Design and optimization of a devulcanization process for butyl rubber

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Summary

The ever-growing problem of end-of-life tires has been receiving more attention over the past years, resulting in increased regulations on the management of tire waste. Part of the solution for this problem can be the efficient recycling of rubber from tires, in order to be repurposed for new tires or other products. While there is extensive research done on the use of silanes as a devulcanization aid for several types of rubber, this is not yet achieved for butyl rubber. Therefore, inner tubes originating from truck tires were selected as feedstock material in this study to design and optimize a devulcanization process for butyl rubber.

Butyl rubber inner tubes are processed into granulate and devulcanized thermo-mechanically in the presence of a devulcanization aid. This leads to a devulcanized butyl rubber of which the quality should be optimized, to make it applicable in industry. The method used for optimization is Design of Experiments, in which the various parameters are explored, and information is gathered about their effects and interactions. This is used to tailor the devulcanization process accordingly. Mechanical tests are used to assess the quality, while specific testing for devulcanized material determines the amount and efficiency of devulcanization. The optimal parameters within a factorial design are used to further optimize and therefore improve the material quality.

Resulting from this study, there is a strong effect of the amount of devulcanization aid. An excess of devulcanization aid could cause oligomerization of the silane, reducing the overall quality of the material. Furthermore, a combination of high shear, long time and high temperature generally results in too much degradation in the material, while an increase of these parameters separately has a positive effect on the tensile strength. An increased fill factor can improve the material by providing higher shear forces for a short period of time. Finally, some considerations have to be made for future research, such as compatibility between the polymer and processing oil, effects observed from varying milling time and the effects of error in the measurements on the statistical analysis.

1 Introduction

Over the last centuries, rubber has become one of the most essential materials used in a variety of applications, such as seals, gaskets, conveyor belts and tires. Rubber is a thermoset polymer that presents significant challenges in recycling due to its inability to be easily reprocessed after curing, akin to materials such as epoxy or polyurethane. Nowadays, there is a growing awareness of the waste problem, which is especially substantial for tires. In the European Union alone over 300 million end-of-life tires are discarded every year, while globally this is estimated to be 1 billion tires. [1] This includes passenger car tires, which are mainly produced from synthetic rubber, as well as truck and airplane tires, produced from mainly natural rubber. This diversity and complexity in tire materials also adds to the difficulty in recycling, as materials often have to be separated first.

The EU has prohibited the landfilling of tires, recognizing the environmental risks associated with the unregulated disposal of tires, such as fire hazards, mosquito breeding, and the leaching of harmful chemicals into soil and groundwater. [2] However, despite these regulations, loopholes remain. For instance, nearly one million tons of rubber waste are exported from the EU each year, a figure that is steadily increasing. [3] This exported waste is not regulated post-export, leading to inconsistencies in waste regulation, and giving industry the possibility to cause pollution by moving rubber waste elsewhere. Furthermore, while it is legal in the EU, stockpiling of tires is a suboptimal solution that fails to address the underlying problem and emphasizes the need for sustainable, long-term waste management strategies.

To mitigate these issues, a variety of rubber waste management methods have been developed. Techniques such as tire retreading, where only the worn tread is replaced, significantly reduces waste. Additionally, methods like material and energy recovery are employed to process end-of-life tires through pyrolysis—a thermochemical decomposition which produces useful byproducts such as recovered carbon black, steel, and pyrolytic oil and gas. [4, 5] Despite the benefits, these processes alone are not long-term solutions to manage end-of-life tires globally, and there is a need for long-term, sustainable solutions.

Alternative strategies for the reuse of tire material have been explored, including shredding tires to create granulate used in applications like synthetic turf infill or molded products such as playground equipment. However, the demand for these products is limited, and the material is of lower quality.

A potential long-term approach to process end-of-life tires is devulcanization, which aims to break crosslinks that formed during vulcanization, while keeping the polymer chains intact. This is the technique that will be explored and optimized, in order to find a balanced trade-off, keeping the polymer chain intact. In practice, devulcanization always goes hand in hand with polymer chain degradation.

This study aims to design and optimize a devulcanization process for butyl rubber inner tubes from truck tires, a very elastic material known for its exceptionally low gas permeability. Using Design of Experiments (DOE) methodology, this project explores various process conditions, their effects and their interactions to identify optimal conditions for producing high-quality devulcanized butyl rubber. This experimental design uses resources efficiently and gives more information, relative to the traditional method of One-Factor At a Time (OFAT). The availability of waste material that only contains butyl rubber was limited, but Rubber Resources in Maastricht could provide butyl rubber originated from truck tire inner tubes. For this material the devulcanization process will be optimized, using bis(triethoxysilylpropyl)tetrasulfide (TESPT) as a devulcanization aid. TESPT is a silane widely used in the rubber industry and already successfully used as devulcanization aid for passenger car tire devulcanization by Ghosh et al. [6] Therefore it is a safe and known choice, applied to a different material.

2 Waste management and recycling

Vulcanized elastomers are difficult to recycle or reprocess in part due to the existence of crosslinks, chemical bonds that increase the strength and toughness of a material, make it less prone to permanent deformation, prevent flow and improve the elastomeric qualities. [7] Furthermore, similarly as thermoset plastics, they can not be reprocessed or melted. Also, the number of different additives and formulations of tire rubber makes the issue more complicated. There are two main sustainability problems occurring in the use of tires:

- The management of end-of-life tires themselves after use
- The domain of tire wear particles that are emitted during and after the lifetime of a tire

The issue of tire wear particles is more related to tire properties and testing methods; hence the focus will not be on this domain. However, the different methods of processing end-of-life tires will be discussed.

Figure 1: Waste hierarchy [8]

2.1 Tire waste management

A tire can be landfilled, stockpiled, incinerated, used to recover material, reused, or recycled. Outside the EU, the tire waste management practices vary greatly. The most noticeable regions globally in their tire waste recovery rates are Europe, Japan and the US, where the recovery rate is between 80 % and 90 %, excluding export and retreading. However, other countries are still lagging behind. Landfilling is a common practice, often with financial incentives.

Figure 2 and Figure 3 show a tire graveyard in Kuwait and a tire graveyard fire, both in 2021. [9] A report from 2008 from the World Business Council for Sustainable Development illustrates the differences in tire waste management more clearly. [10] There is not always data available, and if there is, the definition of recovery can vary. Thus, it is unknown if the number of generated tires is much larger, or if recovery rates are directly comparable between countries. Interestingly, while Australia and New Zealand are considered as developed countries, their recovery rates are low, 30 % and 15 % respectively, and the remaining tires are landfilled, stockpiled or discarded as waste. [11] In many countries, the landfilling of tires is a common practice, and countries that do not contribute directly to landfilling, are financially incentivized to export tire waste to countries where it can be landfilled, stockpiled or incinerated. [12] Seeing that the EU is relatively far in their progression handling tire waste, this study will discuss the most significant processing methods and current difficulties in the EU.

Figure 2: Tire graveyard in Kuwait, 2021 [9]

Figure 3: Tire graveyard on fire, 2021

2.1.1 Prevention

The most environmentally preferred option is prevention of waste, which is also highlighted in the waste hierarchy pyramid in Figure 1. Prevention in the case of tire waste is the preferred objective, to the extent that this is possible. The best way to reduce tire waste is to reduce road transportation. This can take the form of shifting to local production, or reducing cars in certain areas, such as city centers, something that is already happening in the Netherlands. [13] In recent years, more cities have embraced this reduction of cars in city centers, in order to repurpose the resulting space for walking and cycling infrastructure. It reduces air pollution, makes a city greener, and with less asphalt and concrete the formation of urban heat islands is reduced. [14] But a reduction of tires is only realistic to a certain extent. This is even more relevant when considering truck tires, which are logistically necessary in order to transport goods. Truck tire use can only be reduced by shifting production locally, or by replacing the transport method, with for instance trains. However, these options are limited. Therefore, other methods to handle the increasing amount of tire waste globally are necessary.

2.1.2 Landfilling and export

Landfilling and stockpiling of tires can pose risks for soil and groundwater, serve as a nesting area for mosquitos, and create a toxic fire hazard. [15] Within the EU the landfilling of whole tires is prohibited since 2003 and for shredded tires since 2006. [2] Instead, as a more cost-effective option in industry, tire waste can be exported from the EU, to be processed or landfilled. In November 2021 a ban on exporting waste was presented by the European Commission, which would prevent the export of hazardous materials and plastics to non-OECD (Organisation for Economic Co-operation and Development) countries, unless there is proof of the recycling capabilities. [16] This follows an already existing regulatory framework that banned landfilling, causing only 5 % of ELTs to not go through any recycling process, which used to be 50 % in 1996. [5] As illustrated in Figure 4, the annual export of waste rubber from EU-countries has increased by over 100 % from 2012 to 2021. However, the proposed ban would not prevent export from the EU to non-EU OECD countries. An example of the shifting in waste export was seen when China posed restrictions on the import of plastic waste in 2018. Since then, export has shifted to other Asian countries as well as Turkey, where recently also restrictions have been implemented to decrease their import of plastic waste. [17] Furthermore, the statistics on export of ELTs and rubber waste need some clarification, as this doesn't cover the complete picture of waste export. As mentioned by the European Tyre & Rubber manufacturers' association, 95 % of ELTs in 32 European countries are either recycled or used for energy recovery. Unfortunately, it is unclear what portion of ELTs might still be exported, especially when in the form of rubber waste. When classified as rubber waste, there is no more insight over the number of ELTs that is exported. The remaining 5 % that is not processed, used or recycled is usually stockpiled, as a result of the landfilling ban in the EU. [18]

Other options are incineration or another form of energy or material recovery. This can, depending on which method, contribute to greenhouse gas emissions (GHG), but still recovers energy and prevents landfilling this way. Reusing tire rubber is another option commonly used for applications where material quality is not the leading factor. Ground tire rubber can be used on artificial grass fields as infill substance, a topic that has become quite controversial due to the possible pollution by tire particles and the leaching of chemicals. It is also often used in playground areas, rubber mats, or civil engineering applications such as rubber traffic bollards. [19] The European Recycling Industries Confederation presented plans in 2022 to reclassify rubber infill as intentionally added microplastics, which would ban the use of it in sports pitches and other applications. [20]

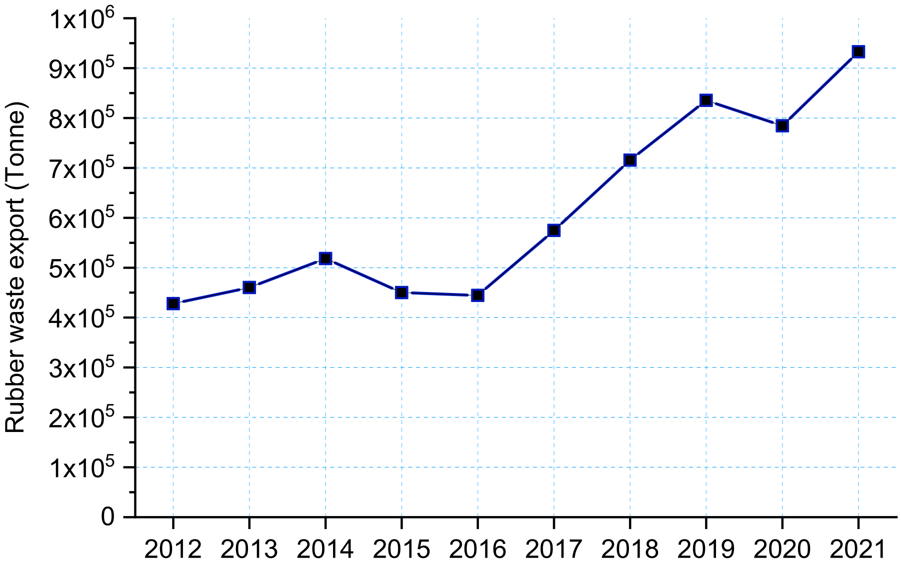


Figure 4: Annual rubber waste export in the European Union [3]

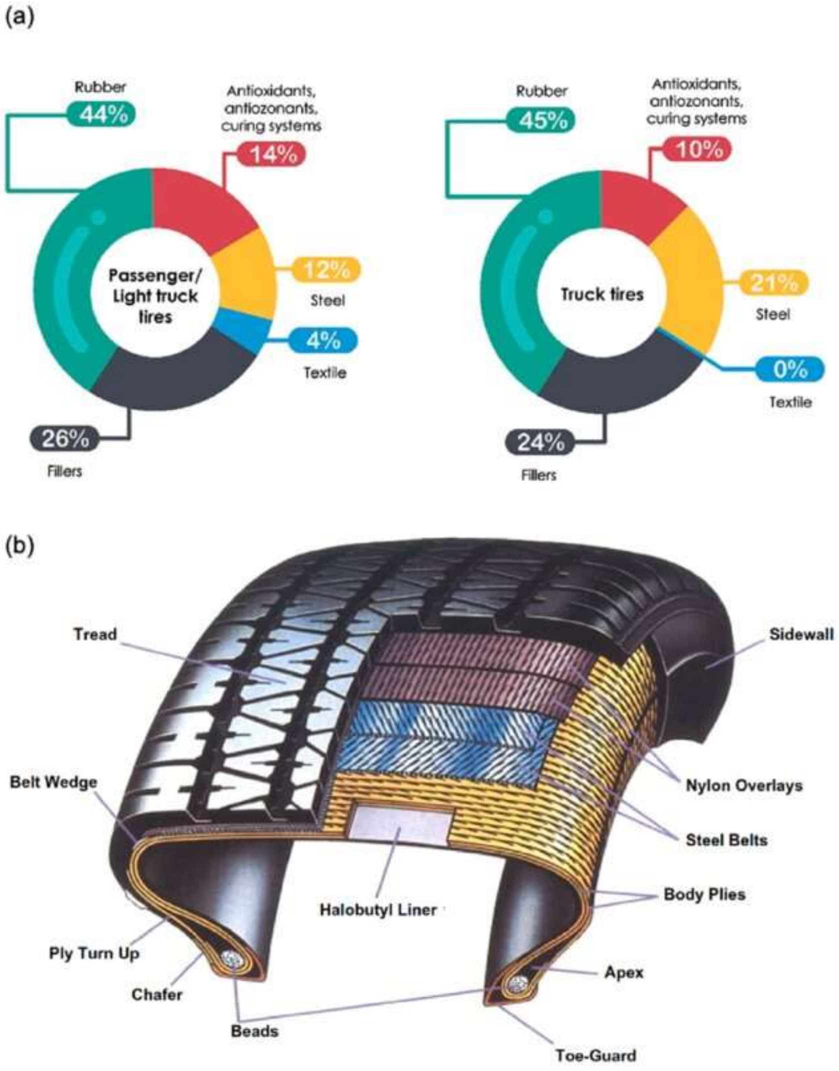


Figure 5: (a) Typical compositions of passenger car tires vs truck tires (b) Visualization of different tire components [21]

As passenger car tire rubber is discarded in high volumes, the focus in most research is on the devulcanization of this type of GTR. But there is a range of different tires and tire parts to be considered, such as truck tires, bicycle tires and airplane tires, which all have very different ingredients and consist of several parts with different compounds. For instance, truck and airplane tire treads use more natural rubber, while passenger car tire treads consist of more synthetic rubbers such as SBR and BR. They also contain inner liners and inner tubes, which are often made from butyl rubber due to its low gas permeability.

3 Devulcanization

The devulcanization of rubber describes the cleavage of the chemical crosslinks previously formed during vulcanization. The main focus is on finding a balance between the scission of crosslinks, while keeping the polymer backbone intact, as this is what retains the quality of the material. Chemically, this means that both S-S and C-S bonds are targeted, while C-C bonds of the polymer chain are avoided.

A different method related to devulcanization is reclamation, where rubber is also processed, replasticized and then used for new products. The difference between the two is that devulcanization refers to selectively targeting crosslinks, while minimizing damage to the polymer chains. Reclaiming on the other hand aims to make the rubber processible again by softening it, without specifically targeting crosslinks. This means that this processing method is less specific on retaining the material properties but is also less expensive in production.

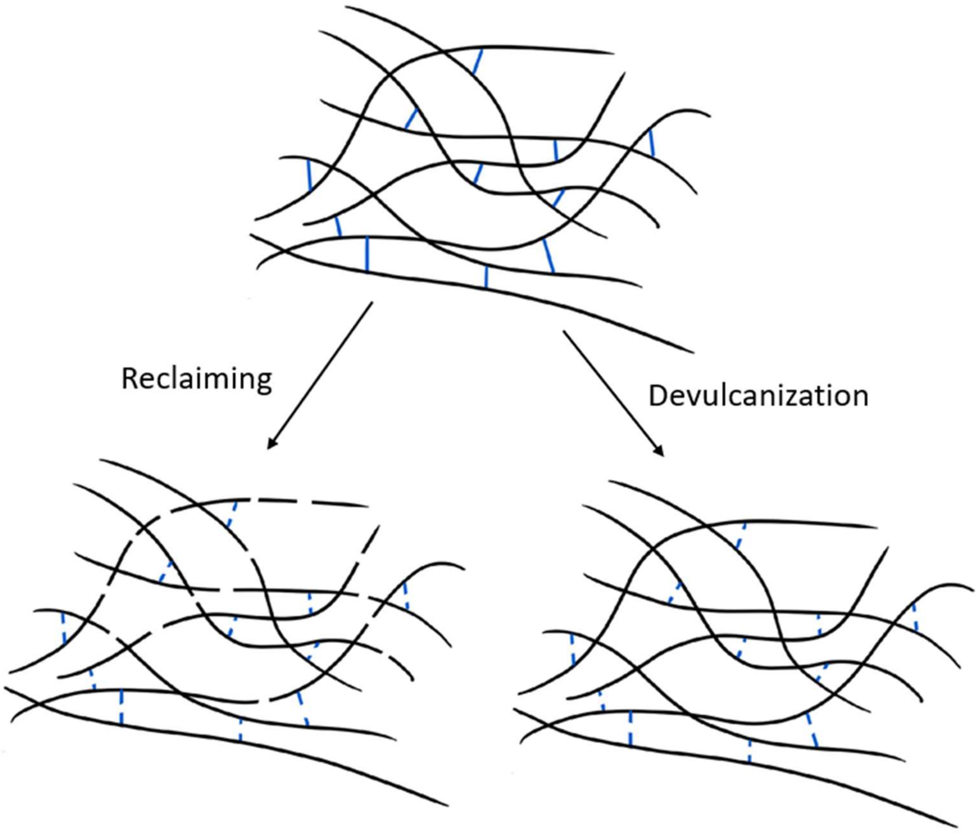


Figure 6: Reclaiming versus devulcanization

3.1 Devulcanization process

The devulcanization process consists of several processing steps. The process can take place with different devulcanization initiation methods. For example, extensive research has been done on the use of ultrasonic, microwave and biological devulcanization. [22-24] Although these approaches can be used for devulcanization, thermo-mechanical processes are still considered the most practical solution, as they can be applied in industry using existing equipment already used in the rubber industry. [25]

First, the vulcanized rubber waste is reduced in size, to make it processible. This is the grinding process, when the rubber is reduced to a granulate that can be processed. After grinding, depending on the type of devulcanization process, the rubber needs to be prepared for devulcanization, for instance by swelling it with processing oil and a devulcanization aid. This process ensures that the devulcanization aid is sufficiently incorporated inside the rubber particles and will improve the devulcanization efficiency.

Then the material is added to the mixer or extruder, where it is devulcanized under set conditions. For example, there is control over the temperature, rotor speed, the total treatment time, and the amount of material, processing oil and devulcanization aid that are added. After devulcanization, depending on the devulcanization efficiency and polymer chain degradation, the rubber can be crumbly, or can be more tacky.

After the devulcanization stage, the material has to be milled and processed into a sheet of rubber, which can be stored and used. The replasticized rubber in combination with oil has a tendency to clump together during milling, if the nip gap is sufficiently small to press the material. After it has formed a sheet, it should be stored overnight, after which curatives can be added. The additional curing package is necessary, as the previous curing system is already used during the first vulcanization process, and remnants of the curatives can also leach out over time. Therefore, it is necessary to add a new curing system to the material, to prepare it for revulcanization and testing. The mentioned steps are illustrated in Figure 7.

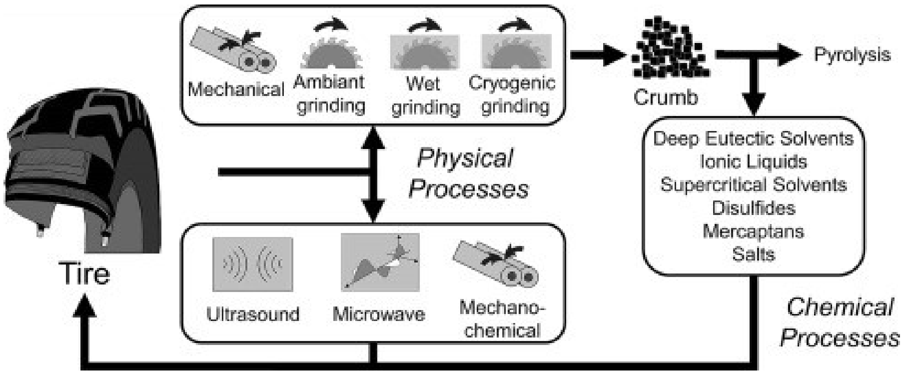


Figure 7: Thermo-mechanical devulcanization process steps [26]

3.1.1 Grinding and Swelling

Rubber grinding is not only a preparation for devulcanization and reclamation, but also occurs in order to process a powder or granulate into different products without replasticizing it. However, for devulcanization the grinding method can severely influence the devulcanization process. The most common grinding methods are ambient grinding, cryogenic grinding and wet grinding. Ambient grinding consists of mechanically breaking the rubber into particles at ambient temperature. This is generally an easy and inexpensive process, but the amount of heat generated can degrade the crumb rubber. It also becomes a more expensive process when finer particle sizes are required. [27]

Cryogenic grinding involves grinding mechanically after the rubber is submersed in liquid nitrogen, to bring the rubber into its glassy state, making it brittle and easier to break, as well as prevent the rubber from sticking and clogging the grinder. This process is faster and generates less heat but is also more expensive. Besides these practical differences, there is variation in morphology and structure of the ground rubber between these two methods. Cryogenic grinding causes smoother particles, but also generates a wider range of particle sizes, making it challenging to obtain efficient devulcanization. Finally, wet grinding involves water as both a lubricant and cooling agent. This creates a fine rubber crumb that has a large surface area, making it suitable for composites and devulcanization. However, this does involve a separate drying step after grinding. [27]

3.1.2 Mixing and Milling

The devulcanization itself generally takes place in an internal mixer or extruder. A twin-screw extruder, as shown by van Hoek et al., has the advantage of precise control over the temperature in different zones, the pressure, and atmospheric conditions within the extruder. [28] The disadvantage is that this is a much larger scale process, and thus is not as suitable for small scale research with limited feedstock material. At the University of Twente a small internal mixer is available for devulcanization. The mixing chamber can be separated from oxygen only to a certain extent, by sealing the inlet with paraffin wax. With this mixer, it is possible to make lab scale batches with little amount of material. Furthermore, there is more control over temperature and shear force.

3.1.3 Revulcanization and Testing

After the process is optimized for devulcanization efficiency, with as goal a high quality devulcanizate, the result is a rubber material that can be used in production of rubber products again. As the devulcanized material still contains vulcanized particles and/or includes damaged polymer chains, it is not equal in quality to virgin rubber before vulcanization. For high-quality rubber products the mass percentage of devulcanized rubber has to stay relatively low to ensure a quality end-product. For instance, Ghosh et al. found that addition of silane-aided devulcanized passenger car tire material can be added to new tires up until 20 wt%, before the tensile strength undergoes a significant reduction. [29] For products that do not have strict requirements on mechanical properties or degradation, the rubber can be produced from fully devulcanized rubber. The financial feasibility and energy usage can still be a considerable factor in the application of recycled rubber in cheap, low requirement products. Furthermore, the usage of chemicals or solvents has to be considered in order to determine the sustainability of the process.

Evaluation of devulcanization and network breakdown

To evaluate the degree of devulcanization, there are a few testing methods developed in research. One method to show the efficiency of the devulcanization process is a Horikx-Verbruggen plot, which typically uses curves as shown in Figure 8. The Horikx-Verbruggen analysis shows the degree of random scission and crosslink scission using the soluble fraction and crosslink density as parameters. In the Horikx-Verbruggen plot there is an indicated optimal target area, where the network breakdown is between 70-90 % as shown in Figure 8. If the network breakdown is higher, the compound will have more random scission, as the difference between the curves reduces to zero at 100 % network breakdown.

