TRANSFORMING SILICA-SILANE REINFORCED RUBBER INTO A HIGH QUALITY DEVULCANIZATE

ROUNAK GHOSH
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উত্তিষ্ঠত জগ্রত প্রাপ্য বরান্নিরোধত।
- ব্যামী বিবেকানন্দ

Arise, awake, and do not stop till the goal is reached.
- Swami Vivekananda
TRANSFORMING SILICA-SILANE REINFORCED RUBBER INTO A HIGH QUALITY DEVULCANIZATE

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CHAPTER 1
INTRODUCTION

This chapter provides a comprehensive overview of the context and research background that motivates the investigation. It outlines the overarching research objective and delineates the structure of the thesis by highlighting subsequent chapters.
1.1 Historical background

Rubber is a highly valuable and indispensable material in contemporary society, finding diverse applications in aircraft, automotive, trains, power transmission belts, household products, and various other sectors. Its versatility and utility have made it an integral component of modern industrial and domestic life¹.

The origins of rubber can be traced back to the 15th century when indigenous people on Haiti extracted a fluid from local trees to create a ball for their traditional game. This fluid was also employed to render their clothing waterproof. In their native tongue, the tree was known as 'caa-o-chu', signifying the 'weeping tree'. Subsequently, the botanical name for this species was designated as *Hevea Brasiliensis*, and the fluid was termed latex². It was not until 1736, that rubber was introduced in Paris, specifically in the Academy of Science. Initially, dried latex was utilized to erase pencil marks by rubbing, leading to the material being named "rubber"³.

For several decades, the stickiness of rubber, its susceptibility to degradation, and exceptional flow properties limited its practical utility. However, a pivotal development occurred in 1839 when Charles Goodyear fortuitously discovered the process of sulphur vulcanization⁴. This process was named after the Roman God of Fire, Vulcan. In 1840, the first rubber product emerged in the form of footwear, sparking a rapid expansion in the diversity of rubber goods¹.

With the advent of automobiles, rubber assumed a critical role in mitigating road-induced jolts and vibrations. The initial tire design consisted of fabric-covered solid rubber sheets⁵. Notably, in 1845, the Scottish scientist Robert William Thomson obtained a patent for a tire comprising a hollow rubberized fabric tube filled with air⁶. By the late 19th century, André Michelin pioneered the invention of the first pneumatic tire, while John Dunlop concurrently developed a similar pneumatic tire design⁷. These innovations marked significant milestones in the evolution of rubber technology and its pivotal role in transportation and industrial sectors.

Over the years, tire properties have seen significant advancements in terms of reliability, safety, fuel efficiency, and lifespan. The construction and rubber compositions used in tire manufacturing have been meticulously adjusted to meet the ever-evolving and demanding requirements. The rubber formulations for each tire component have been finely tuned to cater to specific needs, one of them being the resistance to wear. Because every tire has a finite lifespan, end-of-life tires pose a formidable challenge due to their intricate composition and resistance to decomposition⁸.

1.2 Research background

The challenge of recycling rubber is closely tied to the unique material structure of vulcanized elastomers, which fall into the category of thermosetting materials. In the realm of polymers, materials can broadly be categorized as either thermoplastics or thermosetting materials. Thermoplastics become pliable and can be reshaped when heated to higher temperatures. In contrast, thermosetting materials such as rubber undergo crosslinking when heated, rendering them impervious to softening or reshaping through temperature increases. This inherent property makes thermosets significantly more challenging to recycle compared to thermoplastics. The recycling process, known
as "reclaiming," necessitates the breakdown of the three-dimensional network created by either sulphur crosslinks that connect polymer chains or carbon-carbon bonds within the polymer structure. Preferably, the focus is on breaking the crosslinks while preserving the integrity of the polymer backbone.

One of the most promising solutions to this recycling challenge is to restore rubber to its reusable state by reversing the vulcanization process responsible for imparting its specialized properties, returning it to "green" state. This intricate process is known as "devulcanization".

Successful devulcanization processes have been developed for Ethylene-Propylene-Diene rubber (EPDM) and Natural Rubber (NR). Saiwari and van Hoek have established a proof of concept for devulcanizing Styrene Butadiene Rubber (SBR) and various tire rubbers using both laboratory-scale batch processes with a Brabender internal mixer and continuous processes with an extruder. Furthermore, a small-scale processing line for continuous devulcanization of Ground Tire Rubber (GTR) has been devised, and subsequent investigations have focused on the implications of utilizing the devulcanized material in car tire compounds. Within the study of this thesis, the earlier gained knowledge is used in these developments.

These research studies served as the motivational foundation and initial impetus for this investigation. It is essential to note that one of the major variations in tire rubber is the type of filler: carbon black establishing a physical interactions with the polymer, whereas silica forms a chemical bond with the polymer matrix. While the devulcanization of carbon black-filled tires primarily entails the breakdown of polymer crosslinks, the devulcanization of silica-filled tires necessitates the concurrent rupture of filler-polymer bonds in addition to polymer crosslinks. This duality in bond disruption is what renders the devulcanization of silica-filled tires comparatively more challenging when contrasted with carbon black-filled tires. The principal focus of this investigation was the devulcanization of silica-filled passenger car tire rubber.

1.3 Aim of the research

The research is aimed to attain a high-quality devulcanizate through the development of an environmentally sustainable devulcanization process for rubber sourced from passenger car tires. To accomplish this objective, the research was structured around distinct topics, as delineated below:

1. Comparing the efficiencies of potential new sustainable silane based devulcanization aids (DA's).
2. Devulcanization process optimization with the best DA using a model tire tread compound and ground passenger car tire (GTR) rubber.
3. Reactivity of different types of DA's.
4. Elucidation of the devulcanization reaction mechanism.
5. Improvement of the devulcanizate quality by additives.
7. Application study by blending of devulcanizates with virgin compounds.
8. Comparative study of commercial devulcanizates.
Chapter 1

1.4 Structure of the thesis

Chapter 2 provides an extensive literature review covering various aspects, including passenger car tire tread compounding, ingredients, silica silane technology, an overview of devulcanization, devulcanization mechanisms, and the most recent discoveries concerning the devulcanization of GTR.

Chapter 3 involves evaluating various devulcanization aids for passenger car tire tread granulates, followed by a comparative analysis to identify the most promising silane to be used as DA.

Chapter 4 focuses on optimizing devulcanization parameters using a vinyl silane with peroxide (VP) for model passenger car tire tread materials, with a detailed comparative analysis to identify the best devulcanization parameters. The investigation extends to whole passenger car tire (WT) granulates, conducting a thorough comparative analysis to determine the optimal devulcanization process parameters using VP.

Chapter 5 is dedicated to the examination of three principal domains, which include the assessment of varying combinations of devulcanization aids, the exploration of the impact of individual constituents of the best DA, and the investigation of devulcanization solely employing peroxides.

Chapter 6 is dedicated to the investigation of the devulcanization reaction mechanism of vinyl silane (VTEO) and VP in conjunction with a liquid model compound. A comprehensive analysis of the model compound, both in its devulcanized and revulcanized state, using gas chromatography and NMR spectroscopy elucidated the network degradation mechanism.

In Chapter 7, devulcanization of rubber granulate was conducted employing the most efficient DA, with variations in processing aid (PA). The central objective of this investigation encompassed two primary goals: firstly, to assess the influence of diverse process aids on the devulcanization procedure, and secondly, to pinpoint an optimal process aid for enhancing the devulcanization process.

Chapter 8 delves into an examination of the influence of fillers and the effect of the silanization reaction on devulcanizates. Additionally, it encompasses the process of blending devulcanizates and ground rubber with a virgin compound for the purpose of conducting a comparative analysis of the influence of the recycled rubber on the properties.

The principal objective of this research was to establish a closed-loop tire manufacturing system through the incorporation of a high-quality devulcanizate in new tire compounds. In Chapter 9, the best devulcanizate was blended with a model tire tread compound, and a comprehensive analysis was conducted, with particular emphasis on its applicability in the context of tire requirements.

Chapter 10 primarily involves a comparison between the newly developed devulcanizates and commercial counterparts, along with the establishment of a correlation between tensile strength and miscibility for samples that have undergone devulcanization using various DAs and under diverse process conditions.
Chapter 11 encompasses all results and transfers them to an upscaled extruder process, with particular attention to the transition from a batch process to a continuous one, with the aim to achieve increased productivity and facilitate industrialization. This upscaling effort involved modifications of the screw configuration and process optimization.

The flowchart of the investigation is shown in Figure 1.1.

Figure 1.1. Flowchart of the investigation

1.5 References

3. Hoffmann, W., 1996. Rubber technology handbook, Publisher: Hanser, Germany.
The chapter offers an in-depth examination of tire technology, with particular emphasis on the constituents involved in passenger car tire tread compounding. It includes a part on the advancements in silica-silane technology, which is the predominant filler in modern passenger car tire treads playing a crucial role in devulcanization.

It also provides a comprehensive overview of devulcanization, encompassing various devulcanization techniques and the role of devulcanization aids in the process. Finally it underscores the noteworthy developments that have transpired in the field of tire devulcanization over the past five years. This chapter is based on a review article published in the Tire Tech Annual Review Journal 2023.
2.1. Overview of tire technology

Gum rubber, in its raw form, typically has limited utility in commercial applications due to its inherent mechanical weakness. To transform gum rubber into a rubber compound and, subsequently, into a highly specialized product, it is necessary to meet specific requirements. These requirements are met by incorporating various ingredients into the rubber, a process commonly referred to as compounding. The essential characteristics of the resulting rubber compound such as its resistance to chemicals and temperature, are primarily determined by the inherent properties of the rubber itself, whether it is a single polymer or a blend of polymers\(^1\).

The crosslinking system in rubber compounds comprises the crosslinker itself and an accelerator system. These components collectively influence the vulcanization process in terms of its duration and speed, as well as the density and length distribution of crosslinks formed. Furthermore, they have a significant impact on the mechanical and dynamic properties of the rubber, as well as its stiffness and ageing behavior\(^1,2\).

To optimize the processing characteristics and intrinsic properties of the rubber, lubricants such as various oils or liquid polymers are typically introduced into the compound. Additionally, a range of other ingredients including antioxidants and processing aids, may be incorporated as well\(^1,3\). However, aside from the polymer itself, fillers or filler systems play a crucial role in determining the ultimate properties of the end product. Fillers primarily serve several key purposes: reinforcing the compound to enhance its strength, or change the colour or conductivity of the product, as well as reduction of production costs etc\(^1-3\).

To amalgamate all constituents, they must undergo mixing, typically within an internal mixer and/or an open mill. This mixing procedure can be categorized into multiple stages, and the incorporation of ingredients can occur at various points in the process. The optimization of the mixing process necessitates careful consideration of factors such as mixing duration, temperature, and energy consumption. Moreover, it must serve specific objectives, including the attainment of a uniform compound, the dispersion and even distribution of all incorporated ingredients within the rubber, and, in the case of a silica-silane system, functioning as a chemical reactor\(^1-3\).

The concluding phases in manufacturing of rubber products encompass molding and vulcanization. In the tire industry, the prevailing method for vulcanization is compression molding. During this process, the blended compound is introduced into a preheated mold and subjected to pressure to assume its intended shape. By judiciously selecting appropriate chemical additives during the compounding phase, the crosslinking reaction is induced within a matter of minutes. This catalytic transformation leads to the formation of the final rubber product\(^1,2\).

The recycling challenge is primarily rooted in the three-dimensional network structure of vulcanized rubber, rendering rubber products insoluble and infusible. Since a significant portion of rubber products comprises tires, and the thesis is centered on devulcanizing passenger car tires, it includes a concise overview of various tire types and provides a brief description of the compounding ingredients found in passenger car tires.
2.2. Classification of tires

Various types of tires exist, including those designed for trucks, cars, aircrafts, tractors, and off-road applications, each distinguished by unique constructions and significantly varying rubber compositions, and properties tailored to their specific purposes\textsuperscript{4-6}. Table 2.1 summarizes the property range of various tire tread materials from literature\textsuperscript{2-6}.

I. Truck tires are engineered for carrying heavy load, extended mileage and incorporate a relatively high proportion of natural rubber (NR) in their treads.

II. Aircraft tires must withstand extreme forces and heat generated in the tread due to the high acceleration during landings and the high speeds achieved during rollouts. This necessitates specialized compound properties and a substantial quantity of NR.

III. Tractor tires are required to efficiently transmit forces in soft soil at low speeds, often incorporating specialized tread surface pads. They must also exhibit a high level of resistance to punctures. Typically, these tires are composed of NR filled with carbon black.

IV. Off-road tires must exemplify outstanding puncture resistance, especially against sharp stones, while also demonstrating crack growth resistance while effectively transmitting significant forces at low speeds. Generally, tires for off-road applications are comprised of NR filled with carbon black.

V. Passenger car tires require wear resistance, good wet grip, and low rolling resistance. Typical tread compounds consist of blends of Styrene-Butadiene rubber (SBR) and Butadiene rubber (BR).

<table>
<thead>
<tr>
<th>Tire types</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Viscosity [ML(1+4) at 100\textdegree C]</th>
<th>Hardness (Shore A)</th>
<th>Rebound resilience (%)</th>
<th>Tear strength (kN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter passenger car</td>
<td>14-22</td>
<td>300-500</td>
<td>50-80</td>
<td>60-70</td>
<td>45-65</td>
<td>15-25</td>
</tr>
<tr>
<td>Summer passenger car</td>
<td>16-25</td>
<td>350-500</td>
<td>50-80</td>
<td>60-70</td>
<td>50-70</td>
<td>15-25</td>
</tr>
<tr>
<td>Truck</td>
<td>20-30</td>
<td>300-450</td>
<td>50-90</td>
<td>65-75</td>
<td>60-80</td>
<td>20-30</td>
</tr>
<tr>
<td>Off-road</td>
<td>20-35</td>
<td>250-400</td>
<td>60-100</td>
<td>55-75</td>
<td>60-80</td>
<td>20-35</td>
</tr>
<tr>
<td>Air-craft</td>
<td>25-40</td>
<td>200-350</td>
<td>70-100</td>
<td>60-80</td>
<td>70-90</td>
<td>25-35</td>
</tr>
</tbody>
</table>

These distinctive properties, associated constructions, and compound compositions render it undesirable to intermix them when seeking to recycle rubber for use within the same kind of applications. In the context of truck and passenger car tires, the material utilization is elucidated in Table 2.2\textsuperscript{6}.
Table 2.2. Compounding materials in tire construction

<table>
<thead>
<tr>
<th>Materials</th>
<th>European Union</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Passenger Truck</td>
<td>Passenger Truck</td>
</tr>
<tr>
<td>Natural rubber (%)</td>
<td>22</td>
<td>14</td>
</tr>
<tr>
<td>Synthetic rubber (%)</td>
<td>23</td>
<td>27</td>
</tr>
<tr>
<td>Filler content (%)</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>Steel (%)</td>
<td>13</td>
<td>14-15</td>
</tr>
<tr>
<td>Fabric and other chemical ingredients (%)</td>
<td>14</td>
<td>14-15</td>
</tr>
<tr>
<td>Average weight of new tire (kg)</td>
<td>8.5</td>
<td>16-17</td>
</tr>
<tr>
<td>Average weight of scrap tire (kg)</td>
<td>7</td>
<td>45</td>
</tr>
</tbody>
</table>

% = weight percentage; kg = kilogram

2.3. Passenger car tire compounding

The focus of the thesis centers on the devulcanization of passenger car tires, which primarily consist of a SBR-BR polymer system and a silica-silane filler system in the tread. It is crucial to comprehend the role of each component in order to achieve successful devulcanization, with particular emphasis on the significant contributions of the polymer and filler systems. In this section, the literature on passenger car tire tread compounding ingredients and silica-silane technology is briefly summarized. Table 2.3 gives an overview of the property range for various components of passenger car tire materials.

Table 2.3. Requirements of different components of passenger car tire

<table>
<thead>
<tr>
<th>Tire components</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Viscosity [ML(1+4) at 100°C]</th>
<th>Hardness (Shore A)</th>
<th>Rebound resilience (%)</th>
<th>Tear strength (kN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tread</td>
<td>14-22</td>
<td>300-500</td>
<td>50-80</td>
<td>60-70</td>
<td>50-70</td>
<td>15-25</td>
</tr>
<tr>
<td>Undertread</td>
<td>12-20</td>
<td>250-400</td>
<td>40-70</td>
<td>60-70</td>
<td>45-65</td>
<td>12-20</td>
</tr>
<tr>
<td>Sidewall</td>
<td>12-18</td>
<td>400-600</td>
<td>50-70</td>
<td>55-75</td>
<td>40-60</td>
<td>20-30</td>
</tr>
<tr>
<td>Belt plies</td>
<td>20-30</td>
<td>200-300</td>
<td>55-85</td>
<td>65-80</td>
<td>60-70</td>
<td>25-35</td>
</tr>
<tr>
<td>Innerliner</td>
<td>8-10</td>
<td>400-800</td>
<td>30-60</td>
<td>55-70</td>
<td>30-50</td>
<td>10-20</td>
</tr>
<tr>
<td>Bead filler</td>
<td>4-8</td>
<td>100-200</td>
<td>30-50</td>
<td>40-40</td>
<td>20-40</td>
<td>5-10</td>
</tr>
</tbody>
</table>

2.3.1. Synthetic rubbers

Considering the usage of synthetic rubbers used in passenger car tire tread compounding, this study primarily focuses on SBR and BR. SBR stands as the predominant synthetic rubber for passenger car tires, finding application in various tire components, excluding the inner liner. To enhance the low temperature properties, BR is often blended with SBR in tread compounds. The microstructure of these rubber materials has a direct impact on the glass transition temperature (Tg) of the elastomer, a crucial parameter influencing the overall compound properties. The details about SBR and BR are described below.
2.3.3.1. Styrene-Butadiene rubber (SBR)

In terms of production and usage quantities, SBR stands as the most prevalent synthetic rubber\textsuperscript{11}. It is constituted as a copolymer encompassing styrene and butadiene moieties. The polymer’s macrostructure, which profoundly influences its ultimate application, is determined by the ratio of these components and the copolymerization technique. SBR is fabricated through emulsion polymerization (ESBR) or solution polymerization (SSBR). However, for silica-filled passenger car tire tread applications, SSBR is predominantly chosen owing to its higher molecular weight and narrower molecular weight distribution. Although mechanical properties exhibit marginal disparities between ESBR and SSBR, SSBR outperforms in terms of elasticity, resilience, and resistance to heat build-up. Furthermore, SSBR displays enhanced compatibility with silica and silane coupling agents, consequently yielding superior rolling resistance\textsuperscript{12}.

Modifying the polymer backbone and chain ends with a functional group is common practice for SSBR to enhance the polymer-filler coupling reaction resulting in an improvement of the tire properties. Hence, SSBR became one of the preferred choices for tire compounding. It is noteworthy that elevating the styrene content in SBR results in an increased glass transition temperature (Tg) of the polymer due to the steric hinderance caused by the bulky styrene monomer, which restricts the segmental motion of the branched polymer chain and reduces polymer flexibility\textsuperscript{8}. Figure 2.1 illustrates the polymeric structure of SBR.

![Figure 2.1. Microstructure of SBR\textsuperscript{13}](image)

The polybutadiene component within SBR exhibits three distinct structural configurations, namely cis, trans, and vinyl. A comparative analysis was conducted on SBRs featuring varying levels of styrene and vinyl content within a conventional SBR/BR silica-filled tire tread formulation. The outcome revealed that polymers with elevated styrene content yielded compounds characterized by lower Mooney viscosity and enhanced wet-traction performance\textsuperscript{13}. Compounds with a high vinyl content demonstrated superior rolling resistance\textsuperscript{13-14}.

SSBR typically employed in passenger car tires predominantly comprises a styrene content ranging from 24% to 29%, a vinyl content ranging from 65% to 70%, and in case of a functionalized polymer 1% to 4% of functionalized groups. The Tg of this rubber
Chapter 2

falls within the range of -20°C to -30°C, while its viscosity typically ranges between 45 and 55 MU measured as ML(1+4) at 100°C.\textsuperscript{15,16}

2.3.3.2. Butadiene rubber (BR)

Butadiene rubber, a homopolymer of 1,3-butadiene (C\textsubscript{4}H\textsubscript{6}), is produced through solution polymerization in the presence of a transition metal (Ti, Ni, or Co) catalyst complex or an alkyl metal catalyst, butyl lithium (BuLi). This process results in the formation of three isomers of BR: cis-1,4-, trans-1,4-, and 1,2-vinyl-butadiene, as depicted in Figure 2.2.

![Figure 2.2. Isomers of BR\textsuperscript{17}](image)

Within the tire industry, BR with a high cis-content (>90%) is predominantly favoured due to its exceptional attributes including elasticity, abrasion resistance, and rebound resilience.\textsuperscript{7,17} BR manufactured using nickel (Ni) catalysts exhibits the highest cis-content, reaching up to 98.2%. This particular grade demonstrates enhanced resistance to fatigue, abrasion, and reduced heat build-up when compared to BR's produced with cobalt (Co) or titanium (Ti) based catalysts.\textsuperscript{18} However, owing to its low glass transition temperature (Tg), BR presents challenges in terms of processability and wet traction behaviour. Hence, it is often blended with high Tg rubbers like SSBR to ameliorate the rolling resistance of tire treads.

In literature, it has been ascertained that high cis-content BR is better suited for tire tread compounds. The majority of BRs used in passenger car tire treads contain a cis-content exceeding 92%, possess a Tg below -80°C, and exhibit a viscosity ranging between 42 to 45 MU measured as ML(1+4) at 100°C.\textsuperscript{19}

2.3.2. Silica

Silica is an amorphous white substance composed of silicon (Si) and oxygen (O) atoms. It forms a three-dimensional network of Si-O-Si bonds, featuring surface silanol groups (Si-OH).\textsuperscript{20} Silica can be generated through two distinct methods: fuming or precipitation. For adhesives, sealants, coating, paints etc., fumed silica is used. However, for tire applications, precipitated silica is the predominant choice. Precipitated silica comprises clusters of silica containing interconnected primary particles. In the context of rubber reinforcement, there are small silica clusters that serve as the effective units.\textsuperscript{21} Silicas with high surface areas are often challenging to disperse uniformly within the rubber matrix. Nevertheless, specially functionalized, highly dispersible grades facilitate better
dispersion, leading to enhanced mechanical properties. The typical size of primary silica particles falls within the range of 10 to 30 nanometer, corresponding to a surface area of 125 to 250 m²/g. The surface area of silica can be quantified using methods such as the Brunauer-Emmett-Teller (BET) and cetyltrimethylammonium bromide (CTAB) absorption techniques.

The silica surface features several functional groups including isolated, geminal, and vicinal silanols, and siloxane bridges (Figure 2.3). Among these, the geminal and isolated groups exhibit high reactivity with coupling agents, whereas vicinal groups do not actively participate in the coupling reactions. Water preferably forms hydrogen bonds with the silanol groups, further enhancing the polarity of silica.

![Figure 2.3. Surface chemistry of silica](image)

The manufacturing process of precipitated silica can be categorized into several sequential steps: precipitation, filtration, drying, milling, and granulation. Silica can be classified into distinct grades based on its structure, with categories including conventional, semi-dispersible, and highly dispersible (HD-silica). HD silica exhibits a lower presence of undispersed particles when compared to conventional silica. In the presence of high shear forces, polymers infiltrate the voids within HD-silica clusters and disintegrate them during the mixing process. Consequently, a higher structural quality of silica results in improved dispersion behavior. The structure of silica can be quantified using parameters such as the oil absorption number (OAN) or dibutyl phthalate (DBP) number. Grunert and Blume have reported a correlation between the dispersion coefficient and the DBP number.

### 2.3.3. Silane

Silica exhibits a surface covered with silanol groups, rendering it highly polar. In contrast, general-purpose rubbers such as SBR and BR possess a predominantly non-polar nature, which poses a challenge in forming silica-polymer linkages within these rubbers. Consequently, coupling agents are employed in the compounding process to mitigate this surface energy mismatch. The closer the surface energy of silica aligns with that of the base polymer, the better the compatibility. In 1972, Degussa introduced...
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bis(triethoxy-silyl-propyl) tetra sulphide (TESPT), marketed under the trade name Si 69®, as the preferred silane coupling agent for the rubber industry.

These coupling agents, commonly referred to as silanes, can be categorized into two types: monofunctional and bifunctional. Monofunctional silanes attach to the polar surface of silica, enhancing processability by reducing viscosity, yet without forming a chemical interaction between the filler and polymer. Conversely, bifunctional coupling agents like TESPT possess two functional segments: a hydrophobic backbone with sulphur atoms and two identical hydrophilic end groups. The chemical linkage between the alkoxy groups of the hydrophilic part of the molecule and the polar silica surface forms during mixing. This linkage not only renders the silica surface more hydrophobic, but also lowers compound viscosity, thereby enhancing processability. During vulcanization, the hydrophobic backbone containing sulphur atoms facilitates the connection of silica particles to the polymer. The quantity of silane in the compound formulation is typically adjusted based on the surface area of the silica: a higher surface area necessitates increased silane content.

Two commonly employed silanes in the rubber industry are TESPT and bis(triethoxy-silyl-propyl) disulphide (TESPD). TESPT exhibits a sulphur ranking of approximately 4, while TESPD has an approximate ranking of 21,25. During processing, the ethoxy groups of these silanes react with the hydroxyl groups on the silica surface, while the sulphur moiety interacts with the polymer. TESPT, owing to its poly-sulphidic moiety, can release active sulphur into the rubber matrix under high-temperature and shear conditions during mixing, potentially causing processability issues, often referred to as "pre-scorch." Consequently, compounds containing TESPT require a narrow processing temperature range (145°C – 155°C). In contrast, TESPD, characterized by a shorter sulphur chain length, offers improved thermal stability and a slightly wider processing window. However, substituting TESPT by TESPD necessitates additional sulphur to maintain an equivalent crosslink network due to the lower sulphur content.

In recent times, a sterically hindered mercapto silane and a blocked mercapto silane have gained attention from the rubber industry. A blocked mercapto silane, notable for its high coupling efficiency, features sulphur atom blocking through the octanoyl carboxylate (thio ester), preventing a reaction of the silane with the non-polar rubber during compounding. The octanoyl thio ester group subsequently reacts with the diphenyl guanidine (DPG) accelerator, facilitating silica-silane-polymer coupling during vulcanization.

The coupling efficiency of a blocked mercapto silane also reduces filler-filler interactions, resulting in an easier processable compound with lower viscosity. The mercapto silane comprises a free mercapto group on the polymer-active end and a combination of an ethoxy group with polymeric and amphiphilic substituents on the silica-active end. The presence of polymeric moieties with polar characteristics enhances silica affinity, ensuring rapid adsorption and reaction on the silica surface. Figure 2.4 illustrates the hydrophobation effect of the silica surface by mercapto silane.
2.3.3.1. Silanization reaction

The chemical process wherein silanol groups on the silica surface react with silane is referred to as silanization. Silanization occurs during the compounding process and necessitates careful control, given the influence of various parameters such as temperature, moisture content, and the generation of ethanol. The degree of silanization exerts an impact on filler-filler interactions, consequently shaping the dispersion of silica in the cured compound. Figure 2.5 outlines the factors that influence the silanization reaction.

The silanization reaction unfolds in two distinct stages: the primary and secondary reaction. During the primary reaction, an alkoxy group on the silane undergoes hydrolysis in the presence of moisture, subsequently forming a siloxane moiety as it

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**Figure 2.5. Influencing factors of silanization reaction**

- **Optimum silanization and short mixing times**
- **Fast transportation processes** 
  - $\eta \downarrow$ at $T \uparrow$

- **Best suitable silica/silane system**

- **Reduced re-agglomeration** 
  - $\eta \uparrow$ at $T \downarrow$

- **Fast silanization reaction** 
  - $T \uparrow$ at $t \uparrow$

- **Best rotor and mixing chamber geometry**
attaches to the silica surface. The secondary reaction involves the potential hydrolysis of one or two ethoxy groups of the silane molecule bond to the silica surface, and a condensation reaction that produces either water or ethanol. Recent findings suggest that the slowest reaction, regarded as the rate-determining step, is the adsorption of silane onto the silica surface. In the presence of water, a hydrolysis reaction transpires at the Si-unit of the silane, leading to the release of ethanol. Subsequently, the hydrolysed Si-unit partakes in a condensation reaction with a silanol group located on the silica surface (Figure 2.6)\(^{27}\). It has been established that the secondary reaction proceeds at a pace at least 10 times slower than the primary reaction\(^{29}\). Notably, it has been reported that only 20% to 30% of all silanol groups on the silica surface undergo hydrophobization by silane\(^{29,32}\).

![Figure 2.6. Role of water on the silanization reaction\(^{27}\)](attachment:Figure_2.6.png)

To achieve a successful silanization reaction, several key factors must be considered. Firstly, the mixing time should be sufficiently long in order to complete the silanization reaction, and the mixer temperature should be appropriately high. Additionally, it is essential to promptly remove the alcohol formed during the silanization process to achieve coupling of the silane to the silica. Consequently, silica and silane should be introduced together in the initial mixing cycle\(^{22}\). Inadequate silanization reactions can lead to compromised mechanical strength due to insufficient polymer-filler bonding.

A higher degree of silanization not only enhances reinforcement but also contributes to improved abrasion resistance and rolling resistance. Therefore, achieving an optimal degree of silanization is crucial not only for ensuring superior reinforcement but also for specific application requirements.

2.3.3.2. Polymer silane coupling

The coupling reaction between the silica-silane filler and the rubber primarily occurs during vulcanization, but to a certain extent, it also takes place during the mixing process. Bifunctional sulphur-containing silanes require a minimum of two sulphur atoms to facilitate a reaction with the polymer as they split up within the sulphur moiety and the sulphur forms the bond to the polymer\(^{22-25}\).
Furthermore, the reactivity of sulphur-bridged silanes increases with sulphur chain length, as less energy is needed to break longer polysulphidic linkages. Consequently, TESPT exhibits higher reactivity than TESPD, posing the risk of premature coupling with the rubber during the mixing phase. Additionally, the introduction of free sulphur and accelerators plays a pivotal role in silane-rubber coupling, as they enhance the speed and efficiency of the reaction\textsuperscript{32-36}. Figure 2.7 illustrates the silica-rubber coupling reaction with TESPT.

### 2.3.4. Compounding additives

In the formulation of tire tread compounds, various additives are necessary not only to enhance the final properties but also to facilitate the processing. The following compounding additives are described below:

#### 2.3.4.1. Polymer silane coupling

Plasticizers are employed in rubber compounds to enhance processability by reducing compound viscosity. They function as lubricants between polymer macromolecules,
thereby diminishing structural rigidity. Additionally, plasticizers aid in filler dispersion, decrease hardness, and improve low-temperature flexibility. Based on a literature study\textsuperscript{37}, TDAE oil is identified as the optimal choice for the SBR/BR system not only for compounding, also for devulcanization.

2.3.4.2. Activators

Zinc oxide (ZnO) and stearic acid represent the most prevalent and effective activators in the sulphur vulcanization system. Stearic acid contributes to rubber processability and reacts with ZnO to create an activating complex described by Ikeda. This complex enhances accelerator activity and improves curing efficiency\textsuperscript{38}.

2.3.4.3. Accelerators

Accelerators serve to increase the rate of crosslinking and enhance crosslink density within the rubber compound. Accelerator systems often include multiple accelerators to optimize their effectiveness. They are categorized into two types: primary and secondary, depending on their reactivity during vulcanization. Primary accelerators are the faster-acting ones, while the addition of secondary accelerators alongside primary accelerators further enhances the rate and efficiency of vulcanization.

Sulfenamide-type accelerators, such as cyclohexyl benzothiazole sulphonamide (CBS), are commonly employed as primary accelerators in the SBR/BR system. In silica-filled tire rubber compounding, 1,3-diphenyl guanidine (DPG) is a widely utilized secondary accelerator. DPG also reduces the polarity of silica by adsorbing onto the silica surface and has the capability to accelerate the silanization reaction\textsuperscript{27}. Due to environmental sustainability concerns associated with DPG, alternative amines like cyclohexyl amines may serve as potential substitutes\textsuperscript{39}.

2.3.4.4. Elemental sulphur

A widely employed curing system for rubber products is the sulphur-based one. Elemental sulphur exists in its most common form as rhombic sulphur (S\textsubscript{8}). Vulcanization denotes the crosslinking reaction responsible for forming a three-dimensional network of chemically bonded polymer chains, as illustrated in Figure 2.8. The resulting cured rubber material exhibits dimensional stability, heat resistance, and improved mechanical properties\textsuperscript{36-38}. 

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2.4. Overview on devulcanization

Vulcanized rubber comprises three distinct networks: a polymer network formed by the physical entanglements of the polymer chains; a crosslinked network between the polymer chains resulting from the vulcanization process; and additionally physical or chemical crosslinks between fillers and polymer chains depending on the type of filler system.

The devulcanization process is generally unaffected by physical entanglements within the polymer chains, and as such, it was not a focal point of concern. In the conventional vulcanization process, sulphur enables the creation of sulphidic crosslinks between polymer chains, which, in turn, enhances mechanical strength and dimensional stability. In various devulcanization systems, the formation of different types of bonds is contingent on the specific curing system and the type of polymer, varying according to the degree of unsaturation.

In crosslinked systems, the role of fillers is significant, alongside the formation of polymer crosslinks. It's crucial to differentiate between carbon black and silica in this context. Carbon black establishes a mechanical interlock with the polymer, whereas silica forms a chemical bond with the polymer matrix. When it comes to devulcanization, the process for carbon black-filled tires primarily involves breaking down polymer crosslinks. However, devulcanizing silica-filled tires requires not only breaking of polymer-polymer bonds, but also simultaneously disrupting the filler-polymer bonds. This dual bond disruption makes the devulcanization of silica-filled rubber more challenging compared to carbon black-filled material.

Most recycling methods predominantly focus on random cleavage of the network, whereas there is a crucial need for the selective breakdown of the crosslinks to enhance the quality of recycled rubber. It is imperative to preserve the integrity of the polymer chains to the greatest extent possible, thereby introducing the concept of devulcanization\[^{2,40-42}\]. Devulcanized rubber exhibits superior mechanical properties.
compared to reclaimed rubber, attributed to the higher proportion of intact polymer backbones. Consequently, devulcanization is widely recognized as the most sustainable and valuable approach to rubber recycling. Figure 2.9 presents a comparative schematic diagram illustrating the processes of rubber reclaiming and devulcanization.

Figure 2.9. Schematic diagram of reclamation and devulcanization

2.5. Devulcanization triangle

The devulcanization process comprises three interrelated parameters: crosslink density, length of the crosslinks, and the efficiency of the devulcanization aid (DA). Considering these factors, the “devulcanization triangle” can be established. When considering these three parameters as the axes, the enclosed area within the triangle represents the efficiency of devulcanization, as illustrated in Figure 2.10. The black dotted lines signify the axes, while the grey dotted triangle delineates the optimal and balanced conditions among these three parameters. The bond length and crosslink density exhibit a direct correlation with factors such as filler-polymer interaction, the type of crosslinking system, the quantity of crosslinking aids, the type of coupling agent, and the vulcanization system, among others.

The blue triangle represents a material with a higher crosslink density and shorter bonds. This can be caused by an increase in filler-polymer interaction through the judicious use of a silane coupling agent. In the same system, by reducing the elemental sulphur content and increasing the concentration of accelerators, the vulcanization system shifts towards a more efficient configuration, resulting in shorter crosslinks, primarily monosulphidic. In this scenario, characterized by a high crosslink density and short bond length, devulcanization becomes notably challenging, resulting in lower DA efficiency, as indicated in the blue triangle.

Conversely, if the crosslink density is lower and the crosslink bridges are longer, the sample becomes comparatively more amenable to devulcanization. This implies that the utilization of efficient DAs can lead to a higher degree of devulcanization, as depicted in the orange triangle.

Between the orange and blue triangles, a transitional scenario may exist, where both crosslink density and length of crosslinks are high. In this case, the extent of devulcanization is contingent upon the efficiency of the DA. If the DA is highly efficient, the position shifts towards the orange region, while less efficient DAs result in a shift.
towards the blue region. These conditions fall between the orange and blue regions, as represented by the violet triangle.

![Efficiency of devulcanization aid](image)

Figure 2.10. Devulcanization triangle

In the context of silica-filled passenger car tires, the parameters of crosslink length and crosslink density are typically predetermined and considered as fixed factors. The primary objective of this investigation is to attain the maximum achievable degree of devulcanization, as depicted within the green triangle, through the optimization of DAs to enhance their efficiency.

### 2.5.1. Crosslink density measurement techniques

This approach requires that the crosslink density is measured. There are different possibilities to determine the crosslink density, the commonly used methods are described below:\(^43^:

A. Equilibrium volume swelling:

In this approach, a rubber sample undergoes immersion in a solvent until reaching equilibrium swelling. The Flory-Rehner equation correlates the equilibrium swelling ratio with the crosslink density of the rubber: a higher swelling volume indicates a lower crosslink density.

B. Mooney-Rivlin method:

This method applies uniaxial stress to the material and measures its strain response. Analysing the strain behaviour of the rubber under stress provides insights into its crosslink density using the Mooney-Rivlin equation.
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C. Freezing point depression:

A rubber sample is immersed in a suitable solvent and part of the polymer is dissolved, which causes a depression in its freezing point. By comparing the freezing point of this solution with that of the pure solvent, the crosslink density of the rubber can be estimated.

D. Temperature scanning stress relaxation (TSSR):

In this method, a rubber sample undergoes a gradual increase in temperature while being subjected to constant strain. The resulting stress response as a measurement of the relaxation behaviour is monitored and related to the crosslink density. This provides insight into its structural properties.

2.6. Devulcanization aids for passenger car tires

This section provides a summary of devulcanization aids and associated processes that are suitable for passenger car tire treads, which predominantly consist of SBR/BR blends. Morphologically, this process involves the devulcanization of crosslinked polystyrene and polybutadiene units along with the silica-polymer network.

The filler system plays a pivotal role in the devulcanization process; however, during the thermo-mechanical process, most of the bonds between the filler and the polymer and among fillers become distorted. In the case of a silica-silane filled systems, the disruption of the filler-polymer network is a crucial aspect of the devulcanization process\textsuperscript{40,41}. The primary challenge of this project lies in achieving controlled breakdown of polymer crosslinks and the filler-polymer network while preserving the integrity of the main polymer backbone.

Devulcanization mechanisms can be broadly classified into different categories: ionic and covalent reactions, and other processes, as categorized in Figure 2.11. It is worth noting that all the chemicals capable of forming covalent bonds are not suitable for devulcanization, owing to limitations related to temperature stability, molecular mobility, and processability. Taking these factors into consideration, suitable ions and the required chemical moieties are listed below\textsuperscript{2, 40-49}. 
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Figure 2.11. Classification of devulcanization mechanisms

Appropriate cations for facilitating the devulcanization mechanisms include imidazolium, pyridinium, quaternary ammonium, and quaternary phosphonium ions. Likewise, anions such as halogen, triflate, tetrafluoroborate, and hexafluorophosphate can also be employed in this context\(^\text{46}\). These chemical species are predominantly in a liquid form and exhibit stability throughout the devulcanization process. The structural representations of these ions are provided in Figure 2.12.

Figure 2.12. Ionic liquids; a. Imidazolium b. Pyridinium c. Quaternary ammonium d. Quaternary phosphonium e. Halogen f. Triflate g. Tetrafluoroborate h. Hexafluorophosphate\(^\text{47,49}\)

Various proton donors such as organic acids and transition metal complexes can serve as potential aids for breaking crosslinks. However, a significant limitation associated with these chemicals is their low thermal stability\(^\text{47}\). Therefore, careful selection of DAs bearing such moieties is essential for selective breakdown of crosslinks; otherwise premature thermal degradation of DAs can cause breakdown of polymer backbones.

The most prevalent and effective devulcanization mechanism involves the rearrangement of covalent bonds. Disulphides represent the most commonly employed
moieties for devulcanization, with bis(3-triethoxysilyl propyl) disulphide (TESPD), diphenyl disulphide (DPDS), tetramethyl thiuram disulphide (TMTD), tetrabenzyldimethyl thiuram disulphide (TBzTD), tetaethyl thiuram disulphide (TETD), and 2,2-dibenzamidodiphenyl disulphide (DBDPD) being highly efficient disulphide-type DA's reported as devulcanization aids. However, in compliance with European environmental regulations, thiuram is banned from the market due to its potential to form carcinogenic nitrosamines and explosive mixtures with air. Consequently, TMTD and TETD cannot be utilized. An alternative devulcanization aid featuring polysulphide bonds is bis(3-triethoxysilyl propyl) tetrasulphide (TESPT). Within a controlled temperature range, TESPT can effectively break crosslinks and subsequently recombine with them, resulting in an efficient devulcanization process as stated by Ghorai et al.

The patent by Recker et al. outlines a method for devulcanization using a DA comprised of di-thio-phosphoryl polysulphides and/or silanes possessing a polysulfane group. The patent specifies a range of devulcanization aids that can be employed including TESPT, TESP, bis(O,O-2-ethyl-hexyl)thio-phosphoryl polysulphides, N-cyclohexyl-2-benzothiazole-sulfenamide (CBS), diocyl penta-sulphide, and bis(trialkoxy-silyl)propyl polysulfane. The DA concentration is stipulated to be within the range of 2% to 15%, and the devulcanization process is conducted utilizing a mixer and extruder, with a process duration spanning from 5 to 35 minutes. The temperature conditions fall within the range of 80°C to 150°C, and the addition of 2% to 15% TDAE oil is recommended for the process. The method is applicable to various rubber types, encompassing NR, BR, IR, SBR, SSBR, NBR, HNBR, and EPDM, while demonstrating efficacy.

Phenolic-based devulcanization aids may encompass thio-bisphenol types such as 4,4-dithiobis(2,6-di-t-butylphenol), and various types of phenolic resins like bis-trialkyl phenol sulphide (TAPS). Amines and diamine-type chemicals also exhibit some efficiency as devulcanization aids by substituting sulphur crosslinks. Examples include tributyl-amine (TBA) and 1,3-dimethylbutyl-phenyl-phenylene diamine (6PPD).

Imines, which share properties with amines, can also serve as suitable devulcanization aids. N-Cyclohexyl benzothiazole-2-sulphenamide (CBS) contains nitrogen-sulphide moieties capable of efficiently breaking sulphur crosslinks, making CBS a potential devulcanization aid.

Furthermore, phosphine-type chemicals, such as triphenylphosphine and 1,8-diazabicycloundec-7-ene, may have potential as devulcanization aids. Mercapto silanes and blocked mercapto silanes are also effective candidates in the realm of devulcanization aids.

