**TAMPEREEN TEKNILLINEN YLIOPISTO**
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JOONAS PEKKONEN
NITROSAMINE FREE RUBBER COMPOUNDS – REPLACING A
HAZARDOUS THIURAM ACCELERATOR WITH SAFE ALTERNA-
TIVES

Master of Science Thesis

# ABSTRACT

**JOONAS PEKKONEN**: Nitrosamine Free Rubber Compounds – Replacing a Hazardous Thiuram Accelerator with Safe Alternatives
Tampere University of technology
Master of Science Thesis, 74 pages, 4 Appendix pages
November 2018
Master's Degree Programme in Science and Engineering
Major: Chemistry
Examiner: Adjunct Professor, University Lecturer Terttu Hukka
Keywords: rubber compound, vulcanization, accelerator, tetramethylthiuram disulfide, nitrosamine, health, work safety

Vulcanization is the process of cross-linking rubber to form a three-dimensional network giving rubber its characteristic properties. The most common form of vulcanization is sulfur vulcanization, where sulfur atoms form the cross-links in the structure. Accelerators are used in sulfur vulcanization to boost the vulcanization, i.e. to reduce the time and temperature required for the reaction between polymers.

Tetramethylthiuram disulfide (TMTD) is a fast thiuram accelerator, often used in combination with other accelerators to boost their performance. Using TMTD causes a problem, as potentially carcinogenic nitrosamines can form as byproducts in the vulcanization.

The purpose of this thesis was to improve the safety of rubber manufacturing and rubber products by replacing TMTD with a safer accelerator. The goal was to find replacements for TMTD and create new recipes for the two rubber compounds studied. The studied compounds were a mixture of natural rubber and bromobutyl rubber, denoted as compound A, and a mixture of styrene butadiene rubber and acrylonitrile butadiene rubber, denoted as compound B. Both compounds originally had a vulcanization system, where TMTD was used in combination with the dibenzothiazyl disulfide (MTBS) accelerator.

Test compounds were mixed from both compounds and tests were carried out to determine the effects of varying the accelerators and their amounts on the properties of the rubber compounds. The tested accelerators for compound A were tetrabenzylthiuram disulfide (TBzTD) and Vultac TB710. The choice for compound B was limited, because this compound is used in a food contact application and it needs to fulfill regulations. Thus, the only test accelerator for compound B was zinc dibenzyldithiocarbamate (ZBEC).

For compound A, a successful replacement for TMTD was found from Vultac TB710, used in combination with the *N-tert*-butyl-2-benzothiazole (TBBS) accelerator. The correct amounts of MBTS and ZBEC for compound B were found using central composite design (CCD) method and analyzing and optimizing the results with the Design Expert 11 statistical program.

This thesis confirms that a nitrosamine producing accelerator such as TMTD can be replaced by a safer alternative without altering the compound in other ways. Two different types of cases have been demonstrated and these examples propose a good basis to extend the replacement to other rubber compounds and other hazardous nitrosamine producing accelerators.

# TIIVISTELMÄ

**JOONAS PEKKONEN**: Nitrosoamiinittomat kumisekoitukset – Haitallisen tiuramsulfidikiihdyttäjän korvaaminen turvallisilla vaihtoehdoilla
Tampereen teknillinen yliopisto
Diplomityö, 74 sivua, 4 liitesivua
Marraskuu 2018
Teknis-luonnontieteellinen diplomi-insinöörin tutkinto-ohjelma
Pääaine: Kemia
Tarkastaja: Dosentti, Yliopistonlehtori Terttu Hukka
Avainsanat: kumisekoitus, vulkanointi, kiihdyttäjä, tetrametyylitiuramdisulfidi, nitrosoamiini, terveys, työturvallisuus

Vulkanointi on prosessi, jossa kumin reaktiiviset elastomeeriketjut silloittuvat muodostaen kolmiulotteisen verkon, ja saa sille tyypilliset ominaisuudet. Yleisin vulkanointimuoto on rikkivulkanointi, jossa rikkiatomit muodostavat ristisiltoja elastomeeriketjujen välille. Kiihdyttäjiä käytetään rikkivulkanoinnissa tehostamaan vulkanointia, t.s. alentamaan reaktioon tarvittavaa lämpötilaa ja lyhentämään siihen kuluvaa aikaa.

Tetrametyylitiuramdisulfidi (TMTD) on nopea tiuramdisulfidikiihdyttäjä, jota käytetään usein muiden kiihdyttäjien kanssa nopeuttamaan niiden toimintaa. TMTD:n käytössä piilee ongelma, sillä vulkanointireaktiossa voi muodostua sivutuotteena mahdollisesti karsinogeenisiä nitrosoamiineja.

Tämän diplomityön tarkoituksena oli parantaa kumin valmistuksen ja kumituotteiden turvallisuutta korvaamalla TMTD turvallisemmalla kiihdyttäjällä. Tavoitteena oli löytää TMTD:lle suoria korvaajia ja luoda uudet reseptit kahdelle tutkitulle kumisekoitukselle. Työssä tutkitut kumisekoitukset olivat luonnonkumin ja bromibutyylikumin sekoitus, nimeltään sekoitus A, sekä styreenibutadieenikumin ja nitriilikumin sekoitus, nimeltään sekoitus B. Molemmissa kumisekoituksissa oli alun perin vulkanointisysteemi, jossa TMTD:tä käytettiin yhdessä dibentsotiatsyylidisulfidikiihdyttäjän (MBTS) kanssa.

Molemmista sekoituksista tehtiin koesekoituksia, joita testattiin eri kiihdyttäjien ja niiden määrien vaikutuksen määrittämiseksi. Testikiihdyttäjät sekoitukselle A olivat tetrabentsyylitiuramdisulfidi (TBzTD) ja Vultac TB710. Sekoitus B:n vaihtoehdot olivat suppeammat, sillä tätä kumisekoitusta käytetään elintarvikekontaktimateriaalina ja sen täytyy täyttää sille asetetut vaatimukset. Tämän vuoksi ainut testattu kiihdyttäjä sekoitukselle B oli sinkkidibentsyyliditiokarbamaatti (ZBEC).

Sekoitukselle A onnistunut TMTD:n korvaaja löytyi Vultac TB710:sta, jota käytettiin yhdessä butyylibentsotiatsolisulfenamidikiihdyttäjän (TBBS) kanssa. Sekoitus B:lle MBTS:n ja ZBEC:n oikeat määrät löydettiin käyttämällä CCD-koetta (central composite design) sekä analysoimalla ja optimoimalla tulokset Design Expert 11 -ohjelmistolla.

Tämä diplomityö vahvistaa, että nitrosoamiineja muodostava kiihdyttäjä, kuten TMTD, voidaan korvata turvallisemmalla vaihtoehdolla muuttamatta kumisekoitusta muilla tavoilla. Työssä on osoitettu kaksi erilaista esimerkkiä ja näiden perusteella vastaavanlaisia korvauksia voidaan laajentaa koskemaan myös muita kumisekoituksia ja haitallisia nitrosoamiineja muodostavia kiihdyttäjiä.

# PREFACE

This thesis was made for Teknikum Group Ltd, at the Research & Development department in the company headquarters in Sastamala between May and November 2018. I want to thank Teknikum for providing me with the chance to write my thesis on this interesting subject, familiarize with the rubber industry and gain valuable experience.

I also want to thank the examiner of my thesis Terttu Hukka for constructive feedback and advice in the writing process and regarding the structure of the thesis. I am especially grateful for Mira Juutilainen, my instructor on behalf of Teknikum, who gave valuable advice and guidance in my work often before I even realized to ask for it. Thanks to the team in the Teknikum R&D department for taking me in and teaching me methods and sharing their knowledge required for the studying and developing of rubber compounds.

These six and a half years studying at TUT have definitely been the best of my life so far. I have met many wonderful people and got to be a part of things I never would have imagined. I am grateful for the friends I have made, Ξspecially in Kultahippu, Hiukkanen and TTYY. With you I have experienced a lot and grown as a person. Finally, I want to thank Marikki for support and always being there and believing in me when I found it difficult.


Sastamala, November 6th, 2018

Joonas Pekkonen

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# LIST OF ABBREVIATIONS AND NOTATIONS

| | |
|---|---|
| ANOVA | Analysis of variance |
| ASTM | ASTM International, an international standardization organization formerly known as American Society for Testing and Materials |
| BfR | Bundesinstitut für Risikobewertung (The German Federal Institute for Risk Assessment) |
| BIIR | Bromobutyl rubber |
| BPTD | Bis-($N$-benzyl piperazine) thiuram disulfide |
| CBS | $N$-cyclohexyl-2-benzothiazolesulfenamide |
| CCD | Central composite design |
| CMR | Carcinogenic, mutagenic or reprotoxic substance |
| CRU | Constitutional repeating unit |
| CV | Conventional vulcanization system |
| dNm | Decinewton meter |
| DOE | Design of experiments |
| DSC | Differential scanning calorimetry |
| DTA | Differential thermal analysis |
| ECHA | European chemical agency |
| EPTD | Bis-($N$-ethyl piperazine) thiuram disulfide |
| EU | European Union |
| EV | Efficient vulcanization system |
| FDA | Food and Drug Administration |
| IARC | International Agency for Research of Cancer |
| IIR | Butyl rubber (isobutyl isoprene rubber) |
| IR | Infrared radiation |
| ISO | International Organization for Standardization |
| MBT | 2-mercaptobenzothiazole |
| MBTS | Dibenzothiazyl disulfide |
| MCV | Model compound vulcanization |
| MDR | Moving-die rheometer |
| MH | Moment highest, the highest torque value during a rheometer test |
| ML | Moment lowest, the lowest torque value during a rheometer test |
| MPTD | Bis-($N$-methyl piperazine) thiuram disulfide |
| NBR | Acrylonitrile butadiene rubber |
| NDBzA | $N$-nitrosodibenzylamine |
| NDMA | $N$-nitrosodimethylamine |
| NMR | Nuclear magnetic resonance |
| NR | Natural rubber |
| PBT | Persistent, bio-accumulative and toxic substance |
| phr | Parts per hundred rubber, a measure of amount in rubber recipes |
| pphm | Parts per hundred million |
| PPTD | Bis-($N$-phenyl piperazine) thiuram disulfide |
| PVI | Premature vulcanization inhibitor |
| REACH | Registration, Evaluation, Authorization and Restriction of Chemicals |
| ShA | Shore A hardness scale |
| SBR | Styrene butadiene rubber |
| SVHC | Substance of very high concern |
| $t_{10}$ | Scorch time, time for rheometer torque to reach 10% of the difference between its minimum and maximum values. |

| | |
|---|---|
| $t_{90}$ | Optimum vulcanization time, time for rheometer torque to reach 90% of the difference between its minimum and maximum values. |
| TBzTD | Tetrabenzylthiuram disulfide |
| TMTD | Tetramethylthiuram disulfide |
| TBBS | *N-tert*-butyl-2-benzothiazole |
| TR10 | Temperature at which the TR test sample has retracted 10% from the elongated value |
| TR test | Low temperature retraction test |
| vPvB | Very persistent and very bio-accumulative substance |
| ZBEC | Zinc dibenzyl dithiocarbamate |
| ZnO | Zinc oxide |

# 1. INTRODUCTION

Rubber is an elastomeric material, which has been used industrially since the 17th century. It is still extremely important due to its exceptional properties of being able to reversibly withstand high deformations. Rubbers do not consist of one material, instead they are a carefully made mixture of base elastomers and a large variety of other ingredients, which all affect the resulting rubber compound. Rubber is used for a large variety of products such as car tires, hoses, shock absorbers and protective gear.

Vulcanization is an irreversible process, where cross-links are formed between the elastomer molecule chains. Through vulcanization rubber gains its desired and signature properties, which include elasticity, flexibility, strength and the ability to restore its original shape after stretching. In the vulcanization, the elastomer chains are joined together, and they form a three-dimensional network. When the network is formed, rubber becomes very insoluble and its flow properties decrease dramatically. There are different types of vulcanization, classified by the types of reactions and bonds forming between the elastomer chains. (De & White 2001, pp. 1-10; Coran 2013)

The rubber compounds studied in this thesis are a mixture of natural rubber (NR) and bromobutyl rubber (BIIR) and a mixture of styrene butadiene rubber (SBR) and acrylonitrile butadiene rubber (NBR). Later in this thesis these two compounds will be denoted as compound A and compound B, respectively. NR is the most widely used elastomer and SBR, NBR and BIIR are synthetic elastomers, each with different properties and uses.

The original vulcanization system in both studied rubber compounds in this thesis includes a combination of two accelerators dibenzothiazyl disulfide (MBTS) and tetramethylthiuram disulfide (TMTD). Their chemical structures are presented in Figure 1.
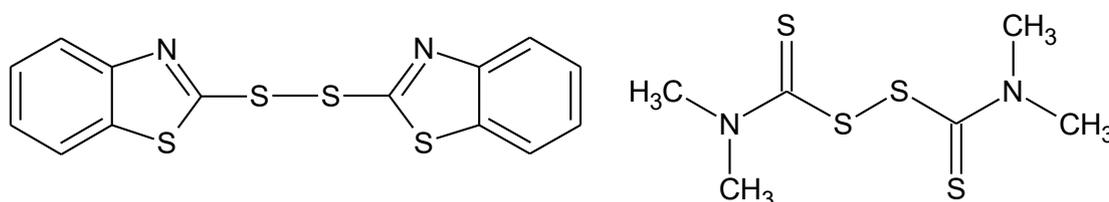


*Figure 1. The molecular structures of MBTS and TMTD.*

MBTS is categorized as a thiazole accelerator and TMTD is a thiuram accelerator. MBTS is a primary all-purpose accelerator, which can be used in many types of rubber. TMTD is a relatively fast accelerator and it is considered as a secondary accelerator, meaning that it is often used in combination with other primary accelerators and rarely on its own.

When these two accelerators are used together, they produce a slow start, which helps processing, then a fast propagation of vulcanization and a high degree of cross-linking altogether.

The issue with using TMTD is the possible formation of nitrosamines, which are known carcinogens. The nitrosamines can form either during production or in the finished products. The formation of nitrosamines and the use of their precursors is already regulated in some countries and the availability of ingredients such as TMTD has decreased. The chemical regulations will likely get tighter in the future and this creates a need for companies to evaluate the used ingredients and switch to safer alternatives.

The purpose of this thesis is to improve the safety of rubber production and the end products by removing the potentially hazardous TMTD from use. The aim is to investigate vulcanization accelerators, which do not produce hazardous nitrosamines and find a replacement for TMTD, which is currently used in production by Teknikum Group Ltd. Teknikum is a Finnish company which manufactures technical rubber and plastic products and rubber compounds in three different countries, so replacing TMTD with a safer accelerator would have a wide impact on the health and safety of both workers and downstream users of rubber products. The goal is to create new recipes for nitrosamine free rubber compounds, which will replace the current potentially hazardous compounds and make the production process and the end products safer. (Teknikum Group Ltd)

The presumption is that the original compounds will have high cross-link densities and good properties and they can be used as good baselines to compare the properties of the test compounds. The expectation is also that straight replacements for TMTD will be found for both studied rubber compounds so that the recipes do not need to be modified in other ways besides changing the vulcanization systems. The new compounds which will hopefully be created in this thesis must have properties which are equal to or better than those of the original compounds.

The thesis consists of a literature part and an experimental part. The literature part consists of an introduction to the basics of rubber manufacturing, discussion on the health and safety of rubber production, the vulcanization of rubber and a review on the possible alternative accelerators to replace TMTD. Based on the review, the available alternatives were evaluated, and the most promising ones were chosen for laboratory tests. The experimental part consists of designing the test rubber compounds, describing the different methods used and then reporting the results, analyzing them and finally concluding the thesis.

# 2. RUBBER MANUFACTURING

Rubber manufacturing is a step process, which in general can be divided into the following parts: compound design, mixing, forming, vulcanization and finishing. This chapter will introduce these different steps to show how rubber products are made. All the different ingredients and processing steps have their role in rubber manufacturing and they all affect the end properties of a product.

## 2.1 Compounding

Compounding is the process of designing and modifying a rubber formula to meet the required properties. The ingredients which make up a rubber are divided into the following categories: elastomers, fillers, vulcanization system, stabilizers and special materials. (B. Rodgers & Waddell 2013)

The rubber compounds are mixed according to a recipe, which tells us which ingredients make up the rubber. Recipes are often devised by rubber chemists, who study and test them thoroughly, before they are put into large scale production. The rubber industry uses a specific way to write the amounts of materials in a recipe. The unit used is phr, parts per hundred rubber. This means that in a recipe, the amount of total elastomer is almost always 100 and the other ingredients are added in proportion to the elastomer by weight. An example of a rubber recipe and the function of different ingredients is presented in Table 1.