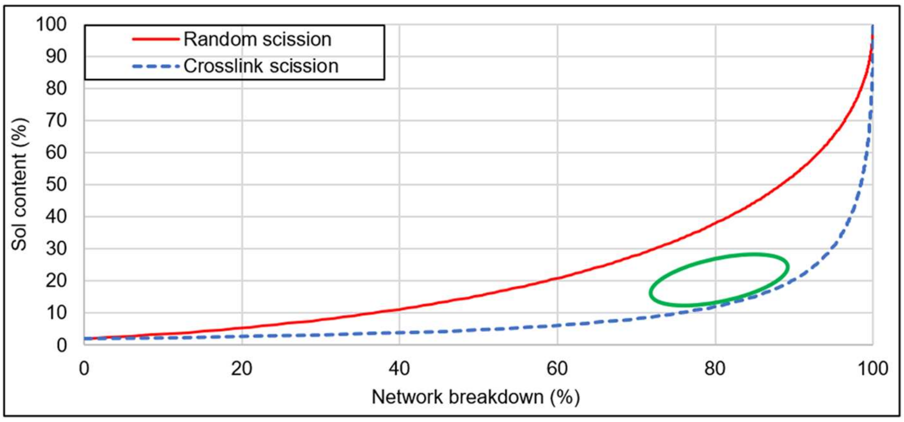


Figure 8: A typical Horikx-Verbruggen plot showing the random scission and crosslink scission curves based on the network breakdown and soluble fraction [30]

Another method to quantitatively analyze the devulcanization efficiency, is the white rubber analysis. As the name implies, the devulcanized material is blended with a white compound. Because of the contrast with the white compound, this shows the still vulcanized particles that did not get devulcanized in the process. Furthermore, the white rubber will turn grey, depending on the degree of devulcanization. If the material turns to a darker grey, this means that there was a higher degree of network breakdown. It should be noted that there is no differentiation between random scission and crosslink scission in this case, unlike the Horikx-Verbruggen analysis. When the sample is analyzed under a digital microscope, it is possible to analyze it based on the number of visible particles, as well as the particle size. This makes it possible to compare devulcanized rubber based on undevulcanized particles in the material. An example of a white rubber sample with clearly visible particles is shown in Figure 9.

Figure 9: White rubber sample with clearly visible particles

3.2 Devulcanization mechanisms

Devulcanization describes the process of breaking crosslinks in rubber. Conventional rubber is cured using sulfur, that forms mono-, di- and polysulfidic crosslinks between the polymer chains. In the design of devulcanization processes, the primary goal is to break these crosslinks while keeping the backbone of the polymer intact, and to prevent degradation of the material as much as possible. An important distinction is made between random scission and crosslink scission, where crosslink scission should be maximized and random scission minimized to get an optimal quality devulcanizate.

The devulcanization reaction is a result of both sufficient energy input that breaks the chemical bonds in a crosslink, as well as a devulcanization aid that attacks crosslinks. Because this study is focused on sulfur-crosslinked rubber, these bonds are either C-S or S-S bonds. In a thermos-mechanical process, the energy input needed to break these bonds is provided by thermal energy and mechanical shear. In the context of an internal mixer, this is translated to the set temperature and the shear forces during mixing, resulting from the rotor speed, the type of rotors, but also the viscosity of the material. During the devulcanization process, the rubber is first softened by sufficient shear force and temperature. It then heats up and due to the thermal and mechanical energy the crosslinks can be broken. In a crosslinked polymer system, the carbon-carbon bonds possess the highest bond energy and will therefore require more energy to break compared to lower energy bonds. The respective bond energies are shown in Table 1. While C-C bonds are strongest, the difference in bond strength between C-C bonds and the sulfur bonds is relatively small, causing the difficulty of selectively breaking C-S and S-S bonds while keeping C-C bonds intact. Even though the types of crosslinks are similar in different types of rubber, the devulcanization efficiency can vary. This is due to differences in heat resistance, structure, and possible secondary reaction mechanisms with the devulcanization aid, that depend on the structure of the polymer.

Bond	Average bond energy (kJ/mol)
C-C	345
C-S	260
S-S	215

Table 1: Bond energies of C-C, C-S and S-S bonds [31]

When there is no devulcanization aid used, the crosslinks can recombine after cleavage, which would limit the devulcanization efficiency, as well as change the structure of the network, diminishing the overall quality. To prevent this, a devulcanization aid such as TESPT can be used, which reacts with the cleaved crosslinks, preventing recombination of said crosslinks. The mechanism for TESPT as recombination inhibitor is shown in Figure 10.

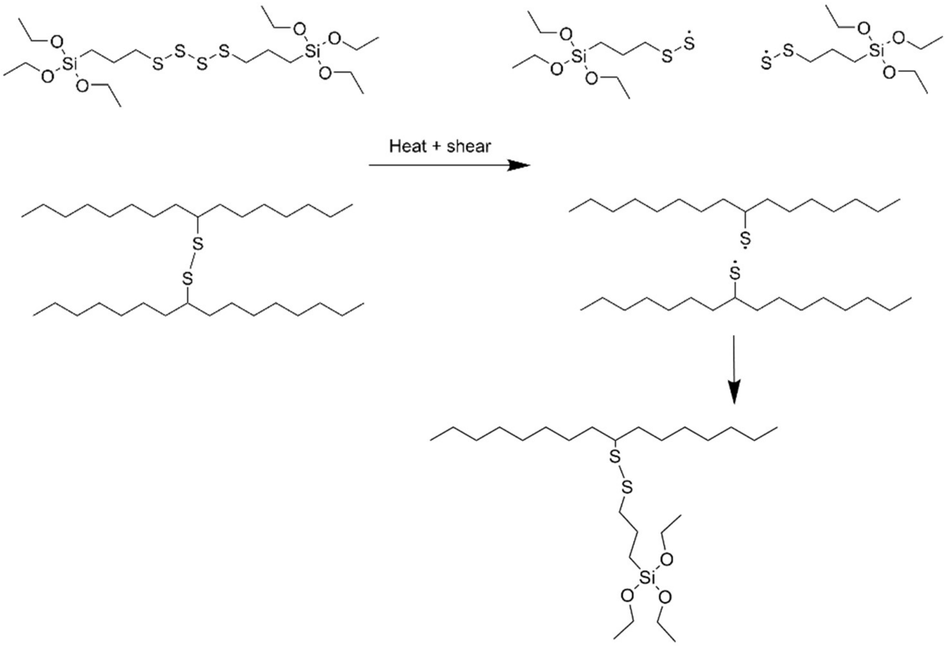


Figure 10: TESPT reaction mechanism as recombination inhibitor

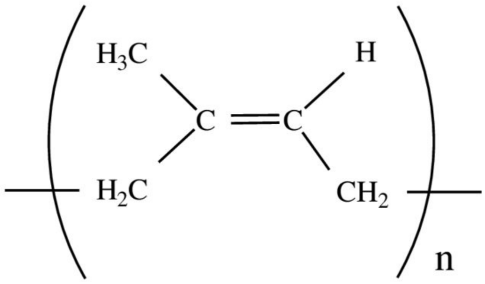


Figure 11: Molecular structure of poly(cis-1,4)isoprene (natural rubber) [32]

In Figure 11 the molecular structure of cis-1,4-polyisoprene is shown. Natural rubber is relatively easy to reclaim, because it is more prone to degradation. However, the ease of devulcanization is mostly due to natural rubber being a forgiving material, that even after significant random scission will still have decent properties. Here the ‘self-healing' properties of natural rubber play a role, caused by the system of proteins and peptides. In devulcanization, since the goal is to selectively target crosslinks while keeping the polymer chains undamaged, a low heat resistance can hamper the devulcanization efficiency, as it increases random scission. On the other hand, unlike SBR and BR, natural rubber is less prone to recombination of crosslinks during the devulcanization process. [33]

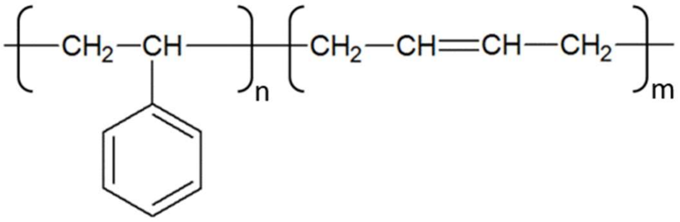


Figure 12: The molecular structure of styrene-butadiene rubber [34]

The molecular structure of styrene-butadiene rubber (SBR) is shown in Figure 12. In contrast to polyisoprene, this co-polymer has a lower concentration of double bonds, and additionally contains an aromatic ring. These molecular properties cause the polymer to be more heat resistant, and therefore less prone to thermal degradation. This is similar in the case of butyl rubber, which is a co-polymer of isobutylene and small amounts of isoprene, as shown in Figure 13. [33] The lower concentration of double bonds gives butyl rubber high heat resistance, and again, as mentioned for SBR, it is positive in terms of preventing random scission.

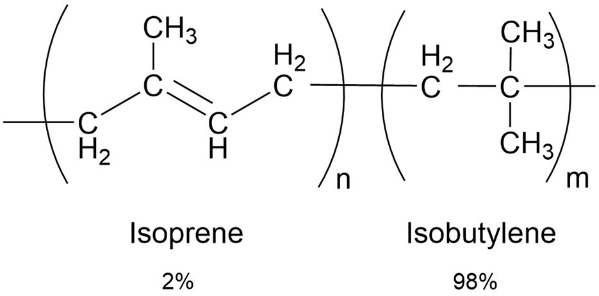


Figure 13: Molecular structure of non-halogenated butyl rubber

On the other hand, as mentioned in a study by Saiwari et al. the devulcanization of chlorinated butyl rubber (C-IIR) gives data points in the Horikx-Verbruggen plot that indicate a rapid increase in sol content, paired with limited network breakdown. [35] Therefore, these data points are located above the random scission line, which is mainly an indication of the devulcanization mechanism of the rubber. In this case, the vulcanized particles undergo a so-called ‘onion peeling’ mechanism, where the particle is not homogenously devulcanized, but instead, the outer layer is devulcanized first. This leads to an increase in sol content but leaves a core that is still vulcanized. Usually, this mechanism is the result of a low compatibility between the polymer and the swelling chemicals, which are the processing oil and devulcanization aid. If these are swelled homogenously through the particle, this onion peeling mechanism does not occur. [36]

3.3 Devulcanization aids

Different devulcanization aids have been studied in order to create efficient and effective devulcanization. In Table 3 a list of various devulcanization aids described in literature is shown, together with the main application of the chemical besides devulcanization. This will also shed some light on the sustainability of the process, using the various safety warnings assigned to each chemical. The focus will be on the most common type of devulcanization, a thermo-mechano-chemical process in which shear force, higher temperatures and a devulcanization aid are combined.

In the selection of devulcanization aids a number of factors are important. A progressively significant factor is the sustainability of the DA, including possible harmful reaction products like hydrogen disulfide as a result of devulcanization. Also, the melting temperature of the DA can vary, for instance diphenyldisulfide (DPDS) melts at 59 °C while dibenzamidodisulfide (DBD) melts at 140 °C, which has a significant influence on the possible process. [28] A common method to distribute the DA in the rubber is swelling of the ground tire rubber (GTR) with processing oil and the devulcanization aid. When the DA has a high melting point, it is not possible to properly swell the rubber beforehand for extended periods of time, because at higher temperatures the GTR will degrade further. On the other hand, a higher boiling point is preferred for a devulcanization aid, as mentioned by Saiwari et al.

To assess the compatibility of a devulcanization aid and a polymer, the solubility parameters can be used as a guide. If the solubility parameters are closer, this means a higher compatibility. [37] For this the Hansen solubility parameters can be used, which are calculated in various ways. One method is to use the HSPiP Hansen Solubility software, that contains a database of chemicals, and can also calculate the solubility parameters based on a chemical input. The solubility parameter is split into three components, representing the dispersion (δD), polar (δP), and hydrogen-bonding (δH).

One risk in devulcanization processes is recombination of rubber chain segments during the reaction after the crosslinks are broken. This is especially relevant for passenger car tire rubber, which mainly consists of SBR (styrene-butadiene rubber), BR (butadiene rubber) and NR (natural rubber). SBR and BR are more likely to recombine at elevated temperatures, if the process is not optimized. [37] Devulcanization process optimization therefore is key to efficient devulcanization of passenger car tires. However, recombination is also a risk for other types of rubber, and so the use of a devulcanization aid can help prevent this recombination mechanism.

Another aspect that makes the implementation less complex is if the DA is already used in the rubber industry, which can provide a quicker but also cheaper introduction of the DA into the process. The implementation of a new or unconventional chemical will usually be more costly and time-consuming and is therefore not preferred.

When a devulcanization aid is selected for a process, besides the efficiency also sustainability concerns are an issue, as well as how realistic the DA can be implemented. Certain devulcanization aids are more suitable both at laboratory and factory scale simply because of better processing or increased safety.

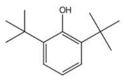
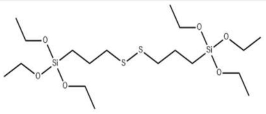
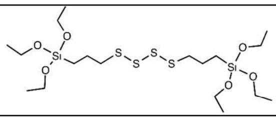
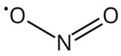
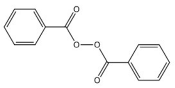
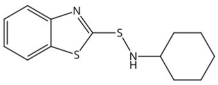
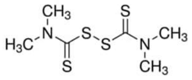
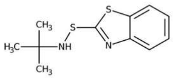
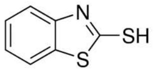
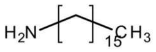
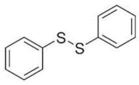
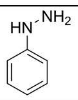
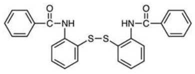
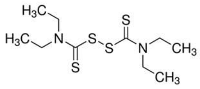
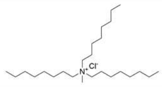
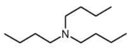
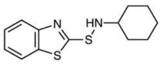
Devulcanization aid	**Structure**	**Other applications**	**Safety and sustainability**
thiobisphenols (4,40-dithiobis(2,6-di-t-butylphenol))		X	Unknown
TESPD (bis(3-triethoxysilylpropyldisulphide)		Silane-coupling agent	X
TESPT (bis(3-triethoxysilylpropyltetrasulphide)		Silane-coupling agent, reinforcing filler, vulcanization agent	Irritant
N2O (nitrous oxide)		Anaesthetic, oxidizer	Oxidizer, compressed gas
BPO (benzoyl peroxide)		Bleaching agent for flour, oil; polymerization catalyst; non-sulfur vulcanization	Explosive, flammable, irritant
CBS (N-cyclohexylbenzothiazole-2-sulphenamide)		Accelerator	Irritant, environmental hazard
TMTD (tetra methyl thiuram disulphide)		Fungicide, animal repellant, rubber accelerator	Health hazard, environmental hazard
TBBS (N-tert-butyl-2-benzothiazyl-sulphenamide)		Accelerator	Health hazard, environmental hazard
MBT (2-mercaptobenzothiazol)		Accelerator, metal industry (anti-corrosion, antifreeze, detergent)	Environmental hazard
HDA (hexadecylamine)		Lubricant, source for chemical manufacturing	Corrosive, irritant, health hazard, environmental hazard
DPDS (Diphenyldisulfide)		Preparation of thiols, coupling reactions	Acute toxic, health hazard, environmental hazard
PH (phenyl hydrazine)		Found in mushrooms	Acute toxic, health hazard, environmental hazard
DBDPD (2,2-dibenzamidodiphenyldisulphide)		Fuel, plasticizer in rubber	X
TETD (tetraethylthiuramdisulphides)		Accelerator	Acute toxic, irritant, health hazard, environmental hazard
Methyl-tri-octyl ammonium chloride		Surfactant, pesticide	Corrosive, acute toxic, irritant, environmental hazard
TBA (tributyl-amine)		Hydraulics, pesticides, solvent	Acute toxic, irritant
IPPD (N-cyclohexylbenzothiazole-2-sulphenamide)		Anti-ozonant, anti-oxidant	Irritant, environmental hazard

Table 2: List of devulcanization aids [30, 38, 39]

4 Butyl rubber

Butyl rubber is a co-polymer of the monomer units isobutylene and small amounts of isoprene. The isoprene unit provides a double C-C bonds which make it possible to vulcanize, in contrast to the otherwise inert polyisobutylene. It is a relatively soft and flexible rubber, often used for applications where gas permeability should be avoided, such as inner tubes in bicycle and truck tires. The structure of regular butyl rubber molecules is shown in Figure 14, consisting of 2 % isoprene units. There are two types of butyl rubber: regular butyl rubber (IIR) and halogenated butyl rubber (X-IIR). Regular butyl rubber consists only of isoprene and isobutylene units.

Halogenated butyl rubber is mainly used in applications where co-vulcanization is required, such as for inner liners in tires. Due to the difference in curing behavior between regular butyl rubber and elastomers such as SBR, BR and NR, these cannot be co-cured properly. Halogenation shortens the curing time and provides better compatibility with other polymers.

Halogenated butyl rubber can be either bromobutyl rubber (B-IIR) or chlorobutyl rubber (C-IIR) with a bromide or chloride side group respectively. For instance, halogenated butyl rubber is faster to vulcanize with different or less curatives, making it more suitable when co-curing it with other compounds. Due to the low polarity of the material, IIR is preferably used with paraffin oil as processing aid. [40, 41]

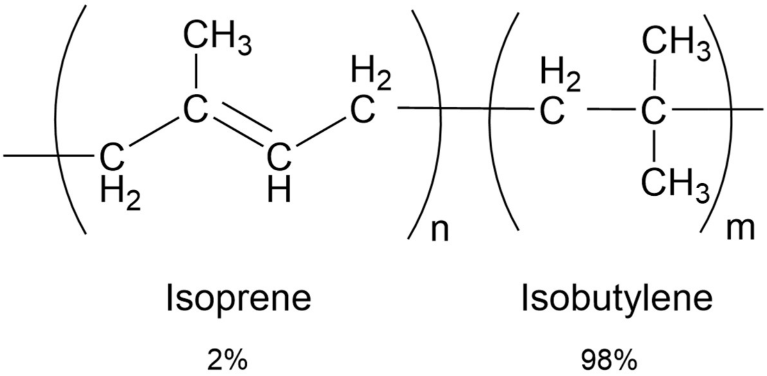


Figure 14: Regular butyl rubber consisting of 98 % polyisobutylene

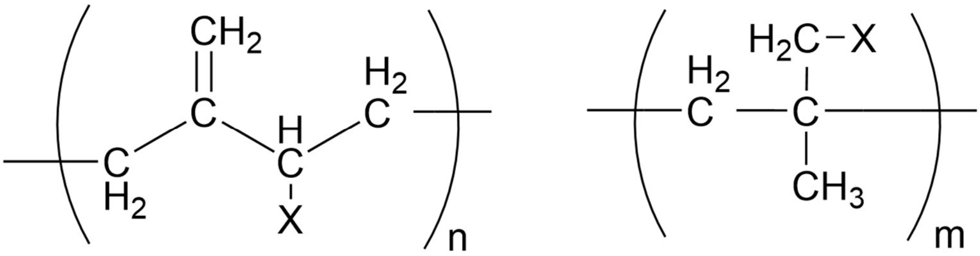


Figure 15: Halogenation of butyl rubber at the isoprene and isobutylene units

Butyl rubber is also relatively oxidation resistant: due to the low amount of double bonds, oxygen can not easily react with the polymer, preventing main chain breakage. Furthermore, there is a low rate of motion on a molecular level, a property responsible for the low gas permeability and ozone resistance. [42]

4.1 Devulcanization and Processing

Some considerations should be made on the processing of butyl rubber, as it is a softer, tackier rubber compared to SBR, BR or NR. This means also that when milling, the material is more likely to stick to the two rolls, making it more difficult to mill according to the general milling procedure. However, butyl rubber is easier to masticate in the devulcanization procedure, as it is softer and more pliable. This also means that even if the devulcanization efficiency is low, the material is still possible to process, in contrast to passenger car tire rubber. In a Design of Experiments procedure, it is important that all the experimental runs can be completed and therefore tested. If the devulcanizate is too crumbly to form into a sheet, it is difficult to accurately test, mold and process. In this case, it should not be included in the results. Butyl rubber is relatively easier to mill into a sheet due to the tacky nature of the material, making it possible to test and mold properly, even if the devulcanization efficiency is very low. Grinding is however a bit more complex if done at room temperature. Due to the elasticity and tackiness, the material is prone to get stuck between the blades and the chamber while grinding, also causing more heat buildup in the material as a result. This is because the grinder keeps rotating against the material even if it is stuck, increasing the shear forces and therefore increasing the temperature.

Furthermore, butyl rubber is especially known and used for its low gas permeability, a property very relevant in inner tubes and inner liners of tubeless tires. Therefore, in processing, this can create problems with trapped air in the polymer. During milling and molding the processing conditions have to be adapted, to prevent trapped air. One method that can aid in this problem is to form the material into a thicker sheet that can be cut to the size of the mold, without separate pieces or folds in the material.

4.2 Compatibility with devulcanization aid and processing oil

The Hansen Solubility parameters are calculated for butyl rubber, TESPT, paraffinic oil and TDAE oil. This gives an indication of the compatibility of the DA and processing oil with the feedstock material. As a comparison, styrene-butadiene rubber (SBR) and polyisoprene (representative of NR) are included. For butyl rubber, polyisobutylene is taken as polymer. For the TDAE oil, one of the aromatic components is taken as representative, which is benzo(a)antracene. Paraffinic oil is characterized by being a standard alkane with n being between 20 and 40.

If the solubility parameters are closer together, this means they are more compatible. It is quite clear that in this case paraffinic oil is preferred for polyisobutylene compared to TDAE oil. Furthermore, the DA is much closer to polyisobutylene in solubility values, indicating they are compatible. However, it is possible that the presence of TDAE hampers the ability of the devulcanization aid to swell into the rubber, as these are not compatible together.

	Polyisobutylene	TESPT	TDAE (benzo(a)antracene)	Paraffin - (standard alkane (n=31))	Polystyrenebutadiene	Polyisoprene
δD	16	14.6	14.1	15.9	13.5	11
δP	0.2	6	2.1	0.1	0.1	0.1
δH	0.2	3.4	35.3	0.1	12.9	5.8

Table 3: Solubility parameters

Furthermore, the degree of crosslink scission and random scission determine the overall quality retained in the devulcanizate. Random scission should therefore be minimized, as this is the cleavage of polymer chains, reducing the material properties. Crosslink scission is targeted in devulcanization and should be maximized.

5 Design of Experiments

The traditional way to identify factors and their influence in experimentation is the variation of only one factor while keeping others constant, which is called the One-Factor-at-A-Time method (OFAT). This method is deeply ingrained in research and is still used a lot. It is a simple and clear way to experiment, but also comes with the disadvantage of using more resources and time, and reducing the amount of information that can be obtained within the scope of a research project. On the other hand, there is the method called Design of Experiments, which does not have a long history, and is not yet as established in research. However, it can be advantageous in research, as it can identify the significance of each factor, and measure interaction effects between factors, something that can not be done using OFAT. It also is generally more efficient, as it can get more information using less experiments, comparatively.

In order to design and optimize a devulcanization process with a relatively large number of factors, design of experiments can therefore help finding the optimal parameters more efficiently and will therefore be used in this project. Often an experimental design is some form of a factorial design, where the number of runs is defined by:

$$Number\ of\ runs = Levels^{Factors}$$

Levels is in this context the variation of a factor. For instance, in a two-level design, there can be two values chosen to be tested for one factor. Factors are the influencing effects that can be controlled. In a devulcanization process, temperature and rotor speed are quite accurately controlled, thus making them suitable to choose as factors. On the other hand, there are factors that are hard to control, such as the amount of oxygen reaching the mixing chamber, or the environmental conditions in the lab.

A factorial design combines settings of factors, often called treatments, in order to vary in such a way that all main effects of the factors and interactions can be discovered. In order to save resources and time, a fractional factorial or Taguchi array can be used, but it does come with a trade-off in information. For screenings especially this might be useful, depending on the number of factors needed.

5.1 Minitab Statistical Software

In order to design and analyze factorial designs, a statistics software program called Minitab is used. This program can do a wide range of statistical tests and analyses. In this context it will mainly be used to design a factorial design based on a number of inputs, and in turn to analyze the results of this factorial design and provide the statistical data necessary to draw conclusions from it.

Minitab is one of the main software programs used to design and analyze factorial designs efficiently. It is widely used in quality control purposes and therefore will be the main tool used in the experimentation and analysis. It will generate factorial designs and a lot of other types of experimental designs based on inputs, but it can also be used for a wide variety of statistical tests.

5.2 Blocking & Confounding

To remove the influence of external, hard to control factors, blocking and confounding can be used. For example, when not all tests can be run under the same conditions, for instance on the same day or by the same person, these changes can affect the results. Blocking is a method that separates the total experimental runs based on a confounding factor. A common method to do this is to use the highest order interaction, and construct blocks based on this interaction. The generated conditions are then sorted based on this highest interaction. As can be seen in Table 4 in the last column, the first block here only contains the ‘high' levels of 1 for ABC, while the second block contains all the ‘low' levels of -1 for ABC. The result is that this interaction effect can not be separated from its individual components, and so this is only a sound method when this interaction effect is not as important.

Another example is to use blocking and confounding on a 2^4 factorial design. This means that the interaction ABCD is used to form blocks. The effect of this interaction can therefore not be determined in the analysis as it is confounded.

RunOrder	Blocks	A	B	C	AB	BC	AC	ABC
1	1	-1	-1	1	1	-1	-1	1
2	1	1	1	1	1	1	1	1
3	1	-1	1	-1	-1	-1	1	1
4	1	1	-1	-1	-1	1	-1	1
5	2	1	-1	1	-1	-1	1	-1
6	2	1	1	-1	1	-1	-1	-1
7	2	-1	1	1	-1	1	-1	-1
8	2	-1	-1	-1	1	1	1	-1

Table 4: Full effect table of a 2^3 factorial design used for blocking & confounding

5.3 Screening

A screening with less experiments is often used to get an initial idea of the parameters needed before optimization. In contrast to OFAT, design of experiments allows for a more efficient scan for parameters and finding a preliminary optimal region to use for optimization. By varying the multiple factors at a time, with less experiments there is more information on the influence of each factor and the products of factors, also called interactions.

