item	Methodology	GTR-MW	GTR+0.25B-MW	GTR+0.5B-MW	GTR+1.0B-MW	GTR+2.5B-MW
Weight loss after MW treatment (%)	Analytical electronic balance	0.59	0.53	0.38	0.36	0.37
Average temperature of GTR after MW treatment (°C)	Thermal camera	197.7	236.1	176.8	159.6	162.6
Maximal temperature of GTR after MW treatment (°C)		303.8	274.4	230.4	207.3	214.2

3.2. WD-XRF Analysis of Reclaimed GTR

For a better understanding of this phenomenon, elemental analysis of studied materials was performed using wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) and the obtained results are presented in Table 4.

Table 4. WD-XRF analysis for studied samples.

Element (wt %)	Methodology	Untreated GTR	GTR-MW	GTR+0.25B-MW	GTR+0.5B-MW	GTR+1.0B-MW	GTR+2.5B-MW
Si	WD-XRF	1.72	1.88	2.66	2.66	2.55	2.90
S		1.91	1.33	1.97	1.86	1.91	2.16
Zn		2.33	1.12	1.55	1.58	1.65	1.68
Ca		0.38	0.40	0.62	0.58	0.61	0.62
Al		0.07	0.08	0.1	0.12	0.12	0.14
Mg		0.06	0.06	0.07	0.08	0.06	0.09
Fe		0.14	0.04	0.05	0.05	0.05	0.07

This non-destructive method allows rapid and quantitative determination of content of silicon (Si), sulfur (S), zinc (Zn), calcium (Ca), magnesium (Mg), aluminum (Al), and iron (Fe) in rubber compounds [27,28]. Miskolczi et al. [29], and recently Liang et al. [30], confirmed that the most intense signal from X-ray fluorescence spectrometry corresponds to zinc, and it is related to its high concentration in GTR. In the studied case the range is 1.22–2.33 wt %. It was noticed that Zn concentration significantly decreased after MW treatment compared to untreated GTR. This could be explained by partial thermal decomposition of zinc stearate (activator used during rubber compounding) present on the vulcanized rubber surface [31], which, according to the literature, occurs at around 250 °C.

Another strong signal detected by WD-XRF is related to sulfur, commonly used as a curing agent in rubber compounds. The results showed that sulfur concentration in studied samples was in the range of: 1.33–2.16 wt %. The lowest value was determined for GTR-MW sample, while the highest was found in case of the sample with 2.5 phr of bitumen (coded as GTR+2.5B-MW). Sulfur is responsible for the formation of cross-linking bonds during vulcanization. Therefore, its content could put some insight on cross-link density of studied samples. Based on this assumption, the sulfur content value indicates that scission of cross-linking sulfide bonds occurs more efficient for GTR-MW sample than for GTR+2.5B-MW sample. The measurements obtained by oscillating disc rheometer discussed later seem to confirm this statement. On the other hand, it should be pointed out that there is no simple correlation between sulfur content and cross-link density [30,32]. Higher sulfur content in the case of GTR samples modified with bitumen could also be explained by sulfur derivatives (such as hydrogen sulfide, carbon disulfide, etc.) present in the bitumen [33].

Silicon content determined by WD-XRF was in the range of 1.72–2.90 wt %, which corresponds with the presence of silica—commonly used as filler incorporated to tires in order to decrease their rolling resistance. Moreover, WD-XRF analysis detected Ca—0.38–0.62 wt %, Al—0.07–0.14 wt %, Mg—0.06–0.09 wt %, and Fe—0.04–0.14 wt %. It was found that microwave treatment of GTR did not affect the content of Si, Ca, Al, and Mg, while the concentration of Fe significantly decreased. This could be related to partial iron oxidation supported by microwave treatment. As could be observed, bitumen plasticization of GTR resulted in a higher content of Si, Ca, Al, Mg, Fe in GTR+2.5B-MW sample comparing to GTR-MW sample or untreated GTR. This phenomenon can be explained by possible migration of silica and other inorganic particles into GTR surface due to the higher mobility of polymer chains resulted from combined impact bitumen plasticizer and microwave treatment. Additionally, it should be mentioned that these elements can also be present in bitumen [34].

3.3. SHS-GC-MS Analysis of Reclaimed GTR

During further studies, we decided to estimate the impact of bitumen plasticizer content on the emission of volatile organic compounds (VOCs) during MW treatment. It is well known that VOCs have a negative impact on the environment, which might be a serious problem for novel technologies due to environmental regulations. However, assessment of VOCs released from polymers and recycled polymers as a function of variable processing conditions is rather poorly described in the literature [35–37]. Volatile organic compounds identified using a SHS-GC-MS method are presented in Table 5. Applied measurement conditions allows for determination of seven compounds: acetone (content in the range of: 1.5–2.5 mg/kg), methacrolein (0.5–0.9 mg/kg), 2-methylfuran (0.6–1.3 mg/kg), methyl vinyl ketone (0.9–1.6 mg/kg), methyl isobutyl ketone (3.9–8.3 mg/kg), cyclohexanone (1.6–2.4 mg/kg), and benzothiazole (6.5–7.9 mg/kg). Regardless of GTR treatment conditions, methyl isobutyl ketone and benzothiazole were determined in the highest concentration. Methyl isobutyl ketone is the main component during synthesis of antiozonant 6PPD—commonly applied in tires. Benzothiazole is the partial structure of vulcanization accelerators used during manufacturing of rubber compounds. Detection of benzothiazole corresponds to the presence of unreacted curing system or scission of sulfide cross-linking bonds presented in GTR.

Table 5. Volatile organic compounds determined using a SHS-GC-MS method.

Compound (mg/kg of Sample)	Untreated GTR	GTR-MW	GTR+0.25B-MW	GTR+0.5B-MW	GTR+1.0B-MW	GTR+2.5B-MW
Acetone	2.2	2.1	2.3	2.5	2.3	1.5
Methacrolein	0.9	0.5	0.7	0.6	0.7	0.5
2-methylfuran	1.3	0.6	0.9	0.8	0.9	0.6
Methyl vinyl ketone	1.6	0.9	1.3	1.0	1.3	0.9
Methyl isobutyl ketone	8.3	3.9	5.9	5.3	5.9	4.4
Cyclohexanone	2.4	1.6	2.2	1.9	2.2	1.8
Benzothiazole	6.5	6.9	7.9	7.6	7.9	7.6
Total content	23.2	16.5	21.2	19.7	21.2	17.3

The presence of ketones in reclaimed GTR indicates its partial oxidation during microwave treatment. Morand et al. [38] proved that methacrolein and methyl vinyl ketone are products formed during oxidation of polyisoprene, while other determined volatile compounds were also detected in natural rubber [39]. This suggests higher oxidation of natural rubber phase than synthetic rubber phase in GTR. Obtained results corresponds with observations described recently by Sousa et al. [40], who performed comprehensive studies of chemical modifications and thermo-oxidative degradation behavior of GTR as a function of the microwave radiation time.

Surprisingly, the highest total content of VOCs was determined for unmodified GTR, which could be related to SHS-GC-MS analysis conditions, because studied samples were pre-heated at 150 °C for 20 min (see Table 2). This could cause additional emission of VOCs from GTR. It should be also pointed out that formed VOCs could act like plasticizers [41], while their interactions with polymeric matrix could affect the results of SHS-GC-MS. Furthermore, it was observed that volatile organic compounds were omitted directly to the environment after MW treatment of GTR, which also affected the total content of VOCs in studied samples. These factors resulted in a lack of simple correlation between bitumen plasticizer content and determined VOC amounts.

3.4. TGA-FTIR Studies of Reclaimed GTR

Kleps et al. [42] and Scuracchio et al. [43] proved that thermogravimetric analysis (TGA) could be a useful analytical tool to estimate the changes in the chemical structure of reclaimed rubber. In this study, we expanded this methodology using TGA conjugated with FTIR, which allowed more detailed characterization of the chemical structure of reclaimed GTR. The curves of thermogravimetric analysis and derivative thermogravimetry (DTG) are presented in Figure 3.

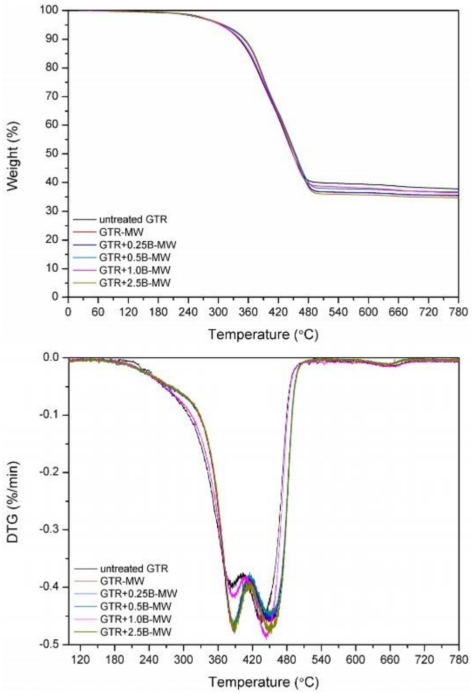

Figure 3. TGA and DTG curves of studied samples.

Thermal analysis was conducted in a nitrogen atmosphere and carried out to complete degradation of the organic components of the sample, in order to determine the stability of the samples and the amount of final residue. The obtained results are summarized in Table 6.

Table 6. Thermal decomposition characteristics of reclaimed GTR estimated from TGA data.

Sample	$T_{-2\%}$ (°C)	$T_{-5\%}$ (°C)	$T_{-10\%}$ (°C)	$T_{-50\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	Char Residues at 750 °C (%)
untreated GTR	258.5	304.3	341.3	448.6	384.8	434.4	40.0
GTR-MW	255.8	310.8	352.1	451.9	387.4	447.7	35.5
GTR+0.25B-MW	250.5	307.0	351.2	452.4	387.5	452.0	35.6
GTR+0.5B-MW	253.6	309.8	352.6	454.3	387.8	452.3	36.8
GTR+1.0B-MW	254.6	303.8	343.5	449.0	387.4	443.6	36.6
GTR+2.5B-MW	254.7	310.6	353.1	452.0	387.5	451.8	34.8

The data showed that $T_{-2\%}$ temperature, which corresponded to the 2% weight loss, was lower for the sample treated with microwaves (GTR-MW) than for untreated GTR. This is due to the reclaiming effect of the microwaves which cause scission of the chains and, subsequently, a higher amount of products susceptible to degradation at lower temperatures.

However, $T_{-5\%}$, $T_{-10\%}$, and $T_{-50\%}$ temperatures increased after the MW treatment. This phenomenon corresponds to the volatile degradation products generated by the scission of polymeric chains during MW reclaiming process. Partial evaporation of volatile compounds caused that the remaining material becomes more thermally stable after MW treatment.

Char residue results are in line with the usual contents of carbon black in GTR. After MW treatment char residues in GTR are lower, which is related to the elimination of low molecular weight compounds formed during the devulcanization. Garcia et al. [22] proved that carbon black present in GTR could adsorb low molecular volatile compounds generated during thermal degradation (barrier effect), and this phenomenon can improve thermal stability of reclaimed GTR.

The results showed that adding bitumen to the samples has three predominant effects. Firstly, according to the temperature measurements presented before, bitumen decreases the general temperature of the GTR after MW treatment, protecting and preserving its degradation. Secondly, bitumen acts as plasticizer that promotes the diffusion and elimination of low molecular weight compounds by improved mobility through the polymeric chains. Thirdly, factor affecting obtained results is the thermal stability of pure bitumen.

These effects are combined in the studied samples. When adding 0.25 phr bitumen, according to the temperatures determined by the thermal camera, the average temperature achieved was higher than in the case of GTR-MW. This amount of bitumen is insufficient to maintain the sample at a relatively low temperature. The effect of the MW treatment on this sample is similar to the sample without bitumen, therefore scission of chains are comparable. $T_{-2\%}$, decreases from 255.8 °C for sample GTR-MW) to 250.5 °C determined for sample GTR+0.25B-MW. This decrease is also related to the plasticizing effect that, as exposed above, favors migration of the low molecular weight degradation products and causes a higher weight loss at lower temperatures. The difference between these two samples at $T_{-5\%}$, $T_{-10\%}$, and $T_{-50\%}$ is not as large as in the case of $T_{-2\%}$. Once the low molecular compounds evaporate, the removal of the remaining components is not so favored by the plasticization. The progressive addition of bitumen to the GTR samples tend to increase the $T_{-2\%}$, $T_{-5\%}$, $T_{-10\%}$, and $T_{-50\%}$. For example, sample GTR+0.25B-MW has a $T_{-2\%}$ of 250.5 °C while the GTR+2.5B-MW sample presents a $T_{-2\%}$ of 254.7 °C. The increment of temperatures depends on the amount of bitumen, reaching a maximum when adding 2.5 phr.

According to the measurements performed with the thermal camera (see Table 3), the GTR+2.5B-MW sample achieved lower temperature after MW treatment than GTR+0.25B-MW sample or reference sample (GTR without bitumen). In this case, the bitumen acted as a protective agent (insulator) that preserves from degradation and consequently decreases the amount of volatile products emitted from the samples.

The third of the described effects is more evident in the case of GTR+2.5B-MW sample containing 2.5 phr of bitumen and predictably for samples with higher content of bitumen plasticizer. This effect is related to thermal degradation of bitumen. This plasticizer contains low molecular weight components that evaporate and degrade below 300 °C, and also some stable molecules that degrade over 400 °C. Those two facts are the cause of the shift of the decomposition temperatures ($T_{-10\%}$ and $T_{-50\%}$) of the GTR+2.5B-MW sample towards higher levels when compared to the GTR-MW sample.

Figure 4 shows DTG curves with two peaks corresponding to the two main components of GTR. The first one is related to the maximum rate of thermal degradation of NR around 390 °C and the second to styrene-butadiene rubber around 450 °C [44]. The relative intensity of the DTG peaks suggests that the impact of the MW treatment on the samples is different in the NR and SBR domains when bitumen is included. The relative difference of height of the peaks corresponding to NR and SBR is substantial in the case of the sample GTR-MW (without bitumen) while the difference in the relative height of the peaks of the sample GTR+2.5B-MW is smaller. Moreover, it was observed that a higher content of bitumen shifted T_{max2} towards higher temperatures, while T_{max1} values for GTR samples treated by MW were similar. This suggests that SBR domains are more preserved when adding bitumen, that would indicate that the distribution of bitumen on the GTR shows preference for SBR while the NR, less encapsulated by the bitumen is more affected by the MW treatment. This observation corresponds with the results of SHS-GC-MS, which confirms the formulation of volatile organic compounds related to natural rubber/polyisoprene decomposition.

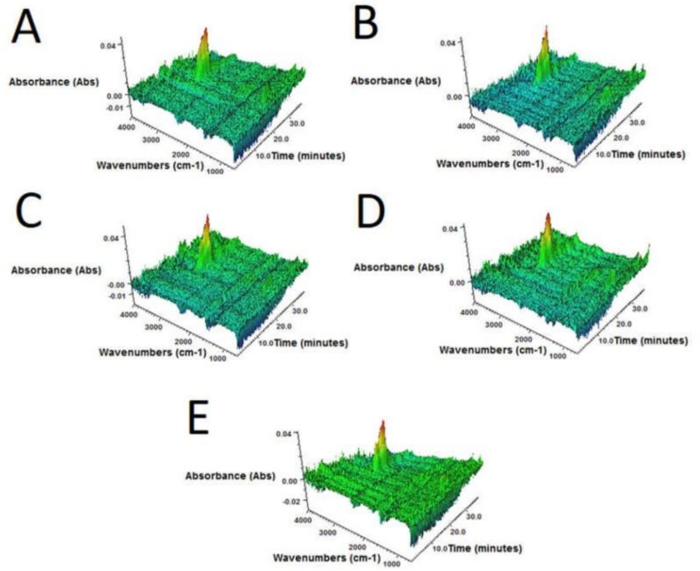

Figure 4. 3D FTIR plots determined for volatile products emitted during thermal decomposition of sample: (**A**) GTR-MW; (**B**) GTR+0.25B-MW; (**C**) GTR+0.5B-MW; (**D**) GTR+1.0B-MW; and (**E**) GTR+2.5B-MW.

3D FTIR spectra of volatile degradation products emitted during thermal decomposition of samples are present in Figure 4.

It was found that, regardless of bitumen content, for all samples 3D FTIR spectra were similar. The strongest absorbance bands, situated in the 2800–3000 cm^{-1} region were observed. These signals are attributed to the symmetric and asymmetric stretching vibrations of C–H bonds in CH_2 groups present in gaseous degradation products of GTR. This indicates that during slow pyrolysis (TGA in inert atmosphere), the main emitted products are aliphatic hydrocarbons, what corresponds with the literature data [45,46].

3.5. Curing Characteristics of Reclaimed GTR

The effect of bitumen plasticizer content on curing characteristics of microwave treated GTR is shown in Table 7. It was found that samples GTR-MW and GTR+0.25B-MW were characterized by the lowest minimal torque (M_L) value, 16.9 dNm, and 17.9 dNm, respectively. These results confirm that microwave treament of GTR enhances processing (M_L is strongly correlated with rubber compound viscosity) of the obtained reclaimed rubber. This is due to the high temperatures generated in these samples by the microwave treatment (maximal temperature respectively: 303.8 °C and 274.4 °C, Table 3), which induce scission of cross-linking bonds and cause partial degradation of the polymer main chains. The addition of 0.5 phr bitumen into GTR (sample GTR+0.5B-MW) resulted in a significant increase of M_L, around 40% compared to sample GTR+0.25B-MW. On the other hand, the application of higher bitumen content cause decrease of M_L, which confirms that the plasticization effect of GTR by bitumen occurs.

Table 7. Curing characteristics of tested samples.

Curing Characteristics at 150 °C	**GTR-MW**	**GTR+0.25B-MW**	**GTR+0.5B-MW**	**GTR+1.0B-MW**	**GTR+2.5B-MW**
M_L (dNm)	16.9	17.9	29.5	28.1	24.4
M_H (dNm)	40.9	40.4	51.0	48.9	46.0
ΔM (M_H-M_L) (dNm)	24	22.5	21.5	20.8	21.6
t_2 (min)	2.5	2.6	2.5	2.5	2.5
t_{90} (min)	11.6	11.2	11.5	11.6	12.3
CRI (min^{-1})	10.9	11.6	11.1	11.0	10.2
R_{300} (%)	0.3	0.1	0.1	0.3	0.5

For a better understanding of the synergistic effects of bitumen plasticization and microwave treatment on short-term devulcanization of GTR the relationship between minimal torque, the average temperature of GTR after MW treatment and $T_{-2\%}$ determined by TGA as a function of bitumen content is presented in Figure 5. It could be noticed, that higher content of bitumen (above 0.25 phr) resulted in a decrease of the minimal torque and the average temperature of GTR, while $T_{-2\%}$ parameter after MW treatment increased. These combined results, which are directly related, indicate that at the higher content of bitumen the plasticization effect of GTR is more prevailing than the consequences of the microwave treatment. In this case, bitumen acting as plasticizer preserve oxidation of GTR during the microwave radiation and simultaneously improves processing of reclaimed GTR.

Maximal torque corresponds with stiffness and shear modulus of vulcanized samples and torque increment (ΔM) is correlated with their cross-link density. The obtained results showed that samples with higher bitumen content have higher stiffness, which confirms that for these samples the microwave treatment had less influence than for sample GTR+0.25B-MW characterized by very a low content of bitumen. On the other hand, scorch time (t_2), optimal cure time (t_{90}), cure rate index (CRI), reversion degree (R_{300}) and torque increment (ΔM) of all studied samples were rather similar, some slight differences could be explained by the complex composition of GTR produced from waste tires.

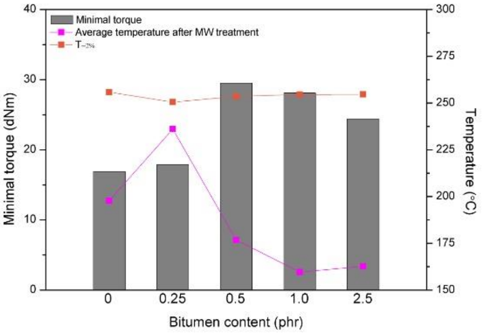

Figure 5. The relationship between minimal torque, average temperature after MW treatment of GTR and $T_{-2\%}$ determined by TGA as function of bitumen plasticizer content.

3.6. Static Mechanical Properties of Reclaimed GTR

Static mechanical properties of vulcanized reclaimed GTR are summarized in Table 8.

Table 8. Mechanical properties of tested samples.

Tensile Properties	GTR-MW	GTR+0.25B-MW	GTR+0.5B-MW	GTR+1.0B-MW	GTR+2.5B-MW
TS_b (MPa)	5.3 ± 0.7	5.9 ± 0.2	5.2 ± 0.8	6.1 ± 0.7	5.9 ± 0.7
E_b (%)	126 ± 15	139 ± 1	109 ± 5	138 ± 12	134 ± 13
M_{100} (MPa)	4.0	4.0	4.7	4.1	4.1
H (°Sh A)	64	63	67	67	65

As could be observed, all studied samples showed similar tensile properties, tensile strength (TS_b) in the range of: 5.2–6.1 MPa, elongation at break (E_b) 109–139%, modulus at 100% elongation (M_{100}) 4.0–4.7 MPa and hardness (H) 63–67° Sh A. This denotes a lack of simple correlation between bitumen plasticization effect and tensile properties of reclaimed GTR. The microwave treatment and bitumen plasticization of GTR result in partial devulcanization and degradation. Then, the obtained reclaimed GTR should be considered as a heterophase composite rather than a homopolymer matrix. Reclaimed GTR is formed by a gel fraction (cross-linked GTR particles that remain after the treatments) and sol fraction (the sum of the devulcanized, degraded and plasticized rubber phase). The formation of a network between cross-linked GTR particles and these different elastomeric chains present in the samples, could explain the slight differences in tensile properties observed for reclaimed GTR. Similar observations have been reported for polyethylene cross-linked waste [47,48]. In order to confirm these assumptions for GTR, tensile properties of obtained reclaimed GTR were compared with other reclaimed rubbers prepared by different methods, as presented in Table 9.

The results from literature showed that reclaimed GTR tensile strength presents a variation of 3.2–8.4 MPa, and elongation at break values are situated in a range comprised in 109–202%. The tensile properties of the studied materials correspond with these values. However, it should be mentioned that apart of the reclaiming method and GTR characteristics (particle size, composition), some other variables related to curing conditions (e.g., curing system, vulcanization settings) have a strong influence on the final performance properties of reclaimed rubber. These considerations have been highlighted in our previous work [54].

Table 9. Comparison of tensile properties of reclaimed GTR prepared by different methods.