*Table 1.*     *A general rubber recipe.*

| Ingredient | phr | Explanation |
|---|---|---|
| NR | 50 | Elastomer |
| SBR | 50 | Elastomer |
| Carbon black | 50 | Reinforcing filler |
| Plasticizer | 9.0 | Tunes hardness and improves processability |
| ZnO | 3.0 | Activator |
| Stearic acid | 2.0 | Activator |
| Stabilizer | 3.2 | Protects from degradation |
| CBS | 0.8 | Accelerator |
| Sulfur | 1.5 | Vulcanizing agent |

This recipe tells in what proportion to add the ingredients. When a rubber batch is mixed, the recipe is converted into masses to fit a particular mixing mill, which will be used. (Laurila 2007, pp. 39-44)

## 2.1.1 Elastomers

The elastomers, which are used in production come from two different origins, natural and synthetic. The most used variety of all elastomers is natural rubber, which is gathered mainly from rubber trees (Hevea brasiliensis). The trees produce a latex, which is gathered by hand. The latex is coagulated using acids, then dried, washed, ground into small granules and packed into bales, which are shipped to rubber factories. Synthetic rubbers are made of cracking by-products from petroleum refineries. These byproducts are different types of monomers, which are polymerized into the wanted elastomers. The main elastomers, which are discussed in this thesis are NR, SBR, NBR and BIIR. (Hofmann 1989)

Natural rubber has one of the best combinations of physical properties and it is relatively cheap. It is resilient, it has high tensile strength, high abrasion resistance, good low-temperature endurance, good dynamic properties and low heat build-up. These properties make it irreplaceable in certain applications. (Hofmann 1989, pp. 11-36)

The molecular structure of NR is that of 1,4-polyisoprene, where the constitutional repeating units (CRU) are in *cis*-configuration. (Klingensmith & Rodgers 2004) The CRU of NR is presented in Figure 2.
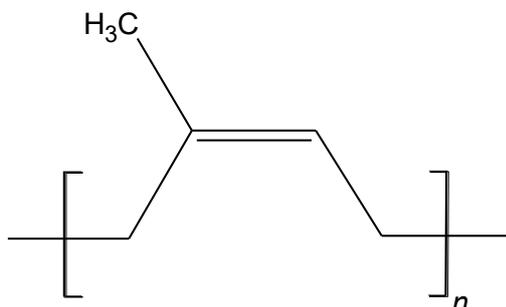


*Figure 2. The molecular structure of natural rubber.*

The structure is quite simple, and the backbone has unsaturation, which enables sulfur cross-linking. In the past natural rubber has been used for almost every rubber product due to its well-balanced properties. Nowadays it has been replaced in the most technical applications, but it is still used in great quantities, especially in blends with other elastomers. (Hofmann 1989, pp. 11-36)

Styrene butadiene rubber is the most common and inexpensive synthetic rubber. It is ductile, and it has good abrasion resistance, although it is inferior to NR. SBR can withstand acids and bases well, but it will swell in oils and fuels. The CRU of SBR is presented in Figure 3.
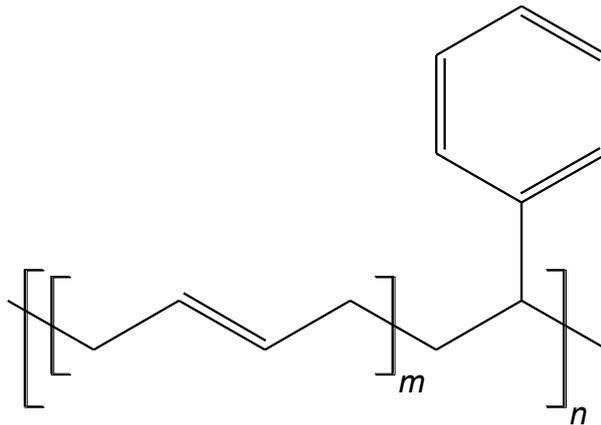
*Figure 3.* *The molecular structure of styrene butadiene rubber.*

The structure consists of m number of butadiene units per one styrene and this chain is repeated n times. The styrene content of the molecule can vary from close to 0 to 50%. Increasing the styrene content increases hardness but reduces abrasion resistance and worsens the dynamic properties. (Laurila 2007, pp. 53-56)

Acrylonitrile butadiene rubber (nitrile rubber) is a copolymer of butadiene and acrylonitrile. It has good oil and fuel resistance, moderate temperature resistance, good physical properties and low ozone and polar solvent resistance. The CRU of NBR is presented in Figure 4.
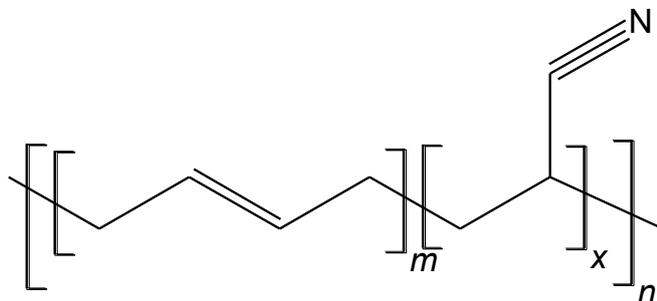


*Figure 4.* *The molecular structure of acrylonitrile butadiene rubber.*

The acrylonitrile content of NBR can vary from 18 to 51%. The acrylonitrile content influences the polarity of the rubber and the low temperature flexibility. Increasing the acrylonitrile content makes NBR more polar, and thus more resistant to oils and gasolines, but at the same time worsens the low temperature properties. The polarity of the rubber also affects how it may be compounded with other elastomers. The solubility of sulfur into NBR is worse than that of other common elastomers, so sulfur donors and more effective accelerators such as thiurams are often used. (Hofmann 1989, pp. 67-78; Laurila 2007, pp. 60-63)

Butyl rubber (IIR) is one of the oldest specialty rubbers. Its other name is isobutylene-isoprene rubber, which also yields the abbreviation. The CRU of IIR is presented in Figure 5.
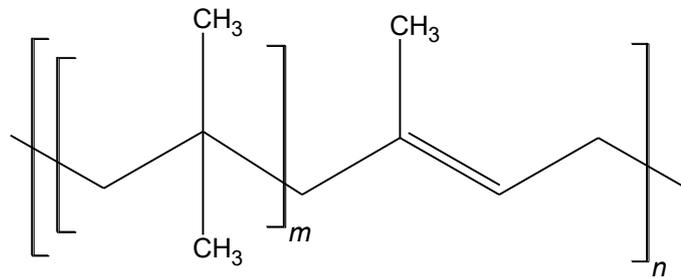


*Figure 5.* *The molecular structure of butyl rubber.*

IIR consists of isobutylene and isoprene molecules chained together. The content of isoprene is low, only about 0,5-3 mole%. In IIR, the isoprenyl units are mainly in the *trans*-configuration. The function of isoprene in the structure is to provide unsaturation to enable sulfur vulcanization. Due to the low unsaturation, IIR vulcanizes slowly and requires fast accelerators. The low levels of unsaturation give IIR extremely good resistance to weathering, ozone degradation, heat and chemicals. The structure also gives IIR very low gas permeability, which is a required property in certain applications. (Hofmann 1989, pp. 88-91)

Bromobutyl rubber is a derivative of IIR, obtained by reacting IIR with bromine. The structure of BIIR is like IIR, with the bromine affecting only the isoprenyl units. The reaction with bromine can yield different kinds of structures which are presented in Figure 6. (ExxonMobil)
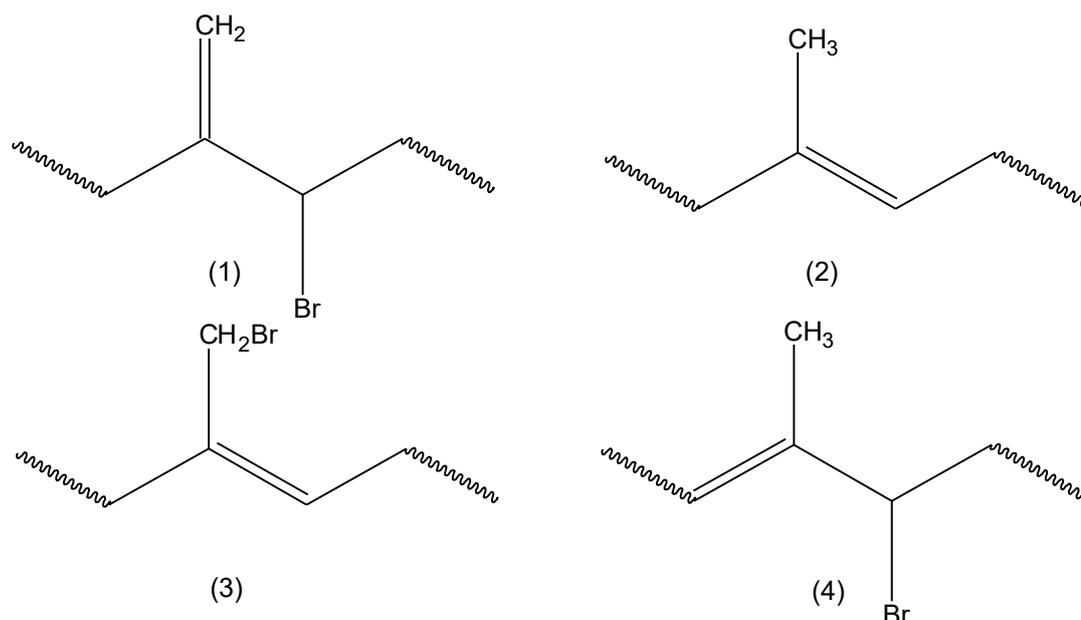
*Figure 6. The molecular structure of isoprenyl units in bromobutyl rubber.*

All these structures are present in the BIIR chains, but in different proportions. The structure distribution is the following: (1) 50-60%, (2) 30-40%, (3) 5-15% and (4) 1-3%. The amount of the isoprenyl units in BIIR is the same as in IIR. The halogenation improves the cure reactivity compared to IIR. The vulcanization rate, state of cure and co-vulcanization with other diene rubbers all improve due to the allylic halogen structures (1) and (4). The properties of BIIR are quite like IIR, except that they are enhanced. BIIR is especially useful for products which require low permeability to gases and liquids, for example hoses, seals and membranes. (Hofmann 1989, pp. 92-93; ExxonMobil)

## 2.1.2  Fillers

Fillers are important for rubber products and the biggest reason to add them is to improve the strength of the products, especially for synthetic rubber, which is not strong by nature. There are different types of fillers and they can be divided into active and non-active fillers depending on their role. The role of active fillers is to improve the properties of the vulcanizate and the role of non-active fillers is to reduce costs of final products. The most used fillers are carbon black, silica, calcium carbonate and clay, of which carbon black is by far the most important. Most carbon black is manufactured by the oil furnace process, in which oil is fed to a reactor and burned with gas and then quenched with water. The process can be tuned and different kinds on carbon blacks can be produced. (Laurila 2007, pp. 41)

There is a variety of different carbon blacks, which differ by their particle size, size distribution, structure and surface activity. The primary particles of carbon black are paracrystalline and they form clusters which are called aggregates. These aggregates are the smallest dispersible units of carbon black and they in turn form agglomerates which

make up the structure of the carbon black. Carbon black also contains small amounts of other functional groups besides carbon. Its surface can contain for example phenol, quinone, carboxyl and hydrogen groups. These functional groups are essential for the carbon black to bind itself into the elastomer chains. The adsorption of elastomer to the surface of carbon black is both a physical and a chemical process, so it depends both on the effective surface area and surface chemistry of the carbon black.

The carbon blacks used in rubber production have different numbers designated by the ASTM International. There are two different series, the N series which contains normal curing blacks and the S series which contains slow curing blacks. The number represents particle size range, with increasing size as the number increases. The numbers range from 100 to 900 and for example N550 is a commonly used medium to coarse range carbon black.

Carbon black is not always the choice of filler for rubber products, especially if the goal is to make products of other color besides black. Silica is the most important non-black filler and its properties are the closest to carbon black. The properties of silica beat carbon black in certain tire functions, but it is more expensive and harder to process. The main problem with silica is that it is hydrophilic, compared to elastomers which are hydrophobic. The result is that silica tends to agglomerate and the dispersion in rubber is not good. This effect can be overcome by using silane coupling agents, which chemically modifies the surface of silica to improve its effectivity.

Calcium carbonate and clay can work both as reinforcing or just a cost reducing filler. They are both available in different particle sizes, where the smaller particles are reinforcing and the larger are not. The particle sizes obtained depend on the way of production. Calcium carbonate and clay can also be treated with silane to improve the reinforcement. Other types of white fillers are also available, but their purpose is mainly to reduce the costs of the final products, not improve the properties. (De & White 2001, pp. 131-162)

### 2.1.3  Vulcanization system

The vulcanization system includes the chemicals which are required for the vulcanization to take place. The vulcanization system determines the way the elastomer chains are cross-linked to one another and it has a decisive role regarding the end properties of the products. There are different types of vulcanization, of which accelerated sulfur vulcanization is by far the most common and widely used method. Other vulcanization methods include peroxide, metal oxide and resin vulcanization.

In sulfur vulcanization the elemental sulfur rings open and form sulfur bridges of different lengths between the elastomer chains. Vulcanization with only elemental sulfur is a slow

process, which can take hours. To speed up this process, different vulcanization accelerators and activators are used. The role of accelerators is to reduce the time and temperature required for the vulcanization. Accelerators modify the scorch time, speed of reaction and the final extent of vulcanization. Activators improve the functioning of the accelerators and increase the final cross-linking density of the products. The most common activators used are zinc oxide and stearic acid. Zinc will form an active complex with the accelerator, which speeds up the sulfur vulcanization. Stearic acid is added to form a salt with zinc to make the zinc more soluble in rubber and help with dispersion. A typical vulcanization system for rubber consists of elemental sulfur, one or two accelerators, ZnO and stearic acid. Sulfur vulcanization and the chemistry related to it will be discussed in chapter 4. (De & White 2001, pp. 167-184; Laurila 2007, pp. 84-98)

Peroxide vulcanization requires organic peroxides, which decompose at high temperatures and initiate the crosslinking in the rubber. Peroxides have a general structure R-O-O-R, where R is an organic group. Metal oxides, such as MgO and ZnO can be used to vulcanize halogenated butyl rubber. Phenolic resins can be used to cure diene rubbers. The cross-links formed by the different types of vulcanization are presented in Figure 7.
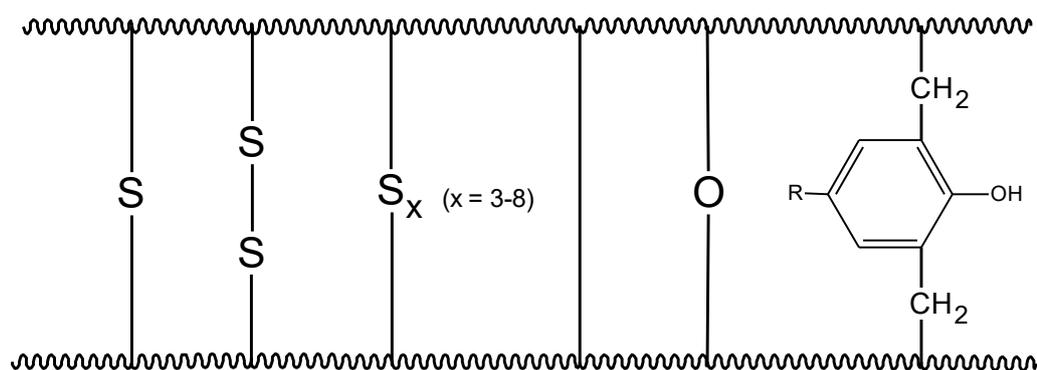


*Figure 7.* *Simple molecular structures of different types of rubber cross-links.*

Sulfur vulcanization can form mono-, di- or polysulfidic cross-links which have different kinds of properties. These links are formed between unsaturated carbon atoms. Peroxide vulcanization happens through a radical reaction, so it can be used to vulcanize saturated molecules as well and the result is a carbon-carbon bond. In the metal oxide reactions, the cross-link is formed due to the reaction between the halogen and metal oxide. The resulting cross-link can either consist of a carbon-carbon bond or an oxygen. In resin vulcanization the reactions happen in a similar way as with sulfur rubber and the resulting links are formed from the phenolic compound. (Laurila 2007, pp. 84-98; Coran 2013)

The sulfur vulcanization systems can also be categorized into different systems, called conventional vulcanization system (CV), efficient vulcanization (EV) and semi-EV. These systems differ by the amounts of sulfur and accelerator and their ratios. The CV system typically contains about 1,5-2,5 phr of sulfur and 0,5-1,0 phr accelerator. If the accelerator amount is increased, the sulfur amount must be lowered to achieve the same

cross-link density. This way the system is shifted from a CV to an EV system. In a CV system the sulfur to accelerator ratio is over one and in an EV system it is below one. The semi-EV system lies in between these two. In an EV system, the sulfur content can be reduced more by using a sulfur donor. It is a compound, which can donate sulfur to form cross-links. There are also chemicals, which can function both as an accelerator and a sulfur donor. The different vulcanization systems yield different kinds on cross-link structures. The CV system gives mainly polysulfidic cross-links and the EV system gives mono- and disulfidic structures. These different structures also result in different vulcanizate properties. In general CV systems give better strength and EV systems give better heat and reversion resistance. This is due to the shorter sulfur cross-links, which do not break as easily as longer chains. (Hofmann 1989, pp. 221-233)

Sometimes the tweaking of the vulcanization system with the vulcanizing agents and accelerators is not enough and retarders or premature vulcanization inhibitors (PVI) must also be used. The ideal PVI works so that it improves the scorch resistance of the compound, without slowing the rate of vulcanization too much. (Coran 2013)

## 2.1.4 Stabilizers

Diene rubbers are susceptible to degradation by heat, oxygen and ozone due to their unsaturated structure. This raises the need to protect and stabilize rubber to maintain its performance over time. The factors which affect rubber degradation are heat, heavy metal contact, sulfur, light, moisture, dynamic fatigue, oxygen, ozone and exposure to oils or solvents. Ozone is especially harmful for diene rubbers. Ozone can attack the double bonds and cause cracking in the rubber. The reactions between ozone and a double bond are presented in Figure 8. (Ohtake 2007)
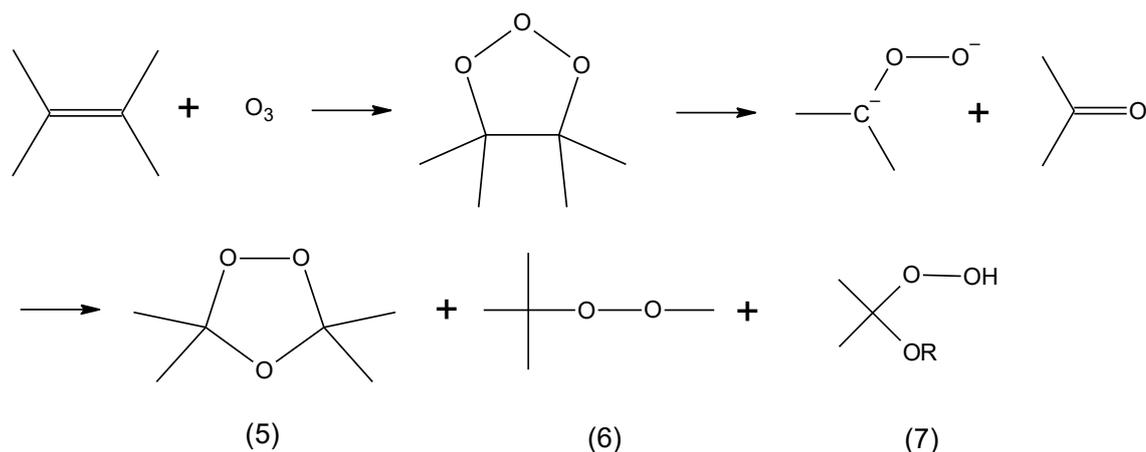