There are a number of considerations to be made before creating a screening design. One of the main issues is that curvature is an important metric in DOE to determine a general trend in screening results. When doing a 3-level factorial design it is possible to show this curvature, but it also drastically increases the number of experiments needed. Another method to show curvature in a screening is to use center points. Especially when using a larger number of factors this can reduce the extra runs needed to investigate curvature, by taking a center point which consists of all the ‘middle' values of all factors. This can also be displayed by the cube construction, as shown in Figure 16. In this case the number of factors is equal to the number of axes, corresponding with a low and high level.

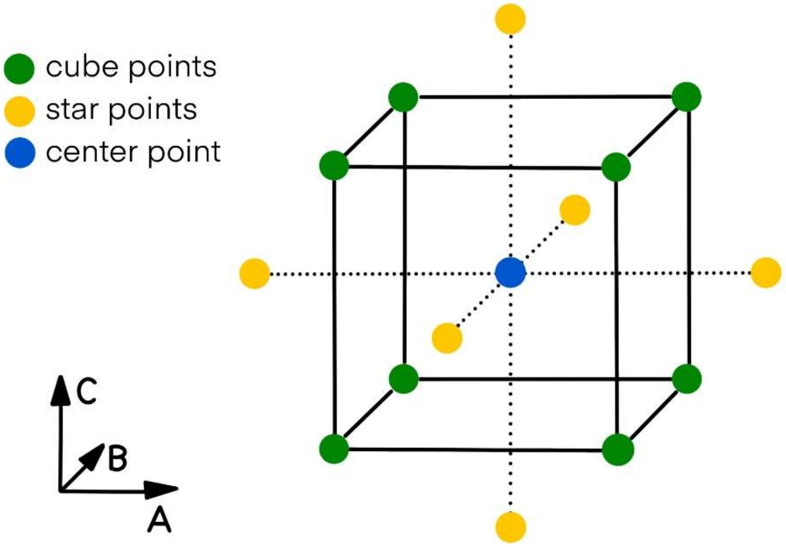


Figure 16: DOE cube including a center point and star points

For the screening it is important to choose ‘extremes' of what is realistically within range for each factor, so for instance if literature on a topic gives certain minimum and maximum values for factors in these processes, then we can take these as ‘high' and ‘low'. There needs to be enough distance between the values to vary and to see an effect. At the same time, the values should not be too extreme, as this can change the fundamental process. One example is choosing a range for the temperature values. In material science the phase of the material is a consequence of the chosen temperature. If that phase changes throughout the process, then the experimental design is not testing a consistent process, as the process parameters are highly influenced by the phase of the material. For example, if temperatures would get below the glass transition temperature of a rubber compound, then the material changes to a glassy state, in which it is brittle and has completely different properties. These properties are not comparable to the usual properties of an elastomer, and therefore the process tested becomes inconsistent. Similarly with addition of processing oil to rubber. A certain amount of oil can still be swelled into the rubber, but any excess oil will not be absorbed. Instead, this excess oil can influence the reliability of the experimental design if it does not contribute similarly like low amounts of oil, for instance by flowing out of the mixer, or acting as a lubricant between the material and the rotors. For these reasons, parameters should not be chosen in too extreme ranges, as the material might not be processible, measurable, or have a different mechanism responsible for the properties.

5.4 Analysis

The analysis of a factorial design and what conclusions can be drawn as a result depend largely on the factorial design itself and different considerations made. The addition of center points, as mentioned before, adds more information to the analysis about curvature in the results, which can point to an optimal region for further testing. Blocking causes external hard to control factors to be less significant by confounding these effects. The general conclusions about a factorial design can be drawn from the main effects & interactions, which are each represented by a P-value, indicating the significance of the effect. When choosing a standard confidence interval of 95 %, a P-value of 0.05 or smaller indicates a significant effect.

5.4.1 Main effects & interactions

The most important results of a factorial design are the main effects and interactions of the factors. For example, Table 4 shows the full effect table of a 2^3 design, including the main effects A, B and C, and interactions AB, BC, AC and ABC. When blocking based on the highest interaction as generator, this means this interaction is not relevant for analysis anymore, as it is confounded, and therefore it will not be included as an effect. Each main or interaction effect can have an influence on the process, and the significance of these effects is analyzed based on the response values. The response values can be any tested parameter that results from the experimental design, but for optimization it is best to use a parameter that should be either minimized or maximized.

5.4.2 Error

In a factorial design one important measure for error is the degrees of freedom. The total degrees of freedom in a design equals the number of observations minus 1. Furthermore, every main effect, interaction effect, blocking measure and center points absorb degrees of freedom, after which finally the error degrees of freedom are left, indicating how much room there is left for error.

5.4.3 Results

The results of a factorial analysis consist of the main effects and interactions table, accompanied by the effect plots that show the relationship between factors and resulting values. The effects table shows among other information the P-values of each effect or interaction. The P-value is a measure of significance, and an effect or interaction is considered significant when the P-value is below 0.05, with a confidence interval of 95 %.

Furthermore, a lower P-value means a higher significance of the effect. This is also the case for other terms, such as curvature. The center points compared to the low and high values give an estimate of the curvature in the model. If the P-value of the curvature is below 0.05, that means there is significant curvature in the model.

Optimizing a full factorial design can be done by removing terms that are not considered significant. Often, these are the terms with high P-values, center points and higher order interactions. In order to visualize the results, there are multiple options such as graphs showing the relation between two parameters, but also 3D contour plots can be used to show relations between 3 parameters in one plot. When there are more parameters than can be shown in the plot, these will be fixed, and so will not contribute to the effect. It has to be taken into account that these plots may vary when choosing a different fixed parameter.

6 Original research plan

Due to unforeseen circumstances, the topic of this research has changed over time. The original research plan aimed to develop a devulcanization process for passenger car tire rubber using a newly developed substance as devulcanization aid. In comparison to more conventional DA's, this substance has the capability of being traced due to the phosphorous group in the substance. One significant challenge in this was the extremely high viscosity of the liquid polymer devulcanization aid. Furthermore, a seemingly advantageous property of the DA was the stickiness. This might have contributed to the processability of the material, as it was easier to form into a sheet by milling, even if the devulcanizate was very crumbly after devulcanization.

6.1 Devulcanization process

The devulcanization process can be divided into 5 stages, which are explained below.

Stage 1: Preparation

To prepare the material, the raw material needs to be reduced in size, by grinding. In the first experimental setup, when the passenger car tire rubber was used, this was already done by the supplier. After grinding, the material is swollen with oil, in order to incorporate the processing oil into the rubber for easier processing. Furthermore, if a devulcanization aid is used, this is swelled into the rubber after oil swelling. These steps ensure the oil and DA are as homogenously distributed throughout the mixture as possible. After this, the material is ready for devulcanization.

Stage 2: Devulcanization

Devulcanization at laboratory scale takes place using an internal mixer. This makes it possible to produce small batches of devulcanizate with differing parameters, and small amounts of material. In an internal mixer, the rotor speed and temperature can be controlled. Furthermore, using the torque versus temperature curve, the process can be monitored. This method is quite flexible but also prone to external factors.

The other option at larger scale is an extruder, which is more suitable for continuous processes at larger scale and retains more control on the parameters, such as pressure and temperature.

The amount of time the material is in the devulcanization stage is called the residence time and can be counted from the first peak in the torque, after the crumb rubber is added. This peak is shown in Figure 17. This is to ensure that the differences in the time required for putting the material into the mixer do not add to the residence time. While the rubber is being added portion by portion, it can start masticating but since the mixer is not filled within the same period of time, this cannot be considered equal for every batch. The amount of material added to the mixture, relative to the total volume of the mixer, is called the fill factor (FF). This is either a percentage or ratio to the full volume. Finally, the amount of devulcanization aid and oil mixed into the rubber influences the properties. The mentioned parameters already have clear interactions. For example, temperature influences the viscosity of the material, and therefore influences the shear forces in the mixer. Fill factor also influences shear forces, as well as the rotor speed. The amount of oil similarly influences shear forces and acts as a processing aid, and finally the residence time influences the final increase in temperature. If the temperature and shear forces are too high, more degradation of the main chain will occur, and thus the quality will decrease. If these factors are too low, the material will not devulcanize enough. The balance between these factors is what makes optimization an important tool to develop the highest quality devulcanized material.

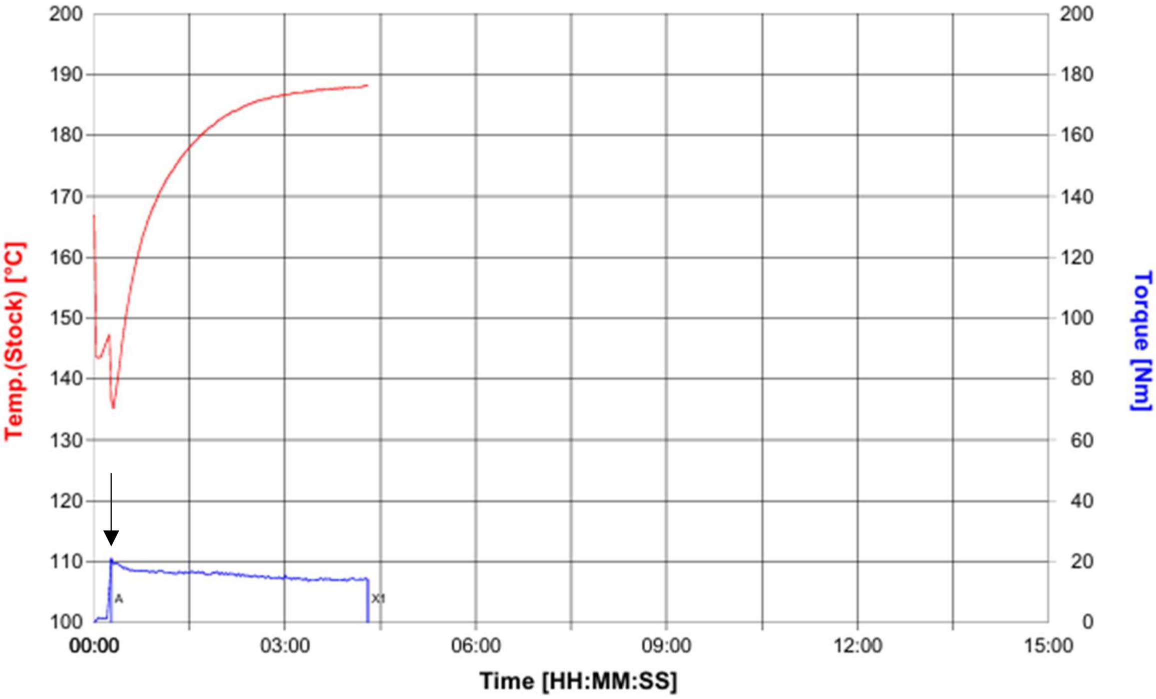


Figure 17: Devulcanization mixing curve

Stage 3: Milling

After the devulcanization stage in the mixer, the resulting material should cool down for a few minutes and then processed on a two-roll mill in order to form a homogenous sheet. Milling should be performed with a sufficiently small nip gap in order to press the rubber to a sheet, but too much shear and a too long milling time should be avoided, as this will further break the polymer chains.

Stage 4: Compounding and milling

Furthermore, the devulcanizate has to be compounded with curatives, before it can be revulcanized. One day after devulcanization the material can be mixed with curatives, and then again milled for 2-3 minutes to form a homogenous sheet.

Stage 5: Molding

Finally, one day after addition of curatives the material is ready for molding. The ideal curing time can be determined from a rheometer test, measuring a cure curve of the specific material. Based on the shape and thickness of the samples, some extra time needs to be added to the curing time. The devulcanizate can be revulcanized in a compression molding machine in the desired molds for specific types of tests. After molding, the samples need to rest for one day before testing.

6.2 Screening design

In order to estimate optimization parameters, a screening is done first. This screening aims to get a preliminary set of parameters to base the optimization process on. Using a full factorial 2^4 design with additional center points will give enough information while limiting the number of experiments.

A 2^4 factorial will give a total of 16 runs, meaning 16 batches of material that will be devulcanized, revulcanized and tested separately. Adding center points to the design gives extra information about curvature in the results, by testing the middle values of all factors. If the curvature shows that the optimal parameters are between the low and high levels, then this can be taken into account for optimization. Furthermore, blocking and confounding is a significant method to reduce external effects. This is especially relevant because of time limitations, causing the screening to be split in two blocks, with each block signifying a day of devulcanization. In order to mitigate the differences in uncontrollable, external factors between days, each block is chosen in such a way that these effects are confounded.

Confounding is done by splitting the experimental runs into blocks, using a generator that is least relevant to the research. Usually, the highest order interaction between factors is used, as this interaction is rarely significant and can therefore be confounded. In a four-factor design this is the interaction ABCD, where each letter is one of the chosen parameters. For each block, two center points are added, in order to add information about curvature to the design.

Generally, in experimental designs it is useful to randomize the order of the experiments, in order to mitigate possible factors that could negatively influence the accuracy of the results. In the case of devulcanization, there is one factor that prevents full randomization, which is temperature. The mixing device used for devulcanization takes a short time to heat up, and a long time to cool down, which makes randomization impossible due to time constraints. To account for this, it is chosen to first randomize the experiments, and then order the runs again for each block, based on temperature. This way the mixer only needs to heat up three times for one day of the screening.

This experimental design was carried out divided into two blocks. Unfortunately, during the first day of devulcanization, it became clear that the smell was unusual and therefore had to be evaluated before continuing. Because the smell strongly resembled Bisphenol A, a harmful substance, the research was stopped and it was decided to look at the chemical reactions possible, to identify what fumes could have come out. After a brainstorm with colleagues, it was concluded that phenol could come out as a result of the devulcanization reaction, and the smell of phenol resembled the smell during devulcanization. To ensure this was the case, the fumes were collected from one batch and then analyzed using liquid gas chromatography, and it was determined that the substance indeed was phenol, a harmful substance that is also present in cigarettes, for instance. The decision was made by the lab management to immediately stop all devulcanization and reactive mixing, even without the generation of phenol. In order to ensure future safety, the decision to make a fume hood for the internal mixer was made. This meant no devulcanization was possible until then, and the ordering and production of this fume hood could take up to two months.

This would severely hamper the project, and thus it was discussed to make a temporary fume hood from leftover materials in storage. At this time, there was a lot of see-through covid screens leftover from the pandemic, both tall ones on wheels and shorter screens to place on tables. With these materials it was possible to make a temporary fume hood that could be placed over the mixer when necessary. The result is shown in Figure 18.

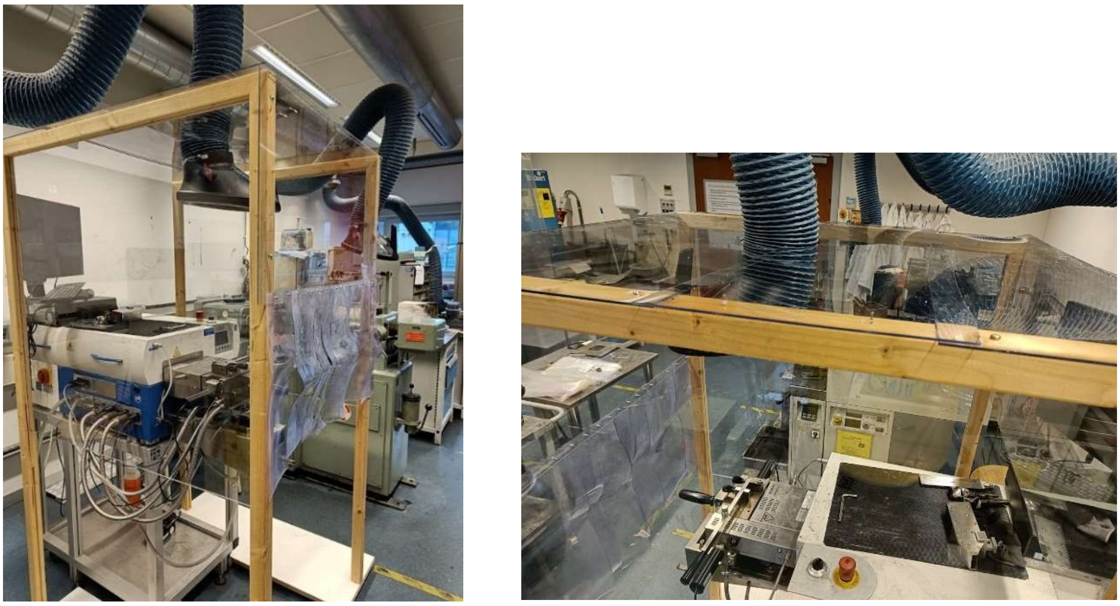


Figure 18: Temporary fume hood

However, the initially used devulcanization aid was not regarded as safe, regardless of the presence of the fume hood, and therefore the material had to be changed. It was decided to use a conventional devulcanization aid, in combination with a different rubber feedstock. TESPT is a well-known silane used for silica-silane coupling reactions, and therefore is already established in the rubber industry. As studied by Ghosh et al., this silane has the possibility to prevent recombination of crosslinks during the devulcanization process. It has therefore been used in this study to devulcanize passenger car tire rubber, as well as the model compound based on the feedstock. [6] However, it has not been used in combination with butyl rubber yet, which is why the choice was made for this feedstock. Butyl rubber is present in inner liners and inner tubes of different types of tires and has not been as much researched in devulcanization studies. Therefore, this is a good candidate to design and optimize a devulcanization process for. Due to this change in research topic, there was limited time for the experimental work for the devulcanization of butyl rubber, which made the experimental work a bit more complex in terms of planning.

7 Experimental

For the experimental part, first the designed experiments are discussed. After that, the materials and methods used, as well as the devulcanization procedure itself are described. The experimental design of the study is further described and explained for this specific process.

7.1 Design of Experiments

The design of experiments method was used to make a randomized factorial design using Minitab Statistical Software. The study consists of three segments done in chronological order, as each part builds onto the previous results. The three segments of the study are as follows:

1. Screening

The screening includes a factorial design of 20 runs, including 2 blocks and 4 center points. This is aimed to get a broad idea of the effect of all parameters. The resulting tensile values will be the response values that the optimization in the next step is based on. This is because an experimental design is most effective if the response value should be minimized or maximized. While the tensile strength can be maximized, this is not the case for the Horikx-Verbruggen results, which is a data point that should reach a target area and consists of two response values. Therefore, the tensile results are used as response value that should be maximized.

2. Optimization

The optimization segment is a continuation of the screening, and the parameters are chosen based on the results from the screening. As the screening indicates optimal values at the limits of the chosen parameters, these parameters should be broadened. The goal is therefore to explore beyond the previous model, to determine whether this improves the previous results. In this case that means broadening the parameters beyond the previous model. In this optimization segment, not only mechanical testing is done, but also specific tests for devulcanization quality, namely the white rubber analysis and the crosslink density. However, these are less suitable to use as response values, as they should not necessarily be maximized or minimized. The optimization segment consists of 10 runs, of which 2 center points.

3. Final iterations

The final iterations are aimed to choose some last options that might improve the results. In this case, it was chosen to test a higher fill factor, to increase the shear forces. This can have a positive effect on the devulcanization efficiency, as indicated by the previous results. For instance, a higher speed is indicated as optimal, but since this cannot be increased more, instead the resulting shear forces can be increased in another way. Furthermore, a reference compound is produced, and while this reference is tested for its properties, part of it is devulcanized in order to revulcanize, to compare the effect of devulcanization on the feedstock material. This is to see the effect of aging and contamination on the devulcanization process, as well as to get a more accurate measure on how the material properties change purely due to the devulcanization and revulcanization process.

7.1.1 Factors

There are a number of factors identified to take into account when generating an experimental design plan. Some of the factors involved in the process are controllable, some are varied on purpose, and some are hard to control and can therefore generate error in the results.

Temperature is a controllable factor and can be set in the mixer and depending on the order of experiments can be assumed to stay as set in the Brabender Plastograph software, called WinMix. However, it is possible for a discrepancy between the material temperature and the mixer temperature. The main practical problem of the temperature control is cooling down the mixer, a time-consuming process as the mixer does not have an active cooling system. Therefore, it was decided to order the experiments so that within a mixing day, the temperature does not have to decrease between experiments. Furthermore, rotors can be programmed at a certain speed. This factor is accurately controlled and is one of the main factors determining the amount of shear forces in the material during devulcanization. While the rotor speed can be controlled precisely, the resulting shear forces depending on this speed can vary based on a number of other factors, including the viscosity of the material, which again results from the material properties, the temperature, fill factor, etc. An overview of identifiable factors and whether they are fixed, hard-to-control or varied on purpose is shown in Table 5.

Factors	**Unit**	**Fixed**	**Hard-to-control**	**Varied**
Temperature	°C			x
Residence time	Minutes			x
Rotor speed	rpm			x
Devulcanization aid amount	wt %			x
Oil content	wt %	x		
Fill factor	vol %	x		
Oxidation	-		x	
Milling time	Minutes	x		

Table 5: Identified factors in the process, divided into fixed, varied and hard-to-control factors

Minitab software can generate a full factorial experimental table that includes all factors and preferences. There are two blocks made to account for possible differences in two screening days, so the screening is split up in two segments. Furthermore, to account for curvature between the high and low levels of each factor, two center points for each block are used.

7.2 Screening

The screening aims to take a wide range in parameters, to give an indication what influence different parameters have on the process. The parameters that have been varied for the screening are temperature, rotor speed, residence time and concentration of DA. The oil concentration and fill factor have already been optimized during previous studies, for instance by Ghosh et al., using a similar devulcanization procedure in the same internal mixer. Based on this optimization, these values will be kept constant at respectively 5 wt% oil and 80 % fill factor. [6]

The 4 parameters are varied based on 'extreme' but realistic ranges of the values. For instance, the devulcanization aid concentration is based on Ghosh et al., who used 4 wt% and 6 wt% of TESPT. Based on this, the values are extended to 3 wt% for the low value and 7 wt% for the high value. The rotor speed has also been optimized in the same study, where the highest setting was the optimal setting, while for a different devulcanization aid and process it was optimized with 50 rpm as optimal value, in a study done by van Hoek et al. Since the feedstock material is significantly different from passenger car tire rubber, it was decided to use 50 rpm as low value as used by Van Hoek et al,. and 150 rpm as high value, as used by Ghosh et al. [28, 29] Furthermore, the chosen temperature values were initially chosen as 130 °C and 170 °C, while the residence times were 3 minutes and 9 minutes. Based on these values, two test batches were done to control the processibility of the material, and for these batches the lowest and highest values were used, as shown in Table 6. As a result, the material was not tested but visually judged on the perceived strength, and the ability to process into a sheet. If the material is overly viscous and sticky, this means that the polymer is significantly degraded, and that high random scission is likely. If the material is very brittle, crumbly, and difficult to form into a sheet, a low degree of devulcanization can be assumed.

Test batch	**Temperature**	**Speed**	**Residence time**	**DA%**
Test low	130 °C	50 rpm	3 minutes	3 %
Test high	170 °C	150 rpm	9 minutes	7 %

Table 6: Test batch values for 1 'low' batch and 1 'high' batch

As a result of these test batches, it was concluded that the residence time and temperature were chosen as too extreme values. The 'high' batch produced a devulcanizate that was highly sticky and was visually judged as highly degraded also. During the devulcanization process, the temperature reached above 200 °C during devulcanization, and since a too high temperature causes degradation, it was chosen to lower the high value to 160 °C. This would lower the resulting temperature during the devulcanization to approximately 185 °C to 190 °C, assuming the same relative increase in temperature. However, a longer residence time can also cause the temperature to rise further, and thus lowering both can prevent thermal degradation and chain scission to a certain extent. The residence time, however, was considered too short for the 'low' batch, as the material was crumbly and did not seem to have enough time to properly masticate. When taking the middle of all values, the center point is defined as 145 °C, 100 rpm, 5 % DA at 6 minutes.

