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Microwave treatment in waste rubber recycling – recent advances and limitations

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Abstract. Environmentally-friendly microwave heating is increasingly used in polymer chemistry and technology. The selectivity and highly efficiency in the heat transfer present a huge advantage in systems based on recycling, improving their productivity and economic competitiveness. In case of the industrial recycling of waste rubbers, especially end-of-life tires, microwave-induced devulcanization and pyrolysis are nowadays considered as promising approaches. This work aims to report the recent progress in microwave treatments of vulcanized rubbers with different compositions. Special attention is focused on the correlation between microwave processing parameters and devulcanization/pyrolysis efficiency, which have a significant impact on the structure-property relationships of the obtained products. Moreover, the main challenges affecting the future of the industrial application of the microwave technology in rubber recycling are also discussed.

Keywords: *recycling, waste rubber, microwave radiation, devulcanization, pyrolysis*

1. Introduction

Three-dimensional network present in cross-linked polymers improves their performance, including mechanical properties, chemical resistance and thermal stability. On the other hand, these features caused that cross-linked polymers, such as thermosetting resins, cross-linked polyolefins, polyurethane foams and vulcanized rubbers are very difficult to recycle [1]. As a consequence, recycling of these materials is still very limited and the principal method of reusing them is through energy recovery or landfilling. Landfilling is illegal in the European Community and many countries.

The presented work is focused on the problem of waste rubbers recycling as a continuation of the authors' research in this field [2–6]. According to data provided by The Freedonia Group – Industry Market Research, the global production of tires is projected to rise by 4.1% per year through 2019. This indicates that the demand on tires is continuously increasing every year, corresponding to the dynamic development of automotive industry which grows in number of total vehicles and the increase in average annual vehicle mileage, boosting tire replacement rates. Simultaneously, around 1000 million of waste tires are discarded worldwide each year and more than 50% of them are directly discarded, landfilled or burned. Moreover, estimated data shows that in 2030, this number can reach 1200 million annually [7, 8]. It should be mentioned that illegally dumped or stockpiled waste tires can collect stagnant rain water pools in their curvy structures, where the rubber can leach compounds that are toxic to aquatic organisms [9]. Additionally, the high humidity existing inside landfilled waste tires creates ideal breeding grounds for rodents and mosquitoes, which can carry diseases [10]. Uncontrolled fire of disposed waste tires constitutes another serious threat, which affects the environment

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*Corresponding author, e-mail: kformela.ktp@gmail.com and human health. Although tires are materials relatively difficult to ignite, their fire is very hard to extinguish [11]. Many incidents have been reported, for example in 2016 the biggest illegal waste tire landfill in European Union caught fire. It was happened in Seseña a village near to Madrid (Spain), where 70000–90000 tons of tires had been illegally accumulated for more than 15 years. The fire of that illegal landfill caused evacuation of that around 9000 people from their houses due to environmental pollution by gaseous products, such as polycyclic aromatic hydrocarbons and other hazardous compounds [12, 13]. The increasing number of waste tires is a serious threat for the environment and currently one of the biggest challenges of the 21st century waste management.

Several attempts have been made in order to manage the recycling of the whole end-of-life tires. Recently, Grupa Recykl S.A. (Poland) opened an interesting online shop called 'OPONUM' which sells used tires for the automotive sector. Prior to reuse, the recycled tires are subjected to a meticulous quality control. The company estimates that the annual scale of used tires trade in Poland is around 1.5–2 million tires (several thousand tons).

In terms of currently conducted research work, the recycling of waste tires can be categorized into three main strategies: i) *grinding technologies and application of ground rubber;* ii) *pyrolysis* and iii) *reclaiming/devulcanization of waste tires.*

The size reduction of waste tires in the form of grinding is among the most commonly applied recycling technologies [14]. The mechanical disintegration of the cross-linked rubber is generally conducted at ambient temperature until the required particle size has been reached. In some cases, cryogenic conditions with liquid nitrogen as freezing medium are also applied. However, ground tire rubber (GTR) obtained via ambient grinding possesses better developed surface than ground rubber obtained by cryogenic method [15]. Surface area and particle size of cross-linked waste rubber are the most important parameters affecting the interphase interactions between matrix and ground tire rubber. The limitations in particle size are related to the energy consumption of the grinding process, which is obviously increased with the size reduction of waste tires, strongly affecting the final costs of GTR.

GTR can be moulded in simple shapes by application of high pressure and temperature causing reactive sintering [16]. This process can be performed in the presence of a curing system or without any additives. However, this method is limited, as mentioned above, to the production of low-cost products with simple shapes and low quality requirements. In order to improve their processing and performance properties, GTR particles need to be modified or blended with other polymeric matrix.

With the purpose of obtaining materials able to be used in applications with higher added value, attempts to include GTR as filler in elastomers, thermoplastic polymers and thermosets have been made. The results show that a high amount of GTR in polymer compositions deteriorate their mechanical properties, what is related to the weak interfacial interactions between the polymer matrix and GTR filler. Therefore, promoting interfacial interaction between GTR and polymer matrix is necessary and can be induced by the use of appropriate compatibilizers. The structure-property relationships of various polymer/GTR systems and different strategies to enhance the compatibility of studied materials have been comprehensively described in works [17–19].

The idea of combining GTR with a matrix has been also applied to the inclusion of GTR in construction and building materials, usually as modifier of cement, concrete and bitumen [20]. The literature data have confirmed that road pavements modified with GTR exhibit higher toughness and resistance to climatic factors, which have a beneficial influence on their durability and maintenance costs. The main factors limiting the common use of bitumen modified with GTR are the low stability and high viscosity causing some inconveniences in its storage and consequent further application. Comprehensive literature reviews about recent progress in this field have been presented in works [21, 22].

Other promising routes for industrial recycling of waste rubber are pyrolysis or reclaiming/devulcanization technologies. Both methods allow a controlled decomposition of waste rubber. Pyrolysis is the thermal decomposition (~500 °C or more) of waste rubber conducted under an inert atmosphere. The obtained products can be categorized into three main streams: gaseous products, pyrolytic oils and pyrolytic carbon. The research works in this area are dedicated mostly to the kinetics of waste rubber decomposition (optimization of the process) and valorization/activation of pyrolytic carbon in order to improve its further application as active carbon or reinforcing filler.

Comparing to pyrolysis the temperature during reclaiming (sometimes called in the literature as devulcanization process) is much lower (~200 °C) and usually do not use inert atmosphere. This process involves destruction of the three-dimensional network present in cross-linked rubber by using thermal, mechanical or chemical energy. The obtained products, called reclaimed rubbers, can be easily processed, shaped and vulcanized. Moreover, the final properties of obtained reclaimed rubber can be successfully tailored by changing the reclaiming conditions [23, 24]. Many attempts in this field have been described in the literature, what was comprehensively summarized in works [25–27].

Saiwari *et al*. [28] investigated the effect of the temperature on the reclaiming efficiency of different unfilled elastomers. The devulcanization of four types of unfilled vulcanizates based on styrene-butadiene rubber, butadiene rubber, natural rubber and chlorinated butyl rubber (all commonly used in tires) was examined. The results indicated that devulcanization should be performed at a reasonably low temperature, which allows a high ratio of cross-linking bonds to main chain scission, and a homogenous breakdown of the vulcanized network. Gągol *et al*. [29] indicated that low temperature during reclaiming of GTR reduces the amount of volatile organic compounds emitted during reclaiming. Other advantages of low temperature devulcanization are related to reduction of energetic costs (heat is generated by high shear forces) and limitation of secondary cross-linking. Song *et al*. [30] examined the samples of GTR with a variable content of soybean oil, which were treated by hot-air at 150 °C for 4 h. The results showed that the cross-linked network present in GTR was destroyed heterogeneously at relatively low temperature, due to the synergistic effects of the soybean oil and controlled oxidation. Moreover, it was found that carbon black separated from the cross-linked network of GTR in highly degraded samples. On the other hand, the low temperature during devulcanization might cause technological problems with further processing of reclaimed GTR [31].

Recently, Dobrotă and Dobrotă [32] described a grinding technology supported by ultrasonic treatment, which allows the production of ultrafine rubber particles with dimensions in the range of 100–150 μm. The authors pointed that ultrafine rubber particles (probably with partially devulcanized surface) can be successfully incorporated as a substitute of reclaimed rubber in rubber compounds. The physico-mechanical properties of vulcanizates with ultrafine rubber particles were higher (or comparable) to those determined for reference sample. In addition, the application of the ultrasound treatment during the grinding of waste rubber reduced energy consumption in 2–2.5 times comparing to conventional grinding and simultaneously increased the process throughput.

The works mentioned above confirm that the research performed on low temperature 'green' reclaiming/devulcanization methods should aim to the optimization of the process, especially on devulcanization time in order to reduce the energy consumption and also to the improvement of the properties of obtained reclaimed rubbers. This approach would allow the sustainable development of the reclaiming/devulcanization technologies and would fulfill the strict requirements of the environment protection. Therefore, further research studies in this field is fully justified.