In addition to chemical aids, the use of supercritical carbon dioxide, microwave irradiation, ultrasound, and bacteria can also be employed to disrupt sulphur crosslinks. Liquid rubbers like L-SBR and L-BR have the capacity to induce a replasticization effect in ground vulcanized rubber during mechanical breakdown, presenting a promising avenue for further investigation in the realm of potential devulcanization processes. Comprehensive details regarding various prospective devulcanization aids are provided in Table 2.4.
**Table 2.4. List of potential devulcanization aids**

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of DAs</th>
<th>Chemical structure of DAs</th>
<th>Devulcanization process</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TESPT (bis-3-triethoxy-silyl-propyl-tetra sulphide)</td>
<td><img src="image1" alt="Chemical structure of TESPT" /></td>
<td>1. NR, SBR, GTR granules + 3-5% DA + 5-10% TDAE oil. 2. 140°C – 160°C in an internal mixer for 4 - 8 mins. 3. Milling on a two roll mill after devulcanization in a mixer. 4. Also suitable for extruder processes.</td>
<td>1. The output was a good quality devulcanized rubber in terms of viscosity and mechanical properties. 2. Efficient crosslink scission. 3. Environmentally friendly. 4. 13-14 MPa tensile strength, 200-250% elongation at break &amp; 80-90 MU viscosity was reported for NR based unfilled material.</td>
</tr>
<tr>
<td>2</td>
<td>TESPD (bis-3-triethoxy-silyl-propyl-disulphide)</td>
<td><img src="image2" alt="Chemical structure of TESPD" /></td>
<td></td>
<td>1. Trials are required. 2. Process conditions must be optimized. 3. Good potential as devulcanization aid.</td>
</tr>
<tr>
<td>3</td>
<td>Sterically blocked mercapto silane (tri-alkoxy-mercapto-alkyl-silane)</td>
<td><img src="image3" alt="Chemical structure of Sterically blocked mercapto silane" /></td>
<td>1. Reported to be suitable for NR, SBR and SBR/BR. 2. Addition of process oil and DPG (diphenyl guanidine) is required. 3. Suitable for internal mixer and extruder.</td>
<td>1. Trials are required. 2. Process conditions must be optimized. 3. Good potential as devulcanization aid.</td>
</tr>
<tr>
<td>4</td>
<td>Blocked mercapto silane (octanoyl mercapto propyl triethoxy silane)</td>
<td><img src="image4" alt="Chemical structure of Blocked mercapto silane" /></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Chapter 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical (Name and Description)</th>
<th>Formula</th>
<th>Process Conditions</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>CBS (N-cyclohexyl benzothiazole-2-sulphenamide)</td>
<td><img src="image" alt="CBS" /></td>
<td>4 phr CBS + 5 phr TDAE oil, devulcanized for 6 min at 160ºC in an internal mixer.</td>
<td>1. 12 MPa tensile strength, 150% elongation at break &amp; 105 MU viscosity was reported for NR based tire devulcanizate. 2. Effective for twin screw extruder processes.</td>
</tr>
<tr>
<td>6</td>
<td>IPPD (N-isopropyl-N'-phenylene-diamine)</td>
<td><img src="image" alt="IPPD" /></td>
<td>1-2 phr IPPD + 10 phr aromatic oil, devulcanized for 10-15 min at 60ºC in an internal mixer.</td>
<td>1. Effective for twin screw extruders 2. Good mechanical &amp; visco-elastic properties of devulcanized and revulcanized rubber.</td>
</tr>
<tr>
<td>7</td>
<td>6PPD (N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine)</td>
<td><img src="image" alt="6PPD" /></td>
<td>1. Reported to be suitable for NR, SBR and SBR/BR. 2. Process oil is required. 3. Suitable for mixer and extruder.</td>
<td>1. Trials are required. 2. Process conditions must be optimized. 3. Can be a potential devulcanization aid.</td>
</tr>
<tr>
<td>8</td>
<td>DPDS (Diphenyl disulphide)</td>
<td><img src="image" alt="DPDS" /></td>
<td>1. Proved its efficiency in GTR, NR and SBR. 2. Suitable for mixer and extruder.</td>
<td>1. 6-8 MPa tensile strength, 100-150% elongation at break &amp; 80-100 MU viscosity was reported for passenger car tire devulcanizate. 2. Very effective crosslink scission.</td>
</tr>
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<td>Chapter 2</td>
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</table>
| 9 DBDPD (2,2-Dibenzamido-diphenyl disulphide) | ![Chemical Structure](image1) | 1. 1 - 4 phr DBDPD + 5 - 10 phr TDAE oil in a twin screw extruder.  
2. Efficient in internal mixer as well. | 1. Causes sufficient degree of devulcanization.  
2. Devulcanizates showed mechanical properties similar to DPDS devulcanizates. |
| 10 Methyl-tri-octyl ammonium chloride (quaternary ammonium salt) | ![Chemical Structure](image2) | Overnight refluxed with benzene, aq. NaOH and 2.5 - 7.5 phr quaternary ammonium salt. | 1. Reduces crosslink density by up to 74% compared to the feed material along with good revulcanization properties.  
2. Trials in internal mixer required. |
| 11 PH (phenyl hydrazine) | ![Chemical Structure](image3) | PH with ferrous chloride and methanol is added to ground rubber and fluxed at 30 ºC for a few hours. | Very good reduction in crosslink density, sufficient level of mechanical properties. |
| 12 TAPS (bis-trialkyl phenol sulphides) | ![Chemical Structure](image4) | 4 to 10 hours, 149ºC in thermo-mechano-chemical process. | Significant reduction in crosslink density is reported. |
| 13 TBA (tributyl-amine) | ![Chemical Structure](image5) | 1 – 4 phr TBA + molten CuCl at 150ºC for 5 to 20 min. | Suitable for devulcanization in a twin screw extruder and internal mixer. |
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<table>
<thead>
<tr>
<th></th>
<th>BPO (Benzoyl peroxide)</th>
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<tbody>
<tr>
<td>14</td>
<td><img src="image" alt="BPO molecule" /></td>
<td>1. Reported to be suitable for NR, SBR and SBR/BR.</td>
<td>1. Trials in internal mixer required for process optimization.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. For mixer and extruder processes.</td>
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<table>
<thead>
<tr>
<th></th>
<th>Thiol-amine combination</th>
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</thead>
<tbody>
<tr>
<td>15</td>
<td><img src="image" alt="Thiol-amine" /></td>
<td>1. Potentially suitable for NR, SBR and SBR/BR.</td>
<td>1. Peridium propane-2-thiolate ion pair forms, which causes devulcanization.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Suitable for mixer and extruder.</td>
<td>2. It has enhanced nucleophilic properties.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. No additional process aid.</td>
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<thead>
<tr>
<th></th>
<th>Triphenyl phosphine</th>
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<tbody>
<tr>
<td>16</td>
<td><img src="image" alt="Triphenyl phosphine" /></td>
<td>1. Potentially suitable for NR, SBR and SBR/BR.</td>
<td>1. It does not result in crosslink scission, but reacts with the broken crosslinks and prevents recombination.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Suitable for mixer and extruder.</td>
<td>2. Trials are required to determine efficiency.</td>
</tr>
</tbody>
</table>
2.7. Devulcanization mechanisms of potential devulcanization aids

Within this study, six different silanes from five distinct categories were chosen as potential DAs. The screening process was conducted with focus on evaluating the likely devulcanization mechanisms and assessing the efficiency. This section provides a description of the possible reaction mechanisms associated with the selected silanes as reported in literature.

2.7.1. DAs with disulphide moieties

Bis(3-triethoxysilyl propyl) disulphide (TESPD) is commonly used as a coupling agent in the silica-silane filler system, but is also reported as a devulcanization aid\textsuperscript{51}.

Proposed reaction mechanism: The disulphide bond of TESPD breaks due to the high temperature (above 160\textdegree{}C) during devulcanization. The sulphur of the TESPD fragment creates a stable bond with the sulphur of a broken crosslink and inhibits a possible recombination as shown in Figure 2.13. According to the literature, TESPD will increase the efficiency of devulcanization of sulphur crosslinks\textsuperscript{40-42}.

![Figure 2.13. Educts and products of the devulcanization reaction with disulphidic silane (based on\textsuperscript{41})](image)

TESPD can break the filler polymer network in the silica filled system. Ghosh et al.\textsuperscript{41} and Ghorai et al.\textsuperscript{42} claimed the efficiency of TESPD as a devulcanization aid in a SBR/BR-silica system and particularly for passenger car tires. The educts and products for the devulcanization of the filler-polymer bond is described in Figure 2.14\textsuperscript{41}.

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2.7.2. DAs with polysulphide moieties

Bis(3-triethoxysilyl propyl) tetrasulphide (TESPT) is another commonly used coupling agent for the silica-silane filler system, but it is also described in literature\textsuperscript{41,42} as a very efficient devulcanization aid for sulphur vulcanized rubber products.

Figure 2.15. Educts and products of devulcanization reaction of with polysulphidic silane (based on\textsuperscript{41})

Reaction mechanism: De et al.\textsuperscript{44}, Mondal et al.\textsuperscript{45} and Ghosh et al.\textsuperscript{41} proved the efficiency of TESPT as a devulcanization aid to complete the cradle to cradle loop of passenger car tire rubber. It was reported that the polysulphide linkage of TESPT would create a
stable bond with the broken sulphur crosslinks during the thermo-mechano-chemical devulcanization process as shown in Figure 2.15 and thus inhibit the recombination.

During the devulcanization process, the polymer-TESPT adducts can further react in the presence of moisture. There are two possibilities: the first one is that an ethyl moiety of the attached TESPT fragments is substituted by a hydroxyl moiety and generates one molecule of ethanol. The detailed reaction mechanism of the hydrolysis reaction, water and alcohol formation is described in Section 2.3.3.1, Figure 2.6. Another possibility is that two separated polymer chains oligomerize via the attached TESPT fragments and eject two molecules of ethanol\textsuperscript{42}. This ethanol formation is not desired during the devulcanization process, so temperature control during the reaction is very important. The educts and products of the hydrolysis and oligomerization reaction during devulcanization are illustrated in Figure 2.16.

![Figure 2.16. Educts and products of ethanol formation during devulcanization (based on\textsuperscript{41})](image)

The educts and products for the recombination of the filler-polymer bond with TESPT are described in Figure 2.17.
2.8. Latest developments in ground tire rubber (GTR) devulcanization

Recycling of tire rubber is a widely recognized technology. Specifically, devulcanization is a sustainable innovation, as most traditional methods rely on grinding only or followed by regeneration. During the regeneration process, the breakdown of the network is non-selective regarding the type of bonds that are broken. As a result, polymer chains are broken resulting in small fragments, leading to reduced strength properties after revulcanization. Devulcanization aims at selectively breaking down crosslinks while preserving the polymer chains, resulting in better properties compared to reclaimed rubber\(^40\). The latter therefore encounters limitations in both quality and quantity for reuse.

Besides the quality of the recycled rubber, legal constraints have an impact on the development of rubber recycling technologies. The European Committee for Risk Assessment (RAC) has proposed a complete ban on the use of rubber granules in artificial turfs. This ban would be implemented after a 6-year transition period to mitigate the release of microplastics into the environment\(^53\). Additionally, the European Chemicals Agency (ECHA) conducted a study in 2017 to assess the health risks associated with exposure to rubber granules through skin contact, inhalation, or ingestion. The study focused on the presence of polycyclic aromatic hydrocarbons (PAHs) in rubber granules derived from end-of-life tires (ELTs). The results indicated a very low risk, as the concentrations of PAHs measured in various European countries were within limits regarded as safe\(^54\). However, to further minimize potential risks, new regulations have been established. As of August 2022, the maximum allowed concentration of PAHs in granules and mulches used as artificial turfs or on playgrounds is reduced to 20 mg/kg, representing an approximate 80% reduction from the previous limit\(^55\). These regulations will strongly reduce the application of granulated tire rubber, thus making it a necessity to find alternative forms of recycled rubber and applications.
This part of the chapter primarily focuses on the most recent developments (last five years: 2018~2023) concerning devulcanization conducted on end-of-life (EOL) tires, with particular emphasis on the most commonly utilized rubber classes for this purpose, namely, natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR). It also centers around sulphur vulcanization, which is the vulcanization technique used in this application. Besides, the filler system significantly influences the devulcanization process: In carbon black filled systems, the reinforcement is primarily through physical interaction with the polymeric matrix. In contrast, for silica filled systems, covalent filler-polymer bonds are formed which have to be broken during the devulcanization process. Breaking of physical interaction is comparatively easier than chemical bonds\textsuperscript{40,56}.

The different crosslinks present in a sulphur cured rubber network and their bond strengths are: -C-S-C- (285 kJ/mol), -C-S-S-C- (268 kJ/mol) and –C-Sx-C- (251 kJ/mol)\textsuperscript{56}. The energies needed to break the targeted S-S and C-S bonds are only slightly lower than the ones required to break the C-C (347 kJ/mol) bonds\textsuperscript{56,57}. Additionally, devulcanization of synthetic rubber proves to be more challenging compared to NR due to differences in polymer chain structures and/or variations in the type, distribution, and density of crosslink sites. For all rubber types, a higher selectivity in the devulcanization process leads to better mechanical properties in the devulcanized and revulcanized material\textsuperscript{47}. Chemical breakdown contributes to controlled crosslink scission, which is a highly selective network breakdown. The combination of thermal, mechanical and chemical processes can be considered as devulcanization, but compared to the chemical devulcanization they are less selective due to the contribution of the thermo-mechanical part, which causes random scission. Rubber recycling can be classified into four main techniques and different combinations of those. The classification is listed in Table 2.5\textsuperscript{40,41,47,48,58-65}.

\textit{Table 2.5. Overview of tire recycling techniques}\textsuperscript{40,41,47,48,58-65}

<table>
<thead>
<tr>
<th>A. Thermal</th>
<th>Pyrolysis, thermolysis etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. Mechanical</td>
<td>Shearing, cracking, grinding, extrusion etc.</td>
</tr>
<tr>
<td>C. Chemical</td>
<td>1. Ionic Cationic; anionic; proton donors; metal complex etc.</td>
</tr>
<tr>
<td></td>
<td>2. Covalent Peroxides; bifunctional additives (silanes); disulphides; polysulphides; phenols; amines; imines; nitrogen-sulphides; phosphines etc.</td>
</tr>
<tr>
<td>D. Thermo-mechanical</td>
<td>Combinations of A and B</td>
</tr>
<tr>
<td>E. Thermo-mechano-chemical</td>
<td>Combinations of A, B and C</td>
</tr>
<tr>
<td>F. Other techniques</td>
<td>Microwave, ultrasonic, bacterial, fungal, supercritical CO\textsubscript{2} etc.</td>
</tr>
</tbody>
</table>

This work critically reviews and consolidates the recent developments since 2018, in the devulcanization techniques and various applications of tire devulcanizates, emphasizing their potential in compounding with diverse polymeric matrices to create sustainable polymer blends with suitable application properties. Moreover, the study highlights the significance of adopting a circular economy approach for the tire industry.
2.9. Main development of devulcanization over time

2018

A study on thermo-mechanical-chemical devulcanization was performed by Vorobyev et al.\textsuperscript{66} for GTR with 1,8-diaza-bicyclo-undec-7-ene, triphenyl-phosphine, and a product of petroleum distillation as DA’s. The process involved blending GTR and the devulcanizing agents in a mixer, followed by extrusion at temperatures ranging from 45°C to 65°C. The tensile strength of the devulcanized rubber ranged from 12.4 MPa to 13.6 MPa. The elongation at break values for the reclaimed rubber ranged from 350% to 390%. In comparison, the tensile strength and elongation at break for reclaimed GTR without the devulcanizing agents was 4.8 MPa and 225% respectively.

Walvekar et al.\textsuperscript{67} conducted a study on the devulcanization of waste tire rubber using amines in combination with ultrasonic treatment, exploring different temperatures and rubber-to-amine ratios. It was noted that a tertiary amine, 3-amino-propyl-trimethoxy silane, yielded superior results compared to a primary amine, (n-diethyl-3-amino propyl) trimethoxy siloxane. The optimal sonication temperature for the process was stated to be 50°C. For the treatment using the tertiary amine, the gel content of the devulcanized rubber ranged from 63% to 77%. In contrast, the use of primary amine resulted in a higher gel content, ranging from 75% to 87%.

Walvekar et al.\textsuperscript{68} also explored the use of a deep eutectic solvent (DES) as a DA. Using an ultrasonic method, with zinc chloride (ZnCl\textsubscript{2}) and urea at different mole ratios of 2:7 and 1:4, they investigated the devulcanization process at temperatures of 30°C, 130°C, 150°C, and 180°C. For the DES with ZnCl\textsubscript{2}:urea in a ratio of 2:7, the optimal devulcanization occurred at 130°C. At higher temperatures, bond reformation was observed, resulting in reduced devulcanization efficiency. Conversely, for a ZnCl\textsubscript{2}:urea ratio of 1:4, higher temperatures beyond 130°C were required to achieve effective devulcanization. Based on the high sol fraction of over 85% obtained, the study concluded that the DES consisting of ZnCl\textsubscript{2} and urea demonstrated excellent effectiveness for GTR devulcanization.

Chen et al.\textsuperscript{69} devulcanized GTR in a twin-screw extruder with a screw rotation speed of 140 rpm. Notably, supercritical CO\textsubscript{2} was directly injected into the extruder barrel during the extrusion process. The resulting devulcanize of GTR exhibited a tensile strength of approximately 10.4 MPa and an elongation at break of 312% after revulcanization.

Li et al.\textsuperscript{70} studied the impact of temperature on the devulcanization of passenger car tire sidewalls in a twin screw extruder using supercritical ethanol and diphenyl disulphide (DPDS) as DA. As the reaction temperature was raised from 240°C to 270°C, the sol fraction significantly increased from 25% to 55%. This increase was attributed to ethanol reaching its supercritical state, facilitating its penetration into the vulcanized structure of the GTR and influencing the breakdown of the crosslinked network.

Diaz et al.\textsuperscript{71} employed a novel thermomechanical devulcanization approach for GTR using two distinct metallic-cone-like high shear mixers. The setup involved one static cone and another rotating cone that pressurized the system. The study explored variations in rubber temperature and mechanical energy consumption during the process followed by water cooling. Large GTR chunks were fed into the equipment, and
the machinery effectively reduced the particle size through controlled shear. As a result, the devulcanization process led to a reduction in particle size, an increase in the soluble content of the rubber from 25% to 40%, and a decrease in its crosslink density to around 50%.

2019

Seghar et al.\textsuperscript{57} investigated the impact of temperature ranging from 80°C to 220°C on the devulcanization of NR using an industrial extruder with a constant feeding rate of 5 kg/h and a screw speed of 240 rpm. The study revealed that the degree of devulcanization could reach approximately 90% of network breakdown across all temperature ranges. However, the best quality of devulcanized rubber was observed within the temperature range of 80°C to 100°C. Within this temperature range, the highest tendency for sulphur bond scission was observed, leading to a high degree of devulcanization. The study claimed that a maximum of 65% of virgin NR can be substituted by the devulcanized rubber. Consequently, they concluded that a relatively low energy input is sufficient to perform devulcanization of NR effectively.

Sheng et al.\textsuperscript{72} conducted the extrusion of GTR without any additives using a single-screw extruder with screw speeds ranging from 90 rpm to 125 rpm. Subsequently, the material was cooled to temperatures between 50°C and 60°C before being further extruded using a twin-screw extruder with screw speeds ranging from 55 rpm to 70 rpm. The resulting devulcanizate demonstrated a tensile strength ranging from 9.1 MPa to 9.7 MPa and an elongation at break ranging from 286% to 308%.

Kaewpetch et al.\textsuperscript{73} reported that \textit{Bacillus Cereus} effectively devulcanized NR vulcanizates. The bacteria exhibited the ability to oxidize the sulphide crosslinks and partially cleave the main carbon chain in the rubber. The Horikx-Verbruggen analysis revealed that the primary mechanism of the bacteria was the cleavage of sulphur crosslinks, which occurred early in the devulcanization process. After 20 days of devulcanization, crosslink density and gel fraction analysis indicated a significant reduction compared to the control sample before bacterial treatment. FTIR spectra demonstrated characteristic peaks for S=O stretching (1088 cm$^{-1}$) and C=O stretching (1730 cm$^{-1}$), supporting the oxidation of sulphide crosslinks to form carbonyl and oxygen-containing sulphur-based groups. X-ray photoelectron spectroscopy results confirmed a decrease in C-S and S-S bonds after treatment, along with a decrease in C-C intensity. These findings suggest that \textit{Bacillus Cereus} can be utilized for recycling of end-of life rubber.

Dierkes et al.\textsuperscript{74} developed a cradle-to-cradle loop for elastomeric products through a thermo-mechanical-chemical devulcanization process, employing hexadecyl-amine as DA. The process proved to be highly effective for rubber with a saturated polymer backbone, and lead finally to successful industrial implementation. Moreover, the method holds the potential for devulcanizing other elastomers such as SBR, BR, NR, and IIR.

Joseph et al.\textsuperscript{75} conducted devulcanization of carbon black filled NR using a water-cooled two-roll mixing mill (15 cm x 30 cm) with a friction ratio of 1:1.25. The achieved degree of devulcanization ranged from 20% to 37.8%. The study demonstrated that controlled
heating was essential for achieving effective decrosslinking during the devulcanization process.

Van Hoek et al.\textsuperscript{76} conducted an investigation into the impact of resins in ground passenger car tire devulcanizates. The study compared GTR samples and model tire formulation compounded with resins (poly-terpene/hydrocarbon/terpene-phenol). All the samples are devulcanized with DBD (2,2’-dibenzamido diphenyl disulphide) in optimum devulcanization parameters. The processing resulted in a notable reduction in viscosity, but no further enhancements in tensile properties or hardness were observed. However, the resin-compounded devulcanizate exhibited a significant increase in wet grip performance and a slight increase in rolling resistance.

\textbf{2020}

Worlee et al.\textsuperscript{56} conducted an investigation to elucidate the mechanism of the thermo-chemical devulcanization process. The study identified two primary steps: firstly, the generation of radicals resulting from breakage of polymer chains at elevated temperatures, and secondly, the capture of these radicals by the DA: DPDS was employed in this study, to prevent recombination. The research revealed that polymers with different molecular structures exhibited varying devulcanization efficiencies due to differences in heat resistance: lower heat resistance led to a higher degree of random scission. Moreover, higher loadings of carbon black induced uncontrolled thermal scission of both the elastomer and filler network. Depending on the polymer type, recombination of polymer fragments and the formation of a new polymer network were also observed as potential outcomes.

Zhang et al.\textsuperscript{77} performed devulcanization of GTR using a combination of softeners (coal tar, aromatic hydrocarbon oil, pine tar, tall oil, dipentene, paraffinic oil, oleic acid, cottonseed oil, rosin) and DAs (aromatic hydrocarbon disulphide, multi alkyl phenol sulphide, phenyl-mercaptan, amine compounds). The GTR and softeners were premixed and then fed into a twin-screw extruder. The residence time in the extruder ranged from 1 to 6 minutes at temperatures of 100°C to 340°C, followed by cooling. Next, the partially devulcanized rubber was introduced into a multi-screw extruder at variable temperatures between 20°C to 110°C for 1 to 6 minutes followed by refining. The resulting devulcanizate exhibited a tensile strength ranging from 15 MPa to 16.3 MPa and an elongation at break ranging from 480% to 535% after revulcanization.

Ghosh et al.\textsuperscript{41} conducted a mechano-chemical devulcanization study using TESPT for SBR-based silica-filled granulates on a two-roll mill. The devulcanization process resulted in a significant increase in sol content reaching up to 24.5%, and a high extend of network breakdown. A 30% devulcanizate blend exhibited a tensile strength of 10.3 MPa and an elongation at break of 451%, along with homogeneous dispersion in the matrix visualized by SEM analysis. The study suggests that up to 30% (w/w) of virgin SBR rubber can be effectively replaced with devulcanized rubber in various applications.

Teixeira et al.\textsuperscript{78} employed auxiliary additives, namely silica, resin, oil, and catalysts, for devulcanizing GTR. The GTR and auxiliary additives were premixed and introduced into an extruder. The devulcanization process was conducted at temperatures ranging from 120°C to 500°C and under a pressure of 80 bar to 100 bar. Subsequently, the material
was cooled with water to a temperature of 20°C to 30°C. The resulting devulcanizate exhibited a tensile strength ranging from 8 MPa to 12 MPa and an elongation at break ranging from 300% to 350%.

Noordermeer et al. developed a devulcanization process utilizing amines as devulcanizing agent (DA). The study highlights that compared to shear and devulcanization time, devulcanization temperature exerts a more significant influence. Depending on the application, the devulcanizate can replace 50% or more of virgin rubber. For elastomers containing butadiene such as SBR and BR, the critical parameter is the devulcanization temperature, which should be kept below 220°C. Additionally, employing a protective atmosphere to exclude oxygen, minimizing shear during devulcanization, and rapid and efficient cooling are essential to prevent radical recombination of broken chains and network fragments. Optimizing these conditions will allow to achieve high degrees of devulcanization up to 80-90%, limited primarily by the presence of mono-sulphidic crosslinks and bound rubber.

2021

Van Hoek et al. investigated the devulcanization of GTR using a co-rotating twin-screw extruder, examining the influence of screw configuration, residence time, extruder temperature, and efficiency of DA (diphenyl disulphide and dibenzamido diphenyl disulphide). Lower temperatures did not significantly affect the remaining crosslink density, but inadequate residence time in the extruder led to insufficient devulcanization. The devulcanizates showed a tensile strength of around 9 MPa and 180% elongation at break after revulcanization. Increasing the concentration of DA resulted in a higher degree of crosslink to random scission. Under the optimal conditions, the devulcanization degree reached 80% to 90%. The produced devulcanizate can substitute up to 30% of virgin rubber as a feed material of new tires.

Zhang et al. investigated the use of hydrogen peroxide (H₂O₂) in the thermo-oxidative reclaiming process of solid styrene-butadiene rubber (SBR) vulcanizates at low temperatures, aided by soybean oil. The reclaiming process was conducted in a drying oven and lasted for a duration of 0.5 to 4 hours. The findings indicated that SBR vulcanizates underwent complete transformation into liquid rubber, yielding a sol fraction of 100% when exposed to a temperature of 100°C. This transformation was achieved with the presence of 100 phr (parts per hundred rubber) soybean oil and a 3%wt. solution of H₂O₂ at a concentration of 2 phr.

Zhou et al. investigated microwave devulcanization of GTR using a combination of additives including stearic acid, palm oil, rosin, calcium bicarbonate, and a natural resources reclaiming agent derived from lemon, orange, or grapefruit peel, with an activator. The process involved pre-mixing GTR with calcium bicarbonate, followed by ultrasonic treatment for 1-3 minutes. The composition was then mixed at 80-100°C for 5-10 minutes in a mixer with a rotor speed of 500-1000 rpm. Microwave treatment of the GTR blend with the additives for 3-10 minutes was performed, followed by refining. The resulting devulcanizate exhibited a tensile strength ranging from 10.9 MPa to 12.1 MPa and an elongation at break ranging from 347% to 535% after revulcanization.
Wisniewska et al. 83 conducted extrusion of GTR with a granulate size of 0.6 mm, pre-blended with dicumyl peroxide and 0–15 phr ethyl vinyl acetate, using a co-rotating twin-screw extruder. The extrusion process was carried out at a temperature of 130°C and a screw speed of 150 rpm. The resulting devulcanizate exhibited a tensile strength ranging from 2.6 MPa to 9.3 MPa and an elongation at break ranging from 78% to 225%.

Simon et al. 84 performed an extrusion process for GTR with a granulate size ranging from 0.2 mm to 0.4 mm. The extrusion was carried out using a co-rotating twin-screw extruder at temperatures ranging from 140°C to 240°C and at a screw speed of 60 rpm to 180 rpm. The resulting composites of reclaimed GTR with NR demonstrated a tensile strength of around 15 MPa and an elongation at break of approximately 340%.

Efimov et al. 85 introduced a novel thermo-mechanical devulcanization method utilizing tandem extrusion. The process involved feeding GTR granulates into a twin screw extruder, followed by single screw extrusion and calendaring on a mill. Throughout the process, screw speed, temperature, and feed rate were varied. The study identified the process's suitability for SBR vulcanizates, highlighting its potential as a devulcanization technique for tire applications.

Ghosh et al. 2 conducted a study to assess the effectiveness of conventional rubber additives, specifically two silanes commonly used as coupling agents for silica, TESPT [bis(3-triethoxy-silyl-propyl) tetrasulphide] and TESPD [bis(3-triethoxy-silyl-propyl) disulphide], and the accelerator CBS [N-cyclohexyl-2-benzothiazole sulfenamide], as DA. The research focused on evaluating the processibility, devulcanization efficiency, and mechanical properties. The outcome suggests that the devulcanizate obtained from this process can be utilized in the production of technical rubber goods such as shock absorbers, floorings, or insulation materials, using 100% recycled material. Additionally, the devulcanizate can be blended with virgin rubber compounds in significant quantities to create high-performance rubber products like tires, seals, and conveyor belts.

2022

Bhadra et al. 86 developed a thermo-mechanical devulcanization method utilizing a co-rotating twin screw extruder with variable screw speed ranging from 400 to 1000 rpm. The process is applicable to various rubber types including NR, SBR, BR, and IR, either individually or in combination, with particle sizes ranging from 3 to 12 mm. The devulcanization process was carried out within a temperature range of 50°C to 250°C, and the feed rate was set at 2-10 kg/hour. As a result, a devulcanizate with a Mooney viscosity in the range of 30 to 70 MU at 100°C was achieved.

Wisniewska et al. 87 conducted an extrusion process for GTR with a granulate size of 0.6 mm. The GTR was pre-blended with dicumyl peroxide and elastomers with concentrations in the range of 2.5 to 15 phr. The extrusion was performed using a co-rotating twin-screw extruder at a controlled temperature of 60°C and a screw speed of 150 rpm. The resulting devulcanizate exhibited a tensile strength ranging from 5.2 MPa to 8.1 MPa and an elongation at break ranging from 113% to 136% after revulcanization.

Colombani et al. 88 developed a devulcanization process utilizing a combination of an acid-base adduct from carboxylic acid and substituted urea, and peroxide as DA. Carboxylic acids with carbon chain lengths ranging from 2 to 18 were used, along with
mono-, di-, or tri-substituted derivatives of urea. In a screening, dicumyl peroxide turned out to be the best choice. The concentrations of additives were varied from 0.5% to 5%, while the peroxide concentration ranged from 0.1% to 3%, and the operational temperature was maintained between 20°C to 80°C.

2023

Ghorai et al.\textsuperscript{89} described the simultaneous devulcanization with TESPT [(bis (3-triethoxysilyl propyl) tetrasulphide] as devulcanization aid (DA) and silica reinforcement for NR based GTR. The devulcanizate not only replaced the fresh natural rubber, but also facilitated the silica dispersion. It is stated that the pendent ethoxy group in the devulcanizate assists homogeneous distribution of silica in the blend or composite system. A 50% (w/w) blend of devulcanizate with a unfilled virgin compound showed a tensile strength of 16.7 MPa and 882% elongation at break. A 60% (w/w) devulcanizate blend showed a tensile strength of 17.9 MPa and 863% elongation at break. The investigation also claims an improvement in abrasion loss, tear strength, ageing and rolling resistance.

Burkhart et al.\textsuperscript{90} developed a devulcanization process using a twin screw extruder with a 60 L/D ratio, followed by a single screw extruder, preferring a particle size range of 0.1 mm to 20 mm as feedstock. The devulcanization process involved the presence of plasticizers, silanes (without specific details disclosed), and stabilizers. The plasticizers used included mild extraction solvents (MES), treated distillated aromatic extracted (TDAE), and heavy naphthenic oils. Stabilizers employed in the process belonged to phenolic, diamine, or imidazole types. The devulcanization temperature was maintained within the range of 100°C to 200°C, while a preferable screw speed of 100 rpm was chosen. It was stated that the resulting devulcanizates have a potential for tire compounding up to a certain level without significant reduction in properties.

Mondal et al.\textsuperscript{91} conducted a study to assess the effectiveness of TESPT [bis(3-triethoxysilyl-propyl) tetrasulphide] as a devulcanizing agent for 40 mesh GTR particles. The mechano-chemical devulcanization process was carried out using an open two-roll mill at room temperature for a duration of 40 minutes. Their best devulcanizate exhibited a sol content of 25% and a degree of network breakdown of 32%. A 40% (w/w) devulcanizate blended with 60% (w/w) virgin compound demonstrated a tensile strength of 7.2 MPa and processable Mooney viscosity. Scanning Electron Microscope (SEM) images and Fourier Transform Infrared (FTIR) analysis of the devulcanizates confirmed successful devulcanization and uniform dispersion of the devulcanizate within the blend.

Mutlu et al.\textsuperscript{92} conducted a recycling technique for rubber particles smaller than 50 microns. The method involves processing the rubber particles in a reactor with a rubber to water ratio of 1:10, while maintaining pressure within the range of 150-250 bar and a rotating speed of 0-500 rpm. The devulcanization process takes place at temperatures ranging from 150°C to 300°C for a duration of 2-6 hours. Although specific properties of the devulcanizates were not disclosed, the process is claimed to be applicable to various rubber types, including NR, BR, SBR, IR, NBR, IIR, HNBR, EPDM, CR, CSM, and ACM.

Morimoto et al.\textsuperscript{93} developed a devulcanization process utilizing alkyl sulfonamides as DA. DAs were stearyl-amides, hexadecyl-amides or alkyl-sulfonamides with variable
carbon chain lengths ranging from 12 to 25 carbons. The concentration of the DA was systematically varied from 1 to 30 phr to optimize the devulcanization process.

Ghosh et al.\textsuperscript{1} studied a thermo-mechanical-chemical devulcanization processes using disulphidic, polysulphidic, amino, mercapto, and alkenyl silanes as DAs for SBR-BR based silica-filled passenger car tire tread granulates. Among the DAs tested, alkenyl silane with an activator under optimized conditions (5% DA and 5% process oil at 155\degree C temperature for 6 minutes residence time in an internal mixer with rotor speed 150 rpm) demonstrated the best results: a network breakdown of 55-60\%, with a tensile strength recovery of 50-55\% for revulcanization of 100\% devulcanizate.

Justin et al.\textsuperscript{94} developed a devulcanization process for GTR by introducing a gas flow in the reactor to generate high turbulent flow and collisions resulting in micronization and fracture of the particles. The process is claimed to be suitable for particle sizes of 0.001 mm to 10 mm but preferably between 2 mm to 8 mm. The temperature of the reactor increased up to 350\degree C and the residence time was 1 to 2 seconds. Inert gasses like nitrogen were used, and the devulcanizate was described as tacky and fluffy.

2.10. Conclusions

The devulcanization process involves three interconnected factors: crosslink density, crosslink length, and the effectiveness of the DA, collectively forming the "devulcanization triangle". Vulcanized rubber consists of three primary networks: a physical polymer network of entangled polymer chains, a network of crosslinks between polymer chains formed during vulcanization, and chemical crosslinks between filler and polymer in case of a silica-silane reinforcement. In devulcanization, the focus is not on the physical entanglements within the polymer chains, but primarily on breaking the crosslinks created during vulcanization. The type of crosslinks formed depends on the curing system and polymer type. Fillers, particularly carbon black and silica, play significant roles. Carbon black causes polymer adhesion, while silica chemically bonds with the polymer matrix. Devulcanization of carbon black-filled tires rubber involves breaking polymer crosslinks, while silica-filled tires require disrupting both polymer crosslinks and filler-polymer bonds, making the process more challenging. Many recycling methods randomly cleave the network, but selective crosslink breakdown is essential for higher-quality recycled rubber.

The most effective devulcanization mechanism primarily involves the reconfiguration of covalent bonds. Efficient DAs generate free radicals or other reactive species during the process, which then recombine with disrupted crosslinks, forming stable bonds. Among these, disulphides and polysulphides, such as TESPD, DPDS, TESPT etc. are reported to be highly efficient. The process is applicable to various rubber types and filler systems, providing an environmentally compliant devulcanization solution.

This assessment revealed that the quality of devulcanized rubber is notably contingent upon several factors including the composition of the feed material, the type of crosslinking and filler systems employed, and the effectiveness of the devulcanization process. Figure 2.18 illustrates the variation in devulcanizate quality after revulcanization.
Figure 2.18. Comparative stress-strain analysis: 100% devulcanizate compounded and re-vulcanized

In summation, the thermo-mechanical-chemical approaches exhibited superior stress-strain and controlled network breakdown properties when contrasted with purely mechanical or thermo-mechanical methods for recycling rubber.

In terms of achieving a closed-loop system for tire recycling, the review demonstrated that efficiently devulcanized GTR can be integrated into new tire production, comprising a significant proportion depending on the desired final properties and the quality of the devulcanizate. For products where strength is not the primary requirement, higher quantities of devulcanized rubber or complete substitution of the virgin compound is possible. Furthermore, the incorporation of devulcanized rubber led to an enhancement in the material's resistance to ageing.

The significance of rubber devulcanization is steadily growing, especially in light of the vision for tire production sustainability by 2030. This presents a crucial opportunity to incorporate high-quality devulcanizate into new tires. Given that tires are among the most widely used rubber products, the adoption of devulcanized rubber to a certain extent in new tire manufacturing can bolster the circular tire economy and lead to a greener future with reduced carbon footprint.
The uniqueness of our research lies in the devulcanization of a specific type of tire, namely the silica-silane filled SBR/BR based passenger car tires. Additionally, our study introduces a new class of DAs: bifunctional and monofunctional silanes are screened. The distinctive aspect lies not only in evaluating sulphidic moieties but also exploring the potential of mercapto, amino, and vinyl moieties as active constituents of DAs. This comprehensive screening of diverse moieties and the specific polymeric and filler system adds novelty to our investigation.

2.11. References
3. Hoffmann, W., 1996. Rubber technology handbook, Publisher: Hanser, Germany.


Chapter 2


carrying out the method and use of the device for the devulcanization of a vulcanized rubber mixture.


90. US2023012369A1, Burkhart, A., Wolf, H., Efimov, K., Völker, T., 2023. Method for the devulcanisation of a vulcanized rubber mixture, device for carrying out the method, as well as a rubber mixture and vehicle pneumatic tyre, comprising a component made of the rubber mixture.


94. NL2029863B1, Justin, M. D., Christopher, M. T., Jan, A. J., 2023. A process for devulcanizing tyre rubber particles.
CHAPTER 3
SCREENING OF DEVULCANIZATION AIDS

This chapter is based on the publication entitled “New route for tire rubber devulcanization using silanes” in the journal ‘Polymers’, volume 15, issue 13, (https://doi.org/10.3390/polym15132848) on 28th June 2023.

In this study, an investigation was conducted to assess potential devulcanization aids (DAs) for passenger car tire tread granulates. A comparative analysis of the obtained results was performed, leading to the identification of the most promising silane as DA, which was chosen for subsequent optimization processes.
3.1. Introduction

Figure 3.1. Flowchart of the study up to Chapter 3

In this study, different silane-based DAs are screened and the devulcanizates are analyzed by the degree of network breakdown, mechanical properties of the revulcanized material, and miscibility of the devulcanized rubber with a virgin compound. A silica-filled SBR-BR-based model tire tread compound was used as the feed material for the devulcanization process. Commercially available silane coupling agents with disulphide, polysulphide, amino, vinyl, and mercapto moieties were selected as potential DAs for the screening trials. The DAs are selected considering the active chemical moieties for devulcanization and processibility. Moreover, sustainability, environmental and health impacts, EU safety regulations, innovation, and commercial feasibility are considered for this development.

3.2. Materials and methods

The experimental process can be classified into three parts:

i. Preparation of the model compound
ii. Devulcanization process
iii. Characterization process

A brief description of each component of the experimental process is described below and the flowchart is shown in Figure 3.2.

Figure 3.2. Flowchart of the experimental process
3.2.1. Model compound preparation

A SBR-BR-based silica-filled model tire tread compound was prepared as feed material for the devulcanization process. The different stages of the model compound preparation are described below.

3.2.1.1. Materials

The model tire tread formulation is given in Table 3.1.

### Table 3.1. Compounding formulation of the model tire tread compound

<table>
<thead>
<tr>
<th>Function</th>
<th>Ingredient</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Quantity (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>SSBR ¹</td>
<td>Sprintan 4601</td>
<td>Trinseo</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>BR ²</td>
<td>CB 24</td>
<td>Arlanxeo</td>
<td>30</td>
</tr>
<tr>
<td>Filler system</td>
<td>Silica</td>
<td>ULTRASIL® 7000 GR</td>
<td>Evonik</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Silane</td>
<td>Si 266®</td>
<td>Evonik</td>
<td>5.8</td>
</tr>
<tr>
<td>Activators</td>
<td>Zinc oxide</td>
<td>Merck Zinc Oxide</td>
<td>Sigma-Aldrich</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
<td>Merck Stearic Acid</td>
<td>Sigma-Aldrich</td>
<td>2</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>TDAE oil ³</td>
<td>Vivatec</td>
<td>H &amp; R</td>
<td>25</td>
</tr>
<tr>
<td>Curing system</td>
<td>Curing aid</td>
<td>Merck Sulphur</td>
<td>Sigma-Aldrich</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Primary accelerator</td>
<td>Santocure CBS</td>
<td>Flexsys</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Secondary accelerator</td>
<td>Perkacit DPG</td>
<td>Flexsys</td>
<td>2.5</td>
</tr>
</tbody>
</table>


The list of the DAs for screening, reference DAs, and chemicals used for the characterization processes are described in Table 3.2.

### Table 3.2. Chemicals used for devulcanization and characterization processes

<table>
<thead>
<tr>
<th>Notation</th>
<th>Chemical Identification</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Polysulphide: bis-triethoxy-silyl-propyl tetrasulphide</td>
<td>Evonik</td>
</tr>
<tr>
<td>DS</td>
<td>Disulphide: Bis-triethoxy-silyl-propyl disulphide</td>
<td>Evonik</td>
</tr>
<tr>
<td>ME</td>
<td>Triethoxy-silyl-propyl mercapto silane</td>
<td>Evonik</td>
</tr>
<tr>
<td>AM</td>
<td>Triethoxy-silyl-propyl amino silane</td>
<td>Evonik</td>
</tr>
<tr>
<td>VN</td>
<td>Triethoxy-silyl-vinyl silane</td>
<td>Evonik</td>
</tr>
<tr>
<td>VP</td>
<td>Triethoxy-silyl-vinyl silane with activator</td>
<td>Evonik</td>
</tr>
<tr>
<td>DPDS</td>
<td>Di-phenyl di-sulphide</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>DBD</td>
<td>Di-benzamido di-phenyl di-sulphide</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Acetone</td>
<td>Acetone</td>
<td>Boom Lab.</td>
</tr>
<tr>
<td>Toluene</td>
<td>Toluene</td>
<td>Boom Lab.</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
<td>VWR Chem.</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>MBTS</td>
<td>Mercapto-benzothiazole sulphenamide</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
3.2.1.2. Compounding

Compounding was performed in two stages: the first step was performed in a 390 mL internal mixer (Model-350S) from Brabender GmbH & Co., Germany. The first step of mixing was conducted with a fill factor of 70%, initial temperature of 80°C, and initial rotor speed of 70 rpm. During the initial step of the compounding process, the polymer underwent mastication to facilitate the incorporation of fillers and other compounding ingredients. As the temperature increased, the viscosity of the polymer decreased. Simultaneously, the addition of fillers led to an increase in viscosity. To ensure optimal reaction conditions for the silica–silane interaction, a temperature of 145°C¹,², known to be the optimum reaction temperature, was selected. Consequently, the starting temperature and rotor speed of the internal mixer were adjusted accordingly to achieve and maintain the desired temperature throughout the compounding process. Due to the high shear forces in the internal mixer during the addition of the polymer, filler, and other compounding ingredients, the temperature increased from 80°C to 145°C. Isothermal mixing and silanization was performed at 145°C for 5 min by adjusting the rotor speed. The steps of the mixing process are detailed in Table 3.3.

### Table 3.3. Mixing process of the model tire tread compound

<table>
<thead>
<tr>
<th>Masterbatch (First) Step</th>
<th>Final (Second) Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Action</td>
<td>Time [mm:ss]</td>
</tr>
<tr>
<td>Polymer</td>
<td>00:00–00:30</td>
</tr>
<tr>
<td>Mastication</td>
<td>00:30–01:30</td>
</tr>
<tr>
<td>½ (Silica + silane)</td>
<td>01:30–02:00</td>
</tr>
<tr>
<td>Mixing</td>
<td>02:00–03:00</td>
</tr>
<tr>
<td>½ (Silica + silane) + other additives</td>
<td>03:00–03:30</td>
</tr>
<tr>
<td>Mixing (140–150°C)</td>
<td>03:30–04:30</td>
</tr>
<tr>
<td>Ram sweep</td>
<td>04:30–05:00</td>
</tr>
<tr>
<td>Mixing (target 145°C)</td>
<td>05:00–09:00</td>
</tr>
<tr>
<td>Discharge and sheeting</td>
<td>-</td>
</tr>
</tbody>
</table>

The masterbatch, the material produced after the first mixing step, was kept for one day at room temperature before final mixing. Final mixing was done on a lab scale two-roll mill (9 cm in diameter) of Schwabenthan GmbH & Co.; the curatives were added at room temperature. The detailed process is described in Table 3.3. After the final mixing the compound was kept for one day at room temperature before curing.

3.2.1.3. Curing

The optimum cure time was measured in a RPA Elite from TA Instruments, Delaware, USA. The samples were cured at 160°C according to the T⁹⁵ value. Compression molding was performed in an automatic press of Wickert Maschinenbau GmbH, Germany, with 200 mm × 200 mm × 4 mm or 80 mm × 80 mm × 2 mm mold. After curing, the tensile strength of the vulcanized sheets was around 16 ± 1 MPa and elongation at break was around 310 ± 30%.
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3.2.1.4. Chopping and grinding

Chopping of the vulcanized sheets was performed with a bale cutter. The pre-treatment for cryogenic grinding of the chopped samples was conducted by dipping them into liquid nitrogen for 4–5 min to achieve a temperature below the glass transition, followed by grinding at room temperature. Grinding was performed in a mechanical grinder from Fritsch, Germany, with a 0.7 mm mesh screen.

3.2.1.5. Revulcanization

The devulcanized rubber samples were compounded and revulcanized for measuring the stress–strain properties. The revulcanization formulation is shown in Table 3.4.

<table>
<thead>
<tr>
<th>Function</th>
<th>Component</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base polymer</td>
<td>Devulcanized rubber sample</td>
<td>100</td>
</tr>
<tr>
<td>Activators</td>
<td>Zinc oxide</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Curing aid</td>
<td>Sulphur</td>
<td>2</td>
</tr>
<tr>
<td>Accelerator</td>
<td>CBS</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.4. Revulcanization formulation

The compounded devulcanized rubber was tested in the RPA 2000 Elite of TA Instruments, Delaware, USA, at 160°C for 30 min according to ASTM D7750-123 to determine the optimum cure time. Sheets of 2 mm thickness were molded at 160°C according to the T95 value in an automatic compression molding machine from Wickert Maschinenbau GmbH, Germany.

3.2.2. Devulcanization process

The ground model tire tread rubber was the feed material for the devulcanization process. It was swollen with oil and DA before performing the devulcanization reaction. A brief description of the devulcanization process is given below.

3.2.2.1. Swelling

The rubber granulate was first mixed with the process oil (TDAE) and subsequently with the DA at room temperature. After each addition, the samples were kept for one day at room temperature for swelling. The kinetic viscosity of the TDAE oil at 40°C was 331 mm²/s and at 100 °C it was 18.4 mm²/s. Due to the high viscosity of the TDAE oil, the rubber granulate was mixed with the oil and manually stirred. The oil-swollen sample was then re-swollen with the DA and kept for one day for migration of the DA into the particles. The swelling of DPDS and DBD was done separately according to the optimum swelling process described in the literature.

3.2.2.2. Devulcanization

The thermo-mechanical–chemical devulcanization process was performed in a Plastograph EC internal mixer from Brabender GmbH & Co., Germany, with a mixing chamber volume of 50 cc. Non-intermeshing counter-rotating rotors and a telescopic ram were used. To minimize oxidation at high temperatures, the cavity was sealed with paraffin wax.
A two-roll mill from Schwabenthan GmbH & Co., Germany, with 200 mm in length and 80 mm in diameter was used at room temperature, with a 1.25 speed ratio and at 30 rpm for milling of the devulcanized rubber. The nip gap was reduced gradually from 1 to 0.1 mm, and the devulcanized rubber formed a band.

According to pre-trial data, the variable and constant process conditions for the devulcanization were selected. For the reference sample, DPDS (diphenyl disulphide) and DBD (2-2′-dibenzamido-diphenyl disulphide) were used as DAs and processed according to conditions obtained from literature\(^4\). The sample details, including the variable and constant parameters for the DA screening trials, are shown in Table 3.5 and Figure 3.3.

![Chemical structure of the silanes used as DA](image)

*Figure 3.3. Chemical structure of the silanes used as DA (sample notations are explained in Table 3.2) (R = hydrocarbon chains)*
Table 3.5. Details of devulcanization process optimization

<table>
<thead>
<tr>
<th>Devulcanization aid screening</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Name of DA</td>
</tr>
<tr>
<td>1–4</td>
<td>PS</td>
</tr>
<tr>
<td>1–4</td>
<td></td>
</tr>
<tr>
<td>5–8</td>
<td>DS</td>
</tr>
<tr>
<td>9–12</td>
<td>ME</td>
</tr>
<tr>
<td>17–20</td>
<td>AM</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Benchmark samples</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>DA</td>
</tr>
<tr>
<td>1</td>
<td>DPDS</td>
</tr>
<tr>
<td>2</td>
<td>DBD</td>
</tr>
</tbody>
</table>

3.2.3. Characterization process

The characterization process consisted of three parts: degree of devulcanization as deducted from the Horikx-Verbruggen plot, stress-strain properties in tensile mode, and white rubber analysis.