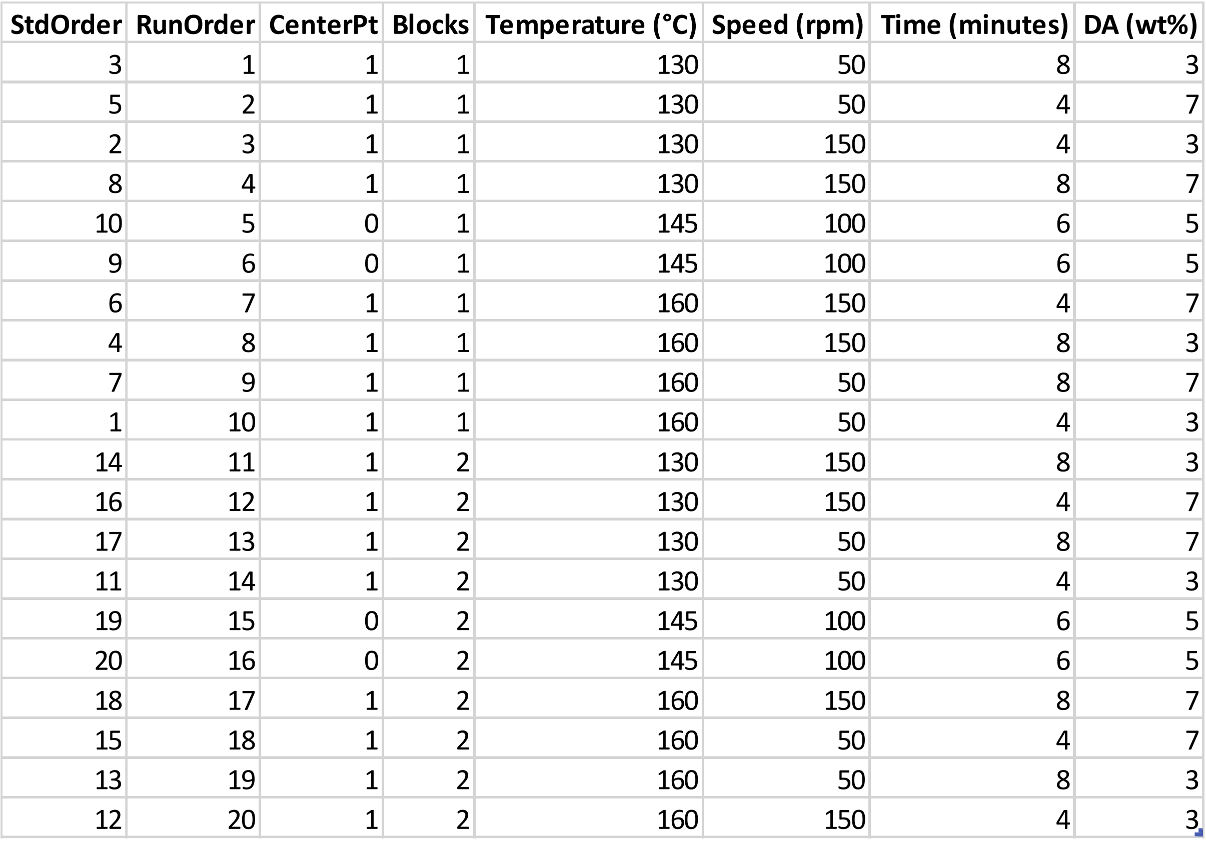
	Low	**High**
Temperature	130 °C	160 °C
Speed	50 rpm	150 rpm
Residence time	4 minutes	8 minutes
DA%	3 %	7 %

Table 7: Resulting low and high values for the experimental design

Using these 4 variable factors, a two-level factorial design is generated by Minitab. To account for external factors between days of devulcanization, the design is split into two blocks, that are confounded by the highest interaction in the model, ABCD. In order to identify curvature between the low and high levels, 4 center points are added, of which 2 in each block. This ensures that in both blocks the error between batches can be estimated, as well as accounting for the error between blocks. In the generated experimental design, a center point is indicated as ‘0' while the other runs are indicated as ‘1'. The blocks are indicated by the column, showing the runs that belong to block ‘1' and block ‘2'.

After generation and randomization by Minitab, the ordering of experiments is changed so the temperature only increases within one day. This is due to the lack of cooling in the internal mixer, making cooling down very time consuming. The resulting factorial design is shown in Table 8.

As the screening is quite extensive with 20 samples, only the tensile tests are used for optimization. In this case, the tensile strength is the response value that is maximized in the model. While tensile strength is not a complete measure of material quality, it gives a strong indication, especially concerning polymer chain scission.



StdOrder	RunOrder	CenterPt	Blocks	Temperature (°C)	Speed (rpm)	Time (minutes)	DA (wt%)
3	1	1	1	130	50	8	3
5	2	1	1	130	50	4	7
2	3	1	1	130	150	4	3
8	4	1	1	130	150	8	7
10	5	0	1	145	100	6	5
9	6	0	1	145	100	6	5
6	7	1	1	160	150	4	7
4	8	1	1	160	150	8	3
7	9	1	1	160	50	8	7
1	10	1	1	160	50	4	3
14	11	1	2	130	150	8	3
16	12	1	2	130	150	4	7
17	13	1	2	130	50	8	7
11	14	1	2	130	50	4	3
19	15	0	2	145	100	6	5
20	16	0	2	145	100	6	5
18	17	1	2	160	150	8	7
15	18	1	2	160	50	4	7
13	19	1	2	160	50	8	3
12	20	1	2	160	150	4	3

Table 8: Factorial design of screening

7.3 Optimization

The optimization is based on the results of the screening. It focuses on the optimal screening parameters in order to further improve the quality of the devulcanizate. Based on the highest tensile strength obtained, the optimal conditions are determined from the screening. It was determined from these results that the optimal values might lie beyond the chosen parameters of the screening as the best conditions are at the border values. For this model, a high amount of devulcanization aid had a strong negative effect, with the optimal sample using 3 wt%. Therefore, for the optimization, the values of 1 and 3 wt% DA were chosen in order to explore beyond the model. Furthermore, rotor speed had a positive effect on the tensile strength, but because this was in the model at the highest possible value of 150 rpm, it was chosen to keep this value constant and therefore not further optimize it.

Generally, the effects show that a lower amount of devulcanization aid, a higher temperature, and a higher speed with lower residence time has a positive effect on the tensile strength, on which the optimization design was based on. The low and high temperature values were chosen to be increased to 160 °C and 180 °C. And finally, the residence time was slightly decreased to 2 minutes and 6 minutes as low and high value. The resulting factorial design is shown in Table 9.

StdOrder	RunOrder	CenterPt	Blocks	Temperature (°C)	Time (minutes)	DA (wt%)
3	1	1	1	160	6	1
1	2	1	1	160	2	1
7	3	1	1	160	6	3
5	4	1	1	160	2	3
9	5	0	1	170	4	2
9	6	0	1	170	4	2
2	7	1	1	180	2	1
8	8	1	1	180	6	3
6	9	1	1	180	2	3
4	10	1	1	180	6	1

Table 9: Factorial design of the optimization stage

7.4 Finalization

For the finalization, a number of last iterations were produced and tested. These samples are further explained in Chapter 8, as these samples are based on the results from the screening and optimization. The same devulcanization procedure is used as described earlier. A reference compound is made based on an inner tube formulation as given by Arlanxeo. [40] This reference compound is tested as well as devulcanized in order to compare the differences. The formulation and mixing stages are described in Table 10.

First stage	**phr**
Regular butyl rubber (IIR)	100
Stearic acid	1
Paraffinic oil	25
Carbon black N660	70
Zinc oxide	3
Second stage	**phr**
Masterbatch	199
Sulphur	1.25
CBS	1.75

Table 10: Formulation of the reference compound [40]

7.5 Materials

Function	Type	Material	Grade	Supplier
Devulcanization	Vulcanized compound	Truck tire inner tubes (post-consumer)		Rubber Resources
	Silane	Si 69	Technical grade	Evonik
	Processing oil	TDAE-oil	Technical grade	
Reference	Polymer	Regular Butyl Rubber	Technical grade	
	Processing oil	Paraffin oil	Technical grade	
	Filler	Carbon black N660	Technical grade	
White rubber analysis	Polymer	Butadiene rubber Buna CB24	Technical grade	Lanxess
	Filler	Titanium dioxide	Technical grade	
Curing package	Activator	Zinc oxide	Technical grade	
	Activator	Stearic acid	Technical grade	
	Accelerator	MBTS	Technical grade	
	Accelerator	CBS	Technical grade	
	Vulcanizing agent	Sulfur	Technical grade	
Cleaning/testing	Polymer	Natural rubber	Cleaning grade	
	Abrasive material	Silica	Technical grade	
	Cleaning product	Bitumen cleaner	Technical grade	
	Solvent	Acetone	Technical grade	
	Solvent	Iso-propanol	Technical grade	
	Solvent	Toluene	Technical grade	
	Solvent	Tetrahydrofuran	Technical grade	

Table 11: Materials and suppliers

7.6 Methods

Machinery	Function
Wickert press	Molding
Brabender Plastograph EC	Devulcanization/mixing
Brabender Internal mixer 350 S	Mixing
Swabenthan two-roll mill	Milling
Universal testing machine Zwick-Roell	Tensile testing
Montech rebound tester	Rebound testing
Soxtherm automatic extraction	Extraction
Hardness durometer	Hardness testing
RPA TA instruments	Rheocurve test
RPA Alpha Technologies	Mooney viscosity
SEM EDX	Halogenation test
Digital microscope Keyence VHX 5000	White rubber analysis
Hot air oven	Drying after extraction
Vacuum oven	Drying after swelling
Fritsch grinder	Grinding

Table 12: Machines and corresponding functions

7.7 Sample preparation

The supplied feedstock material was received as inner tube flakes from truck tires of approximately 5-7 cm in diameter. These had to be reduced in size, using a Fritsch Grinder with a 2 mm mesh. The rubber was submersed in liquid nitrogen in a beaker for 5 minutes, after which the remaining liquid nitrogen was disposed of, and the material was fed into the grinder. It should be noted that the material should be processed in small batches to prevent the grinder from stopping due to an overload of material. If this happens, the material heats up and is clamped between the metal parts.

The resulting granulate is then kept at room temperature without coverage for an hour, in order to let moisture evaporate. After that, the material is weighed and mixed with TDAE oil for swelling. 5 wt% of TDAE oil was used for all experiments, therefore the material was swollen in one batch. Mixing was done manually. Swelling was done for one day at room temperature, before the devulcanization aid was added.

Not all samples contained devulcanization aid, and the weight percentage varied. For this reason, smaller batches were prepared for each DA concentration. For one batch of devulcanizate in a 75 cc mixer volume, 66 grams of swollen material was needed, to fulfill the 80 % fill factor, based on a measured density of 1.1 g/cm^3. This amount includes the weight of the DA and oil, so the final weighing was done after the swelling of both oil and DA.

7.8 Devulcanization procedure

The devulcanization reaction takes place in a Brabender Measuring Mixer 50 EHT, using cam mixer blades. These are high shear rotors that also provide a larger volume of 75 cm^3. Furthermore, a loading chute with weight is used. This loading chute is mounted on the opening of the mixer, through which the material can be added. After adding the material, the ram is pushed in, and the weight put on top to secure it. In order to minimize oxygen flow to the material, the edges between the loading chute and mixer are closed with strips of paraffin wax, sealing the gaps.

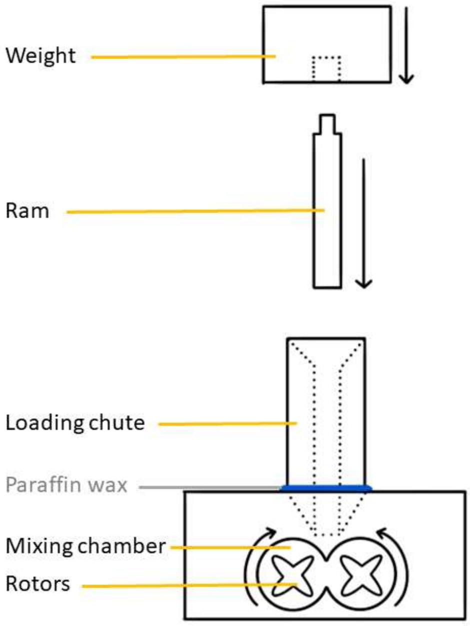


Figure 19: Internal mixer set-up for devulcanization

The mixer is heated up to the desired temperature, and when ready the program is started. After the automatic calibration of the mixer ensuring an accurate torque, the material can be added. As soon as a significant torque is measured by the machine, the torque and temperature curves are shown. The material should not be added too quickly, to prevent it from clogging the loading chute. A brass scraper is used to push the material in. The residence time is counted from the first peak in torque, an indicator that all the material has been added and the rubber starts softening. The mixing fingerprint with the indicated torque peak is shown in Figure 20. After the counted residence time, the mixer is stopped, the material is put into the collection drawer and cooled in ambient air until approximately 60-80 °C.

When sufficiently cooled down, the material will be processed through a two roll mill with a 1.5 mm nip gap. After running it through for 2-3 times, the nip gap is increased to 3 mm and the total milling time, including the initial step, will be 2 to 3 minutes, when it has formed a homogenous sheet. After this, the material is stored in a closed zip lock bag for one day before adding a curing package.

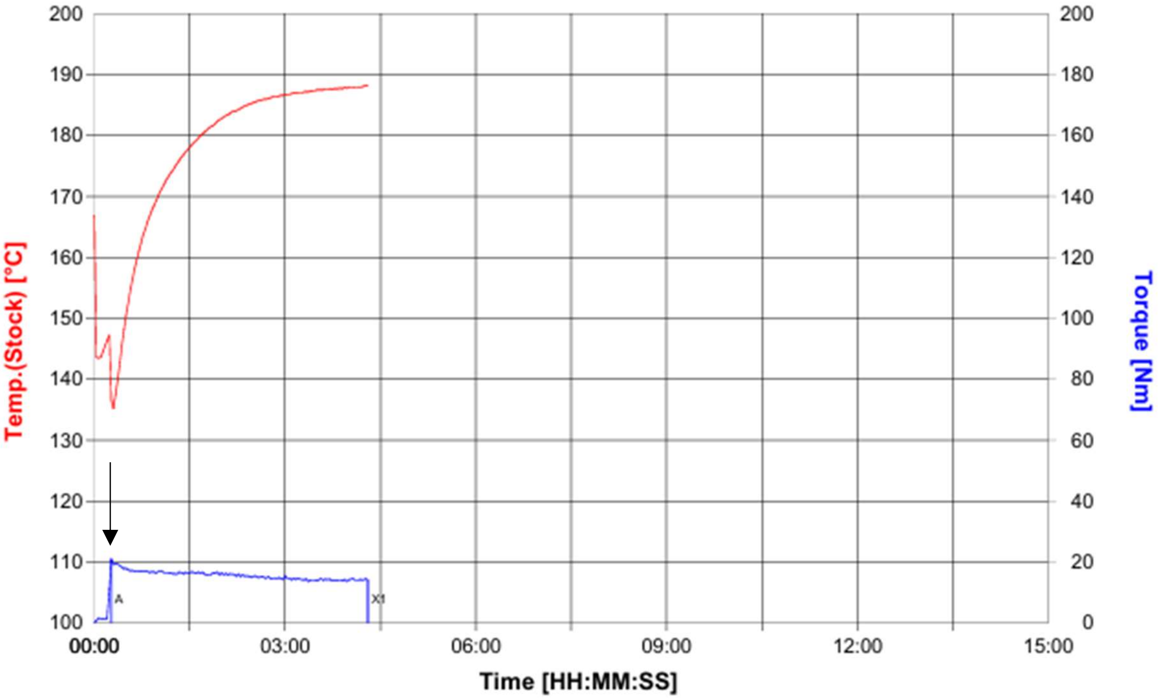


Figure 20: Devulcanization process curve

7.9 Compounding

To make revulcanization and testing possible, a curing package has to be added. For this procedure a standard sulfur curing package is used for all compounds, as shown in Table 13. The mixing procedure for the addition of the curing package is shown in Table 14. These are mixed with the devulcanizate in the Brabender Plastograph EC using roller type blades.

Material	**phr**
Devulcanizate	100
Zinc oxide	4
Stearic acid	2
Sulfur	2
CBS	1

Table 13: Addition of curing agents to the devulcanized compound – values in phr (parts per hundred rubber)

Time	**Step**
00:00	Add devulcanizate
00:10	Close mixer
00:30	Add zinc oxide + stearic acid
1:00	Close mixer
2:00	Add sulfur + CBS
2:30	Close mixer
5:00	Stop mixer and remove material

Table 14: Mixing procedure for addition of curing package to the devulcanizate

7.10 Vulcanization

All vulcanization was done using a Wickert Press at 160 °C. The curing times were evaluated using a TA instruments rheometer measuring for 60 minutes. The cure curves obtained had a marching modulus that significantly varied in shape between samples. The marching behavior was generally more pronounced in samples with a higher amount of devulcanization aid, such as for the 130 °C/50 rpm/4 min/7 wt% sample shown in Figure 21. One method that was attempted is using the tangential method for curves with a marching modulus as used by Mihara et al. [43] Although this method can give a reasonable cure time for regular silica compounds, the curing curves of the devulcanized material did not all have linear parts at the start, and the resulting cure times were therefore extremely different and too subjectively obtained. Therefore, it was chosen to get an estimate of one cure time using this method and using this cure time for all samples. This cure time was 27 minutes for the devulcanized butyl rubber, and 18 minutes for the reference compound. Only for the rebound molding, 5 minutes was added due to the thickness of the sample.

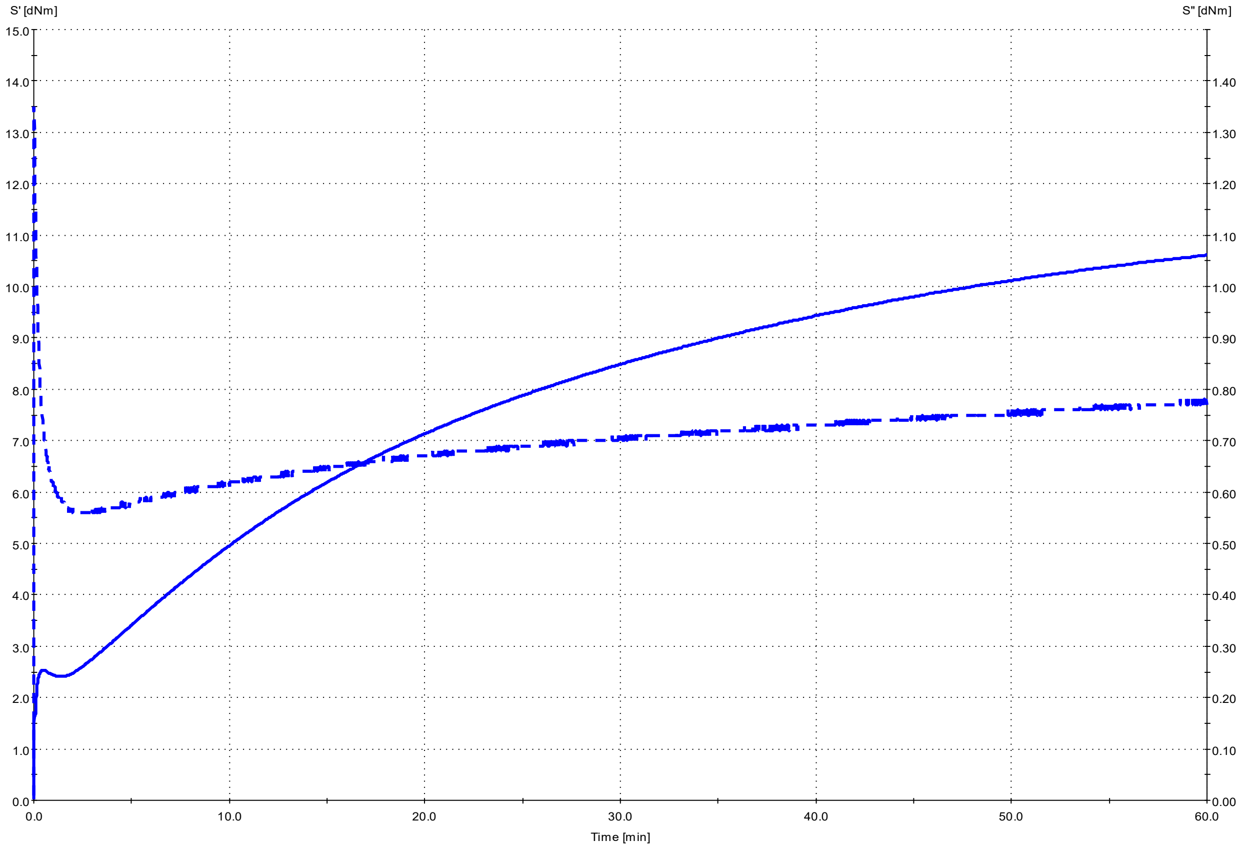


Figure 21: Cure curve from one of the screening batches, showing marching behavior

During the screening, there were some blisters formed in the material when removing it from the mold. The most extreme sample exhibiting this behavior is shown in Figure 22. This can be due to volatiles in the sample, possibly resulting from the remaining chemicals and/or contamination within the feedstock. The forming of blisters was reduced when molding evenly thick sheets the size of the mold. These blisters are different from air bubbles, the latter which capture air into a closed pocket, while the blisters formed visible outlines after removing it from the mold.

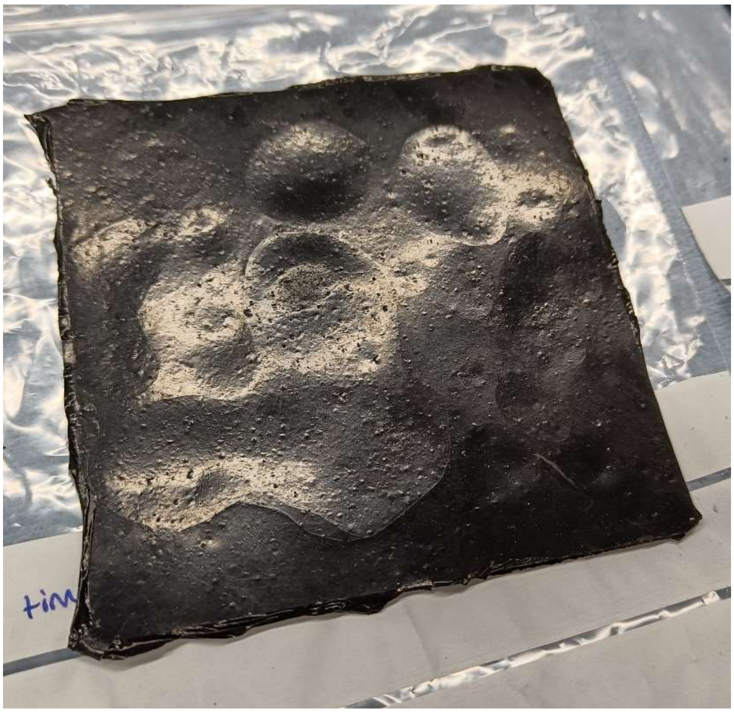


Figure 22: Sample with blisters after removal from the mold

Furthermore, the material is relatively prone to forming air bubbles when molded incorrectly. Most effective is preventing the build up of layers when filling the mold, but instead preparing the rubber in the shape of the mold. Air bubbles did not form a problem in the devulcanized compounds, but only in the reference compound. This is likely due to the homogeneity of this compound causing it to be much less gas permeable. If the compound contains particles, these can be textile, metal, or non-devulcanized particles. then the interface between matrix material and particle is a weak spot in terms of gas permeability.

7.11 Testing

The screening samples are only mechanically tested to determine overall quality of the devulcanizate. Tensile, rebound and hardness testing is done. The optimization and final batches are tested more extensively, in order to determine exactly the degree of devulcanization, by measures such as network breakdown, soluble content, and the number of still vulcanized particles in the material. These tests will be described extensively in the following.

7.11.1 Mechanical testing

Tensile testing is a standard test in material science and is done using the Zwick-Roell universal testing machine. The standard set-up for tensile testing is used, including extensometers for the measuring of elongation. When calibrated correctly, this can accurately measure tensile strength and elongation at break, the two main properties used in this test. This test is done according to the standard ISO-37:2017 for the determination of tensile stress-strain properties for elastomers. [44] Rebound is a test measuring the energy dissipation on single impact. It is performed by the swinging of a pendulum to a rubber sample, and measuring how far it bounces back. The standard used for this method is ASTM D7121-05. [45] Finally, a hardness test is performed, according to ASTM D2270 with a type A indentor. Hardness in elastomers is correlated with the elastic modulus and can therefore be used as an indicator of this. Furthermore, if the hardness values of samples are far apart, it is no longer accurate to compare other mechanical values for these materials.

7.11.2 White rubber analysis

The white rubber analysis aims to show the still vulcanized particles of the devulcanized material by blending it with a white compound for contrast. The ratio between white rubber and devulcanizate is 10:1 in weight. The white compound is produced using butadiene rubber (BR) with titanium dioxide as filler. Titanium dioxide in large quantities ensures the rubber to be as white as possible. Furthermore, processing oil is avoided due to staining properties, and a non-staining accelerator is used. After compounding, the material is blended with the devulcanizate on a two-roll mill, until homogenously mixed. The samples are cured in a circular mold of 3 cm in diameter and 7 mm in thickness. After curing, the top layer of the sample has to be removed to reveal the cross-section with vulcanized particles visible. The sample is submersed in liquid nitrogen for 10-15 minutes and is then sanded with 120 grit sandpaper. Cooling with liquid nitrogen of the samples prevents the rubber from deforming, or particles being pulled out by the sandpaper.

The immediate result shows differences in samples in the number of visible particles, the respective area that is covered by particles, and the color of the sample. If the rubber is more degraded or devulcanized, the sample has a darker color and there are less and/or smaller visible particles. The samples are quantitatively analyzed using a

Keyence 5000 digital microscope, that is able to capture a high-resolution image of the surface, and using the embedded software, to measure the number of visible particles and their size. These values are a measure to determine how well the sample is devulcanized, as higher devulcanization efficiency correlates with less and/or smaller visible particles. [6]

7.11.3 Crosslink density

To measure the crosslink density, the material is extracted first to remove polar and non-polar components. Because the material of the feedstock contains curatives, remaining chemicals and other contaminations, these are for the most part removed before performing the equilibrium swelling test, for a better comparison of the reduction in crosslink density. This reduction is plotted as ‘network breakdown'.

First, the material is extracted with acetone, in a Soxtherm automatic extractor. The program parameters are summarized in Table 15. For the devulcanized feedstock, one has to deal with larger errors due to the inconsistency of the samples than for regular compounds, therefore a larger sample is taken of approximately 5 g. This sample is packaged in filter paper and a 0.035 wire mesh filter. To avoid leakage and identify the samples, the sides are stapled. It is weighed accurately after packing. Boiling stones are added at the bottom of the extraction unit and the program is ran for approximately 4 hours, after which the solvent has boiled off and the extracted mixture is at the bottom. The sample is then dried for 16 h at 70 °C in a hot-air oven to evaporate the solvent. After this, the sample is weighed again and then extracted using the same procedure, but with tetrahydrofuran. The only change in program parameters is the reduction interval that is changed to 5 minutes, according to the machine manual. Acetone is extracting the polar components in the rubber, while THF is extracting for the non-polar components. After this extraction, the sample is again dried for 16 hours and weighed. The setup during extraction is shown in Figure 23.