Application of microwave radiation for low temperature and short-term devulcanization technologies seems to be promising approach. The first tests using of microwave devulcanization of waste rubber were patented by Novotny *et al*. [33] from The Goodyear Tire & Rubber Company. The microwave radiation, acting on the GTR, causes its controlled thermal degradation/oxidation in a process of high efficiency and environmentally-friendly character. Besides, compared to other heating methods based on convection or conduction, microwaves allow a precise and fast increase of the temperature inside the heated material.

Although the use of microwave energy in waste rubber recycling is known for 40 years, its industrial application is still very limited. In this work, the recent progress in microwave-induced waste rubber devulcanization and pyrolysis is presented, including a discussion of their advantages and limitations. The influence of the microwave treatment parameters on the final properties of waste tires recycling products is also exposed.

2. Microwave treatment of rubber – basic concepts

The efficient use of the energy is a priority in industry. In chemical processes, the importance of achieving a way of providing a precise amount of energy, in a specific location, is paramount in order to obtain a better control of the chemical reactions. Microwaves have been used in laboratories and industry because of their efficiency, easiness of application, possibilities of energy regulation and temperature control.

These advantages have motivated the use of microwaves to the vulcanization and devulcanization of rubber as an alternative to conventional heating. In a microwave heater, the magnetron is the source of microwaves. The radiation produced is driven to a cavity, where the waves interact with the sample. The electric field of the microwaves generates heat in the sample by:

i) Dipole rotation: the dipoles present in the sample tend to align following the oscillating electric field, this rotation results in an increase of temperature of the sample.

ii) Ionic conduction: if there are any free ions or ionic species in the sample, the electric field generates ionic motion. Metals, very conductive, can cause an explosion when introduced into a microwave oven. They act as reflectants of the microwave energy. The microwaves do not penetrate the metal surface, instead the waves are reflected and the induced voltage generates electrical discharges.

iii) Interfacial polarization (so-called Maxwell-Wagner effect): it is observed in systems where inclusions of conductive materials in a nonconductive matrix are present. In this situation, the material exhibits good absorption of the microwave radiation.

The behavior of a sample, when exposed to a microwave radiation, depends on its participation in those mechanisms. The material can be conductive, as in case of metals, and then acts as an opaque material, reflecting the radiation. Other materials behave as insulators, like the hydrocarbons. They are transparent to the microwaves, which pass through them without any interaction. Finally, the absorbers are characterized as high dielectric loss materials and are susceptible to heating (e.g. water).

The main parameter related to the susceptibility of a material to being heated by microwaves is the loss tangent which is defined as Equation (1):

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{1}$$

where ε' and ε'' are respectively the dielectric constant and dielectric loss of the material. That defines the capacitive and conductive components of the complex relative permittivity ε^*, as presented in Equation (2):

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{2}$$

According to these considerations, microwaves differ from conventional heating in several aspects that acquire special relevance when applied to chemical reactions or controlled decomposition of waste rubbers. First, the microwaves interact directly with the polar molecules or ions, the heat is generated from the inside of the material to the outside. Instead, in conventional heating, the heat is transferred to the surface and then into the material following conduction, convection, and radiation mechanisms. In case of microwave radiation, the increase of temperature is faster than in conventional heating and a high energy amount can be applied in a short time. The existence of materials that are transparent to the microwaves opens the possibility of constructing vessels and containers that are not affected by the radiation. Plastic materials as polypropylene, polyethylene have been used and also, because of its resistance to high temperatures, polytetrafluoroethylene.

As mentioned previously, the devulcanization processes aim to achieve the breakage of the sulfide bonds with the minimum degradation of the main polymeric chains of the rubber. This objective is based on the lower dissociation energy of the monosulfidic, disulfidic and polysulfidic cross-links (285, 268 and below 268 kJ/mol, respectively) compared to the main C–C (351 kJ/mol) [34]. The possibility of controlling precisely the amount of microwave energy delivered, by tuning the processing parameters (e.g. magnetron power, treatment time), increases the selectivity of the sulfidic cross-linking bonds scission vs main chain degradation, which allows the tailoring of the final properties of prepared reclaimed rubber.

The application of microwaves to the devulcanization of rubber has also drawbacks. First the rubber must be exempt of metals impurities. This is particularly relevant in case of scrap tire rubbers, because they contain inherently wires that are removed when the tires are processed for recycling. However, the process does not always ensure their complete removal, leaving a small amount of metallic impurities inside the ground rubber. Second, some rubbers are non-polar (e.g. EPDM) and non-affected by the microwave radiation. In some cases, the presence of common fillers like carbon black (an excellent microwave absorbent) induces the heating of non-polar rubbers.

The microwaves technology has been applied since 1950 to several industrial processes. In the field of polymer chemistry and technology, continuous and periodic microwave-induced vulcanization is one of the most important applications of microwave heating to polymeric materials [35]. In case of applying microwaves to the synthesis and preparation of other polymeric materials, the development was rather slow due to the lack of reproducibility of the results. In an attempt to solve this problem, different types of microwave ovens have been designed and modified.

The two main types of microwave ovens are the multimode and the single mode. The multimode type is the equivalent to the domestic microwave ovens. There is a cavity where the radiation produced by the magnetron is transmitted. The walls of the cavity are built on metal, a microwave reflective material. When the microwaves are irradiated in the cavity, they are reflected by the opposite wall and there is a constant bouncing of the radiation that produces a permanent transit of the waves in two opposite directions. Furthermore, only few microwave frequencies are dedicated for devices used in industry, science and medicine (the most common MW frequencies are 0.915 and 2.45 GHz). Based on these specifications, the chamber of the oven is designed with appropriate dimensions in order to achieve the resonance of the waves within the frequency width of the band. An optimized design aspires to achieve a constant intensity through the cavity. This implies that the cavity should be designed with a shape and dimensions that produce many modes to be excited at the same time and the overlapping of the areas of high and low energy produced by each individual mode can act compensating the lower energy of one mode with the higher of the other and resulting in each area of the cavity recieving equal amount of energy. In practice, this is difficult to achieve, because some parts receive more energy than others and relatively small changes in shape might result in big differences in the number of excited modes or field patterns. More homogenous results are obtained with the inclusion of stirrers or ventilation fans which act at the same time as wave reflectors. The existence of areas receiving high energy or hot spots in microwaves ovens has been comprehasively described in work [36]. As a result, the use of microwaves to induce chemical reactions (e.g. rubber decomposition) has been often regarded as a procedure with scarce reproducibility.

The single mode ovens have been designed in order to improve the reproducibility of the multimode ovens. In the single mode ovens, only one wave is generated during the irradiation and the cavity is designed for the length of only that wave. The energy inside the cavity can be then distributed homogeneously and is usually higher than in multimode ovens. These ovens include usually control of temperature and pressure.

The devices used normally in the literature related to waste rubber recycling are prototypes and variations of domestic ovens. In most studies, the cavity of the oven is basically empty, a relatively small amount of sample is deposited inside and it is irradiated. If the sample is large, the differences in the amount of energy existing in different points of the cavity can be compensated by the movement and volume of the sample, which absorbs most of the energy produced. If the sample is very small, a big part of the microwave energy is wasted and the incidence of the hot spots is higher, the position of the sample in the cavity is also relevant. This implies that the reproducibility of the tests performed might be difficult when a slight change in the equipment takes place. A good practice that could help to the comparison of these data would be the inclusion of a temperature map of the sample after the treatment. While accepting that this information can be difficult to obtain in many cases, these data could be used to compare the effect produced by the microwave radiation in a sample independently from the piece of equipment used and some of the process variables.

The differences in composition of tires, their complex nature, due to the presence of other compounds, such as extender process oil, fillers, additives, curing agents and plasticizers, the size of the particles and their shape, all these factors can affect significantly to the behavior in a microwave field and consequently reproducibility of obtained results.

3. Microwave devulcanization of variable waste rubbers

3.1. Model compounds

Kleps *et al*. [37] investigated the effect of microwave exposure time on structural changes in model vulcanizates based on natural rubber (NR), styrene-butadiene rubber (SBR) and ethylene-propylene-diene rubber (EPDM). In this work, for the first time, thermogravimetric analysis (TGA) as analytical technique was used for evaluation of microwave devulcanization efficiency in cross-linked rubbers. It was found that, regardless of rubber type, MW treatment of studied vulcanizates resulted in a decrease of the total content of organic component and a simultaneously increase of carbon black/carbon residue. In addition, the authors confirmed that TGA is a very useful tool to establish the optimal parameters of the devulcanization process.

Hirayama and coworkers [38, 39] examined the impact of carbon black content (in the range of: 0–100 phr) on microwave devulcanization of SBR model compounds. It is important to notice that carbon black particles (as conductive filler) in the rubber matrix are responsible for the heating of vulcanizates during microwave processing. Figure 1 presents the correlation between temperature after MW treatment and carbon black content. The results showed that microwave devulcanization is more effective for SBR vulcanizates with higher content of carbon black and was verified in samples with more than 60 phr of this reinforcing filler.