*Figure 8.* *The reaction between ozone and a double bond.*

First the ozone attacks the double bond and forms an ozonide. The ozonide is unstable, so it will break, giving an aldehyde or a ketone and a zwitterion. The zwitterion can be stabilized by three different ways. Most likely it will recombine with the aldehyde or ketone, forming a stable ozonide (5). It can also form a polymerizable peroxide (6). Third, it can also form a hydroperoxide (7) in the presence of a correct solvent. In all the cases, the attack results in scission of the polymer chain. A rubber surface contains minor flaws, which can act as starting points for ozone cracking. The cracking is increased, when the rubber is elongated, so the higher the elongation, the faster and worse the ozone damage will be. When the elastomer chains are broken, the chain ends retract from stress and this causes the signature ozone cracks. (Ohtake 2007)

The lifetime of a rubber article can be affected by choosing the correct elastomers, cure system and stabilizer system. Saturated and peroxide cured rubbers tend to perform better over time, so diene rubbers especially require stabilizers. The oxidation in a rubber has two main mechanisms, cross-linking and chain scission. In cross-linking the polysulfidic network breaks into shorter cross-links which increases hardness, stiffness and reduces fatigue resistance. In chain scission the elastomer chains break which causes softening and decreasing tensile properties. (De & White 2001, pp. 185-193)

There are different criteria which can guide the choice of anti-degradant chemicals used in rubber products. These are: discoloration and staining, volatility, solubility, stability, optimal concentration and the health and safety. Anti-degradants can be divided into different types, which are non-staining antioxidants, staining antioxidants, antiozonants and waxes. When used in a carbon black filled product, staining is often not an issue regarding the color of the product, unless the chemical can cause staining by touch for example when the material comes into skin contact. Antiozonants are required in products, which are susceptible to ozone attack under deformation. They function by migrating to the surface of the rubber and react with the ozone, protecting the rubber itself below. Waxes can also be used for ozone protection, but they function in a different way. They also migrate to the surface and they form a barrier and offer physical protection. Waxes and antiozonants are often used together, as waxes help the antiozonants to migrate to the surface. Waxes come in two main types, paraffinic and microcrystalline, which function best in different temperatures. Waxes can only be used in static conditions, where the protective film stays intact. (B. Rodgers & Waddell 2013)

## 2.1.5  Other ingredients

This category fits other ingredients, which are not part of the previously mentioned categories. The other ingredients include oils, plasticizers, peptizers, resins and pigments. The role of oils and plasticizers is to improve the processability of the rubber, make it softer and reduce overall costs. Oils consist of aromatic, naphthenic and paraffinic oils, which are categorized by the most common structure of an oil. Plasticizers include esters, polyethylene waxes, tars and factices.

Peptizers are used to chemically masticate elastomers. They lower the molar mass and thus the viscosity of the elastomers. They either speed up the oxidation of the elastomer chains or work as radical acceptors to prevent recombination of chains. Different kinds of resins can also be added to rubber. The resins can function as processing aids, tackifiers or curing resins. Pigments are used in rubber, when there is a need to produce colored compounds. (De & White 2001, pp. 198-203; B. Rodgers & Waddell 2013)

## 2.2   Rubber mixing

The purpose of rubber mixing is to combine all the required rubber ingredients into a homogenous compound and to modify the viscosity of the mixture to a desired level. Mixing is a complex process and can be done in various ways. During the mixing there are actually three different processes, which go on at the same time. These are incorporation, dispersion and distribution. Incorporation means combining the separate materials into a uniform mass. In dispersion, the agglomerates are broken into smaller pieces and squeezed into the rubber matrix. In distribution the mass is homogenized, and the components are spread evenly into the rubber.

In practice the rubber mixing process includes weighing of the materials, mixing and after treatment. In large volume production the weighing is an automated process and the large volume chemicals often come from silos straight into the mixing machine.

There are three types of mixing machines, which are used. These are two-roll mills, internal mixers and continuous mixers. A two-roll mill consists of two rolls next to each other, which rotate in opposite directions. The rolls have water circulating in them, which can be used to control the temperature. Two-roll mills are nowadays seldom used for the complete mixing process, except in a laboratory or otherwise for small batches. They can also be used as secondary mixers to add curatives into compounds.

Internal mixers are the most common machines used for rubber mixing. The rubber ingredients are dropped through a feeding door into the mixing chamber, which contains two rotors. A ram presses down the rubber and hold pressure in the chamber. When the mixing is ready, the discharge door at the bottom of the machine opens and discharges the rubber batch. There are two main types of rotors, tangential and intermeshing rotors. The rotors are shaped differently and thus the forces and mixing are a bit different in the machines. The shear forces are higher and dispersive mixing is better with tangential rotors and the distributive mixing is better with intermeshing rotors. The machine sizes can vary from small laboratory scale machines with batches of just a few kilograms up to large industrial machines which can hold hundreds of kilograms of rubber.

Rubber mixing is often a batch process to make sure that the compounds are uniform, and the ingredients are in the correct ratio according to the recipe. Certain rubber compounds can also be mixed in a continuous process, for example with an extruder. The difficulty

with this process is that it requires free flowing ingredients in the form of granulates or powders and they must be processed into this form before use.

Rubber mixing can be done in several phases, where for example first all other ingredients are mixed together except for the vulcanization system. This mixture is called a masterbatch. Then the vulcanization system is added to the masterbatch to produce the final rubber compound. This is done to prevent the compound from gaining excess heat history and causing scorch issues.

After the mixing, the rubber compound must be treated and sent for the next processing stage. There are two general ways to process the mixed compound, either two-roll mills or batch-off extruders. The idea is that the rubber is dropped from the mixing machine straight onto a mill or an extruder, where it is processed some more and formed into a band. The band is applied with an anti-tack agent, cooled and then packed into rolls or boxes, which are then used to make products. (Laurila 2007, pp. 107-128)

## 2.3   Forming

After the final rubber compound has been mixed to the desired composition, it will be formed into the shape of the final product. The main forming processes are mold working, extruding, calendering, latex dipping and casting. Mold working is the most common process and it can be used to make complex shapes. The different types of mold working are compression molding, transfer molding and injection molding. These differ on how the raw rubber is placed into the mold and how complex shapes can be achieved. Overfill is common and essential for all molding types. It ensures that the molds will be filled properly, but it also generates material loss.

Extrusion can be used to manufacture products with a certain cross-sectional profile, for example hoses. The rubber is fed into an extruder screw, which feeds it into a die, which determines the profile of the product.

Calenders are machines consisting of several rolls, which are used to make rubber into a thin sheet or film. They are also used to coat textiles with rubber, to be used as a reinforcement for example in hoses. Calenders can consist of two to four rolls, depending on the need and wanted end product.

Latex dipping is used to make thin rubber products, such as protective gloves or condoms. The mold is dipped into rubber latex and rubber coagulates on the surface of the mold. This process can completely automated.

Casting can be used to make products from liquid ingredients. Examples of these are polyurethane elastomers and silicones. The final compound consists of at least two components. These are mixed together in the mold and they react with each other forming the final structure. (Laurila 2007, pp. 129-179)

## 2.4   Vulcanization methods

After the rubber article has been formed into the wanted shape, it must be vulcanized so it will maintain its shape and gain the required properties. The vulcanization is closely connected to the forming process and sometimes they cannot be distinguished from one another. Vulcanization can be achieved in many ways but in general it requires heat and pressure.

Mold vulcanization is the most common type of vulcanization and it happens simultaneously with mold working. The rubber is pressed into the mold, which is heated and the vulcanization initiates. Sufficient pressure in the mold cavity is achieved by slight overfill. The scorch safety of products is essential here, as the mold must fill completely before vulcanization starts.

Extruded products are often vulcanized by a continuous vulcanization method, as vulcanization can be induced straight after the continuous product leaves the extruder die. Methods for this are for example hot air vulcanizing, salt bath vulcanizing and vulcanization by micro-waves. The continuous methods often do not include pressure, so this must be considered when choosing the recipe.

Another method which can be used for products, which are made on a mold, such as hoses or rubber gloves is vulcanization in an autoclave. An autoclave is a container, which is pumped full of hot steam to achieve a high pressure and temperature. (Laurila 2007, pp. 168-171)

After the product has been vulcanized, it is almost ready for use. Many products require some finishing, such as cleaning the excess material produced by mold overfill or cutting extruded products into desired lengths. The freshly vulcanized products are hot, so they need to be properly cooled and then they can be packed and sent to their destinations.

## 2.5   Technical rubber products

The designing of technical rubber products is a task which requires precision and time. The main factors which need to be considered are the chemical environment and the mechanical design. The circumstances which the product will face must be carefully investigated to be able to choose the correct ingredients for the product. These include the working temperature and fluctuations, contact with chemicals, mechanical stress and form of stress, which can be static or dynamic. The correct elastomer and other ingredients are chosen based on these demands. Also, the price and productional factors must be considered. There rarely is a choice of elastomer, which fills all the required properties and thus compromises must be made.

Teknikum Group Ltd provides solutions for wear and corrosion protection, hoses and assemblies for handling materials and liquids and customer-specific designed polymer products. Examples of technical rubber products made are fuel hoses, pipe coatings and mill linings. Fuel hoses are often made of NBR, which is the best choice due to its good oil and gasoline resistance. The polarity of NBR makes it a good electrical conductor, which is also important for a fuel hose to prevent spark discharge. Rubber coatings are used in cases where a maintenance free protection is required, such as pipes and containers in chemical plants. The rubber lining protects the structure of the containers from corrosion and wear. Halobutyl rubbers are ideal for these applications, as they have the lowest permeability levels and good chemical resistance. Mill linings are sacrificial wearing parts used in large mining mills. They are typically made of NR or SBR due to their ductility and good abrasion resistance. (Hofmann 1989, pp. 67-85; Laurila 2007, pp. 60-66; Teknikum Group Ltd)

These products were just a few examples of the vast variety of technical products which are made of rubber. They all face different environments, which require different designs and compounding.

# 3. HEALTH AND WORK SAFETY IN RUBBER PRODUCTION

The rubber industry uses a wide variety of different chemicals and machinery, which can affect the health of workers. The workers must be well acquainted with their work, know the possible risks and use the correct protective gear. The risks caused by exposure to chemicals is typical in the rubber industry and of interest regarding this thesis. Chemical exposure can happen throughout the rubber manufacturing process, from the mixing process until finishing the products. Long-term and recurrent exposure can also develop effects inconspicuously.

Dust, fumes and solvents are the most common things rubber workers are exposed to. Dusts arise from ingredients used in rubber production, mainly fine-grained fillers such as carbon black or talc. Fumes are produced when rubber is heated during mixing, processing and vulcanization. Solvents are used both as ingredients and in production to prevent tack in molds and to clean tools and work stations. It is necessary to continuously assess the risks related to different tasks and take the required measures to ensure safe working. Basic methods for controlling chemical exposure include for example substitution of certain compounds, containment of material, segregation of certain processes, improvement of ventilation and using personal protection equipment as the ultimatum. (Chaiear & Saejiw 2010)

There are many hazards produced by the different ingredients, but when assessing the risks of the complete manufacturing process, the substances created in the process must also be considered. This is a very complicated process, especially in the production of rubber, as there are various competing chemical reactions taking place, all of which are not even known. The important factor is to identify the substances which may cause possible harm and even more importantly, find out their quantities and where they are produced. When these factors are known, the right actions can be taken to avoid the exposure or prevent the creation of these substances completely.

Air monitoring is the most important way of providing information regarding the exposure of workers to chemicals. The ways of monitoring can vary according to the desired results. For example, detecting certain high concentration spots, individual employee exposure or complying with legal restrictions require different measurement types and set ups. Exposure to chemicals, which cannot be detected by people are often the most dangerous ones and can produce significant harm in the long run. The goal of companies is to continuously improve the safety of workers as this also positively affects the productivity in the long run. (Willoughby 2003, pp. 31-73)

## 3.1 REACH

Regulation, Evaluation, Authorization and Restriction of Chemicals (REACH) is a regulation set by the European Union in 2007 aiming at the protection of people and the environment. REACH defines the correct procedures on how to collect and assess the information regarding the properties and hazards of chemicals. The implementation of REACH also set up the European Chemicals Agency (ECHA), which manages the administration regarding REACH.

REACH places a responsibility on companies, as they need to recognize and control the risks which are connected to the chemicals they manufacture and market in the EU in order to meet the requirements set by the regulation. Companies must show ECHA how substances can be used safely, and they must inform about necessary measures to their customers. Companies must register the chemicals they produce and import in collaboration with others producing and importing the same substances. ECHA receives the registrations and the member countries of EU evaluate substances to settle the concerns regarding the safety of humans and the environment. Authorities and the special committees assigned by ECHA evaluate if certain risks are manageable. If risks cannot be managed, authorities can ban the use of certain chemicals. The allowed amounts of substances can also be restricted or make them subject to licenses. The long-term goal is to replace the most hazardous chemicals with safer alternatives.

According to REACH a company can have three roles: a manufacturer, an importer or a downstream user. Manufacturers produce the chemicals either for their own use or to be delivered to others. Importers buy substances from outside the EU. These substances can be either pure chemicals, mixtures or finished products. Downstream users handle chemicals in their activities and can also have responsibilities according to REACH.

The registration of substances is required if companies produce or import a chemical over one ton per year. The registration is based on one substance, one registration principle, which means that the producers and downstream users of a substance must provide the registration together. The registration also requires tests, which can raise the costs quite high, especially in the case of specialty substances, which are not used by many companies.

The implementation of REACH has brought three notable lists, which catalogue chemicals of different dangerousness. These lists are the REACH annex XVII, REACH annex XIV and substances of very high concern (SVHC). The annex XVII is the restricted substance list, which contains substances and their restriction conditions. The annex XIV is the REACH authorization list, which contains substances selected from the SVHC list, which can only be used or produced with authorization from ECHA. The SVHC list is a candidate list for authorization, and it is the first step for the restriction of the use of a chemical. A substance may be proposed as a SVHC if it meets one or more of the criteria

given by the Article 57 of REACH. These criteria are: the substance is carcinogenic, mutagenic or toxic to reproduction (CMR), the substance is persistent, bio-accumulative and toxic (PBT), the substance is very persistent and very bio-accumulative (vPvB) or there is evidence of similar concern regarding the substance. (ECHA - European Chemicals Agency)

REACH has already had a large effect on the rubber industry and it will continue to do so. The general trend is that the restrictions will get stricter and more ingredients will have to be replaced or their use limited. This will affect the properties of products and bring new challenges to the design of rubber products. The requirement for registration will also keep the variety of ingredients and the number of importers low.

## 3.2 Nitrosamines

Nitrosamines are the chemical compounds which contain the group >N-N=O. Most of these compounds are potential carcinogens and they are produced in the nitrosation reaction of secondary amines. Secondary amines are created as by-products in the vulcanization reaction with certain accelerators, so they give rise to the formation of nitrosamines. The nitrosamine of interest in this thesis is $N$-nitrosodimethylamine (NDMA) or dimethylnitrosamine, which can be produced from dimethylamine. The formation of NDMA is presented in Figure 9. (Goss et al. 2006; Alam et al. 2012)
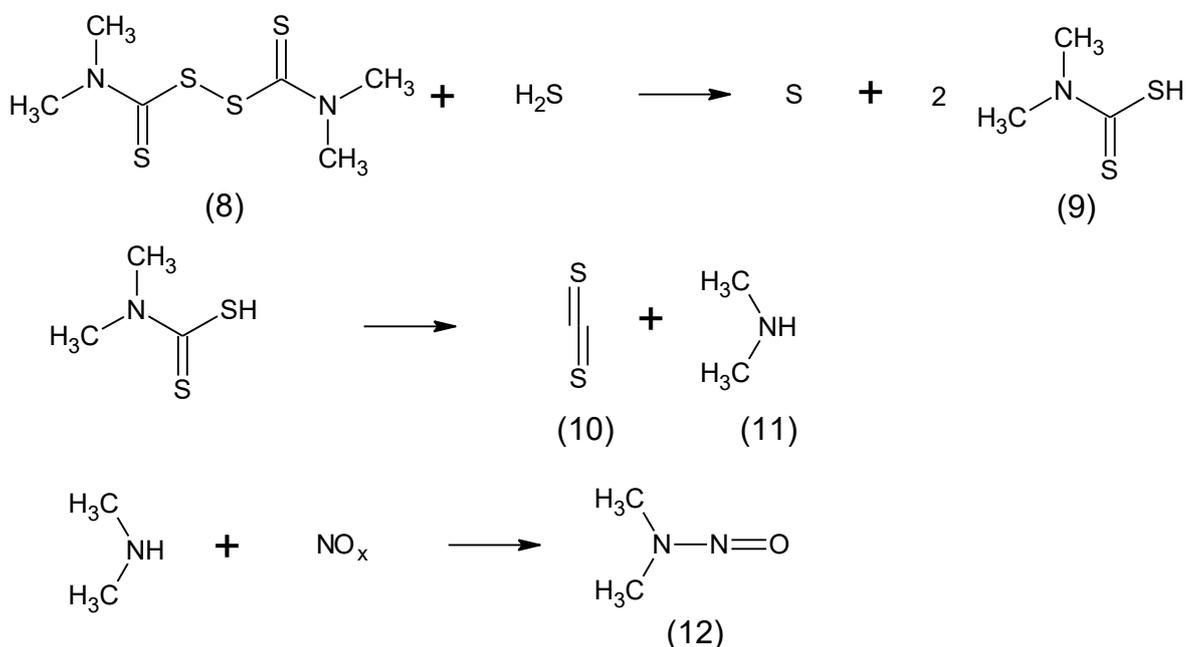
**Figure 9.** *Formation of dimethylnitrosamine in rubber vulcanization.*

When TMTD (8) functions as an accelerator, it will decompose in to dimethyldithiocarbamic acid (9). This thiocarbamic acid can decompose into carbon disulfide (10) and dimethylamine (11), which can undergo nitrosation under the right conditions and NDMA (12) will form.