Reclaiming Method	GTR (mm)	Tensile Properties of Reclaimed GTR		Ref.
		TS_b (MPa)	E_b (%)	
Bitumen plasticization/microwave treatment	0.50	5.2–6.1	109–139	This study
Bitumen plasticization at ambient temperature	0.80	3.3–5.5	154–194	[49]
Microbial desulfurization	0.05	3.3	191	[50]
Shearing in pan mill reactor	0.25	4.2–8.4	109–202	[51]
Grinding, ultrasonically treated, ozone/ultrasonically treated	0.50	3.2–5.1	135–160	[52]
Thermo-mechanical in counter- and co-rotating twin screw extruder	1.50	3.3–6.5	114–180	[53]

4. Conclusions

The synergistic effects of bitumen plasticization and microwave treatment on short-term devulcanization of GTR and structure-properties of obtained reclaimed GTR was investigated. The obtained results confirmed that bitumen plasticization of GTR affects the efficiency of microwave treatment and consequently short-term devulcanization course. It was found that during MW treatment bitumen acts as an insulator, which protects GTR from uncontrolled oxidation and ignition. Additionally, bitumen as plasticizer has a beneficial impact on temperature distribution after MW treatment of GTR and improved processing of obtained reclaimed GTR. Furthermore, in the studied conditions, the impact of bitumen plasticizer on performance properties of reclaimed GTR was negligible.

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Publication 3: Reactive Sintering of Ground Tire Rubber (GTR) Modified by a Trans-Polyoctenamer Rubber and Curing Additives

Article Summary

The proposed method of ground tire rubber (GTR) utilization involves the application of trans-polyoctenamer rubber (TOR), a commercially available waste rubber modifier. The idea was to investigate the influence of various curing additives (sulfur, N-cyclohexyl-2-benzothiazole sulfenamide (CBS), dibenzothiazole disulfide (MBTS) and di-(2-ethyl)hexylphosphorylpolysulfide (SDT)) on curing characteristics, physico-mechanical, thermal, acoustic properties as well as the morphology of modified GTR, in order to evaluate the possibility of reclaiming GTR and the co-cross-linking between applied components. As reference samples, a pure GTR and GTR modified by TOR without any chemical treatment were used. All samples were reclaimed using a two-roll mill and then reactively sintered according to the optimum curing time.

Materials preparation

Mechano-chemical reclaiming was conducted at ambient temperature utilizing the two-roll mills. The whole process time was set to 10 min and the application order and time of used components were as follows: GTR (start), TOR—Vestenamer 8012 (after 1 min), and curing additives (after 7 min). The following two-roll mills settings were used: ambient temperature, friction equaled 1.08 and the gap width varied between 0.2 and 3 mm. The GTR/TOR (100/10) samples were mixed with 5 different curing agents (Sulfur, S-80, CBS, MBTS, and SDT in amount 3.0, 3.75, 3.0, 3.75, and 6.0). The variable amount of additives in the presented composition results from the need to recalculate them so that the same amount of active compound (3 phr—parts per hundred rubber) is added to each sample. After the mastication samples were submitted to the revulcanization process by forming them into sheets with 2 mm thickness and cured in an electrically heated press at 180°C under the pressure of 4.9 Mpa according to the optimum cure time.

Methodology

- Curing Characteristics
- Fourier-Transform Infrared Spectroscopy
- Physico-mechanical properties
- Thermogravimetric Analysis
- Scanning Electron Microscopy
- Acoustic Properties
- Differential Scanning Calorimetry

polymers

MDPI

Article

Reactive Sintering of Ground Tire Rubber (GTR) Modified by a Trans-Polyoctenamer Rubber and Curing Additives

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Abstract: The proposed method of ground tire rubber (GTR) utilization involves the application of trans-polyoctenamer rubber (TOR), a commercially available waste rubber modifier. The idea was to investigate the influence of various curing additives (sulfur, N-cyclohexyl-2-benzothiazole sulfenamide (CBS), dibenzothiazole disulfide (MBTS) and di-(2-ethyl)hexylphosphorylpolysulfide (SDT)) on curing characteristics, physico-mechanical, thermal, acoustic properties as well as the morphology of modified GTR, in order to evaluate the possibility of reclaiming GTR and the co-cross-linking between applied components. The results showed that the presence of the modifier without the addition of curing additives hinders the physico-mechanical properties of revulcanized GTR. The addition of SDT, CBS, MBTS and sulfur change the melting kinetics of TOR, indicating partial degradation and/or co-cross-linking between components. In the studied conditions, the best mechanical properties were obtained by the samples cured with sulfur. The morphology analysis, combined with the physico-mechanical results, indicated that when the surface of the GTR is more developed, obtained by the addition of TOR, the properties of the GTR improve.

Keywords: ground tire rubber; modification; compatibilization; waste management; reclaiming; recycling

1. Introduction

The growing demand for tires, due to increasing consumerism and logistics solutions, contributes to the generation of an increase in waste rubber, which is structurally challenging to recycle [1,2]. Researches, and activities of national governments, have been undertaken for years in order to find appropriate solutions to treat this problematic material which presents a threat to the environment and human health [3]. Consequently, developing an environmentally friendly process for the disposal of waste tires is one of the most important tasks of the 21st century for state authorities, manufacturing companies, and scientists.

At present, the most applied method for waste rubber utilization is energy recovery [4]. The caloric value of a tire has been estimated at 32 MJ/kg, which is comparable with other types of fuels, such as coal, which has the caloric value at 26 MJ/kg [5]. However, compared to the energy required to produce

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one tire (87–115 MJ/kg) [3] the possible output of energy recovery from an end-of-life tire is quite low and a claim for a process that, instead of wasting generated energy, would allow the recycling and the preparation of products with satisfactory properties, suitable for industrial applications, has arisen.

A high number of published studies, covering the subject of waste rubber management, focus on specific recycling that uses ground tire rubber (GTR) as input material. The rubber in this form can be processed via methods that generate shear forces, transforming part of the material into sol by the scission of cross-links and main chains [6,7]. The product in this state can be more easily processed and vulcanized than raw GTR [8,9]. Its structure mostly consists of a sol fraction covering untouched rubber particles [10,11]. The ratio of rubber to a soluble part depends on the reclaiming method [12], which usually has a mechanical, physical, chemical, biological, or combined background. Such treatment produces not only scission of the cross-links and main chains, which translates to an improvement of flowability, but also oxidization of the surface, resulting in the appearance of hydroxyl groups [13]. This phenomenon can be used for the compatibilization of GTR with other matrices, such as polymers, bitumens, or concretes.

The application of GTR in a thermoplastic matrix is a well-known strategy among which blending, compatibilization via surface modification [14,15], and the use of functionalized block copolymers can be applied [16]. The idea of using GTR in thermoplastics has a very good economic and ecological basis, resulting from the assumption that every treatment of GTR should be cost-effective, while the final product is expected to have satisfactory properties. The fact that thermoplastics are one of the more economically viable plastics also encourages their use in GTR management technologies. However, the application of thermoplastics with GTR also has its limitations. As mentioned before, the plastic needs to be modified, and this results in additional costs connected to the treatment process. Moreover, increasing the content of GTR in many cases causes a deterioration of mechanical properties. In such a case, it is preferable to use a material with a good affinity for GTR.

Among commercially available products a trans-polyoctenamer rubber (TOR) can be found under the tradename Vestenamer 8012. It is a semicrystalline polyolefin additive with a high proportion of trans double-bonds, which is dedicated to waste rubber recycling. The additive plays two important roles in terms of GTR recycling. First, it acts as a plasticizer that helps the processing of the cross-linked waste rubber. Second, due to the presence of unsaturated bonds, it takes part in the vulcanization process that facilitates the cross-linking of the GTR and also the co-cross-linking between GTR and TOR [17].

The available literature reports and patents mainly concern the application of TOR in asphalt mixtures, to which GTR is added [18–20]. Arti et al. [21] investigated the influence of three types of peptizers: Vestenamer 8012, Aktiplast 8, and Rhenosin 145 on the mastication of natural rubber/butadiene rubber blends, proving that Vestenamer 8012 can significantly increase mechanical properties while optimizing the mastication process.

Wang et al. [22] prepared blends based on recycled PE (rPE) and GTR with GTR contents ranging from 0% up to 90%. Among the samples, several were selected and then modified by adding the commercially available copolymers Vestenamer 8012 and Engage 8180. The materials were melt blended via extrusion and injection molded to obtain specimens for tests. The mechanical properties of rPE/GTR (10/90) compatibilized with 9 phr of the cited copolymers showed significant superiority of Vestenamer 8012 (tensile strength approx. 2.1 MPa and elongation at break approx. 70%) over Engage 8180 (tensile strength approx. 0.9 MPa and elongation at break approx. 72.5%). The SEM analysis indicated that the addition of the mentioned copolymers had a positive effect on the morphology of the studied materials.

Herrmann et al. [23] modified GTR with mercaptobenzothiazole (MBT) and sulfur by compounding in a fluid mixer. The same modification was carried out melting GTR blended with TOR. Such treated waste rubber was mixed with a natural rubber/styrene-butadiene rubber blend (in ratio 70/30), including components typically used for truck treads, and then vulcanized at 155 °C. The physico-mechanical analysis indicated that the incorporation of modified GTR (regardless of the type of modification) did not improve the bonding between the matrix and the GTR particles (unmodified GTR—14.9 MPa, 426.6%; GTR/TOR—14.9 MPa, 436.1%; GTR/TOR/MBT—15.6 MPa, 430.0%; GTR/TOR/MBT/Sulfur—16.1 MPa; 421.8%). The authors also introduced modified GTR in a natural rubber matrix. The addition of the modified GTR caused a decrease in parameters, and any expected differences between the types of modified GTR (GTR, GTR/TOR, GTR/TOR/MBT, or GTR/TOR/MBT/sulfur) in the analyzed composition were possibly masked by the much stronger matrix of natural rubber.

All of the published studies used TOR as a compatibilizer between GTR and various matrices. However, according to our knowledge, there is no published report about the influence of curing additives on cross-linking and co-cross-linking of TOR and GTR.

In the presented work, GTR was mechano-chemically reclaimed in the presence of common curing additives used in the rubber industry: accelerators and two types of sulfur. The choice of using these systems without applying any other typical compounds generally included in the vulcanization, responds to the need for achieving a process to recycle GTR that must be as economically viable as possible. Moreover, it has been proven that, when preparing mixtures using waste rubber, there is a migration of unreacted components, including accelerators or plasticizers [24,25]. Therefore it is theoretically possible to carry out reclaiming and revulcanization processes using, for example, sulfur alone. The modified reclaimed rubbers have undergone a reactive sintering process, and the obtained revulcanizates were characterized by curing and swelling characteristics, tensile tests, hardness, density, Fourier-transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, acoustic properties, and differential scanning calorimetry.

2. Experimental

2.1. Materials

Ground tire rubber (GTR) was received from Grupa Recykl S.A. (Śrem, Poland). The particle size distribution of the used GTR is presented in Figure 1. The material was obtained by grinding at the ambient temperature of end-of-life tires (mix of passenger car tires and truck tires).

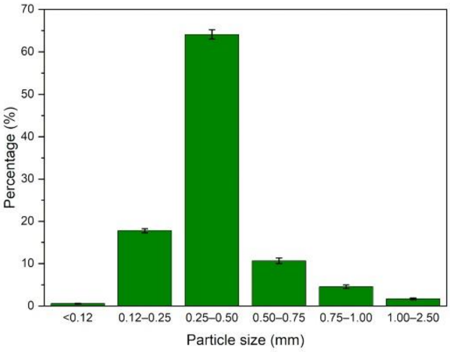

Figure 1. Ground tire rubber (GTR) particle size distribution.

Vestenamer® 8012 was provided by Evonik Resource Efficiency GmbH (Essen, Germany). According to the manufacturer, a small addition to a compound improves the mixing and processing of a sample. Moreover, it enhances the dispersion of difficult polymer blends, reducing the viscosity of the compound, and acts as a compatibilizer between different rubber types. Vestenamer 8012 is a trans-polyoctenamer rubber (TOR) whose characteristics are presented in Table 1.

Table 1. Characteristics of trans-polyoctenamer rubber (Vestenamer 8012) *.

Property	Mooney Viscosity ML(1 + 4) at 100 °C (MU)	Glass Transition Temperature (°C)	Melting Point (°C)	Crystallinity (%)	Thermal Degradation (°C)	Tensile Strength (MPa)	Elongation at Break (%)
Method	DIN 53 523	ISO 11357-1/-2	ISO 11357-1/-3	DSC (2nd heating)	TGA	ISO 527	ISO 527
Value	<10	−65	54	~30	275	8.5	400

* Information according to datasheet from the producer.

Sulfur was provided by Standard Sp. z o.o. (Poland, Lublin), while N-cyclohexyl-2-benzothiazole sulfenamide (CBS), dibenzothiazole disulfide (80%) dispersed in elastomer binder (20%) (Rhenogran® MBTS-80), di-(2-ethyl)hexylphosphorylpolysulfide (50%) dispersed in elastomer binder (50%) (Rhenogran® SDT-50) and sulfur (80%) dispersed in elastomer binder (20%) produced by Lanxess (Cologne, Germany).

2.2. Sample Preparation

Mechano-chemical reclaiming was conducted at ambient temperature utilizing the two-roll mills model 14201/P2 from Buzuluk (Komárov, Czech Republic). The whole process time was set to 10 min and the application order and time of used components were as follows: GTR (start), TOR—Vestenamer 8012 (after 1 min), and curing additives (after 7 min). The following two-roll mills settings were used: ambient temperature, friction equaled 1.08 and the gap width varied between 0.2 and 3 mm.

The composition of the obtained samples is presented in Table 2. The variable amount of additives in the presented composition results from the need to recalculate them so that the same amount of active compound (3 phr—parts per hundred rubber) is added to each sample. After the mastication samples were submitted to the revulcanization process by forming them into sheets with 2 mm thickness and cured in an electrically heated press (PH-90, Nysa, Poland) at 180 °C under the pressure of 4.9 MPa according to the optimum cure time determined as stated in ISO 3417 standard. To make it simple, special coding of tested samples was used according to GTR/TOR^X where GTR is a ground tire rubber, TOR stands for Vestenamer 8012 and X stands for applied curing agent/accelerator.

Table 2. The composition and coding of studied samples.

Components (phr)	Sample Code						
	GTR	GTR/TOR	GTR/TOR^S	GTR/TOR^{CBS}	GTR/TOR^{MBTS}	GTR/TOR^{SDT}	GTR/TOR^{S80}
GTR	100	90	90	90	90	90	90
TOR	-	10	10	10	10	10	10
Sulfur	-	-	3	-	-	-	-
CBS	-	-	-	3	-	-	-
MBTS-80	-	-	-	-	3.75	-	-
SDT-50	-	-	-	-	-	6	-
S-80	-	-	-	-	-	-	3.75

2.3. Measurements

The vulcanization process of prepared samples was investigated via a Monsanto R100S rheometer with an oscillating rotor (Monsanto Company, St. Louis, MO, USA) in accordance with ISO 3417. In order to determine the cross-linking rate, the cure rate index (CRI) was calculated according to Formula (1) [26]:

$$\mathrm{CRI} = \frac{100}{\mathrm{t}_{90} - \mathrm{t}_2} \tag{1}$$

where: t_{90} is the optimum vulcanization time, min and t_2 is the scorch time, min.

Determination of the R_{300} parameter led to investigation of the aging resistance of prepared samples at a raised temperature. R_{300} is calculated from the time at which torque reaches the maximum value ($M_{max.}$) and it describes the percentage of reversion degree after a period of 300 s [27]. It was calculated according to the Formula (2):

$$R_{300} = \frac{M_{max} - M_{300}}{M_{max}} \times 100\% \quad (2)$$

where $M_{max.}$ is the maximum torque, dNm and M_{300s} is the torque 300 s after the occurrence of the maximum torque, dNm.

The tensile strength and elongation at break were estimated in accordance with ISO 37. Tensile tests were carried out on the Zwick Z020 machine (Ulm, Germany) at a constant speed of 500 mm/min. Direct extension measurements were conducted periodically using an extensometer with sensor arms. The reported results stem from five measurements for each sample. Shore hardness type A was assessed using the Zwick 3130 durometer (Ulm, Germany) according to ISO 7619-1.

Based on the Archimedes method, explained in ISO 1183, the density of the vulcanized samples was determined. Measurements were carried out at room temperature in a methanol medium, without exception.

The swelling degree of vulcanized samples (0.2 g) was estimated via a swelling test carried out in toluene at room temperature. The swelling degree was calculated according to Equation (3):

$$Q = \frac{m_t - m_0}{m_0} \times 100\% \quad (3)$$

where Q is the swelling degree, %; m_t is the mass of the sample swollen after time t, g; and m_0 is an initial mass of the sample, g.

Sol fraction was calculated in accordance with formula (4):

$$\text{Sol fraction} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (4)$$

where: W_1 is a mass of the vulcanized sample before swelling, g; and W_2 is the mass of the vulcanized sample after extraction, g.

Acoustic properties were measured using a two-microphone impedance tube Brüel and Kjaer type 4206 (Darmstadt, Germany) in the frequency range 100–6500 Hz, according to ISO 10534-2, which describes the test method for impedance and absorption of acoustical materials using a tube, two microphones and a digital frequency analysis system. The sound absorption coefficient (α) is defined as the ratio of energy absorbed by the sample (E_a) to the total incident energy acting on the sample energy (E_i) on a sample, as presented in equal (5):

$$\alpha = \frac{E_a}{E_i} = 1 - \left(\frac{n-1}{n+1}\right)^2 \quad (5)$$

where the parameter n parameter is correlated to the ratio between the measured maximum (p_{max}) and the minimum (p_{min}) sound pressure inside the tube, as shown in the Equation (6):

$$n = \frac{p_{max}}{p_{min}} \quad (6)$$

The morphology of GTR and reclaimed GTR was characterized by a JEOL 5610 scanning electron microscope (Tokyo, Japan). Before the analysis, samples were coated with a thin layer of gold.

The FTIR spectra were measured in the range of 4000 to 650 cm^{-1} with a Nicolet iS50 FT-IR spectrometer (Waltham, MA, USA) equipped with the Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory. Spectral analysis was controlled by the OMNIC software package version 9.8.372.

The thermal analysis of GTR and modified GTR was performed using TGA (thermogravimetric analysis) model TG 209F3 from the Netzsch Group (Selb, Germany). Samples were weighed to approx. 10 mg and placed in a corundum pan. The study was conducted in an inert gas atmosphere containing nitrogen (flow rate of 20 mL/min) in the range from 35 to 820 °C with a heating ramp of 20 °C/min.

The thermal behavior and crystallization of the samples were measured by differential scanning calorimetry (DSC). The measurement was carried out on a DSC 204 F1 Phoenix apparatus (Netzsch Group, Selb, Germany). Samples of approx. 9 to 10 mg were placed in an aluminum pan and heated from 20 °C up to 250 °C at the rate of 10 °C/min. The cooling was carried out from 250 to −80 °C at the rate of 10 °C/min; subsequently, materials were heated a 2nd time from −80 to 250 °C at the rate of 10 °C/min.

3. Results and Discussion

3.1. Curing Characteristics

The effect of used additives on the curing characteristics of GTR modified with TOR is presented in Figure 2 and summarized in Table 3. As can be seen for samples GTR and GTR/TOR the curing data were not recorded. This is due to the fact that those samples do not contain any cross-linking supporting components. It is well-known [28,29] that during the compounding of GTR, the shear forces acting on the material not only cause the scission of polymeric chains and/or cross-links but also support migration of unreacted components (for example sulfur or accelerators) and carbon black from the ground tire rubber to another polymeric matrix or within the waste material itself. This phenomenon could influence the curing of GTR and GTR/TOR and the results in a typical curing curve course. However, the amount of released components is too small, being impossible to observe the differences in curing behavior by an oscillating disk rheometer. For further analysis of those samples, the curing time was set to 5 min. For other studied materials, the curing took place and the most crucial parameters were measured and listed in Table 3.

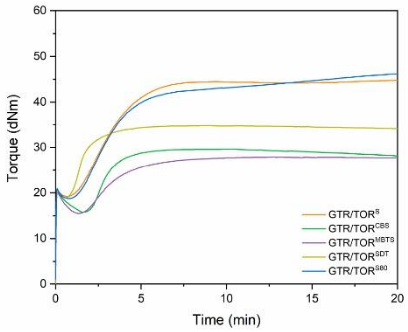

Figure 2. Curing curves of studied samples performed at 180 °C.

Table 3. Curing characteristics of studied samples performed at 180 °C.

Properties	GTR	GTR/TOR	GTR/TOR^{S}	GTR/TOR^{CBS}	GTR/TOR^{MBTS}	GTR/TOR^{SDT}	GTR/TOR^{S80}
Minimal torque (dNm)	-	-	19.2	15.8	15.5	18.9	18.7
Maximal torque (dNm)	-	-	44.5	29.7	27.9	34.8	41.6
ΔM (dNm)	-	-	25.3	13.9	12.4	15.9	22.9
Scorch time (min)	-	-	1.5	2.3	2.2	1.1	1.5
Optimum cure time (min)	5.0	5.0	4.6	4.5	6.3	3.4	4.2
Cure rate index (min^{-1})	-	-	31.9	44.6	24	42.7	38
Thermal aging resistance (%)	-	-	0.7	2.1	0.5	0.9	−3.5

Minimal torque ($M_{min.}$) is a value that gives the first insight into the processing of a sample. The lower the $M_{min.}$, the better are the processing properties of the sample. In this case, the value depends on the type of applied agent and decreases as follows: 19.2 dNm (S), 18.9 dNm (SDT), 18.7 dNm (S80), 15.8 dNm (CBS) and 15.5 dNm (MBTS). During compounding, high shear forces are generated, which favors rubber reclaiming. The presence of some chemical agents may enhance the effect [30]. If an applied agent can create free radicals and has an affinity to the sulfur, as do typical commercially available rubber vulcanization accelerators, they produce a more effective reclaiming and hence, better processing; for example, tetramethyl thiuram disulfide (TMTD) or even CBS or MBTS. This is reflected in the presented results, where the lowest values were obtained for the mentioned accelerators, while the highest was observed for sulfur. The small difference between S and S80 may result from the fact that S80 is dispersed in an elastomeric binder. Regarding GTR/TOR^{SDT}, the minimal torque is rather high compared to CBS and MBTS, even though it is a commercially used accelerator and reacts as a sulfur donor. It may be that during the sample preparation the revulcanization process partially occurred. Those assumptions are supported with the scorch time and optimum cure time results, which are the lowest for the SDT sample (1.1 and 3.4 min, respectively).

The maximal torque ($M_{max.}$) value, which translates to the stiffness of a material, differs significantly depending on the accelerator type and decreases as follows: 44.5 dNm (S), 41.6 dNm (S80), 34.8 dNm (SDT), 29.7 dNm (CBS) and 27.9 dNm (MBTS). The same trend is noticeable for torque increment (ΔM) (25.3 dNm, 22.9 dNm, 15.9 dNm, 13.8 dNm, and 12.4 dNm for S, S80, SDT, CBS, and MBTS, respectively. This shows how efficient, in the case of revulcanization, is every particular component.