These observations correspond with work of de Sousa and Scuracchio [40], who studied the role of carbon black on MW devulcanization of natural rubber. The authors pointed out an important issue. In case of microwave treatment applied to ground rubber, the differences in particles size should not have an impact on the devulcanization process, because microwave heating is volumetric and less dependent of conduction or convection phenomena. Figure 2 shows samples with variable content of carbon black (in the range of: 0–80 phr). As could be observed, temperatures achieved by 2 or 5 min of microwave treatment increase with the carbon black content. The carbon black promotes increase of temperature during MW treatment of waste rubber. The values of gel content for sample with the MW irradiation for 2 min do not show a big change. As the gel content is related to the cross-linking of the sample, the results indicate that the energy produced by the microwave treatment in 2 min is not enough to significantly alter the cross-linked structure of the samples. On the other hand, when the MW treatment is prolonged to 5 min, an increase of temperature after MW treatment and consequently decrease of the gel content are observed. This indicates that the increase of temperature after MW treatment of the vulcanizates is the main factor affecting devulcanization efficiency (measured as change of gel content), which is dependent on microwave exposure time and carbon black content.

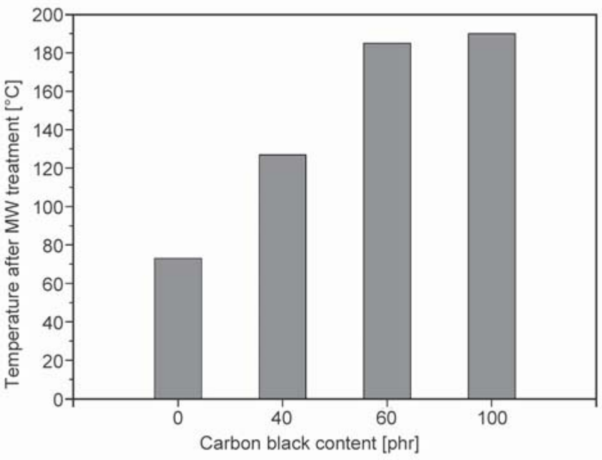

Figure 1. The effect of carbon black content on temperature of reclaimed SBR based model vulcanizates after MW treatment (devulcanization conditions: Magnetron power: 700 W, time: 2 minutes, speed of stirring: 40 rpm) (Data adopted from [38, 39]).

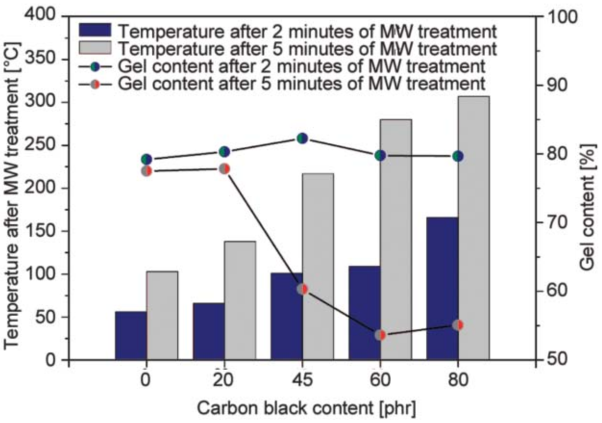

Figure 2. The correlation between temperature after MW treatment and gel fraction as functions of carbon black content and MW treatment time (Data adopted from [40]).

Based on the literature data, the MW devulcanization efficiency of SBR and NR model compounds was compared and summarized in Table 1. As could be observed, under the studied conditions, the changes in temperature after MW treatment and gel fraction content values for SBR were noticeably higher compared to NR. This indicates that the efficiency of SBR devulcanization was higher than for NR, although NR is more prone to thermal degradation than synthetic rubbers [41]. This phenomenon could be related to differences in: i) level of carbon black dispersion and its distribution into both rubbers, ii) microwave

Table 1. Comparison of MW devulcanization efficiency of SBR and NR model compounds (Data adopted from [38–40]).

MW devulcanization conditions	Rubber matrix	Carbon black content [phr]	Temperature after MW treatment [°C]	Gel content [%]		Ref.
				Vulcanized rubber	Devulcanized rubber	
Magnetron power: 700 W, time: 2 minutes, speed of stirring: 40 rpm	SBR	0	73	90.5	90.5	[38, 39]
		60	185	87.0	77.1	
	NR	0	56	83.0	79.2	[40]
		60	109	82.7	79.8	

specific energy *E* value [Wh/kg] (the parameter discussed in Equation (3)) or iii) design of the microwave oven (e.g. chamber dimensions, stirring, hot spots issues, etc.), which could affect the microwave treatment efficiency. However, that should be explained during further research studies in this field.

3.2. Waste tire rubber

The final properties of waste tire recycling products and the repeatability strongly depend on their chemical structure and composition. As presented in Table 2 composition of tires is very complex and obvious differences between passenger car tires and truck tires can be observed.

Truck tires contain more natural rubber and less carbon black comparing to passenger car tires. This is due to the different requirements on the properties of passenger car tires (e.g. low rolling resistance, improved skid resistance and good wear) [42]. The results obtained for model compounds presented in the previous sub-section, indicate that the differences in composition (especially in carbon black content) affect the MW devulcanization process. Additionally, truck tires include a higher content of steel reinforcement and the metal impurities remaining in the GTR might cause uncontrolled discharge during MW treatment. The information about carbon black content and presence of metal impurities is very important in order to achieve reproducibility of the experiments performed by different research groups. Another influential factor that should be considered during research is the weight of sample. The microwave specific energy *E* [Wh/kg] during microwave treatment can be estimated by Equation (3):

Table 2. Typical composition of passenger and truck tires in Europe [42].

Composition	Passenger car tire	Truck tire
Natural rubber	22%	30%
Synthetic rubber	23%	15%
Carbon black	28%	20%
Other additives (e.g. curing system, fibers, processing aids, etc.)	14%	10%
Steel	13%	25%
Estimated average weight of new tire	8.5 kg	65 kg

$$E = \frac{P \cdot t}{m} \tag{3}$$

where P – microwave power [W], t – radiation time [h] and m – weight of sample [kg].

When planning and designing experimental works in this field, these technological issues should be taken into account.

Scuracchio *et al.* [43] perfomed thermal analysis of GTR devulcanized by microwaves. GTR obtained from the treads and sidewalls of passenger car tires was treated by microwaves at constant power of magnetron (700 W) and a variable time (in the range of: 1–5 minutes). The obtained results are summarized in Table 3. Generally, it was found that longer microwave exposure time increases maximal temperature of GTR after MW treatment and at the same

Table 3. Temperature after MW treatment, gel content, mass loss between 200–350 °C and T_g of GTR as function of MW radiation (Data adopted from [43]).

Sample	Temperature after MW treatment [°C]	Gel content [%]	Mass loss between 200–350°C determined by TGA [%]	T_g determined by DSC [°C]
Untreated GTR	–	85	17.1	–59.7
GTR 1	95	85	16.6	–
GTR 2	141	84	12.3	–59.6
GTR 3	236	64	10.1	–60.1
GTR 4	282	54	10.3	–46.8
GTR 5	312	GTR turned to char	4.9	Not detected

time decreases gel content in the sample, that confirms more efficient degradation of three-dimensional network present in GTR. On the other hand, glass transition temperature (T_g) determined by differential scanning calorimetry (DSC) increased after 4 minutes of treatment, while after 5 minutes of the exposure the parameter cannot be determined due to GTR carbonization. These observations are in agreement with the values of mass loss between 200–350 °C measured by TGA, which confirms that this technique can be successfully applied for the evaluation of devulcanization process.

Garcia *et al*. [44] studied the physico-chemical changes that occur in GTR after different microwave exposure periods (in the range of: 3–7 minutes). Used GTR (0.25 mm) was obtained by grinding of truck tires tread layers. The microwave specific energy (E) during MW treatment of the studied samples varied in the range of: 227.8–1594.4 Wh/kg. It was confirmed that a long time of microwave treatment results in many structural changes in GTR. The following conclusions can be drawn: i) a partial decomposition of NR chains resulted in increase of carbon black content; ii) carbon black adsorbs the volatile degradation products formed during MW treatment, which enhances thermostability of reclaimed GTR; iii) high temperature and pressure during rheological analysis did not revulcanize treated GTR; iv) carbon black particles migrate from NR to SBR phase in case of samples treated at higher microwave specific energy and v) the morphology of reclaimed GTR is very similar to a droplet dispersion, NR drops in a continuous phase of SBR.

Colom *et al*. [45] evaluated the impact of MW treatment on GTR with different contents of organic compounds (elastomers, plasticizers, etc.), carbon black and ash. The analysis of chemical structure using FTIR spectroscopy indicates that the microwave treatment of GTR resulted in thermal oxidation reaction which converts part of carbon black into carbon dioxide. Additionally, a correlation between the amount of silica present in GTR and degree of devulcanization was observed. GTR with higher content of silica was characterized by higher degree of devulcanization, which indicates that hydrophilic silica enhanced microwave treatment efficiency. This phenomenon suggests that water absorbed by hydrophilic silica (e.g. during storage of GTR) evaporate when GTR is treated by microwaves, enhancing its devulcanization process.