Nitrosamines of this type have been found in rubber vapors and extracts and they can cause severe problems. NDMA has been classified as a Group 2A carcinogen by the International Agency for Research on Cancer (IARC). This classification means that the substance is probably carcinogenic to humans. (IARC) The formation of nitrosamines can happen with a variety of nitrosating agents, such as nitrous acid or different oxides of nitrogen. These are not always present in the rubber itself, and the formation of nitrosamines can happen during the production, storage or use of the products. (Willoughby 2003, pp. 39-45)

TMTD is not the only accelerator of concern regarding nitrosamines, although it is one of the most commonly used. All the compounds which contain secondary amine structures can possibly form nitrosamines in the presence of nitrosating agents. The accelerator classes, which possess these risks are dithiocarbamates, sulfenamides, thiurams and certain sulfur donors.

The methods to reduce or remove nitrosamine creation include the use of inhibitors, using accelerators which do not produce nitrosamines and using accelerators which produce non-regulated nitrosamines. Inhibitors are used in certain applications in the food industry, but they are not of significance in rubber production. The use of accelerators which do not produce nitrosamines could certainly be the safest option. However, the choice of the correct and suitable accelerator system is often the combination of many factors and completely ruling out certain accelerator classes narrows the possible choices. Choosing accelerators which produce non-regulated nitrosamines is based on the different molecular masses and reactivities of nitrosamines. Nitrosamines with larger functional groups and higher molar masses are less volatile and they will not readily migrate from the rubber matrix, tackling the issue. (Goss et al. 2006)

TMTD is not yet classified on any of the substance lists maintained by ECHA. Some countries like Germany and the Netherlands have set regulations on the amounts of suspected carcinogenic nitrosamines in work areas. They have also set regulations for nitrosamine and nitrosamine precursor amounts for rubber products. This is a likely world-wide trend and thus it is reasonable for companies to replace accelerators which produce hazardous nitrosamines with other alternatives. (Goss et al. 2006)

## 3.3   Regulations on using rubber as a food contact material

It has been established that rubber is a material, which consists of various ingredients. Some of these ingredients can possess risks for the environment or the safety of humans.

Due to its unique properties, rubber is used in several applications in the production and storage of food, such as hosing, seals and linings. The properties of rubber also give rise to possible problems. The easy mobility of elastomer chains also means that low molecular weight compounds can migrate from the rubber matrix rather easily and this could cause issues. Rubbers and especially diene rubbers are susceptible to degradation and this can cause possible reactions when in contact with food materials. The use of stabilizers prevents these reactions but on the other hand adds more chemicals which may migrate from the rubber. When rubber products are used in food applications, they must be carefully designed and regulated to prevent harm to humans. The effect on smell, taste or appearance of food products are also important factors. Even if a substance was otherwise harmless, it will not be usable in food contact materials if it affects these.

Different legislative bodies have produced regulations for food contact materials, which contain lists of substances which are allowed and their maximum amounts. Two commonly used regulations are provided by the United States Food and Drug Administration (FDA) and by the German Bundesinstitut für Risikobewertung (BfR). To gain approval, a product must be manufactured from the materials listed in the regulations and it must pass the required migration tests. The regulations have different limits and categories for different kinds of products, based on the area, time and temperature of the food contact with the rubber material. The recommendations provided by these regulations are not accurate legal norms, but they are still followed by many companies. When a product has been approved by such a regulation, it is a guarantee for both the producer and the downstream user that such a product is safe for use. These regulations protect people, but they also make the rubber product design more difficult, as the choice of ingredients is greatly reduced. (Forrest 2005)

# 4. VULCANIZATION

Vulcanization of rubber is a complex process, which is not completely understood. There are suggestions and predictions as to what could happen in the molecular level, but no precise knowledge. What is known and studied well, is the effect of vulcanization on the properties of rubber. These effects are presented in Figure 10.
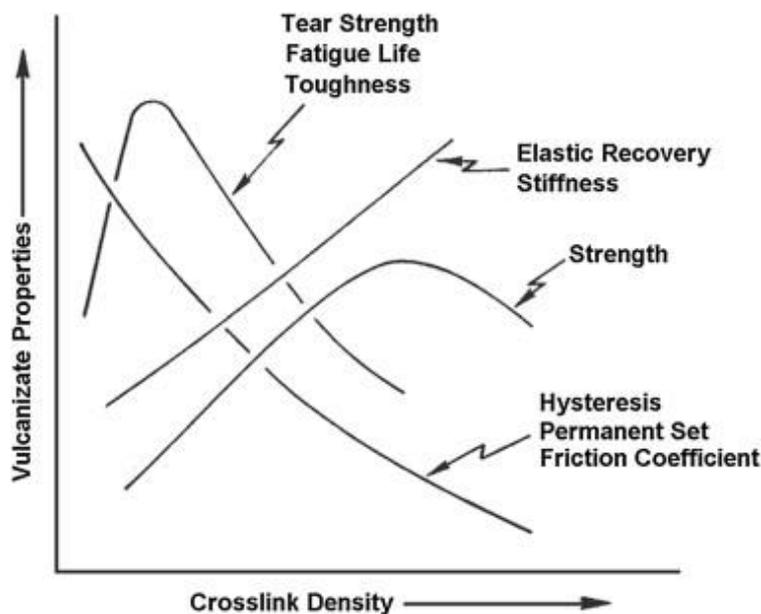


***Figure 10.*** *The effect of cross-link density on the physical properties of a vulcanizate. (Coran 2013, p. 339) (p. 339)*

Figure 10 shows that different physical properties go through large changes during the curing of rubber. These properties are not universal for all types of rubber compounds and the actual values depend on many things in addition to cross-link density, such as the elastomer, fillers and vulcanization system. For example, the tensile strength of a material increases while at the same time its maximum elongation decreases when the cross-link density increases. Thus, a compromise must always be found between these two properties. What is common for all products, is that the good flow properties and moldability are wanted during production and the final product must meet its standards. Thus, it is important that the vulcanization happens only after the rubber has been processed into its final shape. (Coran 2013)

The characteristics of vulcanization are often practically studied in a rubber laboratory by measuring the rubber's rheological properties on a Mooney viscometer or a rheometer. These tests give information on how fast and at which temperatures the vulcanization happens. The time before cross-linking initiates, rate of cross-linking, the final extent of cross-linking and the behavior after vulcanization can all be studied in a rheometer test. A typical curve given by a rheometer test is presented in Figure 11.
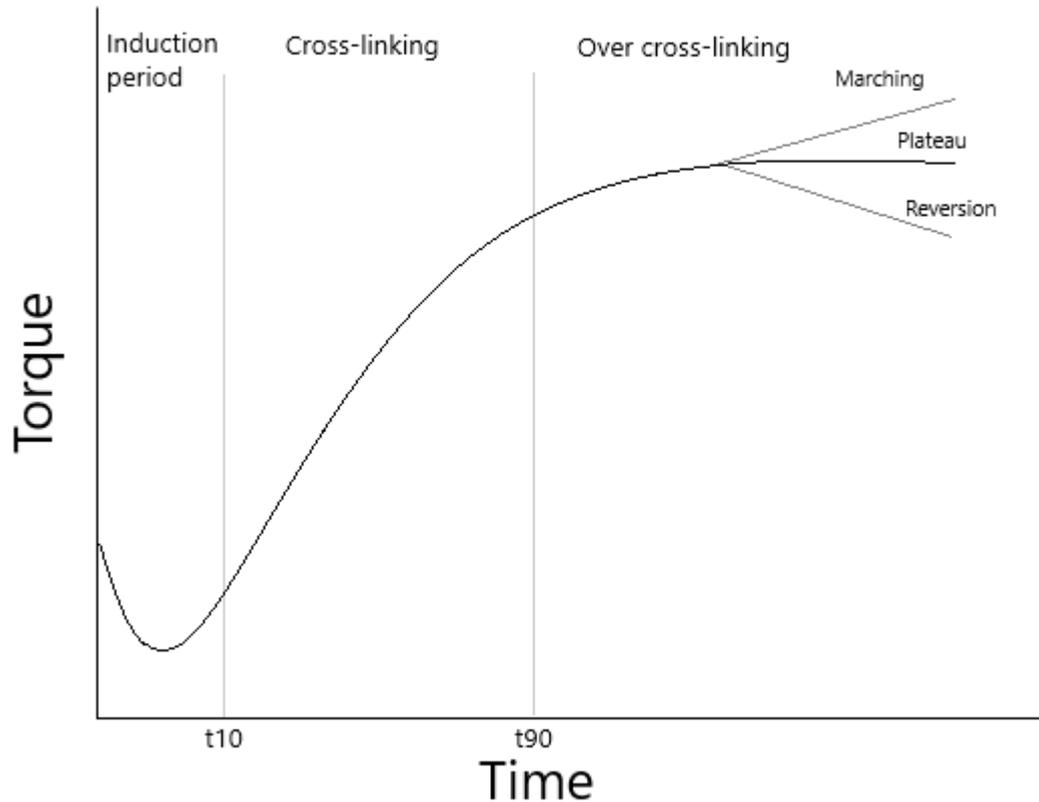
***Figure 11.*** *A curve produced by a rheometer test.*

The vulcanization process is divided into three stages in Figure 11. First is the induction period, also named as scorch time. This measures the compound's resistance to scorch, meaning how long it can be exposed to the processing temperature before the vulcanization starts. A long enough delay is required for forming, so the product can take its final shape before curing. The beginning of vulcanization can be determined from the torque starting to rise. The scorch time can have several determinations and one is time $t_{10}$, which is the time for the torque to increase by 10% of the difference between its minimum and maximum values.

The second stage is the curing, where the torque rises rapidly as the cross-links are formed. This phase is preferably fast to minimize the effective time in production. The optimum cure time is often defined as $t_{90}$, which is when the torque has increased to 90% of the difference between its minimum and maximum values.

These time values are important in the production of rubber, as a too short $t_{10}$ means that the vulcanization will initiate too early, leading to waste. Also, a too long $t_{90}$ means that the vulcanization will be long, and the production is not efficient. The vulcanization temperatures and times vary depending on the rubber compounds, vulcanization methods used, sizes, geometries and thermal conductivities of the products. For molded products, the temperatures vary from 150 °C to 200 °C and the times can range from just a few

minutes to over an hour. Certain specialty rubbers are also made which can vulcanize even in room temperature, but naturally this is a much slower reaction.

The third stage is over cross-linking or over curing and the aim is to get the product out of the mold and cool it fast to prevent unwanted phenomena. In ideal vulcanization, the torque value reaches a plateau at the end, as the vulcanization ends. Marching cure or reversion can also happen. Marching can result in a product that is too stiff and hard for the suggested use. Reversion is a result of thermal aging and often happens with rubbers with an unsaturated carbon backbone. Both effects need to be avoided, as otherwise the properties of the vulcanizate will deteriorate. (Coran 2013)

## 4.1   Research techniques for vulcanization

Vulcanization and the chemistry and mechanisms behind it can be studied using a variety of different methods, which together can give insight into the properties and structures of the vulcanized rubber. Examples of such methods include Model-Compound Vulcanization (MCV), thermoanalytical methods and different types of spectroscopy. MCV namely uses low molecular weight compounds, which are used to model the vulcanization of certain rubber molecules. The model compounds need to have similar functional groups as the example rubber compounds. MCV is good for determining certain reactions and the model compounds are often quite easy to analyze. A commonly used MCV is squalene, which is presented in Figure 12. (Nieuwenhuizen et al. 1997, pp. 370-381)
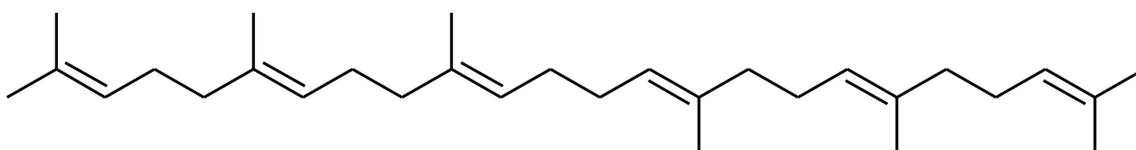


*Figure 12.*        *The molecular structure of squalene.*

Squalene has a repeating symmetrical structure and unsaturation in the chain, so it can be used to model a rubber chain when studying vulcanization. MCV is combined with other research methods to analyze the results. (Vidal-Escales & Borrós 2004)

Thermoanalytical methods, such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) can give information about the vulcanization process as a whole, but the effect of single ingredients and changes is challenging to measure.

Relevant spectroscopy methods for the researching of rubber vulcanization include infrared (IR) and Raman spectroscopy, Nuclear Magnetic Resonance (NMR) and X-ray diffraction. IR and Raman spectroscopy work best, when used complementarily, as both IR and visible light can be used to detect certain bonds and structures related to the vulcanization. NMR can be used to study the nature and concentration of chemical structures, which are formed during vulcanization. (Nieuwenhuizen et al. 1997, pp. 370-381)

As it can be seen from the variety of research techniques, it is not easy to find reliable data regarding the chemistry of rubber vulcanization. Data must be gathered in parts and interpreted correctly to make accurate and verified conclusions.

## 4.2 Accelerators

Vulcanization accelerators can be classified for example into the following categories: thiazoles, sulfenamides, guanidines, thiurams, dithiocarbamates, dithiophosphates, xanthates and other miscellaneous accelerators. The common feature in all chemicals which, can function as accelerators, is the presence of a tautomer. Most of the accelerators used contain the group -N=C-S-H. (De & White 2001, pp. 173-183; Laurila 2007, pp. 84-98) The most common groups of accelerators and their general structures are listed in Table 2.

***Table 2.***     *The most common vulcanization accelerators.*

| Accelerator type | General structure |
|---|---|
| Thiazole |  |
| Sulfenamide |  |
| Guanidine |  |
| Thiuram* |  |
| Dithiocarbamate |  |
| Dithiophosphate |  |
| Xanthate |  |
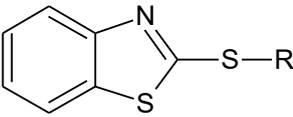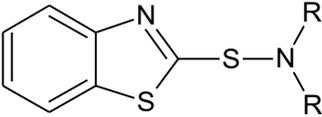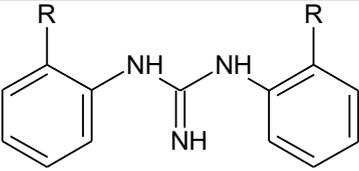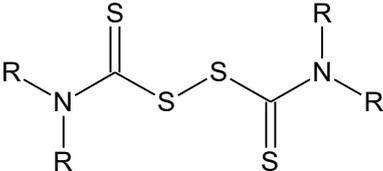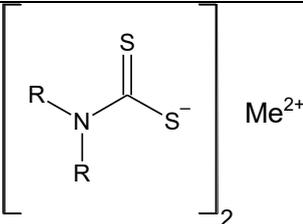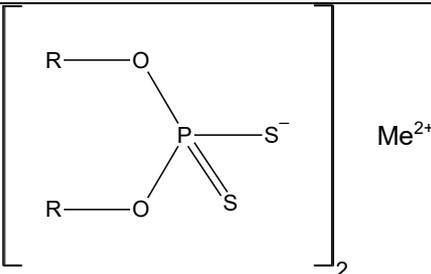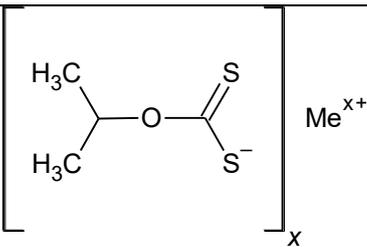
*The sulfur bridge length in thiurams can vary.

The R groups in the molecular structures can be any atoms or functional groups and the Me are metal ions, such as $Zn^{2+}$. The categorization of these accelerators is not always similar, as for example thiazoles and sulfenamides can be interpreted as the same class, originating from the most basic thiazole, 2-mercaptobenzothiazole, MBT (where R = H in the structure). Thiurams and dithiocarbamates are related in the same way, as thiurams are produced by oxidizing the dithiocarbamate salts. Their relation can also be seen in the acceleration speeds. They function in a similar manner, but dithiocarbamates are faster, as thiurams need to first decompose into the dithiocarbamates before they can function as accelerators.