Samples cured with sulfur (GTR/TOR^{S} and GTR/TOR^{S80}) show scorch and optimum cure times similar to each other (1.5 and 4.6 min scorch and 4.2 min optimum cure time, respectively). For samples cured with sulfur, the inversion was noticed. This means that after reaching the alleged maximum torque, set by the software, additional reactions took place. This phenomenon has been confirmed using the DSC method and commented later in the manuscript.

In the case of the accelerators applied, the scorch time was 2.3, 2.2 and 1.1 min and the optimum cure time was 4.5, 6.3, and 3.4 min, respectively, for GTR/TOR^{CBS}, GTR/TOR^{MBTS}, and GTR/TOR^{SDT}. In general, the vulcanization of rubber only with a help of an accelerator is rather limited in the absence of sulfur. However, it can happen when a high temperature, close to the decomposition temperature of the accelerator, is applied. The processing of GTR, especially when it is not highly reclaimed, is limited and requires high temperature and high pressure, which favors revulcanization solely with the presence of an accelerator. The difference between the obtained results is mainly due to the type of decomposition products and their vulcanization mechanics e.g., CBS decomposes under high temperature (205 °C) to 2-bisbenzothiazole-2,2′-disulfid (MBTS), 2-bisbenzothiazole-2,2′-polysulfides (MBTP), 2-bisbenzothiazole-2,2′-monosulfide (MBTM), 2-mercaptobenzothiazole (MBT), and N-cyclohexylamino-2-benzothiazol polysulfides (CBP) and 2-N-cyclohexylaminobenzothiazole (CB) [31]. Upon prolonged heating, only MBT and CB remain. Even though the revulcanization process takes place at 180 °C (which is lower compared to the decomposition temperature of CBS), high pressure is applied, which compensates for the temperature difference resulting in the creation of the aforementioned CBS decomposition products. The difference in the type of the products shifts the time required to obtain a material with optimal properties, which is visible when the optimum curing time of GTR/TOR^{CBS} is compared to GTR/TOR^{MBTS} (4.5 and 6.3 min, respectively).

The parameter R300 for the tested samples was 0.7, 2.1, 0.5, 0.9, and −3.5% for GTR/TOR^{S}, GTR/TOR^{CBS}, GTR/TOR^{MBTS}, GTR/TOR^{SDT}, and GTR/TOR^{S80}, respectively. The parameter was not determined for GTR and GTR/TOR due to the fact that for these samples the cross-linking efficiency cannot be measured by an oscillating disc rheometer. The negative value for GTR/TOR^{S80} is due to the fact that the sample additionally cross-links after reaching maximum torque; this is explained in the further parts of the manuscript (DSC).

3.2. FTIR Analysis

The FTIR spectra of studied samples are presented in Figure 3. The analysis of obtained results shows that there are no significant differences between specimens. The bands of C–H bonds of CH_2 groups existing in the aliphatic chains of elastomers are located at 2915 cm^{-1} and 2850 cm^{-1}. The peak at approx. 1437 cm^{-1} is associated with C–H bonds of $–C=CH_2$, while the band at approx. 1367 cm^{-1} can be connected with C–H bonding of the $–CH_3$ groups. As can be noticed, the intensity of those two bands is rising with the presence of TOR, which is rather an obvious output due to its structure. The same phenomenon occurs also for band 965 cm^{-1}, which corresponds to a trans-C–H out-of-plane bend. Another interesting band that appears due to the presence of TOR in the GTR/TOR compounds is at 700 cm^{-1} that is assigned to the cis-C–H out-of-plane bend. The band at 807 cm^{-1} corresponds to the skeletal vibration of C–C bonds. In the range of 1100 cm^{-1} to 880 cm^{-1}, C–O–C bonding as well as S=O, C–C, and C–O bonds are present, which are detected due to the structure of applied components and their transformation (oxidation of GTR, revulcanization etc.). The presented results indicate that the chemical structure of modified GTR has not changed regardless of the presence of TOR and/or a curing agent, or that these changes are too small to be observed by the FTIR technique.

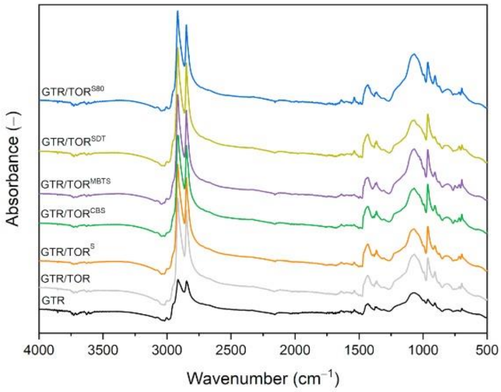

Figure 3. FTIR spectra of the studied compounds.

3.3. Physico-Mechanical Properties

The physico-mechanical properties of studied samples are presented in Table 4. For a better presentation of the results, the strain–stress curves are shown in Figure 4. Samples without cross-linking additives, coded as GTR and GTR/TOR, were prepared in the same manner as the others, while the curing time was set for 5 min. The results for tensile strength and elongation at break are as follows: 3.1 ± 0.1 MPa (GTR), 2.4 ± 0.2 MPa (GTR/TOR), 5.5 ± 0.3 MPa (GTR/TOR^{S}), 3.5 ± 0.3 MPa (GTR/TOR^{CBS}), 3.3 ± 0.2 MPa (GTR/TOR^{MBTS}), 4.7 ± 0.3 MPa (GTR/TOR^{SDT}), 5.8 ± 0.4 MPa (GTR/TOR^{S80}) MPa and 198 ± 3% (GTR), 111 ± 13% (GTR/TOR), 167 ± 8% (GTR/TOR^{S}), 128 ± 14% (GTR/TOR^{CBS}), 132 ± 11% (GTR/TOR^{MBTS}), 164 ± 8% (GTR/TOR^{SDT}) and 186 ± 5% (GTR/TOR^{S80}). The addition of TOR caused a drastic drop in tensile strength and elongation at break values for approx. 23% and 44% compared to unmodified GTR. This shows that the addition of TOR, without any chemical treatment, has a negative impact on the final tensile properties. The absence of any curing agent prevents chemical reclaiming, cross-linking of TOR, and any co-cross-linking between GTR and TOR. The presence of the uncured component disrupts the sintering process of GTR, so the properties of GTR/TOR are the combined results of the hampered sintering process and uncured TOR (proved by the increase of sol fraction), which has resulted in a lower tensile strength and elongation at break than those of GTR. The possibility of a lack of compatibility with the matrix was ruled out by SEM analysis (see subchapter 3.5). The change of M100 (1.6 ± 0.1 to 2.2 ± 0.1 MPa), hardness (56 ± 1 to 68 ± 1 Shore A), density (1.178 ± 0.002 to 1.145 ± 0.008 g/cm^3), swelling degree (163.5 ± 3.2 to 172.1 ± 4.2%), and sol fraction (10.5 ± 0.1 to 20.5 ± 0.5%), with the addition of TOR, results from the characteristics of the modifier.

Table 4. Physico-mechanical properties of the studied samples.

Properties	GTR	GTR/TOR	GTR/TOR^S	GTR/TOR^{CBS}	GTR/TOR^{MBTS}	GTR/TOR^{SDT}	GTR/TOR^{S80}
Tensile strength (MPa)	3.1 ± 0.1	2.4 ± 0.2	5.5 ± 0.3	3.5 ± 0.3	3.3 ± 0.2	4.7 ± 0.3	5.8 ± 0.4
Elongation at break (%)	198 ± 3	111 ± 13	167 ± 8	128 ± 14	132 ± 11	164 ± 8	186 ± 5
M100 (MPa)	1.6 ± 0.1	2.2 ± 0.1	3.3 ± 0.1	2.8 ± 0.1	2.7 ± 0.1	3.0 ± 0.1	3.2 ± 0.1
Hardness (Shore A)	56 ± 1	68 ± 1	72 ± 1	72 ± 1	70 ± 1	71 ± 1	72 ± 1
Density (g/cm^3)	1.178 ± 0.002	1.145 ± 0.008	1.164 ± 0.001	1.146 ± 0.003	1.150 ± 0.008	1.141 ± 0.002	1.153 ± 0.002
Swelling degree (%)	163.5 ± 3.2	172.1 ± 4.2	138.9 ± 8.7	170.7 ± 1.6	176.4 ± 1.3	159.8 ± 0.4	149.3 ± 0.4
Sol fraction (%)	10.5 ± 0.1	20.5 ± 0.5	9.8 ± 0.4	15.9 ± 0.3	17.9 ± 0.1	12.5 ± 0.1	10.4 ± 0.1

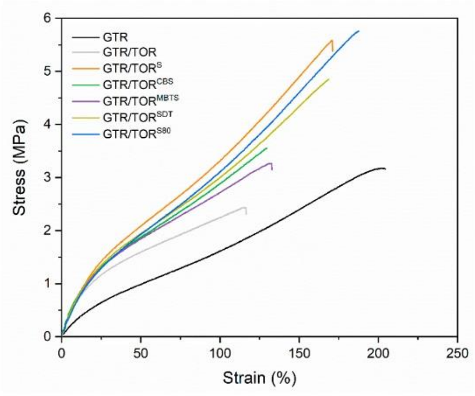

Figure 4. Stress–strain curves of the studied samples.

Among the studied materials, there are two samples cross-linked with sulfur, however, one of them is dispersed in ethylene–propylene–diene monomer rubber (EPDM) (80% sulfur). The physico-mechanical characteristics of GTR/TOR^S and GTR/TOR^{S80} are different, and the specific parameters are: 5.5 ± 0.3 and 5.8 ± 0.4 MPa (tensile strength), 167 ± 15 and 186 ± 19% (elongation at break), 72 ± 1 and 72 ± 1 Shore A (hardness), 1.164 ± 0.008 and 1.153 ± 0.002 g/cm^3 (density), and 138.9 ± 8.7 and 149.3 ± 0.4% (swelling degree) and 9.8 ± 0.4 and 10.4 ± 0.1% (sol fraction), respectively for GTR/TOR^S and GTR/TOR^{S80}. For the S80 curing agent, EPDM acts as a physical binder, which facilitates the access of sulfur to the unsaturated bonds and free radicals obtained during the sintering process. However, as it was confirmed by the inversion phenomenon (curing characteristics) and DSC analysis, the presented properties apply to samples that are not fully cross-linked.

A similar analysis was carried out for samples cross-linked with CBS, MBTS, and SDT accelerators, showing that SDT has the highest influence on the physico-mechanical properties of the studied specimens. It provided the highest tensile strength (4.7 ± 0.3 MPa), stiffness (3.0 ± 0.1 MPa), hardness (71 ± 1 Shore A), and density (1.141 ± 0.001 g/cm^3) compared to GTR/TOR^{CBS} and GTR/TOR^{MBTS}.

The sol fraction increases as follows: GTR/TOR^S (9.8 ± 0.4%), GTR/TOR^{S80} (10.4 ± 0.1%), GTR (10.5 ± 0.1%), GTR/TOR^{SDT} (12.5 ± 0.1%), GTR/TOR^{CBS} (15.9 ± 0.3%), GTR/TOR^{MBTS} (17.9 ± 0.1%)

and GTR/TOR (20.5 ± 0.5%). GTR/TOR^{S}, GTR/TOR^{S80}, and GTR have similar values indicating the mentioned sulfur cross-linking of GTR and TOR. Among the applied accelerators, the lowest sol fraction was obtained by SDT, which is in accordance with the physico-mechanical properties. MBTS and CBS have similar cross-linking characteristics, however, the sol fraction of GTR/TOR^{MBTS} is higher. This phenomenon can be related to partial devulcanization of GTR produced by the used accelerators, which corresponded with a lower value of minimal torque measured during the study of the curing characteristics.

The basic physico-mechanical properties (tensile strength, elongation at break and hardness) of the studied samples were compared with the results reported by different research groups and our previous studies and are shown in Table 5. The table consists of materials, whose main component is GTR (similar to the present study) and materials with much lower content of waste rubber. It can be seen that the designed systems meet or even exceed results published by independent research groups. In case of samples with similar GTR content (GTR/recycled PE/TOR 90/10/9, GTR/EVA 100/10 and GTR/Bitumen/PCL 90/10/10), materials presented in this study (GTR/TOR/active compound 90/10/3) are characterized with higher tensile strength (~2.1, 2.7–3.4, 2.1–2.4 and 3.1–5.8 MPa, respectively) and elongation at break (~70, 125–164, 89–92 and 128–198%, respectively). Even for the material in which the amount of GTR was reduced more than twice and dynamically vulcanized with a complete sulfur curing system in the presence of TOR (GTR/PP/TOR/curing system 60/40/10/9), the obtained results are characterized with higher tensile strength (137% of GTR/TOR^{S80}) and significantly reduced elongation at break (13.4% of GTR/TOR^{S80}). Considering the significant reduction of waste material and the significant decrease of elongation at break, the materials presented in this article show satisficing performance properties.

Table 5. Physico-mechanical properties of GTR-based blends reported by different groups and previous studies.

Sample Composition	Sample Preparation	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Ref.
GTR/TOR/active compound 90/10/3	mixing at ambient temperature compression molding 180 °C	3.1–5.8	128–198	56–72	This study
GTR/recycled PE/TOR 90/10/9	extrusion at 150–180 °C injection molding at 180–190 °C	~2.1 *	~70 *	~78 *	[22]
GTR/bitumen/PCL 90/10/10	mixing GTR with bitumen at ambient temperature, then mixing with PCL at 120 °C compression molding at 120 °C	2.1–2.4	89–92	61–63	[32]
GTR/EVA 100/10	extrusion at 60 °C, compression molding at 140–180 °C	2.7–3.4	125–164	63–65	[33]
waste thermoplastic polyurethane/waste SBR/PE-*g*-MA 90/10/5	mixing at 170–175 °C compression molding at 170 °C	4.8	280	81	[34]
recycled LDPE/GTR/EVA 30/40/30	extrusion at 165–175 °C injection molding at 165–190 °C	~7.8 *	~180 *	unknown	[35]
GTR/PP/TOR/curing system 60/40/10/9.5	mixing at 180 °C (dynamic vulcanization)	~8.0	~25	unknown	[36]

* the value estimated from graphs.

3.4. Thermogravimetric Analysis

The results of the thermogravimetric analysis of GTR, GTR/TOR, GTR/TOR^{S}, GTR/TOR^{CBS}, GTR/TOR^{MBTS}, GTR/TOR^{SDT,} and GTR/TOR^{S80} are presented in Figure 5 and summarized in Table 6. As can be seen, the addition of TOR shifts the thermal stability of GTR/TOR (compared to GTR) towards higher values ($T_{-2\%}$—258.0 to 261.2 °C and $T_{-5\%}$ 315.5 to 318.7 °C). This is due to the good thermal stability of TOR—275 °C. The scale of changes is small, which is a result of the amount of the additive used. The rest of the curing agents caused a shift of thermal stability towards lower values compared to GTR/TOR sample ($T_{-2\%}$ −261.2. 245.9. 225.9. 253.2. 250.6 and 243.1 °C along with

$T_{-5\%}$—318.7, 313.4, 290.9, 303.2, 295.6 and 305.6 °C, respectively for GTR/TOR, GTR/TOR^{S}, GTR/TOR^{CBS}, GTR/TOR^{MBTS}, GTR/TOR^{SDT}, and GTR/TOR^{S80}). The thermal stability of rubber increases with an increasing degree of cross-linking. However, in this case, the opposite phenomenon takes place. The presence of any cross-linkers and accelerators may decrease the thermal stability of rubber products [37]. These components can be thermally decomposed by the effect of elevated temperatures, forming free radicals. Such decomposition products have a significant ability to initiate reactions involving main chains and network nodes affecting the thermal stability of the material. The same phenomenon is commonly used to carry out processes of thermo-chemical reclaiming of GTR.

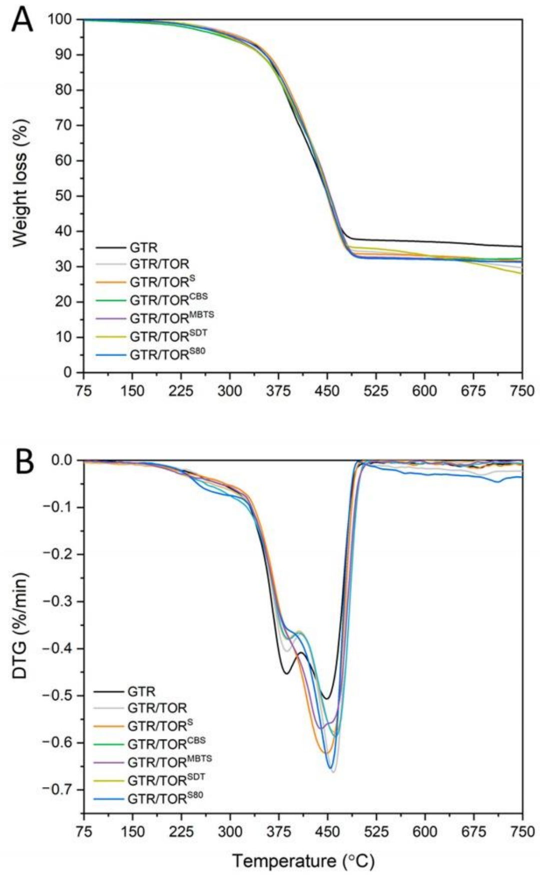

Figure 5. (**A**) TGA and (**B**) DTG curves of the studied samples.

Table 6. Thermal decomposition characteristics of tested samples estimated from TGA data.

Sample	$T_{-2\%}$	$T_{-5\%}$	$T_{-10\%}$	$T_{-50\%}$	Char Residues at 750 °C
GTR	258.0	315.5	355.5	450.5	35.7
GTR/TOR	261.2	318.7	356.2	453.7	29.7
GTR/TOR^{S}	245.9	313.4	358.4	448.4	31.6
GTR/TOR^{CBS}	225.9	290.9	345.9	453.4	32.3
GTR/TOR^{MBTS}	253.2	303.2	348.2	453.2	31.3
GTR/TOR^{SDT}	250.6	295.6	348.1	450.6	28.1
GTR/TOR^{S80}	243.1	305.6	353.1	450.6	31.4

The aforementioned accelerated decomposition also affects DTG (derivative thermogravimetry) curves (Figure 5B). The change of intensity and the shift of two characteristic decomposition peaks of GTR (approx. 390 °C—natural rubber and approx. 445 °C—styrene-butadiene rubber [37]) can be a result of cross-linking and co-cross-linking between the rubber matrix and the TOR, as well as reclaiming. The content of char residues read at 750 °C varies up to 30% for all samples containing TOR. Changes of 2% to 4% cannot be very significant if a sample of about 10 mg is analyzed. The high value of char in GTR is reasonable due to the presence of carbon black, SiO_2 and inorganic impurities.

3.5. Scanning Electron Microscopy

The impact of TOR and applied chemical modifiers on the morphology of the studied samples is presented in Figure 6. SEM images show the surface area perpendicular to the direction of strain, which was created by the breaking of the samples subjected to a static tensile test (the cross-head speed was 500 mm/min). As can be seen, all of the studied samples are characterized by a rather rough surface, however, a few distinctive features can be noticed. Figure 6A represents the GTR sample, which reveals outgoing fibers (residues from tire reinforcements) as well as the voids and gaps created by the rubber particles being torn out during the tensile test. For the GTR/TOR (Figure 6B), the same observations were made, except for the increase in surface roughness. This change was caused by the addition of TOR, which is compatible with GTR. Despite this compatibility, the mechanical properties of the sample are lower than those of the reference. The forces acting on the specimen have been partially transferred to the TOR. The mentioned additive was not cross-linked due to the lack of curing agents and it could not carry the applied load. In the case of pure GTR, the material was sintered and there was no TOR hindering the process, which resulting in superior mechanical properties.

The sample cured with sulfur (Figure 6C) is very similar to the reference sample with visible waste rubber particles, while sulfur dispersed in ethylene–propylene–diene monomer rubber (EPDM) (Figure 6G) is characterized by a rough and shredded surface, which indicates a more developed structure. As mentioned before, the EPDM may act as an additional binder facilitating the cross-linking process by reactive sintering.

The sample treated with CBS (Figure 6D) is relatively smooth with few voids and gaps. The presence of CBS supports the process of reactive sintering and the tested area is the most homogenous among the tested samples. The surface of GTR/TOR^{SDT} (Figure 6F) has a well-developed surface and this is reflected in its mechano-physical properties. GTR/TOR^{MBTS} (Figure 6E) also shows good surface development, however, its properties are not as good as those of GTR/TOR^{SDT}.

The results show that the type of accelerator has an influence on TOR dispersion between rubber particles, but the most important factor is the curing mechanism, which depends on the type of curing agent. Moreover, the smooth surface, which is commonly associated with the appropriate dispersion of components and their good compatibility, does not correlate completely in the presented study. Only a properly developed surface, increasing the possibility of reactive sintering and the creation of a higher number of cross-links, combined with a properly selected cross-linking system, allows obtaining a product with satisfactory parameters. Due to the cross-linked structure it is rather hard to properly develop a convenient surface of GTR. However, the application of TOR, which is compatible with GTR, makes this possible.

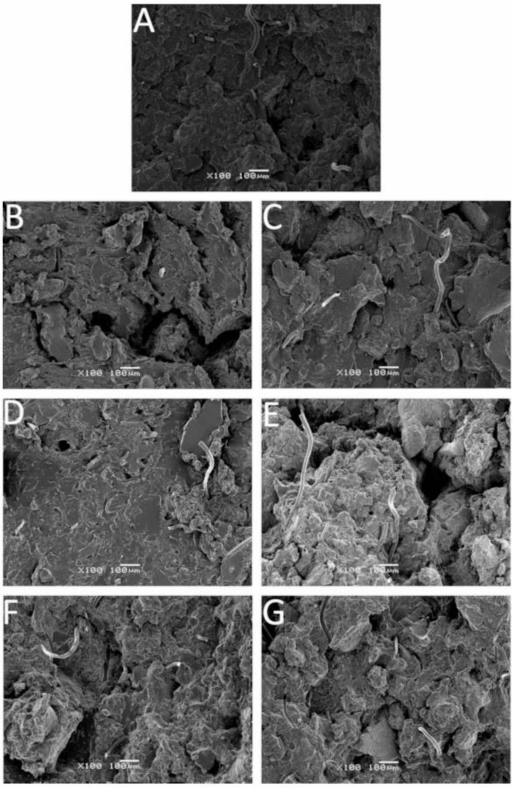

Figure 6. SEM images of samples: (**A**)—GTR; (**B**)—GTR/TOR; (**C**)—GTR/TOR^{S}; (**D**)—GTR/TOR^{CBS}; (**E**)—GTR/TOR^{MBTS}; (**F**)—GTR/TOR^{SDT}; (**G**)—GTR/TOR^{S80} (magnification ×100). Abbreviations: GTR—ground tire rubber; TOR—trans-polyoctenamer rubber.