Ateeq and Al-Shamma'a [46] investigated the impact of MW treatment parameters on the morphology of reclaimed GTR and its interactions with bitumen. Used GTR (2–6 mm) was obtained by mechanical grinding of waste trucks tires. During the experiment, the authors determined the effects of the following parameters: i) five different power levels of magnetron were applied in range of: 250–1000 W; ii) five different distances of the sample from the radiation source (defined as height of samples position in range: on the turntable to 8.5 cm high) and iii) radiation time in range of: 0–80 minutes. To the best of our knowledge, the authors used the longest microwave treatment of waste rubber described in the literature. Sample of GTR (15 g) was treated for 50 minutes when magnetron power was 750 W (microwave specific energy $E = 41\,666.7$ Wh/kg) and up to 80 minutes for magnetron power 50 W (microwave specific energy $E = 4444.4$ Wh/kg). Novotny *et al*. [33] in the patent about microwave devulcanization of rubber claimed that for microwave frequency between 915 and 2450 MHz, the dose should be in the range of: 90.2–389.4 Wh/kg, which resulted in elastomer temperature in the range of: 232–427 °C. Surprisingly, the authors did not mention the decomposition of the rubber or its carbonization, although microwave specific energy used was much higher in comparison to other previously discussed works. Moreover, the presented SEM images show that the surface of treated GTR is smoother compared to unmodified GTR, while the cross-linked rubber structure seems to be preserved. These unexpected observations should be verified and explained.

Recently, de Sousa *et al*. [47] indicated that the temperature reached by GTR after MW treatment is one of the most important factors affecting the course of devulcanization (selective scission of sulfide cross-linking bonds vs main chain degradation). It was also confirmed that natural rubber phase in GTR undergoes a higher degree of degradation than styrene butadiene rubber phase. The authors explained this phenomenon by higher affinity of carbon black filler to NR phase compared to the SBR phase.

3.3. EPDM rubber

Bani *et al*. [48] studied the impact of MW radiation time (in the range of: 5–7 minutes) and magnetron power (40 and 80% of maximum power – no information about this value) on the devulcanization of waste EPDM. The results indicated that the effective devulcanization process of EPDM starts at temperatures above 300 °C and the obtained products showed satisfactory physico-chemical properties. The authors also mentioned technical problems linked to the use of the microwave oven in devulcanization at laboratotry scale. The main difficulties are related to: i) homogeneous distribution of temperature profile inside the MW reactor and ii) the design of an affordable temperature record and control system.

Pistor and coworkers [49, 50] analyzed the impact of paraffinic oil on microwave devulcanization of EPDM from the automotive industry (average particles size = 0.71 mm). It was found that temperatures after MW treatment were higher for waste EPDM without paraffinic oil than those measured for the waste EPDM with a plasticizer. This is related to evaporation of gaseous products from waste EPDM (low molecular weight additives, e.g. paraffinic oil, etc. and also volatile degradation products) after MW treatment. Therefore for a better control of devulcanization process, prior to MW treatment, the paraffinic oil should be extracted from waste rubber. Additionally, in order to prevent waste rubber degradation, the microwave treatment time should be very short (up to 4 minutes). The authors pointed also that evaporation of low molecular compounds increased the total carbon black content in processed waste rubber. This phenomenon has a significant impact on MW treatment efficiency.

3.4. Other elastomers

Landini *et al*. [51] applied microwave processing for recycling of post-production rubber caps (used in pharmaceutic industry) based on bromo-butyl rubber. Authors evaluated the effects of magnetron power (in the range of: 1000–3000 W) and MW treatment time (in the range of: 9–25 minutes). The measurements of the temperatures of the samples, before and after the MW treatment, were comprised between 25 °C (room temperature) and 550 °C. Surprisingly, the authors did not mention high degradation, carbonization or burning of the studied samples. Similar observations were described in work [46]. This phenomenon could be related to the absence of carbon black and plasticizers (susceptible to evaporation by heating) in studied waste rubber. However, the composition of examined waste rubber was unknown. The best results were obtained for the sample treated at 2000 W and 13 minutes.

Scagliusi *et al*. [52] evaluated the progress of devulcanization of waste chloroprene rubber as a function of microwave treatment time (in the range of: 0.5–6 minutes) and magnetron power (in the range of: 1000–3000 W). The results showed that MW treatment resulted in significant deterioration of mechanical properties for studied samples. Comparing to untreated sample (tensile strength: 9.8 MPa, elongation at break: 500% and hardness: 57 °Sh A), the obtained products were characterized by tensile strength in the range: 0.6–6.1 MPa, elongation at break in the range: 100–700% and hardness in the range: 45–52 °Sh A, depending on their MW treatment conditions.

As mentioned above, the results of these works suggest that, regardless of waste rubber type, the most important factor affecting MW devulcanization is the temperature reached by the reclaimed rubber after MW treatment. Based on that assumption, we have included the literature data in Figure 3, which presents the temperature after MW treatment of waste rubber as a function of radiation time, in order to compare the observations made by independent research groups. However, it should be noticed, that these results are affected by many factors, such as: i) design and construction of microwave oven (e.g. chamber dimensions, Faraday cage effectiveness in domestic microwave oven with stirring system, etc.); ii) microwave specific energy applied; iii) temperature measurement conditions (e.g. used equipment) and iv) other factors (e.g. composition of used waste rubber).

As could be observed in Figure 3, the temperatures achieved by the samples, are not consequent with the

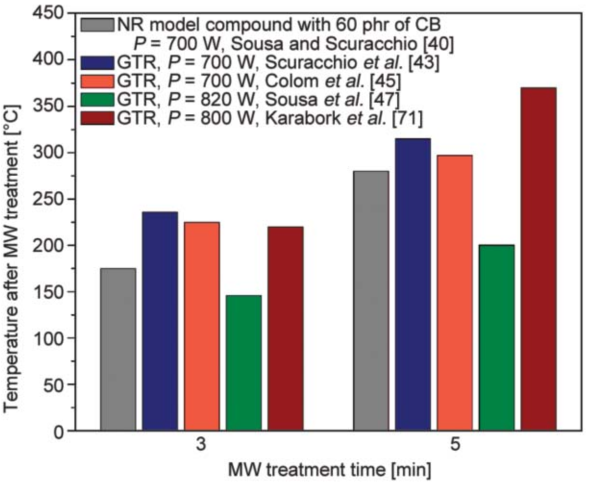

Figure 3. The effect of time on temperature after MW treatment – a comparison of literature data.

conditions of the experiments. This indidactes a serious problem with the reproducibility of obtained results and difficulties with their proper interpretation. Therefore, in order to avoid that lack of reproducibility and to set a parameter that is directly related to the devulcanization/reclaiming phenomena in the sample, we propose to refer to the temperature of the sample as a more indicative factor than (e.g. the magnetron power, treatment time, etc.).

4. Additives and modifiers used in MW devulcanization

The application of variable chemical additives and modifiers in the microwave treatment of waste rubber is a relatively new approach of research. Recent progress in this area over the last ten years is summarized in this section. In 2008, Vega *et al*. [53] investigated the vulcanization/devulcanization behavior of the squalene (model compound for natural rubber) modified with diphenyl disulfide (DPDS) and treated by microwaves. The results indicated that using of DPDS during rubber compounding enhanced devulcanizing ability controlled by microwave treatment power, which affecting devulcanization temperature. The authors showed that DPDS by itself is active only when the scission of disulfidic bonds occurs (temperature above 180 °C). Devulcanization mechanism during microwave treatment of vulcanizates modified with disulfides is presented in Figure 4. In the studied case, DPDS radicals are able to recombine with macro-radicals formed during MW treatment of cross-linked rubber. This phenomenon prevents the unfavorable phenomenon of secondary cross-linking of waste rubber.

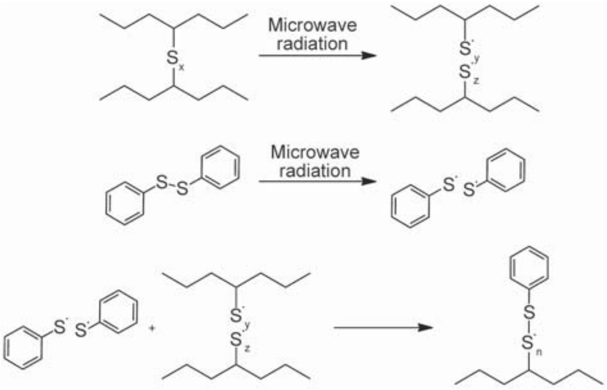

Figure 4. Devulcanization mechanism during microwave treamtent of vulcanizates modified with disulfides (Based on [53]).

Paulo *et al*. [54] studied the microwave devulcanization of waste rubber modified with inorganic salts and nitric acid. Microwave treatment conditions were constant for the studied samples. Changes in the chemical structure of MW processed waste rubber were analyzed by Soxhlet extraction and infrared spectroscopy. The waste rubber modification procedures and the gel content results after MW treatment are presented in Table 4. As can be observed, using metallic ions and nitric acid enhanced the microwave devulcanization of waste rubber (the exception was $CdCl_2$). FTIR studies showed that microwave treatment leads to the formation of carbonyl (band at 1700 cm^{-1}) and C–O (band at 1200 cm^{-1}) groups in devulcanized GTR. This confirms the partial oxidation of GTR, which occurs simultaneously with its devulcanization.

Poyraz *et al*. [55] present interesting results about using of microwave treatment for GTR devulcanization and subsequently modification with carbon nanotubes (CNT). The procedure for the synthesis of devulcanized GTR modified with CNT (CNT/dGTR) is presented in Figure 5. At the beginning, GTR was treated by microwaves in order to its partial devulcanization, which resulted in increased mobility of rubber chains. In the next steps, devulcanized GTR

Table 4. Waste rubber modification procedure and gel content after MW treatment (Data adopted from [54]).