3.2.3.1. Degree of network breakdown

ASTM D 6814-02\textsuperscript{5} describes the standard procedure for the evaluation of the crosslink density according to the equilibrium volume swelling method and Flory–Rehner equation\textsuperscript{9}. At first, the samples were extracted in acetone for removal of the polar components, then dried. To remove the non-polar parts, the material was extracted with tetrahydrofuran.

The samples were then swollen in toluene at room temperature for 72 h, according to the ASTM standard. The volume fraction of the sample in the swollen gel ($V_r$) was determined using the additivity rule of volumes as given in Equation 1\textsuperscript{5}:

$$V_r = \frac{W_r / \rho_r}{W_r / \rho_r + W_s / \rho_s}$$

where $W_r$ is the weight of the rubber specimen, $W_s$ is the weight of the absorbed solvent, $\rho_r$ is the density of the rubber, and $\rho_s$ is the density of the solvent. The apparent crosslink density ($V_c$) was calculated according to Flory–Rehner using Equation 2\textsuperscript{6}:

$$V_c = \frac{1}{2M_c} = -\frac{[\ln(1 - V_r) + \chi \cdot V_r^2]}{V_s \cdot (\frac{1}{V_c} - \frac{1}{V_s})}$$

where $V_r$ is the volume fraction of the polymer in the swollen specimen, $\chi$ is the Flory–Huggins polymer–solvent interaction parameter, $M_c$ is the molecular weight between crosslinks, and $V_s$ is the molar volume of the solvent. For the SBR–toluene system\textsuperscript{7} the value of $\chi$ was 0.38 and the molar volume ($V_s$) and the density values of toluene were 106.2 cm\textsuperscript{3}/mol and 0.866 g/cm\textsuperscript{3}, respectively. The percentage of network breakdown was calculated according to Equation 3\textsuperscript{8,9}:
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Network breakdown percentage (%) = \[ \frac{V_{c1} - V_{c2}}{V_{c2}} \]  

(3)

where \( V_{c1} \) and \( V_{c2} \) are the crosslink densities of the samples before and after devulcanization, respectively\(^5\).\(^8\).\(^9\).

The crosslink density according to the Flory–Rehner equation was not the actual one in a filled compound. To determine the exact crosslink density, the Kraus correction was applied.

\[ V_{\text{actual}} = \frac{V_{\text{apparent}}}{1 + k \times \Phi} \]  

(4)

\[ \Phi = \frac{\text{Weight fraction of the filler} \times \text{density of the compound} \times W_b}{\text{Density of the filler} \times W_a} \]  

(5)

where \( V_{\text{apparent}} \) is the measured crosslink density according to the Flory–Rehner equation and \( V_{\text{actual}} \) is the actual crosslink density after correction for the filler. \( k \) is a constant for a given filler, \( \Phi \) is the volume fraction of the filler in the specimen, \( W_b \) is the weight of the specimen before extraction, and \( W_a \) is the weight of the specimen after the extraction of all soluble material, such as polymer sol fraction, oil, and soluble chemical residues\(^8\).\(^9\).

The limit of the random scission and crosslink scission were calculated by measuring the sol-content of feed material according to the Horikx–Verbruggen method\(^9\). Plotting the values of the sol fraction and network breakdown of the devulcanizates in the graph, the type of network breakdown can be predicted. For one network breakdown versus a sol-content data point, the average result of five samples was calculated.

In Figure 3.4, the marked green zone is the targeted area for the devulcanized rubber considering the minimum sol fraction with maximum devulcanization percentage. To achieve higher values, monosulphidic bonds have to be broken, which goes together with a higher degree of random scission. Moreover, bound rubber cannot be dissolved, limiting the sol content.

![Figure 3.4. Sol content versus network breakdown percentage for random and crosslink scission according to the Horikx–Verbruggen plot](image-url)
3.2.3.2. Stress–strain properties

Stress–strain properties of the revulcanized rubber were measured with a Z010 tensile tester manufactured by Zwick Roell GmbH & Co., Germany, according to ASTM D412\textsuperscript{10}. For each sample, a total of seven tensile dumbbells were tested and, among those, five significant values were plotted in one data point with their average values and error bars.

3.2.3.3. Miscibility

After the devulcanization process, there may still be undevulcanized particle cores in the devulcanizate. Devulcanized polymer chains are homogeneously miscible with a compatible polymer or compound; however, undevulcanized particle cores are not under the same conditions. Considering this, it is important to analyze the number, size, and total area of these undevulcanized particle cores. For this purpose, the white rubber analysis (WRA) was developed. In this quantitative analytical method, the devulcanizate was blended with a bright-white polybutadiene-based compound colored with titanium dioxide. The white colorant was judiciously selected to create a high contrast between the background and devulcanizate, which led to a quantitative characterization process.

White rubber compounds are polybutadiene and titanium dioxide based. The samples were prepared by mixing 10% devulcanizate into this white rubber compound. This resulted in a gray compound, in which the remaining non-devulcanized particles were visible as brownish spots. The digital analysis of the particles and particle size distribution was performed using a VHX 5000 digital microscope from Keyence.

3.2.3.4. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was carried out using a Spectrum 100 spectrometer manufactured by PerkinElmer, based in Massachusetts, USA. The experiments were conducted at room temperature, with each sample undergoing 16 scans, and the results were averaged and plotted after baseline correction.

3.3. Results and discussion

This part was classified into the three main properties: degree of network breakdown, stress–strain properties, and homogeneity. Finally, the reaction mechanism was elucidated.

3.3.1. Network breakdown

In Figure 3.5, the network breakdown versus sol-content data of six silane devulcanized samples along with DPDS and DBD devulcanizates as reference are plotted. Network breakdown and sol content gradually increased with increasing residence time and temperature. It can be concluded that, on an average, VP showed the highest efficiency and ME was the least efficient one in terms of network breakdown and sol content. Using VP as DA, the network breakdown reached 57.1% at a sol content of 13.4%: the latter being much lower than the random scission limit. The more efficient crosslink scission of VP compared to the other chemicals tested as DAs is due to the presence of the vinyl moiety and the activator in VP. VN resulted in a network breakdown of app. 45% on average with a sol content of 9% for the best processing conditions.
Figure 3.5. DA screening: network breakdown analysis (sample notations are explained in Table 3.2)

With PS, the network breakdown percentage increased from 25% to 40% with an increasing residence time of 4 to 6 min, for a devulcanization temperature of 140°C. When the temperature was increased to 160°C at a residence time of 6 min, the sol content increased from 6% to 10% and the network breakdown percentage increased to 53%. The breaking of the crosslinks and reaction with the DA to hamper the recombination and to form sulphur–silane bonds was a probable reason for the higher degree of devulcanization. For the samples devulcanized with DS, AM, and ME, the data points were mostly close and above the random scission line. The points are on the left side of the graph, which indicates insufficient devulcanization of the granulate. It can be concluded that the disulphidic, mercapto, and amino moieties are less efficient than the vinyl and polysulphide groups in this process window.

3.3.2. Stress–strain properties

Based on Figure 3.6, the results reveal that the increase in curing torque is lowest for the DPDS samples, and highest for the PS samples followed by the VP samples. This can be attributed to the presence of unreacted polysulphide moieties in the PS samples, which contributed to the formation of additional crosslinks and resulted in a greater curing torque increase. Furthermore, compared to the VN samples, the VP samples exhibited increased curing torque due to the contribution of the activator. Additionally, the samples with a lower degree of network breakdown exhibited a lower increase in torque, indicating less formation of additional crosslinks.
The comparative analysis of the tensile strength of the revulcanized samples is shown in Figure 3.7. The tensile strength of the revulcanizate varied with increasing time and temperature. The best stress–strain properties were obtained for the VN and VP devulcanized samples. The tensile strength was in the range of 8 to 9.4 MPa. From these screening trials, it can be concluded that VP and VN as DA resulted in the best mechanical strength.
A comparative analysis of the elongation at break values of the revulcanized samples is shown in Figure 3.8. For the reference DAs as well as for PS, DS, and AM devulcanized samples, elongation at break was in the range of 60% to 80% and did not show any significant change with increasing time and temperature. For ME as DA, the range was between 50% to 65%, and for VN the range was 75% to 95%. The best elongation at break values were found for the VP samples, which were in the range of 95 to 110%.

![Figure 3.8. DA screening: elongation at break (sample notations are explained in Table 3.2)](image)

From this screening, it can be concluded that VP resulted in the best stress–strain properties, followed by VN. Considering the tensile strength of the feed material, the tensile strength recovery was around 50–55%. This fits well with the findings of the network breakdown analysis: VP showed the best performance as DA.

### 3.3.3. Miscibility analysis

The homogeneity of the DA optimization trials was elaborated in the white rubber analysis. From the statistical analysis of the brownish devulcanize dispersed in the white rubber matrix, the total number of visible particles and the particle size distribution were analyzed. The series of samples devulcanized at 160°C for 6 min was selected. The comparative results for devulcanizates using different DAs are shown in Figure 3.9.

For the samples devulcanized with VP or AM, the particle size distribution was on the finer side, and the total number of visible particles was higher than for all other samples. The samples devulcanized with DS, PS, VN, ME, and DPDS were comparatively coarser with a lower number of visible particles. This shift in the particle size distribution was an effect of the devulcanization efficiency and mechanical grinding processes occurring in the early stages of the devulcanization process.
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Figure 3.9. DA screening: white rubber analysis (sample notations are explained in Table 3.2).

Figure 3.10. Correlation between tensile strength and total area of visible particles (sample notations are explained in Table 3.2).

In Figure 3.10, the total area of visible particles (TAVPs) is plotted against the tensile strength (TS). With an increasing devulcanization efficiency, as indicated by a smaller TAVP, the TS improved. For ME devulcanized samples, the TAVP had the highest value,
resulting in the lowest TS, and for VP as devulcanization aid, the TAVP showed the minimum value resulting in the best TS, fitting with the explanation mentioned above.

### 3.3.4. Model devulcanization mechanism

The vinyl silane with activator showed the best performance within this group of potential DAs. From a mechanistic view, one of the reasons was the presence of the unsaturated carbon–carbon bond. The proposed reaction mechanism is that the vinyl silane and polymer react and experience a chain-transfer reaction, in which the vinyl moiety becomes attached to the broken crosslinks and restricts further recombination, as shown in Figure 3.11.

![Figure 3.11. Radical addition reaction between vinyl silane and polymer crosslinks](image)

After the radical addition reaction, the molecule experiences a disproportion reaction to achieve higher chemical stability. The activator in the vinyl silane improved the reactivity of the latter during devulcanization, as shown in Figure 3.12.
Figure 3.12. Disproportionation reaction between vinyl silane and polymer crosslinks

The model compound used as the feed material for the devulcanization process contained carbon–carbon double bonds: the base polymers were unsaturated rubbers such as SBR and BR. In the preparation of the model compound, TESPD was employed as a coupling agent to enhance silica reinforcement; ethoxy groups react with silanol moieties and form a stable bond to the filler. VN contains both: ethoxy groups and carbon–carbon double bonds, and can react with silica as well as the radical chain fragments; they are bifunctional. The comparative peak intensities can provide an insight into the progression of the devulcanization reaction, as shown in Figure 3.13.

In the devulcanizate, a reduction in the intensity was observed for the peaks at 2850 cm\(^{-1}\) and 2917 cm\(^{-1}\), which corresponded to the asymmetric and symmetric stretching of C–H bonds of the alkanes and alkenes. The devulcanization reaction did not result in the formation of new moieties in the final product; it was primarily a chain-transfer reaction. No other significant peaks were observed\(^{11}\). 
Figure 3.13. FTIR spectra of the model compound, VN, and VN devulcanizate (sample notations are explained in Table 3.2)

In comparison to pure VN, several peaks disappeared in the devulcanized sample. A peak at 1166 cm\(^{-1}\) corresponding to C–O stretching was noted, indicating the involvement of this functional group in the devulcanization process. Additionally, a peak at 754 cm\(^{-1}\) associated with the C=C bending of an alkene, was detected, signifying the reactivity of VN during devulcanization. These observations provide evidence of the reactivity and transformation of VN during the devulcanization process\(^{11}\).

3.4. Conclusions

The devulcanization efficiencies of the different silanes in terms of mechanical properties, network breakdown, and miscibility were comparatively analyzed in this study. The SBR-silica network is the main challenge for passenger car tire rubber devulcanization, and a potential solution was developed by using vinyl silane as a devulcanization aid (DA). The efficiency of this silane as DA was further improved by the presence of an activator; this combination turned out to be the most promising DA for passenger car tire rubber devulcanization.

Vinyl silane and vinyl silane with activator devulcanized samples showed the best mechanical and network breakdown properties, followed by the ones devulcanized with a polysulphidic and amino silane. Compared to other silanes, the vinyl and the variant with the activator showed a higher crosslink-to-random-scission ratio, resulting in a better devulcanizate quality. A greater extent of devulcanization in rubber leads to an increased number of free polymer chains, resulting in enhanced miscibility. Conversely, reduced devulcanization leads to a reduced presence of free polymer chains, resulting in decreased miscibility and an increased quantity of immiscible particles. A linear correlation was established between the devulcanizate quality in terms of tensile
strength and the total area of visible, insufficiently devulcanized particles for all silane devulcanized samples.

Considering the properties of the feed material, the recovery of the tensile strength was around 50–55%, and the network breakdown percentage was 55–60%: these are rather high percentages for a SBR–silica system due to the strong filler–polymer network. An optimization of the process parameters is required for the further improvement of the devulcanize quality. A reaction mechanism was proposed; however, further research on and analysis of the devulcanization reaction are required.

3.5. References

11. IR Spectrum Table, 2023, Sigma Aldrich.
CHAPTER 4

DEVULCANIZATION PROCESS OPTIMIZATION

This chapter can be categorized into two principal sections:

4A - The first section is dedicated to the optimization of devulcanization process parameters using vinyl silane with peroxide (VP) for a model passenger car tire tread material. A comprehensive comparative analysis of the results was undertaken in order to discern the most favourable process parameters.

4B – This section also centers on the investigation of devulcanization process parameter optimization using VP, but this time, for whole passenger car tire (WT) granulate. A meticulous comparative analysis of the acquired results from variable process conditions was conducted with the objective to identify the optimal process parameters.
4A. Devulcanization process optimization for a model passenger car tire tread compound

4.1. Introduction

The flowchart of the study up to this chapter is sketched in Figure 4.1. An extended investigation was carried out using the most promising DA (vinyl silane with peroxide or VP) from the screening as reported in Chapter 3 within a wider range of experimental conditions. The primary objective of this part of the investigation was to further finetune the operational parameters for devulcanization using VP. The optimization of the devulcanization process parameters encompassed variations in devulcanization temperature, residence time, shear rate, and DA concentration. The outcome of this optimization effort will be further applied to enhance the devulcanization process for whole passenger car tire (WT) rubber (see Section 4B).

4.2. Experimental process

The experimental process can be categorized into 3 parts:

i. Preparation of the model compound
ii. Sampling procedure
iii. Testing process

4.2.1. Preparation of model compound

The preparation of the model compound was executed in accordance with the procedure outlined in Chapter 3, Section 3.2.1.

4.2.2. Sampling procedure

Four devulcanization process parameters were optimized in this investigation. The parameter windows were selected based on the experimental data from Chapter 3. 5% process oil and 80% fill factor was kept constant and stepwise optimization was done:

i. Devulcanization temperature (7 samples): 130°C to 180°C with an interval of 10°C. Constant: 5% VP, 6 min residence time, 150 RPM.
ii. Residence time (4 samples): 4 minutes to 7 minutes with an interval of 1 minute with optimum temperature. Constant: 5% VP, 150 RPM.
iii. Shear rate (5 samples): 50 RPM to 150 RPM with an interval of 25 RPM with optimum temperature and residence time. Constant: 5% VP.

iv. DA concentration (6 samples): 2% to 7% with an interval of 1% with optimum temperature, residence time and shear rate.

All the samples were devulcanized by maintaining the same procedure as mentioned in Chapter 3, Section 3.2.2. All the samples were revulcanized using the same formulation as described in Chapter 3, Section 3.2.1.5.

4.2.3. Testing procedure

The testing process contains three parts: degree of devulcanization as determined by a Horikx-Verbruggen plot, stress-strain properties in tensile mode and homogeneity evaluation by white rubber analysis. The detailed descriptions of these testing procedures are given in Chapter 3, Section 3.2.3.1 to 3.2.3.3.

4.3. Results and discussion

The results and discussion can be classified into four sections: temperature, residence time, shear rate and DA concentration optimization. Each section is separated into three main properties in terms of stress-strain behaviour, degree of devulcanization and homogeneity.

4.3.1. Results of temperature optimization

According to Figure 4.2, the tensile strength values were between 9.1 MPa to 9.5 MPa in the temperature range of 140°C to 170°C. At a temperature of 130°C, the stress-strain properties were poor, probably due to an insufficient devulcanization reaction. With further increase in temperature beyond 170°C, the tensile strength decreased again.

![Figure 4.2. Temperature optimization trials: stress-strain properties](image-url)
The maximum elongation at break was around 110% within the range of devulcanization temperature of 150°C to 155°C. Above 155°C, elongation at break started to decrease again and got reduced to 80% at a temperature of 180°C.

**Figure 4.3. Temperature optimization trials: network breakdown analysis**

The network breakdown and sol content percentage of the devulcanized material with increasing temperature are shown in Figure 4.3. With increasing temperature, both increased gradually. At 130°C, network breakdown was around 35 to 40%, which increased up to 60-65% at a devulcanization temperature of 170-180°C. The sol content was noted around 7-8% at 130°C and increased to 15-18% at 180°C.

All devulcanized samples were in-between the random and crosslink scission line (Horikx-Verbruggen limits). Samples devulcanized at temperatures exceeding 170°C exhibited elevated sol-content, approaching the threshold of random scission, signifying polymer degradation under high temperature conditions.

In Figure 4.4, the white rubber analysis of the model compound is plotted versus devulcanization temperature. With increasing temperature, the total number of visible particles increased gradually, particles became finer and the number of bigger particles got reduced. The particle size distribution shifted towards the finer side which indicates a higher efficiency of the devulcanization process at elevated temperatures.
Figure 4.4. Temperature optimization trials: white rubber analysis

4.3.2. Discussion on temperature optimization

At a devulcanization temperature of 130°C, poor stress-strain properties were observed, resulting from insufficient devulcanization. This restricts the number of free polymer chains, subsequently leading to diminished tensile strength and elongation at break after revulcanization. Furthermore, temperatures exceeding 170°C caused a decline in tensile strength, accompanied by increased sol-content. This phenomenon can be attributed to thermal degradation of the main polymer chains at elevated temperatures, which results in shorter polymer chains, subsequently affecting tensile strength and elongation at break. Inadequately devulcanized samples displayed lower miscibility as indicated in the analysis in white rubber. Ultimately, based on both tensile strength and elongation at break, 155°C was identified as the optimal devulcanization temperature for the model compound.

4.3.3. Results of residence time optimization

According to Figure 4.5, tensile strength and elongation at break increased with increasing residence time, but above 6 minutes both started to decrease again due to degradation of the main polymer chain at longer residence times. Around 9.5 MPa tensile strength and 115% elongation at break were noted for a residence time of 6 minutes; this turned out to be the best residence time. This period of time was therefore selected as the optimum and used for the further optimization process.
Figure 4.5. Residence time optimization trials: stress-strain properties

According to Figure 4.6, it was noted that the network breakdown percentage increased from 45% to 55% with increasing residence time from 4 to 7 minutes. The sol content percentage increased from 10 to 15% within the same residence time window. The increase in sol content and network breakdown percentage with increasing residence time was due to the cumulative amount of shear forces for longer residence times.

Figure 4.6. Residence time optimization trials: network breakdown analysis
In Figure 4.7, the total number of visible particles increased from 1513 to 1612 when the residence time increased from 4 to 7 minutes. The number of finer particles increased and bigger particles got reduced in number with increasing residence time.

4.3.4. Discussion on residence time optimization

As the residence time increased, both tensile strength and elongation at break exhibited an initial augmentation; however, beyond a duration of 6 minutes, a subsequent decline was observed. This decline was attributed to the prolonged residence time inducing degradation in the main polymer chains. This outcome finds support in the generation of shorter polymer chains, which, in turn, contributes to diminishing tensile strength and elongation at break properties as the residence time extends.

The observed increase in both network breakdown and sol content is ascribed to uncontrolled breakdown induced by elevated shear forces. This phenomenon is characterized by a shift towards the random scission line. While controlled temperature and shear force were anticipated to facilitate an effective devulcanization process, surpassing an optimal threshold was associated with undesirable random polymer breakdown and the consequent production of a devulcanizate of inferior quality.

4.3.5. Results of shear rate optimization

According to Figure 4.8, tensile strength and elongation at break both increased gradually with increasing shear rate. In typical rubber compounds, there is often an inverse relationship between tensile strength and elongation at break. However, when it comes to devulcanized rubber, the situation is unique. To achieve a better devulcanization outcome, in which more polymer chains are successfully restored, it leads to an increase in the number of free polymer chains available during the

\[ \text{Figure 4.7. Residence time optimization trials: white rubber analysis} \]

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Revulcanization process. As a result, both tensile strength and elongation at break experience an increase. With increasing shear rate from 50 RPM to 150 RPM, tensile strength increased significantly from 5.2 MPa to 9.4 MPa; similarly, elongation at break improved from 42 to 115%. 150 RPM was the maximum possible rotor speed of the Brabender Plastograph EC, so further optimization at higher rotor speed was not possible.

**Figure 4.8.** Shear rate optimization trials: stress-strain properties

**Figure 4.9.** Shear rate optimization trials: network breakdown analysis
In Figure 4.9, with increasing shear rate from 50 to 150 RPM, the network breakdown percentage increased from 20% to 55%, and the sol content increased from 4 to 14%. It can be concluded that the optimum shear rate for the most efficient devulcanization process is 150 RPM, the highest possible shear rate of the mixing device.

According to Figure 4.10, with increasing shear rate from 50 RPM to 150 RPM, the total number of visible particles increased from 1257 to 1537. With increasing shear rate, the particles became finer and the number of bigger particles got reduced.

### 4.3.6. Discussion on shear rate optimization

A notable disparity in particle size distribution underscores the significance of shear rate in the process of devulcanization. Experimental assessments were extended to the uppermost limit of the instrument's capacity, motivated by the notion that the application of elevated shear force has the potential to diminish residence time. The total shear force, a product of shear rate and residence time, was considered in this context.

Observations revealed that an escalation in shear rate corresponded to enhancements in network breakdown and stress-strain properties. This implies that, at least within the test conditions, a higher shear rate correlates with an increased degree of devulcanization.

### 4.3.7. Results of devulcanization aid concentration optimization

In Figure 4.11, the stress-strain properties of the devulcanized and revulcanized samples with variable DA concentrations are plotted along with the feed and reference compound. The reference compound was devulcanized with DPDS, and the feed material was a model tire tread compound. Tensile strength and elongation at break showed almost similar values within the range of 4% to 7% DA concentration. The...
sample with 2% VP was also tested, but did not form a uniform band; further mixing, revulcanization and stress-strain testing was not possible. The tensile strength was around 9.4 MPa with an elongation at break of 115% at 5% VP concentration. Further increase in DA concentration was not reflected in any further improvement in stress-strain properties.

![Figure 4.11. DA concentration optimization trials: stress-strain properties](image)

![Figure 4.12. DA concentration optimization trials: network breakdown analysis](image)
According to Figure 4.12, with increasing VP concentration, the network breakdown increased and the sol content decreased gradually. At 2% DA concentration, the network breakdown was around 45%, and it reached 55-60% at a concentration of 5 to 7%. The sol content percentage started around 14% at the lowest DA concentration, and decreased to 11% when it is devulcanized with 7% DA concentration. The lower sol content at higher DA concentrations was due to the higher ratio of crosslink to random polymer scission.

In Figure 4.13, the white rubber plot of the devulcanized sample with increasing VP concentration is shown: The total number of visible particles was constant within a range of 1400 to 1500 for all samples. However, with increasing DA concentration, the particle size distribution got shifted towards the finer side indicating higher miscibility at higher VP concentration.

### 4.3.8. Discussion on devulcanization aid concentration optimization

As the concentration of VP increased, there was a corresponding rise in devulcanization efficiency which also leads to the plasticization of the material. This reduction in polymer content may serve as a limiting factor for achieving further enhancements in tensile strength at higher DA concentrations.

Based on the stress-strain properties, it is suggested that a 4% concentration is optimal for VP. The Horikx-Verbruggen analysis illustrates a shift in network breakdown from random scission towards the crosslink scission limit with increasing VP concentration. Notably, the improved network breakdown value does not directly translate into enhanced mechanical properties, owing to the concurrent reduction in polymer content and the counteractive plasticization effect observed at higher DA concentrations.
Considering the values of the feed material (tensile strength of 16.1 MPa and 310% elongation at break), a recovery of 55%-60% of the strength and 30%-35% of the elongation was preserved. The optimized process parameters and related properties of the devulcanizate are summarized in Table 4.1.

**Table 4.1. Optimized process parameters and related properties for model granulates**

<table>
<thead>
<tr>
<th>Feed material</th>
<th>Model compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devulcanization aid</td>
<td>VP</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>9.4 MPa</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>112%</td>
</tr>
<tr>
<td>Network breakdown</td>
<td>60%</td>
</tr>
<tr>
<td>Temperature</td>
<td>155°C</td>
</tr>
<tr>
<td>Residence time</td>
<td>6 min</td>
</tr>
<tr>
<td>Process oil</td>
<td>5%</td>
</tr>
<tr>
<td>DA concentration</td>
<td>4-5%</td>
</tr>
<tr>
<td>Rotor speed</td>
<td>150 RPM</td>
</tr>
<tr>
<td>Fill factor</td>
<td>80%</td>
</tr>
</tbody>
</table>

**4.4. Conclusion of devulcanization process optimization for a model passenger car tire tread compound**

Optimization of the devulcanization parameters was conducted, revealing an optimal devulcanization temperature of 155°C, a residence time of 6 minutes, and a rotor speed set at the upper limit of the equipment of 150 rpm. Notably, mechanical strength exhibited no further improvement beyond a 4% concentration of VP. This finding aligns with the observed plateau in mechanical strength beyond this concentration. These results contribute valuable insights for the controlled devulcanization of rubber compounds. Concurrently, an escalation in network breakdown was observed, coupled with a reduction in sol content. This trend signifies a high degree of crosslink scission while minimizing polymer scission with increasing VP concentration. The analysis of the mechanical properties indicates that the optimum concentration of the DA can be considered as 4% VP.
4B. Devulcanization process optimization with whole passenger car tire (WT) rubber granulate

4.5. Introduction
As described in Section 4A, the optimization of devulcanization process parameters was primarily conducted for model granulates simulating passenger car tire treads. However, available in the market are whole tire (WT) granulates. Given the research focus of devulcanization of passenger car tire rubber, the gained knowledge and investigation was transferred to optimization of the process using WT granulates as feed material and the most efficient DA from the earlier study (Chapter 3).

Within the framework of this extended investigation, a broader range of experimental conditions was applied, using VP as DA. The principal objective of this extended study was to ascertain the optimal operational parameters for the devulcanization process of WT granulates when employing VP. In pursuit of this objective, the optimization of devulcanization process parameters entailed the systematic manipulation of key variables, including devulcanization temperature, residence time, and the concentration of the devulcanization aid. Furthermore, an analysis of the feed material compositions was conducted through assessments of particle size distribution and thermogravimetric analysis.

4.6. Experimental process
The experimental process is the same as mentioned in Section 4.2. The additional information for the WT rubber granulate is mentioned below:

4.6.1. Preparation of WT rubber granulates
The WT rubber granulate used in this study was provided by Genan GmbH. The granulate underwent a swelling procedure involving the use of 5% (w/w) TDAE oil, which lasted for one day at room temperature (RT). Subsequently, it was subjected to an additional swelling process with the devulcanization aid (DA), also conducted at room temperature for one day. This pre-treatment is similar to the swelling procedure as described in Chapter 3, Section 3.2.2.1.

4.6.2. Sampling procedure
As the shear rate was optimized up to the highest instrumental limitation (150 RPM) in the study described in Section 4A and no further fine-tuning to higher rates was possible, only the other three parameters of the devulcanization process were optimized for this material. The parameter windows were selected based on the experimental data from Section 4.3.

i. Devulcanization temperature (7 samples): 145°C to 195°C with an interval of 10°C. Constant: 4% VP, 6 min residence time.
ii. Residence time (5 samples): 4 minutes to 8 minutes with an interval of 1 minute with optimum temperature. Constant: 4% VP.
iii. DA concentration (7 samples): 0% to 6% with an interval of 1% with optimum temperature and residence time.
iv. Reference samples: DPDS was used as DA, and devulcanizates were prepared as described in Chapter 3, Table 3.5.

4.6.3. Testing procedure

The testing process contains six parts:

i. Degree of devulcanization as determined by the Horikx-Verbruggen plot
ii. Stress-strain properties in tensile mode
iii. Homogeneity evaluation by white rubber analysis
iv. Processability of the rubber in terms of viscosity
v. Particle size distribution by optical analysis
vi. Thermogravimetric analysis of the feed material

A detailed description of the first three tests is given in Chapter 3, Section 3.2.3.1. to 3.2.3.3. The remaining test procedures are described below.

4.6.3.1. Viscosity

The viscosities of the devulcanized rubber samples were determined using an MV 2000 VS viscometer supplied by Alpha Technologies GmbH, Germany, following the guidelines specified in the ASTM D1646-19a standard. In this testing procedure, a large rotor (ML) with a diameter of 38.1 mm was employed, and the test temperature was maintained constant at 100°C. A fixed sample weight of 20 grams was pre-heated for one minute, and the viscosity, recorded in Mooney units (MU), was obtained after another 4-minute duration. It is important to note that all measurements were conducted under rigorously controlled and consistent conditions.

4.6.3.2. Particle size distribution

The particle size distribution analysis of the WT rubber granulate was conducted using a VHX 5000 digital microscope provided by Keyence, Japan. The maximum length of each particle was measured under full ring light conditions at a 20X zoom level. In order to ensure statistical significance, random sampling is done for multiple times sourced from the same batch.

4.6.3.3. Thermogravimetric analysis

Thermogravimetric Analysis (TGA) was performed using a TGA 550 instrument supplied by TA Instruments, Delaware, USA. The test was conducted in nitrogen atmosphere with a flow rate of 50 mL/min, ram speed of 10°C/min, and ranging from 30°C to 600°C. Subsequently, the test was continued in a synthetic air atmosphere comprising 70% nitrogen and 30% oxygen, with the same flow rate and ramp speed and in a temperature range from 600°C to 900°C. Equilibration was performed at three different temperatures, namely, 30°C, 600°C, and 900°C, each for a duration of five minutes.

4.7. Results

The results and discussion part is classified into five sections: particle size distribution and thermogravimetric analysis of the feed granulate along with the temperature, residence time, and DA concentration optimization. Each parameter optimization section is classified into four main properties: stress-strain behaviour, viscosity, degree of devulcanization and homogeneity.
4.7.1. Particle size distribution of feed granulates

For this study, the size distribution of the feedstock, WT granulate, was measured. Due to the irregular shapes of the samples, this was based on the maximum length. To address this, the maximum length within the particle or, hypothetically if the particle was enclosed in a sphere, the diameter of that sphere, was considered in this analysis. A microscopic image of the WT rubber granulate is shown in Figure 4.14.

![Microscopic image of WT granulates](image)

**Figure 4.14. Microscopic image of model granulates (left), WT granulates (right)**

Subsequently, a particle size distribution graph was generated, as illustrated in Figure 4.15, comparing the ground model passenger tire tread compound with the WT rubber granulate. On the Y-axis, the frequency or the number of particles in a certain range, and on X-axis the maximum particle length was given. The analysis revealed that the 6 highest frequencies of the model granulates predominantly fell within the range of 500µm to 900µm. For the WT rubber granulate, these 6 frequencies were detected in
between 1300 µm to 2000 µm. WT granulates exhibited a coarser size profile compared to the model compound particles.

### 4.7.2. Thermogravimetric analysis

The results obtained from the WT and the model rubber granulate exhibited similar trends, but with different magnitudes. The discrepancies in the values can be attributed to variations in the feed material: The WT material comprised granulates from different tire types and various tire parts, introducing variations in polymer content, filler ingredients, and ageing, while the model compound does not show this variation.

To quantify this variation, a TGA analysis of the feed materials was done. The TGA results of the WT rubber granulate are shown in Figure 4.16. Six random samples were selected from the same lot for the analysis. The volatiles were released within a temperature range of 250°C to 300°C, and around 450°C all the polymer was degraded. A further decrease in weight was noticed above 600°C, where carbon black got oxidized in the presence of oxygen. The residual was considered as silica and zinc compounds.

![Figure 4.16. TGA of the WT rubber granulates](image)

The polymer content varied within ±5% (w/w), but the main variation was noticed in the filler system. The TGA curve of Sample 3 indicates almost same curve as the model compound. As shown in Table 4.2, the variation in the residue showed the presence of silica content in some of the samples. The carbon black percentage indicates the variation in filler type and content.
A comparative analysis of the WT samples and the model compound is given in Table 4.3. The volatile content of the WT sample was lower compared to the model sample: the model compound was not aged, while the WT samples got aged during their service life as tire. Volatile components like oil partially evaporate from the tire surface as tires are kept in an open environment.

The filler system of the model compound was completely silica-based, but for the WT granulates it was a mixture of silica and carbon black (CB) compounds. Mainly 3 types of compounds were identified in terms of filler variation: around 25-30% CB with 10-12% silica; around 10-15% CB with 20-25% silica and around 30-32% silica with 2-3% CB. The variation of CB and silica concentration results from particles of different tire parts in the same batch as summarized in Table 4.3.

### Table 4.3. Comparison of whole tire material and model granulates

<table>
<thead>
<tr>
<th></th>
<th>WT granulates (w/w)%</th>
<th>Model granulates (w/w)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>46-54</td>
<td>46</td>
</tr>
<tr>
<td>Silica + ZnO</td>
<td>7-32</td>
<td>37</td>
</tr>
<tr>
<td>CB</td>
<td>2-29</td>
<td>0</td>
</tr>
<tr>
<td>Oil &amp; Additives</td>
<td>12-14</td>
<td>17</td>
</tr>
</tbody>
</table>

#### 4.7.3. Results of temperature optimization

In Figure 4.17, the tensile strength values of the devulcanized and revulcanized WT rubber granulate are plotted with respect to the devulcanization temperature. The tensile strength values were in-between 8.2 MPa to 8.6 MPa in the temperature range of 155°C to 185°C. With increasing devulcanization temperature, tensile strength got increased gradually up to 180°C and then decreased again: At lower temperatures (less than 155°C), the granulate was insufficiently devulcanized, and at higher temperatures (more than 180°C). With increasing devulcanization temperature, the error got reduced as the material became gradually more homogeneous as supported by white rubber analysis.
Figure 4.17. Temperature optimization trials of WT granulates: tensile strength

Figure 4.18. Temperature optimization trials of WT granulates: elongation at break
According to Figure 4.18, the maximum elongation at break was 162% for the samples devulcanized at 180°C. Elongation at break showed the same trend as tensile strength: it increased with increasing devulcanization temperature. At 145°C, elongation at break was around 138%; this low value was due to insufficient devulcanization. At 180°C, elongation at break reached a maximum, and beyond this temperature, it started decreasing.

![Figure 4.19. Temperature optimization trials of WT granulates: network breakdown analysis](image)

In Figure 4.19, the network breakdown and sol content of the devulcanized material are plotted with increasing devulcanization temperature. The sample devulcanized at 145°C showed a network breakdown of around 57% and sol content of around 14%. With increase in temperature, both increased gradually. The sample devulcanized at 195°C showed 75% network breakdown and 23% sol content.

According to Figure 4.20, the viscosity of the devulcanized samples decreased gradually with increasing devulcanization temperature. The samples devulcanized at 145°C showed a viscosity of around 102 MU and it got reduced to 75 MU when devulcanization took place at 195°C.
Figure 4.20. Temperature optimization trials of WT granulates: viscosity

Figure 4.21. Temperature optimization trials of WT granulates: white rubber analysis
According to Figure 4.21, the total number of visible particles increased up to the devulcanization temperature of 165°C, and then started decreasing with further increase in devulcanization temperature. At higher temperatures, the particle size distribution shifted towards the finer side.

4.7.4. Discussion on temperature optimization

With increasing devulcanization temperature, tensile strength exhibited a gradual rise up to 180°C, after which it declined. Below 155°C, the granulate was inadequately devulcanized, limiting the number of free polymer chains in the devulcanizate, resulting in diminished tensile and elongation at break properties after revulcanization. Undevulcanized particles exhibit a higher amount of remaining crosslink density compared to the devulcanized phase. Upon revulcanization, additional crosslink formation occurs, likely exceeding the optimum level resulting in a reduction in tensile properties. The variation in modulus between undevulcanized particles and the devulcanized phase after revulcanization may also contribute to defective interphases, potentially being another reason for the observed failure in tensile strength. Conversely, temperatures exceeding 180°C led to thermal degradation of the main polymer chain, causing shorter polymer chains and, consequently, poor tensile and elongation at break properties.

Network breakdown analysis mirrored the stress-strain results, with increased network breakdown and sol content at higher temperatures. Insufficiently devulcanized samples displayed reduced miscibility in the white rubber analysis, and higher devulcanization temperatures improved miscibility. With rising devulcanization temperature, enhanced miscibility is achieved by an increased portion of detached polymer chains through random and crosslink scission. Considering that the highest tensile strength and elongation at break were observed at 180°C, this temperature was selected for further optimization.

4.7.5. Results of residence time optimization

According to Figure 4.22, the tensile strength of the devulcanized and revulcanized samples increased with increasing residence time up to 6 minutes of devulcanization time; at further increase, the strength started decreasing again. For the 4 minutes residence time samples, tensile strength was around 7.8 MPa: the low value was due to insufficient devulcanization. Samples devulcanized for 6 minutes showed a maximum of around 8.6 MPa tensile strength. The error bars got smaller with increasing residence time, as the samples became more homogeneous.
Figure 4.22. Residence time optimization trials of WT granulates: tensile strength

Elongation at break showed the same trend as tensile strength as seen in Figure 4.23. Around 150% to 165% elongation at break was noted in the residence time range of 5 minutes to 8 minutes; it reached a maximum at 6 minutes.

Figure 4.23. Residence time optimization trials of WT granulates: elongation at break
According to Figure 4.24, the network breakdown percentage increased from 60% to 75% with increasing residence time from 4 minutes to 8 minutes. Similarly, the sol content increased from 16% to 27% in the same time interval.

Figure 4.25. Residence time optimization trials of WT granulates: viscosity
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The viscosity of the devulcanized samples decreased gradually with increasing residence time, as shown in Figure 4.25. The samples devulcanized at 4 minutes showed a viscosity of around 90 MU, and it got reduced to 74 MU for the samples devulcanized for 8 minutes.

As seen in Figure 4.26, the total number of visible particles increased up to 6 minutes residence time and then started decreasing for longer times. At 4 minutes, the total number of visible particles was around 1308, which increased up to 1497 at 5 minutes residence time and then got reduced to 1133 for the 8 minutes residence time samples.

![Figure 4.26. Residence time optimization trials of WT granulates: white rubber analysis](image)

4.7.6. Discussion on residence time optimization

Insufficient devulcanization occurred at lower residence times (below 5 minutes), while thermal degradation of the main chain is unavoidable in a thermo-mechanical process becoming more dominant at longer residence times (beyond 6 minutes). Tensile strength and elongation at break increased with extended residence time, peaking at 6 minutes. However, beyond this point, both properties declined due to the degradation of the main polymer chain caused by high shear force, resulting in shorter polymer chains and diminished mechanical properties.

Higher residence times led to increased network breakdown and sol content, approaching the random scission line due to uncontrolled breakdown from higher shear force due to longer residence times. While a controlled temperature and shear forces were expected to facilitate devulcanization, excessive shear forces due to long residence time led to undesired random polymer breakdown, resulting in poor
devulcanizate quality. Longer residence times also shifted the particle size distribution towards finer particles, and with an increased number of fully devulcanized particles improving miscibility. Consequently, the total number of visible particles decreased with extended residence time. The optimum residence time determined from these measurements was 6 minutes, selected for further optimization processes.

4.7.7. Results of devulcanization aid concentration optimization

In Figure 4.27, the tensile strength values of the devulcanized and revulcanized samples with variable VP concentrations are plotted along with the reference compound. The reference compound (according to Chapter 3, Table 3.5) was devulcanized with DPDS at a concentration of 30 mmol/100 g of granulate according to the literature\(^1\). The feed material for the 0% DA sample was only swollen with the oil.

![Figure 4.27. DA concentration optimization trials of WT granulates: tensile strength](image)

The sample without DA showed a tensile strength of around 6.2 MPa, and the DPDS reference showed a value of around 7.7 MPa. The highest tensile strength value was around 8.6 MPa in the range of 4% to 6% VP concentration. The strength increased with increasing VP concentration up to 4% and then showed a plateau: with increasing DA concentration the devulcanization efficiency increases, improving tensile strength of the revulcanized sample.

According to Figure 4.28, elongation at break showed the same trend as tensile strength with increasing VP concentration, like seen earlier in this study. Without VP, elongation at break was around 95%, which increased up to 165% in the range of 4% to 6% DA concentration. For the DPDS reference sample, elongation at break was around 130%.
Figure 4.28. DA concentration optimization trials of WT granulates: elongation at break

Figure 4.29. DA concentration optimization trials of WT granulates: network breakdown analysis
As shown in Figure 4.29, with increasing VP concentration the network breakdown increased and the sol content decreased gradually. For the DPDS reference sample, network breakdown was around 57% with 18% sol content. The sample without VP showed a network breakdown around 45% with 26% sol content, which is far above the random scission limit. It proves that without addition of a DA, chain scission is mostly random. However, this does not explain the position of the data points above the random scission line. At 6% DA concentration the network breakdown was around 73% with a sol content of approximately 19%. The increase in network breakdown and reduction in sol content indicates a higher degree of crosslink scission by keeping the main polymer breakdown as low as possible in the presence of an increasing amount of DA: This proves the efficiency of VP as DA. With a VP concentration of 4% and higher, the data points are closer towards the crosslink scission line with a significant network breakdown, which indicates the overall efficiency of the devulcanization process at higher DA concentrations.

![Figure 4.30. DA concentration optimization trials of WT granulates: viscosity](image)

The viscosity of the devulcanized samples decreased gradually with increasing VP concentration, as shown in Figure 4.30. The samples devulcanized without VP showed a viscosity of around 105 MU, and the viscosity got reduced to 74 MU for the samples devulcanized with 6% VP: With increasing DA concentration, the degree of network breakdown increased and the devulcanization process became more efficient. For the DPDS reference sample, the viscosity was around 95 MU.

As seen in Figure 4.31, the particle size distribution shifted towards the finer side with increasing VP concentration. The reference sample and the sample without DA showed a relatively higher number of coarse particles and a total number of visible particles of around 1398 and 1180 respectively.
4.7.8. Discussion on devulcanization aid concentration optimization

Increasing the concentration of VP from 0% to 6% resulted in a higher devulcanization efficiency, but it also led to a decrease in polymer content within the compound, akin to the plasticization effect of oil which reduces mechanical properties above 5% DA concentration. According to literature\(^1\), a sacrifice of 1% in tensile strength is reported for every 1% increase in process oil concentration. However, it is crucial to note that this is a generalized estimate, and the actual impact can vary substantially based on the reference formulation, including the polymer-to-filler ratio and the specific concentration of process oil utilized.

This limitation in tensile strength improvement at higher DA concentrations may be attributed to the delicate balance between increased devulcanization efficiency and reduced polymer content. The presence of natural rubber and carbon black in the feed material likely contributed to the higher values of elongation at break compared to the results obtained with the model compound.

In earlier work\(^2\), an ‘onion peeling mechanism’ was proposed: the devulcanization starts from the outer surface of the particles, which is completely devulcanized and therefore the polymer dissolves resulting in a high percentage of sol content. The core is devulcanized to a lower extent and features a high crosslink density. This combination of a low degree of devulcanization and a high sol content give the data points a position above the random scission line.
With increasing DA concentration, the particles became finer and the total number of visible particles got increased. Additionally, the finer particles got completely devulcanized and are no longer detected, which is the reason for the reduction in total particle number for the samples with 3% to 6% DA. The parameters and the optimized properties achieved in this investigation are summarized in Table 4.4.

### Table 4.4. Optimization summary of process optimization with WT granulates

<table>
<thead>
<tr>
<th>Devulcanization aid</th>
<th>VP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>8.6 MPa</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>162%</td>
</tr>
<tr>
<td>Network breakdown</td>
<td>75%</td>
</tr>
<tr>
<td>Viscosity</td>
<td>75 MU</td>
</tr>
<tr>
<td>Temperature</td>
<td>180°C</td>
</tr>
<tr>
<td>Residence time</td>
<td>6 min</td>
</tr>
<tr>
<td>Process oil</td>
<td>5%</td>
</tr>
<tr>
<td>DA concentration</td>
<td>4-6%</td>
</tr>
<tr>
<td>Rotor speed</td>
<td>150 RPM</td>
</tr>
<tr>
<td>Fill factor</td>
<td>80%</td>
</tr>
</tbody>
</table>

#### 4.7.9. Correlation analysis

The mechanical grinding effect in the early stages of devulcanization resulted in breaking up larger particles and formation of ones with a smaller size, contributing in the increase of the total number of visible particles. The tensile strength of the devulcanizate did not correlate with the total number of particles; the total area of visible particles (TAVP) provided a better indication.

A higher degree of grinding led to a higher TAVP, while devulcanization increases the miscibility, resulting in reduced TAVP. As the degree of devulcanization is an important indicator of the quality of the devulcanizate, a correlation between tensile strength of the revulcanizates and the TAVP of the devulcanizates was established.

