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PHD THESIS BOOKLET

UPCYCLING OF GROUND TIRE RUBBER VIA
DEVULCANIZATION

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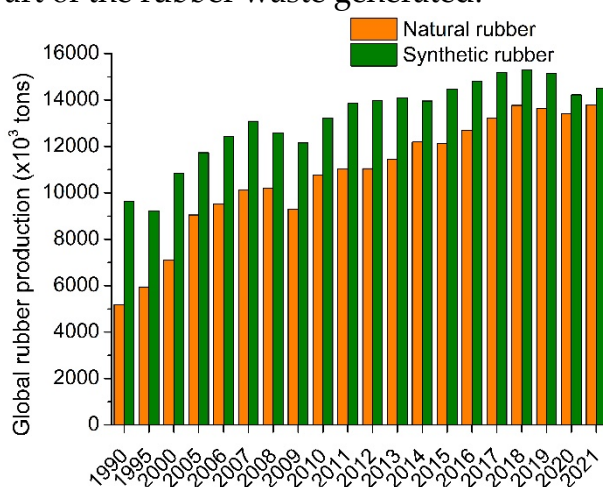
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1. INTRODUCTION

The extensive use of rubber started with vulcanization. The rubber macromolecules can be transformed into a cross-linked structure during this process, mainly using sulphur and compounds containing sulphur. Elastomers have many positive properties: they can undergo large reversible deformation of up to several hundred per cent over several cycles under low stress. Their properties can be varied over a wide range with additives.

However, due to their cross-linked structure, rubbers also have a significant disadvantage: difficult recyclability. This is because vulcanized rubber cannot be directly recycled with conventional polymer processing technologies (extrusion, injection moulding). For this reason, in the past, most rubber waste was landfilled or incinerated.

However, these methods have resulted in significant environmental pollution, and today there are strict regulations governing the management of rubber waste. The problem is getting more severe because the amount of rubber is increasing (Figure 1), which means that more and more rubber waste has to be managed each year. The majority of the rubber produced (~65-70%) is used for tire production and thus accounts for a large part of the rubber waste generated.



1. Figure Global natural and synthetic rubber production from 1990 to 2020 source: *Varnava C. K., Patrickios C. S.: Polymer networks one hundred years after the macromolecular hypothesis: A tutorial review. Polymer, 215, 123322 (2021)*

Due to the difficulty of recycling tires, used tires are turned into ground tire rubber (GTR). GTR as a product is commercially available and therefore easily accessible. GTR is one of the most promising ways to recycle rubber.

GTR can be used without any treatment as an additive in many applications, for example, in playground rubber mats or mixed into asphalt. It can also be used in elastomers, thermosets and thermoplastic polymers. The problem with these

applications is that they are not able to accommodate the increasing amount of waste rubber, and there are also compatibility issues. Therefore, a number of methods have been developed to conserve and recover the high levels of raw materials and energy invested in production.

The ideal solution would be to convert the rubber entirely to its pre-vulcanization state. This is the aim of the devulcanization process. Several processes have been developed: microwave, thermomechanical, chemical, biological and ultrasound devulcanization. In my thesis, I chose microwave and thermomechanical devulcanization because many studies have achieved positive results, and the required equipment and the devulcanization process is simple. The advantage of these methods is that they allow a quick and efficient treatment of the GTR. In addition, it is not necessary to add chemical reagents to the process.

During devulcanization, the mobility of the surface molecules of the rubber particles can be increased by breaking the carbon-sulphur and sulphur-sulphur cross-links. Such molecules are able to form bonds, either with each other or with molecules of the matrix, thus significantly increasing adhesion. That is why devulcanized tyre rubber can be used to replace and increased weight % of the primary rubber without a major loss of mechanical properties compared to compounds containing untreated GTR.

Thermoplastic vulcanizates can be produced by combining devulcanized GTR (dGTR) with a thermoplastic polymer. These are two-phase systems in which rubber particles are dispersed in a continuous thermoplastic matrix. If vulcanization and dispersion of the rubber phase in the thermoplastic phase take place simultaneously, we speak of dynamic vulcanization, and a thermoplastic dynamic vulcanizate (TDV) is produced. TDV production needs high shear, which is most easily achieved in an internal mixer or a twin-screw extruder. The combination of shear and high temperature causes the rubber mixture to vulcanize "in situ".