GTR modification procedure	Sample code	Chemical modifier	Gel content [%]
Procedure I: The inorganic salts $CuSO_4$, $ZnCl_2$, $CdCl_2$ and $Bi(NO_3)_3$ were dissolved in 60 ml of water and incorporated to 25 g of GTR. Modified GTR was dried for 4 h at 100 °C and than treated by microwave radiation.	GTR	–	85.2
	GTR-Cu	Cu^{2+}	43.8
	GTR-Zn	Zn^{2+}	87.0
	GTR-Cd	Cd^{2+}	97.7
	GTR-Bi	Bi^{3+}	32.5
Procedure II: The inorganic salts $CuSO_4$, $ZnCl_2$, $CdCl_2$ and $Bi(NO_3)_3$ were dissolved in 60 ml of a solution of nitric acid at 25% v/v. The inorganic salts content was calculated based on the hypothetic stoichiometric reaction between metallic ions and sulfur present in the rubber. $Bi(NO_3)_3$ was used 25% of the stoichiometric weight due to difficult for dissolution in 60 ml of nitric acid at 25% v/v.	GTR-H	HNO_3	89.0
	GTR-HCu	HNO_3–Cu^{2+}	45.1
	GTR-HZn	HNO_3–Zn^{2+}	35.6
	GTR-HCd	HNO_3–Cd^{2+}	41.2
	GTR-HBi	HNO_3–Bi^{3+}	39.7

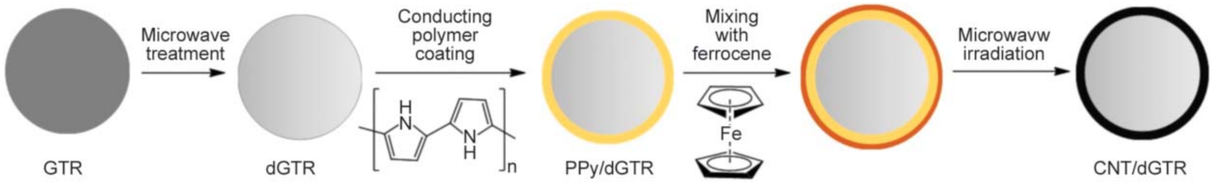

Figure 5. Procedures for synthesis of devulcanized GTR modified with CNT (CNT/dGTR) (Based on [55]).

was coated with conducting polymer (polypyrrole) and mixed with organic metallocene precursor (ferrocene). In the last operation, coated GTR was treated by microwave radiation in order to the formation of CNT on its surface.

Liu *et al*. [56] modified GTR by barium ferrite ultrafine powder. The modification of GTR with variable content barium ferrite ultrafine powder (in the range of: 0–50 wt%) was performed in high-speed mixer for 1 hour. Next, the GTR/barium ferrite powder composition (~100 g) was placed in ceramic dish and microwave treated for various times (in the range of: 0–4 minutes). Subsequently, prepared samples were compression molded at 145 °C for 10 minutes. It was found that barium ferrite, as the magnetic filler, improved microwave devulcanization and activation of GTR. The proposed method allows producing the low-cost flexible magnetic materials, which is a promising approach to extend the up-cycling of waste tire rubber.

Seghar *et al*. [57] used the ionic liquid (pyrrolidinium hydrogen sulfate) in order to improve the microwave devulcanization efficiency of styrene-butadiene rubber vulcanizates. Prior to microwave treatment, ground SBR was mixed for 10 minutes with 10 wt% of ionic liquid pyrrolidinium hydrogen sulfate (mixture was left to stand for at least 1 hour). The results showed that temperature reached by ground SBR exposed to microwave irradiation was favored by pyrrolidinium hydrogen sulfate additive, regardless of used microwave energy value. Moreover, authors indicated that promising approach for waste rubber devulcanization include also combined methods based on mechanical (shear forces) and microwave treatment.

Recently, Mohaved and co-workers performed comprehensive investigations about application of variable chemical agents on microwave devulcanization of ground tire rubber [58], waste EPDM [59] and butyl rubber [60]. Authors evaluated the combined effects of chemical agent type, its concentration and temperature generated during MW treatment. Devulcanization temperature oscillated in the range of: 140–280 °C and as chemical agents CBS (*N*-cyclohexyl-2-benzothiozyl sulfenamide), DPTT (dipentamethylenethiuram tetrasulfide), DPDS (diphenyl disulfide), MBT (mercaptobenzothiazole), MBTS (2-mercaptobenzothiazole disulfide), TMTD (tetramethylthiuram disulfide) and HDA (hexadecylamine) were used. Generally, the results confirm that chemical agents enhanced MW devulcanization efficiency. The GTR modification procedures and observations after MW treatment are summarized in Table 5. The observed differences are related to devulcanization mechanism, which affects the devulcanization efficiency. Process supported by commercial accelerators (CBS, DPTT, DPDS, MBT, MBTS, TMTD) as chemical agents is similar to this proposed in Figure 4. In case of waste rubber modified by HDA ionic devulcanization occurs and proposed mechanism is presented in Figure 6.

Zedler *et al*. [61] investigated the synergistic effects of bitumen plasticization and microwave treatment on short-term devulcanization of GTR. The selected properties of GTR modified with bitumen and treated by microwave are summarized in Table 6. The obtained results showed that bitumen plasticizer (in range of: 0–2.5 phr) acts as insulator which prevent oxidation of GTR during microwave treatment and simultaneously improves processing and thermal stability of obtained reclaimed rubber. Additionally, in studied case, the combined impact of microwave treatment and bitumen plasticization on tensile properties of reclaimed GTR was negligible. This indicates that reclaimed GTR should be considered as a heterophase composite composed from: gel fraction (cross-linked GTR particles that remain after the treatments) and sol fraction (the sum of the devulcanized, degraded and plasticized rubber phase). Slight differences in tensile properties observed for reclaimed GTR could be related to formation of a network between cross-linked GTR particles and these different elastomeric chains (soluble fraction).

Table 5. Effect of selected chemical agents on microwave-induced devulcanization of variable waste rubber (Data adopted from [58–60]).

Waste rubber characteristic	Chemical agents	GTR modification conditions	Observations	Ref.
GTR (passenger car tires) Median particle size: 0.31 mm	HDA, DPDS, CBS, MBTS	Appropriate amount of devulcanizing agents were mixed with 30 g oil and then added to 100 g of above mentioned waste powder in a 500 ml glass beaker. The waste powder was soaked in the oil for 12 h at 80 °C in an oven to allow it to penetrate into the rubber fully. Subsequently, microwave devulcanization of GTR was performed.	Final temperature after MW treatment in the range of: 180–280 °C. The best devulcanization parameters were obtained for compound with 30 phr aromatic oil and 6 phr DPDS at 240 °C.	[58]
Waste EPDM (mixture of several aged and new automotive rubber) Average particle size: <1 mm	CBS, DPTT, HDA, MBT, MBTS, TMTD	Chemical agents were mixed with the aromatic/aliphatic oil and then added to the waste powder in a 500 ml glass beaker. The waste EPDM was soaked in the oil for 24 h to allow it to penetrate into the rubber fully. Modified waste EPDM was treated by microwaves.	Final temperature after MW treatment in the range of: 200–260 °C. The highest devulcanization efficiency was obtained with the CBS, HDA, and MBT additives. On the other hand, the best mechanical properties of reclaimed rubber were achieved with the MBTS. For waste EPDM modified with MBTS, the devulcanization was better in aromatic oil than in the aliphatic oil.	[59]
Waste IIR (waste bicycle and motorcycle butyl tubes) Median particle size: 0.279 mm	HDA, DPDS, CBS, TMTD	Four grams of CBS, DPDS, TMTD, and HDA which were used as devulcanizing agents, were mixed with 30 g oil. In next step, the mixture was added to 100 g waste powder in a 500 ml glass beaker. The waste butyl rubber was soaked in the oil for 12 h at 80 °C in an oven to allow it to penetrate into the rubber fully. Subsequently, waste butyl rubber was treated by microwaves.	Final temperature after MW treatment in the range of: 140–260 °C. The best devulcanizing efficiency was achieved for the compound with paraffinic oils and 6 phr HDA, when MW temperature was fixed at 180 °C.	[60]

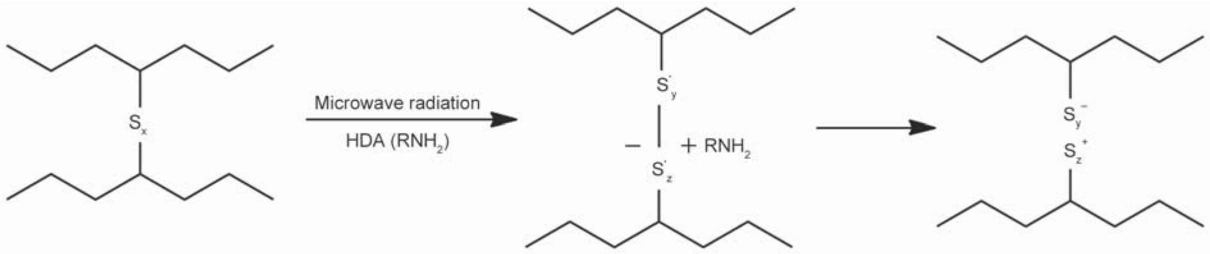

Figure 6. Mechanism of ionic devulcanization of waste rubber modified by HDA (Based on [58]).