3.6. Acoustic Properties

The sound absorption coefficient as a function of the frequency of the studied samples is presented in Figure 7. For all of the tested specimens, a significant peak was recorded at the frequency near 1000–1500 Hz. The acoustic properties depend on the chemical and physical structure of the tested material and they are strongly related to the material's density [38]. Therefore, the acoustic properties result directly from the type of material, particle size distribution, methods of its preparation and thickness [39]. The peak in the 1000 to 1500 Hz range is common for GTR, which has been confirmed by independent studies [38–41], and it can be treated as a material characteristic. Depending on the applied curing system, the intensity of the mentioned peak changes. Additionally, a small band is visible for GTR/TOR, GTR/TOR^{S}, GTR/TOR^{CBS}, GTR/TOR^{SDT} and GTR/TOR^{S80} at 2600 to 3500 Hz.

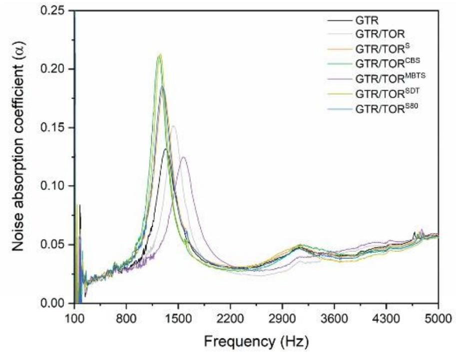

Figure 7. Sound absorption coefficient as a function of frequency.

The sound absorption is related to sample structure, properties, thickness, and surface conditions, as well as to the incident angle and frequency of the sound waves [40]. The measured value changes as the frequency changes from low, through the middle, and up to the high values. In that case, to evaluate the sound-absorbing property one can determine the noise absorption coefficient for specific frequency values (125, 250, 500, 1000, 2000, and 4000 Hz). When the average frequency equals or is higher than 0.2, the tested material can be called "sound-absorbing". In Table 7, the specific values and the average for every tested sample are presented. The results show, that none of the tested specimens fulfills the requirements. The highest value was recorded for GTR/TOR (0.042). However, the applied method misses the frequencies at which tested materials show higher sound absorption. To evaluate the method, another one was used according to the literature studies [41].

Table 7. The changes in the sound absorption coefficient for the studied samples at 125, 250, 500, 1000, 2000, and 4000 Hz.

Frequency (Hz)	Sample Code						
	GTR	GTR/TOR	GTR/TOR^{S}	GTR/TOR^{CBS}	GTR/TOR^{MBTS}	GTR/TOR^{SDT}	GTR/TOR^{S80}
	Sound Absorption Coefficient (α)						
125	−0.07661	0.10734	0.03289	0.0307	−0.07653	0.02072	−0.07766
250	0.01146	0.01599	0.01566	0.01529	0.01709	0.00817	0.01525
500	0.02254	0.01958	0.02348	0.01994	0.02095	0.02025	0.01888
1000	0.02352	0.02251	0.02832	0.02433	0.02644	0.02423	0.0233
2000	0.02689	0.0224	0.03775	0.02053	0.03622	0.02178	0.0209
4000	0.05472	0.0623	0.05146	0.03849	0.04037	0.03726	0.03814
Average	0.01042	0.041687	0.031593	0.02488	0.010757	0.022068	0.006468

Table 8 shows the average sound absorption coefficient at low (100–315 Hz), medium (400–1250 Hz) and high (1600–4000 Hz) frequencies. These values are higher than those presented in Table 6, however, none of them meet the expected requirements.

Table 8. The changes of the sound absorption coefficient for the studied samples at low, medium and high frequencies.

Frequency (Hz)	Sample Code						
	GTR	GTR/TOR	GTR/TOR^{S}	GTR/TOR^{CBS}	GTR/TOR^{MBTS}	GTR/TOR^{SDT}	GTR/TOR^{S80}
	Sound Absorption Coefficient (α)						
100–315	0.06323	0.103741	0.055114	0.056852	0.038187	0.087613	0.051914
400–1250	0.024173	0.02308	0.028704	0.023036	0.025176	0.024022	0.022998
1600–4000	0.038194	0.032915	0.058704	0.025429	0.036743	0.026061	0.025634
Average	0.041866	0.053245	0.047507	0.035106	0.033369	0.045899	0.033515

3.7. *Differential Scanning Calorimetry*

To evaluate the influence of curing additives on the co-cross-linking of TOR and GTR, a DSC study was conducted. The thermogram representing the heating (Figure 8A) and cooling (Figure 8B) process of the revulcanizates is presented in Figure 8. Moreover, enthalpy (ΔH), initial temperature (T_{ω}), peak temperature (T_p), temperature range (D), and time (t) of the melting and crystallization process are presented in Table 9. For better understanding, pure TOR was analyzed.

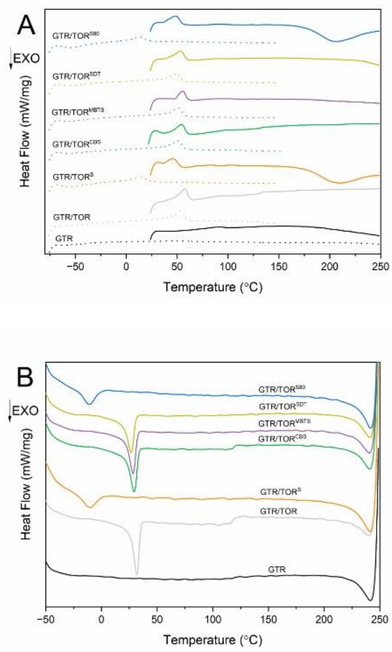

Figure 8. Differential scanning calorimetry (DSC) thermogram evaluating the melting (**A**) and crystallization (**B**) of the studied samples (straight line—1st run; dot line—2nd run).

Table 9. Results of the thermal transitions of the samples studied by DSC.

Sample Code	Melting Enthalpy ΔH_m (J/g)		Initial Melting Temperature ($T\omega_m$) (°C)		Peak Temperature (Tp_m) (°C)		Melting Temperature Range (D) (°C)		Melting Time (t_m) (min)	
	1st run	2nd run	1st run	2nd run	1st run	2nd run	1st run	2nd run	1st run	2nd run
GTR	-	-	-	-	-	-	-	-	-	-
GTR/TOR	5.76	5.06	43.8	39.9	57.6	54.3	19.4	20.4	1.9	2.0
GTR/TOR^S	3.60; −20.83	2.85	36.5	1.5	45.9; 210.4	14.1	17.3; 72.4	24.4	1.7; 7.2	2.4
GTR/TOR^{CBS}	4.86	4.35	39.7	37.5	54.3	51.1	21.9	20.9	2.2	2.1
GTR/TOR^{MBTS}	3.32	4.13	47.3	35.4	55.4	51.3	15.3	24.2	1.5	2.4
GTR/TOR^{SDT}	4.88	3.97	36.0	35.2	53.2	49.4	25.4	21.4	2.5	2.1
GTR/TOR^{S80}	4.30; −25.49	2.70	35.4	−2.4	48.4; 205.7	13.4	20.8; 82.3	27.0	2.1; 8.2	2.7
TOR	85.88	70.79	40.2	25.4	60.1	56.6	36.9	37.6	2.9	3.7

Sample Code	Crystallization Enthalpy ΔH_c (J/g)	Initial Crystallization Temperature ($T\omega_c$) (°C)	Peak Temperature (Tp_c) (°C)	Crystallization Temperature Range (D) (°C)	Crystalization Time (t_c) (min)
GTR	-	-	-	-	-
GTR/TOR	−4.74	38.4	31.7	19.9	2.0
GTR/TOR^S	−2.47	5.3	−10.2	34.0	3.4
GTR/TOR^{CBS}	−4.41	37.5	29.4	22.0	2.2
GTR/TOR^{MBTS}	−4.15	35.3	28.4	19.2	1.9
GTR/TOR^{SDT}	−3.86	35.3	26.7	20.8	2.1
GTR/TOR^{S80}	−2.24	3.8	−10.8	29.1	2.9
TOR	−79.07	39.9	32.4	33.9	3.4

The results show that the only (except the samples cured with sulfur) melting/crystallization peak recorded by the method is associated with TOR. As is well known, the first heating run is conducted to remove the thermal history of a sample, changing the enthalpy and crucial temperatures compared to the second heating run. In the case of GTR/TOR, GTR/TOR^{CBS}, GTR/TOR^{MBTS}, and GTR/TOR^{SDT} the enthalpy changes from 5.76, 4.86, 3.32, and 4.88 J/g to 5.06, 4.35, 4.13, and 3.87 J/g, respectively, while peak temperature changes from 57.6, 54.3, 55.4, and 53.2 J/g to 54.3, 51.1, 51.3, and 49.4 J/g, respectively.

The most interesting results were noticed for samples cured with sulfurs. For GTR/TOR^S and GTR/TOR^{S80} two peaks were recorded: first at 45.9 and 48.4 °C (associated with the melting of TOR), while the second at 210.4 and 205.7 °C, respectively. The second peak was only visible during the first heating run. This phenomenon is associated with the previously discussed, in subchapter 3.1, occurrence and it is correlated with undesirable reactions during DSC analysis. As mentioned before, the cross-linking characteristics indicated that, with the ongoing measurement, the sample does not reach the plateau, and inversion is observed (Figure 2). It was found that the applied conditions were not sufficient to obtain optimum parameters. This is due to the fact that in standard rubber compounds accelerators and activators are used for the cross-linking process with sulfur. The lack of the mentioned additives significantly prolongs this process, which can be observed in the presented paper. The phenomenon was also confirmed by the 2nd heating, which shifts the melting peak to the lower values (45.9 to 14.1 °C and 48.4 to 13.4 °C, respectively for GTR/TOR^S and GTR/TOR^{S80}) and decreases the ΔH_m values. It was also noticed for the crystallization behavior, where the initial temperature shifted from 39.9 °C (TOR) to 5.3 and 3.8 °C. The D_m parameter of the 1st heating for the second peak was 72.4 and 82.3 °C, respectively for GTR/TOR^S and GTR/TOR^{S80}. This shows that the reactions ended approx. at 230 to 240 °C. This exothermic reaction is a vulcanization process. These findings are in accordance with independent studies [42].

4. Conclusions

The proposed method of GTR utilization involves the application of a commercially available waste rubber modifier—TOR (Vestenamer 8012). The idea was to investigate the influence of curing agents/accelerators on curing characteristics, physico-mechanical, thermal, acoustic properties and morphology of the modified GTR. As reference samples, a pure GTR and GTR modified by TOR without any chemical treatment were used. All samples were reclaimed using a two-roll mill and then reactively sintered according to the optimum curing time.

The results show that it is possible to cross-link GTR using only curing additives, without the addition of auxiliary components (plasticizers, activators, etc.). Moreover, curing characteristics depend on the type of compound used, i.e., the most important influence is the nature of the reaction that this compound generates. During the study, GTR/TOR^{S} and GTR/TOR^{S80} showed an inversion phenomenon indicating the appearance of additional chemical reactions after reaching the maximum of vulcanization. This indicates that sulfur can revulcanize GTR, however without accelerators, activators, and plasticizers, the process is unstable.

The physico-mechanical analysis showed a deterioration of GTR/TOR properties compared to pure GTR. This indicates that TOR does not create a cross-link with GTR without additional chemical treatment. Moreover, the presence of TOR hinders the sintering process between GTR particles, unless a curing agent/accelerator is introduced into the rubber mix. The best physico-mechanical properties were obtained by samples cured with sulfurs (5.5 ± 0.3 and 5.8 ± 0.4 MPa—tensile strength, 167 ± 15 and 186 ± 19%—elongation at break, 72 ± 1 and 72 ± 1 Shore A—hardness, respectively GTR/TOR^{S} and GTR/TOR^{S80}). Among the applied accelerators the best properties were obtained for GTR/TOR^{SDT} (4.7 ± 0.3 MPa—tensile strength, 164 ± 8%—elongation at break, 71 ± 1 Sh A—hardness, density g/cm^3—1.141 ± 0.002.

The analysis of the morphology of the tested specimens shows that chemical modifiers influence TOR dispersion as well as the curing mechanism. In the case of the sulfur cured samples, the presence of EPDM in S80 additive influences the development of the GTR particles.

During the DSC tests, the appearance of an exothermic reaction resulting from the presence of sulfur in the composition was observed. The results indicate that the selected process conditions which were sufficient for the vulcanization by accelerators were not sufficient to obtain a product with optimal parameters using only sulfur. Nevertheless, samples treated with accelerators showed decreases in melting enthalpy of TOR compared to GTR/TOR, indicating enhanced TOR degradation and/or co-cross-linking between GTR and the modifier.

The acoustic properties showed that the materials cannot be used as sound-insulating products. However, the proposed method of reclaiming and modification of GTR may allow introducing the tested material into other polymer matrices (polyurethane foams or foamed rotational moulding products), improving their acoustic properties, reducing the cost of production, influencing the ecological aspect of the product, and broadening the range of potential applications.

The presented results indicate that the obtained materials are characterized by good performance properties, compared to the results presented by other research groups (when GTR is considered as the main component of the product). The obtained parameters are sufficient to utilize the recycled GTR as a material for the production of anti-vibration mats, dustbin wheels, water-proof rubber goods and roofing elements (the conclusion drawn after discussions with manufacturers). As part of further work, tests of thermal conductivity and water absorption are planned to determine the susceptibility of the material to the above mentioned purposes.

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Publication 4: Preliminary Investigation on Auto-Thermal Extrusion of Ground Tire RubberArticle Summary

Regarding the management of waste rubber from automobile tires, the methods of extrusion at elevated temperatures are well known. Such an operation makes it possible to obtain a material with a partially degraded structure, which facilitates the recycling of such materials (better processability, higher compatibility with other polymeric matrices, or better dispersion in asphalt mixtures). However, large energy inputs are needed for such a process, which can be reduced. Recently, Seghar et al. [73] studied the effect of the extruder barrel temperature (in the range of 80–220°C) on the thermo-mechanical devulcanization efficiency of post-production waste natural rubber (waste obtained by injection molding). The obtained results indicate the self-heating phenomenon of waste rubber during extrusion in the whole studied range of temperatures. However, this effect was more visible in the lower temperature range (80–140°C). This phenomenon is related to the combined effect of two main factors. The first factor is high shear forces acting on the material, which are transferred into heat during extrusion. The second factor is related to exothermic reactions, which occur during reclaiming/devulcanization of GTR. To sum up, the self-heating phenomenon allows a reduction of energy consumption during rubber recycling [74], which has a beneficial effect on the economic and sustainable development of waste tire recycling. In this paper, preliminary studies on the auto-thermal reclaiming of GTR in a co-rotating twin-screw extruder are presented. Two different heating conditions were applied: (i) constant barrel temperature at 60°C and (ii) auto-thermal (without external heating of extruder barrel).

Materials preparation

The reclaiming of GTR was carried out with the continuous method using a co-rotating twin-screw extruder. It has eleven heating/cooling zones with a screw diameter of 20 mm and an L/d ratio of 40. Ground tire rubber was added into the hopper at constant feed rate using a gravimetric feeder. Two types of heating methods were applied: (i)

Constant barrel temperature at 60°C and (ii) auto-thermal (with disabled barrel heaters). In the first case, all the heating zones were set to 60°C and the process proceeded with a constant heat supply. In the second solution, the heating zones were also heated to 60°C, however, as soon as the process had reached stability, the heating/cooling system was turned off. The reclaimed GTR was further mixed with a sulfur curing system (GTR/Zinc oxide/Stearic acid/N-*tert*-butyl-2-benzothiazole sulfenamide/Sulfur 100/2.5/1.0/0.35/1.5) and then cured in an electrically heated press 150°C to form 2 mm sheets.

Methodology

- Thermogravimetric Analysis
- Static Headspace and Gas Chromatography-Mass Spectrometry
- Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis
- Fourier Transform Infrared Spectroscopy
- Curing Characteristics
- Physico-Mechanical properties

materials

MDPI

Communication

Preliminary Investigation on Auto-Thermal Extrusion of Ground Tire Rubber

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Abstract: Ground tire rubber (GTR) was processed using an auto-thermal extrusion as a prerequisite to green reclaiming of waste rubbers. The reclaimed GTR underwent a series of tests: thermogravimetric analysis combined with Fourier-transform infrared spectroscopy (TGA-FTIR), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and static headspace and gas chromatography-mass spectrometry (SHS-GC-MS) in order to evaluate the impact of barrel heating conditions (with/without external barrel heating) on the reclaiming process of GTR. Moreover, samples were cured to assess the impact of reclaiming heating conditions on curing characteristics and physico-mechanical properties. Detailed analysis of the results indicated that the application of auto-thermal extrusion is a promising approach for the sustainable development of reclaiming technologies.

Keywords: waste tires; recycling; reclaiming/devulcanization; extrusion; auto-thermal extrusion; reclaimed rubber; structure-property relationships

1. Introduction

The ever-increasing development of the global automotive market contributes to the increase in the demand for car tires, and thus the number of waste tires increases. Annually, approximately 1000 million tires are not suitable for further use or retread and according to predictions, this number will increase approximately to 1200 million pieces by 2030 [1]. The most common methods of waste rubber management are dispsal and combustion; the former is forbidden nowadays and the second might increase the production of greenhouse gases (CO_x and NO_x) as well as toxic substances [2]. The legislation on the management of waste rubbers introduced by the European Union in 1999 [3,4] resulted in increased interest in the development of new methods for the utilization of waste rubbers. A promising approach to the material recycling of waste tires is reclaiming [5–7]. Reclaiming of ground tire rubber (GTR) (sometimes called "devulcanization" in the literature) consists in the destruction of the cross-linked structure involving cross-link scission and degradation of polymeric chains. The obtained products (reclaimed GTR) should be characterized by better processing properties than GTR, allowing easier shaping and further vulcanization. Due to the changes in the physical and chemical structure of GTR, the obtained reclaimed rubbers can be used in the manufacturing of new rubber compounds.

Reclaiming of GTR can be obtained by thermal, mechanical, chemical, and biological methods or their combinations, which have recently been described in the literature [8–10]. It should be pointed out that recent studies in this field are usually focused on combining low temperatures and short processing times. For example, Ghosh et al. [11] carried out low-temperature devulcanization of styrene-butadiene rubber (SBR) vulcanizate using bis(3-triethoxysilyl propyl)tetra-sulfide (TESPT) as a devulcanizing agent. Grounded SBR was preliminarily soaked with various amounts of TESPT for 24 h and subsequently transferred to open two-rolls, where it was milled at temperatures between 65 and 70 °C. Obtained reclaimed rubbers were mixed with a curing system and vulcanized according to the curing characteristics. The authors indicated that it is possible to obtain a revulcanized product with superior mechanical and thermal properties using the aforementioned process conditions.

Cheng et al. [12] carried out reclaiming of GTR with aromatic oil at a relatively low temperature. During the process, three different temperatures of 140, 160, and 180 °C were applied. The results showed that the process can be successfully implemented at low temperatures (140 °C) with a high sol fraction content (68.3 wt.%). The reclaiming process of GTR allows for a product with a high sol content to be obtained, which could be used as a plasticizer in rubber compounding and as a modifier in road pavements.

Saiwari et al. [13] reported that the temperature is the most important parameter influencing the efficiency of thermo-mechanical reclaiming of different unfilled elastomers (natural rubber, styrene-butadiene rubber, butadiene rubber, and chlorinated butyl rubber). This confirms that the GTR reclaiming process should be performed at a reasonably low temperature. From an industrial point of view, however, the most crucial parameters to be considered in devulcanization/reclaiming methods would be met by extrusion technologies. This approach allows for continuity and short time, high mixing efficiency, high capacity, and good quality of the obtained products. Moreover, the versatility and diversity of extrusion lines are also a huge advantage for rubber recycling technologies.

Nowadays, reactive extrusion of waste rubbers in twin screw extruders is a relatively well-known method of rubber recycling, which was invented two decades ago by Toyota R&D Division [14]. Although this technology was successfully applied for industrial scale reclaiming of ethylene-propylene-diene monomer rubber, the serious problem is still the reclaiming of GTR [15]. This is due to the presence of styrene-butadiene rubber in waste tires, which has a tendency to secondary cross-linking caused by oxygen and high temperatures. Another issue is the complex composition of waste tires, which can affect process reproducibility and the quality of the obtained products. Moreover, the extrusion parameters involved in the reactive processing must be properly chosen, otherwise the uncontrolled exothermic oxidation in waste rubber may occur, causing degradation of the polymeric chains and the emission of a high amount of odorous and toxic gases [16,17]. In order to reduce or eliminate this technological issue, a relatively low operating temperature during devulcanization/reclaiming via extrusion or high shear thermo-kinetic mixing seems to be a very promising route [18–20]. The literature indicates that low temperature reclaiming of GTR allows for selective scission of cross-linked bonds instead of the main chain scission, directly affecting the mechanical properties of the final product. Moreover, a low temperature affects the intensification of shear forces, limiting secondary cross-linking and reducing energy cost and the amount of emitted gases.

Recently, Seghar et al. [21] studied the effect of the extruder barrel temperature (in the range of 80–220 °C) on the thermo-mechanical devulcanization efficiency of post-production waste natural rubber (waste obtained by injection molding). The obtained results indicate the self-heating phenomenon of waste rubber during extrusion in the whole studied range of temperatures. However, this effect was more visible in the lower temperature range (80–140 °C). This phenomenon is related to the combined effect of two main factors. The first factor is high shear forces acting on the material, which are transferred into heat during extrusion. The second factor is related to exothermic reactions, which occur during reclaiming/devulcanization of GTR. To sum up, the self-heating phenomenon allows a reduction of the energy consumption during rubber recycling [22], which has a beneficial effect on the economic and sustainable development of waste tire recycling technologies.

In this paper, preliminary studies on the auto-thermal reclaiming of GTR in a co-rotating twin-screw extruder are presented. Two different heating conditions were applied: (i) constant barrel temperature at 60 °C and (ii) auto-thermal (without external heating of extruder barrel). Obtained samples were conditioned for at least 24 h. Subsequently, reclaimed GTR was mixed with a sulfur curing system and then vulcanized.

For a better understanding of the changes in the physical and chemical structure of GTR, thermal analysis of GTR samples (reclaimed by the auto-thermal method), taken from different parts of a extruder barrel, was conducted. Static headspace and gas chromatography-mass spectrometry was used to compare the differences in the type and amount of volatile organic compounds (VOCs) generated from GTR samples. Moreover, the influence of the reclaiming method on the curing characteristics and physico-mechanical properties of cured GTR was investigated.

2. Materials and Methods

2.1. Materials

Ground tire rubber (GTR) was received from Grupa Recykl S.A. (Śrem, Poland). GTR was obtained by ambient grinding of used tires (a mix of passenger car tires and truck tires). The particle size distribution of the used GTR is presented in Figure 1. Curing additives of a commercial grade were supplied by Standard Sp. z o.o. (Lublin, Poland).