Parameter	**Acetone**	**Tetrahydrofuran**
T-Classification	200 °C	200 °C
Extraction temperature	170 °C	170 °C
Reduction Interval	4.5 min	5 min
Reduction pulse	2 s	2 s
Hot extraction	1 hour	1 hour
Evaporation A	5 x interval	5 x interval
Extraction time	2 hours	2 hours
Evaporation B	3 x interval	3 x interval
Evaporation C	10 minutes	10 minutes
Program length	3 hours 36 minutes	3 hours 46 minutes

Table 15: Soxtherm extraction parameters for acetone and THF

Figure 23: Extraction running in the Soxtherm extraction unit

The crosslink density is measured using the ASTM standard D6814-02, for equilibrium volume swelling using toluene as solvent. The sample is weighed, then submersed in toluene for 72 hours after which the toluene has swelled into the rubber, depending on the crosslink density and structure. Because the material has already been extracted twice, it is not necessary to replace the solvent. The sample is then taken out and patted dry with paper to remove excess solvent and weighed in a closed dish to avoid further evaporation while weighing. After this, the sample is dried until the weight has stabilized. The Flory-Rehner equation is used to calculate the crosslink density, using the weight of the dry sample, the weight of the swollen sample, the respective densities, the molecular volume of the toluene and the polymer-solvent interaction parameter for polyisobutylene and toluene.

First, the volume fraction of polymer in a swollen network in equilibrium with pure solvent is calculated as:

$$V_r = \frac{Weight\ of\ dry\ rubber\ /\ density\ of\ dry\ rubber}{\frac{Weight\ of\ dry\ rubber}{Density\ of\ dry\ rubber} + \frac{Weight\ of\ solvent\ absorbed\ by\ sample}{Density\ of\ solvent}}$$

Then the effective number of chains in a real network per unit volume is calculated:

$$\nu_e = \frac{-[\ln(1 - V_r) + V_r + \chi_1 {V_r}^2]}{[\frac{V_1 \left(V_r^{1/3} - V_r\right)}{2}]}$$

Where:

$$\chi_1 = polymer - solvent\ interaction\ parameter$$

$$V_1 = molecular\ volume\ of\ solvent$$

To calculate the percentage of network breakdown or devulcanization:

$$Network\ breakdown\ (\%) = \left[1 - \left(\frac{Crosslink\ density\ of\ devulcanized\ rubber}{Crosslink\ density\ of\ control\ crumb\ rubber}\right)\right] \times 100$$

8 Results & Discussion

The results of the different stages of this study are summarized, evaluated and explained. Of each stage, also shown below, the results are shown separately. Furthermore, a statistical analysis of the factorial designs is done in Minitab. The analyses in Minitab can only be done with numerical response values that should be maximized or minimized, in this case the tensile strength. The different devulcanized batches are named by their parameters as follows: temperature/speed/time/devulcanization aid, with the corresponding units °C, rpm, minutes and wt% (weight percentage). The error bars in all graphs represent the 95 % confidence interval.

8.1 Screening

For the screening, the factorial design is again shown in Table 16. This stage of screening will focus on mechanical properties. In the next stage, additional properties are tested. Therefore, the results consist of tensile values, rebound resilience and hardness.

Sample	RunOrder	CenterPt	Blocks	Temperature (°C)	Speed (rpm)	Time (min)	DA (wt%)
130/50/8/3	1	1	1	130	50	8	3
130/50/4/7	2	1	1	130	50	4	7
130/150/4/3	3	1	1	130	150	4	3
130/150/8/7	4	1	1	130	150	8	7
145/100/6/5	5	0	1	145	100	6	5
145/100/6/5	6	0	1	145	100	6	5
160/150/4/7	7	1	1	160	150	4	7
160/150/8/3	8	1	1	160	150	8	3
160/50/8/7	9	1	1	160	50	8	7
160/50/4/3	10	1	1	160	50	4	3
130/150/4/7	11	1	2	130	150	8	3
130/150/4/7	12	1	2	130	150	4	7
130/50/8/7	13	1	2	130	50	8	7
130/50/4/3	14	1	2	130	50	4	3
145/100/6/5	15	0	2	145	100	6	5
145/100/6/5	16	0	2	145	100	6	5
160/150/8/7	17	1	2	160	150	8	7
160/50/4/7	18	1	2	160	50	4	7
160/50/8/3	19	1	2	160	50	8	3
160/150/4/3	20	1	2	160	150	4	3

Table 16: Factorial design of the screening

8.1.1 Mechanical testing

In the testing of stress-strain behaviour, the two most important properties are the tensile strength, and elongation at break. Especially tensile strength is a strong indication of the quality of a material. Elongation at break serves as a related parameter that indicates the elasticity of the material. If the tensile strength is increased, but the elongation at break decreased, this can mean the tensile strength is only indicating a harder, more reinforced material, which is lacking in elasticity. However, this is often the case in reinforced, higher tensile strength materials. Usually this is a trade-off between tensile strength and elasticity. If the tensile value is lower and the elongation at break is higher, this can indicate a lower quality material with more random scission.

The tensile strength and elongation at break values of all screening runs are shown in Figure 24. The center point runs are averaged in order to simplify the graph and are indicated in the factorial design as ‘0' for ‘CenterPt'. In the graph this is indicated as ‘CP'. These will be analyzed using statistical software and then discussed further.

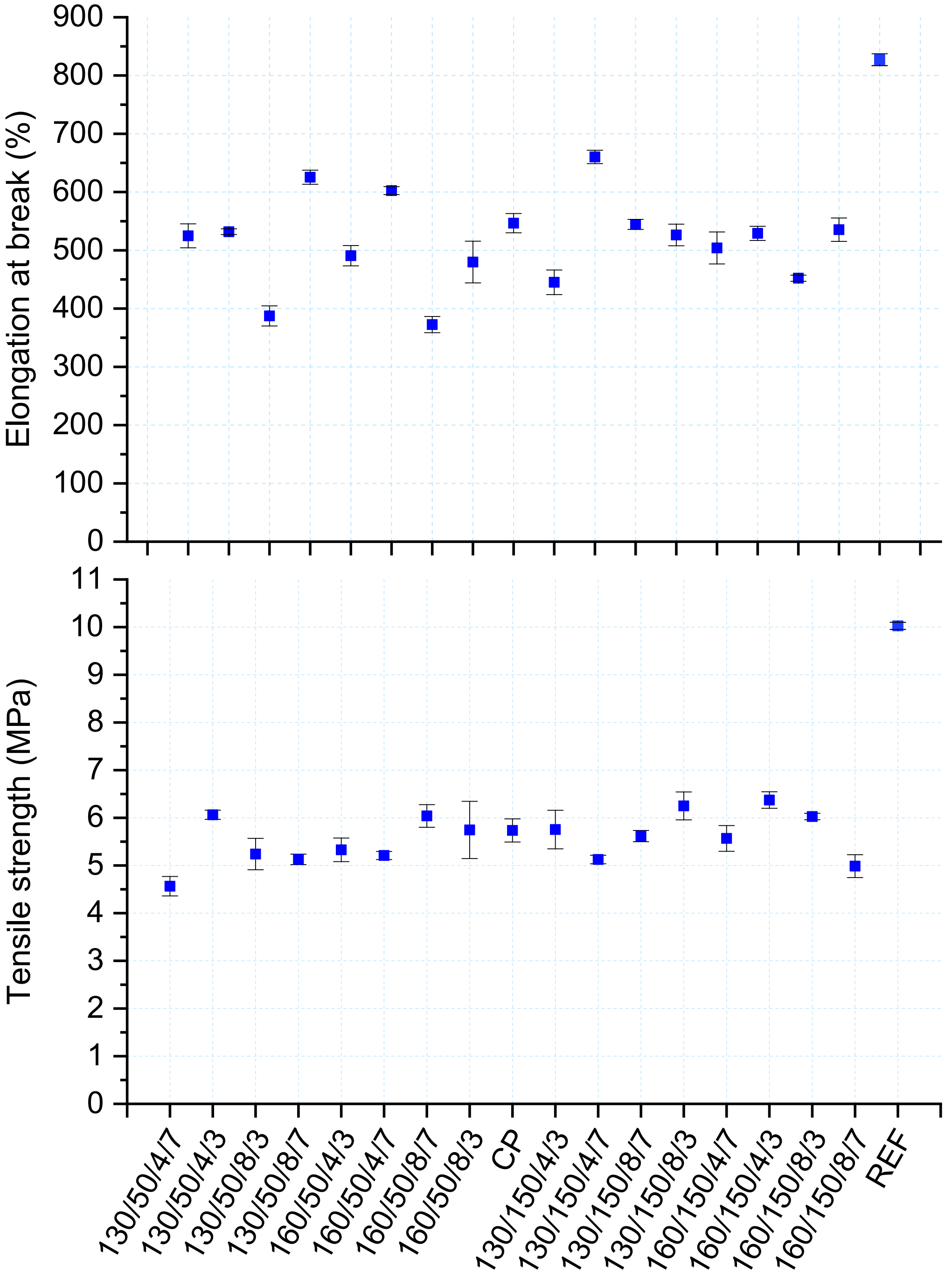


Figure 24: Tensile values of the screening – CP is the center point 145/100/6/5

Furthermore, hardness was tested, as this can show whether these values are within the same range throughout all samples, showing whether they are comparable. Hardness can also be an indication of the modulus of a material. Sample 160/150/8/7, with the most extreme conditions, has the lowest hardness. This can be due to the high amount of TESPT combined with higher energy input, causing more degradation of the polymer and softening it as a result. The TESPT in this case might oligomerize after all the broken crosslinks are bonded to the silane, and possibly form further crosslinks. Similarly, this sample has a high rebound resilience. Rebound resilience and hardness usually show opposing results. Furthermore, the sample with the highest tensile strength has a hardness of 52 Shore A and a rebound resilience of 18%. Based on this sample, it can be concluded that lower quality material can have a too high or too low hardness, as chain softening and chain hardening are the two main types of degradation. Chain softening results from chain scission, which softens the polymer as a result of polymer chains breaking. This causes a deterioration in properties as well as smearing of the rubber. Opposite to this is chain hardening, a result of free radicals produced by heat, oxygen and light. These combine and form new crosslinks, hardening the rubber and making it brittle.

Since most of the hardness data points are below the sample with optimal conditions in terms of tensile strength, it is assumed that mainly chain softening occurs as degradation. This is expected because of the random scission associated with a higher energy input. However, it is also possible that some further crosslinking still occurs, either in the form of silane oligomerization bridging the polymer chains, or at lower DA concentrations if there is not enough silane to prevent recombination.

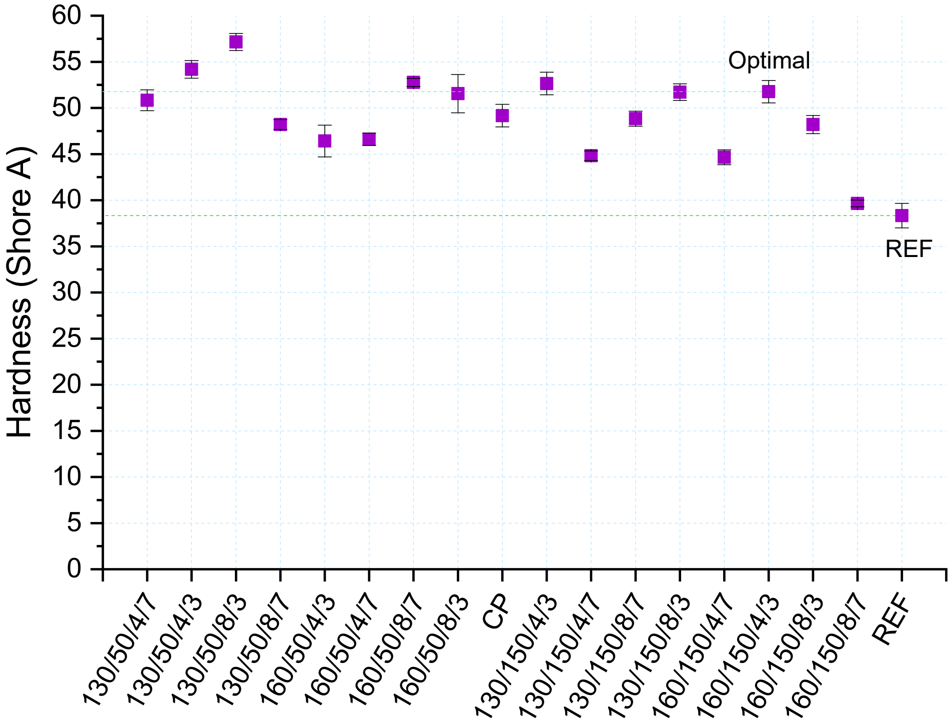


Figure 25: Hardness results of the screening

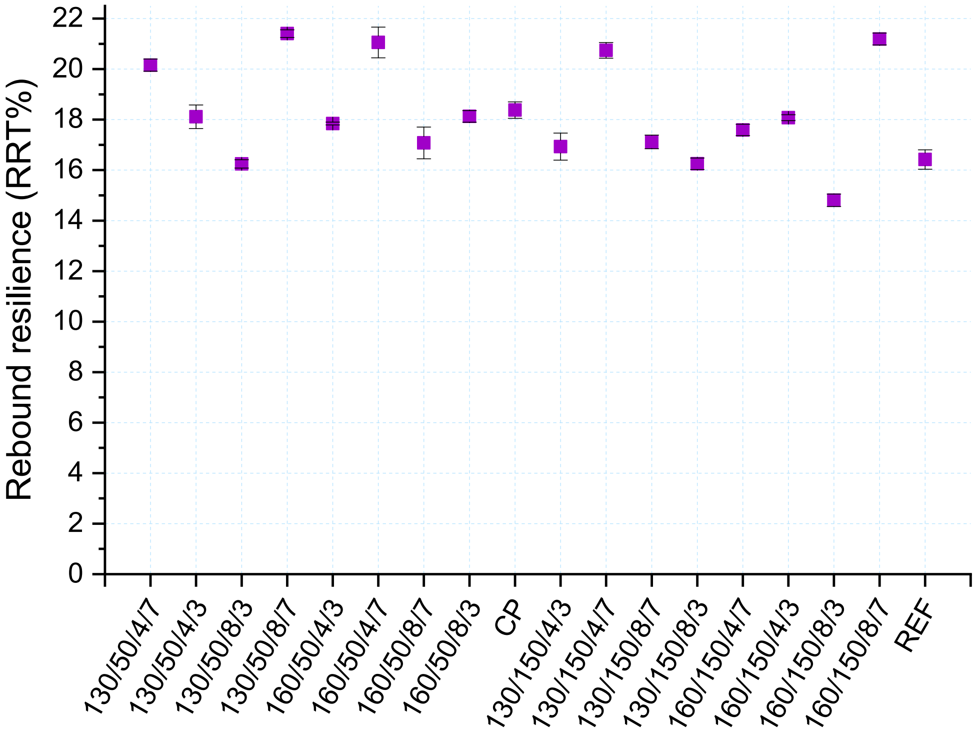


Figure 26: Rebound resilience of the screening

In Figure 24 the tensile strength and elongation at break values from the screening are shown. The last sample in the screening has the highest tensile strength of 6.4 MPa, with an elongation at break of 520 %. This sample is therefore considered the optimal one within the screening, with the following parameters:

Parameter	**Value**
Temperature	160 °C
Speed	150 rpm
Residence time	4 minutes
DA concentration	3 wt%

Table 17: Optimal parameters resulting from the screening

On the other hand, if the tensile value is lower and the elongation at break higher, this indicates more degradation in the material, as the polymer chains break and soften the material. However, in the first two samples in a different effect can be seen. Both samples are devulcanized at 130 °C, 50 rpm and for 4 minutes. The difference is the amount of DA, which varies between 3 wt% and 7 wt%. A higher amount of DA clearly lowered the tensile strength, while the elongation at break remains constant. One possible explanation for this is, that TESPT can react according to several mechanisms. First, the crosslinks and the silane are both broken as a result of energy input and the TESPT attacking the crosslink. Then, the TESPT segments and cleaved crosslinks both contain radicals causing them to react with eachother. However, an excess of TESPT might also react according to different mechanisms. As described by Hayichelaeh et al., there are two silanization reactions possible. The primary reaction takes place as direct condensation of the silane on the silica surface. The secondary reaction is the hydrolysis of the alkoxy groups in the silane, which needs the presence of water, and is shown in Figure 27. As a result, these groups become reactive and the silane particles oligomerize. This reaction, unlike the condensation, can also happens when silica is not present, and is thus a possibility in the devulcanization mechanism. [46]

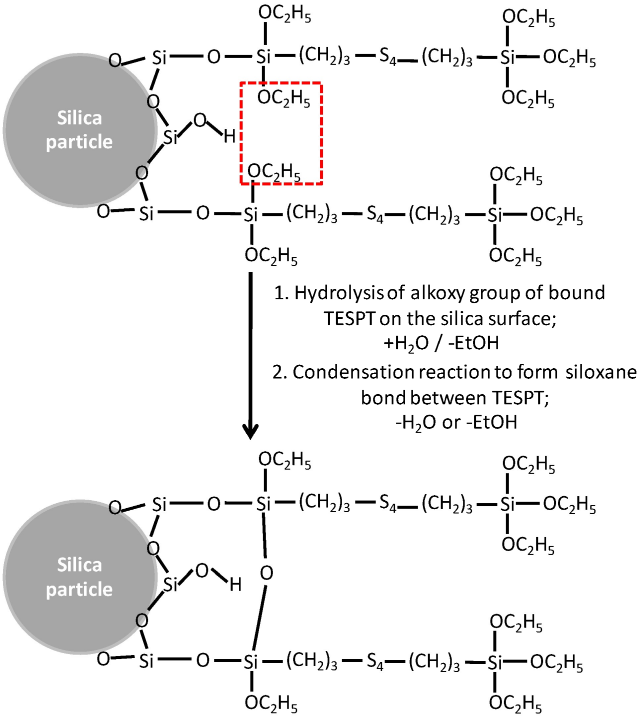


Figure 27: Secondary silanization reaction – hydrolysis and oligomerization of TESPT

Another reaction that might happen instead or simultaneously, is that the TESPT is attacking double bonds, as shown in Figure 28. In other types of rubber this might not be as problematic, but butyl rubber only contains a very low amount of double bonds. Attacking of double bonds could lower this even more, making it very difficult to cure the compound. Finally, if these two reactions are combined, this can mean that the silane is first attacking a double bond, and then oligomerizes further, creating a large side group or even a silane crosslink.

Furthermore, the curing system that was added was later determined to be quite high for a material such as butyl rubber, due to this low double bond density. If even more double bonds are removed, a large part of this curing system remains unused while staying in the compound. [46]

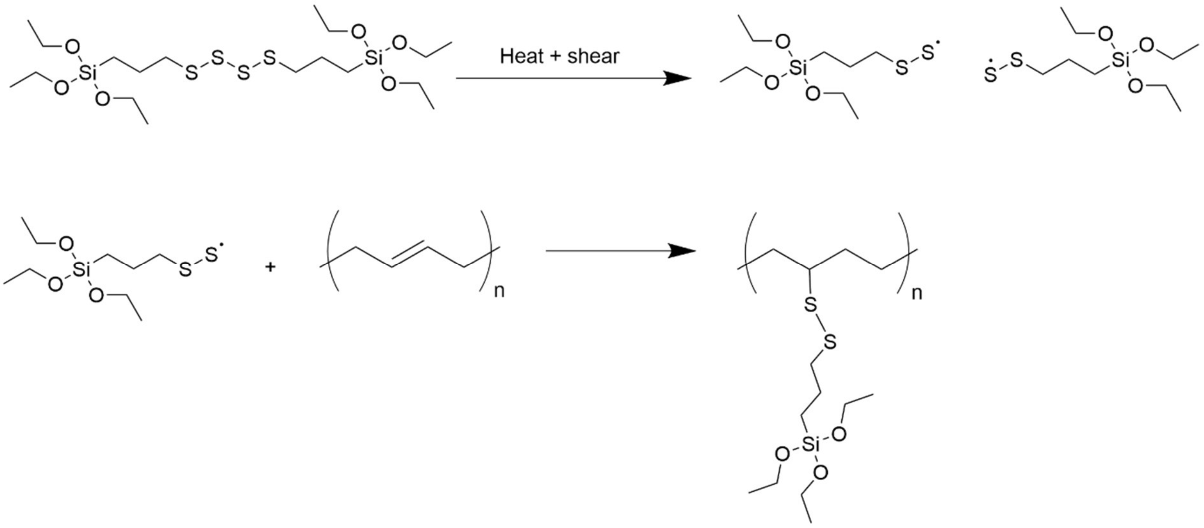


Figure 28: TESPT attacking double bonds in a polymer chain

Interestingly, the compounds showed a migration of powder from the rubber, already after a week of storage. This migration might now be explained by an excess of curatives, as mentioned before. If TESPT attacks the double bonds, this might explain an excess of curatives that can migrate from the rubber, also explaining why this migration was more prominent in samples with a high amount of TESPT.

8.1.2 Minitab statistical analysis - Screening

In Minitab, the design of experiments in combination with the resulting response values are analyzed and the effects resulting of each parameter are calculated. A regression model is generated that under the right conditions can predict the response value based on the given parameters. To determine whether this model can be seen as predictive and accurate, the R-squared value is used as an indication of how well the values fit to the model. A higher R^2 value indicated a better fit, while 100 % means that the model is a perfect fit. In the screening the R^2 is 97.67 %, indicating a good fit.

Furthermore, the center points in the model are an indicator that predicts the variance of the response values. In the final graphs however, the center points are averaged to one value, to simplify the visual. This is because the replications of the center point are only for statistical purposes. The center points are made based on the same parameters and therefore the difference between these can be used as an indicator for the error in the model. If the center points vary more, the pure error value in the model is increased.

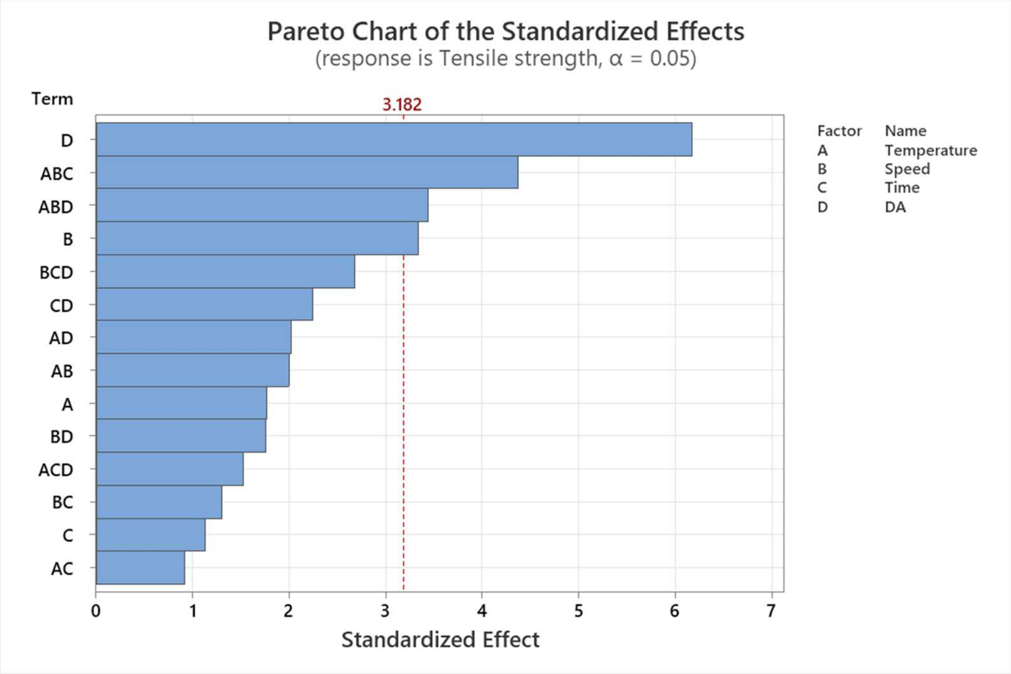
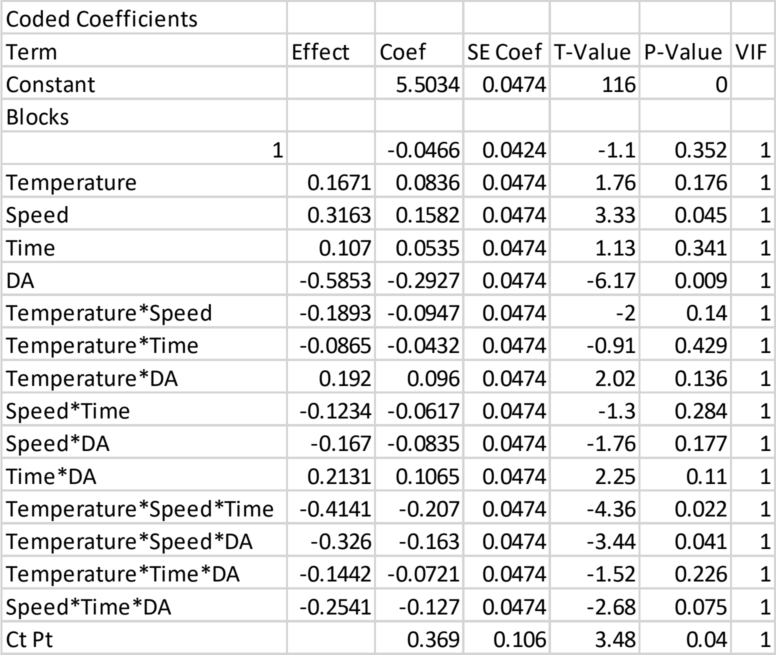


Figure 29: Minitab pareto chart of the screening



Coded Coefficients						
Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant		5.5034	0.0474	116	0	
Blocks						
1		-0.0466	0.0424	-1.1	0.352	1
Temperature	0.1671	0.0836	0.0474	1.76	0.176	1
Speed	0.3163	0.1582	0.0474	3.33	0.045	1
Time	0.107	0.0535	0.0474	1.13	0.341	1
DA	-0.5853	-0.2927	0.0474	-6.17	0.009	1
Temperature*Speed	-0.1893	-0.0947	0.0474	-2	0.14	1
Temperature*Time	-0.0865	-0.0432	0.0474	-0.91	0.429	1
Temperature*DA	0.192	0.096	0.0474	2.02	0.136	1
Speed*Time	-0.1234	-0.0617	0.0474	-1.3	0.284	1
Speed*DA	-0.167	-0.0835	0.0474	-1.76	0.177	1
Time*DA	0.2131	0.1065	0.0474	2.25	0.11	1
Temperature*Speed*Time	-0.4141	-0.207	0.0474	-4.36	0.022	1
Temperature*Speed*DA	-0.326	-0.163	0.0474	-3.44	0.041	1
Temperature*Time*DA	-0.1442	-0.0721	0.0474	-1.52	0.226	1
Speed*Time*DA	-0.2541	-0.127	0.0474	-2.68	0.075	1
Ct Pt		0.369	0.106	3.48	0.04	1

Table 18: Minitab effect analysis of the screening

In Figure 29, the Pareto chart showing the significance of effects is shown as generated by Minitab. Effects larger than the reference line as indicated in red, are considered significant within a 95 % confidence interval.