Dynamic vulcanization can result in the formation of 1–2 μm rubber particles. Due to this fine particle structure, TDVs have excellent fatigue properties, high elongation at break and high tensile strength. Their recyclability is ensured by their thermoplastic nature, which also leads to a low degradation of their mechanical properties, allowing them to be used over several life cycles. These favourable properties make TDVs suitable for use in combination with devulcanized tire rubber.

In my thesis, I use microwave and thermomechanical devulcanization and investigating the structural changes of ground tire rubber after devulcanization. I introduce ground tire rubber into elastomers and thermoplastic dynamic vulcanizates and investigating the physical and mechanical properties of the samples.

2. CRITICAL ASSESSMENT OF THE LITERATURE, AND GOAL OF THE PHD THESIS

Statistics in the literature show that worldwide rubber production is increasing, two-thirds of which is used in the tire industry. Tires are a complex, multi-component composite product with a cross-linked structure, and their recycling is therefore problematic and not fully addressed. In the past, waste tyres were landfilled or incinerated, which had a very serious environmental impact. Therefore, nowadays, there are strict regulations on the management of waste tires, and their recycling must be addressed.

Waste tires are usually recycled in the form of ground rubber (ground tire rubber, GTR). GTR can be used in elastomers, thermoplastic polymers and thermosets. The main goal of research is to improve compatibility between the phases, for which several methods exist. For example, chemical surface treatment, devulcanization, and ionizing radiation.

I chose microwave and thermomechanical devulcanization as the main subjects of my research based on the literature because these methods do not require special equipment, no chemicals are added, and the time required for the treatments is relatively short. These advantages make these methods suitable for industrial-scale applications.

I have learned several analytical methods to detect changes in material structure due to devulcanization. The most used is Soxhlet extraction and the swelling method, which is used to determine soluble content and cross-link density, respectively. The Horikx analysis provides a link between the two properties, allowing us to estimate the degree of the degradation of samples after devulcanization.

Researchers usually use simple household microwave equipment, at which controllability is limited, so the quality of the devulcanized GTR (dGTR) can vary. Devulcanization at 600–900 W and with small, 10–60 g GTR batches resulted in temperatures above 200 °C even for short treatment times of ~1 min, which degraded the natural rubber (NR) phase in the GTR.

In many publications, the classification of devulcanization is based only on the soluble content, which is not sufficient, and the determination of cross-link density is necessary. On this basis, Horikx analysis can be done. The results show whether selective cross-link scission or random chain scission is the main phenomenon during devulcanization. Thus, these methods are of great help for dGTR classification, yet they are missing from many publications.

Various studies have achieved ~15-40% soluble content, and ~20-70% decrease in cross-link density for dGTR, and Horikx analysis has shown mainly random chain scission was the main phenomenon during devulcanization.

In several publications about the thermomechanical treatment of GTR with a co-rotating intermeshing twin-screw extruder, the researchers used very high barrel temperatures of up to 300 °C and high screw speeds, despite the fact that NR is prone to degradation above 200 °C and based on thermogravimetric analysis (TGA), the degradation of NR starts around 250 °C. In the majority of publications on thermomechanical devulcanization, the necessary tests for dGTR assessment were performed. Soluble content was around 15–45%, and a 30–85% decrease in cross-link density was achieved. With gentle devulcanization (low temperature and screw speed), severe degradation of the GTR is avoidable.

I have reviewed the applicability of dGTR and its limitations in various rubber-based compounds and thermoplastic polymers. In most publications on this topic, I observed that dGTR was used only in a low concentration of 10–30 wt%, the effect of higher dGTR content was not investigated, and no attempts were made to improve or modify the formulation of rubber.

Few publications on microwave, thermomechanical, or other high-temperature devulcanization processes paid attention to comparing the degradation behaviour of NR with the temperature during devulcanization.

dGTR is used most commonly in NR- and SBR-based compounds. In general, NR-based blends show a 10% decrease in tensile strength with 10–15 phr dGTR content. A significant decrease in elongation at break only occurs at higher (30–40 phr) dGTR contents.