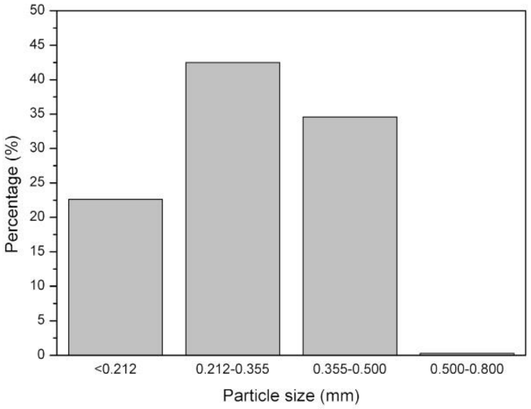

Figure 1. GTR particle size distribution.

2.2. Reclaiming of GTR

The reclaiming of GTR was carried out with the continuous method using a co-rotating twin-screw extruder EHP 2 × 20 from Zamak Mercator Sp. z o.o. (Skawina, Poland). The extruder has 11 heating/cooling zones with a screw diameter of 20 mm and an L/d ratio of 40. Detailed information about the screw configuration was presented in our previous work [18]. Ground tire rubber was added into the hopper at constant feed rate using a gravimetric feeder from Hydrapress Sp. z o.o. (Białe-Błota, Poland).

A summary of the extrusion conditions during the reclaiming of GTR is shown in Table 1. Two types of heating methods were applied: (i) Constant barrel temperature at 60 °C (coded as GTR-EXT) and (ii) auto-thermal (with disabled barrel heaters) (coded as GTR-AUTO EXT). In the first case, all the heating zones were set to 60 °C and the process proceeded with a constant heat supply. In the second solution, the heating zones were also heated to 60 °C, however, as soon as the process had reached stability, the heating/cooling system of the barrel was turned off. The auto-thermal conditions during reclaiming were set up as described in the patent [23]. The process was carried out on a laboratory scale with a capacity of 2.5 kg/h. It should be pointed out that the screw torque values for both heating methods were similar, which indicates that auto-thermal extrusion allows a reduction of the energy used during GTR reclaiming. The appearance of GTR after auto-thermal reclaiming is presented in Figure 2.

Table 1. Extrusion conditions of ground tire rubber (GTR).

Extrusion Parameters	**Sample Code**	
	GTR-EXT	**GTR-AUTO EXT**
Material	GTR 0.4	GTR 0.4
throughput (kg/h)	2.5	2.5
Screws peed (rpm)	250	250
Set barrel temperature (°C)	60	Auto-thermal *
Barrel temperature after process stabilization (from hopper to die) (°C)	32/60/65/65/66/65/66/69/70/85/86	25/39/54/64/69/69/68/70/70/85/96
Pressure on extruder die (bar)	56.7	59.7
Screw torque (Nm)	15.1	15.5
Observations	Frayed GTR ribbon came out from the extrusion die, the material has a temperature over 120 °C. The emission of gases from extruded GTR was observed at the end of the extrusion die.	In auto-thermal conditions, the zones maintained the pre-set temperature. Like in the case of sample GTR-EXT, the emission of gases was observed during processing.

* extruder barrel heating/cooling system turned off.

Figure 2. The appearance of GTR directly after auto-thermal reclaiming.

2.3. Curing of Reclaimed GTR

Reclaimed GTR obtained by the procedure described above was mixed with a sulfur curing system and processed using two-roll mills from Buzuluk (Komárov, Czech Republic). The composition of the tested compounds is presented in Table 2. Tested compounds were formed in sheets with a

2 mm thickness and then cured in an electrically heated press at 150 °C under a pressure of 4.9 MPa for the optimum vulcanization time determined according to the ISO 3417 standard.

Table 2. Rubber composition for testing reclaimed rubber.

Component	Recipe (phr)
Reclaimed rubber	100
Zinc oxide	2.5
Stearic acid	1.0
N-tert-butyl-2-benzothiazole sulfenamide (TBBS)	0.35
Sulfur	1.5

2.4. Measurements

The thermal analysis of GTR and reclaimed GTR was performed using the simultaneous TGA/DSC model Q600 from TA Instruments (New Castle, DE, USA). Samples of reclaimed GTR weighing approximately 10 mg were placed in a corundum dish. The study was conducted in an inert gas atmosphere containing nitrogen (flow rate of 100 mL/min) in the range from 25 to 800 °C with a heating ramp of 20 °C/min. In order to better understand the thermal stability of GTR during extrusion, the TGA measurement in the air atmosphere in the same conditions was also performed. Volatile products that formed during thermal degradation of studied samples were also evaluated using Fourier-transform infrared spectroscopy (FTIR). During the TGA/DSC measurements, the volatile degradation products were directed, using a heated transfer line at 220 °C, to a Nicolet iS10 spectrometer from Thermo Scientific (Waltham, MA, USA). That setup allowed "on-line" characterization of volatile products released during TGA/DSC measurements. The timing offset of FTIR spectra compared to the TGA curves was related to the volume of the thermogravimetric apparatus chamber.

The morphology of GTR and reclaimed GTR was characterized by a Hitachi S3400 scanning electron microscope (Tokyo, Japan). Before the analysis, samples were coated with a thin layer of gold. Qualitative and quantitative analysis of GTR and reclaimed GTR surface composition was performed using energy-dispersive X-ray spectroscopy.

The FTIR spectra were measured in the range of 4000–650 cm^{-1} with a Momentμm microscope attached to a Nicolet iS50 FT-IR spectrometer (Waltham, MA, USA) equipped with the Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory. Spectral analysis was controlled by the OMNIC software package ver 9.8.372.

Volatile organic compounds emitted from reclaimed GTR were determined using static headspace and gas chromatography-mass spectrometry (SHS-GC-MS). Measurements were performed using a Shimadzu GC2010 PLUS GC-MS (Kyoto, Japan) equipped with a split/splitless inlet. The GC-MS system was equipped with an AOC5000 Headspace Auto-Sampler (Shimadzu, Kyoto, Japan). During analysis, the vial was transported by the injection unit from the tray to the agitator. When the sample achieved equilibrium, the headspace sample of a 2.5 mL volume was drawn from the vial and injected into the GC injector. The sampled vial was then returned by the injection unit to the tray.

The curing process of reclaimed GTR samples was investigated at 150 °C using a Monsanto R100S (Columbia City, IN, USA) rheometer with an oscillating rotor according to ISO 3417. For a better understanding of the changes that occurred during the reclaiming process, samples without a curing system were also investigated with the rheometer. Cure rate index (CRI) values were calculated in accordance with Equation (1):

$$\mathrm{CRI} = \frac{100}{t_{90} - t_2} \tag{1}$$

where: t_{90}—optimum vulcanization time, min; t_2—scorch time, min.

In order to determine the aging resistance of the studied vulcanizates at elevated temperatures, the R_{300} parameter was determined. R_{300} defines the percentage reversion degree after a period of

300 s calculated from the time of reaching maximum torque ($M_{max.}$). R_{300} was calculated in accordance with Equation (2):

$$R_{300} = \frac{M_{max.} - M_{300s}}{M_{max.}} \times 100\% \quad (2)$$

where: M_{max}—maximum torque; M_{300s}—torque 300 s after maximum torque.

The tensile strength, elongation at break, and modulus at 100% of elongation (M_{100}) were estimated in accordance with ISO 37. Tensile tests were performed on a Zwick Z020 machine (Ulm, Germany) at a constant speed of 500 mm/min. Direct extension measurements were conducted periodically using an extensometer with sensor arms. Shore hardness type A was estimated using a Zwick 3130 durometer (Ulm, Germany) in accordance with ISO 7619-1. The tensile strength, elongation at break, modulus at 100%, and hardness were estimated based on five repetitions.

3. Results and Discussion

3.1. Thermal Stability of GTR at Different Atmospheres

In order to provide better insight into changes that occurred during the extrusion of GTR, the characteristics of the applied waste rubber were required. Thermogravimetric analysis (TGA) was applied to determine the thermal stability of GTR. The obtained results are presented in Figure 3 and summarized in Table 3. As could be observed in differential thermogravimetric (DTG) curves, two maxima were determined for GTR (384.5 and 435.7 °C, respectively) studied in the inert atmosphere of nitrogen and four maxima for GTR (302.7, 442.0, 521.1, and 581.1 °C, respectively) studied in air atmosphere. The first two peaks in DTG (regardless of the used atmosphere) corresponded to the temperatures of the maximum rate of thermal degradation of natural rubber (384.5 °C—in nitrogen and 302.7 °C—in air) and styrene-butadiene rubber (435.7 °C—in nitrogen and 442.0 °C—in air), which are the main elastomers used in car tire manufacturing [24]. The differences in the maximum rate of thermal degradation of natural rubber results from the thermooxidative degradation due to the presence of the oxygen. Two additional maxima (521.1 and 581.1 °C) for a study carried out in air are the result of carbon black oxidation [25], which corresponds to the char residue value presented in Table 3. Temperatures of $T_{-2\%}$, $T_{-5\%}$, $T_{-10\%}$, and $T_{-50\%}$ are related to the 2%, 5%, 10%, and 50% weight loss, respectively. As could be expected, the thermal stability of GTR was lower in air atmosphere, however, it should be pointed out that thermal decomposition of styrene-butadiene rubber was slower in the presence of air than in nitrogen. This is related to the secondary cross-linking of styrene-butadiene rubber affected by the high temperature in the presence of oxygen.

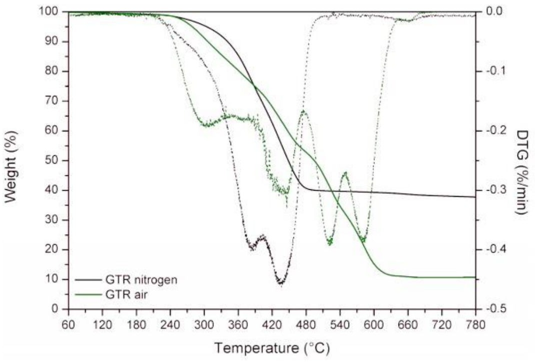

Figure 3. TGA and DTG curves for GTR in nitrogen and in air atmosphere.

Table 3. Thermal decomposition characteristics of GTR in an inert (nitrogen) and in air atmosphere.

Sample Name	Decomposition Temperature (°C)				Maxima from DTG (°C)				Char Residue at 750 °C (%)
	$T_{-2\%}$	$T_{-5\%}$	$T_{-10\%}$	$T_{-50\%}$	T_{max1}	T_{max2}	T_{max3}	T_{max4}	
GTR nitrogen	258.5	304.3	341.3	448.4	384.5	437.5	-	-	38.0
GTR air	253.0	278.8	306.5	494.6	302.7	442.0	521.1	581.1	10.7

The 3D FTIR spectra determined for the volatile products emitted during the thermal decomposition of GTR in an inert atmosphere (A) and in air (B) are presented in Figure 4. In the case of the study carried out in nitrogen, a strong band in the range of 2900–2970 cm^{-1} appeared, which corresponds to the symmetric and asymmetric stretching vibrations of C-H bonds in the CH_2 groups of volatile degradation products formed due to the degradation of hydrocarbons present in GTR. When the sample had access to the oxygen, absorbance maxima appeared at 2349 cm^{-1} and 876 cm^{-1}, representing asymmetric stretching vibrations of CO_2 [26] formed during thermo-oxidative degradation of the sample during thermogravimetric analysis.

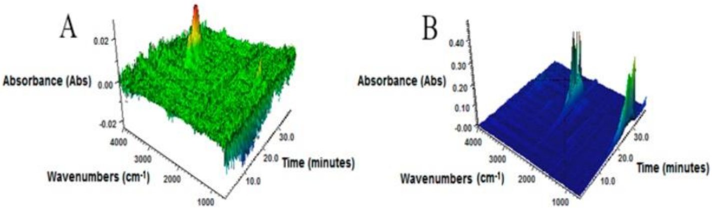

Figure 4. 3D FTIR plots for volatile products emitted during the thermal decomposition of GTR: (**A**) nitrogen, (**B**) air atmosphere (heating ramp of 20 °C/min).

3.2. Thermal Stability of Reclaimed GTR Collected from Different Zones of the Extruder Barrel

In order to investigate the changes that occurred in the GTR structure during the reclaiming process, samples from different zones of the barrel were collected. In this case, samples after auto-thermal extrusion of ground tire rubber were evaluated. The reclaiming process was started and stabilized and after that, the gravimetric feeder and extruder were turned off. Subsequently, the extruder barrel divided in the plane was immediately opened using an electric screwdriver. The appearance of samples collected from different zones of the extruder barrel is shown in Figure 5.

The samples were collected directly from screws and examined using thermogravimetric analysis performed in a nitrogen atmosphere after at least 24 h of conditioning. Kleps et al. [27] confirmed that TGA as an analytical technique is a very useful tool to evaluate reclaimed rubbers and to establish the optimal parameters of the reclaiming/devulcanization process. The results of TGA measurements are presented in Table 4, showing the thermal properties of samples gathered from the same process and from three different barrel zones: Hopper, central, and last zone. As the high shear forces and higher temperature acted on GTR, the reclaiming process occurred, which is connected with the release of low molecular compounds from the complex structure of the waste tires. It was proven by the $T_{-2\%}$ value, which decreased with the progress of the reclaiming process (from 258.5 to 237.7 °C). The shift to a lower value shows either faster evaporation or decomposition of plasticizers or other low molecular additives present in GTR released during the process [28]. The GTR gathered from the last zone shows an increase in the $T_{-2\%}$ value (from 237.7 to 244.6 °C), which is the effect of partial evaporation/decomposition of low molecular compounds during the reclaiming process shifting decomposition temperatures to higher values. The mass loss in the 200–350 °C range did not change significantly with the process progression. The small increase was visible for the sample from the central zone in the range of

200–350 °C (from 11.0% to 13.9%) and the later drop of the value for GTR from the last zone (11.5%). This phenomenon corresponds to the aforementioned release of low molecular compounds and its evaporation/decomposition in a later stage. In the last zone, there is a material, which was influenced by factors favoring the reclaiming process (shear forces, temperature, and time). The scission of cross-links and degradation of main chains facilitated thermal decomposition of reclaimed GTR, which translated into higher values of mass loss in the range of 350–400 °C (hopper—17.6%, central zone—17.0%, last zone—20.4%) and 400–550 °C (hopper—30.8%, central zone—23.5%, last zone—41.2%), which are the temperatures of rubbers degradation. Those results show the partial reclaiming of GTR during the process, which was also confirmed by SEM-EDX described in Section 3.4.

(A) (B)

Figure 5. The appearance of: (**A**) open extruder barrel after stopping of reclaiming process (**B**) GTR collected from different zones of the extruder barrel.

Table 4. Mass loss (Δm) as a function of the temperature range (ΔT) and $T_{-2\%}$ from TGA curves for reclaimed GTR collected from different zones of the extruder barrel.

Sample—Barrel Zone	ΔT (°C)	Δm (%)	$T_{-2\%}$ (°C)
GTR—hopper	200–350	11.0	258.5
	350–400	17.6	
	400–550	30.8	
reclaimed GTR—central zone	200–350	13.9	237.7
	350–400	17.0	
	400–550	23.5	
reclaimed GTR—last zone	200–350	11.5	244.6
	350–400	20.4	
	400–550	41.2	

3.3. *Volatile Organic Compounds of Reclaimed GTR Collected from Different Zones of the Extruder Barrel*

As the volatile organic compounds (VOCs) have a negative impact on the environment, further studies were focused on the estimation of the VOCs emitted during the reclaiming process. Sampling took place on the same basis as in the case of the thermal stability analysis (Section 3.2). The results of the SHS-GC-MS measurement are presented in Table 5. The applied measurement conditions allowed for the determination of seven compounds: Acetone (content in the range of: 2.2–5.5 mg/kg), methacrolein (0.9–2.1 mg/kg), 2-methylfuran (1.3–2.1 mg/kg), methyl vinyl ketone (1.6–3.9 mg/kg), methyl isobutyl ketone (8.3–25.9 mg/kg), cyclohexanone (2.4–9.5 mg/kg), and benzothiazole (6.5–40.6 mg/kg). Regardless of the sampling zone of the barrel, the highest concentration was detected for methyl isobutyl ketone and benzothiazole, which was also confirmed in our previous studies [6]. The first component is used for the synthesis of antiozonant 6PPD (a common component of tires) and the second one can be found as part of the structure of vulcanization accelerators. The presence of benzothiazole correlates with the presence of an unreacted curing system or scission of the sulfide cross-linking bonds present in GTR. Morand et al. [29] indicated that methacrolein and methyl vinyl ketone are formed during oxidation of polyisoprene, while other determined volatile compounds were also detected in natural rubber [30]. The total content of VOCs changed with the progress of the reclaiming process (hopper—23.2 mg/kg, central zone—89.6 mg/kg, last zone—56.8 mg/kg). The highest value was determined for reclaimed GTR from the central zone. The result proves previous assumptions about the release of low molecular compounds during the reclaiming process, which can be evaporated more easily when analyzed by the SHS-GC-MS method. Furthermore, the amount of VOCs for the reclaimed GTR from the last zone was lower than from the central zone, which indicates that part of the low molecular compounds evaporated into the environment during the process. It shows that the analysis of VOCs should be done in every step of GTR processing in order to evaluate changes in the structure of processed material and its influence on the environment.

Table 5. Volatile organic compounds determined using the SHS-GC-MS method.

Compound (mg/kg of Sample)	Sample—Barrel Zone		
	GTR—Hopper	Reclaimed GTR—Central Zone	Reclaimed GTR—Last Zone
Acetone	2.2	5.5	3.8
Methacrolein	0.9	2.1	1.7
2-methylfuran	1.3	2.1	1.9
Methyl vinyl ketone	1.6	3.9	2.8
Methyl isobutyl ketone	8.3	25.9	16.9
Cyclohexanone	2.4	9.5	4.9
Benzothiazole	6.5	40.6	24.8
Total content	23.2	89.6	56.8

3.4. SEM-EDX of Reclaimed GTR

The SEM images presented in Figure 6 unraveled the surface morphology and homogeneity of untreated GTR, GTR-EXT, and GTR-AUTO-EXT. As displayed in the SEM micrographs, there is a minor difference between GTR and thermo-mechanically threated waste rubber. Due to the high shear forces and increased temperature, the reclaiming process occurred on the surface of waste rubber particles, resulting in its smoother surface and the formation of melt-like structures. It is revealed in the amount of white areas, which are increased in the SEM micrographs, especially in higher magnification, for GTR-EXT and GTR-AUTO-EXT compared to GTR. Moreover, the morphological structure of GTR-EXT and GTR-AUTO-EXT is very similar, indicating that heat generated during the process was enough to obtain the same devulcanization degree in both cases.

The elemental composition of the studied samples is presented in Table 6. The results show that GTR and reclaimed GTR are mainly constituted of carbon (86.1–90.1 wt.%). Carbon is a principal element of rubber macromolecules as well as carbon black, which is commonly used as a reinforcement in tires. The presence of oxygen (1.8–5.1 wt.%) and silicon (1.2–3.3 wt.%) is directly related to the presence of silica, which is also used as a reinforcing additive; however, it may also be a result of simple contamination of waste tires by sand. The differences between the amount of detected oxygen and silicon in the tested samples are not a result of the reclaiming process but from the content of silica in GTR, which is in accordance with the oxygen to silicon ratio. Moreover, it might also be due to the presence of unreacted components commonly used in tire manufacturing, such as zinc oxide. The detection of sulfur (1.6–2.0 wt.%) corresponds to the applied vulcanization agents and accelerators. Even a small change in its content is significant due to the overall small amount of sulfur added during tire manufacturing (usually ~1 to 3 phr of sulfur). The decrease of the amount of the element indicates an ongoing reclaiming process, resulting in the scission of S–S and C–S cross-linking bonds and facilitating the evaporation of hydrogen sulfide and sulfide oxide to the atmosphere [10]. The zinc (2.5–3.2 wt.%) is used as a vulcanization activator. The samples were contaminated by iron (0.1–0.2 wt.%) and aluminum (0.1–2.6 wt.%). Both might derive from steel cord (aluminum used as deoxidizer) used in the construction of the tire.

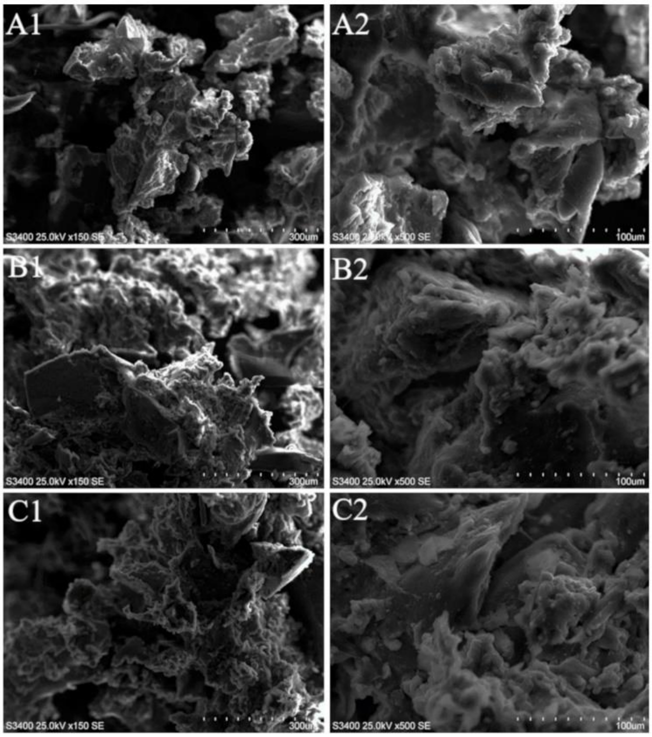

Figure 6. SEM images of: GTR (**A**1—magnification ×150, **A**2—magnification ×500), GTR-EXT (**B**1—magnification ×150, **B**2—magnification ×500), GTR-AUTO-EXT (**C**1—magnification ×150, **C**2—magnification ×500).

Table 6. Elemental composition of GTR and reclaimed GTR determined by energy-dispersive X-ray spectroscopy.