Table 6. Selected properties of GTR modified with bitumen and treated by microwave (Data adopted from [61]).

Property		Standard	GTR – MW	GTR+0.25 B160/220 – MW	GTR+0.5 B160/220 – MW	GTR+1.0 B160/220 – MW	GTR+2.5 B160/220 – MW
Minimal torque	[dNm]	ISO 3417	16.9	17.9	29.5	28.1	24.4
$T_{-2\%}$ according TGA	[°C]	–	255.8	250.5	253.6	254.6	254.7
Tensile strength	[MPa]	ISO 37	5.3	5.9	5.2	6.1	5.9
Hardness	[°Sh A]	ISO 7619-1	64	63	67	67	65

5. Structure and performance properties of polymer matrix – microwave treated rubber systems

5.1. Thermoplastics

Hong *et al*. [62] compared the properties of microwave-treated and ultrasound-treated waste rubber and their application in LDPE/waste rubber composites. In the studied conditions, microwave modification resulted in the higher decrease of gel fraction and cross-link density of waste rubber, which suggested higher degree of devulcanization and probable degradation of polymer main chain. Despite that, SEM images show more regularity in distribution of devulcanization sites for ultrasound-treated rubber. Similar effect was also observed at SEM images of fracture surface of LDPE/waste rubber composites. Samples containing ultrasound-treated rubber show more homogenous structure, which resulted in the best tensile properties. Authors stated that both methods of waste rubber modification are effectively enhancing performance of composites, however presented results suggest that ultrasound treatment is more suitable. Such effect can be associated with lower energy of ultrasound waves, which effectively break S-S bonds, leading to devulcanization, but do not cause decomposition of the polymer main chain.

de Sousa and coworkers [63, 64] prepared dynamically vulcanized HDPE/GTR blends and analyzed the influence of devulcanization process, as well as additional effect of clay content on their structure and properties. Except simple analysis of treatment time, the authors analyzed also multi-step microwave treatment comprising of 2 or 3 shorter steps. Analysis of curing process showed that optimum time and scorch time were noticeably decreased by the application of microwave treatment on GTR particles. Also, one-step exposure caused stronger effect that multi-step one with the same total time. Such effect can be related to higher temperature inside the material for longer exposure periods. The addition of 5 wt% of clay to the blends did not have any significant impact of curing characteristics. Regarding thermal properties, the highest crystallinity of HDPE phase was observed for samples in which GTR was exposed to microwaves for a longer time. Such effect was ascribed to the more developed surface of particles, hence higher possibility of nucleation. In some cases similar effect was observed with addition of clay, however crystallinity of HDPE was more sensitive to changes in the GTR particles. Such effect resulted in the enhanced stiffness of materials and Young's modulus increasing with the exposure time and with the addition of clay.

de Sousa *et al*. [65] studied the influence of extrusion parameters (e.g. screw speed, feeding mode) on the final properties of dynamically vulcanized HDPE/microwave treated GTR blends (in ratio 40/60 wt%). As curing system, sulfur and accelerator *N*-tert-butyl-2-benzothiazole sulfenamide (TBBS) were used. It was found that the finest morphology and the best performance properties were obtained for samples prepared at high screw speed, when microwave treated GTR was feeded directly to molten HDPE (not dosed together with HDPE to hopper). The results confirmed that extrusion parameters allowed matching the residence time with dynamic curing kinetics, what strongly affected cross-linking efficiency of microwave treated GTR and its distribution in thermoplastic matrix. Moreover, authors indicated unsatisfactory compatibility and adhesion between HDPE and microwave treated GTR (regardless of extrusion parameter), what limit potential application of prepared blends.

Simon *et al*. [66] investigated polypropylene based thermoplastic dynamic vulcanizates obtained by twin-screw extrusion. At first they prepared materials containing model rubber comprising in 70% of SBR and in 30% of NR, which was then replaced partially (10, 20 and 30 wt%) by microwave-treated crumb rubber. Introduction of devulcanized crumb rubber resulted in the deterioration of tensile performance of material, however for 10 and 20 wt% content, decrease of tensile strength and elongation at break was very modest. Addition of modified rubber hardly affected hardness, since hardness of microwave-treated rubber was very similar to final hardness of material.

Garcia *et al*. [67] also analyzed the influence of microwave treatment of GTR particles on the structure and properties of PP/GTR blends. Authors confirmed the results presented in other research works, which indicated the increase of the degree of devulcanization with the elongation of microwave treatment, which consequently resulted in decrease of rubber's viscosity. Such effect can be very beneficial during manufacturing of blends and composites containing devulcanized GTR. SEM analysis revealed that the shortest devulcanization times and lowest devulcanization level led to blends with more irregular particles. Longer modification time impacted positively on breaking of GTR particles and avoiding agglomeration during processing. Such effect was later confirmed by 3D images obtained from X-ray microtomography.

It should be pointed out that microwave treatment of GTR could be also very interesting approach for modificiation of asphalts, which similar like thermoplastics, have ability to flow when heated. For example, Yu *et al*. [68] used microwave treatment to modify crumb rubber used in preparation of modified asphalt. Authors applied 5 minute microwave treatment and analyzed the changes in rubber particles with FTIR analysis. It revealed the noticeable decrease of the intensity of signals associated with the S-S bonds, which pointed to successfull devulcanization. Such effect was confirmed by increased equilibrium swelling index. Next, authors analyzed the properties of unmodified asphalt and modified with neat and microwave-treated crumb rubber. Addition of crumb rubber led to 15 °C increase of softening point, but microwave treatment increased this effect by additional 6 °C. Modification allowed also 21% increase and 13% decrease of ductility and penetration, respectively. Such positive effects was ascribed to cleavage of S-S bonds, hence better swelling of modified crumb rubber in asphalt. Authors analyzed also stability of prepared asphalt/crumb rubber mixtures, which showed that for sample containing modified rubber, difference in softening point between top and bottom of material was 1.2 and 1.6 °C, respectively after 48 and 72 hours. Such result is a great improvement comparing to 8.6 and 10.8 °C for asphalt containing unmodified crumb rubber. Presented results clearly indicate that application of microwave treatment might significantly enhance the properties of asphalt/waste rubber mixtures.

5.2. Elastomers

Zanchet *et al*. [69] analyzed the impact of microwave treatment time on the structure and properties of SBR scraps, which were then vulcanized and compared to control sample (primary product). Authors analyzed the effect of MW processing times in the range of: 2–4 minutes. For all times successful devulcanization was observed, which was confirmed by the values of gel content in material, however material obtained after 2 minutes of treatment was not used for vulcanization, because of its low homogeneity with curing system. Vulcanization process of samples was analyzed, which revealed that maximum torque was noticeably decreased due to the reduced cross-link density. Positive aspect of microwave treatment was elongation of scorch time, which enables achieving better process control. Mechanical properties of studied materials were noticeably lower comparing to reference sample. Moreover, elongation of microwave treatment resulted in the slight deterioration of mechanical performance, which is related to the partial degradation of polymer main chain.

In the next work, the same research group [70] selected particular fraction of SBR scraps with the particle size ~0.6 mm and analyzed the impact of microwave treatment on the curing, structure and properties of SBR rubber filled with 80 phr of treated SBR scraps. A decrease of the maximum torque was noticed with the incorporation of SBR scraps. That was related to the reduction of virgin rubber content and the generation of a physical barrier for the cross-linking reactions, which led to the decrease of cross-link density of composites. This phenomenon resulted in a noticeable decrease of compression set values determined for studied composites. Moreover, SBR scraps acted as reinforcing agents, so increase of tensile strength was noted, however microwave treatment had slightly negative effect on its value. In case of elongation at break, treatment of SBR scraps led to the increase of this parameter, however elongation of MW treatment reduced it, probably due to the degradation of polymer main chain. Very interesting was also that authors analyzed the impact of accelerated aging on the mechanical performance of composites. Results indicated that control sample, neat rubber, was more sensitive to the aging effects, than composites containing microwave-treated SBR scraps.

In works published by Karabork and coworkers [71, 72] microwave-treated GTR was used during preparation of SBR-based composites. Authors investigated the effect of MW treatment time (from 1 to 5 minutes) on the properties of modified GTR and its blend with SBR matrix. For preparation of SBR-based composites, samples after 4 and 5 minutes of treatment were used, due to the highest sol content, hence extent of devulcanization. SEM analysis of modified and unmodified GTR particles indicated that microwave-treatment noticeably enhanced the roughness and development of their surface. Such assumptions were confirmed by BET analysis, which revealed that 4 and 5 minutes of treatment increased surface area of particles from 0.0169 to 0.295 and 0.204 m^2/g, respectively. It was revealed that addition of microwave-treated GTR to rubber compounds reduced the scorch time, which according to authors, was associated with the presence of active cross-linking sites on devulcanized GTR particles and possible diffusion of accelerator from GTR to virgin rubber. Optimum vulcanization time was also decreased, which confirms the assumption related to the presence of active functional sites in MW treated GTR. Such effect was also confirmed by the SEM analysis, which pointed the improved adhesion between SBR matrix and microwave-treated GTR. Elongation of MW treatment time had noticeable, positive effect on morphology, which in contrary to samples containing unmodified GTR did not show as much cracks and cavities. This phenomenon strongly affected tensile performance of studied materials. Microwave-treatment increased also friction coefficient of analyzed materials (analysis of non-abrasive surface), which was due to the enhanced strength of interface. On the other hand, the same phenomenon was the reason of deterioration in abrasion resistance after modification of GTR particles.