The compatibility of the phases is a crucial issue with blends of GTR and thermoplastic polymers. It can be improved with several methods: modification of the GTR surface with different acids, plasma spraying, UV radiation, ozone, electron irradiation, gamma radiation, devulcanization, copolymers, coupling agents, and dynamic vulcanization.

With thermoplastic dynamic vulcanization, 1–2 µm rubber particles can be formed. They have excellent mechanical properties, and their recyclability is ensured due to their thermoplastic nature, making them worth blending with dGTR.

Based on the above, I formulated the following goals:

- Microwave devulcanization of ground tire rubber with laboratory microwave equipment. Investigating the changes in the structure of the devulcanized tire rubber to rate devulcanization.
- Thermomechanical devulcanization of ground tire rubber with a co-rotating intermeshing twin-screw extruder. Investigating the changes in the structure of the devulcanized tire rubber to rate devulcanization.
- Investigating the applicability of dGTR in rubber compounds and investigating the physical and mechanical properties of the samples.

3. MATERIALS USED AND METHODS APPLIED

My thesis can be divided into two main parts. In the first part, I perform microwave and thermomechanical devulcanization of ground tire rubber. I investigated the changes in material structure and the applicability of dGTR in rubber compounds. The second part is about the development of thermoplastic dynamic vulcanizates and the investigation of the applicability of dGTR.

I used WJET GTR ground rubber (nominal particle size 0.1–0.2 mm) prepared by Hungarojet Ltd. from truck tyre treads by high-pressure water jet grinding.

I introduced the dGTR in 50, 100 and 185 phr in NR CV 60 natural and SBR 1502 styrene-butadiene rubber-based compounds. Table 1 shows the additives used in the compounding process.

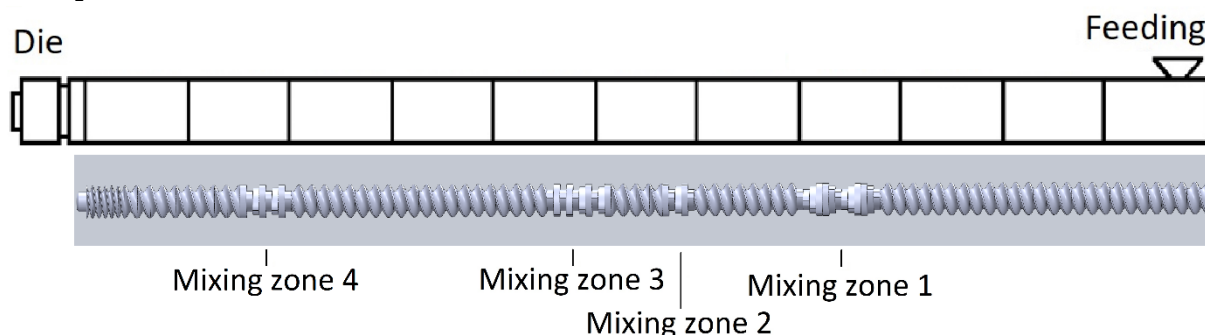
Material	Manufacturer	Brand	Function
N-cyclohexylbenzothiazol-2-sulphenamide (CBS)	Rhein Chemie (Mannheim, Germany)	Rhenogran® CBS-80	Accelerator
Tetramethyl thiuram disulphide (TMTD)	Lanxess (Cologne, Germany)	Rhenogran® TMTD-70	Accelerator
Zinc oxide (ZnO)	Werco Metal (Zlatna, Romania)	ZnO WZ-1	Activator
Stearic acid	Oleon (Ertvelde, Belgium)	Radia0444	Activator
Sulphur	Ningbo Actmix Polymer (Ningbo, Zhujiang, China)	Curekind Sulphur	Cross-linking agent
Naphthenic oil	Hansen und Rosenthal (Hamburg, Németország)	Tudalen 4353	Plasticizer
Paraffin oil	Hansen und Rosenthal (Hamburg, Germany)	Tudalen 3036	Plasticizer
Carbon black N330	Omsk Carbon Group (Omsk, Russia)	N-330 OMSK	Filler
Carbon black N 550	Omsk Carbon Group (Omsk, Russia)	N-550 OMSK	Filler
Carbon black N 772	Omsk Carbon Group (Omsk, Russia)	N-772 OMSK	Filler