Element (wt.%)	Sample		
	GTR	**GTR-EXT**	**GTR-AUTO-EXT**
Carbon	86.1	90.1	89.6
Oxygen	5.1	1.8	3.7
Silicon	3.3	1.2	2.0
Sulfur	2.0	1.6	1.8
Zinc	3.2	2.5	2.7
Iron	0.2	0.1	0.1
Aluminium	0.1	2.6	0.1

3.5. FTIR Spectra of Reclaimed GTR

The FTIR spectra obtained for GTR, GTR-EXT, and GTR-AUTO-EXT are presented in Figure 7. The results show no significant differences between the tested samples. It indicates that regardless of the applied reclaiming method, the chemical structure of the obtained reclaimed waste rubber did not change significantly compared to GTR. The absorbance maxima in the range of 3540–3410 cm^{-1} corresponds to O-H bonds vibrations, which suggest the presence of hydroxyl groups. The bands of C–H bonds of CH_2 groups present in the aliphatic chains of elastomers are located in 2930 cm^{-1} and 2850 cm^{-1}. The bands at approximately 1790 cm^{-1} and 1730 cm^{-1} are attributed to C=O bond vibrations, which occurred as a result of oxidative degradation. The band appears in every analyzed sample, which indicates that partial degradation took place during tire grinding. A characteristic peak for C=C bond present in benzene typical for styrene-butadiene rubber (common elastomer in the tire industry) is visible at approximately 1615 cm^{-1} and 670 cm^{-1}. The characteristic band at approximately 1370 cm^{-1} corresponds to the C–H bonding of methyl groups, which confirms the presence of natural rubber in the examined rubber wastes. Another band for C–H vibrations is located at about 830 cm^{-1}. In the range of 1100 cm^{-1} to 880 cm^{-1}, C–O–C bonding as well as S=O, C–C, and C–O bonds are present in the chemical structure of the samples. The vibrations of C-S bonds can be observed at about 770 cm^{-1}.

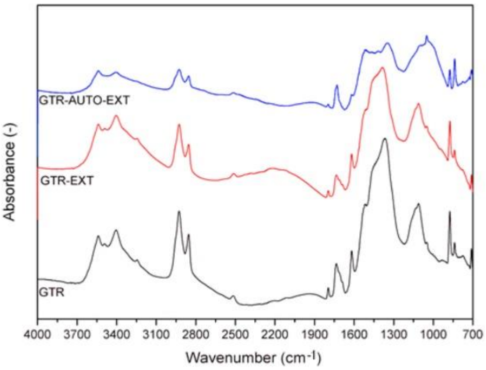

Figure 7. FTIR spectra of GTR, GTR-EXT, and GTR-AUTO-EXT samples.

3.6. *Curing Characteristics*

The curing curves of reclaimed GTR samples without (GTR-EXT and GTR-AUTO EXT) and with a curing system (GTR-EXT + SYS and GTR-AUTO EXT + SYS) are presented in Figure 8. As could be expected, the curing curves for GTR-EXT and GTR-AUTO EXT are almost linear, which indicates that revulcanization of reclaimed GTR without the curing system is rather limited. On the other hand, samples with a curing system (GTR-EXT + SYS and GTR-AUTO EXT + SYS) showed the typical course of curing curves.

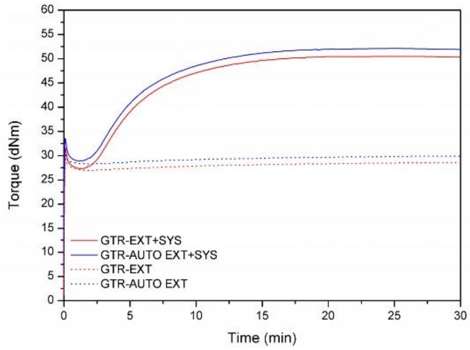

Figure 8. Curing curves for GTR-EXT and GTR-AUTO-EXT samples without and with a curing system (+SYS).

The curing characteristics of GTR-EXT and GTR-AUTO-EXT with and without a sulfur curing system are presented in Table 7. The minimal torque values differ insignificantly depending on the applied reclaiming method (GTR-EXT and GTR-AUTO-EXT: 27.0 and 28.3 dNm, respectively). A similar change was observed for the samples including the curing system (coded as GTR-EXT + SYS and GTR-AUTO-EXT + SYS: 27.4 and 29.0 dNm, respectively). During the extrusion process, high shear forces and high temperatures act on GTR, enhancing the scission of cross-linking bonds and the degradation of polymer chains. This phenomenon causes the formation of low molecular compounds capable of partial secondary cross-linking of the reclaimed rubber structure during the process. This indicates that the auto-thermal method caused a more efficient partial cross-linking during the reclaiming process. The same dependence was observed for samples with the curing system. The minimal torque values of GTR-EXT are similar regardless of the presence of the curing system (27.0–27.4 dNm), and also for samples prepared with the auto-thermal method (28.3–29.0 dNm). The small difference of minimal torque values (in terms of the presence of a curing system) might result from the complex composition of waste tires.

In the case of GTR-EXT and GTR-AUTO-EXT, the torque values increased during the curing process for exactly 1.6 dNm even without the application of a curing system. It proves that the formation of low molecular compounds, capable of cross-linking, occurred during the reclaiming process via extrusion. However, the applied measurement methodology is not suitable for the determination of this phenomenon. The cross-linking process of reclaimed GTR is more efficient when a sulfur curing system is used. For both samples (GTR-EXT and GTR-AUTO-EXT) the torque increament value increased for 23.1 dNm. This shows that in the studied case, regardless of the heating conditions, the curing efficiency of the obtained reclaimed rubbers is the same.

Table 7. Curing characteristics of GTR-EXT and GTR-AUTO-EXT with and without a sulfur curing system.

Item	Sample Code			
	GTR-EXT	**GTR-AUTO EXT**	**GTR-EXT + SYS ***	**GTR-AUTO EXT + SYS**
Minimal torque M_{min} (dNm)	27.0	28.3	27.4	29.0
Maximal torque M_{max} (dNm)	28.6	29.9	50.5	52.1
Torque increment ΔM (dNm)	1.6	1.6	23.1	23.1
Scorch time t_1 (min)	-	-	2.6	2.5
Optimum cure time t_{90} (min)	-	-	11.6	11.8
Cure rate index CRI (min^{-1})	-	-	11.1	10.7
Thermal aging resistance R_{300} (%)	-	-	0.4	0.3

* sample contains a sulfur curing system presented in Table 2.

For GTR-EXT + SYS and GTR-AUTO-EXT + SYS samples, the scorch time was 2.6 and 2.5 min, the optimum cure time was 11.6 and 11.8 min, the cure rate index was 11.1 and 10.7 min^{-1}, and the thermal aging resistance was 0.4% and 0.3 %, respectively. Those minimal changes in the mentioned values also indicate the fact that in the studied conditions, the heating method during extrusion of GTR did not affect its further curing.

3.7. *Physico-Mechanical Properties*

The physico-mechanical properties of the reclaimed rubbers are presented in Table 8. It was observed that for GTR-EXT and GTR-AUTO-EXT samples, the tensile strength (2.7 ± 0.1 MPa) and modulus 100 (1.5 MPa) did not change. A similar phenomenon was observed for the elongation at break values (205 ± 15% and 203 ± 7%, respectively), hardness (47 ± 1 and 51 ± 1 Sh A, respectively), and density (1.16 ± 0.01 and 1.16 ± 0.01 g/cm^3, respectively). Small changes, or their lack, of the above mentioned properties show that the heating method during the reclaiming process had no influence on the physico-mechanical properties of the GTR-EXT and GTR-AUTO-EXT samples.

Table 8. Physico-mechanical properties of GTR-EXT and GTR-AUTO-EXT with and without a sulfur curing system.

Properties	Standard	Sample Code			
		GTR-EXT	**GTR-AUTO EXT**	**GTR-EXT + SYS ***	**GTR-AUTO EXT + SYS ***
Tensile strength (MPa)	ISO 37	2.7 ± 0.1	2.7 ± 0.1	5.1 ± 0.3	4.6 ± 0.1
Elongation at break (%)	ISO 37	205 ± 15	203 ± 7	201 ± 11	196 ± 7
Modulus at 100% (MPa)	ISO 37	1.5	1.5	2.3	2.4
Hardness (Sh A)	ISO 7619-1	47 ± 1	50 ± 1	60 ± 1	59 ± 1
Density at 25 °C (g/cm^3)	ISO 1183	1.16 ± 0.01	1.16 ± 0.01	1.20 ± 0.01	1.19 ± 0.01

* sample contains a sulfur curing system presented in Table 2.

The physico-mechanical properties of reclaimed GTR were enhanced by the addition of a sulfur curing system. The tensile strength of GTR-EXT + SYS and GTR-AUTO-EXT + SYS samples was 5.1 ± 0.3 and 4.6 ± 0.1 MPa, respectively. The difference between the tensile strength values of those samples is negligible. A similar tendency was observed when the rest of the parameters were compared. The elongation at break (201 ± 11 and 196 ± 7%, respectively), modulus at 100% (2.3 and 2.4 MPa, respectively), hardness (60 ± 1 and 59 ± 1 Sh A, respectively), and density (1.20 ± 0.01 and 1.19 ± 0.01 g/cm^3, respectively) did not change significantly for GTR reclaimed by auto-thermal extrusion.

In order to evaluate the physico-mechanical properties of laboratory manufactured reclaimed GTR, the obtained products were compared with commercially available reclaimed rubbers vulcanized in the same conditions as the GTR-EXT and GTR-AUTO-EXT samples. A comparison of the results is presented in Table 9. The results show that, excluding RO-1-S, the tensile strength presents a variation of 4.6 to 5.2 MPa, and elongation at break at 184% to 207%. The high values of the tensile strength (11.0 MPa) and elongation at break (419%) of RO-1-S probably result from the fact that the material used for the reclaiming process did not come from waste tires.

Table 9. A comparison between commercial reclaimed rubbers and reclaimed GTR produced in the laboratory scale (throughput: 2.5 kg/h).

Sample Code *	Supplier	Origin	Physico-Mechanical Properties			
			Tensile Strength (MPa)	Elongation at Break (%)	Hardness (°Sh A)	Density at 25 °C (g/cm^3)
GTR-EXT	Laboratory manufacturing	Poland	5.1 ± 0.3	201 ± 11	60 ± 1	1.20 ± 0.01
GTR-AUTO-EXT	Laboratory manufacturing	Poland	4.6 ± 0.1	196 ± 7	59 ± 1	1.19 ± 0.01
RO-1-S	Geyer&Hosaja	Poland	11.0 ± 1.1	419 ± 11	53 ± 1	1.10 ± 0.05
RSZT	Chemical Worldwide Business	Russia	4.6 ± 0.2	207 ± 13	45 ± 1	1.17 ± 0.02
B-66/TS5	Chemical Worldwide Business	Netherlands	5.2 ± 0.5	184 ± 11	56 ± 1	1.22 ± 0.01

* All studied samples were compounded with a sulfur curing system and vulcanized in the same conditions.

4. Conclusions

The GTR reclaiming process is an important industrial method of rubber recycling, which is highly influenced by temperature. The use of lower temperatures may result in energy savings, which directly affects the reduction of the process costs. On the other hand, high shear forces applied to the cross-linked rubber particles causes their mutual friction and enhances exothermic reactions during reclaiming. As a consequence, a self-heating phenomenon during GTR reclaiming can be observed. The presented preliminary results showed that auto-thermal extrusion of GTR (process carried out without external heating) allows the production of reclaimed rubber with performance properties that are competitive with commercially available products. Moreover, the expected savings of energy and reduced emission of VOCs are also advantages of this method. Further research in this field should be focused on the improvement of processing at low temperatures (e.g. by plasticizers or other chemical additives) in order to ensure easier scale-up of this technology and deep analysis of processing costs.

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Publication 5: Ground Tire Rubber Modified by Ethylene-Vinyl Acetate Copolymer: Processing, Physico-Mechanical Properties, Volatile Organic Compounds Emission and Recycling Possibility

Article Summary

As we already know, the most important factors in GTR recycling are to ensure the continuity of the process, to analyze the impact on the work environment, the costs associated with its processing, and the properties of the final product. In the theoretical part, it was repeatedly emphasized that GTR is a huge problem in terms of its management. This means that products based on recycling of this material will also pose a challenge at the end of their useful life (assuming that the product will not be suitable for use in the second principle of sustainable development, i.e. "reduce"). In the theoretical part, it was repeatedly emphasized that GTR is a huge problem in terms of its management. This means that products based on recycling of this material will also pose a challenge at the end of their useful life (assuming that the product will not be suitable for use in the second principle of sustainable development, i.e. "reuse"). GTR was treated by low-temperature extrusion in presence of two grades of ethylene-vinyl acetate copolymers. The samples were compared with trans-polyoctenamer (a commercial additive dedicated to waste rubber recycling) commercial modified GTR (samples prepared in the same manner).

Materials preparation

Reclaimed GTR modified by thermoplastics was prepared using a co-rotating twin-screw extruder with a L/d ratio of 40. The screw's diameter was 20 mm and their rotational speed was equal to 250 rpm. The extruder was equipped with eleven heating zones. The temperatures in individual heating zones (from hopper to extrusion die) on the barrel of the extruder were: 40/40/60/60/60/60/60/60/60/60/60 °C. Both components, GTR and 10 phr of thermoplastics (TOR-Vestenamer®8012, EVA1—Sipchem EVA 2518 or EVA2 - Escorene Ultra EVA FL00218), were directly introduced into the hopper with a constant feeding rate (2.5 kg/h) that was provided by a gravimetric feeding system. Modified reclaimed GTR was directly formulated into sheets by compression molding for 5 min. under a pressure of 4.9 MPa. In order to better understand the effect of molding temperature on the performance of obtained materials, modified reclaimed GTR samples were compression molded at three different temperatures: 140, 160, and 180 °C.

Methodology

- Temperature and Energy Consumption
- Melt Flow Index
- Mooney Viscosity
- Swelling Behavior
- Physico-Mechanical Properties
- Multiple Reprocessing Assesment
- Volatile Organic Compounds

materials

MDPI

Article

Ground Tire Rubber Modified by Ethylene-Vinyl Acetate Copolymer: Processing, Physico-Mechanical Properties, Volatile Organic Compounds Emission and Recycling Possibility

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Abstract: Ground tire rubber (GTR) was reclaimed and modified with 10 phr of ethylene-vinyl acetate copolymer via low-temperature extrusion process. Processing, physico-mechanical properties, volatile organic compounds emission, and recycling possibility were investigated. In order to better understand the impact of used modifiers, their efficiency was compared with trans-polyoctenamer, which is an additive that is commercially dedicated to waste rubber recycling. The results showed that a relatively small amount of ethylene-vinyl acetate copolymer improves the mechanical properties of modified reclaimed GTR and also allows further recycling by multiple processing without the deterioration of performance after three cycles.

Keywords: ground tire rubber; modification; ethylene-vinyl acetate copolymers; waste management; performance properties; recycling

1. Introduction

Three-dimensional networks present in rubber goods improve their mechanical properties, chemical resistance, and thermal stability. On the other hand, these excellent performances cause difficulties in waste rubbers management and further recycling [1–3].

The mainstream of waste rubbers is end-of-life tires. Gerrard and Kandlikar [4] proposed a breakdown of materials used in a passenger vehicles, which indicated that tires are 3.5%wt., while the other rubber goods are 1.6%wt. The dynamic development in the automotive industry increases the demand for new tires and, consequently, increases the number of waste tires. Estimated data showed that, each year, approximately 1000 million tires are not suitable for further use or retreading. Moreover, according to predictions, this value will increase by 20% by 2030 [5–8]. The current situation is a global environmental problem and a huge challenge for scientists and industry representatives.

At present, energy recovery is still the main method for resolving the issue of waste tires utilization. However, it should be pointed out that material recycling of waste tires is a more environmentally friendly option than their application as an alternative fuel in cement kilns or power plants [9].

During the recycling of waste tires, a common method is used in the form of shredding or grinding, which allows for the disintegration of waste tires into three fractions: steel, cord fibers, and ground tire rubber (GTR). The grinding of tires to a desired particle size distribution is usually performed at ambient temperature. GTR obtained by ambient grinding technology possesses a more developed surface as compared to grinding at cryogenic conditions, which positively affects further applications of GTR [10]. According to data that was presented by the European Tyre and Rubber Manufacturers Association (ETRMA) around 90% of waste tires in the European Union are recycled by this method [11].

Many research works confirmed that GTR can be successfully applied as a low-cost filler or modifier in polymers, bitumens, or concretes, and recent progress in this field was comprehensively described in review works [12–16]. However, usually increasing the content of GTR in a fresh matrix resulted in a deterioration of mechanical properties, which is related to the cross-linked structure of GTR and a rather poor compatibility with matrix.

One promising method to improve matrix-GTR interactions is the devulcanization/reclaiming of GTR, which significantly improves processing (flowability) of waste rubber and improves the interfacial interactions on the phases boundary between GTR and matrix.

Recent trends in this field research show that low-temperature devulcanization is gaining increasing attention [17–19]. The application of lower temperatures during processing allows for limiting the main chain scission and reducing the emission of volatile organic compounds that are characteristic for the reclaiming/devulcanization process. Furthermore, the main advantages of products based low-temperature devulcanization technologies are related to: (i) high quality (e.g., very good mechanical properties); (ii) less odors; and, (iii) reduced energy consumption.

On the other hand, some drawbacks are related to the processing of obtained products. This issue can be resolved by the application of plasticizers, such as bitumens [20] or petrochemical and renewable oils [21–23]. The application of thermoplastics is another possibility to enhance the processing of GTR and the performance of obtained materials [24,25].

Recently, Barbosa and Ambrósio [26] performed a thermo-mechanical devulcanization in the presence of 10%wt. of polypropylene or ethylene-vinyl acetate copolymer. The temperature that was used during extrusion was in the range of 210–270 °C. The authors indicated that a ethylene-vinyl acetate copolymer used during the reclaiming of natural rubber helps in the thermal stabilization of extrusion and it has a beneficial impact on the mechanical properties of the obtained product.

Nunes et al. [27] investigated the effect of polypropylene or low-density polyethylene (in the range of: 15–25%wt.) on the thermo-mechanical devulcanization of GTR. The process was performed in a co-rotating twin-screw extruder at a temperature range of 220–270 °C. The results showed that polypropylene is more effective than low-density polyethylene during the devulcanization process and it promotes the formulation of reclaimed GTR with higher sol fraction.

Wang et al. [28] studied the impact of two compatibilizers: polyolefin elastomer (Engage™ 8180) and trans-polyoctenamer rubber (Vestenamer® 8012) on the properties of recycled polyethylene/ground tire rubber (rPE/GTR) blends (with GTR content in the range of: 0–90%wt.). The samples were prepared in a co-rotating twin-screw extruder with a barrel temperature of between 150–180 °C. The results showed that, for rPE/GTR blend in ratio of 10/90% wt. with 9 phr of compatibilizer, tensile strength is ~2.1 MPa and elongation at break ~70% in the case of Vestenamer® 8012, while, for Engage™ 8180, these parameters were ~0.9 MPa and ~72.5% (values estimated from graphs).

Although, as presented above, thermoplastics were used to support the devulcanization process of GTR, according to the best of our knowledge there are no published data regarding their application in low-temperature devulcanization, which allows for better control of the process by the selective scission of cross-linking bonds. Moreover, the are no data about the impact of used thermoplastics on the possible recycling of GTR modified with a relatively small amount of thermoplastics (up to 10%wt.), while it seems that, in such systems, reclaimed rubber can be formed into the desired shape without the use of a curing system.

In this paper, we propose a new method of GTR treatment by low-temperature extrusion in presence of two grades of ethylene-vinyl acetate copolymers. The modification process was performed in a co-rotating twin-screw extruder. The obtained products were compared with GTR that was modified with trans-polyoctenamer (tradename: Vestenamer®)—a commercial additive dedicated for waste rubber recycling. The processing and performance properties of obtained products have been investigated by the measurement of energy consumption, temperature of reclaimed GTR immediately after extrusion, melt flow index, Mooney viscosity, static mechanical properties, swelling behavior, and volatile organic compounds emission. Moreover, for the first time, the possibility of multiple processing of modified reclaimed GTR was also studied.

2. Experimental

2.1. Materials

In order to produce studied materials, the following components were used:

- Ground tire rubber (GTR)—obtained from passenger and truck tires, with particle sizes up to 0.4 mm, was received from Grupa Recykl S.A. (Śrem, Poland). The basic components of GTR are: natural rubber (NR), styrene-butadiene rubber (SBR), butadiene rubber (BR), additives (curing system, activators, plasticizers, etc.), carbon black, silica, and ash. Thermogravimetric analysis of GTR was presented in the work [29].
- Vestenamer®8012—semi-crystalline thermoplastic elastomer known as trans-polyoctenamer rubber (TOR) imported from the Evonik company (Essen, Germany). This additive acts as a plasticizer during rubber processing or reclaiming. TOR also reacts in the vulcanization process due to the presence of unsaturated bonds in the structure. It is characterized by a high compatibility with other materials.
- Sipchem EVA 2518—ethylene-vinyl acetate copolymer containing 18.2% vinyl acetate, manufactured by Sipchem (Khobar, Kingdom of Saudi Arabia).
- Escorene Ultra EVA FL00218—ethylene-vinyl acetate copolymer containing 18.0% vinyl acetate, obtained from Exxon Mobil Chemical (Machelen, Belgium).

Table 1 summarizes the basic properties of used modifiers provided by the manufacturers.

Table 1. Properties of the used thermoplastic modifiers.

Properties	**Additive**		
	Vestenamer®8012 *	**Sipchem EVA 2518 ***	**Escorene Ultra EVA FL00218 ***
Abbreviation	TOR	EVA1	EVA2
Density at 25 °C, g/cm^3	0.910	0.935	0.940
MFI$_{190\,^\circ\mathrm{C},\,2.16\,\mathrm{kg}}$, g/10 min	13.8	2.5	1.7
Vicat softening temperature, °C	-	64	62
Melting temperature, °C	54	87	87

* Information from technical data sheets provided by producers.

2.2. Sample Preparation

2.2.1. Reclaiming of GTR Modified by Thermoplastics

Reclaimed GTR modified by thermoplastics was prepared using a co-rotating twin-screw extruder model EHP 2x20 Sline from Zamak Mercator (Skawina, Poland) with a L/d ratio of 40. The screw's diameter was 20 mm and their rotational speed was equal to 250 rpm. The extruder was equipped with eleven heating zones. The temperatures in individual heating zones (from hopper to extrusion die) on the barrel of the extruder were: 40/40/60/60/60/60/60/60/60/60/60 °C. Both components, GTR and 10 phr of thermoplastics (TOR-Vestenamer®8012, EVA1—Sipchem EVA 2518 or EVA2 - Escorene Ultra EVA FL00218), were directly introduced into the hopper with a constant feeding rate (2.5 kg/h) that was provided by a gravimetric feeding system from Hydrapress Sp. z o.o. (Białe Błota, Poland).

The extrusion resulted in partial reclaiming of GTR in the presence of thermoplastics, as presented in Figure 1. The appearance of modified reclaimed GTR was similar, regardless of the thermoplastic type.

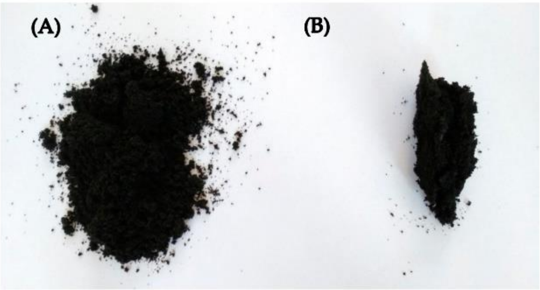


Figure 1. The appearance of products prepared by low-temperature extrusion: (**A**) ground tire rubber (GTR) and (**B**) GTR in presence of thermoplastics.