The total area of visible particles was measured from the white rubber analysis and correlated with tensile strength of the respective revulcanized samples. As shown in Figure 4.32, a second order equation gave the best fit for the correlation between total area of visible particles versus tensile strength. With a decreasing total area of visible particles, tensile strength improved: Well devulcanized rubber shows better miscibility with the rubber matrix, thus a higher degree of homogeneity. This results in less local differences in modulus, the weak spots within the blend.
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Figure 4.32. Correlation of strength and TAVP

![Graph showing correlation between Tensile strength (MPa) and Total area of visible particles (%) for different factors: Temperature (145°-180°), DA concentration (0%-6%), and Time (4min-7min).](image)

- Temperature (145°-180°): \( y = -0.2x^2 + 0.1x + 8.5 : R^2 = 0.98 \)
- DA concentration (0%-6%): \( y = -0.1x^2 - 0.2x + 8.8 : R^2 = 0.99 \)
- Time (4min-7min): \( y = -0.6x^2 + 1.1x + 8.0 : R^2 = 0.95 \)

Figure 4.33. Overall correlation analysis

![Graph showing overall correlation analysis for the devulcanization process optimization.](image)

- Overall devulcanization process optimization: \( y = -0.3x^2 + 0.2x + 8.5 : R^2 = 0.95 \)
A plateau was reached around 8.5 MPa tensile strength and less than 1.5% total area of visible particles. The correlation coefficient was 0.99 for the series with temperature and DA concentration variation, and the overall variation was 0.95 as shown in Figure 4.33.

4.8. Conclusion of devulcanization process optimization for whole tire granulates

The optimization of the devulcanization parameters revealed an optimal temperature of 180°C, a residence time of 6 minutes, and a rotor speed of 150 rpm. A VP concentration of around 5% resulted in the highest mechanical strength of the revulcanized devulcanizate. Further increases in DA concentration led to increased network breakdown with a reduction in sol content, indicating a higher degree of crosslink scission, but no additional improvement in mechanical properties was noticed due to the plasticization effect.

The TGA analysis highlighted variations in filler type and concentration within the WT granulates compared to the model compound, supporting the observed differences in the results. Factors such as feed type, ageing, and filler variation may contribute to the lower tensile strength of the WT material. The model compound, being SBR-BR based, silica-filled, and unaged, differed from the aged, partially NR-based, and carbon black-filled WT granulates. Higher elongation at break and lower viscosity of the revulcanized WT devulcanizate compared to the model compound can be attributed to the presence of natural rubber.

4.9. References

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Chapter 5

Influence of DA Combinations and DA Components on Devulcanization

Chapter 5 is focused on three key areas:

- Evaluating combinations of devulcanization aids (DAs) to determine if there are additional or synergistic effects.
- Investigating the individual impact of constituents within DA’s as each component individually can play a vital role during devulcanization.
- Assessing devulcanization using peroxides as sole agents, which are integral components of the vinyl silane with peroxide (VP).
5.1 Introduction

This chapter is dedicated to the investigation of three primary aspects. Firstly, it seeks to evaluate the influence of different combinations of DAs on the devulcanization process. Secondly, it delves into a comprehensive exploration of the effects stemming from various constituents within the selected DA. Lastly, it undertakes an examination of devulcanization solely employing peroxides, reported as DA in literature1.

5.2 The effect of DA combinations

In this part of the study, various prospective DAs, individually and in combination, were applied in the devulcanization process of WT rubber granulates. These experiments adhered to the previously established optimized parameters with the intention of further enhancing the quality of the resulting devulcanizate, potentially by synergistic effects arising from the combinations of different DAs.

5.2.1 Experimental process

Preparation of the feed material, sampling plan and characterization processes are described in this section.

5.2.1.1 Preparation of feed material

The feed material preparation was done according to the procedure as described in Chapter 4, Section 4.6.1.

5.2.1.2 Sampling plan

Vinyl silane, polysulphide silanes, and their combinations were selected as potential DAs. The chemical structures of the selected DAs are mentioned in Chapter 3, Figure 3.3. Sample details are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>No.</th>
<th>DA + DA combinations</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>VTEO (5%)</td>
<td>Vinyl silane</td>
</tr>
<tr>
<td>2</td>
<td>TESPT (5%)</td>
<td>Polysulphidic silane</td>
</tr>
<tr>
<td>3</td>
<td>VP (2.5%) + TESPT (2.5%)</td>
<td>Vinyl silane with peroxide + polysulphide moieties</td>
</tr>
<tr>
<td>4</td>
<td>VP (2.5%) + DPDS (2.5%)</td>
<td>Vinyl silane with peroxide + diphenyl disulphide moieties</td>
</tr>
</tbody>
</table>

Figure 5.1. Flowchart of the study up to Chapter 5
All the samples were devulcanized using the same procedure as described in Chapter 3, Section 3.2.2. Revulcanization was done using the formulation detailed in Chapter 3, Section 3.2.1.5.

5.2.1.3 Testing process

The testing process contains four parts:

i. The degree of devulcanization as determined by the Horikx-Verbruggen plot

ii. The stress-strain properties in tensile mode

iii. The homogeneity evaluation by white rubber analysis

iv. The processability of the devulcanizate in terms of viscosity

A detailed description of the first three is given in the Chapter 3, Section 3.2.3.1 to 3.2.3.3. The viscosity measurements are detailed in the Chapter 4, Section 4.6.3.1.

5.2.2 Results

In this section, the stress-strain behaviour, degree of devulcanization, viscosity and homogeneity of above mentioned samples (Table 5.1) are shown.

![Figure 5.2. Further optimization with DA combinations: tensile strength](image)

As shown in Figure 5.2, the sample devulcanized with VP showed the best tensile strength, as did the repeatability sample with the same DA and using the same...
processing conditions: This proves the efficiency of vinyl moieties in a DA. With the newly optimized process conditions, the reference sample showed a comparatively better average tensile strength and smaller variation compared to the samples devulcanized according to earlier elaborated reference conditions: an indication of better homogeneity confirmed also via the white rubber analysis as explained later on in this chapter. The tensile strength values the revulcanizates with all DA and DA combination were in the range of 8 MPa to 9 MPa. As the total DA concentration was kept constant for all the samples, no significant synergistic effect was noticed for the DA combinations.

According to Figure 5.3, elongation at break of the VP devulcanized and revulcanized samples was in the range of 160% to 165%, similar to the repeatability sample. With the newly optimized process conditions, the reference sample showed around 140% in elongation at break and smaller error bars compared to the samples devulcanized under earlier elaborated reference conditions. The TESPT devulcanized sample showed a relatively low elongation at break of around 145%, which can be due to the higher crosslink density of the revulcanized sample by an additional filler-polymer network from the reaction of TESPT with silica as well as with the polymer; and the presence of free sulphur. The VTEO and DA combination resulted in an elongation at break of around 150% to 160% of the revulcanized sample. Moreover, like for the strength it can be concluded that the samples with DA combinations result in an average value of elongation at break between the single DA results.

The results of the viscosity analysis are plotted in Figure 5.4. DPDS devulcanized samples showed lower viscosity when the newly optimized process conditions were applied compared to the samples devulcanized under earlier reference conditions: around 85 to 90 MU. All single DA and DA combination samples showed viscosity values
in the range of 80 to 85 MU. As was noticed for the stress-strain properties, here as well the addition of DA combinations resulted in an average value between the single DA results.

**Figure 5.4. Further optimization with DA combinations: viscosity**

**Figure 5.5. Further optimization with DA combinations: network breakdown**
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The Horikx-Verbruggen plot of the samples is shown in Figure 5.5. VTEO and TESPT devulcanized samples showed a network breakdown of around 60% to 65%, but the sol content was comparatively lower for the VTEO samples. This indicates that a more controlled crosslink scission is possible in presence of vinyl moieties compared to the polysulphide moieties. Considering the crosslink density of the feed granulates, VP devulcanized samples showed a network breakdown of around 70% to 75% similar to the repeatability sample, which shows the efficiency of peroxide and vinyl silane as DA. Using the newly optimized process conditions, the DPDS sample showed around 5% improvement in network breakdown keeping sol content in the same range, which proves a better efficiency compared to the old reference conditions. Here again, the samples with DA combinations result in an average value between the samples containing single DA results.

![Figure 5.5. Horikx-Verbruggen plot of the samples](image)

![Figure 5.6. Further optimization with DA combinations: white rubber analysis](image)

As seen in Figure 5.6, the total number of visible particles and particle size distribution didn’t show a significant difference because the samples were devulcanized under the same process conditions and the molar difference in the DA concentrations were also negligible. When comparing TESPT with VTEO or VP as DA, a variation is noticed in the total number of visible particles, but no significant trend can be drawn for the particle size distributions. The total number of visible particles was the lowest for the VP sample, as completely devulcanized particles got miscible supporting the earlier conclusion that this is the most efficient DA. The total number of particles and the particle size distribution of the samples with the DA combinations was in-between the single DA results.
5.2.3 Discussion

Based on the results obtained for tensile strength and network breakdown, it can be inferred that the vinyl moiety exhibited greater efficiency compared to the disulphide (DPDS) and polysulphide (TESPT) moieties. The effectiveness of vinyl moieties was further enhanced in the presence of the peroxide activator. VP demonstrated the highest efficiency as a DA for the whole tire rubber granulates. The sample devulcanized with DPDS under the newly optimized conditions exhibited a finer remaining particle size than the samples devulcanized under the old reference conditions. This is attributed to the application of a higher temperature and shear forces in the newly developed devulcanization process, resulting in a higher degree of network breakdown.

In the combination of VP and TESPT, vinyl and polysulphide moieties participated in the devulcanization reaction. As a result, the tensile strength of the revulcanized sample was between the tensile strength of the 5% VP and 5% TESPT sample. The same trend was also noticed for the VP and DPDS combination, in which vinyl and phenyl disulphide moieties reacted as DA. The tensile strength of the samples with DA combinations result in general in an average value between the single DA results. The DPDS devulcanized sample showed improvement in stress-strain properties, network breakdown and miscibility when processed under the newly elaborated reference conditions compared to the old reference ones. Elongation at break and network breakdown showed a similar trend compared to the tensile strength: The values of the samples with DA combinations were in-between the single DA results.

5.2.4 Conclusions

VP devulcanized samples showed better mechanical and network breakdown properties than TESPT, VTEO and DA combination samples. The reference sample devulcanized with DPDS under newly optimized conditions showed comparatively better properties compared to the sample devulcanized under the earlier elaborated reference conditions. The properties of the samples containing the DA combinations are in-between the properties of samples with a single DA. DA combinations didn’t show any synergistic effect.

5.3 Peroxide and stabilizer optimization experiments

VP is a combination of vinyl silane (VTEO), dicumyl peroxide (DCP), and butylated hydroxytoluene (BHT) in a specific predetermined ratio. It is noteworthy that VTEO has previously demonstrated efficacy as a proficient devulcanization aid, as documented in Chapter 3. The primary objective of this investigation was to scrutinize the devulcanization effectiveness of peroxide, in conjunction with the stabilizer present within the DA system. These stabilizers are incorporated into the composition alongside peroxides to enhance safety during processes, transportation, and storage.

Within the framework of this investigation, WT rubber granulate underwent devulcanization utilizing vinyl silane and peroxide at varying concentrations. Two distinct peroxides were subjected to screening: DCP as present in VP and benzoyl peroxide (BPO) as an alternative, as depicted in Figure 5.7. The selection of BPO aimed to assess its suitability as a DA activator, according to literature¹ and given its distinct chemical composition featuring benzoyl groups in addition to cumyl groups.
Subsequently, the devulcanized sample exhibiting the best mechanical properties and network breakdown characteristics, among others, was chosen for further optimization through stabilizer trials. In addition to VTEO and peroxides, BHT was incorporated into the system at two varying concentrations. The rationale behind this inclusion was to investigate the role of the stabilizer and to quantify its activity as radical scavenger within the devulcanization reaction.

![Chemical structures](image)

*Figure 5.7. Dicumyl peroxide (left), Benzoyl peroxide (middle), Butylated hydroxy toluene (right)*

### 5.3.1 Experimental process

This section provides a comprehensive overview of the procedures involved in the preparation of the feed material, the establishment of a sampling plan, and the characterization processes.

#### 5.3.1.1 Preparation of feed material

The feed material preparation was done according to the same procedure as described in Chapter 4, Section 4.6.1.

#### 5.3.1.2 Sampling plan for peroxide optimization trials

The optimum processing conditions were selected based on the findings of Chapter 4, Section 4.7. The sampling plan and the process conditions are summarized in Table 5.2. The peroxide weights were adjusted considering the required concentration and concentration in the available products. The product specifications of the peroxides are mentioned in Table 5.3.

**Table 5.2. Sampling plan of peroxide optimization trial**

<table>
<thead>
<tr>
<th>DA combination</th>
<th>DA concentration (w/w)</th>
<th>Fixed parameters</th>
<th>Molar concentration* (w.r.t. 100 g granulates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTEO + DCP</td>
<td>5% VTEO + (0.25/0.4/0.55/0.7)% DCP</td>
<td>180°C temperature 6 min residence time 5% TDAE oil 150 RPM 80% fill factor</td>
<td>26.3 mmol VTEO + (0.92/1.48/2.03/2.59) mmol DCP</td>
</tr>
<tr>
<td>VTEO + BPO</td>
<td>5% VTEO + (0.25/0.4/0.55/0.7)% BPO</td>
<td></td>
<td>26.3 mmol VTEO + (1.03/1.65/2.27/2.89) mmol BPO</td>
</tr>
<tr>
<td>VTEO</td>
<td>5% VTEO</td>
<td></td>
<td>26.3 mmol VTEO</td>
</tr>
<tr>
<td>VP</td>
<td>5% VP</td>
<td></td>
<td>20.2 mmol VTEO + 1.48 mmol DCP</td>
</tr>
<tr>
<td>DPDS</td>
<td>5% DPDS</td>
<td></td>
<td>22.9 mmol DPDS</td>
</tr>
</tbody>
</table>

*The amount was calculated according to the active substance in the blend with the carrier.*
Table 5.3. Peroxide specifications

<table>
<thead>
<tr>
<th>Peroxide name</th>
<th>DCP</th>
<th>BPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical name</td>
<td>Dicumyl peroxide</td>
<td>Benzoyl Peroxide</td>
</tr>
<tr>
<td>Commercial name</td>
<td>Perkadox 14-40B-GR-S</td>
<td>Industrial BPO</td>
</tr>
<tr>
<td>Concentration (%)</td>
<td>40% concentrated powder + 60% clay or inert filler</td>
<td>72% concentrated crystals</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>270.37</td>
<td>242.23</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>130</td>
<td>218</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>41</td>
<td>105</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>71</td>
<td>80</td>
</tr>
<tr>
<td>Self-ignition (°C)</td>
<td>380</td>
<td>526</td>
</tr>
<tr>
<td>Half-life time (min/°C)</td>
<td>6 min at 154°C</td>
<td>6 min at 131°C</td>
</tr>
</tbody>
</table>

5.3.1.3 Sampling plan for stabilizer optimization trial

The best tensile strength and network breakdown properties for both peroxides were found in the DA combination of 5% (w/w) VTEO with 0.7% (w/w) peroxide. These optimized conditions were selected for the stabilizer trial at a variable concentration of BHT. The sampling details of the stabilizer optimization trial are summarized in Table 5.4.

Table 5.4. Sampling plan of stabilizer optimization trial

<table>
<thead>
<tr>
<th>DA combination</th>
<th>DA concentration (w/w)</th>
<th>Fixed parameters</th>
<th>Molar concentration (w.r.t. 100 g granulates)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTEO + DCP + BHT</td>
<td>5% VTEO + 0.7% DCP + (0.25/0.5)% BHT</td>
<td>180°C temperature, 6 min residence time, 5% TDAE oil, 150 RPM, 80% fill factor</td>
<td>26.3 mmol VTEO + 2.59 mmol DCP + (1.14/2.27) mmol BHT</td>
</tr>
<tr>
<td>VTEO + BPO + BHT</td>
<td>5% VTEO + 0.7% BPO + (0.25/0.5)% BHT</td>
<td></td>
<td>26.3 mmol VTEO + 2.89 mmol BPO + (1.14/2.27) mmol BHT</td>
</tr>
<tr>
<td>VTEO + BHT</td>
<td>5% VTEO + 0.5% BHT</td>
<td></td>
<td>26.3 mmol VTEO + 2.27 mmol BHT</td>
</tr>
</tbody>
</table>

5.3.1.4 Testing process

The testing process contains four parts:

i. The degree of devulcanization as determined with the Horikx Verbruggen plot
ii. The stress-strain properties in tensile mode
iii. The homogeneity evaluation by white rubber analysis
iv. The processability of the devulcanizate in terms of viscosity

A detailed description of the first three is given in the Chapter 3, Section 3.2.3.1 to 3.2.3.3. The viscosity measurements are detailed in the Chapter 4, Section 4.6.3.1.

5.3.2 Results

This part contains the graphical representation of the results from two optimization series. The first one is the peroxide optimization trial described in Section 5.3.2.1, and the
second one is the stabilizer optimization trial reported in Section 5.3.2.3. The results will be discussed in Section 5.3.3. of this report.

5.3.2.1 Results of peroxide optimization trials

In Figure 5.8, with increasing concentration of peroxides the tensile strength of the revulcanizate increases gradually. The VTEO concentration was constant at 5% for all peroxide variation samples. With increasing DCP concentration from 0.25% to 0.7%, the tensile strength increases slightly from 8.5 MPa to 8.9 MPa. In the same BPO concentration variation, the tensile strength improves from 8.5 MPa to 9.2 MPa. It was expected and actually is reflected in the results that the sample devulcanized by 0.55% DCP with 5% VTEO shows a similar result compared to the VP devulcanized sample of around 8.8 MPa, as VP is a combination of VTEO and DCP with a concentration ratio close to the one used here. The reference DPDS sample shows a strength of around 8.1 MPa, and for the VTEO sample without peroxide it is approximately 8.5 MPa. Taking into account the error bars, the increase observed is not deemed significant. However, there is an overall trend that can be established based on the results obtained.

![Figure 5.8. Peroxide optimization trials: tensile strength](image)

According to Figure 5.9, with the increasing peroxide concentration from 0.25% to 0.7%, elongation at break increases from 145% to 160% for the VTEO+DCP combination and varies from 135% to 145% for the VTEO+BPO combination. The VP sample shows an elongation at break value of around 165%, followed by the VTEO sample with approximately 152% and the DPDS sample of around 140%.
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Figure 5.9. Peroxide optimization trials: elongation at break

As shown in Figure 5.10, the viscosity of the samples decreases slightly with increasing peroxide concentration. With 0.7% DCP, it reaches around 78 MU and with 0.7% BPO, it is around 74 MU. The viscosity of the VP devulcanized sample is around 80 MU and the DPDS devulcanizate shows a viscosity of around 87 MU.

Figure 5.10. Peroxide optimization trials: viscosity
Figure 5.11. Peroxide optimization trials: network breakdown

The network breakdown and the sol-content percentages of the devulcanizates with increasing peroxide concentrations are plotted in Figure 5.11. The sample devulcanized with 5% VTEO and 0.25% DCP shows a network breakdown of around 65% and a sol content of around 15.8%. It increases up to 73% network breakdown and 19% sol content with 5% VTEO with 0.7% DCP. The same trend is noticed for the BPO devulcanized sample: The network breakdown percentage increases from 62% to 72% and the sol content from 16% to 19.2% with an increasing peroxide concentration from 0.25% to 0.7% BPO with a constant amount of VTEO. The network breakdown and the sol content of the DPDS devulcanized sample are around 62% and 18%, respectively.

According to Figure 5.12, no significant difference in the total number of visible particles is found with increasing concentration of peroxide, but BPO devulcanized samples show a lower total number of visible particles compared to DCP devulcanized samples. For the reference DPDS sample, the total number of visible particles is 1508 and for the VP devulcanized sample it is 1289, which indicates higher miscibility for the VP devulcanized samples compared to the reference DPDS samples.
5.3.2.2 Conclusions

According to the results of Section 5.3.2.1, it can be concluded that the addition of peroxides improved the devulcanization efficiency of the vinyl silane. DCP and BPO both resulted in an improvement in mechanical, visco-elastic and network breakdown properties of the revulcanized and devulcanized rubber respectively with increasing concentration.

5.3.2.3 Stabilizer optimization trials

The best results in terms of mechanical properties and network breakdown within the concentration range of this study are found for the combination of 5% VTEO and 0.7% peroxide. An excessive rise in peroxide concentration may have an adverse effect on the devulcanization effectiveness as it is efficient to split the main polymer chains resulting in degradation of the polymer. This might also lead to the formation of new crosslinks, ultimately increasing the resultant crosslink density instead. In the next step, the stabilizer was additionally included as part of the DA system and comparatively analyzed. VP contains VTEO, DCP and BHT; so far the efficiency of the first two components was investigated. The goal of these experiments is to investigate the effect of BHT as DA and optimize the concentration in the DA system.

As seen in Figure 5.13, with increasing stabilizer concentration, the tensile strength of the revulcanized devulcanizate is not improving, but even decreases to some extent. The same DA combination shows better tensile properties without stabilizer.
Chapter 5

Figure 5.13. Stabilizer optimization trials: tensile strength

As illustrated in Figure 5.14, the elongation at break values of the samples are also reduced with increasing concentration of stabilizer. Without stabilizer, the VTEO+DCP combination shows around 160% in elongation at break, which is reduced to 140% with the addition of 0.5% BHT. The same trend was noticed for the VTEO and BPO combination as well.

Figure 5.14. Stabilizer optimization trials: elongation at break
The Mooney viscosity of the samples is increased by around 3MU to 5MU with the addition of 0.5% BHT, as shown in Figure 5.15. The presence of the stabilizer shows the same trend for both peroxides.

**Figure 5.16. Stabilizer optimization trials: network breakdown analysis**
It can be concluded from Figure 5.16 that with increasing concentration of BHT, the network breakdown and sol content both decrease for the devulcanizates. Around 10% reduction in network breakdown and around 3% reduction in sol content are noted in the presence of 0.5% BHT.

![Figure 5.17. Stabilizer optimization trials: white rubber analysis](image)

In Figure 5.17, the total number of visible particles increases with increasing BHT concentration. Without BHT, the number is around 1250 for VTEO+DCP devulcanized samples, which increases to 1375 with the addition of 0.5% BHT. A similar trend was noticed for the BPO+VTEO combinations.

### 5.3.3 Discussion

According to the results of Section 5.3.2, it can be concluded that the addition of peroxides improved the devulcanization efficiency of the vinyl silane. DCP and BPO both resulted in an improvement in mechanical, visco-elastic and network breakdown properties of the revulcanized and devulcanized rubber respectively with increasing concentration.

At the best devulcanization temperature of 180°C, the peroxide bond of the DCP molecule splits and cumyl moieties including an oxygen radical are formed as shown in Figure 5.18². It can be hypothesized that the active radicals of DCP engage in a chemical reaction with the vinyl silane to produce a more efficient component that facilitates devulcanization. The details of the reaction mechanism still have to be elaborated further.
Similarly, at elevated temperatures, BPO undergoes a homolytic cleavage and forms free benzoyl radicals as shown in Figure 5.19. These radicals have the potential to actively break the bonds and recombine with the reactive fragments from the polysulfide, disulfide and carbon-sulphur linkages which results in an effective devulcanization reaction as shown in Figure 5.20.

As shown in Figure 5.8, the tensile strength of the de- and revulcanized samples increased because the devulcanization efficiency is improved with increasing peroxide concentration. This is further proven in Figure 5.11: the network breakdown percentage is increased with increasing peroxide concentration. A higher degree of network breakdown with higher crosslink to random scission ratio causes more intact free polymer chains which contribute to a higher mechanical strength after revulcanization. Additionally the free polymer chains of the devulcanized sample cause a reduction in viscosity as shown in Figure 5.10. The elongation at break is decreased with increasing
peroxide concentration; this is probably due to the presence of unreacted peroxide which contributes to extra crosslink formation during revulcanization. As the extent of network breakdown increases, the particle size distribution becomes finer, and its miscibility improves as well. For the same concentration, BPO showed a higher degree of network breakdown than DCP, which comparatively results in a higher total number of visible particles in the DCP samples as shown in Figure 5.12.

In order to enhance safety during storage and handling, peroxides are commonly packaged with inert fillers. The use of inert fillers such as clay or calcium carbonate, makes it easier to handle peroxides at room temperature. However, it is not clear whether the presence of inert fillers has any effect on the devulcanization process, as this has not been thoroughly studied. During devulcanization, BPO operates in a liquid form, whereas DCP is in a gaseous state as the operating temperature is above its boiling point. This difference in state between BPO and DCP can potentially impact the migration of peroxides within the rubber granules, leading to a change in the efficiency of devulcanization.

As stated in Section 5.3.2.2, BHT as stabilizer had a negative influence on the devulcanization reaction but it is unavoidable to maintain the storage safety of the peroxides. The stabilizing effect of BHT is based on scavenging the oxygen generated in the decomposition of the peroxides and giving stability to the chemicals as shown in Figure 5.21.

During devulcanization, with the increasing concentration of BHT, free DA radicals got scavenged which results in the reduction of network breakdown efficiency as shown in Figure 5.15. A lower extent of network breakdown percentage caused a lower degree of free devulcanized polymer chains. As a consequence, the mechanical properties of the de- and revulcanized rubber were also poor for samples with a higher stabilizer concentration as shown in Figures 5.13 and 5.14. Due to this insufficient degree of devulcanization, the viscosity increases and the total number of visible particles increases as well as shown in Figures 5.15, 5.16 and 5.17.

5.3.4 Conclusion

Samples devulcanized with VTEO+BPO showed better tensile strength, miscibility and viscosity than VTEO+DCP devulcanized samples. Elongation at break and percentage of network breakdown was higher for the VTEO+DCP devulcanized samples compared to the VTEO+BPO combination. Considering this it can be concluded that along with the DCP+VTEO combination (VP), VTEO+BPO can also be a potential DA.
VTEO with 0.55% to 0.7% DCP concentration showed almost the same results as the VP devulcanized material, because this composition mirrors the original VTEO and DCP proportion of VP. BHT had no significant influence on the devulcanization reaction, but was required for maintaining the chemical stability of the peroxides. To achieve the highest mechanical and network breakdown properties, the best choice would be to leave out the stabilizer or using minimum amounts only for the stability of the mixture.

5.4 Trials with peroxide only as DA

Within this section, the devulcanization process was applied exclusively to oil-swollen WT rubber granulate using varying concentrations of peroxides. The primary objective of this investigation was to examine the devulcanization activity and efficiency of peroxides in the absence of vinyl silane (VTEO). Two specific types of peroxides, namely dicumyl peroxide (DCP) and benzoyl peroxide (BPO), were subjected to scrutiny.

The devulcanization experiments were conducted employing two distinct peroxide concentrations, specifically 2% and 5% w/w relative to the WT granulates. The outcome of these trials were subsequently compared to those achieved when employing VTEO, both in isolation and in combination with peroxides, for the devulcanization process.

5.4.1 Experimental process

This section provides detailed information regarding the preparation of the feed material, outlines the sampling plan, and elucidates the testing processes employed for the experiments involving only peroxides as DA.

5.4.1.1 Preparation of feed material

The feed material preparation was done according to the same procedure as described in Chapter 4, Section 4.6.1.

5.4.1.2 Sampling plan for trials with peroxide only as DA

The optimum processing conditions were selected based on the findings of Chapter 4, Section 4.7. The specifications of the peroxides used in this series are mentioned in Table 5.3 of this Chapter. The sampling plan and the process conditions are summarized in Table 5.5. The samples with VTEO and VTEO with peroxide combinations were not tested separately for these experiments; the results from Section 5.3.2.1 were plotted along with the samples devulcanized with peroxide only.

Table 5.5. Sampling plan with peroxide only as DA

<table>
<thead>
<tr>
<th>DA name</th>
<th>DA concentration (w/w)</th>
<th>Abbreviation</th>
<th>Fixed parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCP</td>
<td>2% and 5%</td>
<td>DCP</td>
<td>180°C temperature</td>
</tr>
<tr>
<td>BPO</td>
<td></td>
<td>BPO</td>
<td>6 min residence time</td>
</tr>
<tr>
<td>VTEO</td>
<td>5% VTEO</td>
<td>VTEO</td>
<td>5% TDAE oil</td>
</tr>
<tr>
<td>VTEO +</td>
<td>5% VTEO + (0.25 &amp; 0.7)% DCP</td>
<td>VTEO-D</td>
<td>150 RPM</td>
</tr>
<tr>
<td>DCP</td>
<td></td>
<td></td>
<td>80% fill factor</td>
</tr>
<tr>
<td>VTEO +</td>
<td>5% VTEO + (0.25 &amp; 0.7)% BPO</td>
<td>VTEO-B</td>
<td></td>
</tr>
</tbody>
</table>
5.4.1.3 Testing process

The testing process contains four parts:

i. The degree of devulcanization as determined with the Horikx Verbruggen plot
ii. The stress-strain properties in tensile mode
iii. The homogeneity evaluation by white rubber analysis
iv. The processability of the devulcanizate in terms of viscosity

A detailed description of the first three properties is given in the Chapter 3, Section 3.2.3.1 to 3.2.3.3. The viscosity measurements are detailed in the Chapter 4, Section 4.6.3.1.

5.4.2 Results

In this section, the stress-strain behaviour, degree of devulcanization, viscosity and homogeneity of above mentioned (Table 5.5) samples are shown.

![Figure 5.22. Trials with peroxide only as DA: tensile strength](image)

According to Figure 5.22, the peroxide with VTEO combination (VTEO-D and VTEO-B) showed significantly better tensile properties than the peroxide only samples. For the latter samples, with increasing peroxide concentration, the tensile strength decreased. For both peroxide devulcanizates, DCP and BPO only, at a concentration of 2% tensile strength was around 5 MPa, which got reduced to 3 MPa when 5% peroxide was used as DA. In the presence of 5% VTEO, when the peroxide concentration increased from 0.25% to 0.7%, an increasing trend in tensile strength was noticed; however, without VTEO the trend was the opposite. The peroxide samples exhibited significant deviations in the measured values attributed to undevulcanized particles. Failures in the samples consistently occurred at the weakest points, and the higher presence of undevulcanized particles in peroxide-devulcanized samples resulted in a greater degree of irregularity, as indicated by larger error bars.
The same trend as for tensile strength was noticed for elongation at break of the samples. In Figure 5.23, the VTEO with peroxide samples showed comparatively better elongation at break than the peroxide only samples. Using VTEO-D with 0.7% DCP showed elongation at break values of around 160%, which got reduced up to 80% when the sample was devulcanized with 2% DCP only and further to 30% with 5% DCP. The same trend as for DCP was noticed for the BPO devulcanized samples.

**Figure 5.23. Trials with peroxide only as DA: elongation at break**

**Figure 5.24. Trials with peroxide only as DA: viscosity**
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The comparative results of the Mooney viscosities of the VTEO with peroxide and peroxide only devulcanizates (2% and 5%) are plotted in Figure 5.24. With 5% VTEO and peroxide concentrations of 0.25% and 0.7%, the viscosity showed a decreasing trend, and the value was around 80MU. For peroxide only devulcanized samples, the viscosity increased up to 100MU with 2% peroxide and reached around 115MU with 5%. DCP and BPO showed the same trend.

Figure 5.25. Trials with peroxide only as DA: network breakdown analysis

According to Figure 5.25, a comparative analysis in terms of network breakdown and sol-content is plotted. The sample with 5% VTEO and 0.7% peroxide showed a network breakdown of around 70%. Without VTEO and an increasing peroxide concentration from 2% to 5%, the network breakdown got decreased to 40% and 22% respectively. The sol content and network breakdown decreased gradually with increasing peroxide concentration. During the devulcanization, peroxides may cause additional crosslink formation which increased the resulting crosslink density of the devulcanizate.

As shown in Figure 5.26, the particle size distribution was shifted with increasing peroxide concentration towards the coarser side. The maximum of the particle size distribution of VTEO with peroxide samples is around 100µm, which shifted to 350µm for 2% peroxide devulcanizates and further increased to 500µm for 5% peroxide devulcanizates.
The tensile strength (TS) and total area of visible particles (TAVP) showed a linear correlation in this process window. As seen in Figure 5.27, the TAVP of the VTEO with peroxide samples, both DCP or BPO, were in the range of 2-3%. TAVP values of the 2% peroxide devulcanized samples were around 5%, and further increased up to 7%.
when 5% peroxide was used as DA. This correlation clearly shows the poor miscibility and mechanical properties of the peroxide-devulcanized samples compared to VTEO with peroxide combinations.

![Figure 5.28. Trials with peroxide only as DA: correlation between network breakdown and total area of visible particles](image)

The decreasing network breakdown of the devulcanizates with increasing peroxide concentration correlates with the decreasing tensile strength of the revulcanized samples as shown in Figure 5.28. The samples devulcanized with VTEO and VTEO with peroxides exhibited values positioned in the top left side of the graph, indicating a high degree of network breakdown and a low TAVP. In contrast, samples devulcanized solely with peroxides showed comparatively lower network breakdown and higher TAVP than the VTEO and VTEO with peroxide combinations. The plots further shifted towards the bottom right corner of the graph with increasing peroxide concentration, signifying low network breakdown and high TAVP.

### 5.4.3 Discussion

During devulcanization with peroxide, the granulated sample (average particle size of 1.5 mm to 2 mm) got further particulated (less than 0.5 mm) and didn’t form a smooth band during milling. The devulcanizate was sticky when the VTEO and peroxide combination was used as DA. To make the powdery sample better processable or to be able to incorporate the curatives in the devulcanizates, for peroxide only samples milling was done for a longer time compared to the other silane devulcanized samples. With the increasing concentration of peroxides, the particle size distribution of the undevulcanized particles shifted towards the coarser side, which indicates a lower extent of devulcanization. That may cause decreasing mechanical properties of the revulcanized samples with increasing peroxide concentration (Figure 5.22). The image of the peroxide only and the VTEO devulcanized sample are shown in Figure 5.29.
Figure 5.29. 5% DCP devulcanized (left) and 5% VTEO devulcanized sample (right)

The large undevulcanized particles caused a two-phase system; undevulcanized or additionally crosslinked particles distributed in a partially devulcanized matrix; this can be the reason for increased viscosity of the peroxide devulcanizates. Variation in the quantity of undevulcanized solid particles and the viscous devulcanized phase lead to alterations in the hydrodynamic effect, consequently inducing variations in viscosity. Another effect is a recombination or network formation facilitated by peroxides, which can mitigate the network breakdown resulting in a rather high final crosslink density. The correlation of TS and TAVP shows the insufficient devulcanization of peroxide samples compared to the silane with peroxide combinations.

Figure 5.30. Schematic devulcanization mechanism with peroxide with vinyl silane

During devulcanization, the vinyl silane and the polymer will go through a chain transfer reaction, in which the vinyl moiety gets attached to the crosslink fragments and restricts further recombination. The peroxide initiator improved the reactivity of the vinyl silane during the devulcanization reaction: peroxidic bonds will break and activate the vinyl moieties. This activation of the vinyl silane results in a higher devulcanization efficiency as shown in Figure 5.30.
5.4.4 Conclusions

Peroxide can be used as an efficient DA for saturated rubber like EPDM as shown by the study of Dijkhuis\textsuperscript{4}, but peroxide solely is not efficient as DA for unsaturated polymer systems like natural rubber or styrene butadiene rubber compounds. It results in crosslinking of the polymer network, and thus hinders the devulcanization reaction. The resulting crosslink density of the devulcanizate indicates an insufficient reduction in crosslink density. The combination with a vinyl silane increases the devulcanization efficiency; the peroxide alone does not increase the devulcanizate quality. It can be concluded that peroxide alone is not suitable as DA, a radical scavenger is needed.

5.5 References

CHAPTER 6

CHARACTERIZATION OF THE DEVULCANIZATION MECHANISM

In this chapter, an investigation of the devulcanization reaction mechanism involving vinyl silane (VTEO) and Vinyl silane with Peroxide (VP) was conducted. This investigation employed a Liquid Model Compound (LMC) derived from Liquid Polybutadiene Rubber (LBR) and applied Fourier Transform InfraRed spectroscopy (FTIR), Gas Chromatography (GC), and Proton Nuclear Magnetic Resonance (1H-NMR) for in-depth analysis.
6.1 Introduction

Figure 6.1. Flowchart of the study up to Chapter 6

VP is a blend of additives comprising a vinyl silane (VTEO) in a concentration of 88% to 90% combined with dicumyl peroxide (DCP) with approximately 8-10%, and butylated hydroxy toluene (BHT) in a concentration of around 1-2%. The research findings of Chapter 5 indicated that increasing the DCP concentration from 0.25% to 0.55% in the presence of 5% VTEO led to an enhancement in devulcanization efficiency. The inclusion of stabilizers did not exert a significant influence on the devulcanization reaction. These results raised inquiries regarding the devulcanization potential of peroxides in the absence of VTEO. The investigation of in Chapter 5, Section 5.4 demonstrated that the use of peroxide solely as DA ultimately increased the crosslink density of the devulcanizate, resulting in insufficient devulcanization. Conversely, when peroxide was added in conjunction with vinyl silane, it augmented the efficiency of the devulcanization process.

The primary objective of this investigation was to elucidate the devulcanization reaction mechanism of VTEO and VP. This was achieved by preparing a liquid model compound (LMC) through the compounding of liquid polybutadiene rubber (LBR) with curatives, followed by treatment with VP for devulcanization. The reaction mechanism was characterized using Fourier transform infrared spectroscopy (FTIR). Additionally, a comprehensive characterization of the liquid model compound (LMC), also in devulcanized state, and VP was done by gas chromatography (GC). The study sought to assess the structural alterations within the polymer as a result of the devulcanization process. Furthermore, the decomposition of VP at 180°C was examined by GC and proton nuclear magnetic resonance (1H-NMR).

6.2 Hypothesis for the reaction mechanism

In order to explore the devulcanization mechanism, a working hypothesis was formulated to investigate the reaction involving VTEO, peroxide and VP, and subsequent characterizations were conducted in accordance with this hypothesis.

6.2.1 Devulcanization mechanism with VTEO

The chemical structure of VTEO is illustrated in Figure 6.2. The proposed reaction mechanism is that the vinyl silane and the polymer will react and go through a radical addition reaction, in which the vinyl moiety gets attached to the broken crosslinks and main polymer chains, thus restricts further recombination as shown in Figure 6.3 and Figure 6.4.
Chapter 6

Figure 6.2. Chemical structure of VTEO

Figure 6.3. Breakdown of the polymer crosslinks and main polymer chains

Figure 6.4. Radical addition reaction between vinyl silane with polymer crosslinks (a) and main polymer chains (b)
Chapter 6

After the radical addition reaction, the molecule goes through a disproportion reaction to achieve higher chemical stability. The activator in the vinyl silane improves the reactivity of the latter during devulcanization as shown in Figure 6.5.

![Disproportionation reaction of the addition product of vinyl silane and sulphur](image)

**Figure 6.5. Disproportionation reaction of the addition product of vinyl silane and sulphur**

### 6.2.2 Devulcanization mechanism with DCP

As a consequence of mechanical shear and elevated temperatures, the occurrence of thermal and mechanical breakdown of crosslinks takes place. During devulcanization, DCP splits up at the peroxide moiety, leading to the formation of acetophenone and generating a highly reactive methyl radical as shown in Figure 6.6. Although the reactive methyl radical could attack a crosslink and thus initiate devulcanization, in actual practice this happens only to a small extent. The methyl moiety is highly reactive and reacts preferably with unsaturated double bonds, recombines with broken crosslinks or creates additional crosslinks. This has been concluded based on the results of Chapter 5.

### 6.2.3 Devulcanization mechanism with VP

According to Figure 6.6, due to thermal decomposition, splitting of DCP resulted in acetophenone and a methyl radical. The active methyl radical reacts with the vinyl moieties to create a comparatively more stable secondary radical than the primary radical generated form VTEO. At the devulcanization temperature, this radical reacts with radicals from broken crosslinks, thereby inhibiting recombination and resulting in a net lower crosslink density as shown in Figure 6.7.
Figure 6.6. Decomposition of DCP and activation of VTEO

Figure 6.7. Radical addition reaction with VP

DCP is dissolved in the VTEO matrix, due to the interaction of the vinyl moiety and the methyl radical there is a high likelihood of activation of vinyl moieties by the latter. However, an alternative reaction pathway is also possible. The highly active methyl radicals can directly react with the broken crosslinks or the main polymer chain as shown in Figure 6.8. Additionally, they may attack the unsaturated polymer backbone.

Figure 6.8. Radical addition reaction of methyl radical with polymer crosslinks and main polymer chains

6.3 Experimental process
This section contains four parts:
a. Preparation of the liquid model compound (LMC)
b. Devulcanization of the cured LMC
c. Decomposition of VP
d. Characterization process

6.3.1 Preparation of LMC

The LMC was prepared using liquid polybutadiene rubber and curatives as mentioned in Table 6.1. Mixing was done by a mechanical stirrer, and the mixing temperature was maintained at 80±5°C.

<table>
<thead>
<tr>
<th>Function</th>
<th>Component</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Polymer</td>
<td>Liquid polybutadiene (LBR)</td>
<td>100</td>
</tr>
<tr>
<td>Activators</td>
<td>Zinc oxide</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Vulcanization agent</td>
<td>Sulphur</td>
<td>2</td>
</tr>
<tr>
<td>Accelerator</td>
<td>CBS</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6.1. LMC formulation

After mixing, the compound was kept for 4 hours in a vacuum oven at 160°C for curing. The cured model compound had a jelly-like consistency.

6.3.2 Devulcanization of the cured LMC

The cured LMC was devulcanized by a thermo-mechano-chemical process. 5% VP was added as DA, and devulcanization was done by mechanical stirring at 160°C for 8 to 10 minutes. The jelly-like model compound became less viscous with a honey-like consistency.

6.3.3 Decomposition of VP

VP was encased within an airtight glass vial and subjected to 20 minutes heating at 180°C in an hot air oven, after which the sample was allowed to cool down to room temperature for a duration of 2 hours, followed by subsequent analytical assessments.

6.3.4 Characterization process

The samples were characterized in three ways:

6.3.4.1 FTIR: according to the procedure described in Chapter 3, Section 3.2.3.4.

6.3.4.2 Gas Chromatography (GC)

GC was conducted in a GC 2010 Plus instrument, manufactured by Shimadzu, Japan. The testing parameters employed were as follows:

i. Temperature – 320°C
ii. Air flow – 400 mL/ min
iii. H₂ flow – 40 mL/min
iv. Duration – 39 min

For the analysis, the sample was dissolved in acetone of GC-grade quality at a concentration of 1% (w/w) and subjected to testing using the aforementioned parameters.
6.3.4.3 Proton Nuclear Magnetic Resonance (\(^1\)H-NMR)

\(^1\)H-NMR analysis was conducted using an automated spectrometer manufactured by Bruker, Germany. Deuterated chloroform served as solvent, with the sample being introduced as a minute droplet and subsequently diluted with 1 ml of the solvent. The proton \(^1\)H-NMR test equipment was operated at a frequency of 300 MHz, and data analysis was carried out using the MestReNova software.

6.4 Results and discussion

This section contains three parts: FTIR, GC and \(^1\)H-NMR results analysis.

6.4.1 FTIR analysis

To characterize the devulcanization reaction of the LMC, the latter, VP and the VP devulcanized LMC were analyzed separately by Fourier Transform Infrared Spectroscopy (FTIR). The spectrum was analyzed from 4000 cm\(^{-1}\) to 650 cm\(^{-1}\), but the significant findings were noted between 2000 cm\(^{-1}\) to 650 cm\(^{-1}\).

![Figure 6.9. FTIR spectroscopy of LMC, VP and LMC devulcanize (LMC-DV-VP)](image)

In the spectral plot of Figure 6.9, the yellow line corresponds to the peaks of the LMC, while the blue and orange lines represent VP and VP devulcanized LMC, respectively. Notably, three new peaks were observed in the devulcanized material compared to the original LMC; specifically, the peak at 1738 cm\(^{-1}\) representing the C=O stretching of aldehydes or esters, typically found between 1720 cm\(^{-1}\) and 1740 cm\(^{-1}\). The peak at 1368 cm\(^{-1}\) represents the O-H bending of alcohol or phenol, typically observed between 1330 cm\(^{-1}\) and 1420 cm\(^{-1}\). Lastly, the peak at 1216 cm\(^{-1}\) corresponds to the C-O stretching of ethers, esters or alcohol, usually found between 1130 cm\(^{-1}\) and 1225 cm\(^{-1}\) as mentioned in FTIR data table of Sigma-Aldrich\(^1\).
Compared to VP, certain peaks were found to be absent in the spectra of the devulcanizate, indicating the involvement of VP in the devulcanization reaction: The peak observed at 1164 cm\(^{-1}\) corresponds to the C-O stretching of ester groups, typically detected within the range of 1163 cm\(^{-1}\) to 1210 cm\(^{-1}\). Likewise, the peak at 1075 cm\(^{-1}\) corresponds to the C-O stretching of tertiary alcohols, generally observed between 1124 cm\(^{-1}\) and 1205 cm\(^{-1}\). The peaks at 955 cm\(^{-1}\) and 1010 cm\(^{-1}\) represent the C=C bending of mono-substituted alkenes, which are typically found within the range of 925 cm\(^{-1}\) to 1025 cm\(^{-1}\). Lastly, peaks at 755 cm\(^{-1}\) and 780 cm\(^{-1}\) indicate the C=C bending of di- and tri-substituted alkenes, commonly found within the range of 730 cm\(^{-1}\) to 790 cm\(^{-1}\) as mentioned in FTIR data table of Sigma-Aldrich\(^{1}\).

Devulcanization is primarily breakdown of bonds by heat or shear followed by a chain transfer reaction to restrict the recombination, which does not typically result in the formation of new moieties in the final product to be identified for proof of the reaction mechanism; however, new molecules from a side reaction can be identified and thus confirm the occurrence of the main reaction. In this study, the dicumyl peroxide radical was assumed to react with the active hydrogen radical generated by the disproportionation reaction of the devulcanization process (as shown in Figure 6.5 and 6.7) to form an alcohol, as shown in Figure 6.10. The absence of certain peaks in the devulcanized-LMC compared to pure VP, as well as the appearance of new peaks in devulcanized-LMC when compared to LMC, indicates the occurrence of a side reaction. This side reaction as illustrated in Figure 6.10. can only take place if the primary reaction: devulcanization as shown in Figure 6.5. and 6.7., is also happening, thereby providing support for the devulcanization reaction mechanism.