Accelerators are also often categorized as primary or secondary accelerators. Primary accelerators generally provide a moderate scorch time and medium cure rates. Secondary accelerators often provide fast or extremely fast cure times with little or no scorch delay. Thiazoles and sulfenamides are considered as primary accelerators whereas for example guanidines and thiurams are considered secondary accelerators. The division of accelerators is not always absolute, but in general primary accelerators can be used on their own and secondary accelerators are used in combination with primary accelerators. For example, the accelerator pair MBTS and TMTD studied in this thesis is a pair of a primary and a secondary accelerator. When certain secondary accelerators are used in combination with primary accelerators, they act synergistically, meaning that their combined effect is better than the simple addition of their individual effects. The synergy between these accelerators will be described more in section 4.3.3. (Ignatz-Hoover & To 2004; B. Rodgers & Waddell 2013)

## 4.3 Accelerated sulfur vulcanization

The basic reaction in the accelerated sulfur vulcanization of rubber is that the activators and accelerators form an active complex. This complex reacts with sulfur forming another complex, which then reacts with the hydrogen in the allylic position in the elastomer chain and forms an intermediate. Two different intermediates react together and form a sulfur cross-link between the elastomer chains. The exact reactions and intermediates present are not known for certain and unanimously, but there are several theories and propositions on what could take place. The basic reactions are presented in Figure 13. (Datta et al. 2006)

$$Acc—S-S—Acc \xrightarrow{\quad Zn^{2+} \quad} Acc—S—Zn—S—Acc \xrightarrow{\quad S_8 \quad}$$

(13)                    (14)

$$Acc—S—S_x—Zn—S_y—S—Acc \; + \; |—H \longrightarrow |———S_x—Acc$$

(15)                                         (16)

$$\longrightarrow |—S_x—| \xrightarrow[\text{Chain modification}]{\text{Shortening of cross-links}} \textbf{Final vulcanizate network}$$

(17)
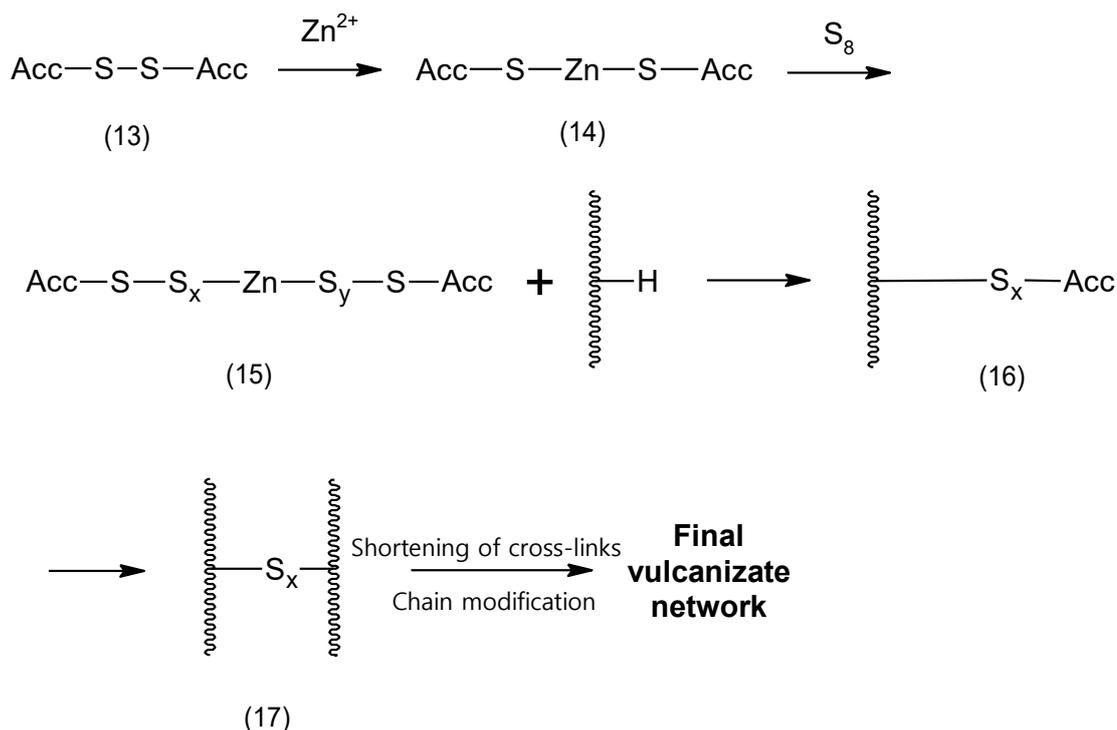
***Figure 13.***      *Schematic of basic vulcanization mechanisms.*

This schematic presents the basic reactions taking place in the accelerated sulfur vulcanization of diene rubber. Compound (13) is a general accelerator with a disulfidic bridge. First, the activator-accelerator complex (14) is formed, which then reacts with elemental sulfur to form an active sulfurating complex (15). The sulfurating complex substitutes an allylic hydrogen and forms a cross-link precursor (16). This cross-link precursor can then substitute another allylic hydrogen to form a cross-link (17). When the cross-link forms, a thiol group is released, which can form a new sulfurating agent and continue the cross-linking process. After the initial cross-links have formed, they can still go through some shortening or there can be modifications to the elastomer chains, such as isomerization. The resulting structure is the final vulcanizate network. (Datta et al. 2006)

Although the reactions taking place are not accurately known, several factors affecting the speed of vulcanization have been discovered. These include the number of double bonds, the polarity of the elastomer, the number of allylic hydrogens and the free volume in the elastomer. The number of double bonds and allylic hydrogens are clearly linked, and it can be deduced that increasing the number of reactive sites also increases the rate of reaction. This can be seen for example when comparing the sulfur vulcanization of NR and IIR. Polarity also increases the reactivity and thus vulcanization rate. (Laurila 2007, pp. 84-93)

These general examples are simplifications of the reactions taking place in the accelerated sulfur vulcanization of diene rubber. To better understand how specific accelerators work,

they need to be examined more carefully on their own and when they are working together in different rubber compounds.

## 4.3.1  Dibenzothiazyl disulfide

MBTS is one of the most commonly used accelerators. MBTS is useful when a good scorch time is required. It has delayed start, which is due to MBTS first having to thermally decompose into MBT, before it can function. The cross-link formation with MBTS is presented in Figure 14. (ExxonMobil)
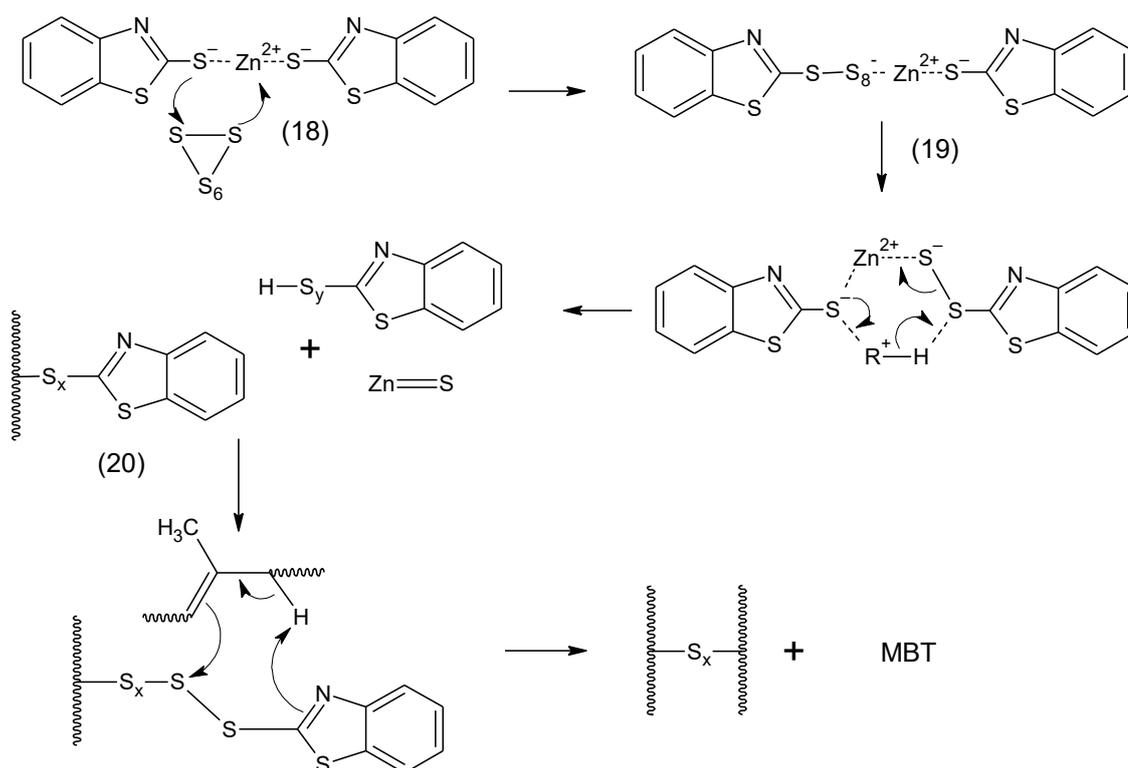


*Figure 14.*        *Vulcanization acceleration mechanism for MBTS.*

MBTS will first form a zinc complex (18), which will then form a sulfurating complex (19) and then a cross-link precursor (20). The cross-link precursor can substitute an allylic hydrogen, and this forms the polysulfidic cross-link. The R in Figure 14 is used to represent a rubber chain to make the structures simpler.

## 4.3.2  Tetramethylthiuram disulfide

TMTD can function both as a vulcanization accelerator and a sulfur donor, which makes it a versatile choice in rubber compounds. As an accelerator, the possible mechanism is like the general mechanism presented earlier. The mechanism is depicted in Figure 15. (ExxonMobil)
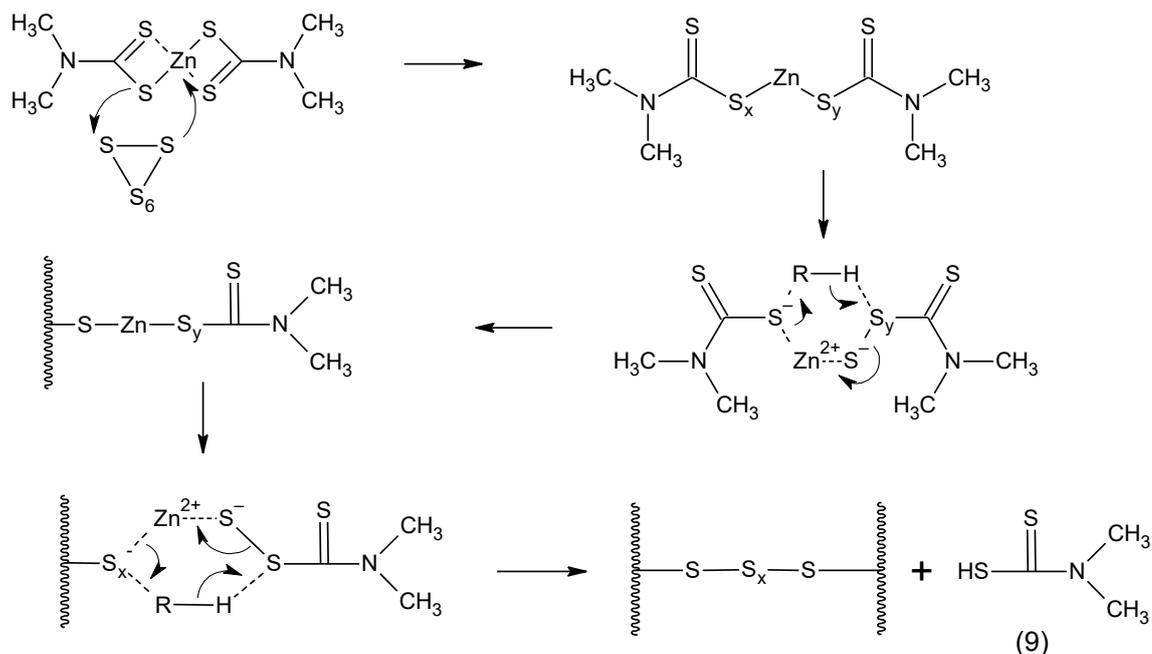
**Figure 15.** *Vulcanization acceleration mechanism for TMTD.*

TMTD will first form a zinc complex, which then reacts with elemental sulfur to form a sulfurating complex and then begins the cross-link formation. The reaction of ZnO is not completely known, but the zinc ion can cleave the sulfidic bond and forming a complex. The zinc can be present in both the activator-accelerator complex as well as in the cross-link precursor. If the zinc is not present in the cross-linking precursor, then the acceleration will proceed in a similar way compared to MBTS. The compound which will be left over after the cross-link formation is dimethyldithiocarbamic acid (9). The formation of this compound and the formation of NDMA was presented in Figure 9, and is the reason for the hazardousness of TMTD.

What is special about TMTD, is that it can also function as a sulfur donor, meaning that vulcanization can occur at very low levels or even in the absence of elemental sulfur. The function of TMTD as sulfur donor is presented in Figure 16. (ExxonMobil)
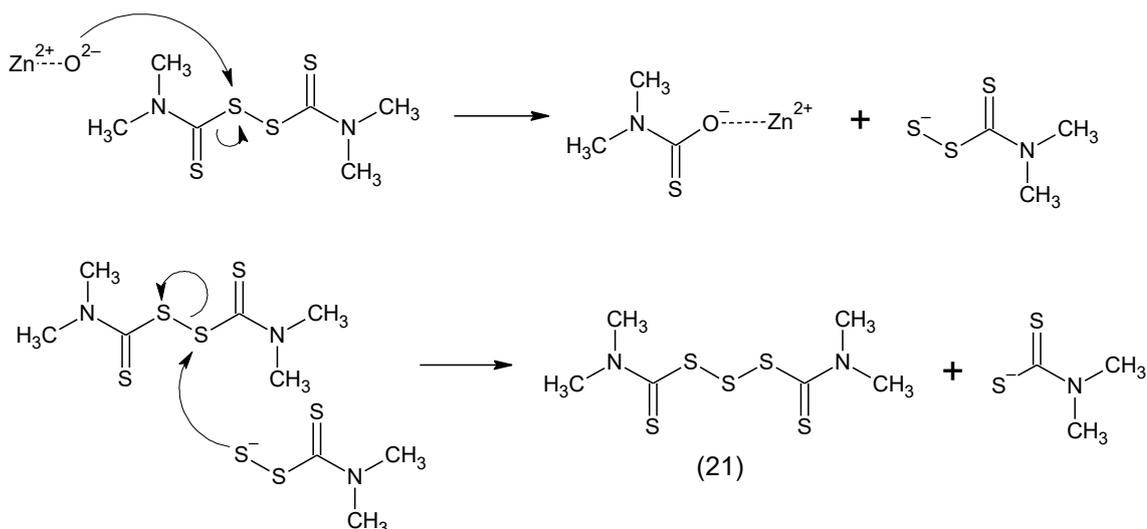
***Figure 16.*** *Mechanism for TMTD functioning as sulfur donator.*

In this mechanism, the sulfurating complex (21) is formed only from TMTD. This complex can then react further with ZnO and form cross-links the same way as before. The key factor here, is that the sulfur link consists of only three atoms, which means that the cross-links formed will be mono- or disulfidic already, without having to evolve.

## 4.3.3 Synergistic action of dibenzothiazyl disulfide and tetramethylthiuram disulfide

In addition to working as accelerators on their own, MBTS and TMTD also work synergistically. This means that together they work better than either of them would work on their own. Synergistic action is common for rubber accelerators and there are many different pairs, which present this kind of behavior. The synergy between MBTS and TMTD is depicted in Figure 17.
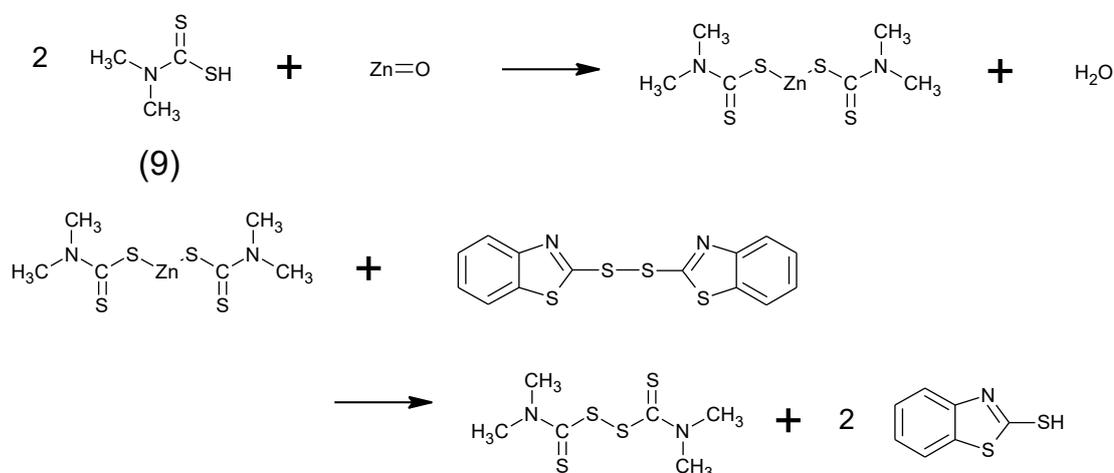


***Figure 17.*** *The recovery of TMTD through the synergistic action with MBTS.*

As was seen earlier in Figure 15, the resulting molecule from the vulcanization reaction with TMTD is dimethyldithiocarbamic acid (9). This molecule can however react with ZnO and MBTS to recover TMTD. At the same time in this reaction MBTS decomposes into MBT, which is required for the MBTS to function as an accelerator. Due to these reactions, the presence of both accelerators in the rubber compound speed up the vulcanization even more. This synergistic action allows this accelerator pair to vulcanize less active rubbers, such as BIIR. (Alam et al. 2014)