2.2.2. Formulation of Modified Reclaimed GTR by Compression Molding

Modified reclaimed GTR was directly formulated into sheets by compression molding for 5 min. under a pressure of 4.9 MPa. In order to better understand the effect of molding temperature on the performance of obtained materials, modified reclaimed GTR samples were compression molded at three different temperatures: 140, 160, and 180 °C. To clarify, Table 2 summarizes the samples formulation conditions and coding. The samples were coded as GTR+X-Y, where X is used thermoplastics (TOR, EVA1, or EVA2), while Y is compression molding temperature (140, 160, or 180 °C).

Table 2. Sample formulation and coding.

Sample Composition *	Compression Molding Temperature (°C)	Sample Coding
GTR + 10 phr Vestenamer®8012	140	GTR+TOR-140 °C
	160	GTR+TOR-160 °C
	180	GTR+TOR-180 °C
GTR + 10 phr Sipchem EVA 2518	140	GTR+EVA1-140 °C
	160	GTR+EVA1-160 °C
	180	GTR+EVA1-180 °C
GTR + 10 phr Escorene Ultra EVA FL00218	140	GTR+EVA2-140 °C
	160	GTR+EVA2-160 °C
	180	GTR+EVA2-180 °C

* All samples were prepared in the same conditions.

2.3. *Measurements*

Energy consumption during the extrusion of GTR was evaluated by two methods. The first method is based on direct measurement of energy consumption by electricity meter (include all items in the extruder, but the main energy consumption is related to barrel heaters and drive motor). The second method determines specific mechanical energy (SME, in kWh/kg—based on energy consumption of drive motor), which was calculated while using Equation (1):

$$\mathrm{SME} = \frac{\mathrm{N}}{\mathrm{Q}} \tag{1}$$

where: N is the consumption of drive motor power (kW) and Q is a throughput (kg/h).

Temperature distribution in GTR that was treated during extrusion was measured using an infrared thermal imaging camera model Testo 872 (Testo SE & Co. KGaA, Lenzkirch, Germany). Table 3 presents the specification during measurements performed by Testo 872.

Table 3. Specification and measurement parameters of Testo 872.

Item	Specification *
Measuring range	−30 to 650 °C
Accuracy	± 2 °C/±2%
Infrared resolution	320 × 240
Thermal sensitivity	60 mK
Geometric resolution	2.3 mrad
SuperResolution	640 × 480 pixels/1.3 mrad
IR image refresh rate	9 Hz
Spectral range	7.5–14 μm

* According to producer data.

The melt flow index of samples was investigated using the Zwick mFlow plastometer (ZwickRoell Group, Ulm, Germany), according to ISO 1133 at 210 °C, with a load of 10 kg.

Mooney viscosity of modified GTR was investigated while using MV 2000 viscometer (Hudson, OH, USA) according to ISO 289 at 125 °C. During measurements, a large rotor was used. The preheating time was 1 min and the measurement time was 4 min. At least three tests were performed for each sample.

The tensile strength and elongation at break of the obtained modified reclaimed rubbers were tested at room temperature according to ISO 37. Tensile tests were carried out on the universal Zwick/Roell Z020 testing machine (ZwickRoell Group, Ulm, Germany) at a constant speed of 500 mm/min. Extensometers were used to exactly measure relative elongation at break of the samples. At least five measurements were performed for each sample.

Shore hardness type A was measured with a Zwick 3130 durometer (ZwickRoell Group, Ulm, Germany) in accordance with the standard ISO 7619-1. The reported results are the means of ten measurements per sample.

The density of the samples was measured by the Archimedes method in accordance with ISO 2781 while using an analytical balance model AS 110.R2 from Radwag (Radom, Poland). The test was carried out at room temperature and it consisted of weighing the material in air and then in a methanol medium. The density value quoted in the paper is the average of at least three measurements per sample.

The determination of the swelling degree of the modified GTR and its cross-link density was carried out on the basis of the equilibrium swelling method. Small pieces of samples weighing approximately equal to 0.2 g were immersed in toluene at room temperature for 72 h. The swelling degree was calculated according to Equation (2):

$$Q = \frac{m_t - m_0}{m_0} \times 100\% \tag{2}$$

where: Q—swelling degree (%); m_t—a mass of the sample swollen after time (g); m_0—an initial mass of the sample (g).

The sol fraction was determined on the basis of the mass difference of the initial sample and the dried sample after extraction according to Equation (3). The remaining part is a gel fraction (4):

$$F_{sol} = \frac{m_0 - m_k}{m_0} \times 100\% \tag{3}$$

$$F_{gel} = 100\% - F_{sol} \tag{4}$$

where: F_{sol}—the content of sol fraction (%); F_{gel}—the content of gel fraction (%); m_0—an initial mass of the sample (g), and m_k—a mass of the dried sample after extraction (g).

Cross-link density was determined according to the Flory–Rehner Equation (5) [30]:

$$v_e = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{[V_1\left(V_r^{\frac{1}{3}} - \frac{V_r}{2}\right)]} \quad (5)$$

where: v_e—cross-link density (mol/cm^3); V_r—gel volume in the swollen sample (cm^3); V_1—solvent molar volume (toluene = 106.2 cm^3/mol), χ—polymer-solvent interaction parameter (in the calculations, it was assumed to be 0.391).

The Flory–Rehner equation is correct for non-filled compounds. The presence of rubber waste in the examined materials causes them to have a high content of carbon black. Therefore the Kraus correction should be included in order to calculate the actual cross-link density. However, in the present study, this correction was omitted, assuming that the filler content in all of the tested samples is the same, which allows for comparison of the obtained values with each other, as suggested by Barbosa and Ambrósio [26].

Total volatile organic compounds (TVOCs) parameter and chemical structure of volatile organic compounds emitted from the modified GTR were determined using microscale stationary emission chamber—Markes Micro-Chamber/Thermal Extractor™—μ-CTE™ 250 (Markes International Ltd., Llantrisant, UK) in which 2.5–3.0 g samples were conditioned for 20 min. at 40 °C. Volatile organic compounds emitted from the modified GTR were collected using stainless steel tubes filled with Tanax TA adsorption bed ((Markes International Ltd., Llantrisant, UK) under the influence of a carrier gas (nitrogen) at a rate of 25 mL/min. Subsequently, the adsorbed analytes were released through a two-stage process of thermal desorption (Markes Series 2 Thermal Desorption Systems; UNITY/TD100, Llantrisant, UK). Subsequently, quantitative and qualitative analysis of analytes that were released from the modified GTR were performed on: GC-FID system (Agilent 7820A GC, Agilent Technologies, Inc., Santa Clara, CA, USA) and GC-MS system (GC Agilent Technologies 6890 and 5873 Network Mass Selective Detector; Agilent Technologies, Inc., Agilent, Santa Clara, CA, USA). More detailed information regarding used equipment and methodology are presented in works [31–33].

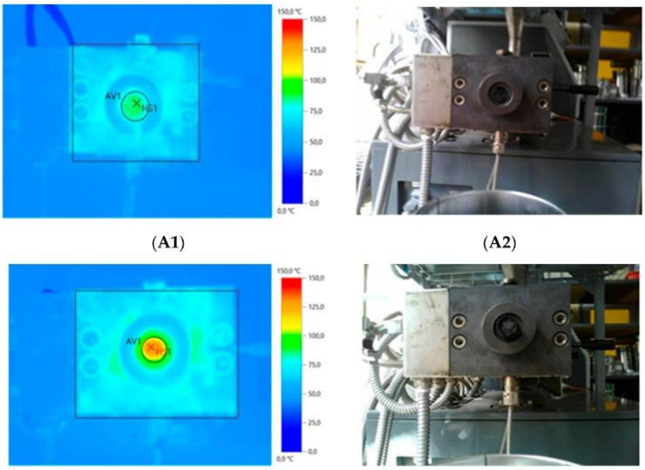
3. Results and Discussion

3.1. Temperature and Energy Consumption Measurements

It was observed that relatively small amounts of thermoplastics (10 phr) during low temperature devulcanization allow for the preparation of modified GTR in form of solid profiles (see Figure 1). Thermoplastics act like a binder that connects GTR particles, which strongly affects the temperature of the material after extrusion. Figure 2 presents the temperature distribution of GTR on the die (Figure 2(A1,A2)) and GTR+EVA2 (Figure 2(B1,B2)) measured by the thermograph IR camera immediately after extrusion.

The results showed that, for pure GTR, the maximal temperature ($T_{Maximal}$) after extrusion was 69.0 °C, while the average temperature ($T_{Average}$) was 63.0 °C. The addition of thermoplastics resulted in a significant increase in the average and maximal temperature of reclaimed GTR. Depending on the thermoplastics used, $T_{Average}$ was 107.4, 110.4, and 102.9, while $T_{maximal}$ was 136.1, 126.9, and 120.3 for GTR+TOR, GTR+EVA1, and GTR+EVA2, respectively.

The evaluation of energy consumption during processing provides useful information about process efficiency and determine the possibility of its application at an industrial scale. A common practice is to measure specific mechanical energy (SME), related to power necessary for driver motor. During presented research, this method was extended by the application of an electricity meter installed in the extruder. In this solution, energy consumption is determined for all of the items in the extruder, but most power is related to the driver motor and barrel heaters. Table 4 shows the results of temperature measurements and energy consumption.



(**A1**) (**A2**)

(**B1**) (**B2**)

Figure 2. IR camera images of: GTR (**A1**,**A2**) and GTR+EVA2 (**B1**,**B2**).

Table 4. Temperature and energy consumption measurements as function of sample composition.

Sample Composition	**Physical form of Extruded Material**	**IR Camera Record**		**Energy Consumption (kWh/kg)**			**Mooney Viscosity ML(1+4) 125 °C (MU)**
		T$_{Average}$ (°C)	**T$_{Maximal}$ (°C)**	**SME**	**Total ***	**SME in Total Energy (%)**	
GTR	**Powder with developed surface**	63.0	69.0	0.142	0.420	33.9	- **
GTR+TOR	Solid profile	107.4	136.1	0.489	0.567	86.3	124.6 ± 0.6
GTR+EVA1	Solid profile	110.4	126.9	0.457	0.545	83.8	150.6 ± 1.7
GTR+EVA2	Solid profile	102.9	120.3	0.423	0.524	80.7	142.3 ± 0.3

* Measured directly by electricity meter installed in extrusion line. ** The viscosity of sample cannot be determined in studied conditions.

Diaz et al. [34] performed thermo-mechanical reclaiming of ethylene-propylene-diene rubber in a special high shear mixer (HSM) designed as a rotor-stator system that was equipped with a cooling system dedicated independently to the rotor and stator to control rubber self-heating phenomenon. In conclusion, the authors indicated that specific mechanical energy can be used as an indicator of rubber reclaiming efficiency. It was observed that the energy needed for the waste rubber treatment decreased with a lower particle size of waste rubber. This trend is also visible in the presented work. The application of thermoplastics resulted in the formulation of a solid profile which significantly increases SME (0.423–0.489 kWh/kg) when comparing to GTR (0.142 kWh/kg) in form of powder with the developed surface, as presented in Table 4. More interesting is the tendency observed for total energy consumption (measured for all items in the extruder, but the main source of power consumption are motor driver and heaters) and percentage content of SME in total energy. The results showed that the application of a relatively small amount of thermoplastics (10 phr) in modified GTR resulted in 24.7–35.0% increase of total energy consumption when compared to GTR (an increase from

0.420 kWh/kg to 0.524–0.567 kWh/kg—depending on used thermoplastic). It was noticed that the GTR percentage content of SME in total energy was 33.9%, while the addition of thermoplastics resulted in an increase of this parameter to values in the range: 80.7–86.3%. This is related to the self-heating phenomenon of GTR with thermoplastics during extrusion, which is caused by increased friction due to the presence of a thermoplastic modifier. It significantly reduces the energy consumption of barrel heaters.

3.2. MFI and Mooney Viscosity Measurements

The MFI of used thermoplastics at 190 °C and 2.16 kg was 13.8 g/10 min. for TOR; 2.5 g/10 min. for EVA1 and 1.7 g/10 min. for EVA2, as presented in Table 1. For modified GTR, the MFI test conditions at 210 °C with load 10 kg (preliminary studies were performed for temperature in the range: 190–210 °C, load: 2.16–10 kg) were used in order to investigate processing properties. In studied conditions, prepared samples have not shown adequate flowability and, therefore, the MFI parameter could not be determined. Samples of modified GTR showed rubber-like behavior with limited flow. During measurement, the ground particles of modified GTR (particle dimension suitable to apply in a plastometer barrel) have merged due to elevated temperature and pressure. This confirms that the pressure is too low to enable the modified GTR to pass through a standard capillary die with a diameter of 2.095 mm. Garcia et al. [35] measured the melt-viscosity of reclaimed rubber using a high-pressure capillary rheometer with a capillary die diameter of 1mm and L/D ratio of 20. The measurement temperature was 190 °C and the shear rate was in the range of: 300–15000 s^{-1}. The authors pointed out that the possibility to determine the viscosity of studied samples was strongly correlated with the devulcanization degree of the sample. The results showed that this method cannot be applied for reclaimed GTR characterized by 83.5% of gel fraction content (the viscosity was measured for samples with gel fraction content lower than 73.0%). The products that are characterized in this research are characterized by a higher value of this parameter (see Table 5).

Table 5. Swelling degree, cross-link density, sol, and gel fraction of GTR modified by ethylene vinyl acetate (EVA).

Sample Coding	Swelling Degree (%)	Cross-Link Density ($mol/cm^3 10^{-4}$)	Sol Fraction (%)	Gel Fraction (%)
GTR-140 °C	166 ± 2	1.64 ± 0.06	9.6 ± 0.1	90.4
GTR-160 °C	163 ± 1	1.65 ± 0.01	9.8 ± 0.1	90.2
GTR-180 °C	169 ± 4	1.55 ± 0.07	10.5 ± 0.3	89.5
GTR+EVA1-140 °C	178 ± 3	1.36 ± 0.02	11.0 ± 0.8	89.0
GTR+EVA1-160 °C	180 ± 1	1.34 ± 0.01	10.9 ± 0.2	89.1
GTR+EVA1-180 °C	184 ± 1	1.29 ± 0.04	10.6 ± 0.3	89.4
GTR+EVA2-140 °C	172 ± 3	1.53 ± 0.06	9.4 ± 0.2	90.6
GTR+EVA2-160 °C	174 ± 1	1.49 ± 0.02	9.6 ± 0.2	90.4
GTR+EVA2-180 °C	178 ± 1	1.40 ± 0.01	10.1 ± 0.1	89.9

Taking into account the above-mentioned examples, it seems that the only way to test the reclaimed rubber with a capillary rheometer or plastometer is to change the standard dimensions of the die, which should be considered during future studies in this field.

During studies, the Mooney viscosity of modified GTR was also investigated and the results are summarized in Table 4. Regardless of the type of used thermoplastics, it was found that the application of thermoplastics allows for the determination of viscosity of modified reclaimed GTR by Mooney viscometer, while measurements for unmodified GTR were not possible. Mooney viscosity —ML(1+4) 125 °C for studied samples were: 124.6 MU for GTR+TOR; 150.6 MU for GTR+EVA1; and, 142.3 MU for GTR+EVA2. The lowest value was determined for the GTR+TOR sample, which is related to the highest MFI value of this thermoplastic modifier (see Table 1). For EVA copolymers, the viscosity of reclaimed GTR modified by EVA1 was slightly higher when compared to reclaimed GTR with EVA2. In this case, there is no simple correlation between MFI of EVA copolymers and Mooney viscosity of reclaimed GTR modified by EVA. This indicates that slight differences between sample GTR+EVA1 and GTR+EVA2 can be related to the complex composition of GTR and its intermolecular interactions with EVA copolymer, which also affect the temperature of material after extrusion (see Table 4).

3.3. Swelling Behavior

The swelling behavior of GTR that was modified by thermoplastics was investigated in toluene at room temperature for 72 h. The appearance of studied samples as a function of time was presented in Figures 3–5. As can be observed in Figure 3(A1–A3), the sample coded as GTR+TOR showed very low toluene resistance. GTR+TOR samples start to disintegrate after a few minutes of solvent extraction. The resistance for toluene increased with higher temperature of sample compression, in the order: GTR+TOR-180 °C > GTR+TOR-160 °C > GTR+TOR-140 °C, as presented in Figure 4.

As presented in Figure 5, samples GTR+EVA1 and GTR+EVA2 were stable after 72 h extraction, which allowed for the determination of their swelling degree, cross-link density, sol, and gel fraction presented in Table 5. For comparison, the results for GTR compressed in the same temperatures are also presented. It was found that for GTR modified with thermoplastics swelling degree is in the range of 172–184%, cross-link density: 1.29–1.49 mol/cm^3 · 10^{-4}; sol fraction: 9.4–11.0% (gel fraction: 89.0–90.6%). The addition of EVA copolymers resulted in the decrease of cross-link density and increase of swelling degree as compared to unmodified GTR, while the effect of this modifier on sol and gel fraction was negligible. Moreover, the presented results indicate that the cross-link density of the material is slightly higher for GTR+EVA2 when comparing to GTR+EVA1. This confirms that the lower temperature of the material after extrusion (see Table 4) resulted in a lower devulcanization degree of GTR during processing, which affects the matrix-filler interactions [36–38].

The analysis of swelling behavior in relation to changes in the sintering temperature shows that, as the temperature of this process increases, the degree of swelling increases and the cross-linking density and the sol fraction decrease. This is due to the fact that, with the increase in temperature, a partial reclaiming/degradation of the GTR takes place during the preparation of revulcanizates.

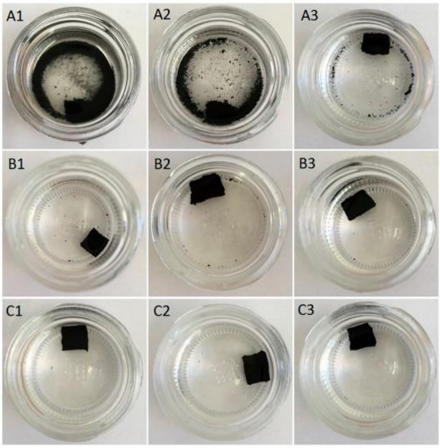


Figure 3. Samples after a few minutes of extraction in toluene: (**A1**) GTR+TOR-140 °C; (**A2**) GTR+TOR-160 °C; (**A3**) GTR+TOR-180 °C; (**B1**) GTR+EVA1-140 °C; (**B2**) GTR+EVA1-160 °C; (**B3**) GTR+EVA1-180 °C; (**C1**) GTR+EVA2-140 °C, (**C2**) GTR+EVA2-160 °C, and (**C3**) GTR+EVA2-180 °C.

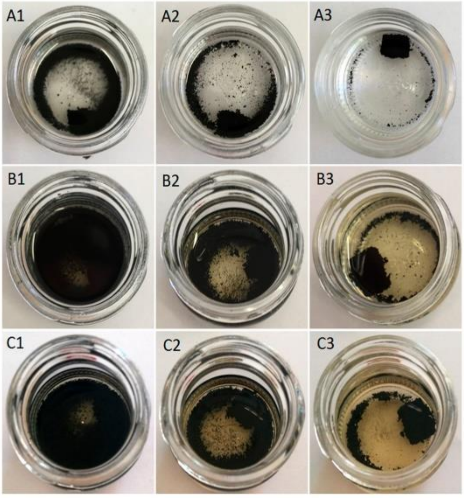


Figure 4. GTR modified with trans-polyoctenamer rubber (TOR); the letters indicate the extraction time in toluene: (**A**) few minutes; (**B**) 24 h; (**C**) 72 h; the numbers indicate the temperature at which the samples were compression molded: (**1**) 140 °C; (**2**) 160 °C; (**3**) 180 °C.

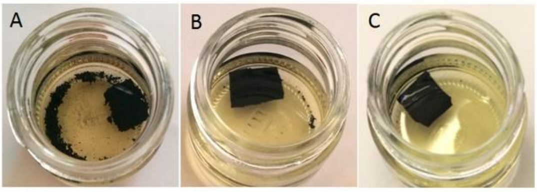


Figure 5. Samples after 72 h extraction in toluene: (**A**) GTR+TOR-180 °C; (**B**) GTR+EVA1-180 °C; (**C**) GTR+EVA2-180 °C.

3.4. *Physico-Mechanical Properties*

Table 6 summarizes the physico-mechanical properties of GTR modified by thermoplastics. For comparison, the results for GTR formulated in the same conditions (pressure, temperature) as GTR modified by thermoplastics are also presented in Table 7. It was found that a relatively small amount of EVA copolymers (regardless of EVA copolymer grade) increased tensile strength by 28%, elongation at break by 98%, and hardness by 12% as compared to values determined for unmodified GTR. Moreover, a slight decrease of density of samples GTR+EVA1 and GTR+EVA2 was observed in comparison to GTR, which is obviously related to the lower density of the thermoplastics when compared to GTR.

Table 6. Physico-mechanical properties of GTR and GTR modified by thermoplastics.

Sample Coding	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Sh A)	Density (g/cm^3)
GTR-140 °C	2.4 ± 0.2	77 ± 7	59 ± 1	1.170 ± 0.002
GTR-160 °C	2.4 ± 0.2	71 ± 6	55 ± 1	1.163 ± 0.006
GTR-180 °C	2.6 ± 0.1	79 ± 4	57 ± 1	1.149 ± 0.007
GTR+TOR-140 °C	1.7 ± 0.2	49 ± 11	63 ± 1	1.090 ± 0.007
GTR+TOR-160 °C	2.1 ± 0.2	73 ± 11	64 ± 1	1.121 ± 0.001
GTR+TOR-180 °C	2.4 ± 0.2	92 ± 14	65 ± 1	1.125 ± 0.003
GTR+EVA1-140 °C	2.7 ± 0.4	125 ± 13	64 ± 1	1.130 ± 0.003
GTR+EVA1-160 °C	3.1 ± 0.1	138 ± 10	64 ± 1	1.123 ± 0.003
GTR+EVA1-180 °C	3.4 ± 0.4	164 ± 14	64 ± 1	1.127 ± 0.003
GTR+EVA2-140 °C	3.4 ± 0.5	147 ± 16	65 ± 1	1.140 ± 0.004
GTR+EVA2-160 °C	3.2 ± 0.5	146 ± 11	63 ± 1	1.132 ± 0.002
GTR+EVA2-180 °C	3.2 ± 0.5	151 ± 21	63 ± 1	1.134 ± 0.003

The results showed that temperature had a significant impact on the values of studied physico-mechanical properties. Usually, the tensile properties increased with higher compression temperature. However, there is no simple correlation between all studied samples. For example, surprisingly, sample GTR+TOR compressed at 140 °C showed the lowest values of tensile strength and elongation at break among studies samples. This indicates that, for this system, 140 °C was too low to allow efficient encapsulation of GTR by TOR. Furthermore, GTR devulcanization during compression was rather limited in this temperature, which also affects the final performance properties of the obtained materials.