![Figure 6.10. Side reaction of active moieties with dicumyl peroxide radicals](image)

### 6.4.2 GC analysis

In Figure 6.11, a comparative GC spectra was generated individually for each of the ingredients used in the preparation of the LMC. Acetone was employed as solvent, and VP was utilized as the DA in this investigation.

Zinc oxide and sulphur did not exhibit any discernible peaks under the test conditions. In contrast, stearic acid displayed two distinct peaks in the chromatogram, one occurring around the 19-minute mark and another around the 21-minute one. This observation
can be attributed to the inherent differences in thermal stability between the hydrocarbon chain and the carboxylic end group present in the structure of stearic acid. Furthermore, a peak was detected for the accelerator CBS at approximately 23 minutes.

![Figure 6.11. Study of the devulcanization mechanism: gas chromatograph of model compounding ingredients](image)

Multiple peaks were observed for the liquid BR (liquid polymer) during the analysis. The variation in polymer chain length within the liquid polymer was identified as the primary factor contributing to this peak height and time variation. These peaks were distributed across a range of 21 to 35 minutes, depending on the polymer chain length. When considering the average distribution of polymer chains, the major peak distribution was found to occur between 26 to 30 minutes. It can be inferred that polymers with shorter polymer backbones exhibited earlier peaks, typically around 21 to 26 minutes, while those with longer polymer backbones displayed peaks between 30 to 35 minutes.

Around the 5 to 6-minute mark, a peak was observed for VP, likely attributed to the formation of acetophenone. At the test temperature of the GC measurement, the decomposition of DCP, an additive in VP, led to the generation of acetophenone. Additionally, at this temperature, a significant portion of VP’s vinyl silane component may have undergone dimerization or oligomerization, resulting in the peak observed around 17 minutes. Subsequent characterization studies were conducted on VP, decomposed VP, and acetophenone using both GC and 1H-NMR techniques to gain a clearer understanding of these compounds.
As depicted in Figure 6.12, comparative GC spectra were generated for the solvent (acetone), uncured LMC, cured LMC, and devulcanized LMC. At approximately 1 minute into the analysis, solvent evaporation occurred, resulting in a prominent peak at 1 minute for all the samples. In the case of the cured model compound (represented by the grey line), no significant peaks were observed, primarily because the crosslinked structure remained mostly intact and did not decompose under the specified test conditions as mentioned in Section 6.3.4.2. A series of minor peaks, detected beyond the 30-minute mark, can be attributed to degradation of the smaller, unbound polymer chains within the crosslinked matrix.

Conversely, the uncured model compound (indicated by the green line) comprised liquid polymers, zinc oxide, CBS, and sulphur, while zinc oxide and sulphur exhibited no discernible spectra when tested separately. This observation suggests that the primary contribution to the peaks in the uncured LMC arose from the presence of free polymer chains of LBR, which displayed the highest concentration of peaks due to the unperturbed state of the polymer chains before compounding.

A similar pattern was observed in the devulcanized LMC when compared to the uncured LMC. In comparison to the cured LMC, the peaks in the devulcanized LMC increased in intensity, indicating the presence of free polymer chains along with small network fragments. Additionally, a few additional peaks were detected, attributed to contributions from VP. Notably, the intensity of the peaks in the devulcanized LMC was relatively lower than that in the uncured LMC. This discrepancy suggests that, even after devulcanization, a part of the crosslinked structure persisted, limiting the complete liberation of polymer chains. That proves the efficiency of the devulcanization reaction in the specified system.
Figure 6.13. Characterization of the devulcanization mechanism: gas chromatograph of acetone, acetophenone, VP, and decomposed VP

Figure 6.13, illustrates the comparative GC spectra of VP, decomposed VP, acetophenone and the pure solvent (acetone). VP primarily comprises vinyl tri-ethoxy silane (VTEO) and dicumyl peroxide (DCP). In case of VP, two distinct peaks appeared at approximately 6 minutes and 17 minutes. For decomposed VP, two distinct peaks emerged at approximately 6 minutes and 23 minutes. It was hypothesized that the peak around 6 minutes corresponds to the decomposition of DCP into acetophenone. To validate this hypothesis, a pure acetophenone sample was analyzed, and the overlapping spectra confirmed the presence of acetophenone in the decomposed VP. Furthermore, during decomposition, VTEO as part of VP underwent oligomerization and exhibited delayed evaporation resulting the shift in the peaks from 17 minutes to 23 minutes.
Figure 6.14. Reaction scheme of VP

Decomposition of DCP present in VP leads to the formation of acetophenone and an active methyl radical, which actively participates in the dimerization and oligomerization of vinyl silane present in VP as illustrated in Figure 6.14. To substantiate the validity of these proposed structures, $^1$H-NMR analysis was conducted.

6.4.3 $^1$H-NMR analysis

The contribution to the $^1$H-NMR peaks of VP was attributed to the presence of the vinyl silane, as depicted in Figure 6.15. A pronounced peak at 1.39 ppm substantiated the existence of hydrogens attached to the primary carbons within the ethoxy silane groups, while the peak at approximately 3.83 ppm confirmed the presence of hydrogens attached to the secondary carbons of the ethoxy group. Peaks falling within the range of 5.2 to 5.4 ppm provided confirmation of the presence of the vinyl group.
Figure 6.15. $^1$H-NMR spectra of VP

The peaks in the range of 7.17 to 7.54 corroborated the presence of DCP. Furthermore, the presence of BHT led to additional peaks in the spectrum, while some peaks remained unidentified.

Figure 6.16 depicts the $^1$H-NMR spectra of decomposed VP, accompanied by structures illustrating the key components. The peak observed at 1.39 ppm corresponds to the presence of hydrogen atoms attached to primary carbon atoms within the ethoxy moieties found in the vinyl silane portion of VP. Likewise, the peak at 3.83 ppm signifies the presence of hydrogen atoms attached to secondary carbon atoms within these ethoxy moieties.
Figure 6.16. $^1$H-NMR spectra of decomposition of VP

Comparing the $^1$H-NMR spectra of VP and decomposed VP, the disappearance of peaks within the range of 5 ppm to 5.5 ppm provides conclusive evidence of dimerization and oligomerization reactions occurring within the vinyl moieties. These reactions involve the conversion of double bonds into stable single bonds, as evidenced by peaks in the range of 1 ppm to 1.17 ppm. The primary hydrogens attached to the ethyl side group contribute to the appearance of a peak at approximately 0.87 ppm.

Additionally, peaks ranging from 7.45 ppm to 7.96 ppm suggest the presence of hydrogen atoms attached to the benzene ring within acetophenone and oxidized BHT. A distinct peak at approximately 10 ppm confirms the oxidation of BHT.

6.5 Conclusions

A reaction mechanism for the two different DAs, VTEO (vinyl silane) and VP (vinyl silane with peroxide), was proposed. The main devulcanization reaction was a radical addition reaction, in which the broken polymer crosslinks combined with the active DA radical.

FTIR characterization of the feedstock and devulcanizates was performed using liquid model compounds, including the analysis of the side products. This study has successfully provided proof of the devulcanization reaction mechanism as illustrated in Figure 6.4 and 6.5, using both VTEO and VP.
GC provides a clear insight into the devulcanization mechanism attributed due to the presence of VP. The concurrent evaporation times observed in the GC spectra for devulcanized LMC and uncured LMC serve as compelling evidence for the effectiveness of the decrosslinking or devulcanization process at the polymeric level.

Both GC and $^1$H-NMR analyses conducted on VP and decomposed VP not only elucidate the structural composition of VP, but also affirm the existence of dimerized and oligomerized structures within the decomposed VP.

6.6 References

1. IR spectrum table of Sigma Aldrich: accessed on 09.04.2023
In this chapter, the devulcanization of passenger car tire rubber granulates was carried out using the most effective devulcanization aid (DA), while varying the process additive. The primary aim of this investigation was twofold: firstly, to ascertain the impact of different process additives on the devulcanization process, and secondly, to identify a superior process additive for optimizing the devulcanization.
7.1 Introduction

The objective of this investigation was to determine the effect of various process additives replacing TDAE oil in the devulcanization process. The processing parameters used in this study have previously been optimized with TDAE oil. Four different alternative process additives were screened at two different concentrations, namely:

1. Sunflower oil (SO)
2. Liquid polybutadiene rubber (LBR)
3. Silane terminated liquid BR (SLBR)
4. Poly-octenamer (PO)

In one series of experiments, the process additives were separately added to the feed material before devulcanization in order to elaborate their effect on the process and product. In a second series, they were added to the devulcanizate. The impact of these additives was evaluated based on network breakdown and viscosity of the devulcanizates, mechanical properties of the revulcanizate, and miscibility as determined by the white rubber analysis. The primary goal of this investigation was to identify the most effective additive for improving the quality of the devulcanizate.

7.2 Experimental process

Preparation of the feed material, selection of the additives, sampling plan and characterization processes are described in this section.

7.2.1 Preparation of feed material

The feed material preparation was done according to the procedure described in Chapter 4, Section 4.6.1.
### 7.2.2 Selection of the process additives

Five different additives and the reasoning for their selection are given in Table 7.1.

**Table 7.1. Details of the selected additives**

<table>
<thead>
<tr>
<th>Name (Notation)</th>
<th>Trade name</th>
<th>Supplier</th>
<th>Chemical structure</th>
<th>Reasons</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDAE oil</td>
<td>Vivatech</td>
<td>H &amp; R</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>1. High thermal stability: boiling point around 450°C, which was expected to provide sufficient stability during the devulcanization process. 2. High compatibility with NR, SBR and BR: ease of migration into the granules.</td>
</tr>
<tr>
<td>Sunflower oil (SO)</td>
<td>AH Zonne bloem olie</td>
<td>Albert Heijn</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>1. Low viscosity: facilitates the migration of additives into the granules. 2. High thermal stability: boiling point of 320°C. 3. A sustainable bio oil, compatible with NR, SBR and BR.</td>
</tr>
</tbody>
</table>
Liquid BR (LBR) | Polyvest | Evonik | 1. Effectiveness of liquid rubbers as process additives.  
2. It was anticipated that the use of LBR as an additive would result in the formation of additional crosslinks with the polymer during revulcanization, leading to enhanced mechanical properties of the revulcanizate³.

Silane terminated liquid BR (SLBR) | Polyvest ST | Evonik | 1. Similar to LBR.  
2. Additionally the expectation that the silane-terminated functionalized LBR would improve polymer-filler interaction⁴.

Poly-octenamer (PO) | Veste-namer | Evonik | 1. The viscosity of PO varies with temperature, being solid at room temperature and having a viscosity of approximately 10 MU at 100°C. The melting point is 55.6°C, so the liquid physical state of PO at the devulcanization temperature is expected to facilitate migration⁵.  
2. PO was selected for its high temperature stability⁵.  
3. Similar to LBR, the expectation was that PO would form additional crosslinks during revulcanization.

All samples were devulcanized by maintaining the same procedure as described in Chapter 3, Section 3.2.2. They were revulcanized using the formulation as given in Chapter 3, Section 3.2.1.5.
7.2.3 Sampling plan for additive screening experiments

The sampling plan for the additive screening experiments is given in Table 7.2.

**Table 7.2. Sampling plan of additive screening experiments**

<table>
<thead>
<tr>
<th>Process additives</th>
<th>TDAE</th>
<th>SO</th>
<th>LBR</th>
<th>SLBR</th>
<th>PO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (w/w)</td>
<td>5% &amp; 10% (w/w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before devulcanization</td>
<td>Additives are mixed directly before devulcanization</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 hours pre-swelling</td>
<td>6 hours at room temperature</td>
<td>6 hours at 80°C#</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 day pre-swelling</td>
<td>1 day at room temperature</td>
<td>1 day at 80°C#</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After devulcanization</td>
<td>Additives are compounded with the devulcanizate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constant parameters</td>
<td>Feed material: Genan WT granulates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Temperature: 180°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Residence time: 6 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Shear rate: 150 RPM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fill factor: 80%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>VP concentration: 5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# The melting temperature of PO is 55.6°C, rendering it in a solid state at room temperature at which swelling was not feasible. Therefore, a temperature higher than the melting point was employed for the swelling process.

7.2.4 Testing process

The testing process consists of four parts:

i. Stress-strain properties in tensile mode.

ii. Degree of devulcanization as determined by the Horikx Verbruggen plot.

iii. Homogeneity evaluation by white rubber analysis.

iv. Processability of the rubber in terms of viscosity.

A detailed description of the first three is given in Chapter 3, Section 3.2.3.1 to 3.2.3.3. The viscosity measurements are detailed in the Chapter 4, Section 4.6.3.1.

7.2.4.1 Correction of the sol content

The sol content of the devulcanizate was determined by the weight reduction observed during THF extraction. For the devulcanized samples with oil addition, the latter gets extracted with acetone; for the polymeric additives (LBR, SLBR, and PO), it was not extracted with this polar solvent. Therefore, for the devulcanized samples with oil addition, only the smaller polymer chain fragments were measured by THF extraction: sol content. For polymeric additives, the latter was also removed in the sol using THF extraction, resulting in a higher extractable content which was not related to polymer fragments generated by random chain scission. To address this, a sol-correction was performed using the following procedure:

1. 100% of a known amount of the additive was extracted using the same procedure (acetone and THF) as used for the devulcanizate.
2. The weight reduction during acetone and THF extraction was recorded.
3. The samples were tested for each additive to get an accurate average result.

The details are explained in Table 7.3.

**Table 7.3. Sol content measurement for 100% polymeric additive samples**

<table>
<thead>
<tr>
<th>Additive</th>
<th>No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO</td>
<td>1</td>
<td>1.56</td>
<td>2.11</td>
<td>3.67</td>
<td>3.50</td>
<td>0.17</td>
<td>1.67</td>
<td>1.83</td>
<td>86.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.68</td>
<td>2.00</td>
<td>3.69</td>
<td>3.49</td>
<td>0.20</td>
<td>1.73</td>
<td>1.75</td>
<td>87.60</td>
<td>86.85</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.83</td>
<td>2.09</td>
<td>3.92</td>
<td>3.73</td>
<td>0.19</td>
<td>1.93</td>
<td>1.80</td>
<td>86.17</td>
<td></td>
</tr>
<tr>
<td>LBR</td>
<td>1</td>
<td>1.56</td>
<td>2.01</td>
<td>3.57</td>
<td>3.33</td>
<td>0.24</td>
<td>1.61</td>
<td>1.72</td>
<td>85.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.67</td>
<td>2.03</td>
<td>3.71</td>
<td>3.50</td>
<td>0.20</td>
<td>1.74</td>
<td>1.76</td>
<td>86.48</td>
<td>85.81</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.81</td>
<td>2.07</td>
<td>3.88</td>
<td>3.69</td>
<td>0.19</td>
<td>1.92</td>
<td>1.77</td>
<td>85.50</td>
<td></td>
</tr>
<tr>
<td>SLBR</td>
<td>1</td>
<td>1.59</td>
<td>2.06</td>
<td>3.65</td>
<td>3.46</td>
<td>0.19</td>
<td>1.69</td>
<td>1.77</td>
<td>86.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.73</td>
<td>2.09</td>
<td>3.82</td>
<td>3.59</td>
<td>0.23</td>
<td>1.79</td>
<td>1.80</td>
<td>86.13</td>
<td>85.76</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.81</td>
<td>2.05</td>
<td>3.86</td>
<td>3.65</td>
<td>0.21</td>
<td>1.91</td>
<td>1.74</td>
<td>85.01</td>
<td></td>
</tr>
</tbody>
</table>

For example: 2.090 g PO was extracted with acetone for 2 days, and after extraction the weight was 2.002 g. The sample was further extracted with THF for 3 days and the residue was only 0.201 g: the weight reduction due to THF extraction is 86.17%. After averaging the results from the five samples, the weight loss percentage of THF extraction was 86.48%. The same procedure was followed for LBR and SLBR, and the weight reduction during THF extraction was 85.80% and 85.76% respectively.

The sol content in the devulcanizate was assessed based on the observed weight reduction during THF extraction as mentioned in Equation 1. The sol content of the devulcanizate was corrected by subtracting the weight contribution from the additive part as mentioned in Equation 2.

\[
S_{DV-O} = W_{R-THF}
\]  
\[
S_{DV-P} = [W_{R-THF} - (P \times W_{R-P} / 100)]
\]

\( S_{DV-O} \) = Sol content of devulcanized sample with oil
\( W_{R-THF} \) = Weight reduction by THF extraction
\( S_{DV-P} \) = Sol content of devulcanized sample with polymeric additive
\( P \) = Polymeric additive percentage (LBR, SLBR, PO at 5% and 10%)
\( W_{R-P} \) = Weight reduction of 100% polymeric additive during THF extraction (values mentioned in column I of Table 7.3).
For example, for the devulcanizate with 5% PO, the sol content was 21.4% including the contribution from the additive. So the correction was \( [21.4 - (5 \times 86.48/100)]\% = 17.1\% \). Similarly for 10% SLBR samples with 23.8% sol content, the correction was \( [23.8 - (10 \times 85.76/100)] = 15.2\% \). The Horikx-Verbruggen plot was drawn using to the corrected sol content results.

### 7.3 Results and discussion

In this section, the stress-strain behaviour, degree of devulcanization, viscosity and homogeneity of the above mentioned (Table 7.1) samples are shown.

![Figure 7.2. Additive screening experiments: tensile strength](image)

Figure 7.2. illustrates the comparison of the tensile strength values of additive samples that underwent devulcanization through four different methods of process additive addition:

i. Direct addition
ii. 6 hours pre-swollen
iii. One day pre-swollen
iv. Compounded after devulcanization

For all samples, in terms of tensile strength, the use of a process additive at a concentration of 5% results in a higher tensile strength compared to not using any one. Considering the average tensile strengths, surprisingly, the addition of 5% additive yields a slightly higher result compared to 10% additive in all cases, probably due to nip slippage at higher additive concentration. An exception was noticed for PO: devulcanized samples containing 10% additive showed higher tensile strength compared to the 5% ones. This might be due to the formation of additional crosslinks from the unsaturated double bonds present in the PO.
SO and TDAE oil addition results in a comparable tensile strength, lower than the one of the other additives. PO addition results in a similar level of tensile strength compared to both LBR types (LBR and SLBR), and these three additives resulted in a higher tensile strength compared to oil addition (TDAE and SO).

The comparison of the tensile strength of the samples pre-swollen for one day before devulcanization compared to six hours indicates similar results. This suggests that a six-hour pre-swelling duration is long enough to achieve sufficient process additive migration resulting in similar levels of network breakdown.

The results of the compounding (addition after devulcanization) of oils (TDAE and SO) show that as the concentration of additive increases, the tensile strength decreases. This may be attributed to plasticization and dilution of the polymer. During the compounding of polymeric additives (PO, LBR & SLBR), the results suggest a slight improvement in tensile strength with the increasing additive concentration. These additives contain a long unsaturated polymeric backbone, and this effect can be due to the formation of an additional polymeric network during curing.

![Figure 7.3. Additive screening experiments: elongation at break](image)

In Figure 7.3, the elongation at break values increased for the 5% additive samples compared to the no additive samples, but decreased with further increase in additive concentration, except for the sample containing PO. This is due to the solid physical state of PO at room temperature making the devulcanizate stiffer, thus resulting in poor elongation at break. Ranking the additives based on their elongation at break performance, SLBR is the best, followed by LBR, TDAE, sunflower oil, and PO, respectively.
The swelling time variation and compounding of LBR and SLBR showed similar trends in elongation at break results when compared to tensile strength. The samples devulcanized in presence of PO and SLBR showed almost similar tensile strength, but significant differences in elongation at break. The stress-strain curves of the samples with 5% PO or SLBR are plotted in Figure 7.4. The lower elongation at break for PO compared to SLBR can be attributed to different factors: PO is solid at room temperature, resulting in a stiffer material with lower elongation, as explained above. On the other hand, SLBR exhibited a higher elongation at break due to the lower viscosity of liquid rubber at room temperature.

![Figure 7.4. Comparative stress-strain properties: PO vs SLBR as additive](image)

In Figure 7.5, the samples devulcanized with 5% additive showed higher viscosity compared to those devulcanized with 10% additive, which is attributed to the liquid physical state of the additives at the test temperature of 100°C. Moreover, the samples devulcanized with 5% additive showed a reduction of 10MU in viscosity compared to those without any additive. This is due to the plasticization effect as well as a higher amount of free polymer chains due to a higher degree of devulcanization with 5% additive (as seen in Figure 7.7). The ranking of the viscosity of the compound samples from lowest to highest was as follows: SO resulted in the lowest viscosity, followed by TDAE oil, LBR, SLBR and PO. The ranking is the same for the viscosity of the additives at 100°C except for PO whose viscosity is positioned between the ones of SO and TDAE. The influence of PO on viscosity was similar to the other additives, as at the viscosity measurement temperature PO is liquid, unlike in the case of elongation at break measurements at which PO was solid.
Comparing the viscosity of samples that underwent pre-swelling before devulcanization for one day and six hours, they showed similar results. This is another indication, that pre-swelling of 6 hours is sufficient to let the additives migrate into the particles. When the additives are compounded after devulcanization, the viscosity decreased with increasing additive concentration, which can be attributed to the plasticization effect as stated above. Compared to the oils, less reduction of viscosity was noticed for the polymeric samples due to higher viscosity of these additives.

Figure 7.5. Additive screening experiments: viscosity

Figure 7.6 presents a comparison of network breakdown versus sol content (Horikx-Verbruggen analysis). Sol-correction as described above was carried out for LBR, SLBR, and PO samples. As the additive concentration increased from 5% to 10%, the degree of network breakdown decreased due to nip slippage during the devulcanization process, which can result in lower efficiency. There is a correlation between the degree of network breakdown and strength of the revulcanized samples: A higher degree of network breakdown resulted in a higher tensile strength of the revulcanizate.

The Horikx-Verbruggen analysis of samples pre-swollen for one day and six hours showed no significant differences, again indicating that a pre-swelling duration of six hours is sufficient to achieve adequate migration to the core of the particles. Similar findings were also reported in the PhD thesis of van Hoek. It was also reported that the distribution of additives is non-uniform, contingent upon the particle size, with small particles absorbing a relatively higher amount of additives due to their higher surface-to-volume ratio compared to larger ones.
Insufficient migration of additives occurred when the process additive was added directly before devulcanization. The study by van Hoek\(^6\) showed that 17 hours is required for optimum migration of TDAE oil for 2 mm granulates for TDAE in whole tire rubber. As a result, the additives did not penetrate into the granulates sufficiently but instead accumulated more on the surface. This led to increased nip slippage and insufficient devulcanization in the samples with directly added additives.

Additionally, the analysis showed that along with the addition of the oils, SLBR and PO exhibited a good compromise between network breakdown and sol content. During the devulcanization, oils and polymeric additives both showed only plasticization effect and no consequence of double bonds from additives was reflected in the devulcanization process. During revulcanization, the unsaturation of the polymeric additives contributed in crosslinking and resulted in additional reinforcement. It can be concluded that apart from TDAE oil, PO and SLBR can be potential process additives for devulcanization.

![Figure 7.6. Additive screening experiments: network breakdown](image)

In comparison to direct addition and compounding of additive samples, the sample pre-swollen for 6 hours and 1 day exhibited superior results in terms of mechanical strength and network breakdown properties. As expected, 6 hours and 1 day pre-swollen samples showed similar trend of results in white rubber analysis. As 1 day pre-swollen samples were used as reference for all investigations, in this chapter also the data for the devulcanizates using the 1-day pre-swollen rubber were illustrated in Figure 7.7. The analysis revealed that with an increase in additive concentration, there was a shift in particle size distribution from finer particles to coarser particles. This observation supports the hypothesis of insufficient devulcanization at higher additive concentrations, which can be caused by nip slippage.
Figure 7.7. Additive screening experiments: White rubber analysis of 1 day pre-swollen devulcanizate

Figure 7.8. Additive screening experiments: correlation between tensile strength and total area of visible particles
In Figure 7.8, a linear correlation between the total area of visible particles (TAVP) and tensile strength of the additive screening experiments is obvious. The sample without any additive exhibited the highest TAVP and lowest tensile strength, highlighting the significance of the process additives. As the additive concentration increased, TAVP increased and tensile strength decreased, except for PO due to the solid physical state at room temperature as explained above.

**Figure 7.9. Additive screening experiments: correlation between elongation at break and total area of visible particles**

Figure 7.9 portrays the correlation between elongation at break and TAVP in the additive screening experiments. The results show a linear correlation between TAVP and elongation at break for the additives except for PO. As previously mentioned, the lower elongation at break of the samples with PO is likely due to its solid physical state at room temperature.

**Table 7.4. Expectations and outcome of the process additives**

<table>
<thead>
<tr>
<th>Name</th>
<th>Expectations from screening</th>
<th>Outcome/findings</th>
</tr>
</thead>
</table>
| TDAE oil | 1. High thermal stability.  
2. Short swelling time for efficient devulcanization. |
| SO     | 1. Low viscosity & compatibility.  
2. High thermal stability.  
2. Same as TDAE oil.  
3. Non-hazardous processing. |
| LBR          | 1. Effectiveness of liquid rubbers.  
2. Additional crosslink formation during revulcanization. | 1. Efficient as process additive.  
2. Compared to oil devulcanizates, higher tensile strength and lower elongation at break supports the expectation. |
|--------------|---------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| SLBR         | 1. Similar to LBR.  
2. The silane functionalization improves polymer-filler interaction. | 1. Similar to LBR  
2. Compared to LBR, it showed higher tensile strength and lower elongation at break supporting the expectation. |
| PO           | 1. Solid physical state at room temperature (RT)  
2. High temperature stability.  
2. Similar to TDAE oil.  
3. Compared to other samples, a lower elongation at break supports the influence of the solid physical state, as the tensile tests were performed at RT. |

### 7.4 Conclusions

The optimal additive quantity was determined to be 5%, as concentrations exceeding this value led to nip slippage in the mixer, resulting in comparatively inferior devulcanizates. Among the devulcanizates, those containing long polymer chains with unsaturated double bonds, specifically SLBR and PO, exhibited superior properties.

A swelling time of 6 hours yielded properties similar to those obtained with a 1-day swelling period, suggesting that 6 hours can be considered the optimum swelling time. Additives compounded after devulcanization induced a plasticization effect.

It can also be concluded that the inclusion of polymeric additives enhanced the quality of the devulcanizate. Samples with polymeric additives, with a 5% concentration and a 6-hour pre-swelling time, demonstrated optimal properties, making them promising candidates for further exploration in devulcanization processes.

### 7.5 References

1. Product safety data sheet; Vivatech 500, H&R Chem Pharm.
2. Product safety data sheet; Sunflower oil, A&H.
5. Product safety data sheet; Vestenamer, Evonik Industries.
This chapter is focused on the investigation of three key aspects. The first two aspects are the influence of additional fillers on the resulting devulcanizate and the impact of an additional silanization reaction on the devulcanizate containing silica.

The third part is an assessment of the effect of blending devulcanizates with a virgin compound. The devulcanizates with different filler quantities are investigated, as well as the ones with varying devulcanization aids. As reference, untreated ground tire rubber, mechanically and cryogenically ground, are also tested in the blend. The results were analyzed in terms of mechanical and viscoelastic properties, network breakdown and miscibility.
8.1 Introduction

This chapter is dedicated to the examination of three fundamental aspects:

1. The investigation scrutinizes the influence of additional fillers on the devulcanizate.
2. It also explores the impact of the silanization reaction on the devulcanizate.
3. It assesses the effect of blending devulcanizates or ground tire rubber with a virgin model compound in a comparative study.

8.2 Effect of fillers on devulcanizates

In this study, both the model compound and WT rubber granulates were subjected to devulcanization under optimized process conditions and subsequently compounded with additional fillers. ULTRASIL® 7000GR grade silica together with TESPD as coupling agent and N330 carbon black were individually incorporated into the devulcanizate at four varying concentrations, while maintaining a consistent revulcanization formulation. The primary objective of this section was to assess the impact of fillers on the resulting revulcanizate, particularly in terms of mechanical properties and filler interaction characteristics.

8.2.1 Experimental process

This section provides detailed explanations regarding the preparation of the feed material, outlines the sampling plan, and elucidates the characterization processes employed.

8.2.1.1 Preparation of feed material

The preparation of the feed material for the model passenger car tire tread granulates followed the same procedure outlined in Chapter 3, Section 3.2.1. The feed material preparation for the whole passenger car tire rubber (WT) granulates was done according to the same procedure as described in Chapter 4, Section 4.6.1.
8.2.1.2 Filler compounding

The fillers were compounded with the devulcanizate using a Brabender Plastograph EC, Germany, with a 50 CC volume and 70% fill factor. The mixer was set to a temperature of 70°C, which was increased to around 130°C for silica compounding. The silica-silane was compounded for 3 minutes at an isothermal mixing temperature of 145°C. For carbon black samples, the temperature increased to around 120°C, and the compounding process, including mastication time, took a total of 6 minutes.

8.2.1.3 Sampling plan

The devulcanizates were prepared by using the optimum devulcanization conditions based on the findings of Chapter 4, for WT rubber granulates. These two types of devulcanizate were compounded separately with two filler systems in four different concentrations. The quantity of silane coupling agent was calculated according to Guy's formula. Considering the surface area of silica and functionality of the silane, 7.5% TESPT relative to the silica is sufficient for silanization under standard processing conditions. The sampling details of the filler optimization trials are given in Table 8.1.

Table 8.1. Sampling plan for filler optimization trials

<table>
<thead>
<tr>
<th>Devulcanizate</th>
<th>Abv.</th>
<th>Silica + Silane (w/w %)</th>
<th>Carbon black (CB w/w %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VP - Model</td>
<td>M-VP</td>
<td>1. 10% Silica + 0.75% Silane</td>
<td>1. 10% CB</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. 20% Silica + 1.50% Silane</td>
<td>2. 20% CB</td>
</tr>
<tr>
<td>VP – WT</td>
<td>WT-VP</td>
<td>3. 30% Silica + 2.25% Silane</td>
<td>3. 30% CB</td>
</tr>
<tr>
<td>granulates</td>
<td></td>
<td>4. 40% Silica + 3.00% Silane</td>
<td>4. 40% CB</td>
</tr>
</tbody>
</table>

All samples were devulcanized applying the procedure detailed in Chapter 3, Section 3.2.2. All samples were revulcanized using the same formulation as described in Chapter 3, Section 3.2.1.5.

8.2.1.4 Testing process

The testing process contains four parts:

i. Stress-strain analysis

Stress-strain properties were measured in tensile mode, and a detailed description of the measurement technique is given in Chapter 3, Section 3.2.3.2.

ii. Dispersion

The macro-dispersion analysis of the silica in the compounded sample was done using a Dispergrader of Alpha Technologies, USA, at full-top light and room temperature. Cylindrical samples with 25 cm in diameter and 12 mm thickness were cut with a sharp knife and the exposed cross-section was analyzed. The distribution of fillers within the revulcanize samples was analyzed depending on the filler concentration.

iii. Payne effect

The Payne effect gives an indication of the micro-dispersion, the filler-filler interactions on small scale, in the compounds. The analysis of the silica-filled revulcanizates was done according to ASTM D8059-19 in a rheometer of TA Instruments, USA. To measure
the Payne effect of cured samples, the samples were revulcanized at 160°C up to t95, and the Payne effect was measured at 60°C in two strain rate sweeps, low to high (from 0.33% to 14.1%) and high to low (from 14.1% to 0.33%) for each sample. The curves from both sweeps were plotted and the difference between the shear modulus at low strain and high strain was reported as Payne effect.

iv. Abrasion resistance

The abrasion resistance of the rubber compounds was determined by the weight loss according to ASTM D5963 on a rotary drum DIN abrasion tester of Montech, Switzerland.

8.2.2 Results

In this section, the stress-strain behaviour, dispersion, filler-filler interaction and abrasion resistance of the above mentioned (Table 8.1) samples are shown. In a polymeric system, the filler system can create either a physical or chemical interaction, depending on the type of filler: carbon fillers create a physical interaction, while a silica-silane system creates a chemical bond with the polymer. As the concentration of filler increases, the mechanical strength of the rubber generally improves up to a certain point. However, if the polymer concentration is insufficient to interact with the further increased filler concentration, this leads to a reduction of the overall mechanical properties of the system.

As shown in Figure 8.2, the tensile strength of the de- and revulcanized samples increased with increasing filler concentration up to a certain level; above that limit reversal took place. For the model compound, the tensile strength reached around...
10.3 MPa at 20% filler concentration, and for WT granulates the maximum was around 9.7 MPa at 30% filler concentration. The samples filled with silica-silane demonstrated slightly higher values in comparison to carbon black. However, the average values of tensile strength follow a trend which allows to conclude that the silica filled material performed in general better. Comparing the original and 20% additionally silica filled model devulcanizate, a significant increase in tensile strength can be considered.

![Figure 8.3. Filler optimization trials: elongation at break](image)

According to Figure 8.3, for both model compound and WT granulates, elongation at break decreased gradually with increasing filler concentration. For WT granulates, elongation at break was around 165% for the unfilled sample, and got reduced to 118% for the 40% silica filled samples and to 137% for the 40% carbon black filled samples. For the model compound, elongation at break was around 116% for original samples, which got reduced to 80% for 40% silica filled samples and 83% for 40% carbon black filled samples.

The dispersion analysis of the WT revulcanizates with increasing silica concentration is shown in Figure 8.4. With the increase in added filler concentration, an elevation in the viscosity of the devulcanize was observed, consequently leading to an increase in shear forces during the mixing process. These higher shear forces contribute to enhanced dispersion of filler particles within the devulcanized matrix.
Figure 8.4. Filler optimization trials: dispersion

Due to instrumental limitations (very high shear modulus), the Payne effect measurement of the 40% filled samples was not possible. The notation L-H stands for the strain sweep from low to high, and H-L is the high to low sweep as mentioned in the legend of Figure 8.5. With increasing silica concentration, the Payne effect increased
gradually which indicates higher filler interactions. Similarly, the difference between the shear modulus values of the two sweeps at low strains also got increased. This can be explained by the change in the elastic behaviour due to less matrix material with an increasing concentration of added filler, which delays the recombination of the filler at higher loadings as shown in Table 8.2.

Figure 8.5. Filler optimization trials: Payne effect of the silica filled samples

The devulcanizates without additional filler exhibited a minimal Payne effect, suggesting that the filler-filler interaction was already disrupted during devulcanization. The strain sweep, conducted from low to high, resulted in breaking of the remaining filler-filler network.

Table 8.2. Payne effect values for filler optimization trials

<table>
<thead>
<tr>
<th>Filler type</th>
<th>Filler quantity (w/w %)</th>
<th>Low to high strain sweep: Shear modulus G' (KPa)</th>
<th>High to low strain sweep: Shear modulus G' (KPa)</th>
<th>Payne effect (KPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Max</td>
<td>Min</td>
<td>Min</td>
</tr>
<tr>
<td>Unfilled</td>
<td></td>
<td>1997</td>
<td>1212</td>
<td>1211</td>
</tr>
<tr>
<td>Silicasilane</td>
<td>10</td>
<td>4867</td>
<td>2163</td>
<td>2147</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>10131</td>
<td>3191</td>
<td>3146</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>18392</td>
<td>5012</td>
<td>4875</td>
</tr>
<tr>
<td>Carbon black</td>
<td>10</td>
<td>6193</td>
<td>2369</td>
<td>2357</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19400</td>
<td>5794</td>
<td>5724</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>28724</td>
<td>7878</td>
<td>7789</td>
</tr>
</tbody>
</table>

*Payne effect = Difference between the maximum and minimum shear modulus of low to high strain sweep
As shown in Figure 8.6 and Table 8.2, the carbon black filled samples showed the same trend in shear modulus as the silica filled samples. The shear modulus values were observed to be higher for the carbon black samples compared to those of silica when compounded at the same weight percentage. This discrepancy in shear modulus is attributed to the higher volume of carbon black, as its density (1.8 g/cc) is lower than that of silica (2.5 g/cc). Consequently, the carbon black samples exhibited a comparatively elevated shear modulus.

![Figure 8.6. Filler optimization trials: Payne effect of the carbon black filled samples](image)

Typically, abrasion resistance is quantified in terms of volume loss, but due to the density variations in the devulcanizate resulting from WT granulates, the abrasion resistance values were expressed in weight loss. The density of the model devulcanizate is constant within the sample as the feed material was uniform. However, for the whole tire (WT) devulcanizate, variations in density were observed, attributed to the diverse origins of granulates from different tires and tire parts.

According to Figure 8.7, the abrasion resistance of the sample with 10% additional silica was similar to the wear of the sample without any additional filler. With further increasing additional filler concentration, abrasion resistance decreased gradually resulting in higher mass losses.
8.2.3 Discussion

The model compound for devulcanization contained 80 PHR silica, a commonly used filler concentration; therefore it has not much capacity for a further filler loading. With increasing additional filler content, the filler-polymer interaction got reduced due to insufficient polymer. Above 20% additional filler loading, tensile strength decreased for the model devulcanizates: this can be considered as the optimum level. WT rubber devulcanizates were also filled with additional silica or carbon black up to a certain extent, and they showed a maximum tensile strength for 30% additional filler loading. Above this concentration the trend reversed. Compared to the model devulcanize, higher elongation at break values for the WT devulcanizates were probably due to the presence of natural rubber and carbon black in the feedstock.

With increasing filler concentration, the macro-dispersion as measured by optical microscopy improved due to increasing shear forces during blending of the compound with the additional filler. However, no quantification could be made based on this dispersion analysis. High contrast microscopy and particle distribution analysis would be more promising for quantifying the dispersion of fillers.

During the Payne effect measurement, at the first sweep, the shear modulus decreases with increasing strain which indicates breakdown of the filler network. During the second sweep from high to low strain, the recombination of the filler network takes place resulting in an increase in shear modulus. With increasing filler concentration, the mobility of the filler in the matrix got reduced resulting in a higher Payne effect indicating less recombination for higher filler loadings. For inadequate dispersion of fillers, the abrasion index is adversely affected leading to increased material loss during abrasion resistance testing.
8.2.4 Conclusions

Compounding of around 20% of additional filler can improve tensile strength of the revulcanizates by up to 15%. In addition to the filler cost, a sacrifice in elongation at break and abrasion resistance was noticed.

In comparison to samples filled with carbon black, those filled with silica did not exhibit significant improvements in mechanical or viscoelastic properties. However, due to silica's status as a sustainable and environmentally friendly filler: it is produced from a sustainable source and its main application is to improve the fuel efficiency of tires, it was prioritized. For further trials, an addition of 20% silica-silane was considered as the best option.

8.3 Effect of silanes on devulcanizates

It was reported in the previous section (Section 8.2) that compounding of the devulcanizate with 20% (w/w) silica-silane improves the tensile strength of the revulcanizates by up to 15% along with a sacrifice in elongation at break, dispersion and abrasion resistance.

In this investigation, the silane relative to the silica concentration was varied. The background of this study was that the WT feedstock already contained carbon black and silica: Carbon black might interfere with the silanization by adsorbing and thus deactivating the silane, and the originally contained silica might get activated and thus consumes some of the added silane.

The devulcanizate was compounded with additional silica and varying amounts of silane. A highly dispersible grade silica (ULTRASIL® 7000GR) and TESPĐ were compounded in six different combinations keeping the same revulcanizate formulation.

8.3.1 Experimental process

The preparation of the feed devulcanizate, sampling plan and characterization processes are described in this section.

8.3.1.1 Preparation of feed material

The feed material for this study was the devulcanizate based on whole passenger car tire rubber (WT) granulate, which was produced according to the procedure described in Chapter 4, Section 4.6.1.

8.3.1.2 Compounding and silanization reaction

The fillers were compounded using a Brabender Plastograph EC with a 50 CC volume and 70% fill factor. The mixer was set to a temperature of 70°C, which was increased to around 145°C to 150°C for silica compounding. For the silanization reaction, silica-silane was mixed for 3-4 minutes at an isothermal mixing temperature between 145-150°C.
The mixing curve illustrated in Figure 8.8 shows the addition of devulcanizate and mastication for 1 minute, addition of silica for 1 minute, ram cleaning and putting back overflowed silica for 30-45 seconds, and finally the silanization reaction during isothermal mixing for 220-250 seconds depending on the time needed for getting escaped silica back into the mixing chamber.

8.3.1.3 Sampling for silanization trials

20% silica with 1.5% silane was reported as the optimal filler concentration in Section 8.2.; the quantity of silane coupling agent was calculated according to Guy et al. To evaluate the effect of silanization, samples without silica and silane were used as references, and the silane concentration was varied keeping the silica concentration constant. The sample without additional silica but with additional silane was tested to assess the reactivation of silica in the devulcanizate. The sampling details of the silanization trials are given in Table 8.3.

Table 8.3. Sampling plan of silanization trials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compounding details</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silica (w/w%)</td>
<td>Silane (w/w%)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Feed material: WT granulates; Temperature: 180°C; Residence time: 6 min; Shear rate: 150 RPM; Fill factor: 80%; VP concentration: 5%
All samples were devulcanized by maintaining the same procedure as described in Chapter 3, Section 3.2.2. They were revulcanized using the same formulation as mentioned in Chapter 3, Section 3.2.1.5.

8.3.1.4 Testing process

The testing process consists of six parts:

i. Stress-strain properties in tensile mode (see Chapter 3, Section 3.2.3.2).
ii. Degree of devulcanization as determined by the Horikx Verbruggen plot (see Chapter 3, Section 3.2.3.1).
iii. Homogeneity evaluation by white rubber analysis (see Chapter 3, Section 3.2.3.3).
iv. Processability of the rubber in terms of viscosity (see Chapter 4, Section 4.6.3.1).
v. Filler interaction by Payne effect analysis (see Chapter 8, Section 8.2.1.4).
vi. Scanning electron microscopy (SEM)

SEM analysis was done using a TableTop SEM by PhenomXL, Germany. The cross-section and fracture surfaces of all the samples were analyzed to evaluate the dispersion of the fillers with variable silane concentrations. The experimental conditions were kept the same for all measurements: Voltage: 5 kV, Beam intensity: Image, Detector: BSD full, Vacuum: Low (60 Pa), Averaging: High, Scan size: 3840X2400.

8.3.2 Results and discussion

Figure 8.9. Silanization trials: stress-strain properties

Figure 8.9 displays the stress-strain characteristics. The sample without additional silica and silane exhibited the lowest tensile strength and the highest elongation at break. When only 1.5% silane was added, no significant increase in tensile strength but a slight
reduction in elongation at break was noticed. In the case of the additionally filled samples, the silica concentration remained constant at 20% (w/w), while the silane concentration was varied from no silane to 4.5% (w/w), while the commonly used concentration is 1.5% (w/w). In this series, the tensile strength improved up to a silane concentration of 3%, beyond which no further enhancement was observed. Elongation at break gradually decreased as the silane concentration increased due to the formation of an additional filler-polymer and polymer-polymer network during the revulcanization process.

Figure 8.10 presents a comparative analysis of the Payne effect for not additionally filled samples and additionally silica-filled samples with varying silane concentrations. The strain sweep curves represented by dotted lines depict the sweep from low to high strain, during which the filler network is broken leading to a decrease in shear modulus. Conversely, the solid curves represent the high to low strain sweep, during which recombination of the filler network occurs, resulting in an increase in shear modulus.

For the samples without additional silica (blue and violet), both sweeps show low shear moduli (Table 8.4), indicating effective dispersion of the filler. Upon the addition of silica, the difference between the shear moduli in first sweep of low to high strain: the Payne effect, got increased, indicating stronger and more interactions between the fillers. As the silane concentration increased, the Payne effect gradually decreased, indicating better dispersion of the filler with less filler-filler interactions: With increasing silane concentration, the Payne effect improved as the degree of silanization got higher, see Table 8.4.
Table 8.4. Silanization trial: Payne effect data - shear modulus

<table>
<thead>
<tr>
<th>Sample details</th>
<th>Low to high strain sweep: Shear modulus G’ (KPa)</th>
<th>High to low strain sweep: Shear modulus G’ (KPa)</th>
<th>Payne effect(^a) (KPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>0% Silica + 0% Silane</td>
<td>1997</td>
<td>1212</td>
<td>1211</td>
</tr>
<tr>
<td>0% Silica + 1.5% Silane</td>
<td>2297</td>
<td>1512</td>
<td>1511</td>
</tr>
<tr>
<td>20% Silica + 0% Silane</td>
<td>9290</td>
<td>2747</td>
<td>2674</td>
</tr>
<tr>
<td>20% Silica + 1.5% Silane</td>
<td>6308</td>
<td>2073</td>
<td>2056</td>
</tr>
<tr>
<td>20% Silica + 3% Silane</td>
<td>5612</td>
<td>1953</td>
<td>1937</td>
</tr>
<tr>
<td>20% Silica + 4.5% Silane</td>
<td>4752</td>
<td>1675</td>
<td>1658</td>
</tr>
</tbody>
</table>

\(^a\)Payne effect = Difference between the maximum and minimum shear modulus of low to high strain sweep

Figure 8.11. Silanization trials: different components of the Payne effect

The Payne effect curves are a product of four variable effects as illustrated in Figure 8.11: filler-filler interaction, filler-polymer interaction, polymer network, and the hydrodynamic effect. For samples without additional silica, the only parameter that improves is the filler-polymer interaction, while the other three parameters remain constant. Conversely, in samples filled with additional silica, an increase in silane concentration results in an increase of the filler-polymer interaction and a gradual decrease in filler-filler interaction. The polymer-polymer network remains unchanged. There might be a slight reduction in the hydrodynamic effect due to the addition of liquid silane. Based on the findings from the Payne effect data, no reduction was observed when silane was introduced to the samples which were not additionally filled. The consistent Payne effect values indicate the absence of silica reactivation: If silane had reacted with silica, a lower Payne effect would have been anticipated. The lack of any alteration in the Payne effect values confirms the absence of silica reactivation.
Figure 8.12. illustrates a comparative analysis of viscosities of the samples with and without additional silica and different silane concentrations. The viscosity of the samples without additional silica was observed to be in the range of 75 MU to 78 MU. Upon adding 20% (w/w) silica, the viscosity increased to approximately 115 MU. In the case of silica-filled samples, the viscosity gradually decreased with increasing silane concentration, reaching around 110 MU. This reduction in viscosity can be attributed to the plasticization effect caused by higher silane concentrations.