## 4.4   Metal oxide vulcanization of bromobutyl rubber

Halobutyl rubbers are special in a sense that they can be vulcanized by using only metal oxides. Zinc oxide is an important reagent here, as it can both act as an activator for sulfur vulcanization and a vulcanizing agent by itself. A proposed mechanism for the zinc oxide cross-linking of halobutyl rubber is presented in Figure 18.
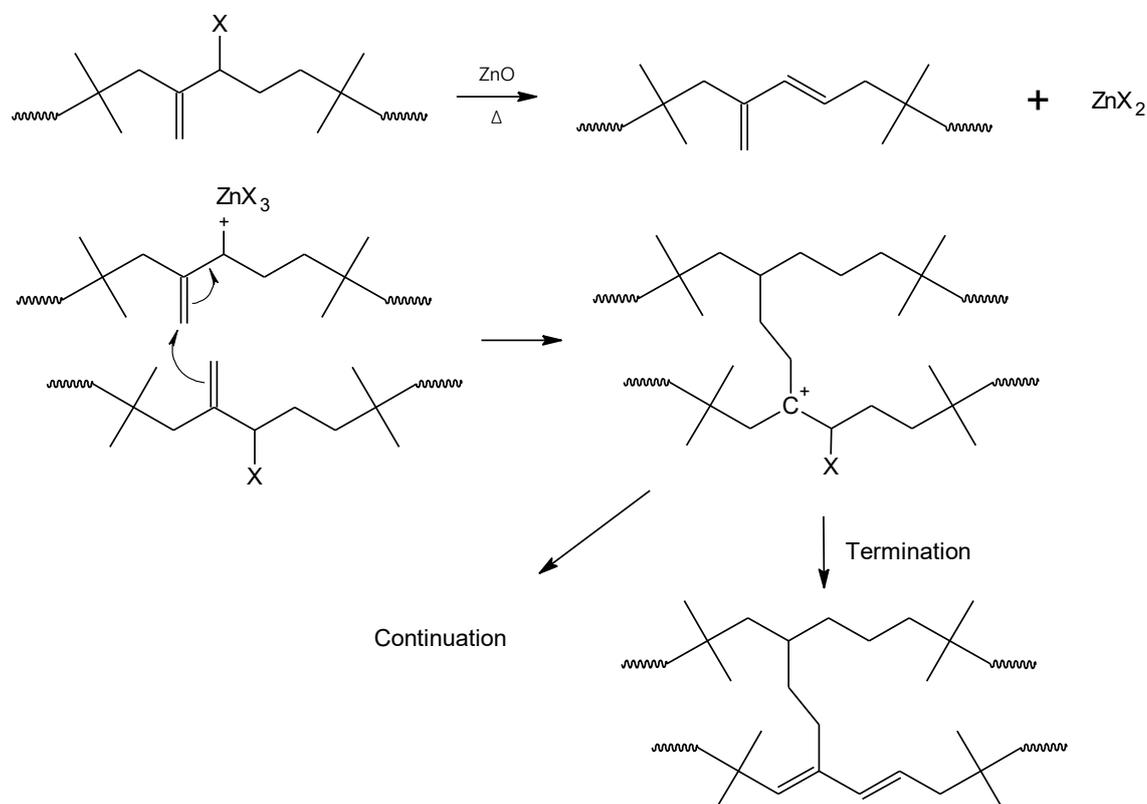


***Figure 18.***        *Zinc oxide cross-linking of halobutyl rubber.*

The zinc oxide will first form a zinc halide, which then catalyzes the cross-linking reaction. After the formation of a cross-link, the reaction can either continue in the same pattern or terminate. (Bayer Polysar Technical Centre - Antwerp 1992)

It is not clear, which vulcanization reaction will happen in BIIR, but it is probable, that both sulfur vulcanization and metal oxide vulcanization will take place in the presence of an accelerated sulfur vulcanization system.

## 4.5   Literature review of nitrosamine free alternatives

The previous sections described the function of the currently used accelerators MBTS and TMTD. They form a well-functioning accelerator pair. However, due to health and availability issues, there is a need to replace TMTD with another accelerator. The function of TMTD as an accelerator was presented in Figure 15, where dimethyldithiocarbamic acid is formed. Dimethyldithiocarbamic acid can decompose and form NDMA, as presented in Figure 9. This formation of NDMA is the reason for the hazardousness of TMTD. The studied rubber compounds are a mixture of NR/BIIR and a mixture of SBR/NBR, so all these different elastomers and their mixtures need to be considered when the accelerator system is chosen. The chosen accelerators need to be fast and efficient and compatible for all the rubber types. The synergy performed by MBTS and TMTD is a great feature, which should be mimicked and pursued when choosing the new accelerator system.

There are several different methods to get rid of the regulated nitrosamines in rubber products. The rubber compounds examined in this thesis are sulfur accelerated compounds and thus the alternatives investigated were all sulfur vulcanization accelerators. There are two main ways to get rid of the regulated nitrosamines in rubber, either using accelerators which do not produce nitrosamines, or using accelerators, which produce non-regulated nitrosamines, which are considered safe. Accelerators, which do not produce nitrosamines and could be used, include dithiophosphates, xanthogens, xanthates and alkylphenol disulfides. If there is a desire to keep the same type of an accelerator, then other dithiocarbamates and thiurams can be considered. These accelerators will also produce nitrosamines, but the key is that the nitrosamines produced are not harmful or they cannot migrate from the rubber matrix. (Goss et al. 2006; M. B. Rodgers et al.)

The different alternatives for TMTD were investigated using available literature. The found results and accelerator choices are discussed in the following sections.

### 4.5.1   Dithiophosphates

Dithiophosphate accelerators chemically resemble the structure of dithiocarbamates, so they could be used to replace dithiocarbamates in some situations. However, they are much slower and more expensive than dithiocarbamates, so their use is not preferred. Accurate test results related to the rubber compounds discussed here were not readily found. (Hofmann 1989, pp. 254-255; Goss et al. 2006)

### 4.5.2   Xanthogens and xanthates

Xanthogens resemble structurally the xanthate accelerators, which were introduced earlier in Table 2. Xanthogens and xanthates are related in the same way as thiocarbamates

and thiurams are, as xanthogens are formed by oxidizing the xanthate salts. Xanthate accelerators are ultra-fast accelerators, which function in lower temperatures than other accelerators. They are often used in the vulcanization of natural rubber latex. The use of xanthates in the vulcanization of butyl and bromobutyl rubber has also been investigated, due to their high reactivity. Xanthates and xanthogens do not exhibit synergistic action with MBTS, but they could still be used to vulcanize BIIR. When they are used in other, more actively vulcanizing rubbers, they cause problems with scorch safety. Also, reversion can become an issue with the fast curing rates in all the rubber types discussed here. (Goss et al. 2006; Tambe et al. 2007)

### 4.5.3 Alkylphenol disulfides

Alkylphenol disulfides are a class of rarer polymeric accelerators, which consist of phenolic groups with an alkyl group in the para-position, which are connected to each other with disulfidic links. An example of an alkylphenol disulfide accelerator is Vultac TB710, which is a para-*tert*-butylphenol disulfide polymer containing 10% of stearic acid. The molecular structure of Vultac TB710 is presented in Figure 19.
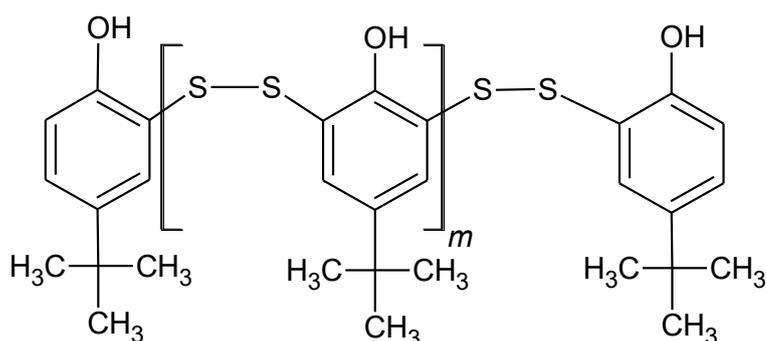


***Figure 19.***      *The molecular structure of Vultac TB710.*

The cross-links formed with alkylphenol disulfides will most likely consist of phenol sulfides, not only sulfur. These accelerators have been reported to be used with butyl rubbers with successful results. Studies of the vulcanization behavior also suggest that alkylphenol disulfides could exhibit synergistic effects when used with MBTS. Alkylphenol disulfides could also possibly function as sulfur donors in the vulcanization, which is also a promising feature. Although these compounds have shown promising results with IIR and chlorobutyl rubber, they can reduce the scorch times in BIIR. This issue could limit their use in BIIR compounds and needs to be tackled. (M. B. Rodgers et al.; ExxonMobil)

### 4.5.4 Dithiocarbamates and thiurams

Different kinds of dithiocarbamates and thiurams are the most studied alternatives for TMTD, which is natural as they have the same basic chemical structure. Examples of these include zinc dibenzyldithiocarbamate (ZBEC), tetrabenzylthiuram disulfide

(TBzTD), bis-(*N*-methyl piperazine) thiuram disulfide (MPTD), bis-(*N*-phenyl piperazine) thiuram disulfide (PPTD), bis-(*N*-ethyl piperazine) thiuram disulfide (EPTD), and bis-(*N*-benzyl piperazine) thiuram disulfide (BPTD). ZBEC is the only dithiocarbamate and its structure is almost like TBzTD, apart from the zinc atom located between the two sulfurs. Therefore, ZBEC is already in the activator-accelerator complex and the vulcanization will be faster. The downside is that ZBEC cannot function as a sulfur donor. The structures of ZBEC and the different thiurams are presented in Figure 20.



ZBEC                                          TBzTD

Bis-(*N*-R piperazine) thiuram disulfide
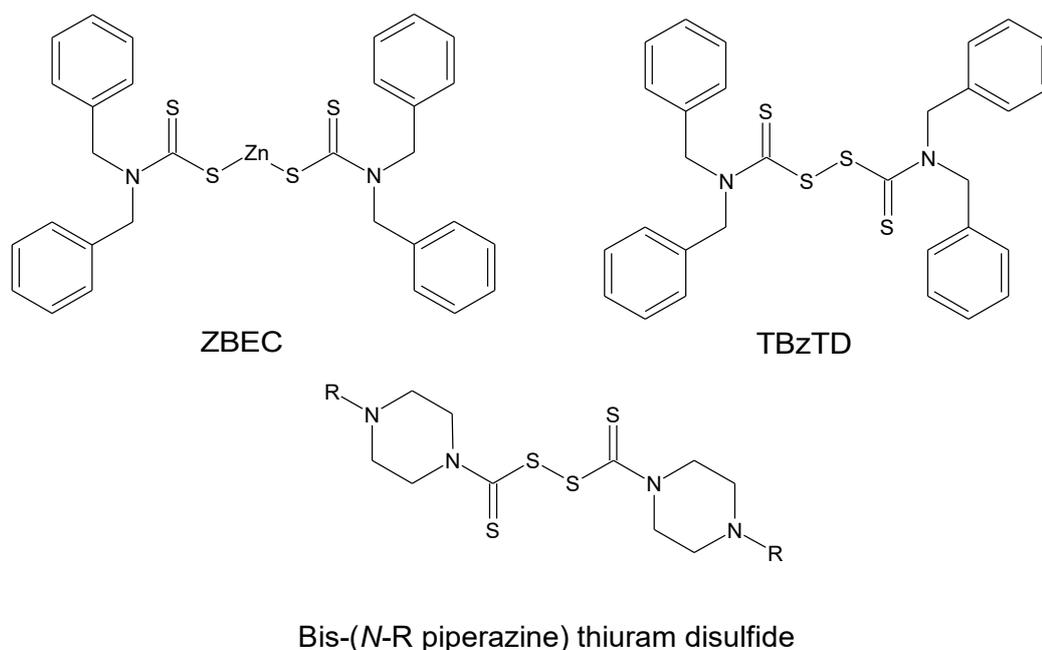
**Figure 20.**        *The molecular structures of ZBEC, TBzTD and other high molecular weight thiurams.*

The other investigated thiurams besides TBzTD are all based on the same structure, with only the carbon group (R) varying at the end of the piperazine group. The mutual feature in all these molecules is their significantly higher molar mass compared to TMTD and other common thiuram accelerators. This makes the created secondary amines less volatile and could cause steric hindrance. These accelerators have been reported as safe, so they could be considered as viable choices. (Goss et al. 2006; Alam et al. 2012; Alam et al. 2014) All these accelerators have been tested with NR and they have functioned quite well, producing similar results as the control compounds with TMTD. The piperazine accelerators have all been synthesized in the laboratory, so their industry scale use is currently not likely. The only accelerator of these that has been reportedly tested with butyl rubber is TBzTD, which also produced promising results according to (Desai & Sheth 2014) The thiurams used here have been combined mainly either with MBT, MBTS or *N-tert*-butyl-2-benzothiazyl sulfenamide (TBBS). (Ferrandino & Sanders 1996; Debnath & Basu 1996; Abhitha et al. 2013)

The secondary amine created from TBzTD is dibenzylamine, which has much lower volatility, higher boiling point and lower reactivity with nitrosating agents than dimethylamine. The boiling point of dibenzylamine is 300 °C and it decomposes before it reaches that, compared to 7.4 °C for dimethylamine. (Ferrandino & Sanders 1996; Willoughby 2003, pp. 41–45) The nitrosamine, which could be created in this case is *N*-nitrodibenzylamine (NDBzA) and its mutagenic potential has also been researched. Compared to NDMA, NDBzA is over 100 times less mutagenic. Combining the low incidence and reactivity of the preceding amine and the lower mutagenicity, TBzTD can be regarded as a safe alternative for TMTD. (Jiao et al. 1997)

### 4.5.5 Accelerators for laboratory testing

Based on the previous evaluation a few alternatives were chosen for laboratory tests. The dithiophosphate, xanthogen and xanthate accelerators did not show promising results in the studied articles. The issues with vulcanization rate were the main concern and thus they did not qualify for further consideration. (Goss et al. 2006; Tambe et al. 2007) Alkylphenol sulfides and thiurams on the other hand had more promising results, which should be investigated more closely. Alkylphenol disulfides possess risks concerning the scorch time, but due to possible synergistic action and sulfur donating capabilities they are still worth examining.

The benefits of thiurams for this compound are clear, as TMTD functions so well already, so applying another safe thiuram in the place of TMTD could provide the most secure and predictable results. As was mentioned earlier, the thiurams were combined with thiazoles or sulfenamides, so it is advisable to test both combinations. The structure of TBBS is presented in Figure 21.
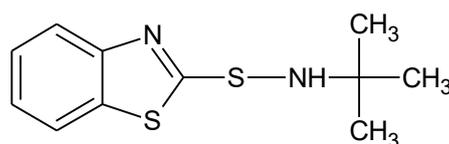


*Figure 21.*     *The molecular structure of TBBS.*

When this structure is compared to the structures of MBT and MBTS, which have been presented earlier, it is clear that all these accelerators are based on the same basic thiazole structure. They have all been reported to function in a similar manner, retarding the start of the vulcanization and exhibiting synergistic action with thiurams. (Hofmann 1989, pp. 246-248; Debnath & Basu 1996)

The two rubber compounds studied in this thesis have different requirements, so also different accelerators were chosen for the testing. The first compound was a mixture of NR and BIIR which is denoted as compound A. The second compound was a mixture of SBR and NBR which is denoted as compound B.

Due to good availability and most promising results, TBzTD was chosen as a thiuram test accelerator for compound A. TBzTD has a much higher molecular weight than TMTD, so a larger quantity should likely be added. Also, the tuning of the sulfur level might be necessary, to compensate for less sulfur being available from the accelerator. The alkylphenol disulfides presented promising results in the studied articles, so Vultac TB710, was also chosen as a test accelerator for compound A. These accelerators will be tested with primary accelerators MBTS and TBBS. (De & White 2001, pp. 181-183)

Choosing the test accelerators for compound B was more complicated than for compound A. None of the studied articles, which were discussed previously in this chapter, had tested the accelerators with SBR or NBR. However, it was mentioned already in the Introduction, that MBTS and TMTD can be used in a wide variety of different rubbers. Other studies were found, where mixtures of SBR and NBR have been successfully vulcanized with different combinations of thiazole based accelerators and thiuram accelerators. (Ramesan & Alex 2001; Chapman & Tinker 2003; Habeeb Rahiman & Unnikrishnan 2006; Essawy et al. 2014) This and the fact that the original vulcanization system contained MBTS and TMTD implies that another similar combination can also be found.

The choice of accelerator for the compound B was more limited, due to regulations. This compound is used in a food contact application and it is designed to meet the regulations set by the BfR. The only one of these nitrosamine free accelerators introduced here, which can be found on the BfR positive list is ZBEC and it was chosen as the test accelerator. TBBS is not on the positive list, so ZBEC will only be tested with MBTS as the primary accelerator. (BfR 2016)

Different accelerator combinations were chosen for the tests for compounds A and B. As a summary, TBzTD and Vultac TB710 were chosen for A and ZBEC was chosen for B as explained above. The testing of these compounds and the rubber recipes used will be discussed in chapter 5.

# 5. EXPERIMENTAL COMPOUNDS AND METHODS

The experimental part of the thesis was conducted at the Research and Development laboratory of Teknikum Group Ltd in Sastamala. The design of the test compounds was done based on the currently used production compounds and the information presented in section 4.5. This chapter describes all the experimental work done and methods used for this thesis. The aim of the experimental work was to find suitable replacements for TMTD in both compounds A and B and create new recipes which perform as well as or better than the original ones.

## 5.1  Design of compounds

Two different rubber compounds with different compositions were studied and modified in this thesis. The compounds were a mixture of NR and BIIR, denoted as compound A and a mixture of SBR and NBR, denoted as compound B. Both had original recipes, which were the starting points of the research. The number of variables in the recipes was kept to a minimum to best study the effects of the chosen variables. The original recipes for compound A and B are presented in Table 3.

*Table 3.*     *The original recipes of the studied rubber compounds.*

| Compound A | | Compound B | |
|---|---|---|---|
| **Ingredient** | **phr** | **Ingredient** | **phr** |
| NR + BIIR | 100 | SBR + NBR | 100 |
| Fillers + Oils | 60 | Fillers + Plasticizers | 75 |
| ZnO + Stearic acid | 5 | ZnO + Stearic acid | 2 |
| Stabilizers | 5 | Stabilizers | 3 |
| Sulfur | 0.5 | Sulfur + Retarder | 2 |
| MBTS | 1.5 | MBTS | 0.1 |
| TMTD | 0.2 | TMTD | 0.5 |

Due to confidentiality reasons, the recipes and the ratios of certain ingredients cannot be presented completely. The original recipes both had their applications and a set of required properties, which must be met also by the new compounds, where TMTD has been replaced. Multiple test compounds were mixed from the masterbatches of both compounds A and B. These individual compounds will be denoted as A/0, A/1, A/2 etc. and B/0, B/1, B/2 etc. A/0 and B/0 are the original baseline compounds used for control and

the others are the test compounds having different vulcanization systems created in this thesis.