As shown, in this screening there are 4 significant effects:

- D: DA%
- ABC: Temperature*Speed*Time
- ABD: Temperature*Speed*DA
- B: Speed

As mentioned in Chapter 5, the P-value is the direct metric used to establish significance of an effect, and can be seen in the effect table as shown in Table 18. In the second column, the effects are quantified and also show whether the effect is positive or negative for the response value. As can be seen, within the boundaries of this model there are a lot of negative effects. For instance, an increasing DA concentration constitutes a negative effect on the tensile strength. Furthermore, time, speed and temperature separately have a positive effect on the tensile strength, although it has to be mentioned that the effect of temperature and time are both not statistically significant. When these effects are combined, the effect becomes negative. This can be an indication that an increase in temperature combined with an increase in the shear forces can cause more degradation in the material, reducing the tensile strength. When analyzing a DOE, there is not one standard method, but instead this analysis depends largely on the type of design and conditions. Reducing the model can help identify other significant effects by removing insignificant effects. Furthermore, the significance of curvature in the model can be identified using the center points.

Finally, contour plots are generated to compare parameters and their influence on the tensile strength, shown in Figure 30. In each plot, two parameters are varied while the other two stay set at the ‘hold values'. The colored regions indicate the tensile strength. In these contour plots it is quickly visible which parameters should be changed in order to optimize the tensile strength. For instance, in speed*temperature the optimal values are at a higher speed and higher temperature. The strongest effects are visible in the contour plots including the devulcanization aid concentration, where a lower DA combined with a higher temperature, lower DA with a higher speed, and a lower DA with lower residence time all give positive effects on the tensile strength, within the boundaries of the model. Time shows a less extreme effect, but still shows that a lower time combined with higher speed could be more optimal. This could be due to the trade-off in energy input. Combining a longer residence time with a higher temperature causes the temperature to also increase to a higher level during devulcanization. This causes thermal degradation that damages the polymer chain.

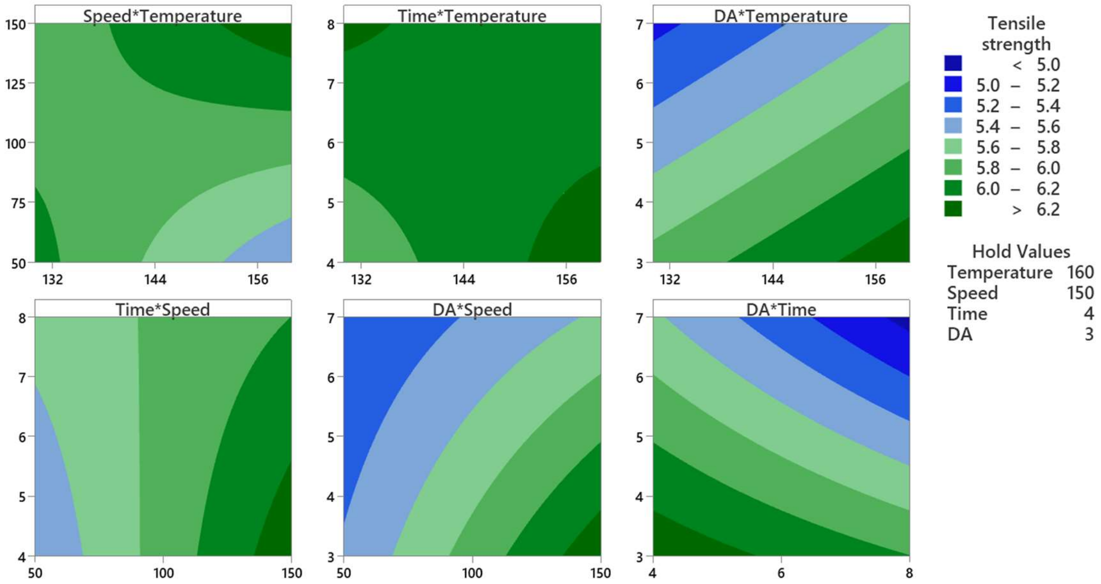
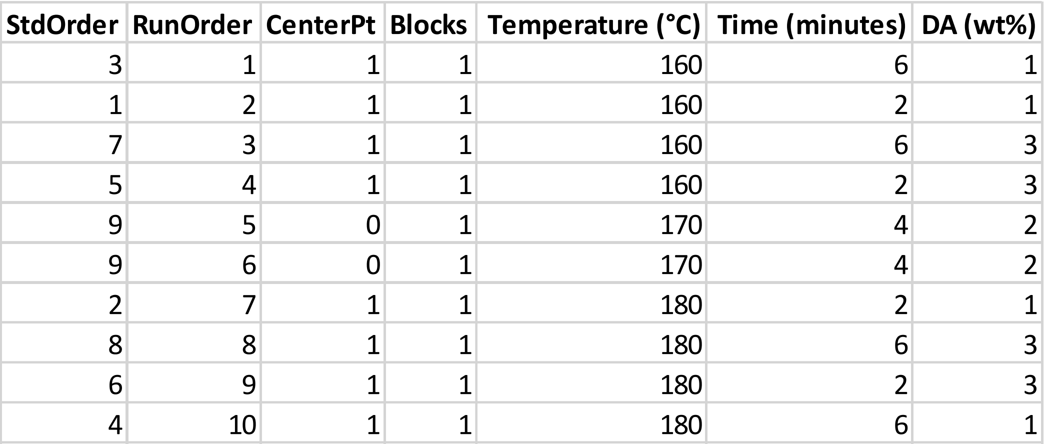


Figure 30: Contour plots of the screening with the optimal parameters as hold values

8.2 Optimization

The optimization design is based on the results of the screening, in order to optimize the quality of the material. From the screening it was indicated that the speed should be increased, but this was already at the practical limit of the mixer. The amount of devulcanization aid had the opposite effect and was therefore chosen to decrease to low and high values of 1 wt% and 3 wt%. The temperature was increased, and the time window was shifted to a shorter time in order to investigate values beyond the lower limits of the model. This is also based on the screening results, showing a lower time generally ensures a higher tensile strength. The resulting DOE is shown in Table 19.



StdOrder	RunOrder	CenterPt	Blocks	Temperature (°C)	Time (minutes)	DA (wt%)
3	1	1	1	160	6	1
1	2	1	1	160	2	1
7	3	1	1	160	6	3
5	4	1	1	160	2	3
9	5	0	1	170	4	2
9	6	0	1	170	4	2
2	7	1	1	180	2	1
8	8	1	1	180	6	3
6	9	1	1	180	2	3
4	10	1	1	180	6	1

Table 19: Factorial design for the optimization

The resulting tensile values are shown in Figure 31. The differences in tensile values remain limited, which can be explained by the reduced difference in values, decreasing their possible effect. However, the effects differ from the screening. The optimal result in this factorial design is achieved by the 170/150/4/2 sample, which is generally in line with the trends seen in the screening. The reference compound is indicated as REF, and is not devulcanized but a model compound of a truck tire inner tube.

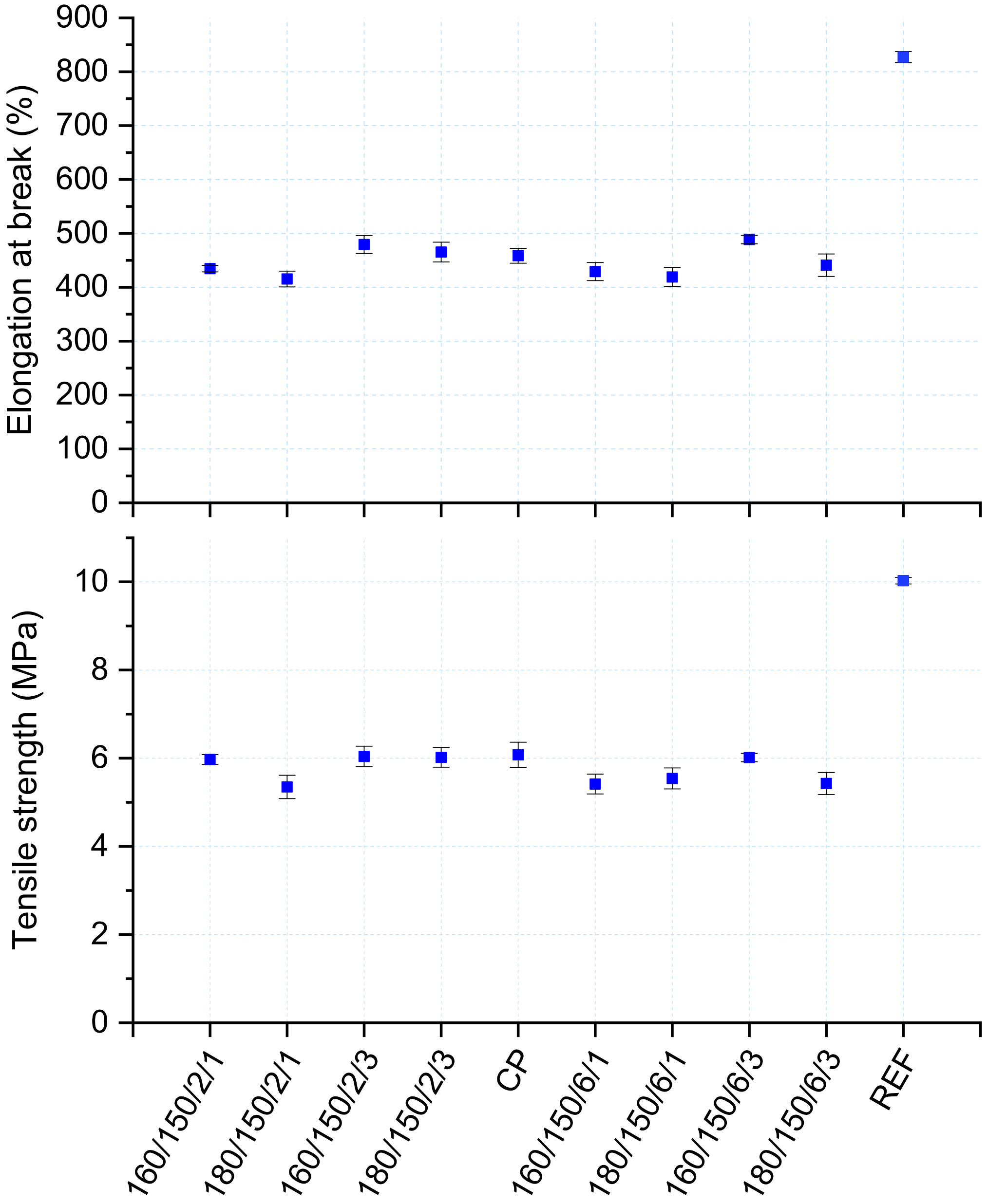


Figure 31: Tensile results of the optimization

8.2.1 Minitab Statistical Analysis - Optimization

In the analysis of the optimization factorial design, the resulting effects were all not statistically significant. This might have several reasons. First, there is error in the results due to inhomogeneity of the feedstock material, which will always cause more error than a model compound. Combined with this, the parameters chosen for this experimental design lie closer together compared to the screening. It is possible that these parameters are too close together, as well as the results, to properly assess the resulting effects. The amount of devulcanization aid had to be lowered, but was already decreased to 1 wt% as 'low' value. It was determined that 0 wt% DA would not be a suitable low value, as it would take out a significant mechanism responsible for targeting the crosslinks selectively, and would also result in more recombination. The temperature could not be increased higher than 180 °C, as this would cause too much thermal degradation. Finally, only the residence time could have been broadened in order to see how strong the effects are.

Coded Coefficients						
Term	Effect	Coef	SE Coef	T-Value	P-Value	VIF
Constant		5.7222	0.0651	87.87	0.007	
Temperature	-0.2765	-0.1382	0.0651	-2.12	0.28	1
Time	-0.2458	-0.1229	0.0651	-1.89	0.31	1
DA%	0.3066	0.1533	0.0651	2.35	0.256	1
Temperature*Time	0.0454	0.0227	0.0651	0.35	0.786	1
Temperature*DA%	-0.029	-0.0145	0.0651	-0.22	0.86	1
Time*DA%	-0.0633	-0.0316	0.0651	-0.49	0.712	1
Temperature*Time*DA%	-0.3294	-0.1647	0.0651	-2.53	0.24	1
Ct Pt		0.355	0.146	2.44	0.248	1

Table 20: Resulting effects of the optimization

As visible in Table 20, none of the effects in this model are significant. Also, when the center point is added into the analysis to estimate curvature, the resulting curvature effect is not significant either. Furthermore, Minitab indicates the presence of unusual observations in all of the data points except the center points. This indicates that these data points do not fit the model. Since all data points have this effect, it can be assumed that the model is not a good fit for the response values. If the parameters are chosen too close, while the error in measurement is too large, this can be the consequence. For instance, the DA concentration, a very significant factor in the screening, is chosen at 1 wt% and 3 wt%, which might be too close to see a visible effect. At the same time, it is already known that using aged feedstock material that is contaminated with a range of other materials and leaching chemicals can greatly increase the variance of the results, especially in batch processing such as is done in this study. For instance, the variation in results can be tested by comparing all center point results. If there is no removal of outliers, the confidence intervals indicate quite a large variance of the results. With a 95 % confidence, the tensile strength ranges between 5.5-5.9 MPa. Similarly, the elongation at break ranges between 527-557 %.

In Figure 32, the resulting contour plots of the optimization are shown, with the previously determined optimal parameters as hold values. It should be noted that while there are no significant effects, the contour plots can still indicate general trends towards optimization, even if they are considered small. The lack of significance is likely because there is a larger error in the model, compared to the distance between values, decreasing the significance of the effects. In contrast to the screening, the plots show that a higher DA concentration increases the tensile strength, combined with a lower temperature and a lower residence time. These results indicate that while this is the optimization step, the optimal parameters might have been already determined within the screening.

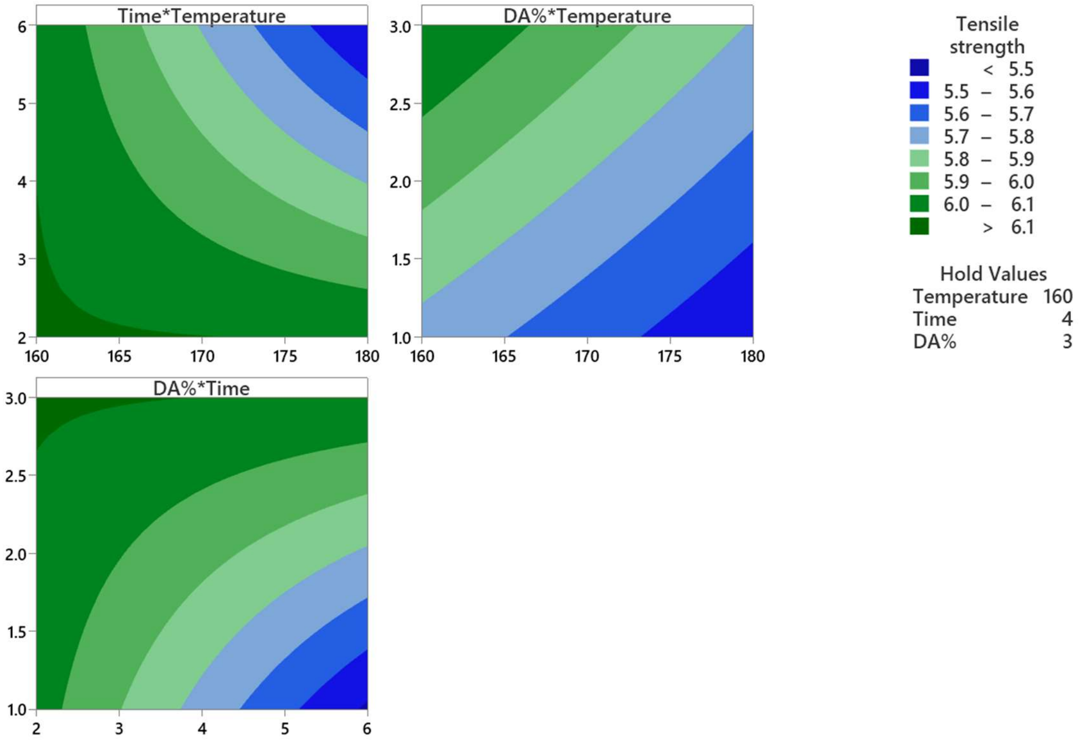


Figure 32: Contour plots of the optimization factors

While tensile strength indicates the quality of the material, and is an appropriate numerical measure for statistical analysis, it does not fully explain the degree of devulcanization or rubber breakdown. The white rubber analysis, while not distinguishing between random and crosslink scission, indicates how well the material is devulcanized and/or degraded, by dispersing it in a white compound. The contrast between the matrix and the still vulcanized particles shows how successful the process has been. Comparing the total area of visible particles to the tensile strength can indicate whether degradation is responsible for a lower number of particles, or if this indicates a higher degree of devulcanization.

In Figure 33, the results of the white rubber measurements are shown in a bar graph, with each sample showing the distribution of particles across categories of particle size, ranging from under 50 to 1000+ µm.

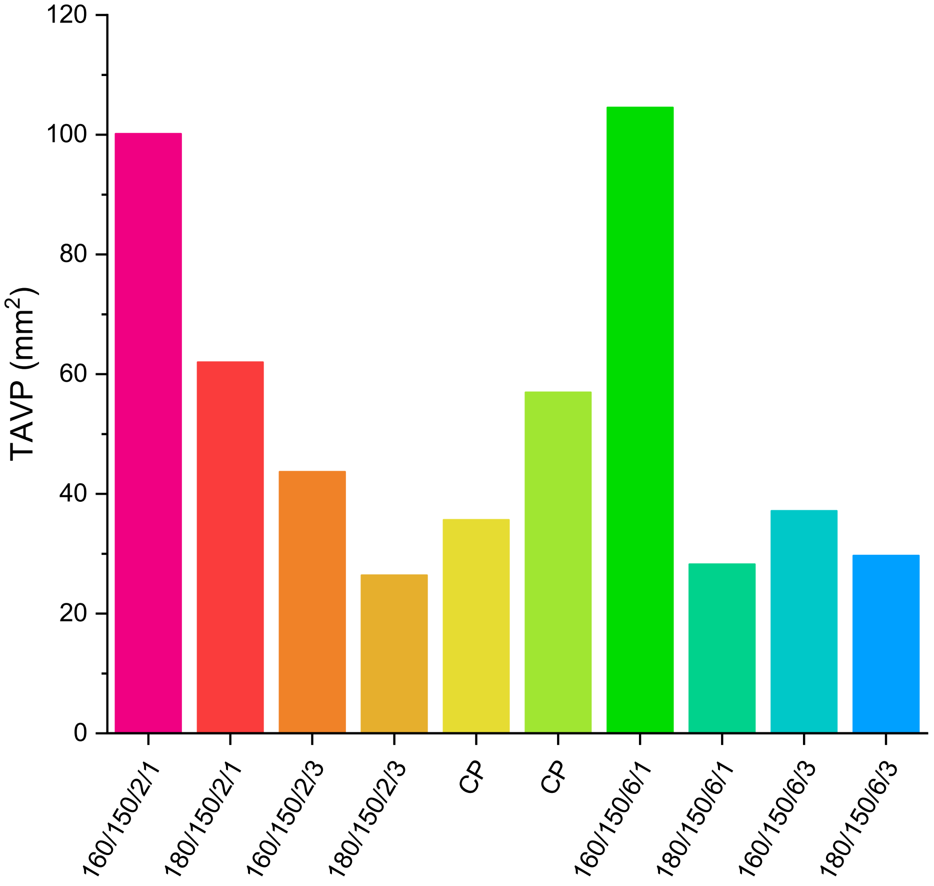


Figure 33: Total Area of Visible Particles (TAVP) of the optimization

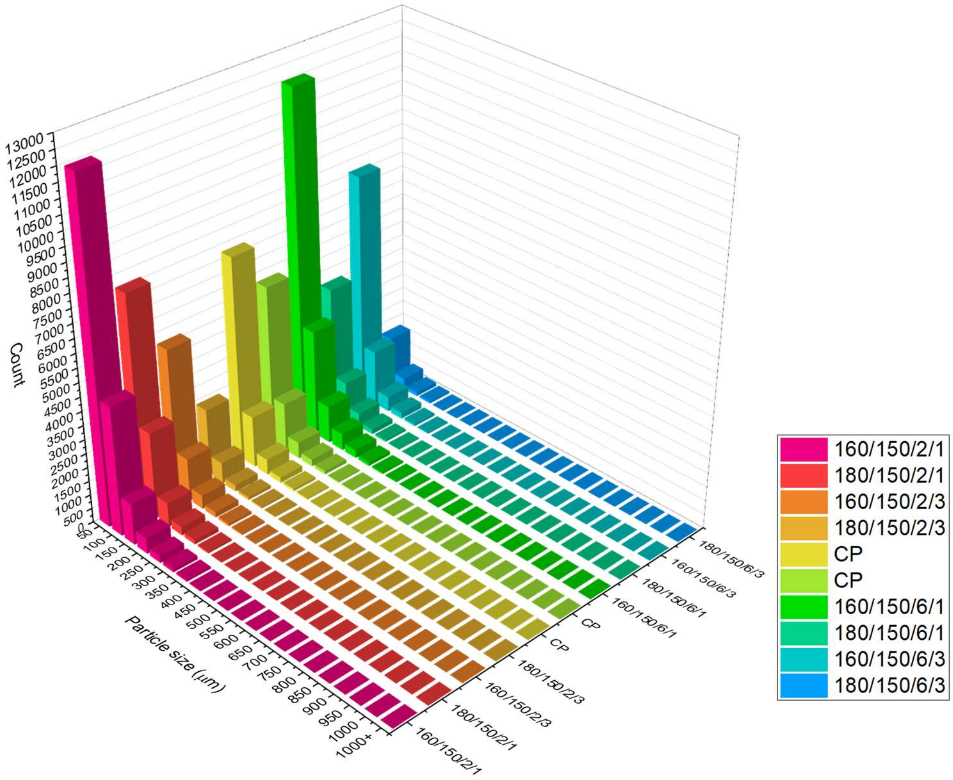


Figure 34: Particle size distribution for the optimization

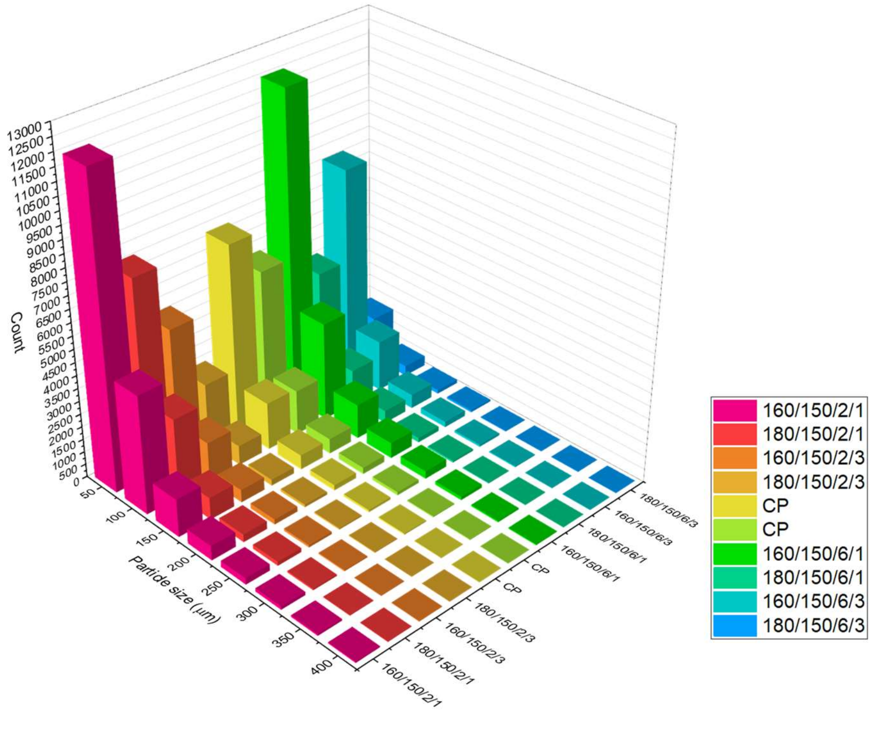


Figure 35: Particle size distribution of the optimization – Focused on particles larger than 400

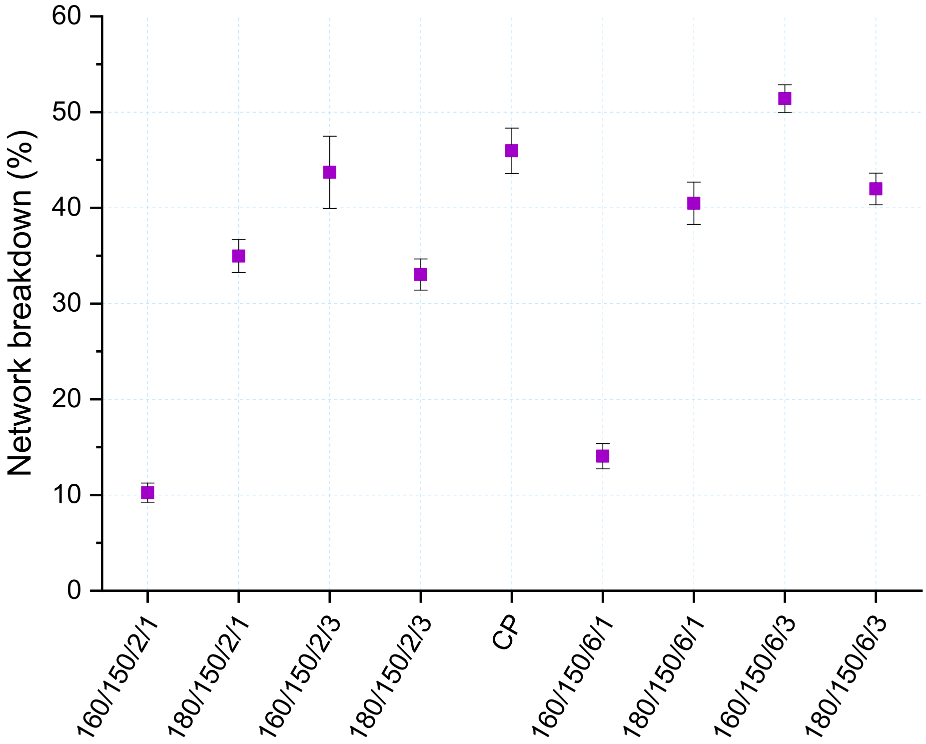


Figure 36: Network breakdown of the optimization

In Figure 36 the network breakdown of the optimization samples is shown. The network breakdown is the percentage in reduction of crosslink density of the devulcanizate, in comparison to the original vulcanized sample. Immediately visible are the first two samples devulcanized at 160 °C, 150 rpm and 1 wt% DA. The difference is in the residence time, showing that 2 minutes results in a lower network breakdown than 6 minutes. The highest network breakdown is obtained in the 160 °C/150 rpm/6 minutes/3 % DA, which is close in parameters to the optimal sample from the screening (160/150/4/3). The tensile strength is however very similar to 160/150/2/3 and 170/150/4/2, but both these samples have a lower network breakdown. This indicates that while the tensile strength is similar, the degree of devulcanization of the 160/150/6/3 sample is higher and so this sample is more optimal.