![Figure 8.12](image)

**Figure 8.12. Silanization trials: viscosity**

Figure 8.13 depicts a comparative Horikx-Verbruggen analysis of samples with and without additional silica with varying silane concentrations. The red line represents the limit of random scission, while the dotted green line represents the limit of crosslink scission. The average values of five samples are plotted in terms of network breakdown and sol-content. All samples underwent the same devulcanization process, followed by separate compounding with silica and silane.

The unfilled samples exhibited a network breakdown ranging from 70% to 75%. Upon the addition of 20% (w/w) silica, when the silane concentration was varied from 0% to 4.5%, the network breakdown percentage decreased from 55% to 45%. The variation in network breakdown was attributed to the increase in silane concentration, as this resulted in an additional polymer-filler network, which counterbalances the reduction in crosslink density in the devulcanization process. Though Krauss filler correction was done, the reduction in network breakdown percentage can be due to the fact that the additional 20% silica forms a different type of reinforcement for which the Krauss correction has limited applicability. With increasing silane concentration, the interaction between the filler and the polymer improved due to the silanization reaction, leading to an additional network and consequently lower net network breakdown.
Chapter 8

Figure 8.13. Silanization trials: network breakdown

Figure 8.14. Silanization trials: white rubber analysis
According to Figure 8.14, samples without silica exhibited a total number of visible particles in the range of 1290-1300. However, with the addition of 20% (w/w) silica together with varying amounts of silane, the total number of visible particles decreased to approximately 920-960: The presence of silica in the additionally filled samples led to a decrease in the total number of immiscible particles compared to not-additionally filled devulcanizate as shown in Figure 8.15. Silica is compatible with the white rubber matrix, and due to the contribution of additional silica the relative volume of undevelopanized particles got reduced resulting in a lower number of visible particles.

*Figure 8.15. Schematic diagram of white rubber analysis: white rubber samples containing vulcanizates with and without additional silica*
According to the observations in Figure 8.16, an increase in silane concentration resulted in improved dispersion of silica: Figure C and D showed comparatively poor dispersion compared to Figure E and F, which correlates with the Payne effect values.

Based on the findings in Figure 8.17, as the silane concentration increased, the material exhibited smoother fracture surfaces compared to no silane samples. With an increasing silane concentration, the silica dispersion became more homogeneous. Fracture is generated from defective spots, therefore a more homogeneous and uniform distribution will cause less defects leading to a smoother fracture surface resulting in better tensile properties (Figure 8.9).
8.3.3 Conclusions

With additional 20% silica and increasing silane concentration, the tensile strength, Payne effect and dispersion got improved due to better polymer-filler interaction by a better silanization. With increasing silane concentration, elongation at break & net network breakdown got reduced due an increase in crosslink density by the formation of short, stable filler-polymer bonds during the silanization reaction. Viscosity got reduced due to the plasticization effect of silanes.
20% silica with 3% silane showed the best properties in terms of mechanical strength, and beyond this concentration no further improvement was noticed: this can be considered as the optimum concentration for the addition of a silica-silane filler system to the devulcanizate.

### 8.4 Blending of the devulcanizate and ground rubber with a virgin model compound

In Sections 8.2 and 8.3, the type and quantity of additional filler, and the concentration of silane in the case of silica addition were optimized in terms of mechanical and viscoelastic properties of the devulcanizates. Considering the main goal of application of the devulcanizates in the new products, it is important to examine the variation in mechanical properties when these devulcanizates are blended with the virgin compound.

The objective of this next step in the investigation was to assess the impact of incorporating these devulcanizates into the model compound on mechanical properties. The model compound was blended with the devulcanizates, and the cured model compound as such was taken as reference. Additionally, the cured model compound was subjected to mechanical and cryogenic grinding, followed by blending with virgin compound to investigate the variation in mechanical properties compared to the devulcanizate blends.

Both unfilled and silica-silane filled devulcanizates were blended with the model compound at varying ratios. The alterations in the properties of the resulting revulcanizates, with increasing devulcanizate concentrations, were assessed in terms of tensile strength and elongation at break. Furthermore, the virgin model compound was combined with devulcanized whole tire material without additional filler to investigate its effect on the mechanical properties for comparison with the benchmark of DPDS devulcanizates.

#### 8.4.1 Experimental process

This section can be classified into four parts: feed material preparation, blending procedure, sampling plan and testing process.

##### 8.4.1.1 Preparation of feed material

The preparation of the feed material consists of three steps:

i. Preparation of the virgin model compound

The detailed description of the model compound preparation is given in Chapter 3, Section 3.2.1.

ii. Preparation of cryogenically and mechanically ground samples

Mechanically ground samples were prepared in the Brabender Plastograph EC. When no devulcanization aids and process oils are used, the rubber is only ground, but not devulcanized. Before grinding, the feed rubber granules were passed through 0.7 mm sieve and the smaller fraction was mechanically ground at 155°C for 6 minutes with a
rotor speed of 100 RPM and 80% fill factor. The resulting ground rubber was then sieved using a 0.2 mm sieve.

For cryogenic grinding, the cured model compound was cooled down to below the glass transition temperature using liquid nitrogen. The cooled rubber was subsequently ground in a Fritsch grinder with a 0.2 mm mesh for around 2 to 3 minutes; the remaining larger particles within the grinder were ground again. The output particle size was around 0.2 to 0.3 mm with a certain amount of finer particles, which was close to the particle size and particle size distribution of the mechanically ground samples.

iii. Preparation of different devulcanized samples using silanes

The swelling for the model granulate was done according to the procedure described in Chapter 3, Section 3.2.2.1. For the whole passenger car tire rubber (WT) granulates, the feed material preparation is described in Chapter 4, Section 4.6.3.1. For the addition of filler to the devulcanizate, 20% (w/w) highly dispersible silica (ULTRASIL® 7000GR) along with 1.5% (w/w) TESPD were mixed into the devulcanizate as described in Section 8.2.1.2.

All samples were devulcanized using the procedure as mentioned in Chapter 3, Section 3.2.2. All the devulcanizates were compounded using the same formulation as detailed in Chapter 3, Section 3.2.1.5.

8.4.1.2 Addition of curatives and blending procedure

After devulcanization, no active curatives were present in the devulcanizate for revulcanization as no raise in torque was noticed when measured in the RPA. Due to the viscosity difference of the virgin compound and devulcanizate (around 25 to 30 MU), uniform dispersion of the curatives is very difficult in the blended matrix. Therefore, devulcanizates were compounded with curatives separately before they were blended with the model compound already containing the curatives.

The virgin model compound also contained curatives before blending with the devulcanizate; therefore no supplementary curatives were introduced into the system when blending devulcanizate and model compound. The addition of curatives to the virgin compound and the devulcanizate, as well as blending of the devulcanizates with the virgin compound were carried out on a two-roll mill manufactured by Schwabenthan GmbH & Co., Germany. It is important to note that no additional curatives were incorporated into the ground rubber, as this is still vulcanized rubber and no additional crosslinking was needed.

8.4.1.3 Sampling plan for blending trials

The blending trials can be classified into three parts:

i. Blending with devulcanizates containing different silanes as DA
ii. Blending with additionally filled and unfilled devulcanizates
iii. Blending of cryogenic and mechanically ground, thus non-devulcanized rubber samples

The sample details are described in Table 8.5, 8.6 and 8.7 respectively.
Chapter 8

Table 8.5. Sampling plan of blends of the virgin model compound with devulcanizate based on different DAs

<table>
<thead>
<tr>
<th>Devulcanizate details</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>WT devulcanizate using VP</td>
<td>VP-WT</td>
</tr>
<tr>
<td>Model devulcanizate using VP</td>
<td>VP-M</td>
</tr>
<tr>
<td>Model devulcanizate using VTEO</td>
<td>VTEO-M</td>
</tr>
<tr>
<td>Model devulcanizate using TESPT</td>
<td>TESPT-M</td>
</tr>
<tr>
<td>Model devulcanizate using DPDS</td>
<td>DPDS-M</td>
</tr>
</tbody>
</table>

Devulcanizate : Virgin (w/w) 10:90, 20:80, 30:70, 60:40, 50:50

Reference = 100% virgin model compound & 100% unfilled devulcanizates

Table 8.6. Sampling plan of blends of the virgin model compound with filled and unfilled devulcanizates based on different DAs

<table>
<thead>
<tr>
<th>Devulcanizate details</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled#</td>
<td></td>
</tr>
<tr>
<td>Model devulcanizate using VP</td>
<td>VP-M</td>
</tr>
<tr>
<td>Model devulcanizate using VTEO</td>
<td>VTEO-M</td>
</tr>
<tr>
<td>Model devulcanizate using TESPT</td>
<td>TESPT-M</td>
</tr>
<tr>
<td>Model devulcanizate using DPDS</td>
<td>DPDS-M</td>
</tr>
</tbody>
</table>

Devulcanizate : Virgin (w/w) 10:90, 30:70, 50:50

Filled with 20% silica + silane

Model devulcanizate using VP               | VP+EX20%Si                 |
Model devulcanizate using VTEO           | VTEO-M+EX20%Si             |
Model devulcanizate using TESPT       | TESPT-M+EX20%Si            |
Model devulcanizate using DPDS     | DPDS-M+EX20%Si             |

Reference = 100% virgin model compound & 100% unfilled devulcanizates
# Unfilled samples are same from Table 8.5.

Table 8.7. Sampling plan of blends of the virgin model compound with devulcanizate and ground material

<table>
<thead>
<tr>
<th>Devulcanizate details</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model devulcanizate using VP</td>
<td>VP-M</td>
</tr>
<tr>
<td>Mechanically ground model compound</td>
<td>Mech-M</td>
</tr>
<tr>
<td>Cryogenically ground model compound</td>
<td>Cryo-M</td>
</tr>
</tbody>
</table>

Devulcanizate or Ground rubber : Virgin (w/w) 10:90, 20:80, 30:70, 60:40, 50:50

Reference = 100% virgin model compound & 100% unfilled devulcanizates

8.4.1.4 Testing procedure

Stress-strain properties were measured in tensile mode, and a detailed description of the measurement technique is given in Chapter 3, Section 3.2.3.2.

8.4.2 Results

This section is classified into 3 parts as mentioned in the experimental section: blends of the model compound with devulcanizates based on different DA’s, a comparison of blends with devulcanizates with and without additional filler, and blends with simply ground rubber.
Tensile strength of the virgin model compound was around 16±1 MPa. According to Figure 8.18, the blends with VP devulcanized rubber did not exhibit a significant decrease in their properties when blended with up to 20% devulcanizate. Moreover, when blended with up to 40% devulcanizate, the average tensile strength of the VP devulcanized blends was above 14 MPa. With increasing devulcanizate concentration, tensile strength decreased gradually. For the same DA, WT rubber devulcanizate blends showed a similar trend and values were also not much lower compared to the model devulcanizate blends.

![Graph showing tensile strength](image)

Figure 8.18. Blends of virgin model compound with devulcanizate based on different DAs: tensile strength

As illustrated in Figure 8.19, elongation at break showed the same trend as tensile strength. VP blends exhibited the best elongation at break among the tested samples, followed by VTEO, TESPT and DPDS. For the virgin compound, the elongation at break was around 310% and got reduced to around 300% for the 10% VP-WT blend, and to around 290% for the 10% VP-M blend. Compared to the model devulcanizate blends, WT devulcanizate blends showed comparatively higher elongation at break.
Figure 8.19. Blends of virgin model compound with devulcanizate based on different DAs: elongation at break

Figure 8.20. Blends of virgin model compound with filled and unfilled devulcanizates based on different DAs: tensile strength
In Figure 8.20, comparative tensile strength results of blends of the virgin model compound with additionally filled and unfilled devulcanizates based on different DAs are plotted. The additionally filled samples exhibited better tensile strength compared to the unfilled ones. For the 10% devulcanizate blends, no significant decrease was noticed for the silane devulcanized samples, but tensile strength decreased gradually with further increasing devulcanizate concentrations. In terms of mechanical properties, blends with VP devulcanizate displayed superior characteristics, followed by VTEO, TESPT and DPDS as DA.

According to Figure 8.21, elongation at break gradually decreased as the devulcanizate/virgin compound ratio increased. For the VP devulcanizate blends, for 10% devulcanizate blends only a small reduction in elongation at break was noticed; when blended with up to 30%, the elongation at break was gradually reduced approximately up to 250%. At a concentration of 50%, around 50% sacrifice in elongation at break was noticed compared to the elongation at break of the 100% model compound.

According to Figure 8.22, blends of virgin compound with devulcanizate (VP-M) have a significantly higher tensile strength compared to blends of the virgin compound with ground rubber. When comparing the samples with ground rubber, mechanically ground rubber results in a higher tensile strength compared to cryogenically ground material. This is due to the higher surface area and morphology, thus increased interaction with the model compound matrix caused by the rough particle surface of mechanically ground rubber.
Figure 8.22. Blends of virgin model compound with devulcanizate and ground material: tensile strength

Figure 8.23. Blends of virgin model compound with devulcanizate and ground material: elongation at break
In Figure 8.23, a decrease in elongation at break was noticed with increasing amount of devulcanizate and ground rubber: high quantities of ground rubber or devulcanizate result in a higher number of undevulcanized or ground particles which leads to an increase in defective spots.

8.4.3 Discussion

Among the tested samples, blends with VP devulcanizates displayed the best mechanical properties, followed by VTEO, TESPT and DPDS. Compared to the benchmark DPDS samples, silane devulcanized samples showed better mechanical properties.

Compared to the model devulcanizate blends, a higher elongation at break was measured for the WT devulcanizate blends. This was attributed to differences in the filler and polymer system: The model compound contains SBR-BR as polymer and was silica filled, the WT material contains natural rubber (NR) and carbon black (CB) filled rubber. At high temperatures (above 180°C), natural rubber shows a softening effect which helps in the devulcanization process, while SBR-BR gets brittle with increase in temperature which hinders the selective network breakdown. For a silica filled rubber, an additional filler-polymer network is formed, which reduces elongation at break values. Carbon black features physical bonding with the polymer resulting higher elongation at break values.

Due to the higher surface area and morphology, a better interaction with the model compound matrix takes place for mechanically ground rubbers compared to cryogenically ground rubbers resulting in higher tensile strength.

8.4.4 Conclusions

Based on the results of these trials, it can be concluded that VP devulcanizates can be blended with a virgin model compound at a level of up to 20% without experiencing a significant reduction in tensile strength. When 50% devulcanizate is blended with the virgin model compound, a sacrifice of around 30% in tensile strength and 50% in elongation at break is observed, while samples with additionally filled devulcanizate did demonstrate relatively higher mechanical properties.

When ground rubber was added to the virgin compound, the loss in properties is significantly higher compared to addition of devulcanizate. In terms of the grinding method, mechanically ground samples resulted in better blend properties compared to cryogenically ground rubber. This can be explained by the higher surface area of the former and thus a better interaction created by the rough particle surface.

8.5 References

The focus of this chapter is to investigate the impact of incorporating devulcanizates in varying proportions, ranging from 10% to 50%, into a virgin model passenger car tire tread compound. Different from the application study in Chapter 8, here the devulcanizates were used produced in an extruder. The examination is directed towards elucidating and understanding how the addition of devulcanizate affects the mechanical, viscoelastic, and other essential properties relevant to tire applications. The objective is to determine the quantity of devulcanizate that can be introduced into new tires without significant variation in tire-related properties.
9.1 Introduction

The objective of this chapter is to investigate the influence of devulcanizates incorporated in various ratios into the virgin model tire tread compound on mechanical, viscoelastic and other properties, and to determine the optimum devulcanizate quantity which can be incorporated in new tire applications without significant sacrifice in tire-related properties. Different from the application study of Chapter 8, Section 8.4, in which the best devulcanizate prepared in the small scale internal mixer was chosen, the devulcanizate within this investigation was produced via a continuous extrusion process. The selection of the blending ratios was guided by the findings in Section 8.4. It was observed that up to 20% devulcanizate in the blend, there was no significant reduction in mechanical and viscoelastic properties. However, a 50% devulcanizate blend was also tested to quantify the changes in tire properties with a higher proportion of devulcanizates. For the comparative analysis within this study, testing was conducted on 100% model compound, 100% devulcanizate, as well as blends containing 20% and 50% devulcanizate. Additionally, to evaluate the influence of the DA on the devulcanizate and the blend quality, a sample devulcanized with a process aid but without DA was also blended with the virgin compound.

9.2 Experimental process

This section can be categorized into five distinct components: preparation of the model compound, production of the devulcanizates, and the blending process involving the model compound and devulcanizates. Additionally, it encompasses the delineation of the sampling plan and the detailed description of the testing procedures employed in the study.

9.2.1 Preparation of the model compound

The detailed description of the SBR-BR based passenger car tire model tread compound preparation is given in Chapter 3, Section 3.2.1. The compound is a 70/30 (w/w) blend of SBR and BR, filled with 80 phr silica and cured using a conventional vulcanization system.
9.2.2 Preparation of the devulcanizate

The feed material preparation for the whole passenger car tire rubber (WT) granulates was done according to the same procedure as described in Chapter 4, Section 4.6.1. For the uniform distribution of the process aid (PA) and DA, the granulates were preswollen for 1 day and subsequently used for devulcanization. For the devulcanizate production, 5% (w/w) VP was utilized as DA, accompanied by 5% (w/w) TDAE oil serving as the PA. The term "Oil Reclaimed" denotes granulates that underwent the process in the extruder without the inclusion of a DA, but were processed with 5% TDAE oil only.

The devulcanization process was conducted using a co-rotating twin-screw extruder manufactured by Krauss Maffei, Germany, featuring a 2.5 cm diameter screw and a length-to-diameter ratio of 42. Two nitrogen (N₂) inlets were employed, with one situated in the feed zone and the other close to the die. Two outlets were sealed to increase the barrel pressure, with the exclusive nitrogen release through the die. Parameters optimized from prior upscaling experiments of the devulcanization process within the extruder were chosen for this specific devulcanization procedure. A uniform devulcanization temperature of 210°C was maintained across all 10 zones, with the extruder operating at a rotational speed of 75 RPM and employing a screw configuration as depicted in Figure 9.2.

![Figure 9.2. Screw configuration for the continuous devulcanization trials](image-url)

All devulcanizates were compounded using the formulation detailed in Chapter 3, Section 3.2.1.5.

9.2.3 Blending procedure

A blending procedure was followed as described in Chapter 8, Section 8.4.1.2.

9.2.4 Sampling plan

The sample details are described in Table 9.1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Model (w/w %)</th>
<th>Devulcanizate (w/w %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Model</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>20% Devulcanizate</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>20% Oil Reclaimed</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>50% Devulcanizate</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>100% Devulcanizate</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
9.2.5 Testing procedure

i. The optimum cure time (T\textsubscript{95}) was measured in the rubber process analyser as described in Chapter 3, Section 3.2.1.3.

ii. Stress-strain properties were measured in tensile mode, and a detailed description of the measurement technique is given in Chapter 3, Section 3.2.3.2.

iii. Viscosity measurements are detailed in Chapter 4, Section 4.6.3.1.

iv. Payne effect and abrasion resistance analysis measurement process details are described in Chapter 8, Section 8.2.1.4.

v. The hardness of the revulcanizates and vulcanized blends was assessed using a Shore hardness tester manufactured by Zwick Roell GmbH & Co., Germany, utilizing the Shore A scale and adhering to the ASTM D2240 standard.

vi. The rebound resilience of the materials was quantified using a 5109 rebound resilience tester from Zwick Roell GmbH & Co., Germany, in accordance with ISO 4662. Rebound resilience was measured at room temperature, and to predict the rolling resistance, rebound resilience was also measured at an elevated temperature of 60°C.

vii. The tear strength of the revulcanizate and the cured blends were determined utilizing a Z010 tensile tester manufactured by Zwick Roell GmbH & Co., Germany, following the guidelines outlined in the DIN 53515 standard.

viii. To assess thermal ageing properties, uncut tensile specimens were subjected to a 22-hour exposure at 100°C in an air-circulating oven. Subsequently, the specimens were allowed to cool to room temperature for a minimum of 18 hours prior to testing. The tensile properties, including modulus, tensile strength, and elongation at break of the thermally aged specimens were evaluated using the same methodology as applied to the unaged specimens.

ix. Dynamic mechanical analysis was conducted using a DMA Explexor 2500 instrument manufactured by Netzsch, Germany. The analysis involved a temperature sweep ranging from -100°C to +100°C, with a heating rate of 2°C per minute, conducted in tensile mode. A limiting load of 25N was applied, with a static load of 1% and dynamic load of 0.3%, while maintaining a frequency of 10 Hz throughout the analysis.

9.3 Results and discussion

As illustrated in Table 9.2 and Figure 9.3, a gradual reduction in the optimum cure time (T\textsubscript{95}), an increase in the cure rate index (Equation 1), and a decrease in the marching modulus (Equation 2) as a consequence of the incorporation of increasing concentrations of devulcanizate into the matrix is measured.
Table 9.2. Cure characteristics of the devulcanizate blends

<table>
<thead>
<tr>
<th>Sample name</th>
<th>(T_{95}) (s)</th>
<th>CRI ((s^{-1}))</th>
<th>MMI (dNm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Model</td>
<td>1610</td>
<td>0.0862</td>
<td>5.55</td>
</tr>
<tr>
<td>20% Devulcanizate</td>
<td>799</td>
<td>0.1606</td>
<td>2.03</td>
</tr>
<tr>
<td>20% Oil Reclaimed</td>
<td>920</td>
<td>0.1744</td>
<td>2.12</td>
</tr>
<tr>
<td>50% Devulcanizate</td>
<td>491</td>
<td>0.2849</td>
<td>-0.36</td>
</tr>
<tr>
<td>100% Devulcanizate</td>
<td>334</td>
<td>0.4075</td>
<td>-2.19</td>
</tr>
</tbody>
</table>

Cure rate index (CRI) = \(100/(T_{90} - T_{min})\) \hspace{1cm} \ldots\text{(1)}

Marching modulus index (MMI) = Torque at 30 min – Torque at 10 min \hspace{1cm} \ldots\text{(2)}

\(T_{95}\) = Time in seconds to reach the 95% of maximum torque

\(T_{90}\) = Time in seconds to reach the 90% of maximum torque

\(T_{min}\) = Time in seconds to reach the minimum torque

Figure 9.3. Application study on devulcanizate blends: rheogram

The model compound primarily consisted of SBR/BR and silica-silane as filler system, while the devulcanizate contained a significant portion of natural rubber (NR) and carbon black (CB) as filler. As a result, the pure model compound exhibited marching behaviour, as often noticed for silica-silane compounds, attributed to both SBR-BR and the silica-filled system. Conversely, the devulcanizate showed a reversal effect indicated by the negative MMI values in Table 9.2. due to the partial degradation of NR caused by the devulcanization process. As the quantity of the devulcanizate increased, there was an associated reduction in the marching modulus due to the resultant effect of both: the marching modulus of SBR/BR-silica and the reversion due to the presence of NR.
During devulcanization, a certain amount of unavoidable polymer chain scission occurs, leading to a reduction in the average polymer chain length of the devulcanizates. The model compound, being virgin material, had longer average polymer chains compared to the devulcanizates. Additionally, the model compound was based on SBR-BR and silica-silane filled while the devulcanizate contains a significant proportion of NR and is CB filled. Due to this, the devulcanizate demonstrates a lower maximum torque compared to the model compound. Consequently, this leads to a gradual decrease in the maximum torque with an increasing quantity of devulcanizate in the virgin compound.

As depicted in Figure 9.4 and 9.5, an incremental inclusion of devulcanizate led to a gradual decrease in both tensile strength and elongation at break. As reported by Birjarimi et al.\textsuperscript{1}, a tensile strength falling within the range of 16±1 MPa and an elongation at break of 300±20% are deemed acceptable for passenger car tire tread compounds. The blend containing 20% devulcanizate fulfils this requirement.

Specifically, when a 20% devulcanizate blend was employed, there was a 7% reduction in tensile strength and a 10% reduction in elongation at break, which is a comparatively minor reduction than reported in literature\textsuperscript{2-4}. At this blend ratio, the tensile strength measured was 15.1 MPa, accompanied by an elongation at break of 281%, rendering it suitable for tire application requirements\textsuperscript{1}.

However, when a 50% devulcanizate blend was analyzed, a more substantial decrease in tensile strength (24%) and elongation at break (25%) was observed. According to literature, the incorporation of devulcanizate (thermo-mechanical-chemical; with the
presence of DA) and reclaim (granulates processed thermo-mechanically without DAs) rubber leads to a reduction in tensile strength at a rate of 1% loss in property per 1% increase in the proportion \(2,3,4\). It can be concluded that devulcanizate blends showed superior mechanical properties compared to the blends with reclaimed rubber.

For 50% devulcanizate blend, the tensile strength was recorded at 12 MPa, with an elongation at break of 234%, making it suitable for use in rubber products with lower performance requirements compared to tire applications. It is noteworthy that the blends with the oil reclaimed rubber exhibited inferior properties compared to the devulcanized samples processed using a DA, underscoring the critical role of the DA in the devulcanization system.

![Figure 9.5. Application study on devulcanizate blends: stress-strain curve](image)

With increasing quantities of the devulcanizate, an increase in the modulus was observed, as illustrated in Figure 9.6. The increase in modulus can be attributed to the presence of a residual rubber network within the devulcanizate, which therefore got cured to a higher extent and contributed to a higher modulus within the blended matrix. Both the 100% and 200% modulus exhibited a consistent trend. In the case of the 100% modulus, the value was at its minimum for the model compound, and it exhibited a gradual rise with increasing concentration of devulcanizate, reaching its highest point for the 100% devulcanizate. For 100% devulcanizate elongation at break was around 175%, so the measurement of 200% modulus of that sample was not possible.

For the oil reclaimed blend, the modulus was comparatively lower in comparison to the devulcanizate blends. It was observed that residual double bonds from VP (vinyl silane with peroxide) facilitated the formation of additional crosslinks (as described in Chapter 6), and a greater number of polymer chains was released compared to the reclaimed...
material (Chapter 5, Section 5.2). Due to the efficient devulcanization process, polymer chains remained intact and these led to the formation of additional crosslinks and stronger networks in the revulcanizate, resulting in a higher modulus compared to the reclaimed blends.

![Figure 9.6. Application study on devulcanizate blends: modulus](image1)

![Figure 9.7. Application study on devulcanizate blends: tensile strength after ageing](image2)
As illustrated in Figure 9.7, the introduction of devulcanizate resulted in a less pronounced reduction in tensile strength for aged samples. Specifically, the tensile strength of the 100% model compound experienced a 9% reduction due to ageing, whereas the 100% devulcanizate sample exhibited only a 4% reduction in tensile strength: This positive effect can be attributed to the fact that the feed WT granulates utilized for devulcanizate preparation were already aged during service life. This suggests that the incorporation of the devulcanizate can enhance ageing resistance properties of the blended material.

Compared to the tensile strength of unaged samples with the same blend ratio, a relative 6.6% reduction due to ageing was observed for the 20% oil-reclaimed blend, and 6.1% for the 20% devulcanizate blend. This finding suggests that controlled crosslink scission does not exhibit any influence compared to reclaim: the ageing of the feed material plays a vital role.

![Figure 9.8. Application study on devulcanizate blends: elongation at break after ageing](image)

As depicted in Figure 9.8, a similar trend was observed in the behaviour of elongation at break, the commonly used indicator for ageing, when compared to tensile strength. The introduction of the devulcanizate resulted in a less significant reduction in elongation at break for the aged samples. In particular, elongation at break of the 100% model compound underwent a 28% relative reduction as a result of the ageing process, while the 100% devulcanizate sample displayed only an 11% relative reduction in elongation at break. In comparison to the 100% model compound, the inclusion of 20% devulcanizate led to an approximate 13% relative reduction in elongation at break.

Similarly, when adding 50% devulcanizate to the compound, an initial 25% relative reduction in elongation at break was observed compared to the 100% model compound.
However, after ageing, the difference in elongation at break between the rubber with 50% devulcanizate and the 100% model compound turned out to be reduced to 17% relatively.

Considering that the devulcanizate had already undergone ageing, it is evident that the incorporation of it enhances the material's resistance to ageing. Therefore, it can be inferred generally, that the addition of devulcanizate exerts a favourable influence on the ageing resistance properties of the material.

As depicted in Figure 9.9, an increase in tear strength values was observed upon the inclusion of 20% devulcanizate. In the case of the 20% blend, the presence of undevulcanized particles appeared to impart resistance to crack propagation, explaining the observed enhancement in tear strength.

When the crack tip encounters the undevulcanized particles, the energy is dissipated as the crack goes around the particles: more energy is consumed for the crack to propagate, ultimately leading to a higher tear strength. However, when higher concentrations of devulcanizate (>20%) are present, the particles are coming closer and there is not enough matrix material to embed them. This means an elevated number of defective spots, resulting in a reduction in the final tear strength.

In comparison to the 20% devulcanizate samples, the 20% oil reclaimed samples displayed relatively diminished tear strength. This observation implies that the oil-reclaimed samples do not provide adequate resistance to the propagation of cracks due the weaker interface between non-reclaimed particles and the matrix due to the shorter polymer chains. As described later on (Chapter 11), the oil reclaimed rubber has a higher number of particles which leads to a higher number of defective spots within the matrix.
For the 50% devulcanizate blend, tear strength was around 7 MPa and got further reduced for the 100% devulcanizate down to 4.3 MPa: crack growth resistance is inferior when the devulcanizate concentration is increased above a certain limit. It can be concluded that for applications such as tire manufacturing or those where crack growth resistance is a critical factor, the incorporation of 20% devulcanizate can potentially lead to a comparative improvement.

Figure 9.10. Application study on devulcanizate blends: viscosity

As illustrated in Figure 9.10, there was a gradual increase in viscosity with increasing quantity of devulcanizate. The viscosity for the 100% model compound was measured as 66 MU, while for the 100% devulcanizate, it was approximately 87 MU.

The viscosity for the 20% devulcanizate blend measured approximately 76 MU, and it increased to 80 MU when the devulcanizate concentration was raised to 50%. The 20% oil reclaimed blend exhibited a viscosity of approximately 78 MU. Therefore, it can be expected that there is a gradual increase in viscosity with an increasing quantity of devulcanizate or reclaim.

In the case of devulcanizate blends, the presence of undevulcanized particles created a two-phase system within the polymeric matrix, contributing to the observed increase in viscosity. Nevertheless, it can be generalized that all the blends remained within the industrially acceptable range of viscosity, which is limited to 80 MU.

As illustrated in Figure 9.11, the inclusion of devulcanizate did not reveal any significant discernible trend in hardness values. Across all samples, hardness measurements fell within the range of 64 to 67 Shore A. This observation suggests that the crosslinking systems for both the virgin and devulcanized phases were comparable, leading to hardness values within a similar range.
The hardness values exhibited a degree of comparability among the model compound, devulcanizate, and devulcanizate blends. This observation enables a meaningful comparison of mechanical, dynamic, and viscoelastic properties among the samples.

**Figure 9.11. Application studies on devulcanizate blends: hardness**

![Hardness Graph](image)

**Figure 9.12. Application study on devulcanizate blends: DMA analysis**

![DMA Graph](image)
According to the data presented in Figure 9.12, several observations were made regarding the impact of increasing devulcanizate concentration. Specifically, Tan δ exhibited a shift towards lower temperatures, as did the glass transition temperature (Tg), and there was an increase in peak height. This behaviour was attributed to the composition differences between the devulcanizate and the model compound. The devulcanizate contained natural rubber and carbon black, while the model compound consisted of SBR-BR and silica fillers.

The Tg of SBR, BR, and NR typically vary, falling around -30°C, -70°C, and -100°C, respectively, depending on the specific polymer grade. This variation can be attributed to distinct factors: The presence of styrene side groups in SBR introduces steric hindrance, leading to an elevation in Tg. Conversely, isoprene groups in natural rubber enable more unrestricted movement at the polymeric level, consequently lowering the Tg. Furthermore, the type of filler system plays a significant role: carbon black primarily establishes mechanical interlocking with and physical adhesion to the polymer, whereas silica forms chemical bonds with the polymer, restricting the movement of the polymer chains to a higher degree and thereby resulting in a higher Tg compared to the carbon black filled samples.

For the 100% model compound, the Tg was approximately -20°C. In the case of the 20% devulcanizate blend, the shift in Tg was negligible. However, with the inclusion of 50% devulcanizate, the Tg shifted to around -25°C, and for the 100% devulcanizate, it was approximately -35°C.

![Figure 9.13. Application study on devulcanizate blends: wet grip prediction](image-url)
Chapter 9

The wet grip performance of tires can be prognosticated by considering the Tan δ value at a temperature of 0°C. A higher Tan δ value at 0°C shows the higher amount of energy dissipation, which is indicative of improved tire performance in wet conditions, while a lower Tan δ value at 0°C suggests poorer wet grip properties. According to the data presented in Figure 9.13, it can be concluded that wet grip properties were enhanced with the inclusion of 20% devulcanizate.

Although the shift in the Tg values was not normalized, the overall conclusion to be drawn is that the model and 50% devulcanizate blend both showed the wet grip prediction in the similar range. The wet grip performance of the 100% devulcanizate was relatively inferior. A similar trend was reported by van Hoek⁴: with increasing concentration of devulcanizate in the virgin blend, up to a 30% devulcanizate content, wet grip performance showed an improvement. In our study as well, the sample with 20% oil reclaim exhibited comparable wet grip as the 50% devulcanizate blend.

There seems to be a certain threshold (20-30%) of devulcanizate incorporation, up to which the blend demonstrates an improvement in wet grip. Beyond this point, with an increase in the concentration of undevulcanized particles and reduction in the quantity of matrix material, the concentration of weak points is higher, resulting in poor energy dissipation indicating inferior wet grip properties.

This study shows that the inclusion of up to 20% devulcanizate is feasible for tire applications, with the most important improvement the increase in wet grip performance.

![Graph showing Tan δ vs Temperature for different blends](image)

*Figure 9.14. Application study on devulcanizate blends: rolling resistance prediction*
The rolling resistance performance of tires can be predicted by assessing the Tan δ value at a temperature of 60°C: A lower Tan δ value at 60°C indicates lower energy dissipation which signifies improved rolling resistance properties, while a higher Tan δ value at 60°C indicates higher energy dissipation resulting poorer rolling resistance. It can be concluded from Figure 9.14 that Tan δ values were in the same range for 100% model, 100% devulcanizate and 50% devulcanizate blends which are comparatively better than 20% devulcanizate and 20% oil reclaimed blends.

Compared to the 100% model compound, there was no significant reduction in rolling resistance for the 100% devulcanizate. However, the 20% devulcanizate blend and the 20% oil reclaimed blend exhibited a slight increase in rolling resistance, implying a small trade-off in rolling resistance performance. The inclusion of devulcanizate led to an increase in the stiffness of the material, primarily attributable to the higher degree of crosslinking in comparison to the virgin model compound as also concluded from the stress train properties (see Figure 9.5 and 9.6).

Little impact on rebound resilience measured at room temperature was observed with increasing devulcanizate concentration, as indicated in Figure 9.15. Both the 100% model compound and the 100% devulcanizate exhibited the same percentage of rebound. A reduction of approximately 7% in rebound resilience was noted for the 20% devulcanizate blend when compared to the model compound. However, for the 50% devulcanizate blend and the 20% oil reclaimed blend, no significant trend was evident.

In terms of predicting rolling resistance for tire applications, rebound resilience was measured at 60°C. A similar trend was observed at this temperature, mirroring the findings at room temperature. Specifically, the model compound displayed the highest...
rebound resilience, followed by the 50% devulcanize blend, a pattern consistent with the results obtained from dynamic mechanical analysis (Figure 9.14). Also a similar trend was observed for rebound resilience with DMA results, in the case of the 100% model and 20% devulcanizate blend.

As plotted in Figure 9.16, there is a trend of increasing loss during abrasion with a rising concentration of devulcanizate, indicative of diminished abrasion resistance. For the whole tire (WT) devulcanizate, variations in density were observed, attributed to the diverse origins of granules from different tires and tire parts. Typically, abrasion resistance is quantified in terms of volume loss but due to the density variations in the devulcanizate resulting from WT granulates, the abrasion resistance values were expressed in weight loss.

In the case of the 20% devulcanizate blend, there was a 10% reduction in abrasion resistance, while the 50% blend exhibited a more substantial decrease of approximately 32% in abrasion resistance. During abrasion resistance testing, the non-devulcanized particles in the rubber matrix tend to break out easily. This observation aligns with the inferior abrasion resistance exhibited by the 100% devulcanized samples when compared to the model compound.
Figure 9.17. Application study on devulcanizate blends: Payne effect of the uncured compound

Table 9.3. Application study on devulcanizate blends: differences in $G'$ and Payne effect

<table>
<thead>
<tr>
<th>Sample</th>
<th>Low to high strain sweep</th>
<th>High to low strain sweep</th>
<th>Payne effect* (KPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shear modulus $G'$ (KPa)</td>
<td>Shear modulus $G'$ (KPa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>min</td>
<td>Max</td>
</tr>
<tr>
<td>Payne effect of uncured samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% model</td>
<td>1212</td>
<td>192</td>
<td>185</td>
</tr>
<tr>
<td>20% devulcanizate</td>
<td>986</td>
<td>183</td>
<td>178</td>
</tr>
<tr>
<td>20% oil reclaimed</td>
<td>874</td>
<td>187</td>
<td>182</td>
</tr>
<tr>
<td>50% devulcanizate</td>
<td>874</td>
<td>177</td>
<td>172</td>
</tr>
<tr>
<td>100% devulcanizate</td>
<td>638</td>
<td>140</td>
<td>133</td>
</tr>
<tr>
<td>Payne effect of cured samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% model</td>
<td>3866</td>
<td>1385</td>
<td>1370</td>
</tr>
<tr>
<td>20% devulcanizate</td>
<td>3665</td>
<td>1155</td>
<td>1140</td>
</tr>
<tr>
<td>20% oil reclaimed</td>
<td>2851</td>
<td>987</td>
<td>973</td>
</tr>
<tr>
<td>50% devulcanizate</td>
<td>2375</td>
<td>1143</td>
<td>1136</td>
</tr>
<tr>
<td>100% devulcanizate</td>
<td>1833</td>
<td>942</td>
<td>935</td>
</tr>
</tbody>
</table>

*Payne effect = Difference between the maximum and minimum shear modulus of low to high strain sweep

As depicted in Figure 9.17 and Table 9.3, an evident trend was observed whereby the Payne effect of the uncured compound got decreased as the concentration of devulcanizate increased. The Payne effect for the 100% model compound was notably high, primarily attributed to its composition which included an 80 phr silica filler system.
In contrast, the feed material for the devulcanizate was passenger car tires from different grades: WT granulates are a blend of different polymers and filler systems. It is globally filled with 55-60 phr carbon black and 5-10 phr silica (as measured in the TGA analysis in Chapter 4, Figure 4.16) and subsequently underwent a high-shear devulcanization process, resulting in a relatively lower Payne effect as seen in this graph for the 100% devulcanizate sample.

As illustrated in Figure 9.18, an analogous trend was observed for the Payne effect of the cured compounds: it decreased as the concentration of devulcanizate increased. The shear modulus values displayed an increase compared to the uncured rubber, primarily attributed to the curing process: The formation of a crosslinked system led to higher shear modulus values.

**Figure 9.18. Application study on devulcanizate blends: Payne effect of the cured rubber samples**
Figure 9.19. Application study on devulcanizate blends: comparison of all properties

In Figure 9.19, all the values were normalized to the model compound set as 100. A higher index number indicates a better result and vice versa. Based on the comparative index, several general conclusions can be drawn:

i. No significant changes were observed in hardness as seen in Figure 9.11, but not depicted here.

ii. The stress-strain properties after ageing displayed an improvement as the concentration of devulcanizate increased.

iii. In the case of the 20% devulcanizate blend, both tear strength and wet grip exhibited enhancements.

iv. Rebound resilience at 60°C improved with increasing devulcanizate concentration.

Compared to the blend containing 20% oil reclaimed rubber, the one with 20% devulcanizate showed improvement in tensile strength, elongation at break, tear strength, abrasion resistance and wet grip properties. Furthermore, it's important to note that, aside from the results mentioned above, all other measured properties exhibited a gradual deterioration with increasing devulcanizate concentration. However, compared to reclaim, the devulcanizate blends always showed better properties.
9.4 Conclusions

One of the most important improvements when adding devulcanize as well as reclaim is the increased resistance to ageing: as the feedstock had already undergone ageing, it is evident that the incorporation of devulcanize and reclaim enhances the material's resistance to ageing. Furthermore, up to 20% devulcanize can be blended into a virgin compound without significant reduction in mechanical properties. When adding 50% devulcanize, around 25% of the mechanical property level got sacrificed. A linear relationship between reduction in tensile strength and elongation at break was noticed with the increasing devulcanize concentration up to 50%. For the 20% devulcanize blend, tear strength and wet grip got improved. Good processability was noticed for the devulcanize while blending and processing. Overall, 20% devulcanize can be used for a high performance application without significant sacrifice in required properties. Compared to the blend with reclaim, devulcanize blends always showed better in-tire properties.

9.5 References

CHAPTER 10

COMPARISON OF NEWLY DEVELOPED DEVULCANIZATES WITH COMMERCIAL ONES

This chapter focuses on comparing the devulcanizates developed in this study with commercial ones. Besides, the earlier stated correlation between tensile strength and total area of visible particles (TAVP) for the devulcanizates within this study is also made for the commercial samples based on different devulcanization aids (DAs) and process conditions.
10.1 Introduction

This chapter is dedicated to the investigation of two distinct facets. The first part involves the comparison between devulcanizates developed within this study and commercially available ones. The second part of this chapter aims to check the earlier established correlation between tensile strength and total area of visible particles (TAVP) for samples that have undergone devulcanization using various DAs under varying process conditions.

10.2 Comparison with commercial devulcanizates

The objective of this investigation was to conduct a comparative analysis between the optimized model as well as WT devulcanizates, and three commercially available devulcanizates. They were compared in terms of their mechanical properties based on stress-strain behaviour, miscibility through white rubber analysis, and material analysis using thermogravimetry and differential scanning calorimetry. The commercial devulcanizates being used for the analysis are sourced from Rubber Resources (Maastricht, the Netherlands), Rubber Green Industries (Frameries, Belgium), and Tyromer (Arnhem, the Netherlands).

10.2.1 Experimental process

The preparation of the devulcanizates developed in this study, sampling details and characterization processes are described in this section.

10.2.1.1 Preparation of newly developed devulcanizates

The feed material preparation for the model passenger car tire tread granulates was done according to the procedure described in Chapter 3, Section 3.2.1. The feed
material preparation for the whole passenger car tire rubber (WT) granulates was
detailed in Chapter 4, Section 4.6.1. All the samples were devulcanized by maintaining
the procedure as mentioned in Chapter 3, Section 3.2.2.

10.2.1.2 Preparation of commercial devulcanizates

Commercial devulcanizates were directly compounded without any modification.

10.2.1.3 Sampling details

All the devulcanizates were compounded only with the curing additives in the formulation
given in Table 10.1.

Table 10.1. Revulcanization formulation for all devulcanizates

<table>
<thead>
<tr>
<th>Function</th>
<th>Material</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base polymer</td>
<td>Devulcanizate</td>
<td>100</td>
</tr>
<tr>
<td>Activators</td>
<td>Zinc oxide</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
<td>2</td>
</tr>
<tr>
<td>Curatives</td>
<td>Sulphur</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>CBS</td>
<td>1</td>
</tr>
</tbody>
</table>

10.2.2 Testing process

The testing process consists of four parts:

i. Stress-strain properties in tensile mode (Chapter 3, Section 3.2.3.2).

ii. Homogeneity evaluation by white rubber analysis (Chapter 3, Section 3.2.3.3).

iii. The material analysis in terms of thermogravimetric analysis (Chapter 4, Section
     4.6.3.3).

iv. Glass transition temperature analysis by differential scanning calorimetry (DSC):

DSC was done in a Netzsch Polyma instrument, supplied by Netzsch Analysing and
Testing, Germany. The test was performed in nitrogen atmosphere with a flow rate of
50 ml/min and a ramp speed of 10°C/min. Two sweeps were performed ranging from
40°C to -115°C and from -115°C to 40°C.

10.2.3 Results

In this section, the stress-strain behaviour, homogeneity, thermal and thermogravimetric
analysis of the above mentioned samples are shown.

Table 10.2. Material analysis of the devulcanizates

<table>
<thead>
<tr>
<th>Devulcanizate</th>
<th>Filler content</th>
<th>Polymer content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial materials: Genan*,</td>
<td>25% – 27% Carbon black</td>
<td>45% - 50%</td>
</tr>
<tr>
<td>Rubber Resources, Tyromer</td>
<td>+ 4 – 5% Silica</td>
<td></td>
</tr>
<tr>
<td>Commercial materials: Rubber Green</td>
<td>30% – 32% Carbon black</td>
<td></td>
</tr>
<tr>
<td>Model devulcanizate</td>
<td>35% Silica</td>
<td></td>
</tr>
</tbody>
</table>

* Feed material for the newly developed devulcanizates
Figure 10.2 shows the TGA analysis curves, and Table 10.2 presents the material analysis of the various devulcanized rubber samples. The commercial devulcanizates have a filler content of 25-27% carbon black and a maximum of 4-5% silica, whereas the model devulcanizate contains around 35% silica. The polymer content of the model devulcanizate is almost the same as the one of the commercial samples.

The TGA curve of the model devulcanizate displays a different slope below 400°C, which is attributed to variation in volatile content, as the model sample is unaged. In the case of WT granulates, the blooming and degradation of oil and other volatiles occurs during their service life, due to the effect of ageing. Therefore, compared to the unaged newly developed (ND) devulcanizates, a lower amount of volatiles is present in the aged WT granulates.

![TGA analysis curves](image)

**Figure 10.2. Comparison with commercial devulcanizates: TGA analysis**

As plotted in Figure 10.3, the comparison of the tensile strength and elongation at break properties of the various devulcanized rubber materials indicate that the Rubber Green material has the highest tensile strength, followed by the devulcanizate from Tyromer, the model material, and the Genan and Rubber Resources devulcanizates. On the other hand the Tyromer devulcanizate has the highest elongation at break, followed by the one from Rubber Green, Genan, Rubber Resources, and then the model devulcanizate.
Figure 10.3. Comparison with commercial devulcanizates: tensile strength

Figure 10.4. Comparison with commercial devulcanizates: white rubber analysis
According to Figure 10.4, the analysis of the particle size distribution of the various devulcanized rubber materials shows that Rubber Green and Tyromer have a higher proportion of fine particles compared to the Model, Genan, and Rubber Resources material.