## 5.1.1  Compound A

The new secondary accelerators chosen for laboratory testing to replace TMTD in compound A were TBzTD (Figure 20) and Vultac TB710 (Figure 19), which were combined with primary accelerators MBTS (Figure 1) and TBBS (Figure 21). This compound was a two-stage compound, where first the BIIR and NR masterbatches were mixed separately and then they were combined, and finally the vulcanization system was added. The BIIR masterbatch was received from the Teknikum rubber mixing factory. The NR masterbatch was mixed at the Teknikum R&D laboratory.

The desired results for compound A were to find a suitable accelerator, which would maintain the fast and efficient vulcanization provided by the original vulcanization system. The mechanical properties should be close to the ones of the control compound. A slight increase in the $t_{10}$ of the compound would also be welcome to improve the scorch safety of the compound. Based on the literature reviewed in chapter 4, TBzTD should provide a straight replacement for TMTD.

A total of 11 compounds were mixed from the masterbatch. The recipes for mixing the masterbatch and the vulcanization systems are presented in Table 4 and Table 5.

***Table 4.*** *The mixing recipes for compounds A/0-A5. Amounts are given as phr.*

|  | Compound | | | | | |
|---|---|---|---|---|---|---|
| **Ingredient** | **A/0** | **A/1** | **A/2** | **A/3** | **A/4** | **A/5** |
| NR/BIIR masterbatch | 170 | 170 | 170 | 170 | 170 | 170 |
| Sulfur | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| MBTS | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| TBBS | - - | - - | - - | - - | - - | - - |
| TMTD | 0.20 | - - | - - | - - | - - | - - |
| TBzTD | - - | 0.20 | 0.40 | 0.60 | - - | - - |
| Vultac TB710 | - - | - - | - - | - - | 1.5 | 2.0 |

Compound A/0 was the original recipe, which was made as a control compound to compare the results. The compounds A/1-A/3 were combinations of MBTS and TBzTD and compounds A/4 and A/5 were combinations of MBTS and Vultac TB710.

***Table 5.*** *The mixing recipes for compounds A/6-A/10. Amounts are given as phr.*

| Ingredient | Compound | | | | |
|---|---|---|---|---|---|
| | A/6 | A/7 | A/8 | A/9 | A/10 |
| NR/BIIR masterbatch | 170 | 170 | 170 | 170 | 170 |
| Sulfur | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| MBTS | - - | - - | - - | - - | - - |
| TBBS | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| TMTD | - - | - - | - - | - - | - - |
| TBzTD | 0.20 | 0.40 | 0.60 | - - | - - |
| Vultac TB710 | - - | - - | - - | 1.5 | 2.0 |

In the compounds A/6-A/10 the MBTS was switched to TBBS, but otherwise the compounds were similar to A/1-A/5. The amounts of TBzTD and Vultac TB710 were estimates based on the studies where they were used. The molecular weight of TBzTD is about 2.25 times the molecular weight of TMTD, which suggests that TBzTD should be used in a larger quantity to achieve the same stoichiometry. However, the situation is not that simple, as the overall dispersion and the recovery of the accelerator during the reaction also influence the required amount. Therefore, the tested amounts of TBzTD were the ones presented in Table 4 and Table 5. Only the amounts of the new accelerators were varied here, everything else was kept constant to minimize the number of variables. At this point, it was advisable to run the tests and decide on the next actions based on their results.

## 5.1.2 Compound B

The secondary accelerator chosen to replace TMTD in compound B was ZBEC (Figure 20), which was used in combination with the original primary accelerator MBTS. The masterbatch was received from the Teknikum rubber mixing factory and the addition of the vulcanization system was done at the Teknikum R&D laboratory.

The aim of the tests for compound B were to find a combination of MBTS and ZBEC which will have similar properties as the control compound. The vulcanization speed is crucial as the compound cannot slow down to maintain productivity in large scale production. Also, the physical properties, more precisely the hardness and moduli of the compound should stay the same for the product to function correctly.

The test recipes for compound B were designed using central composite design (CCD), which is a method in design of experiments (DOE) in response surface methodology. DOE in general means the controlled design of experiments, where hypotheses are made and the effect of certain factors on the results is measured. CCD is useful in finding quadratic effects of variables, which cannot be found by linear test methods. In this case, two

variables were chosen, which were the amount of MBTS and the amount of ZBEC. As these two are the only variables, a broeader experiment is justified here. The experiment design for two factors can be presented using Figure 22.
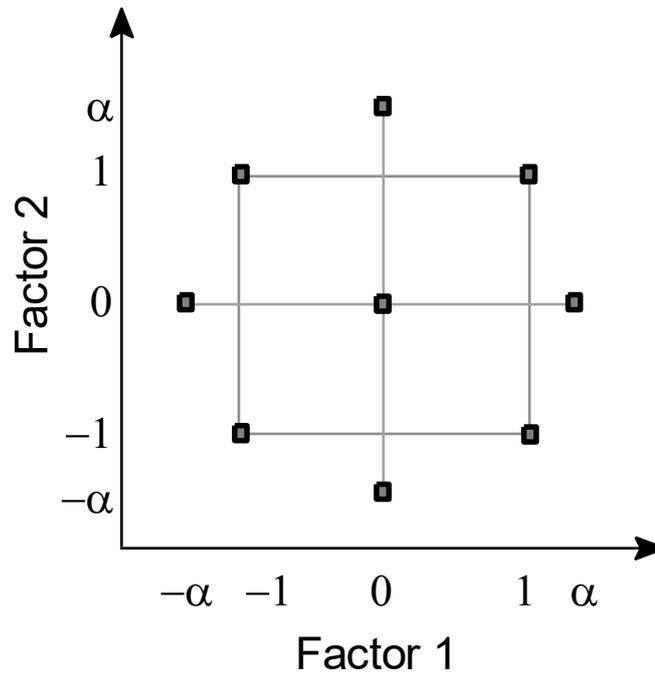


*Figure 22.*        *Central composite design (CCD) for two factors.*

The two variables are presented on the axis and the measurement points are the grey points on the graph. The measurements are done in five levels and the points consist of the edge or factorial points, presented by the square at ±1 and the star points at ±α, which are at the ends of the cross in Figure 22. The center point (0,0), which is often repeated several times, finishes the method. All the different points have different functions in the method. The factorial points model linear and second order effects, the star points model quadratic effects and the repeated center point provides information on the accuracy and error of the design method. The CCD method can also be used for a larger number of variables, which increases the number of required test points. The α is the limit point, which is calculated by $\alpha = 2^{k/4}$, where k is the number of variables in the experiment. Thus, here $\alpha \approx 1.414$. The important issue with CCD is choosing the factor ranges correctly, so desirable results can be obtained. By using this design method, a three-dimensional response surface graph can be created to model the results as factors of the variables. Using this experimental method and calculations, the response in individual compound properties can be plotted as factors of the accelerator concentrations. The desirable properties and values must be decided and from these parameters the ideal combination of the amounts of MBTS and ZBEC can be calculated. The CCD method was chosen here, because the number of available accelerators was restricted, and this method could be used to calculate the optimal accelerator dosages with a limited number of experiments. (Lewis et al. 2003; Whitcomb & Anderson 2016, pp. 141–153)

The ranges chosen for this measurement were 0 to 1.0 phr for MBTS and 0 to 0.9 phr for ZBEC. These specific ranges were chosen to cover a relatively wide combination of accelerator concentrations. In this compound, 1 phr of MBTS should be enough and the limit of 0.9 phr for ZBEC was chosen as the amount of ZBEC cannot exceed 0,5% of the mass of the whole compound according to regulations by BfR. The ranges were set at the limit points and the other amounts were calculated. (BfR 2016)

The code values are given real values according to the equation:

$$Real\ value = (Range/(2*\alpha)) * Code\ value + Mean \tag{1}$$

The calculated real values corresponding to the code values are presented in Table 6.

**Table 6.** *The code values and their respective real values for the amounts of MBTS and ZBEC in compound B.*

| Code values | Amount of MBTS (phr) | Amount of ZBEC (phr) |
|:---:|:---:|:---:|
| -1.414 | 0 | 0 |
| -1.000 | 0.1464 | 0.1318 |
| 0 | 0.5000 | 0.4500 |
| 1.000 | 0.8536 | 0.7682 |
| 1.414 | 1.000 | 0.9000 |

These amounts and the code values were used to generate the complete experiment design for compound B, which is presented in Table 7.

**Table 7.** *The experimental design for compounds B/1-B/11.*

| Compound | Code value | | Real amount (phr) | |
|:---:|:---:|:---:|:---:|:---:|
| | MBTS | ZBEC | MBTS | ZBEC |
| B/1 | -1.000 | -1.000 | 0.1464 | 0.1318 |
| B/2 | 1.000 | -1.000 | 0.8536 | 0.1318 |
| B/3 | -1.000 | 1.000 | 0.1464 | 0.7682 |
| B/4 | 1.000 | 1.000 | 0.8536 | 0.7682 |
| B/5 | -1.414 | 0 | 0 | 0.4500 |
| B/6 | 1.414 | 0 | 1.000 | 0.4500 |
| B/7 | 0 | -1.414 | 0.5000 | 0 |
| B/8 | 0 | 1.414 | 0.5000 | 0.9000 |
| B/9-11 | 0 | 0 | 0.5000 | 0.4500 |

All the compound designs can easily be traced on the graph in Figure 22 according to their code values. The compounds B/1-B/4 are the factorial points, B/5-B/8 are the star points and B/9-B/11 are replications of the center point. (Whitcomb & Anderson 2016, pp. 141–153)

A total of 12 different compounds were mixed from the masterbatch, as also B/0 was mixed as the control compound according to the original recipe which was presented in Table 3. For the other compounds, the only things changed compared to the original recipe were the amount of MBTS and ZBEC, which replaced TMTD. The recipes for mixing the masterbatch and the vulcanization system for compounds B/0-B/5 are presented in Table 8.

***Table 8.*** *The mixing recipes for compounds B/0-B/5. Amounts are given as phr.*

| | Compound | | | | | |
|---|---|---|---|---|---|---|
| **Ingredient** | **B/0** | **B/1** | **B/2** | **B/3** | **B/4** | **B/5** |
| SBR/NBR masterbatch | 182.0 | 182.0 | 182.0 | 182.0 | 182.0 | 182.0 |
| MBTS | 0.1000 | 0.1464 | 0.8536 | 0.1464 | 0.8536 | 0 |
| TMTD | 0.5000 | -- | -- | -- | -- | -- |
| ZBEC | - - | 0.1318 | 0.1318 | 0.7682 | 0.7682 | 0.4500 |

The recipes for mixing the masterbatch and the vulcanization system for compounds B/6-B/11 are presented in Table 9.

***Table 9.*** *The mixing recipes for compounds B/6-B/11. Amounts are given as phr.*

| | Compound | | | | | |
|---|---|---|---|---|---|---|
| **Ingredient** | **B/6** | **B/7** | **B/8** | **B/9** | **B/10** | **B/11** |
| SBR/NBR masterbatch | 182 | 182 | 182 | 182 | 182 | 182 |
| MBTS | 1.00 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 |
| TMTD | -- | -- | -- | -- | -- | -- |
| ZBEC | 0.450 | 0 | 0.900 | 0.450 | 0.450 | 0.450 |

It was mentioned in section 4.5.4 that ZBEC cannot function as a sulfur donor like TBzTD or TMTD, so the issue which could arise is the lack of sulfur in the compound. Despite this, only two variables were chosen to simplify the result analysis.

## 5.1.3  Analysis program

The program used for the analysis of the DOE results in this thesis was Design-Expert 11, a software made by Stat-Ease Inc. It is a program, which is especially designed for DOE tasks. The program has a variety of different experiment settings and analysis tools, which can be used from large screening tests to precise optimization. It can be used for both experiment design and result analysis. The program is easy to use, and it also offers guidance on designing the experiments based on the numbers and types of variables. The significance of each factor is confirmed with analysis of variance (ANOVA). ANOVA is a statistical procedure, which is used to evaluate differences between population means. It is used to determine the fit of certain models to a data set and to rule out the models which are not significant. The program gives 3D plots and contour graphs from the data

and it can be used to predict the optimal process parameters based on the desired results. (Whitcomb & Anderson 2016, pp. 19–25; Stat-Ease)

In this thesis the Design-Expert 11 was used to analyze the results from the CCD experiment setup presented in section 5.1.2. The graphs and optimization results are presented in section 6.2.

## 5.2 Mixing of rubber compounds A and B

The compound A was mixed in two stages. First the NR masterbatch was mixed separately with an internal mixing machine. Then the NR masterbatch was combined with the BIIR masterbatch and the vulcanization system. The NR masterbatch was mixed using a Krupp Elastomertechnik GK 1,5 E laboratory internal mixer, which had intermeshing rotors, ram pressure of 8 bars and a capacity of 1.5 liters. The internal mixer is presented in Figure 23.



*Figure 23.*      *The internal mixer used for mixing the NR masterbatch.*

The NR elastomer was first pre-masticated in the mixer for 1 minute. Then the stabilizers, zinc oxide and stearic acid were added and gradually the oil and fillers. The mixing times were in the order of five minutes.

After the NR masterbatch was complete, it was combined with the BIIR masterbatch and the vulcanization system according to the recipes presented in Table 4 and Table 5. Although zinc oxide and stearic acid are regarded as part of the vulcanization system, they are often added already in the first mixing stage to ensure uniform distribution of zinc, as it is poorly soluble in rubber on its own. The other vulcanization chemicals are added separately to prevent too much heat history. Combining the masterbatches and mixing the vulcanization systems were done using a laboratory scale two-roll mill, which is presented in Figure 24.



**Figure 24.**      *The two-roll mill used in the mixing of the rubber compounds.*

The mixing of compound B only required the addition of the vulcanization system into the masterbatch. The SBR/NBR masterbatch arrived as such and the accelerators were added using the two-roll mill. In this case the sulfur had already been added to the masterbatch, as it is quite insoluble in NBR.

## 5.3   Rheometer and vulcanization

A moving-die rheometer (MDR) is a test machine used to measure the vulcanization characteristics of a rubber. A small piece of unvulcanized rubber is placed in a heated cavity between two dies set at a known constant temperature. The structure of the rheometer is presented in Figure 25.
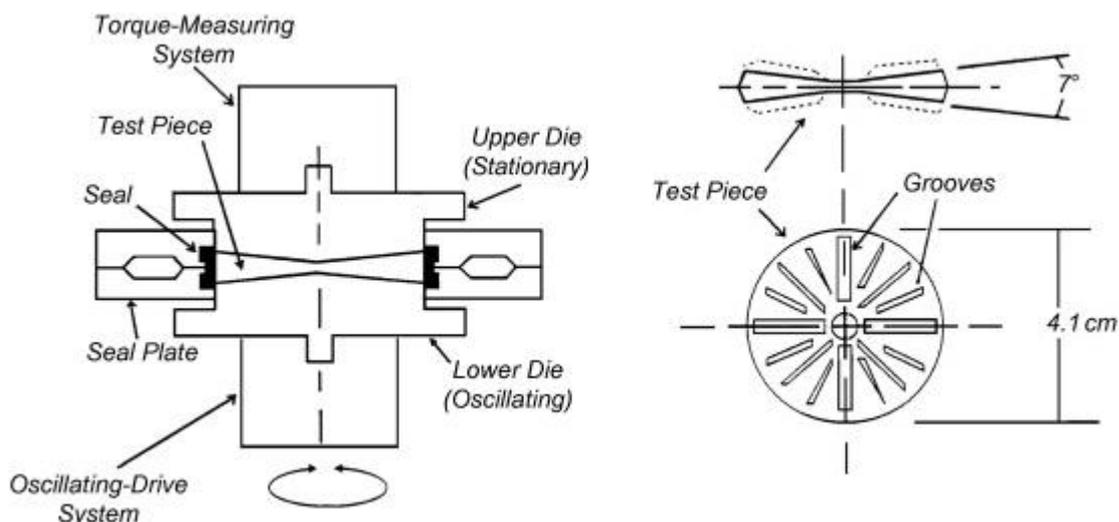
**Figure 25.** *Structure of a moving-die rheometer (MDR). (Coran 2013, p. 343) (p. 343)*

The die is closed, and the rubber is sealed in the cavity. The other die begins oscillating, the other one remains stationary and the torque required to maintain the oscillation is measured. The rubber starts to vulcanize due to the heat and maintaining the oscillation in the die requires more and more torque as the compound is cured. The MDR automatically plots a torque versus time curve, which was presented earlier in chapter 4 (Figure 11). The rheometer test can be used to determine the scorch time and optimum vulcanization time of a rubber compound. The key values given by a rheometer test are ML (Moment Lowest), MH (Moment Highest), $t_{10}$ (in minutes) and $t_{90}$ (in minutes). ML is the lowest value of torque during the test and MH is the highest value of torque during the test, both often given in decinewton meters (dNm). The ML value describes the processability of the rubber, as a low torque in the rheometer means that the rubber will flow easily. The MH value describes the cross-link density and extent of vulcanization of the rubber, as a rubber with higher cross-link density will be stiffer and thus requires a higher torque. Exact values of ML and MH for certain properties cannot bet determined, because they vary with different rubbers, but they can be used for comparison between compounds. The rheometer test is often used in a laboratory to determine the correct curing times for test samples and for general quality control of rubber compounds. (Ignatz-Hoover & To 2004; Coran 2013)

After the rubber mixing was complete, rheometer tests were run for all the compounds at 180 °C for compound A and at 160 °C for compound B, using an Alpha Technologies MDRB to determine the vulcanization characteristics and the correct curing times for each compound.

The samples required for most of the laboratory tests were 2 mm thick plates. Only the De Mattia -tests (see section 5.4.5) for compound B required special samples. The sam-

ples were vulcanized using molds, which were placed in a laboratory scale heated hydraulic press. The vulcanization temperature was 180 °C for compound A and 160 °C for compound B and the cure times for each compound were determined from the rheometer test results.