Furthermore, the combination of a lower DA%, a lower time and lower temperature is negative for the network breakdown. The amount of devulcanization aid of 1 wt% shows varying results, but only gives a higher network breakdown when combined with an increased temperature. When increasing only the residence time to 6 minutes, there is not a high increase in network breakdown, but when increasing the temperature to 180 °C, the network breakdown in significantly increased from 10 % to 35 %. This indicates that 1 wt% of DA is only suitable at elevated temperatures, in this case 180 °C.

8.3 Finalization

Finally, some last changes and variations were made to see the effects. The names are based on which feedstock material is used, IT standing for inner tube, and REF standing for the model compound made according to an inner tube formulation. These are devulcanized with some last variations in parameters. OPT stands for the optimal parameters from the screening, at 160 °C/150 rpm/6 minutes/3 wt% DA. 85 and 90 signify the adjusted fill factor. Initially this was chosen at 80 %, but due to the limitations in increasing shear, combined with the lower viscosity of butyl rubber, a higher shear was achieved by increasing the fill factor to 85 % and 90 % using the optimal parameters. Furthermore, 0OIL indicates no processing oil was swelled into the feedstock, and 0DA indicates that no DA was used. Finally, one reference compound is devulcanized using the parameters from the screening center point to compare the resulting values.

1. IT-0DA – Feedstock devulcanized with optimal parameters, no DA
2. IT-0DA-0OIL – Feedstock devulcanized with optimal parameters, no DA and no oil
3. IT-OPT-85 – Feedstock devulcanized with optimal parameters, increased fill factor of 85 %
4. IT-OPT-90 – Feedstock devulcanized with optimal parameters, increased fill factor of 90 %
5. REF-D – Reference compound devulcanized with optimal parameters
6. REF-CP – Reference compound devulcanized with center point parameters of the screening
7. REF-0DA-0OIL – Reference compound devulcanized with optimal parameters, no DA and no oil
8. REF-0DA – Reference compound devulcanized with optimal parameters, no DA

Also, a reference compound was produced to compare to the devulcanized material. This reference compound was then also devulcanized in order to compare the devulcanized materials. The main differences between the post-consumer inner tube feedstock and the reference material is that the feedstock was already aged, and is contaminated due to collection and processing. In Table 21 the samples with corresponding parameters are shown. Initially a fill factor of 80 % was chosen, due to previous conducted research by Ghosh et al., in which this was optimized for passenger car tires mainly consisting of SBR and BR. However, it was later determined that the difference in softness can influence the devulcanization behavior as the shear forces generated will be different. Butyl rubber is softer and more pliable compared to passenger car tire rubber and will likely generate less shear forces during mixing. Since the speed could not be further optimized, it was chosen to compare a higher fill factor in this finalization step instead, to further increase the shear forces. For the optimal parameters, the fill factor was increased to 85 % and 90 %. Furthermore, the feedstock was devulcanized without DA and without both processing oil and DA, to compare with the previously optimized parameters, and see the influence of the oil and DA on the devulcanizate quality. Furthermore, a reference compound was made according to an inner tube formulation, as described in Chapter 7.4. It was devulcanized with the same parameters as was used for the inner tube feedstock batches. REF-D indicates the optimal parameters in devulcanization of the feedstock, used for the reference compound.

Sample	Feedstock	Fill factor	Oil	Temperature	Speed	Time	DA%
IT-0DA	IT	80	5	160	150	4	0
IT-0DA-0OIL	IT	80	0	160	150	4	0
IT-OPT-85	IT	85	5	160	150	4	3
IT-OPT-90	IT	90	5	160	150	4	3
REF-D	REF	80	5	160	150	4	3
RED-CP	REF	80	5	145	100	6	5
REF-0DA-0OIL	REF	80	0	160	150	4	0
REF-0DA	REF	80	5	160	150	4	0

Table 21: Finalization including devulcanized reference compounds (REF) and inner tube feedstock (IT)

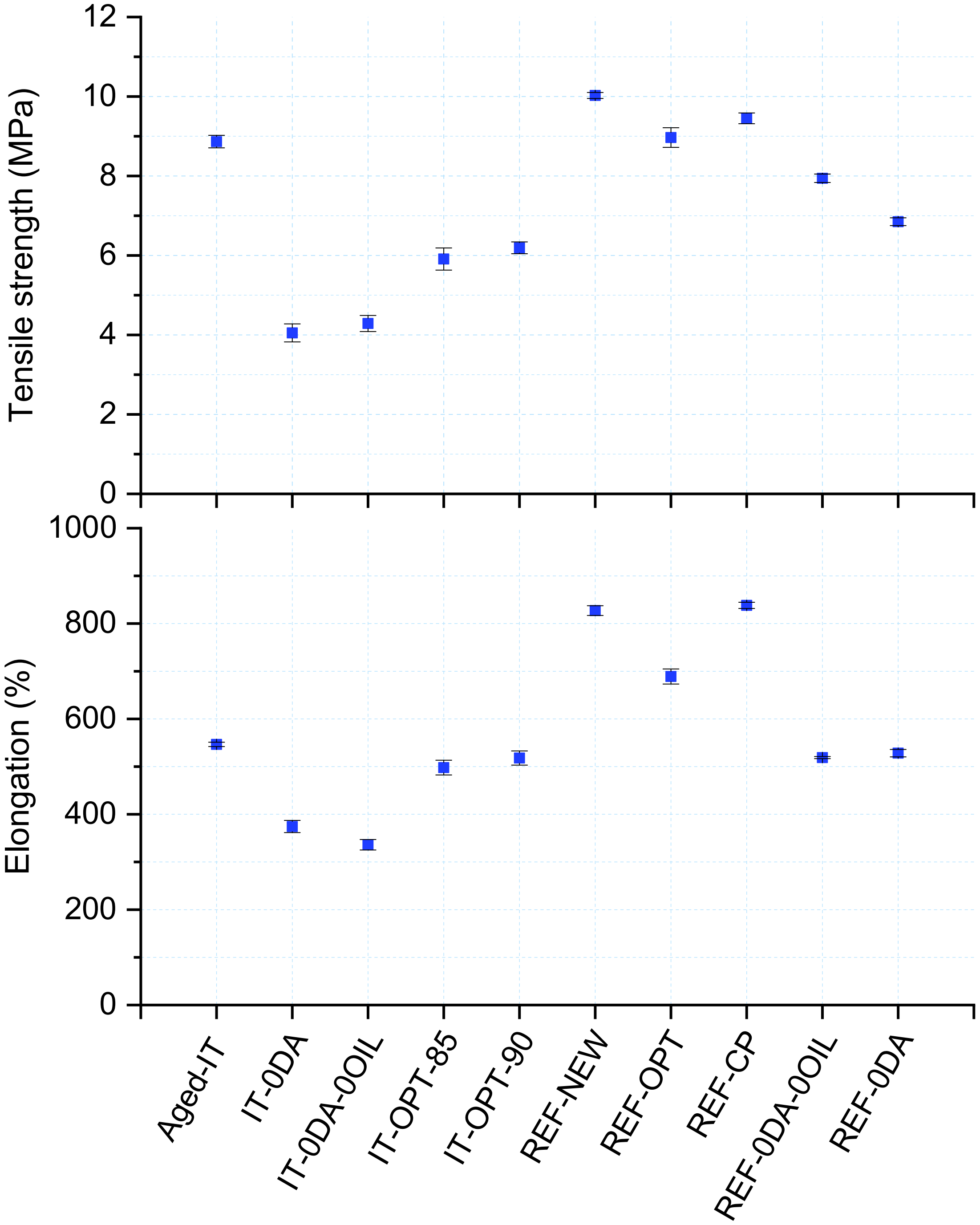


Figure 37: Tensile results of the finalization samples

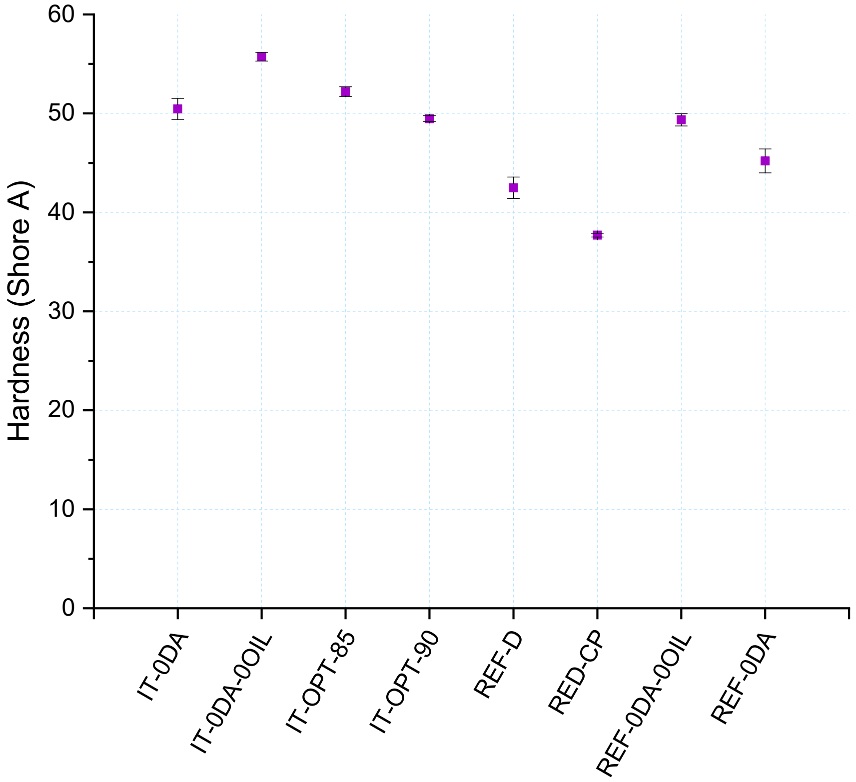


Figure 38: Hardness results of the finalization

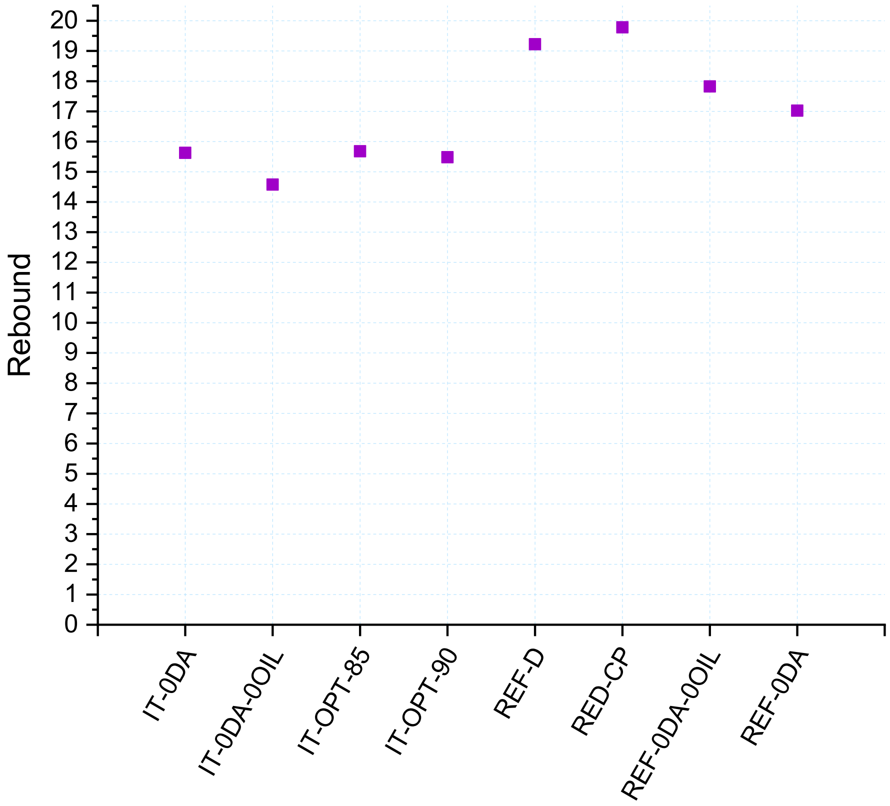


Figure 39: Rebound resilience of the finalization

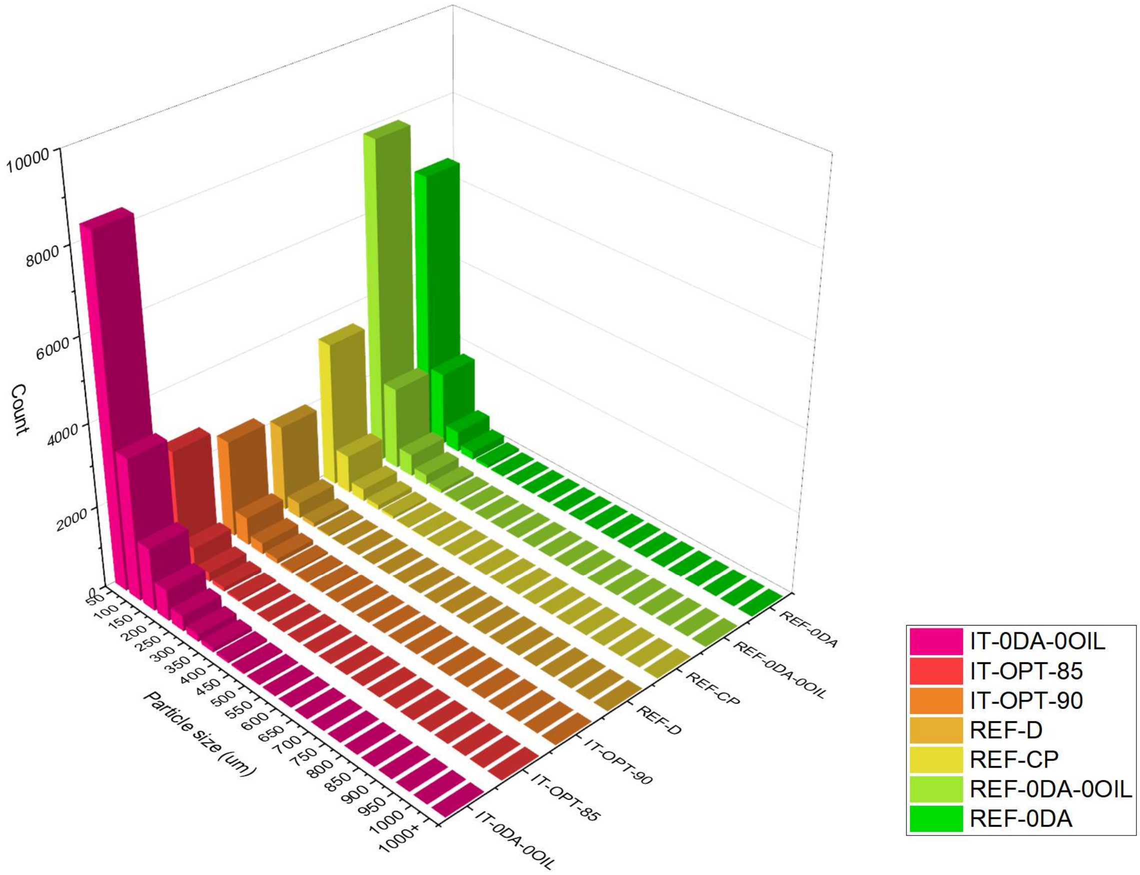


Figure 40: Particle size distribution of the finalization samples

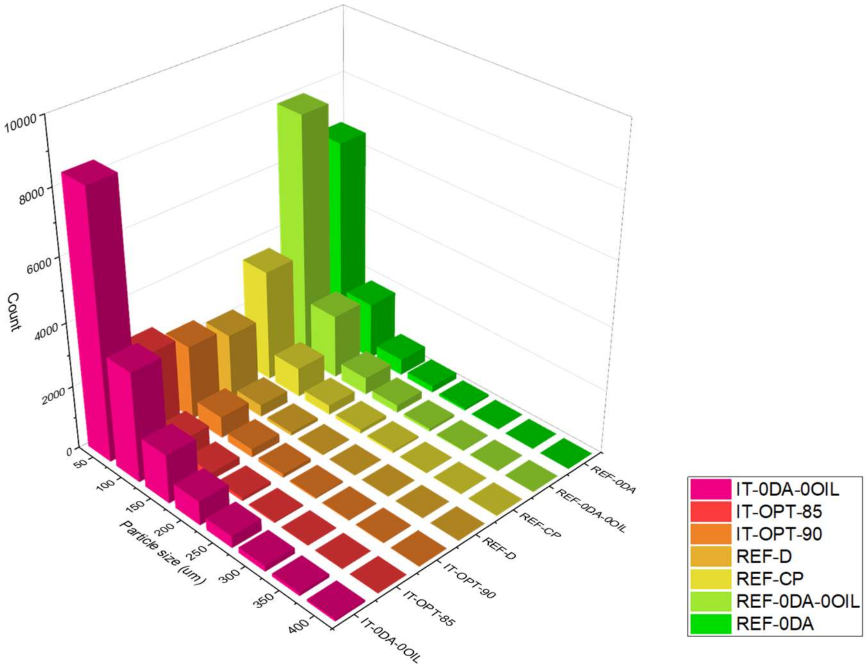
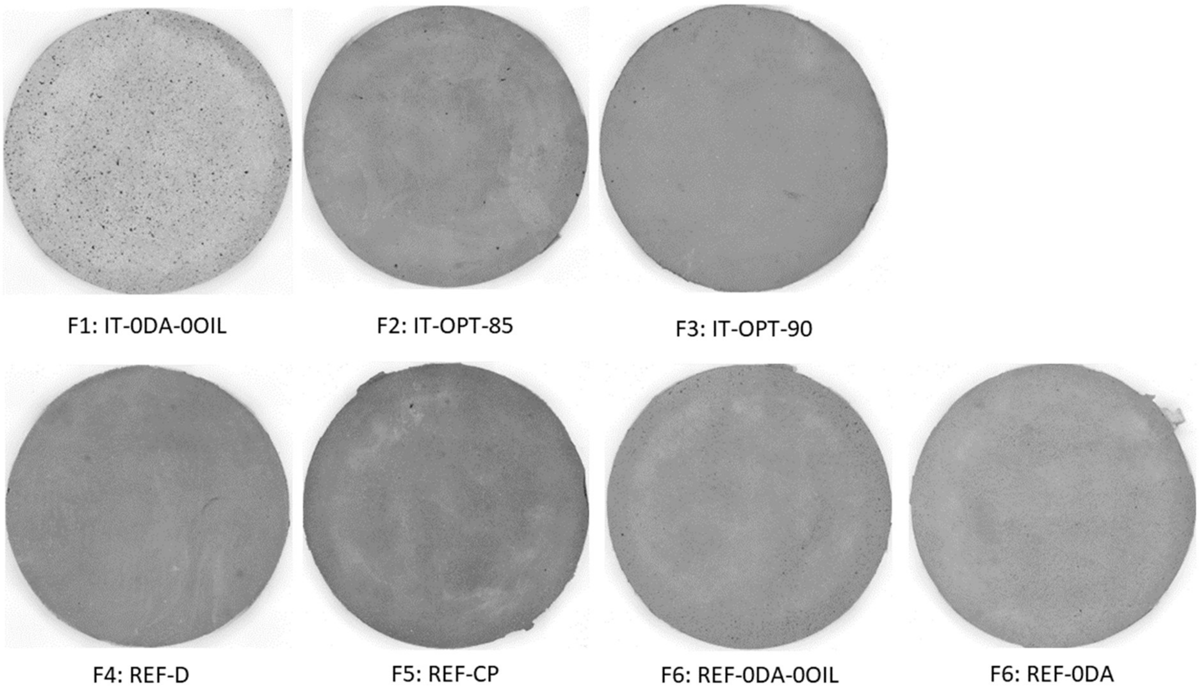


Figure 41: Particle size distribution of the finalization samples, showing particles up to 400 μm



F1: IT-0DA-0OIL

F2: IT-OPT-85

F3: IT-OPT-90

F4: REF-D

F5: REF-CP

F6: REF-0DA-0OIL

F6: REF-0DA

Figure 42: Images resulting from the white rubber analysis

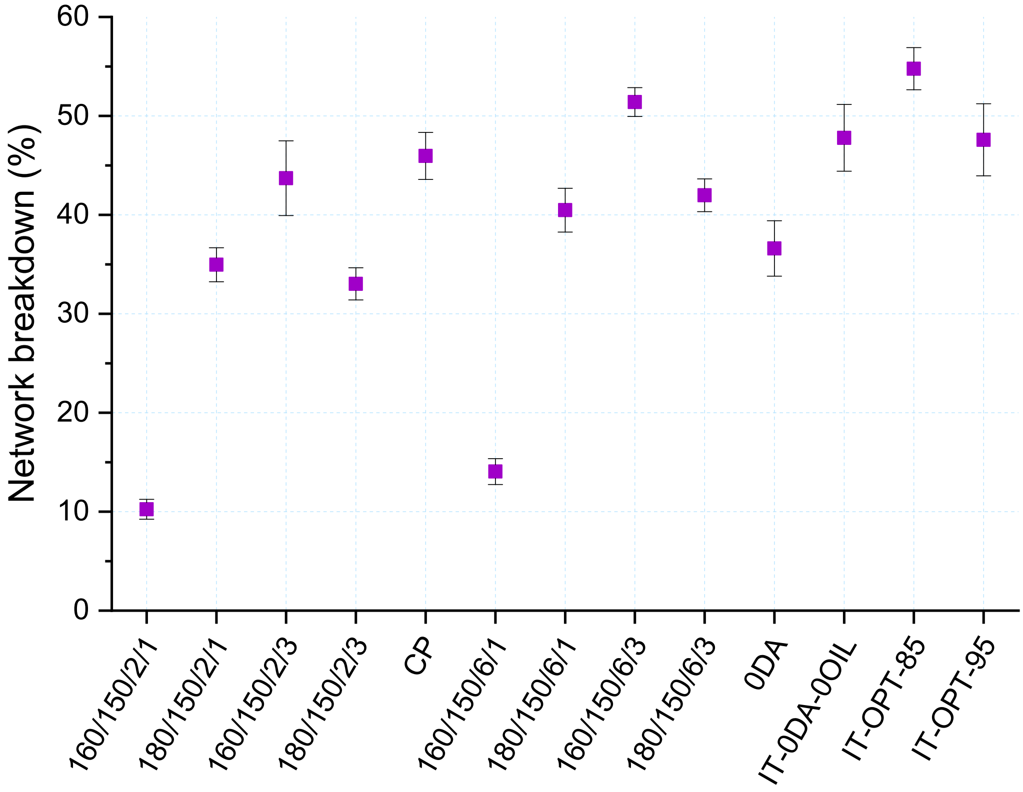


Figure 43: Network breakdown of the optimization and finalization of the feedstock (IT)

9 Application

Finally, one of the goals of devulcanization research is to use the devulcanized material in new products. Since there is insufficient time for a full application study, research about devulcanization blends is used to estimate where the devulcanizate could be applied and to what extent.