![Graph showing tensile strength vs TAVP](image)

**Figure 10.5. Comparison with commercial devulcanizates: tensile strength vs TAVP**

In Figure 10.5, a comparison between the tensile strength of the various devulcanized rubber materials and the total area of visible particles (TAVP) indicates that the Rubber Green and Tyromer samples exhibit better tensile strength and particle area properties in comparison to the other materials. The TAVP comparison demonstrates that Rubber Green material has the smallest TAVP value, followed by Tyromer, Genan, Rubber Resources, and Model, respectively.

If the devulcanizates are categorized, two distinct feedstock types emerge: SBR-BR based (Model and Genan) and NR based (Tyromer, Rubber Resources and Rubber Green). Testing one representative from each category provides an overview of the glass transition (Tg) for all devulcanize samples.
Figure 10.6. Comparison of Model and Tyromer devulcanizates: DSC analysis

The DSC results as shown in Figure 10.6 indicate that the model devulcanizate shows Tg’s at -32°C and -66°C. The base polymers of the model devulcanizate were 70% styrene-butadiene rubber (SBR) and 30% polybutadiene rubber (BR). The Tg of BR is around -95°C and SBR is around -15°C. As the devulcanized polymer chains are not completely free in the matrix, the contribution from the partly devulcanized part may shift the BR peak to a higher Tg as measured of around -66°C. In comparison, the devulcanizate supplied by Tyromer exhibits one Tg of -60°C for natural rubber.

10.2.4 Discussions

The observed differences in mechanical properties may be attributed to variations in the feed material. Rubber Green, Rubber Resources and Tyromer samples were obtained from aircraft tire and truck tire devulcanizates, respectively, which include natural rubber and carbon black as filler. In the case of newly developed devulcanizate, the feed material was passenger car tire devulcanizate, containing SBR-BR and silica-silane as filler. In addition to differences in feed material, variations may also arise from the devulcanization process, which involves the use of supercritical CO₂ and an extruder for the Tyromer devulcanizate.

Additionally, the Tyromer samples exhibit slow burning of carbon black; to reconfirm this the tests were repeated three times and showing the same trend. The reason behind this observation is not obvious as not much is known about the sample composition and the devulcanization process.

Looking at the strength properties, high temperatures and shear forces in the extruder cause a higher degree of polymer breakdown of natural rubber, compared to the SBR-
BR based passenger car tire devulcanizate. A higher degree of devulcanization allows to reform a more controlled new network and thus contributes to a higher tensile strength of the revulcanizate. Additionally, it results in a lower total area of visible particles. Besides, there are unknown industrial details which also play a role for the properties of devulcanized rubber materials.

10.2.5 Conclusions

The comparative analysis reveals that the newly developed devulcanizate exhibits comparable properties to commercial counterparts based on passenger car tire rubber. Variations in feed material such as the presence of NR, the filler system, and devulcanization process account for the differences observed in the properties of devulcanized rubber.

As an outlook, shifting from the batch process to the continuous process may offer opportunities for further improving the quality of the newly developed devulcanizate. Subsequent experiments were conducted to investigate this possibility, and devulcanization was carried out using an extruder.

10.3 Correlation studies on tensile strength and total area of visible particles (TAVP) of devulcanized rubber

Devulcanization of rubber aims at the scission of crosslinks and keeping the main polymer chains intact; however, practically this is not possible. During devulcanization, a certain amount of polymer scission takes place along with crosslink scission. Crosslink scission maintains the mechanical strength of the devulcanized rubber. During random chain scission, the mechanical strength decreases because of the broken polymer backbone, but miscibility improves as the polymer fragments are detached from the network except for entangled polymer chains. Free polymer chains obtained from crosslink or random scission are miscible with the rubber compound, but the undevulcanized particles within the devulcanized rubber matrix are immiscible. Considering this phenomenon, immiscible particles become visible in a blend with white rubber. For poorly devulcanized rubber, the number of undevulcanized particles is higher resulting in more counts of immiscible particles in the white rubber matrix.

Due to the inconsistent particle size distribution among the devulcanizates: The Tyromer and Rubber Green devulcanizates have a considerably higher number of very small particles, a direct comparison with mechanical properties is not feasible. To address this disparity, the measurement of the total area of visible particles (TAVP) was employed, providing an indication of the devulcanizate miscibility.

The aim of this section is to establish a correlation between the tensile strength and TAVP for samples based on different feed material, devulcanized with different DAs and under variable process conditions. A silica-filled SBR-BR-based ground model tire tread compound was devulcanized with VP, VTEO, TESPT and DPDS at variable temperatures, time and rotor speed (Chapter 3). The tensile strength of the de- and revulcanized rubber was measured and correlated to the TAVP of the same sample.
obtained by the white rubber analysis. Samples combining a low TAVP with a high tensile strength feature a high efficiency of devulcanization.

10.3.1 Experimental process

Preparation of the feed material, sampling plan and characterization processes are described in this section.

10.3.1.1 Preparation of the feed material

The feed material preparation for the model passenger car tire tread granulates was done according to the procedure described in Chapter 3, Section 3.2.1. All samples were devulcanized as described in Chapter 3, Section 3.2.2.

10.3.1.2 Sampling details

Five devulcanization parameters were varied in this investigation. The parameter windows were selected based on the experimental data from Chapter 3 and 4. The results obtained from Chapter 4 for the VP devulcanized samples were utilized for this section. Additionally, samples with other devulcanization aids (VTEO, TESPT, and VTEO) were prepared specifically for this study.

i. Devulcanization temperature: 130°C to 230°C at an interval of 10°C.

ii. Residence time: 4 minutes to 6 minutes at an interval of 1 minute.

iii. Shear rate: 50 RPM to 150 RPM at an interval of 25 RPM.

iv. DA type: VP, VTEO, TESPT and DPDS (taken as reference)

v. DA concentration: 2% to 7% at an interval of 1%.

10.3.1.3 Testing process

The testing process contains two parts:

i. Stress-strain properties in tensile mode (Chapter 3, Section 3.2.3.2).

ii. Total area of visible particle evaluation by white rubber analysis (Chapter 3, Section 3.2.3.3).

10.3.2 Results

In Figure 10.7, the correlation of the tensile strength and TAVP of the devulcanized samples are shown with variable DAs and process conditions. The series are named according to the respective DA’s. The letter ‘M’ represents that the feed material is the model compound and the letter ‘R’ represents the reference sample.

The VP devulcanized samples show the highest tensile strength around 9.4 MPa and minimum TAVP around 1%, followed by the VTEO and TESPT devulcanized samples. The reference DPDS sample shows a tensile strength around 7.2 MPa and TAVP around 3%.
### 10.3.3 Discussion

The devulcanization process is a thermo-mechano-chemical process, and each part plays its role effectively during the reaction. However, in a specific process window, one of the components became dominant.

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**Figure 10.7. Correlation between tensile strength and TAVP of devulcanizates**

**Figure 10.8. Components of the TAVP correlation curve**
In Figure 10.8, this series of experiments can be classified into three parts: mechanical, thermal and chemical breakdown. During the process optimization with variable rotor speed and residence time, the mechanical component is dominant: It increases the tensile strength and decreases the TAVP as shown by the dotted blue line with the gradual increase in RPM and residence time from right to left. Thermal degradation starts at lower temperatures but above 180° C, thermal degradation of the SBR-BR blend becomes dominant. Due to this, the tensile strength decreases rapidly as obvious from the brown dotted line. Elevated temperatures transform the SBR-BR-based model compound into hard, brittle rubber prone to be ground. The grinding effect in the early stages of the devulcanization process causes an increase in TAVP. For example, when a few bigger particles got ground, many small particles are formed, resulting in an increase in surface area. Hypothetically, when a cube with a side length of 2 µm is considered, it possesses a surface area of 24 µm² and a volume of 8 µm³. Subsequently, by grinding upon reduction to a cube with a side length of 1 µm, the surface area undergoes an increase to 48 µm² while maintaining the same volume.

On the other hand thermal degradation reduces the TAVP as the rubber gets degraded and miscible and thus particles get smaller. Considering these opposite effects, the slight increase in TAVP for high degradation temperatures demonstrates the balance of the grinding and degradation effect showing a slight dominance of the former. When increasing the DA concentration, tensile strength increases up to a certain level with a gradual decrease in TAVP as shown by the green line which shows improved miscibility at higher DA concentrations.

10.3.4 Conclusions

The components of the devulcanization reaction: thermal, mechanical and chemical breakdown, all have their respective significance during the devulcanization process. With the increase of these three parameters, TAVP decreases gradually showing higher devulcanization efficiency. The devulcanized sample using VP exhibited superior mechanical strength and miscibility, followed by VTEO. TESPT demonstrated a performance between vinyl silanes and the reference DPDS. The efficiency ranking of the devulcanization aids was ranked as VP > VTEO > TESPT > DPDS. Vinyl moieties in the DA displayed enhanced devulcanization efficiency compared to the conventional DPDS. The introduction of peroxide along with vinyl moieties (VP) enhanced the devulcanizate quality further.
This chapter focuses on upscaling of the devulcanization process as developed and optimized on small scale in an internal mixer, and transforming it to a continuous process in an extruder. This includes screw configuration and optimization of the process parameters such as temperature, screw speed, and residence time. Type and concentration of devulcanization and process aids were other factors to be optimized. The final aim of this study is to boost productivity for the production of a high quality devulcanizate and industrialization of the developed technology.
11.1 Introduction

Figure 11.1. Flowchart of the study up to Chapter 11

This chapter is dedicated to upscaling of the devulcanization process in an extruder, with focus on the transition from a batch process to a continuous one and enhancement of devulcanizate quality. The upscaling trials entailed alterations to the screw configuration and process parameters: Initially, temperature optimization was conducted with a reference screw configuration. Subsequently, the optimization process extended to the shear rate and screw profile. Upon optimizing the operating conditions, the final two steps encompassed variations in devulcanization aids and process aids.

11.2 Temperature optimization experiments in an extruder

The devulcanization temperature stands as a paramount parameter in process optimization. Operating below the optimum temperature leads to inadequate devulcanization, while exceeding it results in polymer chain degradation. In the batch process, initially optimized in an internal mixer, the optimal temperature for whole tire (WT) rubber granulates was determined to be 180°C, serving as the starting point for subsequent experiments. The choice of screw configuration and screw speed was guided by the findings of van Hoek\(^1\) from an earlier study using the same feed material and a screw speed of 25 rotation per minute (RPM). Keeping this reference parameter constant, the temperature profile of the extruder was systematically varied to optimize this parameter.

11.2.1 Experimental process

This section provides a comprehensive description of the feed granulate preparation, extruder specifications with screw configuration, sampling procedures, and characterization methods employed in the study. It applies to all optimization steps described in this chapter.
11.2.1.1 Preparation of feed material

The feed material preparation for the whole passenger car tire rubber (WT) granulate was done according to the procedure as described in Chapter 4, Section 4.7. 5% (w/w) VP as DA and 5% (w/w) TDAE oil as the process aid (PA) were employed in these experiments. The term "blank sample" refers to granulates which were extruded without the use of a DA or PA.

11.2.1.2 Extruder specifications and screw configuration

The experiments were done in a twin screw extruder manufactured by Krauss Maffei, Germany. A picture of the extruder is shown in Figure 11.2. The specifications of the extruder are mentioned below:

- Diameter – 2.5 cm
- Length : diameter (L/D ratio) – 42
- Rotor type – Co-rotating
- Power input – 36 kW
- Screw type – Twin screw
- Screw speed limit – 300 RPM
- Screw pressure safety limit – 60 bar
- Operational heating zones – 10 zones including feed zone
- Hopper type – Gravitational feed
- Hopper filling – Manual
- Operation control – Electronic type
- Cooling system – Water cooling
- Venting – 4 vents with N₂ flow set up

Figure 11.2. Extruder employed in the investigation

Screw Configuration 1 as shown in Figure 11.3 was used for these experiments. Four vents were incorporated into the extruder, with one located at the feed zone, another at the die zone, and two positioned in between. In order to mitigate oxidative degradation, nitrogen gas is purged into the barrel. The strategic placement of conveying and shearing zones is carefully executed to uphold barrel pressure within prescribed limits and to achieve the requisite shear force.
11.2.1.3 Sampling details

The initial sampling plan was formulated based on the results obtained from the batch process optimization using identical feed material and a DA, as well as the findings presented in Hans van Hoek's PhD thesis on devulcanization process optimization in the same extruder. Sampling details of the temperature optimization experiments in the extruder are given in Table 11.1.

Table 11.1. Sampling details of temperature optimization experiments in the extruder

<table>
<thead>
<tr>
<th>Screw</th>
<th>Temperature profile (°C X number of zones)</th>
<th>DA + Additive (% w/w)</th>
<th>RPM</th>
<th>Residence time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180X10</td>
<td>5% VP + 5% TDAE</td>
<td>25</td>
<td>6 min 10 s</td>
</tr>
<tr>
<td></td>
<td>200X6 + 180X4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>220X6 + 200X4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>220X10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>210X10</td>
<td>Blank</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>210X10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To measure the residence time, cured white rubber granules (immiscible with black WT granulates) without DA were fed into the extruder alongside WT granules containing the DA. The DA is not migrating from the WT feed material into the white rubber particles; they pass the extruder without major change. The residence time of the granulates in the extruder was determined through manual measurement using a stopwatch, which involved recording both the entry and exit times of the white granulates. With the reference screw configuration (Screw 1) and a screw speed of 25 RPM, the granulates exhibited a residence time of 6 minutes and 10 seconds ± 5 seconds. To restrict thermal degradation of the devulcanizate, it was cooled after extrusion.

All devulcanizates were compounded with the curatives and revulcanized using the formulation given in Chapter 3, Section 3.2.1.5.

11.2.2 Testing process

The testing process consists of four parts:

i. Processability of the rubber in terms of viscosity.
ii. Degree of devulcanization as determined by the Horikx Verbruggen plot.
iii. Homogeneity evaluation by white rubber analysis.
iv. Stress-strain properties in tensile mode.

The viscosity measurements are detailed in the Chapter 4, Section 4.6.3.1. A detailed description of the last three measurements is given in Chapter 3, Section 3.2.3.1 to 3.2.3.3.

11.2.3 Results

In this section, the stress-strain behaviour, viscosity, network breakdown and miscibility analysis of the above mentioned samples are shown. The sample notations are based on the temperature profile and given as °C X number of zones, as indicated also in Table 11.1.

As illustrated in Figure 11.4, a gradual temperature increase led to a corresponding gradual rise in tensile strength, peaking at 210°C with 7.5 MPa, after which a decline was observed. The best results were achieved across all ten zones set to a temperature of 210°C. Blank samples (without DA and PA) exhibited a significantly lower tensile strength of approximately 5.8 MPa after processing at 210°C.

As depicted in Figure 11.5, a progressive temperature increase resulted in a corresponding gradual elevation in elongation at break of the devulcanizate, reaching a maximum of 149% at 220°C, beyond which a decline was evident. Blank samples demonstrated an elongation at break of approximately 118% at 210°C.
As shown in Figure 11.6, a consistent elevation in temperature coincided with a gradual reduction in viscosity, reaching a minimum value of 96 MU at 220°C. At 180°C, viscosity was measured to be 116 MU, which decreased to 103 MU at 210°C. Blank samples exhibited a viscosity of 119 MU at 210°C, demonstrating the necessity of a DA and PA.
The gradual decline in viscosity suggests improved processability of the devulcanizate. However, it needs to be mentioned that the best sample still exceeded the industrially acceptable limit (around 80 MU), necessitating further optimization of the process or post-treatment.

According to the data presented in Figure 11.7, both network breakdown percentage and sol content exhibited a gradual increase as the temperature was elevated. The presence of VP as a DA contributed to an improved degree of crosslink to random scission, thereby enhancing the efficiency of the devulcanization process through more selective breakdown. In the absence of a DA and at temperatures exceeding 210°C, the sol content levels were notably high, indicating a greater degree of random chain scission. Specifically, at a temperature of 180°C, the network breakdown and sol content percentages were 45.3% and 8.2%, respectively. These values increased to 61% for network breakdown and 17.2% for sol content at 210°C. Conversely, the sample without a DA exhibited approximately 49% network breakdown and 17.2% sol content at 210°C, surpassing the threshold for random scission.

As depicted in Figure 11.8, with increased devulcanization temperature the particle size distribution shifted towards finer particles indicating a grinding effect of the larger particles in the feedstock. The sample devulcanized at 180°C temperature showed a total number of undevulcanized particles of 1091, which increased up to 1298 at 220°C temperature. Well-devulcanized samples exhibited better miscibility compared to inadequately devulcanized ones. Notably, samples devulcanized with VP displayed a finer particle size distribution when contrasted with those devulcanized in absence of VP.

**Figure 11.7. Temperature optimization in the extruder: network breakdown**
11.2.4 Discussion

According to the extruder optimization experiments it can be concluded that the devulcanization efficiency got improved up to 210°C in presence of the DA. Beyond this threshold, thermal degradation of the polymer chain became dominant, leading to a decline in stress-strain properties. The inclusion of VP as a DA played a crucial role in augmenting the devulcanization process efficiency by promoting a higher degree of crosslink relative to random scission, which was achieved through a selective network breakdown, scavenging the radicals and restricting recombination mechanism.

In the extruder, the first three zones may be characterized as the feed zone, wherein the material attains the requisite devulcanization temperature. In this zone, conveying elements are employed to restrict the backflow of granulates. Zones 4 through 8 yield a high shear force facilitating the devulcanization reaction by the utilization of shearing elements. The final two zones preceding the die represent the compression zone, wherein conveying elements are utilized.

To mitigate thermal degradation following contact with the air, the temperature of the last few zones is lowered. Achieving efficient reactions across these distinct zones is imperative for the successful execution of the devulcanization process; thus, the judicious configuration of extruder parameters is important. The best devulcanize so far was achieved for Screw Configuration 1 and a temperature of 210°C at 25 RPM, and was characterized with:

a) Tensile strength: 7.5 MPa
b) Elongation at break: 140%
c) Network breakdown: around 61%

d) Mooney viscosity: 103 MU

### 11.2.5 Conclusions

A temperature of 210°C can be deemed as the optimal choice within this study, and should be employed for subsequent experiments. VP demonstrated notable efficiency for devulcanization and resulted in best performance in terms of stress-strain properties, network breakdown, viscosity, and miscibility. Further process optimization steps are necessary to attain an even superior quality of the devulcanizate. Compared to the batch process, the quality of the extruder devulcanizates were comparatively lower. The temperature was optimized in the extruder, but insufficient shear forces may be the primary factor contributing to an inadequate devulcanization process, necessitating the implementation of a high-shear screw configuration.

### 11.3 Shear rate and screw profile optimization in the extruder

In Section 11.2, a temperature of 210°C was identified as the optimal operation temperature within the parameter window of this study. Subsequent optimization efforts were directed towards enhancing the devulcanization process through modifications of the screw profile and configuration as well as shear rate. To achieve a comparable shear force of the continuous process to the batch process, a higher amount of shear forces is required for sufficient devulcanization. The screw profile essentially comprises two components: conveying and shearing zones. The primary objective of these trials was to augment shear forces by expanding the shearing zones. Alternatively, increasing the screw speed can also enhance shear forces, although this adjustment poses a challenge in terms of optimizing reaction time, given that a higher screw speed results in shorter residence times. Thus, a delicate balance is necessitated in this regard.

#### 11.3.1 Experimental process

The feed material preparation, extruder specification and characterization methods are as described in Section 11.2.1. This section provides a comprehensive description of the adjusted screw configuration and sampling procedures employed in the study.

#### 11.3.1.1 Screw configuration

The screw configuration used for these experiments is shown in Figure 11.9. 

---

**Figure 11.9. Screw Configuration 2**
11.3.1.2 Sampling details

Sampling details of the shear rate and screw profile optimization experiments in the extruder are mentioned in Table 11.2. All devulcanizates were compounded only with the curatives according to the formulation given in Chapter 3, Section 3.2.1.5.

Table 11.2. Sampling details of shear rate and screw profile optimization experiments

<table>
<thead>
<tr>
<th>Screw</th>
<th>Temperature profile (°C X number of zones)</th>
<th>DA + Additive (% w/w)</th>
<th>RPM</th>
<th>Residence time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>210 X 10</td>
<td>5 % VP + 5% TDAE</td>
<td>25</td>
<td>6 min 10 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>210 X 10</td>
<td>5 % VP + 5% TDAE</td>
<td>25</td>
<td>7 min 40 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>3 min 55 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>75</td>
<td>2 min 20 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>1 min 25 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>25</td>
<td>7 min 40 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>1 min 25 s</td>
</tr>
<tr>
<td>2</td>
<td>210 X 8 + 200 X 2</td>
<td>5 % VP + 5% TDAE</td>
<td>25</td>
<td>7 min 40 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>3 min 55 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>75</td>
<td>2 min 20 s</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>1 min 25 s</td>
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<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>25</td>
<td>7 min 40 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>1 min 25 s</td>
</tr>
</tbody>
</table>

To reduce the thermal degradation of the devulcanizate due to contact with air, the temperature of the last few zones is lowered. This temperature profile was compared with the setup in which all zones are maintained at the same temperature, to assess the effect of degradation.

11.3.2 Results

This section presents an analysis of the stress-strain behaviour, viscosity, network breakdown, and miscibility of the aforementioned samples. The sample notations are based on the screw speed values in the respective experiments. As depicted in Figure 11.10, a progressive increment in shear rate was associated with a gradual elevation in tensile strength, reaching a peak of 8.7 MPa at 100 RPM with Screw Configuration 2. Further screw speed escalation beyond this point was constrained due to barrel pressure limitations ensuring safety. Blank samples (lacking DA and PA) demonstrated a tensile strength of approximately 6.8 MPa at 100 RPM with the same screw configuration. No significant difference was observed between the results obtained at 210°C within the 10 zones, when compared to the results obtained at 210°C in 8 zones and 200°C in 2 zones. The devulcanizates prepared with screw set up 2 and using a higher screw speed showed comparatively superior tensile strength compared to Screw Configuration 1 after revulcanization.
Figure 11.10. Shear rate and screw profile optimization in the extruder: tensile strength

As illustrated in Figure 11.11, the trend observed for elongation at break closely paralleled that of tensile strength. Specifically, the optimal configuration was observed with Screw Configuration 2, operating at 100 RPM, and a temperature profile of 210°C in 10 zones, yielding the highest elongation at break reaching 162%.

Figure 11.11. Shear rate and screw profile optimization in the extruder: elongation at break
Figure 11.12. Shear rate and screw profile optimization in the extruder: viscosity

As seen in Figure 11.12, a systematic increase in shear rate corresponded to a gradual decrease in viscosity of the devulcanizate, reaching its lowest point at 83 MU when employing a shear rate of 100 RPM and Screw Configuration 2. Blank samples exhibited a viscosity of 119 MU at 25 RPM, which decreased to 102 MU at 100 RPM. The gradual reduction in viscosity implies enhancements in both viscoelastic properties and the processability of the devulcanizate.

The presence of TDAE oil led to swelling of the granulates, and the presence of DA facilitated an efficient devulcanization process. This resulted in a viscosity reduction of approximately 10 MU compared on the basis of equal screw speed. In the case of the blank samples, there was a decrease in viscosity of around 20 MU with an increase in shear rate. Specifically, at a screw speed of 25 RPM, the viscosity was around 120 MU, which subsequently decreased to 100 MU at a screw speed of 100 RPM. It is expected that the mere addition of 5% DA and 5% oil will also result in reduction of viscosity due to plasticization effect.

Figure 11.13 illustrates a gradual increase in both network breakdown percentage and sol content as the shear rate was raised. Specifically, when operating at 25 RPM with Screw Configuration 2, the network breakdown and sol content percentages were 61% and 14%, respectively. These values increased to 68% for network breakdown and 17.1% for sol content at 100 RPM with the same screw configuration. Conversely, the sample lacking a DA exhibited approximately 55% network breakdown and 20.9% sol content at 100 RPM, shifting the data points close to the random scission line.
Figure 11.13. Shear rate and screw profile optimization in the extruder: network breakdown

Figure 11.14. Shear rate and screw profile optimization in the extruder: white rubber analysis

As illustrated in Figure 11.14, the observed trend indicated that with an increase in shear rate, there was a corresponding shift in particle size distribution towards smaller
particles, resulting in an augmentation of the total number of visible particles. Well-devulcanized samples demonstrated enhanced miscibility when compared to inadequately devulcanized counterparts. Importantly, samples subjected to devulcanization in presence of VP exhibited a finer particle size distribution in contrast to those devulcanized without DA. It is noteworthy that the results of the white rubber analysis for the temperature profile of 210°C in 10 zones showed a similar trend as the one for 210°C in 8 zones together with 200°C in 2 zones.

![Figure 11.15. Shear rate and screw profile optimization in the extruder: correlation tensile strength vs TAVP](image)

As plotted in Figure 11.15, with progressively elevated devulcanization temperature and shear rate, there was a gradual increase in tensile strength and a concomitant reduction in the total area of visible particles (TAVP). A lower TAVP signifies enhanced miscibility, indicative of higher devulcanizate quality. Through this optimization process, a reduction of TAVP down to 1.7% was achieved, alongside a tensile strength of 8.7 MPa with Screw Configuration 2 at 100 RPM.

### 11.3.3 Discussion

The selection of parameters for this trial was determined by the findings from the previous serious of experiments focused on temperature optimization. In this trial, the shear rate was varied while maintaining the optimal temperature profile elaborated in the first step. To minimize the degradation upon contact with air, the devulcanizate was rapidly cooled after exiting the extruder by submerging it in water, therefore a temperature reduction of the extruder in the last two zones had no measurable effect on the devulcanizate quality. In comparison to the process optimization achieved in an internal mixer, similar levels of stress-strain properties were attained in this process optimization. However, when considering the TAVP, it can be deduced that the quantity of immiscible particles was higher in the devulcanizates processed in the extruder.
compared to those from the internal mixer. This indicates a potential for further improving the quality of the devulcanizate in terms of miscibility as well as properties.

As the temperature increases, thermal degradation becomes more predominant, leading to lower viscosity and reduced shearing forces. Conversely, at higher screw speeds, a greater amount of shear forces impacts on the granulate. When operating in the optimal temperature range, it was observed that higher screw speeds not only resulted in increased productivity, but also improved the degree of devulcanization. It can be inferred that additional improvements may be achieved through maintaining a balance between screw speed and configuration. Incorporating high shear elements capable of generating a substantial shear force and adjusting the screw speed ensure a sufficient reaction time for devulcanization.

As the shear rate increased and a greater number of shear zones were incorporated into the screw profile, an enhancement in devulcanization efficiency was observed. This improvement is indicated by the enhanced stress-strain properties and the reduction in viscosity, particularly evident in Screw Configuration 2. The inclusion of VP as DA notably enhanced the ratio of crosslink to random scission, thereby augmenting the efficiency of the devulcanization process through selective breakdown mechanisms. In the absence of a DA, sol content levels were markedly elevated, signifying a more pronounced occurrence of random chain scission.

Compared to the temperature optimization process, improvements in mechanical, network breakdown and viscoelastic properties were noticed. For Screw Configuration 2 at a temperature of 210°C for 10 zones and at 100 RPM screw speed, the optimum devulcanizate showed:

- a) Tensile strength: 8.7 MPa
- b) Elongation at break: 162%
- c) Network breakdown: 68%
- d) Mooney viscosity: 82 MU

11.3.4 Conclusions

This process optimization yielded stress-strain properties at levels comparable to those achieved through the internal mixer process optimization. In the internal mixer, the initial temperature was set at 180°C; however, owing to the application of high shear forces, it elevated the stock temperature to a range between 210°C to 215°C. In the extruder a temperature of 210°C maintained across all zones, coupled with an operational screw speed of 100 RPM, can be considered as the optimal configuration within this study and should be utilized in subsequent experiments. Enhancing the number of shearing zones in Screw Configuration 2 may potentially lead to further improvements in devulcanizate quality. Therefore, additional process optimization steps are essential to achieve a further improved devulcanizate quality.

11.4 Temperature and shear rate optimization experiments in the extruder: 2nd iteration

Based on the observations outlined in Sections 11.2 and 11.3, an optimal operating temperature of 210°C for all zones and a screw speed of 100 RPM were identified.
Comparable tensile strength values were obtained from both the internal mixer and extruder trials. However, the TAVP values of the extruder trial samples were comparatively higher than the ones of the internal mixer samples. Consequently, it was determined that there might be potential for further process and product improvement. To address this, additional shearing zones were incorporated into the screw profile. The inclusion of the high-shear screw resulted in the maximum barrel pressure reaching the safety limit, thereby restricting the maximum attainable shear rate to 75 RPM. As the screw configuration significantly influences the temperature profile, finetuning of that parameter was again conducted.

11.4.1 Experimental process

The procedures for feed material preparation, extruder specifications, and characterization methods remained consistent with those detailed in Section 11.2.1. This section offers a thorough account detailing of the screw configuration and sampling procedure utilized throughout the research.

11.4.1.1 Screw configuration

The screw configuration used for these experiments is shown in Figure 11.16.

![Figure 11.16. Screw Configuration 3](image)

11.4.1.2 Sampling details

Table 11.3 provides specific information regarding the sampling procedures employed during the shear rate and temperature optimization experiments conducted in the extruder. According to the preceding investigation, the significance of incorporating high shear elements within the screw configuration was evident. Consequently, for these experiments, a high shear screw was employed. Furthermore, the investigation underscored the critical role of temperature and screw speed in the devulcanization process. It was imperative to explore the impact of temperature and screw speed within the framework of the high shear screw configuration.

<table>
<thead>
<tr>
<th>Screw</th>
<th>Temperature profile (°C X number of zones)</th>
<th>DA + Additive (% w/w)</th>
<th>Speed (RPM)</th>
<th>Residence time</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>180 X 10</td>
<td>5 VP + 5 TDAE</td>
<td>25</td>
<td>8 min 10 s</td>
</tr>
<tr>
<td></td>
<td>200 X 10</td>
<td></td>
<td>50</td>
<td>4 min 10 s</td>
</tr>
<tr>
<td></td>
<td>210 X 10</td>
<td></td>
<td>75</td>
<td>2 min 15 s</td>
</tr>
<tr>
<td></td>
<td>220 X 10</td>
<td>Blank</td>
<td>75</td>
<td>2 min 15 s</td>
</tr>
</tbody>
</table>
As in the former experimental series, the devulcanizates were compounded with curatives only as specified in the formulation detailed in Chapter 3, Section 3.2.1.5.

11.4.2 Results

In this section, an analysis of the stress-strain behaviour, viscosity, network breakdown, and miscibility of the above mentioned samples is presented.

As illustrated in Figure 11.17, a gradual increase in shear rate and temperature up to 210°C was correlated to a progressive elevation in tensile strength, ultimately peaking at 9.6 MPa. The optimal outcomes were consistently attained at temperatures of 210°C, and beyond this point, a decrease in tensile strength was observed due to thermal degradation of the main polymer backbone. Blank samples (devoid of DA and PA) exhibited an approximate tensile strength of 6.9 MPa at 210°C. In the initial trial reported in Section 11.2., the influence of temperature was dominant, particularly as the screw profile had not been optimized. Within the first screw configuration, elevating the extruder set temperature from 180°C to 210°C resulted in an increase in tensile strength from 6.1 MPa to 7.5 MPa at a screw speed of 25 RPM. Conversely, when employing the high shear screw configuration (Screw Configuration 3), the tensile strength exhibited a rise from 8.1 MPa to 9.2 MPa within the operational conditions.

![Figure 11.17. Temperature and shear rate optimization in the extruder: tensile strength](image)

As shown in Figure 11.18, a gradual increase in both temperature and shear rate led to a corresponding gradual rise in elongation at break, culminating at a maximum of 174% at 210°C and 75 RPM; beyond this temperature, a decline in elongation is evident. Blank samples exhibited an elongation at break of approximately 143% at 210°C and 75 RPM. In summary, it can be concluded that the trend in elongation at break mirrored that of the tensile strength.
In the case of virgin compounds after vulcanization, there is typically a reciprocal relationship of elongation at break with tensile strength considering the network density: due to an additional crosslink formation, an increase in tensile strength occurs caused by a stronger network, but that reduces elongation at break simultaneously. However, for devulcanizates, this reciprocal relationship does not hold because stress-strain properties mostly depend on the degree of free polymer chains available due to efficient crosslink scission. When the quantity of free long polymer chains increases, tensile strength and elongation at break both increase gradually. While it may appear surprising, it is a logical observation when considering the varying quality of devulcanizates and revulcanizates.

![Figure 11.18. Temperature and shear rate optimization in the extruder: elongation at break](image)

As depicted in Figure 11.19, a consistent increase in temperature and shear rate corresponded to a gradual decrease in viscosity, ultimately reaching a minimum value of 80 MU at 220°C and 75 RPM. At 180°C and 25 RPM, the viscosity was 95 MU, which subsequently decreased with increasing rotor speed and temperature. In the case of blank samples, a viscosity of 97 MU was observed at 210°C and 75 RPM and for the devulcanizate, a viscosity of 82 MU was observed in the same circumstances. High values of viscosity result in inferior viscoelastic properties, as the processibility of the devulcanizate gets difficult above 90 MU and the final network comprising the remaining and the new network is less controlled. The gradual reduction in viscosity within this range implies improvements in both viscoelastic properties and the processability of the devulcanizate.
According to the data presented in Figure 11.20, both the percentage of network breakdown and sol content displayed gradually increases as temperature and shear rate were raised. The inclusion of VP as DA contributed to an enhanced degree of crosslink to random scission, thereby improving the efficiency of the devulcanization process.
through selective breakdown. Specifically, when operated at 25 RPM and 180°C with Screw Configuration 3, the percentages of network breakdown and sol content were recorded at 62.3% and 14%, respectively. These values increased to 72.1% for network breakdown and 16.2% for sol content when operating at 210°C and 75 RPM with the same screw configuration. In contrast, the sample lacking a DA exhibited approximately 62% network breakdown and 19% sol content at 210°C and 75 RPM, and approaching the limits of random scission.

As illustrated in Figure 11.21, the observed trend indicates that with an increase in devulcanization temperature and shear rate, the particle size distribution shifted towards smaller particles, resulting in an increase in the overall number of visible particles. Notably, samples subjected to devulcanization in the presence of VP displayed a finer particle size distribution when compared to those devulcanized without DA.

![Shear optimization: Screw setup 3 - 210°C X 10 Zones - 75 RPM](image)

**Figure 11.21. Temperature and shear rate optimization in the extruder: white rubber analysis**

As depicted in Figure 11.22, with the progressive increase in devulcanization temperature and shear rate, there was a gradual elevation in tensile strength accompanied by a concurrent decrease in the total area of visible particles (TAVP). A lower TAVP indicates enhanced miscibility, which is indicative of a higher quality devulcanizate. Through this optimization process, a reduction in TAVP down to 0.61% and a tensile strength of 9.2 MPa were achieved. However, the highest tensile strength of 9.6 MPa, coupled with a TAVP of 0.79%, was attained at 210°C using Screw Configuration 3 at 75 RPM. It was noted that the stress-strain, network breakdown, and viscoelastic properties of the same devulcanizate exhibited a variation of ±5%; therefore, this level of variation can be deemed as negligible.
11.4.3 Discussion

An enhancement in devulcanization efficiency was observed as the shear rate increased by a greater number of shear zones incorporated in the screw profile. This improvement is evidenced by the enhanced stress-strain properties and the reduction in viscosity, particularly notable in screw set up 3. It can be inferred that devulcanization efficiency under these circumstances also improved up to 210°C. Beyond this temperature threshold, thermal degradation of the polymer chain became dominant, resulting in a decline in stress-strain properties as also found in the temperature optimization trials mentioned in Section 11.2.

As discovered in the investigation detailed in Section 11.3, there was an improvement in the quality of the devulcanizate with increasing shear rate. A similar trend was also observed in the current investigation. However, it should be noted that the limitations of the extruder prevented operation at 100 RPM with Screw Configuration 3.

The inclusion of VP as a DA played a pivotal role in augmenting the efficiency of the devulcanization process by promoting a higher degree of crosslinking relative to random scission. Compared to the samples without DA, the enhancement was achieved through the selective network breakdown and by restricting the recombination of crosslinks. For screw set up 3, at 210°C temperature for 10 zones and at 75 RPM screw speed, the devulcanizate showed:

a) Tensile strength: 9.6 MPa
b) Elongation at break: 174 %
c) Network breakdown: 72 %
d) Mooney viscosity: 82 MU

Figure 11.22. Temperature and shear rate optimization in the extruder: correlation tensile strength vs TAVP
These are the resulting properties of the best quality devulcanizate obtained up to this level of process optimization.

11.4.4 Conclusions

A temperature of 210°C maintained uniformly across all zones, in conjunction with an operational screw speed of 75 RPM utilizing Screw Configuration 3, may be regarded as the optimal configuration for the extruder operation, and it is recommended for utilization in subsequent experiments.

11.5 Devulcanization aid (DA) variation experiments

In this study, a range of potential DAs was compared in the devulcanization process of WT rubber granules within an extruder. These experiments conformed to the optimized parameters previously established in Section 11.4 for VP, with the objective of evaluating and comparing the quality of the resultant devulcanizate.

11.5.1 Experimental process

The procedures pertaining to feed material preparation, extruder specifications, and characterization methods were upheld in accordance with the descriptions provided in Section 11.2.1. For these experiments, Screw Configuration 3 (as shown in Figure 11.16) was employed. This section provides a comprehensive description of the sampling procedure employed throughout the research.

11.5.1.1 Sampling details

Table 11.4 furnishes details concerning the sampling procedure implemented during the experiments involving variations in devulcanization aids in the extruder devulcanization. It is worth emphasizing that all devulcanizates were compounded exclusively with the curatives as stipulated in the formulation outlined in Chapter 3, Section 3.2.1.5.

<table>
<thead>
<tr>
<th>Screw</th>
<th>Temperature profile (°C X number of zones)</th>
<th>DA + Additive (% w/w)</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>210 X 10</td>
<td>5% VP + 5% TDAE</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5% VP + 5% TDAE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5% VTEO + 5% TDAE</td>
<td></td>
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<td></td>
<td></td>
<td>5% TESPT + 5% TDAE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5% DPDS + 5% TDAE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5% VP + 5% TDAE – Double pass</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blank – No DA + No PA</td>
<td></td>
</tr>
</tbody>
</table>

* Details about the DAs are mentioned in Chapter 3, Table 3.2.

In order to assess the impact of longer residence times during extrusion, extrusion in series (double pass in the extruder) was performed. A sample containing 5% VP and 5% TDAE oil underwent devulcanization at a screw speed of 75 RPM and a temperature of 210°C. Following the cooling of the sample, the resulting output was subsequently reintroduced into the extruder while maintaining the same process conditions. These samples were designated as "double pass samples."
11.5.2 Results

In this section, an analysis of the stress-strain behaviour, viscosity, network breakdown, and miscibility of the aforementioned samples is provided.

Figure 11.23 illustrates the results of the comparative analysis of tensile strength obtained from the DA variation experiments. Among these, VP devulcanized samples containing 5% DA exhibited the highest tensile strength, 9.5 MPa, followed by 5% VTEO samples with a strength of 9.3 MPa. The efficiency ranking for tensile strength based on DA type is as follows: VP > VTEO > TESPT > DPDS. Like in earlier studies, the DA devulcanized samples displayed superior tensile strength compared to the blank samples. Moreover, in comparison to the single pass sample, the double pass sample exhibited relatively inferior properties.

![Figure 11.23. DA variation in the extruder: tensile strength](image)

Figure 11.24 depicts the results of the DA variation experiments, where samples devulcanized with TESPT containing a 5% concentration exhibited the highest elongation at break, measured as 180%. This was followed by the 5% VP samples, which displayed an elongation at break of approximately 175%. Additionally, in terms of elongation at break, the trends observed between DA and blank samples, as well as between single pass and double pass samples, showed similarities to those observed in tensile strength. The double pass samples exhibited relatively subpar stress-strain properties, primarily attributed to an extended extrusion time that resulted in thermal degradation and prolonged exposure to high shear forces, leading to random scission. The efficiency ranking for elongation at break based on the type of DA is as follows: TESPT > VP > VTEO > DPDS.
Figure 11.24. DA variation in the extruder: elongation at break

Figure 11.25. DA variation in the extruder: viscosity

Figure 11.25 presents the results of a comparative analysis of viscosity derived from the DA variation experiments. Among these, VP devulcanized samples containing a 5% DA concentration, when subjected to a double pass in the extruder, exhibited a viscosity of 78 MU, the lowest one in this series. Following closely were the 5% VP devulcanized samples subjected to a single pass, with a viscosity of 80 MU. It is noteworthy that all
the samples with a 5% DA concentration and a single pass displayed viscosities falling within a range of 80 MU to 86 MU. As seen earlier, the DA devulcanized samples exhibited lower viscosities compared to the blank samples, resulting in improved processability. The efficiency ranking for viscosity based on the type of DA is as follows: VP > DPDS > VTEO > TESPT.

Figure 11.26 reveals that the single-pass 5% VP devulcanized sample demonstrated the most favourable equilibrium between network breakdown and sol content, yielding percentages of 73% and 16%, respectively. It was observed that samples containing DAs exhibited a higher ratio of crosslink to random scission in comparison to the blank samples, underscoring the effectiveness of selective devulcanization. In contrast, the double-pass sample exhibited higher network breakdown and sol content, indicating a greater occurrence of random chain scission. The efficiency ranking for network breakdown based on the type of DA is as follows: VP > VTEO > TESPT > DPDS.

As depicted in Figure 11.27, double-passed samples exhibited the highest quantity of visible particles, coupled with a finer particle size distribution, attributable to the grinding effect resulting from high shear forces. DCP will be depleted after the first pass due to the half-life of 2.4 seconds at 210°C, thus there is no activation of the vinyl moieties in the second pass. In contrast, the blank samples displayed a coarser particle size distribution when compared to the DA devulcanized samples.
As illustrated in Figure 11.28, there was a gradual reduction in the total area of visible particles as DA efficiency and concentration increased. For instance, in the case of 5% VP devulcanized single-pass samples, a TAVP of 0.7% was achieved along with a tensile strength of 9.5 MPa. The highest TAVP was observed in the blank samples, which exhibited comparatively inferior quality.
The sample with a 2.5% VP concentration exhibited higher TAVP and relatively lower tensile strength due to the lower devulcanization efficiency. The double pass samples, subjected to higher shear force, displayed increased random chain scission, leading to a reduction in tensile strength. The correlation between DA efficiency for tensile strength and TAVP can be ranked as follows: VP > VTEO > TESPT > DPDS.

11.5.3 Discussion

The comparative analysis of the DA variation experiments revealed that VP exhibited the highest efficiency in terms of tensile strength, network breakdown, miscibility, and processability. The vinyl silane forms active radicals in the presence of dicumyl peroxide and effectively restricts the crosslink recombination, resulting an efficient devulcanization process. The detailed reaction mechanisms of VP and VTEO are explained in Chapter 6.

Furthermore, when comparing DA devulcanized samples to the blank sample, it becomes evident that the former consistently exhibited superior properties in the aforementioned aspects, underscoring the significance of DAs in the devulcanization reaction.

The higher elongation at break observed for the revulcanized sample after devulcanization with TESPT can be attributed to the presence of polysulfide moieties. The unreacted polysulphide moieties donate sulphur which creates additional polysulphidic crosslinks during revulcanization which enhance elongation at break of the revulcanizates. In the context of single pass versus double pass experiments, the single pass approach yielded superior results. This outcome can be attributed to the higher occurrence of random chain scission in the double pass samples, which led to a decline in devulcanizate quality, reflected in higher sol content.

The optimum parameters and related properties from this series of experiments are:

1. Extruder temperature settings: 210°C for all 10 zones
2. Screw configuration 3: high shear
3. Screw speed: 75 RPM
4. Additive type and concentration: 5% VP + 5% TDAE oil
5. Tensile strength: 9.5 MPa
6. Elongation at break: 175%
7. Network breakdown: 72%
8. Mooney viscosity: 82 MU

11.5.4 Conclusions

The significance of DAs was underscored in the devulcanization reaction. VP exhibited a relatively superior efficiency among the screened DAs. The double-pass method did not yield particularly effective results for extruder devulcanization. Further optimization opportunities exist through the variation of process aids.
11.6 Process aid (PAs) variation experiments

The objective of this investigation was to assess the influence of various additives on the extruder-based devulcanization process, within the context of previously optimized parameters using TDAE oil. The study aimed to evaluate the effect of DAs without PAs, in addition to blank samples (devoid of both DA and PA). According to the findings of Chapter 7, sunflower oil (SO), silane terminated liquid polybutadiene rubber (SLRR) and polyoctenamer (PO) can be a potential substitutes of TDAE oil in terms of PA; therefore these additives were selected for these trials as well.

The impact of these additives was assessed based on multiple criteria, including network breakdown and viscosity of the devulcanizates, mechanical properties of the revulcanizate, and miscibility as determined through white rubber analysis. The primary objective of this investigation was to identify the most effective additive for further enhancing the quality of the devulcanizate.

11.6.1 Experimental process

The procedures pertaining to feed material preparation, extruder specifications, and characterization methods were upheld in accordance with the descriptions provided in Section 11.2.1. For these experiments, Screw Configuration 3 (as shown in Figure 11.16) was employed. This section provides a comprehensive description of the sampling procedure employed throughout the research.

The WT granulates were subjected to swelling with TDAE oil, SO, and SLBR for a duration of 1 day at room temperature. PO was employed to swell the WT granulate for 1 day at a temperature of 80°C due to its solid state at room temperature. For achieving uniform mixing of the PAs with the granulates, manual stirring in a container was employed. PA swollen granulates were reswollen with DAs for 1 day at room temperature with manual stirring.

11.6.1.1 Sampling details

Table 11.5 provides comprehensive information. It is essential to highlight that all devulcanizates were exclusively compounded using the curatives as specified in the formulation detailed in Chapter 3, Section 3.2.1.5.