1. table Rubber additives

I used a BP-125/50 laboratory microwave device for microwave devulcanization, manufactured by Microwave Research & Applications Inc., Carol Stream, Illinois, USA. The device can be programmed; the final temperature in °C and the heating rate in 1–100 °C/min can be set. Therefore, it was possible to set different temperature profiles for the treatments. Devulcanization was performed at 140, 160, 180 and 200 °C with heating rates of 2, 3, 6, 12 and 18 °C/min.

Thermomechanical devulcanization of the GTR was carried out in a co-rotating intermeshing twin-screw extruder (LTE 26-44, Labtech Engineering Co., Ltd.,

Samutprakarn, Thailand). Figure 2 shows the configuration of the screw. The treatment was carried out at 140, 160, 180, 200, 210, 220, 230 and 240 °C at 60, 120 and 180 rpm.



2. Figure Screw configuration for thermomechanical devulcanization

I prepared the rubber mixtures with a Brabender Plasti-Corder (Brabender GmbH & Co. KG, Duisburg, Germany) internal mixer at 50 °C and 40 rpm. The blends were vulcanized with a Teach-Line Platen Press 200E hydraulic press (Dr. Collin GmbH, Munich, Germany) at 160 °C at 2.8 MPa until t_{90} , based on the determined vulcanization properties. I also prepared blends with conventional mixing and with two-step mixing that I developed. In the latter, I added activators, plasticizers, accelerators, and vulcanizing agents to the devulcanized tire rubber, and in the second mixing step, I added this mixture to the reference mixture (the starting mixture to which I added the additives).

The soluble solids content, S (%), of the ground rubber was determined by Soxhlet extraction. Toluene was used as a solvent in the tests. Extraction time was 24 h (the ISO 1407:2011 standard requires 16 h), and the samples were dried at 85 °C until equilibrium weight was reached (24 h).

The swelling test was carried out according to ASTM D6814. The samples were soaked in toluene for 72 hours at room temperature until equilibrium swelling was reached. The rubber was dried with paper towels and the swollen mass was measured. The samples were then dried at 85 °C until equilibrium mass was reached (24 h). The cross-link density was determined with the use of the Flory-Rehner theory and the Kraus correction.

The vulcanization properties of rubber compounds were measured with a D-RPA 3000 (Montech Rubber Testing Solutions, Buchen, Germany) rotary vulcometer at 160 °C (the frequency was 1.67 Hz and the amplitude was 1°).

I measured the cross-link density of the rubber samples from the vulcanization properties of the rubbers with a D-RPA 3000 (Montech Rubber Testing Solutions, Buchen, Germany) rotary vulcometer. First, I vulcanized the rubber mixture (160 °C, frequency 1.67 Hz and amplitude 1°) until t_{90} (determining t_{90} required a separate test), then cooled the sample back to 40 °C. This was followed by a heating step at a heating

rate of 5 °C/min, while the storage modulus (G') was recorded. The frequency was 10 Hz and the amplitude was 0.715°. From the storage modulus, the cross-link density can be calculated.

I investigated the morphology of the rubber samples with an atomic force microscope (FlexAFM 5 from Nanosurf (Liestal, Switzerland) in tapping mode, equipped with a BudgetSensors (Sofia, Bulgaria) Tap-190AI-G needle with a needle diameter of <10 nm. The resonance frequency of the needle is 190 kHz. Samples were prepared by microtome cutting (Leica EM UC6, Wetzlar, Germany) at -120 °C.

The tensile and tear tests of the rubber specimens were performed with a Zwick Z020 (Zwick GmbH, Ulm, Germany) universal tensile testing machine, with the use of a 20 kN load cell. All tests were performed at room temperature.