The feedstock material originates from used, aged truck tire inner tubes Ghosh et al. found that devulcanized material from aged rubber, has increased aging resistance as a result, a property that could positively impact the application. [29] However, in inner tubing the most important parameter is gas permeability being the property that prevents tires from deflating and maintaining the right pressure. Other important parameters are tensile strength and elasticity since the tire pressure and the stresses resulting from driving are primary external forces that require a good tensile strength.

9.1 Tires

In tires, the two applications of butyl rubber are inner liners and inner tubes. Inner liners are used in passenger car tires and are co-cured with the rest of the tire. This is also the reason why butyl rubber is a co-polymer, consisting of polyisobutylene and usually about 2 % of polyisoprene units. Here, the latter provides double bonds in the polymer chain making it possible to sulfur cure the polymer, as crosslinks form next to these double bonds. However, due to the low concentration of double bonds, butyl rubber has much longer curing times compared to for instance natural rubber or styrene-butadiene rubber. To make co-curing of the inner liner with the rest of the tire possible, the butyl rubber needs to be halogenated in order to increase its reactivity. Therefore, only halogenated butyl rubber is used in inner liners.

Figure 44: (a) Inner tube of truck tire and (b) Inner tube removed from a bicycle tire [47, 48]

Because of this, the application of devulcanized regular butyl rubber in inner liners might be problematic, if it influences the curing behavior too much. In order to apply the devulcanizate into inner liners, first the curing behavior of the blend should be studied. Devulcanized butyl rubber should be blended in varying ratios with the halobutyl compound for inner liners to see the differences in degree of curing. If these are significant, the curing package should be changed if possible.

Inner tubes on the other hand, are not co-cured with other compounds, making it more flexible as an application for devulcanized butyl rubber. However, the other important properties such as gas permeability and mechanical properties might be limiting to the application of devulcanized material in both inner liners and inner tubes. Especially contamination of the feedstock material can create interfaces between the rubber and contaminants, increasing the gas permeability. However, these properties need to be tested for the specific material.

For this contamination, there are treatments possible to reduce this. One way is to clean the feedstock before grinding, removing most of the external contaminants. Butyl rubber inner tubes are very tacky, making it necessary to powder the material with talcum powder or a similar powder. This is one of the contaminants that gets processed into the devulcanizate if not removed. However, contaminants from other sources than a tire can still be present as a result of the collection, processing and grinding.

The devulcanization efficiency also plays a role in maintaining a low gas permeability. If there are still vulcanized particles, while this can have a positive effect on tear strength, it can increase the gas permeability at the interface spots between the particle and the matrix. This can be problematic again if the material is applied in inner tubes. One method to reduce the vulcanized particles, without increasing the devulcanization efficiency, is refining the material. This is done through a milling technique in which the rolls of the mill have varying gaps. If the nip gap in the middle is smaller than on the outsides of the mill, the particles will move to the outer sides of the material during milling, and that way the still vulcanized particles can be concentrated and removed.

9.2 Mechanical goods

Butyl rubber is used for a range of other applications too Other relevant applications are for instance sports-ball bladders, glove-box gloves. Furthermore, butyl rubber has good weather resistance, making it suitable as a patching material for membrane roofs or a window sealing. However, there needs to be good control over the material quality for these type of applications. One advantage as mentioned before, is the aging resistance, on which devulcanization has a positive effect. This is especially relevant in applications that need a long lifetime and where aging is detrimental to the properties such as sealing applications. Due to the low gas and vapor permeability this also is a good material for gas mask insulation.

Furthermore, waterproofing applications such as tank and pond liners use butyl rubber. Butyl rubber is also regularly used as a vibration dampener, in suspension bushings, automotive applications, shock mounts, etc. Due to its flexibility and sealing properties it is often used in seals, gaskets, O-rings and hoses.

10 Conclusions and Recommendations

10.1 Conclusions

In this study, a Design of Experiments analysis was done to evaluate the effects of different devulcanization parameters and their interactions on the devulcanization process of truck tire inner tubes. Therefore a screening was conducted considering the residence time, temperature, devulcanization aid% and rotor speed as parameters. From the screening, the resulting optimal parameters were a tensile strength of 6.4 MPa and an elongation at break of 529 %. The interactions between parameters that increase the input of energy were relevant in the screening and show that a combination of increased temperature, increased rotor speed and increased residence time has a negative effect on the devulcanizate quality. This can be due to degradation of the main chain. When looking at all of these parameters separately, they each have a positive effect on the tensile strength. The opposite is true for the devulcanization aid. In the screening the higher amounts of devulcanization aid negatively impacted the tensile strength, which could be due to oligomerization of the silane, the forming of silane crosslinks or the attack of the silane on the double bonds in the polymer, affecting the curing behavior of the material.

Based on the results of the screening, an optimization of devulcanization parameters was conducted. Therefore, the rotor speed was fixed at 150 rpm since this was already determined to be optimal considering the limitations of the machine. A second experimental design was conducted but did not result in a further optimization of the devulcanizate quality. Therefore the optimal parameters from the screening as shown in Table 22 resulted in the highest tensile strength, which is 6.4 MPa.

Parameter	**Value**
Temperature	160 °C
Speed	150 rpm
Residence time	4 minutes
DA concentration	3 wt%

Table 22: Optimal devulcanization parameters

The optimization segment showed that a devulcanization aid content of only 1 wt% gave strongly decreased results, unless combined with an elevated temperature. Therefore it is concluded that 1 wt% DA is only suitable with a temperature of 180 °C. This is corroborated with the white rubber analysis and network breakdown. The white rubber analysis also showed a positive result for samples at 180 °C, but this can be due to increased degradation, which is why the tensile strength was lacking. It is concluded that 160 °C is still the optimal temperature. The network breakdown also further supported the findings about the optimal parameters from the screening.

In the finalization, an increased fill factor did not make a significant change to the results. Aging had a clear effect on the inner tube material, reducing the tensile strength and elongation at break. Likely, the primary degradation mechanism during the lifetime of an inner tube is chain hardening. The presence of processing oil has a larger positive effect on the inner tube material, compared to the reference compound.

Finally, three main reaction mechanisms are identified based on the results. The primary mechanism is TESPT acting as a recombination inhibitor by binding to cleaved crosslinks. Besides this main reaction, oligomerization of the TESPT and the attack of TESPT on double bonds are possibilities, especially when there is an excess of TESPT.

10.2 Recommendations

In the pursuit of optimizing the recycling process of truck tire inner tubes, several recommendations are made, based on both experimental findings and theoretical considerations. This chapter describes various strategies aimed at refining the devulcanization process for enhanced efficiency, reduced error, and increased material quality.

Optimization using model compounds

The initial screening and optimization using design of experiments should utilize model compounds to fine-tune the processing parameters to minimize errors in this stage. Once an optimized set of conditions is determined with devulcanization of a model compound, these conditions can then be applied to actual feedstock. Using more replicates with real feedstock can make the estimation of error more robust and lead to a reduction in error and a better measure of effects and interactions in the model.

Extruder trials

Extruder trials offer significant advantages, particularly in controlling processing conditions such as temperature and atmosphere. This controlled environment minimizes external variabilities that could skew results, providing a clearer insight into the processability of materials on a larger scale. However, this should be done at a later stage, as the amount of material needed increases significantly compared to this study.

Compatibility

Compatibility can be increased by replacing commonly used oils with paraffin oil can enhance the efficiency of the recycling process. The choice of oil can significantly affect the properties of the recycled material, as well as the ease of processing. Furthermore the compatibility between the devulcanization aid and the rubber can influence the homogeneity of the devulcanization. A low compatibility can cause an onion-peeling mechanism, resulting in vulcanized particles that are not devulcanized due to a lack of swelled devulcanization aid.

Curing system

Optimizing the curing system for butyl rubber will increase the devulcanizate quality. In this study, it was difficult to assess the curing times of the samples accurately due to the marching behavior of the cure curves. This can be explained by the devulcanization aid playing an additional role in the curing of the material, it should be assessed how the curing behavior changes based on this, as well as if the curing system should be reduced.

Processing White Rubber

A lower percentage of devulcanizate in the white rubber sample can be advantageous for the analysis since the white rubber samples in this study turned relatively dark, making it more difficult to properly analyze the particles. Using less devulcanizate could make the particle analysis clearer, although this also depends on the devulcanization degree.

Milling Time and Techniques

Experimenting with different milling times and techniques can help determine the most efficient method for specific types of rubber, optimizing the particle size distribution and quality of the output.

Ambient, Cryogenic and Wet Grinding

Comparing different grinding methods can reveal their respective efficiencies and limitations. Ambient, cryogenic, and wet grinding each have pros and cons and should be compared for this specific feedstock. However, ambient grinding will likely result in tackiness

Implementing these recommendations can significantly enhance the efficiency and quality of rubber recycling processes. By systematically exploring these areas, recyclers can adapt and optimize their operations to meet the challenges posed by different types of rubber and contamination levels.

References

[1] "LIFE project aims to revolutionise Europe's approach to recycling end-of-life tyres." https://cinea.ec.europa.eu/news-events/news/life-project-aims-revolutionise-europes-approach-recycling-end-life-tyres-2023-12-14_en (accessed 15 October, 2023).

[2] F. Valentini and A. Pegoretti, "End-of-life options of tyres. A review," *Advanced Industrial and Engineering Polymer Research,* vol. 5, no. 4, pp. 203-213, 2022/10/01/ 2022, doi: https://doi.org/10.1016/j.aiepr.2022.08.006.

[3] *Trade in waste by type of material and partner.* [Online]. Available: https://ec.europa.eu/eurostat/databrowser/view/ENV_WASTRDMP__custom_7125627/default/line?lang=en

[4] "Understanding tire pyrolysis and the process." https://contec.tech/what-is-tire-pyrolysis-how-does-it-work/#:~:text=Tire%20pyrolysis%20is%20a%20form,tire%20wastes%20don%27t%20burn. (accessed 25 September, 2023).

[5] P. T. Williams, "Pyrolysis of waste tyres: A review," *Waste Management,* vol. 33, no. 8, pp. 1714-1728, 2013/08/01/ 2013, doi: https://doi.org/10.1016/j.wasman.2013.05.003.

[6] R. Ghosh *et al.*, "New Route of Tire Rubber Devulcanization Using Silanes," *Polymers*, vol. 15, no. 13*,* doi: 10.3390/polym15132848.

[7] A. Y. Coran, "Chemistry of the vulcanization and protection of elastomers: A review of the achievements," (in English), *J Appl Polym Sci,* vol. 87, no. 1, pp. 24-30, Jan 3 2003, doi: 10.1002/app.11659.

[8] "Waste Framework Directive." European Commission. https://environment.ec.europa.eu/topics/waste-and-recycling/waste-framework-directive_en (accessed 20/04/2023.

[9] H. Jamie, "What Happens When Tires Reach The End Of The Road?," in *Forbes*, ed: Forbes, 2022.

[10] "Managing End-of-Life Tires," World Business Council for Sustainable Development, 2008.

[11] "Managing of End-of-Life Tires," World Business Council for Sustainable Development, 2018. [Online]. Available: https://docs.wbcsd.org/2018/02/TIP/End_of_Life_Tires-Full-Report.pdf

[12] "4 Billion Tires in Landfills: A Shifting Problem." https://www.retyre.eco/western-countries-shipping-old-tyres-to-the-landfills/ (accessed 13 December, 2023).

[13] "Netherlands." Sadler Consultants Europe GmbH. https://urbanaccessregulations.eu/countries-mainmenu-147/netherlands-mainmenu-88 (accessed.

[14] M. J. Nieuwenhuijsen and H. Khreis, "Car free cities: Pathway to healthy urban living," *Environment International,* vol. 94, pp. 251-262, 2016/09/01/ 2016, doi: https://doi.org/10.1016/j.envint.2016.05.032.

[15] L. W. Coleman. "Tire Recycling and the Environment: Benefits and Challenges." EHS Daily advisor. (accessed 21/04/2023.

[16] "Waste shipments." European Commission. (accessed April 10th, 2023).

[17] D.-G. f. Environment. "Plastic waste shipments: new EU rules on importing and exporting plastic waste " https://environment.ec.europa.eu/news/plastic-waste-shipments-new-eu-rules-importing-and-exporting-plastic-waste-2020-12-22_en (accessed 05-05, 2023).

[18] "In Europe 95% of all End of Life Tyres were collected and treated in 2019," vol. 2023, ed: European Tyre and Rubber Manufacturers' Association, 2021.

[19] "How are Recycled Old Tires Used?" Compactor Management Company. (accessed April 15th, 2023).

[20] "Burning or recycling? EU considers possibilities regarding end-of-life tires." Klean Industries. (accessed April 12th, 2023).

[21] S. Utrera-Barrios, R. Verdejo, M. Lopez-Manchado, and M. Hernández, "Self-Healing Elastomers: A sustainable solution for automotive applications," *European Polymer Journal,* vol. 190, p. 112023, 05/01 2023, doi: 10.1016/j.eurpolymj.2023.112023.

[22] A. I. Isayev, S. P. Yushanov, S.-H. Kim, and V. Y. Levin, "Ultrasonic devulcanization of waste rubbers: Experimentation and modeling," *Rheologica Acta,* vol. 35, no. 6, pp. 616-630, 1996/11/01 1996, doi: 10.1007/BF00396511.

[23] P. S. Garcia, F. De Sousa, J. De Lima, S. Cruz, and C. Scuracchio, "Devulcanization of ground tire rubber: Physical and chemical changes after different microwave exposure times," *Express Polymer Letters,* vol. 9, no. 11, 2015.

[24] F. Ghavipanjeh, Z. Ziaei Rad, and M. Pazouki, "Devulcanization of Ground Tires by Different Strains of Bacteria: Optimization of Culture Condition by Taguchi Method," *Journal of Polymers and the Environment,* vol. 26, no. 8, pp. 3168-3175, 2018/08/01 2018, doi: 10.1007/s10924-017-1169-0.

[25] S. Seghar, L. Asaro, M. Rolland-Monnet, and N. Aït Hocine, "Thermo-mechanical devulcanization and recycling of rubber industry waste," *Resources, Conservation and Recycling,* vol. 144, pp. 180-186, 2019/05/01/ 2019, doi: https://doi.org/10.1016/j.resconrec.2019.01.047.

[26] L. Bockstal, T. Berchem, Q. Schmetz, and A. Richel, "Devulcanisation and reclaiming of tires and rubber by physical and chemical processes: A review," *Journal of Cleaner Production,* vol. 236, p. 117574, 2019/11/01/ 2019, doi: https://doi.org/10.1016/j.jclepro.2019.07.049.

[27] A. Dorigato, D. Rigotti, and G. Fredi, "Recent advances in the devulcanization technologies of industrially relevant sulfur-vulcanized elastomers," *Advanced Industrial and Engineering Polymer Research,* vol. 6, no. 3, pp. 288-309, 2023/07/01/ 2023, doi: https://doi.org/10.1016/j.aiepr.2022.11.003.

[28] J. W. van Hoek, "Closing the Loop: Reuse of Devulcanized Rubber in New Tires," PhD, University of Twente, 2022.

[29] R. Ghosh, "Transforming silica-silane reinforced rubber into a high quality devulcanizate," Ph.D. Thesis, University of Twente, Netherlands, 2024. [Online]. Available: http://dx.doi.org/10.3990/1.9789036560061

[30] R. Ghosh, "DESIGN OF A DEVULCANIZATION PROCESS FOR TIRE MATERIAL IN A TWIN SCREW EXTRUDER," PDEng, Elastomer Technology & Engineering, University of Twente, 2021.

[31] *Chemistry 2e*, 2 ed. OpenStax, 2019. [Online]. Available: https://openstax.org/books/chemistry-2e/pages/7-5-strengths-of-ionic-and-covalent-bonds.

[32] I. Surya, S. Maulina, and H. Ismail, "Effects of alkanolamide and epoxidation in natural rubber and epoxidized natural rubbers compounds," *IOP Conference Series: Materials Science and Engineering,* vol. 299, p. 012061, 01/01 2018, doi: 10.1088/1757-899X/299/1/012061.

[33] A. Worlee, S. Saiwari, W. Dierkes, and S. S. Sarkawi, "Significant factors affecting the thermo-chemical de-vulcanization efficiency of tire rubber," *Journal of Environmental Treatment Techniques,* vol. 8, no. 3, pp. 1118-1123, 2020/9/20 2020.

[34] "[Styrene-butadiene Rubber]." Taica. https://taica.co.jp/gel/en/support/technical_terms/term_033.html (accessed September, 2023).

[35] S. Saiwari, "Post-consumer tires back into new tires: de-vulcanization and re-utilization of passenger car tires," Ph.D. Thesis, University of Twente, Netherlands, 2013. [Online]. Available: http://dx.doi.org/10.3990/1.9789036535410

[36] J. W. M. Noordermeer *et al.*, "Cradle-to-cradle Devulcanization Options for various Elastomer Types," 2019/10, 2019.

[37] S. Saiwari, W. K. Dierkes, J. W. M. Noordermeer, and A. Blume, "Best Practice for the Devulcanization of Sulfur-cured SBR Rubber," 2015.

[38] National Center for Biotechnology Information [Online] Available: https://www.ncbi.nlm.nih.gov/

[39] S. Saiwari *et al.*, "Upscaling of a Batch De-Vulcanization Process for Ground Car Tire Rubber to a Continuous Process in a Twin Screw Extruder," *Materials (Basel),* vol. 9, no. 9, Aug 24 2016, doi: 10.3390/ma9090724.

[40] M. van Duin *et al.*, *Handbook of Synthetic Rubber*. ARLANXEO Deutschland GmbH, 2020.

[41] M. M. Horikx, "Chain scissions in a polymer network," *Journal of Polymer Science,* vol. 19, no. 93, pp. 445-454, 1956/03/01 1956, doi: https://doi.org/10.1002/pol.1956.120199305.

[42] W. L. Hosch, "butyl rubber," in *Chemical products*, ed. Britannica: Britannica, 2023.

[43] S. Mihara, "Reactive processing of silica-reinforced tire rubber : new insight into the time- and temperature-dependence of silica rubber interaction," Ph.D. Thesis, University of Twente, Netherlands, 2009. [Online]. Available: http://dx.doi.org/10.3990/1.9789036528399

[44] *Rubber, vulcanized or thermoplastic*, ISO, 2022. [Online]. Available: https://www.iso.org/standard/68116.html

[45] *Standard Test Method for Rubber Property—Resilience Using Schob Type Rebound Pendulum*, ASTM, 2018. [Online]. Available: https://www.astm.org/d7121-05r18.html

[46] C. Hayichelaeh, L. A. E. M. Reuvekamp, W. K. Dierkes, A. Blume, J. W. M. Noordermeer, and K. Sahakaro, "Enhancing the Silanization Reaction of the Silica-Silane System by Different Amines in Model and Practical Silica-Filled Natural Rubber Compounds," *Polymers*, vol. 10, no. 6*,* doi: 10.3390/polym10060584.

[47] "Bike tubes." Mr Cycling World. (accessed 20 April, 2024).

[48] "Auto/Light Truck Tubes." TYK Industries. https://tykindustries.com/collections/auto-light-truck-tubes (accessed 21 April, 2024).

[49] F. Beilstein, "Ueber den Nachweis von Chlor, Brom und Jod in organischen Substanzen," 2018/9 2018, doi: 10.1002/cber.18720050209.

Appendix A: Halogenation of butyl rubber

The butyl rubber inner tubes provided were to only consist of butyl rubber. Furthermore, we know that for inner tubes in truck tires, usually non-halogenated butyl rubber is used. However, during processing some indications required confirmation of this. For instance, during molding there was the forming of blisters, round pieces of rubber that swelled up more than the rest of the sheet, and while it did not create air pockets, it might influence the properties. One explanation for this blister forming would be the release of some volatiles during curing. To test if these volatiles could contain halogen compounds from the butyl rubber, first a Beilstein test was performed. This is a simple qualitative chemical test to see if halogens might be present. A copper wire is used together with the material and put into a flame. If the flame turns green, halogens could be present. [49]

The test was performed with a small piece of devulcanizate, and a few granules of the feedstock material. In both cases there was no green flame visible. In order to determine with more certainty that the material is indeed non-halogenated, it was tested using a scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX). Of different regions in the sample a spectrum was generated, showing the atomic composition. Bigger peaks show that certain elements are present. While the results are quantitative, this should not be used as a certain value, also due to the small region that is tested. Furthermore, small peaks should be disregarded because they can be part of the general noise in the measurement. shows one of the microscopic images with the corresponding measured atomic spectrum. From these spectra of five measurements in total it is concluded that if there would be chloride or bromide groups on the polymer chains, this would show much larger peaks than are visible in the spectra. Therefore this can be assumed to be either noise or contamination. The results of this test are described and shown in Appendix A.

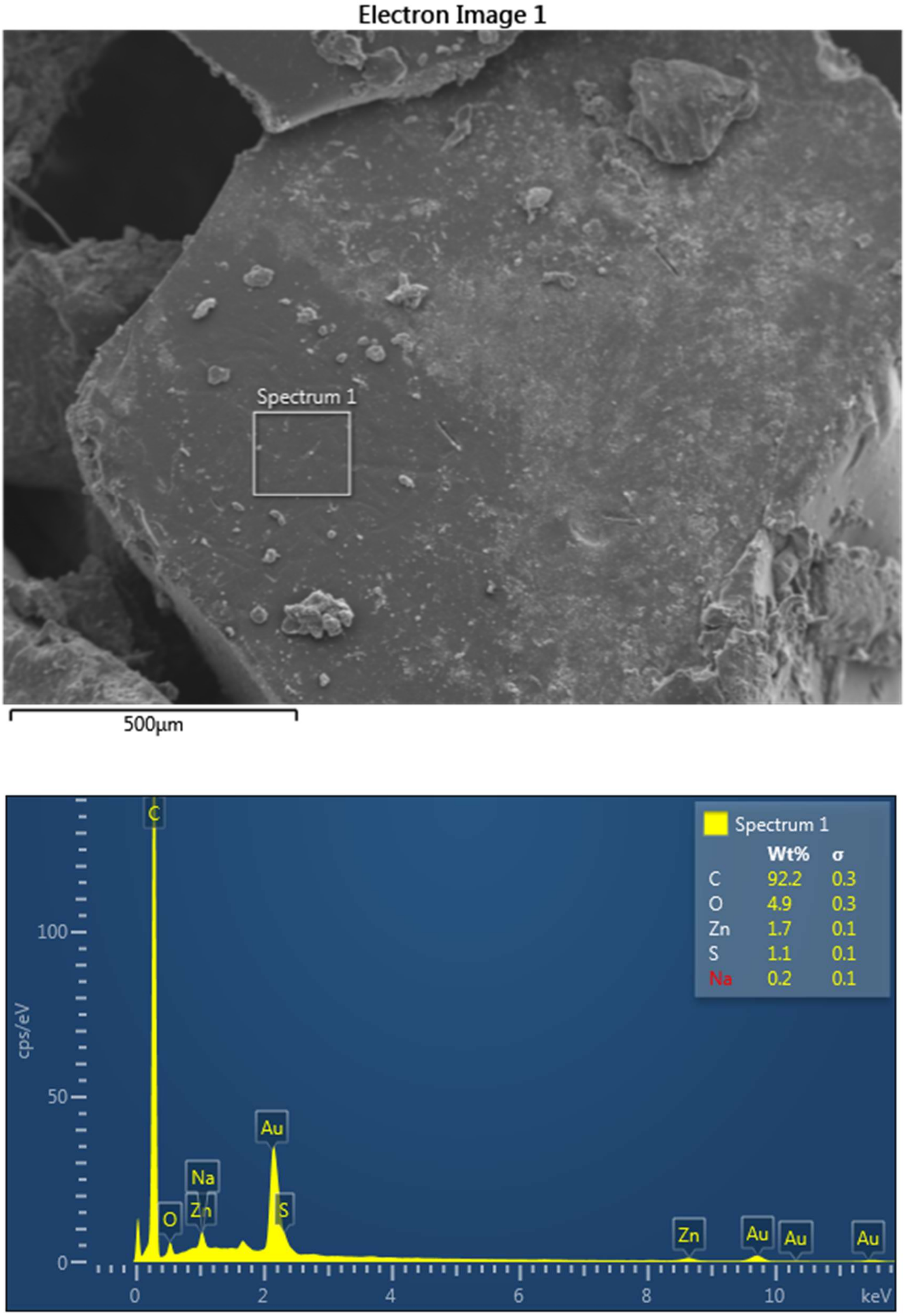


Figure 45: SEM-EDX results showing an atomic spectrum and a microscopic image