Luo *et al*. [73] analyzed the influence of GTR modification method on the properties of NR/GTR composites. Authors used sol-gel method for modification of untreated GTR and GTR treated by microwave radiation. Both types of GTR were swollen in tetraethyl orthosilicate at 40 °C for 48 h and next soaked in a 10% aqueous solution of *n*-butylamine at 40 °C for 24 h. Subsequently, sol-gel modified GTR particles were dried under reduced pressure at 50 °C for several days until constant weight. Such modified GTR was used to prepare NR/GTR composites, which revealed that sol-gel modification was more effective in enhancing the mechanical performance of composites than microwave treatment. However, pretreating of GTR particles with microwaves increased the effectivity of sol-gel modification and led to the 49% increase of tensile strength, 13% increase of elongation at break and 19% increase of tear strength comparing to NR/GTR composite filled with unmodified particles. Furthermore, authors investigated the impact of the content of bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) used to improve the dispersion of *in-situ* generated silica during sol-gel modification. Addition and increasing of TESPT content resulted in the decrease of scorch time and optimum cure time, which was related to the breakage of sulfur bridges in TESPT and additional cross-linking reactions occurring inside the material. Such phenomenon led to the enhancement of materials' modulus, as well as tensile and tear strength. This effect was associated with the more homogenous dispersion and higher wettability of in-situ generated silica with rubber matrix, due to the incorporation of TESPT, which was confirmed by SEM analysis of cryogenically fractured surface and fracture area after tensile tests.

de Sousa *et al*. [74] investigated the reversion process occurring during vulcanization of NR-based composites containing microwave-treated NR waste. As in other, above mentioned works, elongation of treatment time resulted in the decrease of gel content and cross-link density in waste rubber particles. Next, curing characteristics were determined and the percentage of reversion was calculated from the results. Authors indicated that microwave exposure time of NR waste and their content have significant influence on the higher reversion of studied composite during vulcanization, which confirmed the results of previous works. Such effect was directly responsible for deterioration of mechanical properties, such as tensile strength, elongation at break and Young's modulus.

Colom *et al*. [75] except the investigation of irradiation time, analyzed also the influence of GTR source on the structure and properties of NR/GTR composites. Authors used GTR from passenger car tires and truck tires, which have different composition (see Table 2). FTIR analysis of composites revealed that regardless of GTR source, elongation of treatment time resulted in the partial degradation of GTR. However, the source of GTR, hence its composition, had significant impact on formation of unsaturated C=C bonds during microwave treatment. These results are in agreement with the values of cross-link density calculated according to Flory-Rehner equation. As could be expected, mechanical properties of NR/GTR composites were deteriorated comparing to reference sample, due to weak matrix-filler interactions. However, application of microwave treatment resulted in the improvement of tensile properties of composites, because of increased roughness and specific surface area after treatment, which enhanced the compatibility between phases. The effect of treatment was stronger in case of GTR from truck tires, because of higher content of NR and higher degree of devulcanization.

5.3. Thermosets

Recently, Aoudia *et al*. [76] investigated the effects of incorporation (10 wt%) of microwave-treated GTR into bisphenol-A and bisphenol-F based epoxy matrix. The impact of exposure time and microwave power applied during treatment, hence the energy used for GTR devulcanization on the structure and performance of composites was determined. Authors noted that for short microwave treatment time (15 seconds), the level of magnetron power (in the range of: 300–900 W) strongly affected the cross-link density of GTR (measured by equilibrium swelling). For longer time (60 seconds), the influence of used magnetron power on the degree of swelling of treated GTR was negligible. Moreover, presented results show that microwave treatment of GTR enhanced chemical reactivity of particles' surface, which promoted interfacial adhesion between matrix and filler.

Up to 20% enhancement of flexural stress and strain at break was observed for moderate microwave energy values. For microwave energy values exceeding 1250 J/kg, increase of mechanical parameters was noticeably lower. According to authors this is related to partial degradation of microwave-treated GTR particles. Other positive aspect of GTR incorporation into epoxy matrix was enhanced toughness expressed by the decrease of compressive modulus. Generally, modulus was decreasing in the linear manner with the increasing microwave energy. Authors analyzed the structure of materials with SEM microscopy, which revealed noticeable improvement of interface between matrix and filler in case of microwave-treated GTR. Significant enhancement of interfacial adhesion was related to the higher surface reactivity in case of treated GTR.

To the best of our knowledge, the published data about microwave-treated GTR particles into thermosets are very limited. We hope that this review work, encourages the investigation of the potential of microwave-treated/functionalized GTR application into thermoset composites.

6. Waste rubber pyrolysis

It is worth to notice that burning of the waste tires, mainly in cement kilns and power stations, allows only for around 37% of the energy recovery that is used to produce new tires [77]. Waste tires pyrolysis offers the advantages of energy recovery in more sophisticated and environmentally-friendly manner comparing to combustion of tires. The products of waste tires pyrolysis are high value-added compounds (gases, pyrolytic oils and pyrolitic carbons), which can be refined and than used as a alternative source of energy or chemical substrates. Comprehensive literature reviews about progress in this field were presented by Williams [78] and Martínez *et al.* [79]. Application of microwave energy seems to be promising approach for further development of industrial pyrolysis. Microwave-induced pyrolysis overcomes the disadvantages of conventional pyrolysis methods such as slow heating and necessity of feedstock grinding. At the same time, MW pyrolysis improves the quality of pyrolysis products and significantly reduces processing time (energy consumption costs) [80]. Although, microwave-induced pyrolysis has many advantages the published research works about its application in rubber recycling are rather limited and performed mostly in the laboratory-scale. In this sub-chapter, recent developments and future perspectives in field MW pyrolysis of waste rubber are summarized. A special attention was focused on the correlation between microwave-pyrolysis conditions and the final properties of obtained products.

Undri *et al.* [81] examined the microwave pyrolysis of waste tires and characterized the properties of solid, liquid and gas products. The results showed that the process is affected by the MW power (P) and tire mass (M). The ratio between microwave power and tire mass square (P/M^2) has significant influence on working temperature (the authors pointed on the technological issues related to temperature measurement during MW pyrolysis), which consequently affects the efficiency and the composition of products. The correlation between MW processing conditions and the yield of the products is presented in Table 7. The pyrolytic products yields were: 40.6–65.0 wt% for solid, 20.7–44.0 wt% for liquid and 9.0–27.4 wt% for gases. As could be observed, the collected pyrolytic products were characterized by a high calorific value, ~34 MJ/kg for solid, ~45 MJ/kg for liquid, and ~46 MJ/kg for the gas fraction. In the final conclusion, the authors indicated that complete MW

Table 7. The correlation between MW pyrolysis, pyrolytic products yield and their higher heating value (Data adopted from [81]).

P [kW]	M [g]	P/M^2 [kW/kg^2]	T_{max} [°C]	t [min]	Pyrolytic products yields [wt%]			High calorific value of pyrolytic products [MJ/kg]		
					Solid	Liquid	Gas	Solid	Liquid	Gas
6	208.8	137.6	573	14	41.1	31.5	27.4	35	47	46
4.8	212.8	106.0	546	15	40.6	43.1	16.3	36	48	49
3	233.3	55.1	522	39	43.2	42.6	14.1	33	44	49
1.5	252.1	23.6	523	100	65.0	20.7	14.3	30	43	49
3	1501.1	1.3	533	70	50.7	39.3	9.0	34	43	43
3	502.8	11.9	513	59	40.6	44.0	13.4	34	43	42
3	64.1	730.1	453	47	47.5	30.1	22.4	–	–	44

P – MW power; M – tire mass; T_{max} – maximal temperature measured by IR thermometer; t – pyrolysis time pyrolysis of whole tire may be achieved using an appropriate P/M^2 ratio and pyrolysis time.

Song *et al*. [82] investigated microwave-induced pyrolysis efficiency as function of process time (in the range of: 10–30 min.), which allowed determination of yields and composition of obtained products at different stages of process. The pyrolysis products yields at different times indicated that waste tire pyrolysis was relatively complete within 20 min. However, the samples in the center of the microwave reactor were pyrolyzed earlier than those in the surrounding areas. After 24 min, the temperature of GTR stabilized at ~500 °C and remained so until the end of the pyrolysis. It was observed that solid fraction content first decreased from 54 wt% at 10 min to 45 wt% at 20 min, followed by an additional slight decline (43 wt% at 30 min). On the other hand, pyrolytic gases content was ~12 wt% and liquid fraction content was ~45 wt% after 30 min. Generally, longer pyrolysis time resulted in increase of yield for gases and liquid fraction, while solid fraction content decreased. Furthermore, it is worth to notice that the limonene content present in liquid fraction obtained by microwave-induced pyrolysis was evidently higher than that from conventional pyrolysis. More detailed investigation about limonene formation during microwave pyrolysis of waste tire rubber was recently published in work [83]. The results showed that in the laboratory scale (batch size: 30 g) the highest efficiency of limonene was up to 23.4%, when optimal pyrolysis conditions were used (specific micowave power: 15 W/g; weight hourly space velocity: 3.75 h^{-1}; ground tire rubber characteristics: particles size – 0.6 mm without steel impurities). More useful information about the impact of microwave pyrolysis conditions on the final properties of liquid, solid and gases pyrolytic products are presented in works [84–86].