The rubber specimens were tensile tested according to DIN 53504 at a speed of 500 mm/min and a grip length of 60 mm. Tear tests were carried out according to ASTM D624 at a speed of 500 mm/min and a grip length of 56 mm.

The Shore A hardness of the rubber specimens was determined with a Zwick H04.3150 hardness tester (Zwick GmbH, Ulm, Germany). I measured hardness at 10 points on each specimen.

The morphology of the samples was investigated with a Jeol JSM-6380LA (Jeol LTD., Tokyo, Japan) scanning electron microscope.

Thermogravimetric analysis (TGA) was carried out using a Q500 (TA Instruments, New Castle, Delaware, USA) at a heating rate of 10 °C/min in an air atmosphere with a sample mass of 4–5 mg. The maximum temperature was 700 °C.

The differential scanning calorimetry (DSC) tests were performed with a Q2000 (TA Instruments, New Castle, Delaware, USA) apparatus at a heating rate of 3 °C/min from room temperature to 250 °C in air atmosphere with a sample mass of 4-5 mg.

The infrared spectra of the samples were determined using a Bruker Tensor 37 (Bruker Inc., Billerica, Massachusetts, USA) device in the wavenumber range of 4000–400 cm^{-1} in attenuated total reflectance (ATR) mode.

The moisture content of the ground tire rubber was measured with an Aquatrac-3E (Brabender Messtechnik GmbH & CO., Duisburg, Germany) device.

4. SUMMARY

Global rubber production was 28 million tonnes in 2021, 60% of which was used in the tire industry. Despite increasingly stringent waste management regulations, the problem tire recycling is not fully solved, and existing methods cannot accommodate the growing amount of waste.

Recycling tires in the form of regrind is the most practical method. Ground rubber can be used in rubber compounds, thermoplastic polymers and thermosets. The

problem is that rubber is chemically very stable, and the adhesion between the matrix and the rubber particles is weak. Several compatibilization methods have been developed to overcome this problem: oxidation of the surface of the rubber particles, reduction of their surface tension, reduction of the aggregation tendency of the grind, coupling polymers, ionizing radiation, and devulcanization.

In my thesis, I chose devulcanization, which aims to selectively break up the cross-links in rubber. Based on the literature review, I chose the microwave and a thermomechanical devulcanization method and investigated the properties of the devulcanized ground tire rubber.

The results showed that high selectivity (>0.85) can be achieved within a wide range of irradiation energies, which means that cross-links can be broken with high selectivity, i.e. the degradation of the rubber is negligible in the 140–160 °C temperature range. In microwave and thermomechanical devulcanization, the decrease in cross-link density was sufficient (~65%). This was achieved at low (140–160 °C) treatment temperatures, and selective cross-link scission was the main phenomenon. At higher temperatures (180–200 °C), approaching/exceeding the degradation temperature of natural rubber, the decrease of cross-link density reached 85%, but the process was dominated by random chain scission, selectivity was drastically reduced, and severe degradation occurred.

I introduced the devulcanized ground tire rubber in 100 phr to rubber compounds. The tensile strength of the samples decreased by ~60%, and their tear strength by ~80%. When the formula was improved and the amount of vulcanizing agents was increased, tensile strength decreased by a smaller amount of ~45% and tear strength by ~60%, compared to the reference rubber mixture without dGTR. I further improved the mechanical properties by developing a two-step mixing procedure, whereby the increased amount of vulcanizing agents was added in two steps (first to the devulcanized ground tire rubber, and then in the next separate mixing step, this mixture was added to the reference mixture). Compared to the reference, tensile strength was reduced by ~35%, and tear strength increased back to the reference value. This is because the vulcanizing agents acted directly on the surface of the rubber particles, thus increasing the adhesion between the matrix and the rubber particles.

I also investigated the applicability of dGTR in thermoplastic dynamic vulcanizates. This is better than using it in elastomers, as the material produced can be recycled, as it is a thermoplastic; recyclability is retained even at high rubber content.