Table 11.5. Sampling details of process aid variation experiments in the extruder

<table>
<thead>
<tr>
<th>Screw</th>
<th>Temperature profile ( °C X number of zones)</th>
<th>DA (w/w %)</th>
<th>PA (w/w %)</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>210 X 10</td>
<td>0% VP</td>
<td>5% TDAE</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5% VP</td>
<td>0% TDAE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5% TDAE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5% SO</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5% PO</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>5% SLBR</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Blank – No DA + No PA</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
11.6.2 Results

In this section, an analysis of the stress-strain behaviour, viscosity, network breakdown, and miscibility of the above mentioned samples is presented.

According to Figure 11.29 and considering the combinations of DA and PA, the presence of both types of additives had the highest efficiency, followed by DA without PA, PA only, and finally none of them added. All revulcanizates with DA and PA added yielded tensile strengths within the range of 9 to 9.5 MPa: There were no significant deviations observed in terms of tensile strength. Therefore, it is plausible to consider SO, PO, and SLBR as potential alternatives to TDAE oil.

As depicted in Figure 11.30, all samples except for the one containing PO, exhibited similar trends in terms of elongation at break as tensile strength. The likely reason for this deviation for the PO sample is its solid physical state at room temperature. As the tensile strength was measured at room temperature, inclusion of PO enhanced the revulcanizate stiffness resulting in lower elongation at break. The SLBR and VP containing material exhibited the highest elongation at break: 189%, followed by the TDAE oil with VP sample at 175%, and the SO with VP sample at 171%. The sample without VP but with TDAE oil exhibited an elongation at break of 151% because. In the absence of a DA, reclamation instead of devulcanization occurred, leading to inferior devulcanizate quality.
Based on the data presented in Figure 11.31, it can be deduced that samples containing DA and PA exhibited lower viscosity when compared to the blank samples or samples without PA. It is worth noting that the initial viscosity of the PAs as such played a significant role in influencing the final viscosity of the samples. The viscosity of the PAs at 100\(^\circ\)C can be ranked as SLBR>PO>TDAE>SO. However, aside from this influencing factor, all DA and PA devulcanized samples fell within a viscosity range of 78 to 83 MU.
The addition of a polymeric additive resulted in a high amount of weight loss during THF extraction, indicated by a high sol content. To avoid a measurement error, sol correction was done for the PO and SLBR samples as mentioned in Chapter 7, Section 7.2.4.1. Based on the observations presented in Figure 11.32, it can be concluded that variations in PAs did not significantly impact the degree of network breakdown. However, samples lacking both DA and PA displayed a higher degree of random scission, whereas samples with DA but without PA exhibited a lower network breakdown compared to samples devulcanized with both DA and PA as also reported in Chapter 3, 4, 5 and 8. This highlights the influence of PAs in the devulcanization process. All samples devulcanized with PA and DA demonstrated a network breakdown within the range of 71% to 74%, along with a sol content ranging from 16.5% to 17.5%. Therefore, in terms of network breakdown, SLBR, PO, and SO can potentially serve as substitutes for TDAE oil.

Based on the data presented in Figure 11.33, it is evident that samples subjected to devulcanization with both DA and PA exhibited a finer particle size distribution in comparison to samples devulcanized without PA and/or DA. Furthermore, when varying the type of PA, PO and SLBR samples demonstrated a lower total number of visible particles in comparison to samples processed with TDAE oil.
**Figure 11.33. PA variation in the extruder: white rubber analysis**

**Figure 11.34. PA variation in the extruder: correlation tensile strength vs TAVP**
As shown in Figure 11.34, for the absence of both DA and PA, the TAVP was measured to be approximately 3.4%. In contrast, samples with PA but without DA exhibited a TAVP of approximately 2.2%, while the sample with DA but without PA had a TAVP of 1.55%. The samples with both DA and PA displayed the lowest TAVP values ranging from 0.65% to 0.95%.

11.6.3 Discussion

Based on the analysis of tensile strength, network breakdown, and TAVP in the samples with PA variations, SLBR can be considered as the most suitable substitute for TDAE oil. Its polymeric nature contributes to improved compatibility along with the processibility during revulcanization. The presence of free low molecular weight polymer chains with unsaturated double bonds of SLBR creates additional crosslinks during revulcanization resulting in higher tensile strength and elongation at break values for the revulcanizates. This trend was similar to the one noticed in the findings of Chapter 7.

Furthermore, the viscosity of the PAs played a significant role in determining the final viscosity of the devulcanized samples, thereby influencing their processability. For instance, the SO containing samples displayed lower viscosity than the TDAE oil ones due to the inherently lower viscosity of SO as compared to TDAE oil. Three different combinations of samples – those with both DA and PA, those with DA but without PA, and those with PA but without DA - were tested. It can be concluded that the DA facilitates controlled crosslink scission and limiting the recombination reaction, while the presence of the PA enhances the migration of the DA by increasing the inter-polymeric distance. Furthermore, the residual PA and DA from the devulcanization reaction can form additional crosslinks during revulcanization which contributes to improvement of the stress-strain properties of the revulcanizate. These findings distinctly highlight the importance of PA and DA in the devulcanization system. Optimum parameters and properties for this study turned out to be:

1. Extruder temperature settings: 210°C for all 10 zones
2. Screw Configuration 3: high shear
3. Screw speed: 75 RPM
4. Additive type and concentration: 5% VP + 5% SLBR
5. Tensile strength: 9.6 MPa
6. Elongation at break: 189%
7. Network breakdown: around 74%
8. Mooney viscosity: 80 MU

11.6.4 Conclusions of the PA variation trials

SLBR emerges as a feasible alternative for TDAE oil, followed by PO and SO. Importance of PAs in the extruder devulcanization was prominently described.
Chapter 11

11.7 Conclusion of the process upscaling in an extruder

The extruder process has demonstrated the capability to produce devulcanizates of superior quality compared to devulcanization in an internal mixer, as also reported in literature\(^1\). Upscaling of the batch process was performed in a continuous process using an extruder by optimizing screw configuration, temperature profile, screw speed along with the type and concentration of DAs and PAs.

In comparison to the batch process, a significant enhancement of approximately 10-12% was observed in the stress-strain properties, while concurrently maintaining a consistent level of viscoelasticity, miscibility, and network breakdown properties.

The optimized parameters can serve as the initial reference for upscaling the process in an industrial setting. VP stands out as a potential DA compared to the other silanes. In addition to TDAE oil, SLBR emerges as a viable additive as PA.

11.8 References

Summary

This general summary provides a comprehensive overview of the thesis, commencing with the research motivation. The summary highlights the key findings derived from the results of this study and their discussion, and concludes it with the investigative limitations and future research prospects.

Research motivation

Recycling of vulcanized elastomers presents a substantial challenge due to their thermoset nature. In contrast to thermoplastics, when heated, rubber crosslinks preventing reshaping. This renders thermosets more complex to recycle. The commonly used process known as "reclaiming" involves breaking crosslinks but at the same time also scission of polymer chains. A promising solution is "devulcanization," which reverts rubber to a reusable state by selective breakdown of crosslinks. Devulcanization preserves polymer chains, thereby maintaining mechanical properties, and makes it a sustainable rubber recycling solution.

This research focuses on devulcanization of end-of-life tires (ELTs), particularly natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR) based. NR is rather easy to recycle due to its softening effect at high temperatures, whereas SBR-BR rubber becomes brittle, hindering devulcanization. The filler system significantly impacts the process, with carbon black-filled rubber being easier to devulcanize than silica-filled rubbers, in which chemical filler-polymer bonds pose challenges. In the current technology for tire treads, SBR-BR as polymer and silica-silane as filler system are increasingly used due to improved fuel efficiency.

Rubber devulcanization holds increasing importance for sustainable tire production by 2030 and beyond. Incorporating high-quality devulcanized rubber into new tires can enhance the circular tire economy, reduce the carbon footprint and promote a greener future. This study addresses the lack of a dedicated devulcanization process for SBR-BR based silica-silane filled tires, proposing an efficient solution to fill this gap.

This research aims to develop an environmentally sustainable devulcanization process for passenger car tire rubber, resulting in a high-quality devulcanizate which can be reused in considerable quantities in new tires. Earlier work has shown, that silanes are efficient devulcanization aids, besides being commonly used in passenger car tire tread compounding and therefore a non-critical additive to tire rubber. It involves evaluating silane-based devulcanization aids (DA), optimizing the process with model as well as ground tire rubber, investigating the reactivity of the DA's, elucidating the reaction mechanisms, enhancing the devulcanizate quality with additives, exploring applications in tire compounding, and finally upscaling of the developed process in an extruder.
Results summary

In Chapter 3, various silanes were chosen based on existing knowledge about functionalities boosting the efficiency of devulcanization. They were evaluated concerning their effectiveness in devulcanizing a SBR-BR based silica-silane filled model passenger car tire tread rubber, focusing on mechanical properties, network breakdown, and miscibility. The SBR-silica network presented a formidable challenge for devulcanization, with vinyl silane emerging as a promising DA. The presence of a peroxide activator further improved the efficiency of this silane, making it the most promising DA in this study. Vinyl silane (VTEO) and its activated variant (VP) yielded the best mechanical and network breakdown results, with polysulphidic and amino silane also showing favourable outcomes. These silanes demonstrated a higher crosslink-to-random-scission ratio, enhancing devulcanizate quality compared to the traditional ones. An increased degree of devulcanization led to higher miscibility and a low number of immiscible particles. Tensile strength recovery reached approximately 50–55%, with a network breakdown percentage of 55–60%, compared to the feed material. The resulting mechanical and network breakdown properties were 22–25% superior to those of the benchmark devulcanizate.

Based on the screening described in Chapter 3, Chapter 4 is dedicated to the optimization of the devulcanization process parameters. The first part was performed with the model passenger car tire tread material, and the second part with whole passenger car tire (WT) granulates. For both the materials, devulcanization was performed using vinyl silane with peroxide (VP) as DA. The resulting model devulcanizate showed a tensile strength of 9.4 MPa, an elongation at break of 112%, and a network breakdown of 60%. The optimized process parameters are:

- Temperature: 155°C
- Residence time: 6 minutes
- TDAE oil (process oil): 5%
- DA concentration: 5%
- Rotor speed: 150 RPM
- Fill factor: 80%

The WT devulcanizate exhibited a tensile strength of 8.6 MPa, an elongation at break of 162%, and a network breakdown of 75%. The devulcanization process was fine-tuned to a temperature of 180°C, and the other parameters were similar to the ones of the model devulcanizate.

TGA analysis revealed variations in filler type and concentration within the WT granulates. The inhomogeneity of this feed material in terms of type of rubber and filler type as well as content, and ageing during service life contributed to a lower tensile strength observed in WT material compared to the model compound. On the other hand, the presence of natural rubber led to higher elongation at break and lower viscosity in contrast to the model compound.

Chapter 5 is dedicated to three primary aspects:

i. Evaluating combinations of DAs in terms of additional or synergistic effect.
ii. Investigating the impact of individual DA constituents.

iii. Assessing devulcanization using peroxides, which are part of the VP DA, as sole agents.

Samples devulcanized with VP demonstrated superior network breakdown properties and mechanical strength after revulcanization compared to all tested DA combinations: no synergistic effect was measured. Samples devulcanized with the combination of VTEO and BPO (benzoyl peroxide) exhibited better tensile strength, miscibility, and viscosity than those devulcanized with VTEO and DCP: BPO in conjunction with vinyl silane turned out to be a promising DA, surpassing DCP for this purpose. BHT did not significantly impact the devulcanization reaction; however, plays a vital role in maintaining the chemical stability of the peroxide. Peroxides alone were inefficient as DAs for these unsaturated polymer systems based on NR, BR and SBR.

In Chapter 6, the devulcanization reaction mechanisms were investigated for two different devulcanization aids, VTEO (vinyl silane) and VP (vinyl silane with peroxide). The primary devulcanization reaction involved radical addition reactions: recombining broken crosslinks and polymer chains with active DA radicals to achieve stabilization. FTIR characterization including side product analysis was performed on educts and products of the devulcanization reaction using liquid model compounds (LMCs), confirming the proposed devulcanization mechanism. GC analysis provided insights into the efficacy of devulcanization, particularly with VP. Comparable retention times in GC spectra for devulcanized LMC and uncured LMC supported the effectiveness of the decrosslinking process. GC and NMR analyses of VP and decomposed VP confirmed the presence of dimerized and oligomerized structures within decomposed VP.

Chapter 7 investigated the influence of the type of processing aids. This series of experiments was performed with WT rubber granulate and using the most efficient DA. It aimed to achieve two primary objectives: firstly, to evaluate the impact of different process aids on the devulcanization procedure, and secondly, to identify an optimal process aid and concentration for enhancing the devulcanization process and devulcanizate properties. An optimum additive quantity of 5% process aid (PA) was determined, as exceeding this amount resulted in nip slippage in the mixer and comparatively poorer devulcanizate quality. Silane-terminated liquid polybutadiene rubber (SLBR) and Polyoctenamer (PO) exhibited superior properties due to the contribution of the long polymer chains and unsaturation in the backbone compared to other PA’s. Unsaturated PA’s contributed to the additional crosslink formation during revulcanization resulting in superior revulcanizate quality. Samples pre-swollen for 6 hours to let the DA and PA migrate into the granules exhibited similar properties to those pre-swollen for one day. Additionally, additives compounded after devulcanization displayed a plasticization effect rather than an influence on material quality.

Chapter 8 delves into an examination of the influence of a silanization step to activate the silica in the WT rubber, and of separately added silica and silane to the devulcanizates. Additionally, it encompasses the process of blending devulcanizates or ground rubber with a virgin compound for a comparative analysis of the influence of the recycled rubber on the properties of a blend. Compounding with around 20% of additional filler (silica + silane) can improve tensile strength of the revulcanizates by up
Summary

252 to 15%. In addition to the filler cost, a sacrifice in elongation at break, dispersion, and abrasion resistance was noticed. With an additional 20% silica and increasing silane concentration, tensile strength, Payne effect, and dispersion improved due to better polymer-filler interaction from enhanced silanization. However, network breakdown of the devulcanizate (after compounding and before revulcanization) got decreased due to an increase in crosslink density caused by the formation of short, stable filler-polymer bonds during the silanization reaction. The optimum concentration for improvement of the properties of the devulcanizate was elaborated to be 20% silica and 3% silane.

When ground rubber was added to the virgin compound, a significant loss in properties was observed, much more compared to the addition of a devulcanizate. Mechanically ground samples yielded better blend properties than cryogenically ground rubber due to their higher surface area and improved interlocking from the rough particle surface. VP devulcanizes could be blended with a virgin tread compound up to 20% without a significant reduction in tensile strength; a 50% blend resulted in around 25% and 30% sacrifice in tensile strength and elongation at break respectively. Additionally filled devulcanizates exhibited relatively higher mechanical properties compared to the no additionally filled ones. A considerably higher amount of devulcanizate can be used compared to the reclaim or powder.

Based on the promising results of the devulcanizate-virgin rubber blends, in Chapter 9 a more elaborated application study was performed, including also properties relevant for tire applications. An improvement in ageing resistance due to the addition of devulcanizate was clearly observed. Compared to the model compound, for the 20% devulcanizate blend, tear strength and wet grip were improved. The devulcanizates exhibited good processability during blending and processing. Overall, a 20% devulcanizate blend can be utilized for high-performance applications without a significant sacrifice in the required properties, while a 50% devulcanizate blend or 100% devulcanizate is suitable for low-performance applications.

Chapter 10 entails a comprehensive comparison between the developed devulcanizates and their commercial counterparts. The truck tire and aircraft tire tread based samples exhibited similar properties, characterized by a tensile strength of approximately 14 MPa and an elongation at break of around 200%. In contrast, the model devulcanizate displayed a comparatively lower tensile strength (approximately 9.4 MPa) and elongation at break (about 110%). Two other devulcanizates based on truck tire treads and a blend of whole passenger car and truck tire rubber samples demonstrated even lower tensile strength (around 8 MPa) and elongation at break (about 150%). These variations can be attributed to factors such as differences in the devulcanization process and variation in the feed material, especially the presence of natural rubber and carbon black, and variations in the devulcanization process. Higher temperature and shear forces within the extruder facilitated a more extensive network breakdown, contributing to improved tensile strength. However, there is a limit at which polymer scission becomes dominant and properties decrease again. Moreover, a correlation was established between tensile strength of the devulcanizate and miscibility with a virgin compound: VP-devulcanized samples exhibited superior mechanical strength and miscibility, followed by VTEO. TESPT displayed an intermediate performance between
vinyl silanes and the reference DPDS, and their comparative efficiency can be summarized as VP > VTEO > TESPT > DPDS.

Chapter 11 consolidates all the findings and extends them to an upscaled extruder process, with primary focus on the transition from batch to continuous processing to enhance productivity and enable industrialization. This upscaling endeavour entailed adjustments in screw configuration and process optimization. The optimal parameters for the extruder process and the properties were determined as follows:

- Temperature profile: 210°C for all zones
- Screw configuration: high shear screw
- Screw speed: 75 RPM
- DA concentration and type: 5% VP
- PA concentration and type: 5% SLBR
- Tensile strength: 9.6 MPa
- Elongation at break: 189%
- Network breakdown: 74%
- Mooney viscosity: 80 MU

These optimized parameters can serve as an initial reference for further upscaling of the process in an industrial environment. The extruder process has demonstrated its capability to yield superior quality devulcanizates compared to the internal mixer. VP emerges as the most promising devulcanization aid within this study as well, and SLBR proves to be a viable alternative for process aids.

**Outlook**

The future outlook for rubber recycling through devulcanization appears promising, poised to address environmental concerns and foster sustainable practices in the rubber industry. Devulcanization, with its capability to selectively break down crosslinks in vulcanized rubber, presents a key solution for recycling rubber products, particularly tires. Advancements in devulcanization methods, including innovative chemical agents and processing techniques, hold the potential to enhance efficiency and product quality. As research explores alternative devulcanization aids adhering to stringent environmental regulations, the landscape of rubber recycling is expected to evolve further. Integration of more sustainable practices, such as the use of supercritical CO₂ in devulcanization processes, aligns with global efforts toward eco-friendly solutions.

Moreover, the development of continuous devulcanization processes could streamline operations, making rubber recycling more scalable and economically viable. Collaboration between academia, industry, and policymakers is crucial to drive research, implement regulations, and create a supportive framework for the widespread adoption of devulcanization in rubber recycling. As circular economy initiatives gain traction, the role of devulcanization in closing the loop for rubber materials is likely to expand. The future of rubber recycling through devulcanization holds promise for reducing waste, conserving resources, and establishing a sustainable paradigm in the rubber industry.
Deze samenvatting van het proefschrift begint met de motivatie voor het onderzoek, bevat de belangrijkste bevindingen voortkomend uit deze studie en hun discussie, en sluit af met de toekomstige onderzoeksperspectieven.

**Motivatie**

Recycling van gevulkaniseerde elastomeren vormt een aanzienlijke uitdaging vanwege hun structuur als thermoharder: In tegenstelling tot thermoplasten, voorkomen de crosslinks het opnieuw vormgeven bij verhitting. Dit maakt thermoharders complexer om te recyclen. Het veelgebruikte proces dat bekend staat als "regeneratie" omvat het verbreken van crosslinks, maar tegelijkertijd ook de splitsing van polymeerketens. Een veelbelovende oplossing is "devulkanisatie", die rubber terugbrengt naar een verwerkbare en herbruikbare staat door selectieve afbraak van crosslinks. Devulkanisatie is een proces waarin de polymeerketens intact blijven, waardoor mechanische eigenschappen behouden blijven. Dit maakt het een duurzame oplossing voor rubberrecycling.

Dit onderzoek richt zich op de devulkanisatie van afgedankte autobanden, met name op basis van natuurrubber (NR), styreen-butadieenrubber (SBR) en butadieenrubber (BR). NR is relatief eenvoudig te recyclen omdat het bij hoge temperaturen zachter wordt, terwijl SBR-BR rubber broos wordt, wat devulkanisatie bemoeilijkt. Ook het vulstofsysteem heeft een aanzienlijke invloed op het proces: rubber met carbon black is gemakkelijker te devulkaniseren dan rubber versterkt met silica, waarbij chemische bindingen tussen vulstof en polymeer verbroken moeten worden. In de hedendaagse technologie voor bandenloopvlakken worden SBR en BR als polymeren en silica-silaan als vulstof systeem steeds vaker gebruikt vanwege verbeterde brandstoeffefficiëntie van de desbetreffende banden.

Devulkanisatie van rubber is van toenemend belang voor duurzame bandenproductie: Hoogwaardig gedevelopuleerd rubber in nieuwe banden kan de circulaire bandeneconomie naar voren brengen, de CO2 voetafdruk verkleinen en zo aan een duurzamere toekomst bijdragen. Dit onderzoek richt zich op het ontbrekende devulkanisatieproces voor SBR-BR-gebaseerde en silica-silaan gevulde banden, en stelt een efficiënte oplossing voor om dit materiaal te recyclen.

Dit onderzoek heeft tot doel een milieuvriendelijk en duurzaam devulkanisatieproces te ontwikkelen voor rubber van personenwagenbanden, resulterend in een hoogwaardig devulkanisaat dat in aanzienlijke hoeveelheden kan worden hergebruikt in nieuwe banden. Eerder onderzoek heeft aangetoond dat silanen efficiënte devulkanisatie additieven (DA) zijn, naast het feit dat ze samen met silica gebruikt worden in loopvlakken van personenwagenbanden en daarom een bekende en onkritische toeslagstof zijn. De studie binnen dit proefschrift omvat de evaluatie van op silaan gebaseerde DAs, optimalisatie van het devulkanisatie proces met zowel modelrubber als bandenrubber, onderzoek naar de reactiemechanismen van de DA’s, verbetering van de kwaliteit van het devulkanisaaat met verdere additieven, onderzoek naar
toepassing in banden, en uiteindelijk het opschalen van het ontwikkelde proces in een extruder.

**Samenvatting van de resultaten**

In Hoofdstuk 3 zijn verschillende silanen gekozen op basis van bestaande kennis over functionaliteiten voor een efficiënte devulkanisatie. Deze werden geëvalueerd op hun effectiviteit voor een SBR-BR silica-silaan geulde modelrubber voor een personenwagenbanden loopvlak, met nadruk op mechanische eigenschappen, netwerkafbraak en mengbaarheid met een nieuw compound. Het SBR-silica netwerk vormde een uitdaging voor devulkanisatie, en in deze studie kwam een vinylsilaan naar voren als meest belovende DA voor dit specifieke rubber. De aanwezigheid van een peroxide-activator verbeterde de effectiviteit, waardoor deze combinatie het beste DA bleek in deze studie: Vinylsilaan (VTEO) en de peroxide-geactiveerde variant ervan (VP) leverden de beste mechanische en netwerkafbraak resultaten op. Polysulfid- en aminosilanen toonden echter ook goede resultaten: een hoog percentage afbraak van zwavelbruggen tegenover breken van polymeerketens. Dit verbeterde de kwaliteit van het devulkanisaat in vergelijking met de traditionele devulkanisatie additieven. Een hogere devulkanisatiegraad leidde tot betere mengbaarheid en een laag aantal niet-mengbare deeltjes. Vergeleken met het uitgangsmateriaal was de bereikte treksterkte ongeveer 50-55%, met een netwerkafbraak percentage van 55-60%. De resulterende mechanische en netwerkafbraak eigenschappen waren 22-25% verbeterd ten opzicht van het referentie-devulkanisaat gebruik makend van de conventionele DAs.

Hoofdstuk 4 is gewijd aan optimalisatie van de devulkanisatie parameters, gebruik makend van het in Hoofdstuk 3 gekozen DA. In eerste instantie is dit uitgevoerd met het modelmateriaal voor personenwagenbanden loopvlakken, en in het tweede deel is granulaat van hele personenwagenbanden (WT) gebruikt. In beide gevallen werd de devulkanisatie uitgevoerd met vinylsilaan met peroxide (VP) als DA. Het resulterende model-devulkanisaat vertoonde een treksterkte van 9,4 MPa, een rek bij breuk van 112% en een netwerkafbraak van 60%. De geoptimaliseerde procesparameters zijn:

- Temperatuur: 155°C
- Verblijftijd: 6 minuten
- TDAE-olie (procesolie): 5%
- DA-concentratie: 5%
- Rotorsnelheid: 150 RPM
- Vulfactor: 80%

Het WT-devulkanisaat vertoonde een treksterkte van 8,6 MPa, een rek bij breuk van 162%, en een netwerkafbraak van 75%. De optimale condities voor het devulkanisatie proces verschillen alleen qua temperatuur: 180°C voor het WT rubber; de andere parameters waren gelijk aan de devulkanisatie van het modeldevulkanisaat. Een TGA-analyse onthulde variaties qua type vulstof en concentratie in het WT-granulaat en type rubber. Daarnaast droeg de veroudering tijdens gebruik van een band bij aan een lagere treksterkte van het revulcanisaat van WT materiaal vergeleken met modelrubber. Aan de andere kant leidde de aanwezigheid van NR in de WT rubber tot een hogere rek bij breuk en lagere viscositeit in tegenstelling tot het modelmateriaal.
Hoofdstuk 5 is gewijd aan drie aspecten:

i. Evalueren van combinaties van DA’s qua aanvullend of synergistisch effect.
ii. Onderzoeken van het effect van individuele bestanddelen van de DA’s.
iii. Effectiviteit van devulkanisatie met behulp van peroxiden, die deel uitmaken van VP.

Rubber gedevulkaniseerd met VP vertoonde betere eigenschappen qua netwerkafbraak, en na revulkanisatie ook betere mechanische eigenschappen in vergelijking met alle DA-combinaties: Er werd geen synergistisch effect gemeten. Devulkanisaat met een combinatie van VTEO en BPO (benzoylperoxide) vertoonde een hogere treksterkte, betere mengbaarheid en lagere viscositeit dan gebruik van VTEO met DCP (dicumylperoxide): BPO in combinatie met vinylsilaan bleek een veelbelovende DA te zijn, die DCP voor dit doel overtrof. BHT had geen significante invloed op de devulkanisatie reactie; het speelt echter een cruciale rol voor de chemische stabiliteit van het peroxide. Peroxiden op zichzelf waren niet efficiënt als DA’s voor deze onverzadigde polymersystemen op basis van NR, BR en SBR.

In Hoofdstuk 6 werden de mechanismen van de devulkanisatie reacties onderzocht voor twee verschillende DAs: VTEO (vinylsilaan) en VP (vinylsilaan met peroxide). Het devulkanisatie mechanisme omvatte radicaal radicale additie reacties: recombinatie van actieve fragmenten van gebroken crosslinks en polymeer ketens met DA-radicalen. FTIR onderzoek inclusief analyse van bijproducten werd uitgevoerd op educten en producten van de devulkanisatie reactie op basis van laagmoleculaire modelverbindingen (LMC), waarbij het voorgestelde devulkanisatie mechanisme werd bevestigd. GC-analyse bracht verder inzicht in de effectiviteit van devulkanisatie, met name met VP als DA. Vergelijkbare retentietijden in GC-spectra voor ongevulkaniseerde en gedevelopaneerde LMCs bevestigden de effectiviteit van het devulkanisatie proces. GC- en NMR-analyses van VP als zodanig en na degradatie bevestigden de aanwezigheid van dimeren en oligomeren.

In Hoofdstuk 7 is de invloed van het type verwerkingshulpmiddelen onderzocht. Deze reeks experimenten werd uitgevoerd met WT-rubbergranulaat en met behulp van het meest efficiënte DA. Het beoogde twee hoofddoelen te bereiken: ten eerste het beoordelen van de impact van verschillende verwerkingshulpmiddelen op het devulkanisatie proces, en ten tweede het identificeren van het beste verwerkingshulpmiddel en bepalen van de concentratie ervan om het devulkanisatie proces te verbeteren. De optimale hoeveelheid verwerkingshulp (PA) werd bepaald als 5%; hogere concentraties veroorzaakten slip in de menger en daardoor een relatief slechtere devulkanisaat kwaliteit. Vloeibare polybutadienrubber met silaan eindgroepen (SLBR) en Polyoctenamer (PO) vertoonden betere eigenschappen door de bijdrage van lange polymeer ketens en onverzadigdheid in vergelijking met andere verwerkingshulpmiddelen.

Dubbele bindingen in de chemische structuur van de verwerkingshulpmiddelen droegen bij aan de vorming van extra crosslinks tijdens revulkanisatie, resulterend in een betere devulkanisaat kwaliteit. Om het DA en PA in de rubberdeeltjes te laten migreren, werden verschillende tijden aangehouden voor deze voorbehandeling. Monsters die zes uur
waren gezwollen vertoonden vergelijkbare eigenschappen met granulaat na een zweltijd van een dag. Bovendien vertoonden additieven, die na de devulkanisatie waren toegevoegd, alleen een weekmakereffect in plaats van een invloed op de materiaalkwaliteit.

In hoofdstuk 8 werd de invloed van een silaniseringsstap, om silica in de WT-rubber te activeren, onderzocht. Ook werd silica en silaan afzonderlijk toegevoegd aan de devulkanisaten. Daarnaast omvat dit hoofdstuk ook een applicatiestudie: het mengen van gedevoalaniseerd of slechts gemalen rubber met een nieuw mengsel. In deze vergelijkende analyse werd de invloed van het gerecyclede rubber op de eigenschappen van een mengsel met nieuw rubber bestudeerd. Uit deze studie bleek dat de toevoeging van ongeveer 20% extra vulstof (silica + silaan) de treksterkte van de revulkanisaten met maximaal 15% verbeterd. Echter, naast een verhoging van de kosten werd ook een verlies in rek bij breuk, dispersie en slijtvastheid gemeten. Werd bij extra toevoeging van 20% silica ook een toenemende hoeveelheid silaan toegevoegd, verbeterden treksterkte, Payne-effect en dispersie vanwege een intensievere polymeer-vulstof interactie. De graad van netwerkafbraak van het gedevoalaniseerde materiaal (ná toevoeging van de het additionele vulstof-systeem en vóór revulkanisatie) verminderte echter: een toename van de crosslink-dichtheid veroorzaakt door korte, stabiele vulstof-polymerbindingen tijdens de silaniseringsreactie. De optimale concentraties voor verbetering van de eigenschappen van het devulkanisaat waren 20% silica en 3% silaan.

Werd gemalen rubber aan een nieuw mengsel toegevoegd, betekende dat een aanzienlijk verlies aan eigenschappen, veel hoger in vergelijking met de toevoeging van devulkanisaat. Mechanisch gemalen rubber vertoonde betere mengeigenschappen dan cryogeen gemalen rubber vanwege een groter oppervlak en verbeterde verankering door het ruwe oppervlak van de deeltjes. VP-devulkanisaat kon met een concentratie van 20% worden ingemengd in een nieuw loopvlakmengsel zonder significante afname van de treksterkte; toevoeging van 50% devulkanisaat resulteerde in respectievelijk circa 25% en 30% teruggang in treksterkte en rek bij breuk. Bovendien vertoonden de devulkanisaten met extra silica en silaan relatief gezien betere mechanische eigenschappen in vergelijking met de devulkanisaten als zodanig: Bij devulkanisaat kan een aanzienlijk hogere hoeveelheid worden toegevoegd in vergelijking met gemalen rubber.

Op basis van de veelbelovende resultaten van de applicatiestudie werd in Hoofdstuk 9 een uitgebreidere studie uitgevoerd, waarbij ook eigenschappen die relevant zijn voor toepassing in banden werden meegenomen. Er werd een duidelijke verbetering qua veroudering gemeten door de toevoeging van gedevoalaniseerde rubber. In vergelijking met het nieuwe rubber werden scheursterkte en grip op nat wegdek verbeterd voor het mengsel met 20% devulkanisaat. Daarnaast vertoonde het devulkanisaat goede verwerkbaarheid. Over het algemeen kan een mengsel met 20% devulkanisaat worden gebruikt voor hoogwaardige toepassingen zonder een significante teruggang van eigenschappen, terwijl een mengsel van 50% gedevoalaniseerde rubber of zelfs 100% devulkanisaat geschikt is voor laagwaardige toepassingen.
Hoofdstuk 10 bevat een vergelijkende studie van de ontwikkelde devulkanisaten en hun commerciële tegenhangers. De monsters op basis van vrachtwagenbanden en vliegtuigbanden vertoonden vergelijkbare eigenschappen, met een treksterkte van ongeveer 14 MPa en rek bij breuk van ongeveer 200%. Daarentegen vertoonde het devulkanisaat op basis van modelrubber een relatief lagere treksterkte (circa 9,4 MPa) en rek bij breuk (circa 110%). Twee andere devulkanisaten op basis van vrachtwagenbanden en een mengsel van rubber van hele personenwagen- en vrachtwagenbanden vertoonden een nog lagere treksterkte (ongeveer 8 MPa) en rek bij breuk (ongeveer 150%). Deze variaties kunnen worden toegeschreven aan factoren zoals verschillen in grondstof, met name de aanwezigheid van NR en carbon black, en variaties in het devulkanisatie proces. Hogere temperaturen en afschuifkrachten in het extruderproces vergemakkelijken netwerkafbraak, wat bijdroeg aan verbeterde treksterkte. Er is echter een limiet waar polymeerbreuk dominant wordt en de eigenschappen weer afnemen.

In deze studie werd een correlatie gevonden tussen treksterkte van het devulkanisaat en mengbaarheid met een nieuw mengsel: VP-devulkanisaat vertoonde betere mengbaarheid en treksterkte na revulkanisatie, gevolgd door de VTEO variant. TESPT als DA vertoonde een positie tussen vinylsilanen en de referentie DPDS als DA, en hun efficiëntie neemt af in de volgende orde: VP > VTEO > TESPT > DPDS.

Hoofdstuk 11 consolideert alle bevindingen en breidt ze uit naar een opgeschaald extrusieproces, met nadruk op de overgang van batch naar continue verwerking om de productiviteit te verbeteren en industrialisatie mogelijk te maken. Deze opschaling omvatte aanpassingen in Schroefconfiguratie en procesoptimalisatie. De optimale parameters voor het extrusieproces zijn:

- Temperatuurprofiel: 210°C voor alle zones
- Schroefconfiguratie: hoge afschuifkrachten
- Schroefsnellheid: 75 RPM
- DA-concentratie en type: 5% VP
- PA-concentratie en type: 5% SLBR
- Treksterkte: 9,6 MPa
- Rek bij breuk: 189%
- Netwerkafbraak: 74%
- Mooney-viscositeit: 80 MU

Deze geoptimaliseerde parameters kunnen dienen als een eerste referentie voor verdere opschaling van het proces in een industriële omgeving. Het extrusieproces heeft aangetoond dat het in staat is om devulkanisaten van hogere kwaliteit te produceren in vergelijking met devulkanisatie in een interne menger. Binnen deze studie komt VP naar voren als het meest belovende devulkanisatiemiddel, en SLBR blijkt een goed alternatief te zijn als proceshulpmiddel.
Samenvatting

Vooruitzichten

De toekomst van rubberrecycling door devulkanisatie is veelbelovend en een manier om milieuproblemen aan te pakken en duurzame praktijken in de rubberindustrie te bevorderen. Devulkanisatie, door selectief crosslinks in gevulkaniseerd rubber af te breken, biedt een belangrijke oplossing voor het recyclen van rubberproducten, met name voor banden. Vooruitgang in devulkanisatie methoden, waaronder innovatieve chemische middelen en verwerkingstechnieken, heeft het potentieel om de efficiëntie en productkwaliteit te verbeteren. Naarmate onderzoek alternatieve devulkanisatie hulpmiddelen verkent die voldoen aan strenge milieuregels, wordt verwacht dat rubberrecycling zich verder zal ontwikkelen. De integratie van meer duurzame praktijken zoals het gebruik van superkritisch CO₂ sluit aan bij wereldwijde inspanningen voor milieuvriendelijke oplossingen.

Bovendien zou door de ontwikkeling van continue devulkanisatieprocessen rubberrecycling schaalbaarder en economisch haalbaarder worden. Samenwerking tussen academici, industrie en beleidsmakers is cruciaal om onderzoek te stimuleren, regelgeving te implementeren en een ondersteunend kader te creëren voor de brede acceptatie van devulkanisatie in rubberrecycling. Naarmate initiatieven voor de circulaire economie aan momentum winnen, zal de rol van devulkanisatie bij het sluiten van de cyclus voor rubbermaterialen naar verwachting toenemen. De toekomst van rubberrecycling door devulkanisatie belooft afval te verminderen, grondstoffen te sparen en duurzaamheid in de rubberindustrie te vorderen.
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi )</td>
<td>Polymer-solvent interaction parameter</td>
</tr>
<tr>
<td>%</td>
<td>Percentage</td>
</tr>
<tr>
<td>( \mu m )</td>
<td>Micrometer</td>
</tr>
<tr>
<td>(^1)HNMR</td>
<td>Proton nuclear magnetic resonance</td>
</tr>
<tr>
<td>6PPD</td>
<td>Dimethyl butyl phenyl phenylenediamine</td>
</tr>
<tr>
<td>AM</td>
<td>Amino</td>
</tr>
<tr>
<td>AMEO</td>
<td>Amino tri-ethoxy silane</td>
</tr>
<tr>
<td>BPO</td>
<td>Benzoyl peroxide</td>
</tr>
<tr>
<td>BR</td>
<td>Polybutadiene rubber</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon black</td>
</tr>
<tr>
<td>CBS</td>
<td>Cyclohexyl benzothiazole sulphenamide</td>
</tr>
<tr>
<td>CC</td>
<td>Cubic centimeter</td>
</tr>
<tr>
<td>CIIR</td>
<td>Chloro-butyl rubber</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>DA</td>
<td>Devulcanization aid</td>
</tr>
<tr>
<td>DBD</td>
<td>Dibenzamido diphenyl disulphide</td>
</tr>
<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
</tr>
<tr>
<td>DC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>DCP</td>
<td>Dicumyl peroxide</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analyzer</td>
</tr>
<tr>
<td>dNm</td>
<td>Deci Newton meter</td>
</tr>
<tr>
<td>DPDS</td>
<td>Diphenyl disulphide</td>
</tr>
<tr>
<td>DPG</td>
<td>Diphenyl guanidine</td>
</tr>
<tr>
<td>DS</td>
<td>Disulphide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimeter</td>
</tr>
<tr>
<td>ECHA</td>
<td>European chemicals agency</td>
</tr>
<tr>
<td>ELT</td>
<td>End of life tires</td>
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<tr>
<td>EPDM</td>
<td>Ethylene propylene diene rubber</td>
</tr>
<tr>
<td>ESBR</td>
<td>Emulsion SBR</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>G'</td>
<td>Storage modulus</td>
</tr>
<tr>
<td>G&quot;</td>
<td>Loss modulus</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga Pascal</td>
</tr>
<tr>
<td>GTR</td>
<td>Ground tire rubber</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HD</td>
<td>Highly dispersible</td>
</tr>
<tr>
<td>kg</td>
<td>Kilogram</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilo Pascal</td>
</tr>
<tr>
<td>L/D</td>
<td>Length by diameter</td>
</tr>
<tr>
<td>LBR</td>
<td>Liquid polybutadiene rubber</td>
</tr>
<tr>
<td>MBTS</td>
<td>Mercapto benzothiazole disulphide</td>
</tr>
<tr>
<td>ME</td>
<td>Mercapto</td>
</tr>
<tr>
<td>ML</td>
<td>Mooney viscosity with large rotor</td>
</tr>
<tr>
<td>mL</td>
<td>Millilitre</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>MU</td>
<td>Mooney units</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>NR</td>
<td>Natural rubber</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>OAN</td>
<td>Oil absorption number</td>
</tr>
<tr>
<td>PA</td>
<td>Process aid</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly cyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PH</td>
<td>Phenyl hydrazine</td>
</tr>
<tr>
<td>phr</td>
<td>Per hundred rubber</td>
</tr>
<tr>
<td>PO</td>
<td>Polyoctenamer</td>
</tr>
<tr>
<td>PS</td>
<td>Polysulphide</td>
</tr>
<tr>
<td>RAC</td>
<td>European committee for risk assessment</td>
</tr>
<tr>
<td>RPA</td>
<td>Rubber process analyzer</td>
</tr>
<tr>
<td>RPM</td>
<td>Rotation per minute</td>
</tr>
<tr>
<td>S</td>
<td>Sulphur</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene butadiene rubber</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
</tbody>
</table>
Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SLBR</td>
<td>Silane terminated LBR</td>
</tr>
<tr>
<td>SO</td>
<td>Sunflower oil</td>
</tr>
<tr>
<td>SSBR</td>
<td>Solution SBR</td>
</tr>
<tr>
<td>T95</td>
<td>Time to reach 95% of T&lt;sub&gt;max&lt;/sub&gt;</td>
</tr>
<tr>
<td>Tanδ</td>
<td>Loss tangent</td>
</tr>
<tr>
<td>TAPS</td>
<td>Bis trialkyl phenol sulphide</td>
</tr>
<tr>
<td>TBA</td>
<td>Tributyl amine</td>
</tr>
<tr>
<td>TBBS</td>
<td>Tertbutyl benzo thiazyl sulphenamide</td>
</tr>
<tr>
<td>TBzTD</td>
<td>Tetra benzyl thiuram disulphide</td>
</tr>
<tr>
<td>TDAE</td>
<td>Treated distillated aromatic extracted</td>
</tr>
<tr>
<td>TESPD</td>
<td>Bis triethoxy silyl propyl tetrasulphide</td>
</tr>
<tr>
<td>TESPD</td>
<td>Bis triethoxy silyl propyl disulphide</td>
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<tr>
<td>TETD</td>
<td>Tetra ethyl thiuram disulphide</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>Tetra hydro furan</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Maximum curing torque</td>
</tr>
<tr>
<td>TMQ</td>
<td>Trimethyl dihydro quinoline</td>
</tr>
<tr>
<td>TMTD</td>
<td>Tetra methyl thiuram disulphide</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>v/v</td>
<td>Volume by volume</td>
</tr>
<tr>
<td>VN</td>
<td>Vinyl</td>
</tr>
<tr>
<td>VP</td>
<td>Vinyl silane with peroxide</td>
</tr>
<tr>
<td>VTEO</td>
<td>Vinyl tri-ethoxy silane/ Vinyl silane</td>
</tr>
<tr>
<td>w/w</td>
<td>Weight by weight</td>
</tr>
<tr>
<td>WRA</td>
<td>White rubber analysis</td>
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<tr>
<td>WT</td>
<td>Whole tire</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
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</table>
Bibliography

Patents

1 German: Devulkanisierter Kautschuk, Verfahren zur Herstellung von devulkanisiertem Kautschuk und dessen Verwendung. 
English: Devulcanized rubber, process for producing devulcanized rubber and its use.
   Filed: 24.09.2022; Accepted: 24.09.2023

2 Working title: Devulcanization process additives, influence on devulcanizates and revulcanizates
   Filed: February, 2024

Publications

1 New route of tire rubber devulcanization using silanes.

2 GTR devulcanization review.

Working titles of manuscripts submitted or under preparation:

3 Exploring the impact of reinforcing filler systems on devulcanizate composites.
   Submitted to Polymers, special issue: “Application and Characterization of Polymer Composites”

4 Closing the loop of passenger car tire rubber by blending with high quality devulcanizates.

5 Investigation of the devulcanization mechanism in crosslinked polymers using vinyl silane and its derivatives as devulcanization aids.

6 The influence of different compounding additives on devulcanizates and revulcanizates (Patent 2).

7 Optimizing the devulcanization process in a small scale batch mixer and upscaling it to a pilot scale extruder process for passenger car tire rubber.

Authors (3-7): Ghosh, R., Mani, C., Krafczyk, R., Schnell, R., Talma, A., Blume, A. and Dierkes, W.K.
### Conference presentations

<table>
<thead>
<tr>
<th>Date</th>
<th>Conference</th>
<th>Title</th>
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<tr>
<td>28.10.2021</td>
<td>Deutsche Kautschuk Gesellschaft West. Cologne, Germany.</td>
<td>Latest insights into the devulcanization possibilities</td>
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<tr>
<td>10.11.2022</td>
<td>Deutsches Institut für Kautschuktechnologie. Hanover, Germany.</td>
<td>New routes of tire devulcanization with silane coupling agents</td>
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<td>22.03.2023</td>
<td>Tire Tech Expo. Hanover, Germany.</td>
<td>A new approach to devulcanize passenger car tire rubber</td>
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<tr>
<td>20.06.2023</td>
<td>PhD Seminar. Hanover, Germany.</td>
<td>A new approach to devulcanize passenger car tire rubber</td>
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<tr>
<td>18.10.2023</td>
<td>International Elastomer Conference, Rubber Division, American Chemical Society, Cleveland, Ohio, USA.</td>
<td>Closing the loop for silica-filled passenger car tire rubber</td>
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Mani, C., Krafczyk, R., Schnell, R., Paasche, A., Talma, A., Blume, A., Dierkes, W.K.
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- Rounak
The research aims to develop a more environmentally sustainable devulcanization process for rubber sourced from silica-silane based passenger car tires to achieve a high-quality devulcanizate. A comprehensive literature review covers various aspects, including tire tread compounding, devulcanization mechanisms, and recent developments in devulcanization of ground tire rubber (GTR).

A screening of devulcanization aids (DAs) for passenger car tire tread granulate chosen from commonly used rubber chemicals, is conducted to identify the most promising one: vinyl silane with peroxide (VP). Optimization of devulcanization parameters using VP is performed for model tire tread material and whole tire granulate. Further investigations involve varying combinations of DAs assessing a synergistic effect, exploring the impact of individual constituents, and investigating devulcanization solely employing peroxides. The devulcanization reaction mechanism of vinyl silane and VP is analyzed using a liquid model compound.

In the next step devulcanization with variation in processing aid is carried out to pinpoint the optimal one. An examination of the influence of fillers and the effect of the silanization reaction on the devulcanizate properties is conducted. The best devulcanizate is blended with a model passenger tire tread compound, and its applicability for tires is comprehensively analyzed. A comparison between newly developed devulcanizates and commercial counterparts is conducted, establishing a correlation between tensile strength and miscibility for samples devulcanized using various DAs and process conditions.

Results are transferred from a batch process and upscaled to an continuous extruder process, aiming to achieve increased productivity and to facilitate industrialization. The future of rubber recycling through devulcanization holds promise for reducing waste, conserving resources, and establishing sustainability in the rubber industry.