In Table 7, the final properties of modified GTR were compared with other EVA/GTR systems characterized by other research groups. The literature data showed that EVA/GTR systems prepared via melt-blending in ratio 90/10%wt. and 60/40%wt. are characterized by tensile strength in the range ~6–9 MPa, elongation at break ~310–550%, and hardness ~34–81 (Sh A) [39–41], while, for LDPE/GTR/EVA with 40–45%wt. content of GTR [42,43] tensile strength and elongation at break values are ~5–7.8 MPa and ~180–185%, respectively. The presented parameters are higher than those determined for studied materials. However, it should be pointed out that the obtained materials only contain 10 phr (9%wt.) of fresh EVA, while the systems described in the literature are usually modified with 60–90%wt. of thermoplastics. Moreover, analysis of literature data showed that the tensile strength of obtained materials is significantly higher than the 2.0 MPa determined for reclaimed GTR/EVA system in the ratio of 70/30%wt. [44]. Finally, GTR/rPE/TOR 90/10/9 proposed by a different research group [28] shows tensile strength at 2.1 MPa, elongation at break at approx. 70%, and hardness at approx. 78 Sh A, giving lower values than those that are presented in our study.

Table 7. Tensile properties of EVA/GTR systems described in literature.

Sample Composition	Sample Preparation	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Sh A)	References
GTR/EVA 100/10	extrusion at 60 °C, compression molding at 140–180 °C	2.7–3.4	125–164	63–65	This study
GTR/recycled PE/TOR 90/10/9	extrusion at 150–180 °C injection molding at 180–190 °C	~2.1	~70	~78	[28]
EVA/GTR 90/10	batch mixer at 140 °C, compression molding at 123 °C	~9 *	~550 *	~34 *	[39,40]
EVA/GTR 60/40	batch mixer at 140 °C, compression molding at 123 °C	~6 *	~310 *	~81 *	[41]

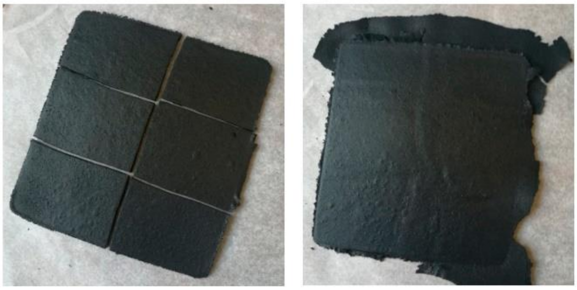
Table 7. *Cont.*

Sample Composition	Sample Preparation	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Sh A)	References
LDPE/GTR/EVA 35/45/20	extrusion at 165–175 °C, injection molding at 165–190 °C	~5 *	~185 *	-	[42]
recycled LDPE/GTR/EVA 30/40/30	extrusion at 165–175 °C, injection molding at 165–190 °C	~7.8 *	~180 *	-	[43]
Reclaimed GTR/EVA 70/30 and 50/50	batch mixer at 120 °C, compression molding at 130 °C	2.0–5.4	300–999	72–80	[44]

* The value estimated from graphs.

3.5. Evaluation of Modified Reclaimed GTR Recycling Possibility

During this study, for the first time, the possibility of modified reclaimed GTR recycling was investigated. The recycling of the GTR+EVA2 sample was simulated by multiple processing (three rounds) in the same conditions (temperature, pressure, and time of compression molding) as a reference sample. The appearance of the sample before and after material recycling is presented in Figure 6. The changes in tensile strength, elongation at break, and hardness as a function of the recycling cycle were studied and the results are summarized in Table 8. The results showed that reclaimed GTR that is modified by EVA copolymers can be successfully recycled without significant deterioration of tensile properties after three cycles of material recycling.



(**A**) (**B**)

Figure 6. Appearance of GTR+EVA2 sample: (**A**) reference sample; (**B**) sample after material recycling (sample compressed in the same conditions as the reference sample).

Table 8. Tensile properties of GTR+EVA2 sample as function of recycling cycles.

Sample Coding	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Sh A)
Reference	3.2 ± 0.5	146 ± 11	63 ± 1
1st round of recycling	2.9 ± 0.4	136 ± 17	63 ± 1
2nd round of recycling	3.1 ± 0.4	143 ± 17	64 ± 1
3rd round of recycling	2.7 ± 0.5	123 ± 25	63 ± 1

3.6. Determination of Volatile Organic Compounds

Two types of analyses were performed in order to determine the emission of volatile organic compounds emitted from modified GTR: gas chromatography with a flame ionization detector (GC-FID) and gas chromatography with mass spectrometry (GC-MS). GC-FID study allows for the investigation of the total volatile organic compounds (TVOCs) emitted from the modified reclaimed rubbers, while the GC-MS analysis provides information about the chemical structure of volatile organic compounds released from prepared materials. Table 9 presents the results of TVOCs analysis for studied samples. It was observed that a relatively small amount of thermoplastics in GTR limits the emission of volatile organic compounds. TVOCs parameter for GTR modified by thermoplastics decreased by 81–105% when comparing to GTR (decrease from 1.56 μg/g to 0.76–0.86 μg/g). This phenomenon is related to the higher thermal stability of thermoplastics when comparing to GTR, which is very important during high-temperature processing via extrusion, injection, or compression molding. For example, Ramarad et al. [44] studied the thermal stability of reclaimed GTR/EVA blends by thermogravimetric analysis. The results indicated that volatile compounds content in reclaimed GTR is 8.25%wt., while for reclaimed GTR modified by 30%wt. of EVA volatile compounds content decrease to 5.40%wt.

Table 9. Total volatile organic compounds (TVOCs) parameter determined for GTR and GTR modified by thermoplastics.

Sample Coding	TVOCs (μg/g)
GTR-180 °C	1.56
GTR+TOR-180 °C	0.86
GTR+EVA1-180 °C	0.76
GTR+EVA2-180 °C	0.78

Table 10 summarizes chemical structures of volatile organic compounds emitted from GTR+EVA2, as determined by GC-MS analysis. The presented results showed that the investigated volatile organic compounds are mostly oxidative degradation products of GTR and EVA. For GTR, determined VOCs can be divided into three groups: (i) residual vulcanization accelerators (benzothiazole, aniline); (ii) natural rubber degradation products (1-butanol; methyl isobutyl ketone; cyclohexanone; cyclooctane); and, (iii) styrene-butadiene rubber degradation products (toluene; xylene; styrene; cyclohexanone; cyclooctane; benzaldehyde; acetophenone). Low molecular compounds that are related to the degradation of EVA are: butanoic acid, ethyl ester; 5-methyl-2-hexanone and 1-butanol, 3-methyl-, acetate.

The highest intensity of peak area was noticed for limonene (13.25%) and benzothiazole (9.87%), which indicates that these two volatile organic compounds should be considered as markers for GTR reclaiming progress. Limonene concentration provides information regarding natural rubber oxidative degradation level. Due to fact that natural rubber is more prone to thermal degradation than synthetic rubbers, limonene concentration is correlated to the level of main chain scission in GTR. On the other hand, the benzothiazole level gives information about vulcanization accelerators present in GTR. Therefore, benzothiazole concentration can be a useful indicator of the disintegration of a three-dimensional network that is formed during sulfur vulcanization (degree of devulcanization).

Table 10. Volatile organic compounds identified by gas chromatography with mass spectrometry (GC-MS) measurement for GTR modified with ethylene-vinyl copolymers.

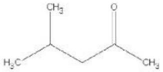
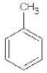
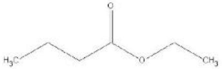
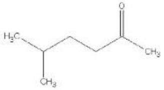
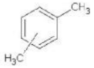
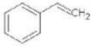
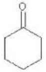
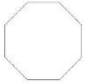
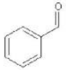
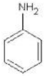
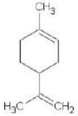
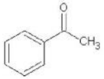
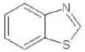
Retention Time (min)	Identified Compound	Chemical Structure	Molecular Weight (g/mol)	Peak Area (%)	Match Quality (%)	Source	References
6.58	1-butanol		74.12	2.68	90	natural rubber present in GTR	[45]
7.92	methyl-isobutyl ketone		100.16	4.74	87	natural rubber and anti-aging agents present in GTR	[18,45,46]
8.64	toluene		92.14	0.84	92	styrene-butadiene rubber present in GTR	[47,48]
8.94	butanoic acid, ethyl-ester		116.16	2.86	89	EVA	-
10.09	5-methyl-2-hexanone		114.19	1.62	91	EVA	-
10.37	1-butanol, 3-methyl-, acetate		130.18	4.67	90	EVA	-
10.59	xylene		106.16	0.58	94	styrene-butadiene rubber present in GTR	[47,48]
11.06	styrene		104.15	1.27	95	styrene-butadiene rubber present in GTR	[47,48]

Table 10. *Cont.*

Retention Time (min)	Identified Compound	Chemical Structure	Molecular Weight (g/mol)	Peak Area (%)	Match Quality (%)	Source	References
11.19	cyclohexanone		98.14	5.33	91	elastomers present in GTR	[48]
11.80	cyclooctane		112.21	4.95	97	elastomers present in GTR	-
12.50	benzaldehyde		106.12	1.43	96	styrene-butadiene rubber present in GTR	[48]
12.70	aniline		93.13	2.30	95	vulcanization accelerators present in GTR	[45]
13.58	limonene		136.23	13.25	94	natural rubber present in GTR	[45,49]
14.36	acetophenone		120.15	1.13	95	styrene-butadiene rubber present in GTR	-
17.37	benzothiazole		135.19	9.87	95	vulcanization accelerators present in GTR	[18,45,47,48]

4. Conclusions

Regardless of the proposed methodology, GTR recycling must be an economically viable and environmentally acceptable process. This means that it must be possible to use the waste material without the need for a selective collection of post-consumer tires, the treatment and modification must be cost-effective, and the products cannot be characterized as hazardous. The recycling and modification methods proposed in the study, as well as the characteristics of the finished products, are part of a pro-ecological approach to the subject. In the paper, GTR was modified by low-temperature extrusion in the presence of two grades of ethylene-vinyl acetate copolymers and trans-polyoctenamer—commercially available additive dedicated for waste rubber recycling. The reclaiming process was analyzed in terms of energy consumption, the temperature generated during self-heating of rubber, melt flow index, and Mooney viscosity. The modified reclaimed GTR samples were reactively sintered under three different temperatures (140, 160, and 180 °C). Subsequently, the samples were analyzed for static mechanical properties, swelling behavior, and VOC emissions. In addition, the possibility of recycling already received revulcanizates was investigated, which is of key importance in terms of the "green" approach. The results showed that the application of 10 phr of thermoplastic facilitates the self-heating phenomenon of GTR, reducing the energy consumption related to heating of barrels (SME of pure GTR—33.9%, SME of modified GTR—80.7–86.3%), while the overall energy consumption was higher (0.420 kWh/kg for GTR and 0.567, 0.545, and 0.524 kWh/kg for GTR+TOR, GTR+EVA1, and GTR+EVA2, respectively). The addition of thermoplastics reduced the amount of VOCs emitted to the atmosphere by 81–105%, which will significantly increase the possibilities for practical use of GTR in industrial applications. Moreover, obtained samples (GTR+EVA1 and GTR+EVA2) were characterized with satisfactory mechanical properties (tensile strength—2.7–3.4 MPa, elongation at break—125–164%, and hardness—63–65 Sh A) and recyclability without significant mechanical property loss per each stage.

Future research in this field should focus on: (i) use of cross-linking systems, plasticizers, or other thermoplastic modifiers to improve processing and tensile parameters, (ii) analysis of in-process energy consumption and evaluation of its reduction possibilities, and (iii) analysis of VOCs generated during processing and assessment of their impact on the environment and human health.

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4. Conclusions on all research carried out in the dissertation.

The topics of my research works include methods of managing waste rubber from waste automotive tires, considering the cost-effectiveness of the processes, risks associated with working on production lines, recyclability, as well as identifying inaccuracies and/or deficiencies in the literature.

Considering the above aspects, the basic ideas and paths while conducting my research have been outlined. Guided by the above assumptions, which were also partly formed during the course of the research, I have conducted a number of studies on ELT management methods, taking into account aspects often bypassed by the community. This research is presented in the five publications (P1-P5) included in this dissertation, which are based on research results from my doctoral study and the main findings are presented below.

The articles **P1** (page 46) and **P2** (page 68) show that, apart from the conclusion that the structure of the crosslinking system influences the process and final product properties, another phenomenon is of great importance for the practical use of GTR-based products. It is the phenomenon of blooming. During the tests, it was observed that white blooming occurred on the surface of the samples. This means that this undesirable phenomenon occurs due to using too much of a vulcanizing system or using a vulcanizing system that is less compatible with the matrix being used. This can have a huge impact on aspects such as: the release of hazardous substances into the environment, a negative impact on the health and life of not only the users of the product but also the production line staff, and a negative perception of the product by the consumer resulting in a decrease in potential sales. Furthermore, too high temperature can lead to ignition of the samples while the bitumen acts as an insulator, reducing the temperature to about 100°C, which protects GTR from uncontrolled oxidation and ignition.

The most important conclusion of the article **P3** (page 76) is related to determining the feasibility of revulcanizing reclaimed rubber using vulcanization accelerators alone, which was confirmed in the study (without sulfur it was possible to record a typical curing curve - ΔM 13.0-15.9 dNm). Moreover, it was determined that it is possible to revulcanize rubber using only sulfur (ΔM 22.9-25.3dNm). However, cyclization during this process is apparent (deviation from the plateau towards higher values – curing curves), which indicates its instability when no additional accelerators are applied to the crosslinking system. This also indicates incomplete vulcanization process, which was confirmed by DSC analysis (two peaks in a diagram for the 1st heating run were present only when sulfur was applied). The presented results show that the obtained materials are characterized by good performance properties, compared to the results presented by other research groups (when GTR was considered as the main component of the product). The defined parameters are sufficient to utilize the recycled GTR as a raw material for producing anti-vibration mats, dustbin wheels, water-proof rubber goods, and roofing elements, which was confirmed in discussions with manufacturers of such products.

Regarding the management of waste rubber from automobile tires, extrusion methods at elevated temperatures are well known. Such an operation makes it possible to obtain a material with a partially degraded structure, which facilitates the recycling of such materials (better processability, higher compatibility with other polymeric matrices, or better dispersion in asphalt mixtures). However, considerable energy inputs are needed for such a process, which. Research presented in the article **P4** (page 97) addresses the phenomenon of self-heating of material during low-temperature extrusion and the associated benefits (barrel temperature after the process stabilization - 25/39/54/64/69/69/68/70/70/85/96, set temperature – ambient with disabled barrel heaters). The use of lower temperatures may result in energy savings, which directly affects reducing the process costs.

On the other hand, high shear forces applied to the crosslinked rubber particles cause their mutual friction and enhance exothermic reactions during reclaiming. As a consequence, a self-heating phenomenon during GTR reclaiming can be observed.

The presented preliminary results showed that auto-thermal extrusion of GTR (process carried out without external heating) allows the production of reclaimed rubber with performance properties that are competitive with commercially available products. Moreover, the expected savings of energy and reduced emission of VOCs are also advantages of this method.

Regardless of the proposed methodology, GTR recycling must be an economically viable and environmentally acceptable process. This means that it must be possible to use the waste material without the need for a selective collection of post-consumer tires, the treatment and modification must be cost-effective, and the products cannot be characterized as hazardous. The recycling and modification methods proposed in the article **P5** (page 115), as well as the characteristics of the finished products, are part of a pro-ecological approach to the subject. It was proven that proper modification of the system could lead to a significant reduction in total VOCs. Moreover, the samples were characterized by good reprocessing parameters, showing that the samples retain their mechanical properties even at the third cycle of revulcanization.

The analysis of the presented publications allows us to draw the following conclusions.

- In order to reduce the price of the product, the typical sulfur-based crosslinking system was reduced to a peroxide-based system. This approach results in a significantly lower amount of additional resources used in the production of revulcanized products. I have shown that using organic peroxides or a simple curing accelerator is possible to produce cross-linked elastomers based on GTR.
- Due to the cross-linked structure of GTR, in products with high GTR content, the degree of physical or chemical bonding of the raw material particles is not high. This property results in the formation of gaps and voids in the structure. Moreover, it hinders the dispersion of the crosslinking system components in GTR, which is due to their limited ability to penetrate the crosslinked network. The cumulative effect of this state of affairs is the migration of excessive amounts of processing components to the

surface of the already vulcanized product, becoming a potential hazard to the environment and the people handling the product.

- Another obstacle at recycling, associated with the crosslinked state of GTR is its processability, which is essential for its recyclability. I have proved that it is possible to modify the GTR using bitumen to obtain a product with the same end properties as the reference material or even better. Unfortunately, due to the complex composition of the asphalt, there is a partial absorption of the crosslinking system reducing its effectiveness. Despite its positive impact, its application forces the use of larger quantities of crosslinking system components, which is economically unviable, particularly given the ratio of a component to matrix price.
- High-temperature processes pose a significant risk due to the potential release of harmful substances into the environment and the risk of ignition of the material. This release is especially important in microwave processes, for which GTR heating is very efficient, which often ends in material ignition. It is worth mentioning that ignition is not reported in the literature, for the conditions used in my work, where I have faced the phenomenon. I have demonstrated that it is possible to control the temperature of the product by adding bitumen, while maintaining an appropriate degree of reclaiming and mechanical properties while improving the processability of the material.
- Improved processability of GTR can be achieved by a small addition of a modifier, such as bitumen. However, due to its ability to partially absorb the crosslinking system, another solution must be found. For this purpose, a commercially available product (TOR) designed to improve waste rubber recycling was used.

However, due to the price of the GTR (approx..130-220 euro/tonne – calculated by the exchange rate on 28.06.2021) the work must be carried out in the idea of low consumption of raw material in order to keep the process cost-effective. Therefore, materials with a small addition of modifier were tested. I have shown that it is possible to obtain a vulcanized product using only vulcanization accelerators (SDT, MBTS, and CBS) and a small modifier (TOR) addition improves the material processability and strength properties.

- The GTR reclaiming process is an important industrial method of rubber recycling, which is highly influenced by temperature. The use of lower temperatures may result in energy savings, which directly affects the reduction of the process costs. On the other hand, high shear forces applied to the cross-linked rubber particles cause their mutual friction and enhance exothermic reactions during reclaiming. As a consequence, a self-heating phenomenon during GTR reclaiming can be observed. I have shown that auto-thermal extrusion of GTR (process carried out without external heating) allows the production of reclaimed rubber with performance properties that are competitive with commercially available products. Moreover, the expected savings of energy and reduced emission of VOCs are also advantages of this method.
- Due to the price and quality of GTR-based products, its recycling should be cost-effective as well as not harm the environment. This means that the treatment and modification must be cost-effective, and the products cannot be characterized as hazardous. I have shown that it is possible to obtain a product based on a waste tire having higher properties than commercially available products, and at the same time it is possible to recycle it again without any loss in final properties, up to three cycles. I also highlighted the quantity and quality of potential volatile organic compounds generated from the product. Further research work will focus on promoting a more conscious approach towards GTR upcycling.

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> *„Nie można zrozumieć procesu przez zatrzymanie go. Zrozumienie musi podążać z biegiem procesu, musi się przyłączyć i płynąć razem z nim.”*
>
> ~Frank Herbert, Diuna

Powyższa praca, jak i dorobek naukowy autora, jest efektem ciężkiej, pięcioletniej pracy w tematyce zagospodarowania odpadów gumowych. Jednakże, aby mogła ona powstać wiele osób użyczyło mi swojej wiedzy, wsparcia oraz czasu, dzięki czemu stałem się lepszym pracownikiem oraz świadomym naukowcem. W związku z tym, chcę w tym miejscu gorąco podziękować tym osobom, bez których nie byłbym tu, gdzie jestem.

Po pierwsze, chcę podziękować mojemu promotorowi prof. dr hab. inż. Józefowi Haponiukowi, który to zdecydował się wziąć mnie pod swoje skrzydła na czas trwania moich studiów doktoranckich. Jestem szczególnie wdzięczny za jego wsparcie, w postaci ogromu przekazanej wiedzy, ale również duchowe, gdyż uśmiech i radość jaką ze sobą na co dzień niesie powinna być przykładem dla każdego pracownika uczelni. Gdyby ludzkość miała tyle radości, szczerości i uśmiechu w sobie co Pan Profesor, zażegnalibyśmy większość światowych konfliktów.

Dedykuję tę pracę również dr inż. Krzysztofowi Formeli. To dzięki jego ciężkiej pracy, wiedzy, zdolnościom i sukcesom byłem w stanie tak szybko się rozwijać i twardo stąpać po uczelnianej rzeczywistości. To mnogość coraz to nowych i zróżnicowanych zadań sprawiła, że uważam się za doświadczonego pracownika. Jednakże, zdolności to nie wszystko. Krzysiek jest przede wszystkim dobrym człowiekiem. Zawsze dba o dobro swojego zespołu, i co według mnie jest najważniejsze, liczy się ze zdaniem każdego z jego członków.

Podziękowania również kieruję do dr inż. Paulinie Kosmeli oraz dr inż. Aleksandrowi Hejnie. Przy nich praca na uczelni nigdy nie była nudna. Czy poprzez przekomarzanie się, czarny humor, czy sesje Energy 2000, zawsze czułem się dzięki nim jako część uczelnianej społeczności.

Natomiast, przede wszystkim, chciałbym podziękować mojej żonie Darce. Jestem pewny, że bez jej wsparcia, miłości i poczucia humoru nigdy nie ukończyłbym studiów doktoranckich. To ona nadaje mojemu życiu sens. I jak praca jest jedynie kroplą w jeziorze mojego życia, tak jej miłość wypełnia pozostałą jego część.

Dziękuję.

Research achievements

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1. Kosmela, P., Olszewski, A., **Zedler Ł**., Burger, P., Piasecki, A., Formela, K., Hejna, A. (2021). Ground Tire Rubber Filled Flexible Polyurethane Foam—Effect of Waste Rubber Treatment on Composite Performance. Materials, 14, 3807. https://doi.org/10.3390/ma14143807
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Projects

1. Position of the contractor of the LIDER project " Opracowanie niskoemisyjnej technologii wytwarzania modyfikowanych regeneratów gumowych jako proekologiczna metoda recyklingu zużytych opon samochodowych" funded by the National Centre for Research and Development.
2. Position of contractor of the LIDER project " Opracowanie technologii wytwarzania spienionych kompozytów poliuretanowo-gumowych do zastosowania w charakterze materiałów tłumiących " 2017 funded by the National Center for Research and Development
3. Participant of the research project "Innovative technology for continuous rubber devulcanization", whose applicant is Recykl Organizacja Odzysku S.A. under 1.2: "Sectoral research and development programs"

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