Song *et al*. [87] examined the effect of steel wires on microwave-induced pyrolysis of GTR. It was observed that discharge triggered by metals under microwave irradiation accelerated the pyrolysis of ground tire rubber, which consequently affected the composition of pyrolytic products and their yield. For example, gas products yield reached up to 35.3 wt%, which is realted to presence of local hot spots (very high temperature) formed during discharging of metals treated by microwaves.

Song and coworkers [88, 89] comprehensively investigated the impact of magnetron power on microwave-assisted pyrolysis of waste tires. The results showed that pyrolysis efficiency increased with increasing microwave energy. In work [88] the final temperature of GTR after pyrolysis reached 415, 498 and 574 °C at specific microwave energy 9, 15 and 24 W/g, respectively. In the second work of the same research group [89], the maximum temperatures after microwave pyrolysis of GTR (batch 30 g) were 350, 365, and 389 °C at power levels of 300 (10 W/g), 500 (16.7 W/g) and 700 W (23.3 W/g), respectively. Observed differences are related with the specification of used microwave reactors. For example, maximal power of magnetron used in work [88] is 900 W, while in work [89] this value is 3000 W.

The above mentioned and discussed laboratory-scale trials are very promising. The preliminary results of investigations about microwave-induced pyrolysis of waste rubber indicate that this technology will be successfully developing in next years.

In our opinion, other promising approaches for further studies in field of microwave-induced thermal decomoposition of waste rubber can be devided into two directions: light pyrolysis and gasification. Light pyrolysis of waste rubber is relatively novel technology and comparing to conventional pyrolysis is performed in lower temperature (usually around 300 °C or less) [90, 91]. In this conditions primary pyrolysis occurs, which combine devolatilization of rubber additives (and other low molecular compounds) and partial thermal decomposition/degradation of waste rubber. This indicates that light pyrolysis can be categorized as a method combining reclaiming and pyrolysis processes. This allows production of new group of waste tires recycling products, which could found application as bitumen modifiers [92], semi-reinforcing fillers [93] or reactive plasticizers [94, 95].

Gasification is another interesting approach which should advance the application of microwave-assisted thermal decomposition in near future. This is a process in which air, oxygen and or steam support decomposition of waste tires to produce mainly syngas (CO and H_2). In 2010, Donaj *et al*. [96] treated automobile shredder residue by microwave pyrolysis combined with high temperature steam gasification. The process was designed in order to improve the conversion of automobile shredder residue into valuable products. Moreover, it should be pointed that flash heating by microwaves might has beneficial impact on gasification efficiency. However, recent development in waste rubber gasification comprehensively described by Machin *et al*. [97] and by

Oboirien and North [98] indicated that application of microwave energy during gasification of waste rubber is still very limited.

7. Advances and limitations in MW treatment of waste rubber

As presented above, the use of microwaves in rubber recycling by devulcanization and pyrolysis is gaining more attention of research groups around the world. Table 8 presents a summary of advantages and disadvantages of MW treatment of waste rubber, which strongly affect development and further industrial application of microwave technology in rubber recycling.

The unique features of the microwaves enable solvent-free, short-time and highly efficient environmentally friendly treatment of waste rubber, which is a huge advance of this technology. In comparison to other methods, the microwave heating occurs in the whole volume of material. It is extremly important in case of waste rubbers for which the thermal conductivity is usually very low. The dosage of microwave energy acting on waste rubber can be simply controlled by magnetron power and time settings, allowing selective breakage of the cross-linking bonds with minimum degradation of the main polymeric chains. However, it should be noticed that settings of time and power do not guarantee completely the amount of energy irradiated to the sample. As mentioned above, the cavity of the microwave oven is not irradiated equally due to presence of hot spots. Obviously, devulcanization or pyrolysis process efficiency and the final quality of obtained products requires a precise control of temperature distribution during MW treatment, what is a common problem in this technology. This problem is solved in professional microwave reactors, but due to high cost their application in waste rubber recycling is rather limited. Other route, commonly used by academic researcher, is modification of low-cost domestic ovens by addition of stirring system. However, it should be pointed out, that such solution might change the microwave power characteristics (e.g. partial waste of MW energy by hole in Faraday cage, partial absorbion of MW energy by parts of stirring system, etc.).

Literature data showed that microwave treatment improved the compatibilty and interfacial adhesion between polymeric matrix and MW treated waste rubber. This is due to higher mobility of polymer chains in partially devulcanized waste rubber, which enhances the physco-chemical interactions on the phase boundary.

Another advantage is possibility of modification/functionalization of GTR by MW treatment, which could found application as reinforcing fillers or engineering materials. Moreover, the suitable modification of atmosphere or temperature conditions during MW treatment of waste rubber allow preparation of novel products, such as reclaimed rubber, oligomers, oils, carbon black and gases with different characteristics.

Although, above discussed laboratory investigations about application of microwave energy in waste rubber recycling are usually conducted by batch process, it should be noticed that this technology can be performed in a continuous manner. This promising industrial approach was described in patents of Hunt Industries Inc. (USA) [99] and Marpo Sp. z o.o. (Poland) [100]. Hunt Industries Inc. [99] presents rubber recycling technology based on continous MW treatment of waste rubber in vacuum, which allow recovering devulcanized rubber or purified carbon and volatiles from a ground rubber feed material. In patent of Marpo Sp. z o.o. [100], waste rubber is subjected to a depolymerization process performed in microwave tunnel at inert atmosphere. Patented apparatus for recycling is equipped with a fan system for absorbtion of the process gases and providing a

Table 8. Advantages and disadvantages of MW treatment of waste rubber – a summary.

Advantages	Disadvantages
Heating in the material volume	High cost of professional microwave reactors
Short-time of process	Problems with efficient mixing
Solvent-free and environmental-friendly process	Hot spots issue
Precise control of MW energy dosage by magnetron power and time settings	Problems with volatile degradation products emission
Possible to perform in continuous manner	
Possible functionalization/modification of GTR	
Improvement of the matrix-GTR interactions	
Preparation of novel products, such as reclaimed rubber, oligomers, oils, carbon black and gases	

light negative pressure. In both patents, the inventors pointed out on the important issue of volatile compounds, which should be collected to condenser during MW processing of waste rubber.

8. Conclusions and future perspectives

Over the last 15 years many attempts in MW treatment during devulcanization and pyrolysis of waste rubber were depicted. The summarized data presented in this paper confirms that MW treatment is currently one of the most promising methods of waste rubber recycling. This approach allows solvent-free, short-time and highly efficient devulcanization and pyrolysis of waste rubber. These processes resulted in a full spectrum of novel products with unique properties, which are suitable for application in different branches of industry. The state of knowledge presented above indicates that the recycling of waste rubber by microwave treatment will continue to grow in the future. However, it seems that the most promising routes for further investigations can be categorized into three main directions. First route, is modification and functionalization of waste rubber during MW treatment. This allows preparation of novel products of waste tires recycling, which could found application as reinforcing (or semi-reinforcing) fillers, engineering materials or low-cost flexible magnetic materials. Furthermore, MW treatment of waste rubber improves its interfacial interactions with different polymeric matrix. Second direction for further reseach should be focused on methodology suitable for evalution of progress in MW treatment of waste rubber. In this field the technical problems with measurements of temperature distribution and emission of volatile organic compounds from waste rubber after MW treatment should be resolved. Due to very promising results in laboratory scale, the third approach will be focused on optimization and up-scaling of microwave devulcanization, pyrolysis or gasification processes (especially in continuous manner) in order to facilitate their industrial implementation.

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Abbreviations

CBS	*N*-cyclohexyl-2-benzothiozyl sulfenamide;
CNT	carbon nanotubes;
DPDS	diphenyl disulfide;
DPTT	dipentamethylenethiuram tetrasulfide;
DSC	differential scanning calorimetry;
EPDM	ethylene-propylene-diene rubber;
FTIR	Fourier-transform infrared spectroscopy;
GTR	ground tire rubber;
HDA	hexadecylamine;
HDPE	high density polyethylene;
IIR	butyl rubber;
LDPE	low density polyethylene;
MBT	mercaptobenzothiazole;
MBTS	2-mercaptobenzothiazole disulfide;
MW	microwave;
NR	natural rubber;
phr	parts per hundred of rubber;
PP	polypropylene;
SBR	styrene-butadiene rubber;
SEM	scanning electron microscopy;
TGA	thermogravimetric analysis;
T_g	glass transition temperature;
TMTD	tetramethylthiuram disulfide

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