I produced polypropylene-based thermoplastic dynamic vulcanizates. The formulation of the rubber phase was like the formulation of GTR. I used an intermeshing co-rotating twin-screw extruder and my specially configured screws. The mechanical properties of my thermoplastic dynamic vulcanizates were close to those of commercially available thermoplastic dynamic vulcanizates. When 50% of the

rubber phase of the thermoplastic dynamic vulcanizates was replaced with dGTR, they still remained usable for their purpose, and by using two-step mixing, I was able to improve their mechanical properties. Thus, when used in thermoplastic dynamic vulcanizates, dGTR has an advantage over the use of GTR.

5. THESES

1. I showed that during the microwave devulcanization of ground tire rubber, high selectivity (>0.85) can be achieved within wide limits, independently of the amount of irradiated energy, with negligible degradation of the rubber waste in 140–160 °C temperature range. In this low-temperature range, the applied heating rate (2–18 °C/min) did not significantly affect the soluble content. Selectivity was not significantly changed. Increasing the treatment time promoted selective cross-link scission. In the higher temperature range (180–200 °C), the heating rate did not significantly affect the decrease in cross-link density, only the soluble content, i.e., increasing the treatment time, random chain scission became stronger, i.e., degradation became more severe.

I verified my results by Soxhlet extraction, swelling tests and Horikx analysis on devulcanized ground tire rubber with a particle size of less than 0.71 mm, obtained from the tread of truck tyres by water jet milling [1-3].

2. I showed that the thermomechanical devulcanization of ground tire rubber with an intermeshing co-rotating twin-screw extruder at a given screw configuration resulted in a ~70% decrease in cross-link density over a wide range of temperatures, and speeds, at lower barrel temperatures (140-160 °C), irrespective of screw speed, with negligible degradation. This is because at lower barrel temperatures, the degradation of NR is not significant at the given extrusion temperature and residence time, even with the temperature increase from external heating and frictional heat. At higher barrel temperature treatments (above 200 °C), also independently of screw speed, the decrease in cross-link density was great, but the ground tire rubber suffered significant degradation. In the intermediate temperature range, at a barrel temperature of 190 °C, a significant ~80% decrease in cross-link density was achieved with minimal degradation.

My results were verified by Soxhlet extraction, swelling tests and Horikx analysis on devulcanized ground tire rubber with a particle size of less than 0.71 mm, obtained from the tread of truck tyres by water jet milling [4, 5].

3. I showed that during microwave and thermomechanical devulcanization with an intermeshing co-rotating twin-screw extruder and during the compounding of rubber mixtures, with the two-step mixing method I developed, the vulcanizing agents act not only on the surface of the rubber particles but also in their entire cross-section. The additional vulcanizing agents added to the devulcanized ground tire rubber formed a stronger adhesive bond with the matrix than with conventional mixing, resulting in an improvement of the mechanical properties of the rubber compounds, especially tear strength (~750%), compared to rubber mixtures with conventional one-step devulcanized rubber granules.

This was confirmed by scanning electron microscopy, energy dispersive spectroscopy, atomic force microscopy, and tensile and tear tests on NR-based mixtures containing devulcanized ground tire rubber with a particle size of less than 0.71 mm produced by water jet milling of truck tyre treads [2-4].

4. I showed that the degree of degradation of the devulcanized ground tire rubber produced with microwave and thermomechanical devulcanization with an intermeshing co-rotating twin-screw extruder in natural rubber-based mixtures produced by two-step mixing has an effect on the tear strength of the samples. Mixtures with a higher degree of degradation of devulcanized ground tire rubber content have higher tear strength. This is due to the fact that in the tear test, the crack runs along the surface of the grains, bypassing the rubber particles. The fragmented molecular chains at the surface of the more degraded rubber particles are more mobile and reactive compared to the less degraded longer molecular chains, resulting in stronger adhesion at the interface of the devulcanized ground tire rubber and the matrix due to the vulcanizing agents introduced by two-step mixing.

This was confirmed by scanning electron microscopy, energy dispersive spectroscopy, atomic force microscopy, and tensile and tear tests on NR-based mixtures containing devulcanized ground tire rubber with a particle size of less than 0.71 mm produced by water jet milling of truck tyre treads [2-4].

6. LIST OF MY PUBLICATIONS

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