## 5.4 Measuring and testing of rubbers

Rubbers can be tested in various ways in a laboratory. Most of the tests done are according to certain standards provided for example by the International Organization for Standardization (ISO) or ASTM International. Standards are made to unify the testing methods and make the comparing of results valid. All the tests made for rubber have certain functions which can help the forecasting of how the material will behave in use. It must be noted that the results from standardized tests done for materials cannot be directly interpolated for products, as the geometries and circumstances vary a lot. Nevertheless, the tests are important and provide valuable information for product development. When required test parameters have been established for a certain product, it will be easier to test and develop new materials when they can be compared to existing results. The methods used, or properties tested for the rubber compounds in this thesis were a moving-die rheometer, tensile properties, hardness, tear resistance, low temperature retraction, ozone resistance and De Mattia. These different tests are described in the following sections.

The required samples for the following tests were cut from the 2 mm thick rubber plates. Before the measurements, the rubber plates and the De Mattia samples were stored in a room with stable atmospheric conditions at 23 °C and 50% relative humidity for at least 16 hours.

### 5.4.1 Tensile properties

The tensile properties of the material are tested using a special machine made for this purpose. The purpose of this test is to measure the behavior of materials when they are strained. The machine measures the force at which the test piece is pulled, and an extensometer measures the elongation. Before the test, the thickness of the test sample is measured to calculate the cross-section of the sample being tested. The test samples have a dumb-bell shape with fixed geometry, presented in Figure 26.
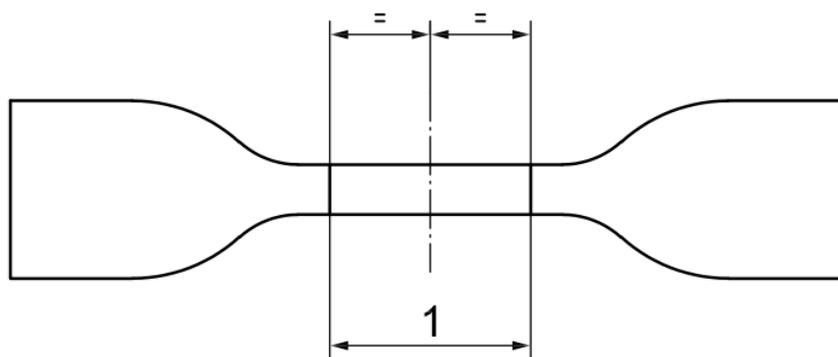
***Figure 26.*** *Shape of dumb-bell test pieces used for tensile tests. (International Organization for Standardization 2017b)*

The dimensions of the samples can vary, depending on the type of test made. The test samples are cut using a fixed die to ensure the consistency of the samples. The properties measured with this test are the tensile strength (in MPa), elongation at break (in %) and the moduli (in MPa), which is the tensile stress at 100%, 200% and 300% elongations. The extensometer is fixed on the test sample before starting the test and it moves along with the test sample, measuring the elongation. The results of the test are presented as a curve, which plots stress versus elongation. The stress is calculated from the measured force divided by the cross-section of the test sample. The tensile stress and elongation at break tell how much stress the sample can withstand and how far it will stretch before it will break. These are ultimate values and a rubber article in use should not come close to these values. The moduli tell about the stiffness of rubber and how it will behave under certain elongations. The stress and elongation do not always increase linearly, and this affects the behavior of different compounds. (International Organization for Standardization 2017b)

The tensile properties were measured using a Gibitre Tensor Check Profile PC machine. The tensile properties measurements were done for three test pieces from each compound. The reported value was the median of the three results for each compound.

## 5.4.2 Tear resistance

The tear resistance test measures how a material resists the growth of cracks or cuts when strained. There are different methods for measuring the tear resistance, the one used here was the type C crescent test sample with a nick. The shape and dimensions for the tear resistance test piece are presented in Figure 27.

**Figure 27.** *Shape of crescent test pieces used for tear resistance tests. (International Organization for Standardization 2015)*

The test samples are cut using a die like in the tensile properties test. A nick is also cut into the sample in the location (1) presented in Figure 27. Before the testing, the thickness of the sample is measured, like in the tensile properties test. The testing machine gives a result of the force required to break the sample. The tear resistance can be calculated from the maximum force divided by the thickness of the sample. The result is given in kN/m. (International Organization for Standardization 2015)

The tear resistance measurements were done with the same machine as the tensile property measurements. The measurements were done for five pieces from each compound and the median value of these five was reported.

## 5.4.3  Hardness

The hardness of a material means its resistance to indentation. The hardness of a rubber is an important property and it can widely affect the use and performance of a material. Rubbers are measured by the Shore hardness scale, of which Shore A is the most common and it is used for rubbers in the normal hardness range. Others which are sometimes used are Shore A00 and Shore D, for very soft gel-like materials and for hard rubbers respectively. The scale of Shore hardness goes from 0 to 100 and the hardness of a material is expressed for example as 50 ShA, meaning that it is 50 is the Shore A scale. The hardness is measured by a device called durometer, which has an indenter which is pressed against the sample at a certain force. The depth of indentation is proportional to the hardness of the material and thus it can be used to determine the hardness. There are two types of durometers, larger table durometers which use a mass to press the sample and hand-held

durometers, which use a spring to press the sample. The larger durometers are more reliable and produce more reproducible results. The hardness of the material can be read from the scale of the durometer. The hardness is determined from a sample, which is at least 6 mm thick and the surface area must permit measurements from at least 12 mm away from the edges of the sample. (International Organization for Standardization 2010)

The hardness measurements were done using a Bareiss BS 61 table durometer in the Shore A scale. The hardness was measured three times for each compound and the median value was recorded.

## 5.4.4  Ozone resistance

The measurement of ozone resistance is a common test for polymeric materials. The risks of ozone attack for diene rubbers were described earlier in section 2.1.4. The ozone resistance test is used to forecast the lifetime of a rubber product. The test samples used are narrow test pieces presented in Figure 28.
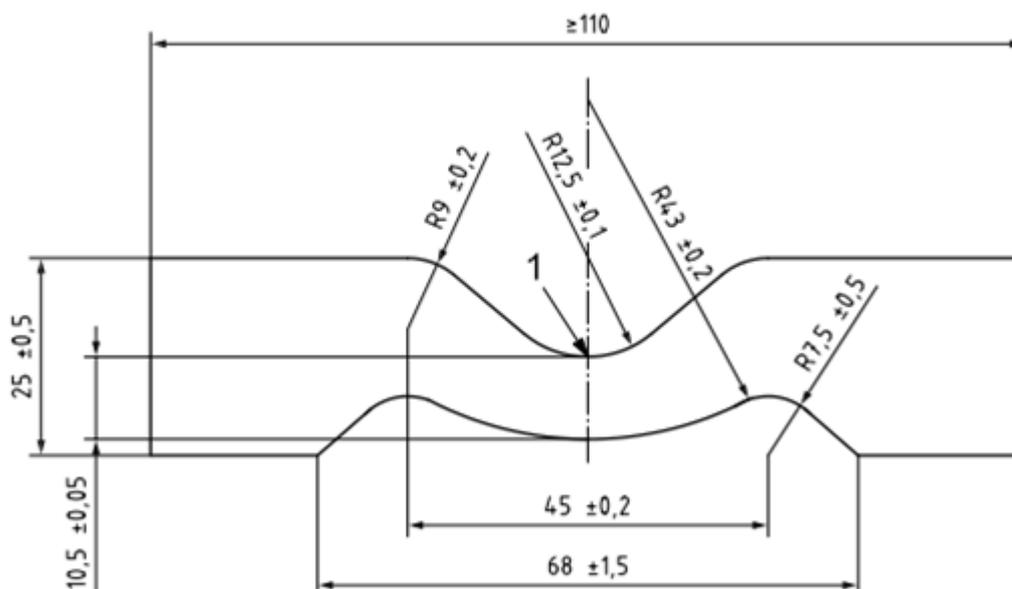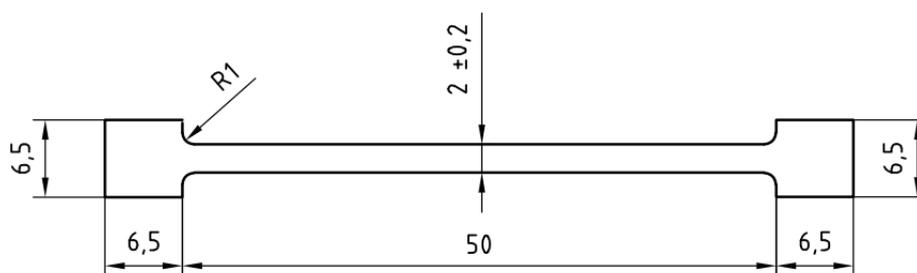


***Figure 28.***      *Shape of narrow test pieces used for ozone resistance tests. (International Organization for Standardization 2012)*

The test samples are placed in a test chamber under static strain at different elongations and examined periodically for the formation and growth of cracks. The temperature and ozone concentration are kept constant. The ozone concentrations, specimen elongations and test times are varied according to the required results. The test is continued until the required time has passed or all the samples have broken. (International Organization for Standardization 2012)

The ozone resistance tests were done using a Hampden 2000-AM ozone test chamber. Three parallel measurements were done for each compound and elongation. The conditions used to the test compound A were 50 pphm ozone concentration and a temperature of 40 °C. The conditions for compound B were 25 pphm ozone concentration at room temperature. The samples were stretched to 5, 10, 15, 20, 30, 40, 60 and 80% static elongations. The samples were stretched and held at room temperature for 72 hours before starting the actual test. The test was run for 96 hours for compound A and 168 hours for

compound B. The samples were checked for defects regularly during the test. The first check was done after 2 hours, then 4, 24, 48, 72, 96 and finally 168 hours.

The compounds A and B have different requirements for ozone resistance and thus different concentrations and test times were used. The results of the ozone test are expressed as the highest elongation in % the compound can withstand at the end of the test without any defects in the sample. If defects occur in all the samples before the end of the test, then the result will be the last time when intact samples were observed and the largest elongation at which they were observed.

### 5.4.5 Low temperature retraction test

The low temperature retraction (TR) test is a test to measure the low temperature behavior of a material. The behavior of rubbers changes drastically as temperature decreases. In their operation temperature, they should be elastic and flexible, but as temperature decreases they can become brittle and hard. The TR test is useful for materials which will be used at lower temperatures to ensure they can cope with these circumstances. The test is done by a special automated TR tester machine. The samples used in this test are like the ones in the ozone resistance test with variance in length. Shorter samples are used for materials, with large elongations and longer samples for materials with small elongations. Smaller elongations are used for compounds which contain NR, due to its cold crystallization potential. The test samples are stretched to a certain elongation, then placed in cold ethanol and the tension is released after a cooling period. The starting temperatures used range from -70 °C to -60 °C, depending on the rubber compound tested. The temperature is then raised constantly which causes the samples to retract towards their original shape. The results are given as a plot of the retraction percentage from the elongated length versus the temperature. Often the results of interest are TR10, TR30, TR50 and TR70, which represent the temperatures at which the measurement sample has retracted 10%, 30%, 50% and 70% from the elongated value, respectively. The results are given as negative Celsius degrees and the test is ended either when 70% retraction is reached or when the temperature reaches 0 °C. A material with good low temperature properties will not become stiff and will retract more at lower temperatures, meaning that the temperatures TR10, TR30, TR50 and TR70 will be colder than for a material with poor low temperature properties. (International Organization for Standardization 2011)

The TR test was done using a Gibitre Low Temperature Check machine and it was done only for compound A. The samples used were 100 mm long and an elongation of 50% was used. First the machine was cooled to -65 °C and then the samples were stretched, immersed and measured. Three parallel samples were measured for each compound and the mean of the results was reported.

## 5.4.6 De Mattia

The De Mattia test is used to measure the fatigue behavior and resistance to cracking or crack growth of rubbers. The aim of this test is to measure what happens to a rubber when it is repeatedly bended or flexed. In the test, a strip of rubber is placed between holders which move up and down periodically, bending and stressing the sample. The strip of rubber has a groove in the middle, perpendicular to the long edge of the sample. There are two types of De Mattia measurements, either with or without a crack introduced to the sample prior to measuring. The test without the crack measures the resistance to cracking and the test with the crack measures resistance to crack growth. The test setup used in a De Mattia test is presented in Figure 29.
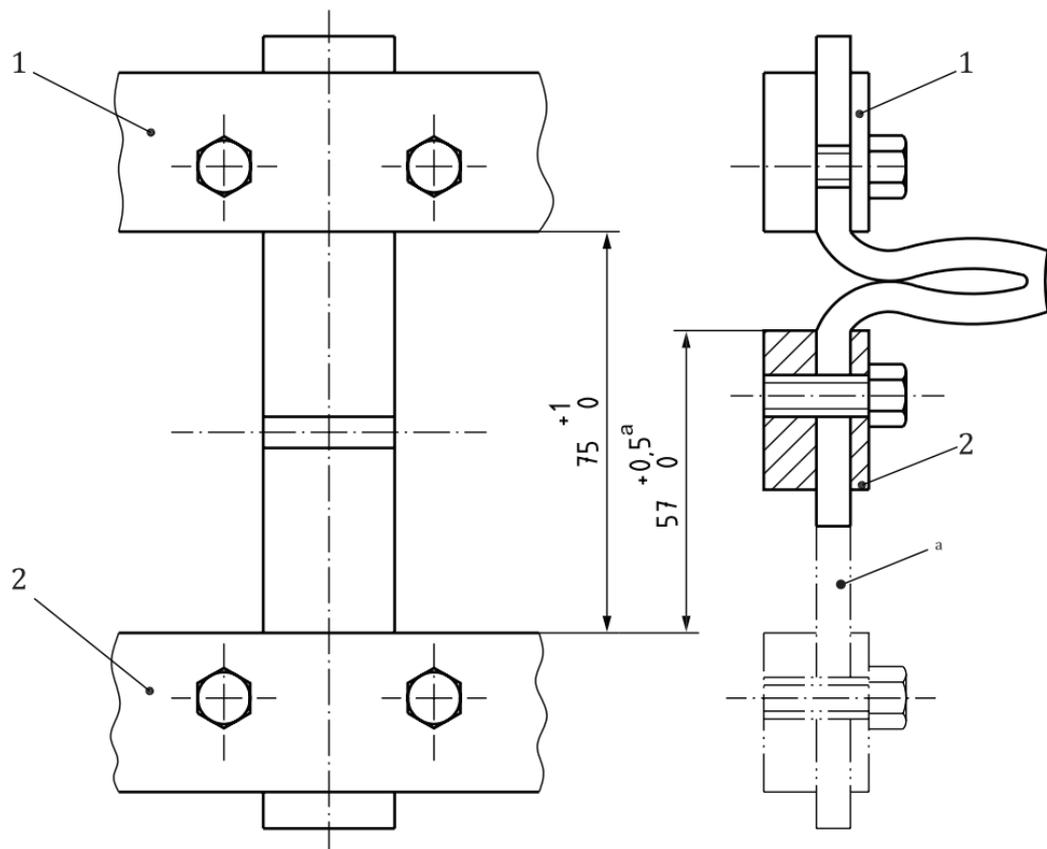


**Figure 29.**    *The setup in a De Mattia type machine. (International Organization for Standardization 2017a)*

On the left, the grips and the sample are presented from the front in a relaxed, upright position. On the right they are presented from the side in a bent position, showing the movement of the bottom grip. If the crack growth is studied, then a 2 mm cut, denoted by L, is made to the center of the groove in the sample. The sample is fastened to the test jig so that the side of the groove will bend outward, causing stress in the sample. The test is run for a certain amount of deformation cycles and the samples are investigated at regular intervals. The test is ended when the cracks are large enough or when a certain threshold of cycles has been reached. (International Organization for Standardization 2017a)

The De Mattia tests were only required for compound B. They were done using a machine that has been assembled in the laboratory. The type of test done was with a crack introduced in the sample. The samples were monitored regularly between the cycles and the results, which are the number of cycles required for the crack to reach L+2, L+6 and L+10 mm, were recorded. The test was done two times for each compound and the mean of these results was reported.

# 6. RESULTS AND DISCUSSION

The results of the laboratory tests and the analyses based on them is presented in this chapter. This chapter has been divided into three sections: compound A, compound B and the future development after this thesis is complete.

## 6.1 Compound A

In general, the results for compound A were unexpected. The presumption was that A/0 would have a high cross-link density and great mechanical properties and it could be used as a good baseline to compare the properties of the other compounds. This was not the case as can be seen from the results presented in this section. The rheometer tests were ran according to the method described in section 5.3 and the results, ML, MH, $t_{10}$ and $t_{90}$ for compounds A/0-A/10 are presented in Table 10.

***Table 10.*** *The rheometer results at 180 °C for compounds A/0-A/10. ML and MH values are given in dNm and $t_{10}$ and $t_{90}$ in minutes.*

| Compound | ML (dNm) | MH (dNm) | $t_{10}$ (min) | $t_{90}$ (min) |
|----------|----------|----------|----------------|----------------|
| A/0 | 0.75 | 5.40 | 0.69 | 2.12 |
| A/1 | 0.77 | 5.46 | 0.76 | 2.43 |
| A/2 | 0.78 | 5.79 | 0.76 | 2.16 |
| A/3 | 0.78 | 6.00 | 0.73 | 2.01 |
| A/4 | 0.75 | 8.10 | 0.67 | 2.43 |
| A/5 | 0.77 | 8.68 | 0.67 | 2.30 |
| A/6 | 0.78 | 6.28 | 1.13 | 3.62 |
| A/7 | 0.78 | 6.11 | 1.03 | 2.87 |
| A/8 | 0.77 | 6.57 | 1.00 | 2.74 |
| A/9 | 0.77 | 8.80 | 0.77 | 2.99 |
| A/10 | 0.80 | 9.44 | 0.75 | 2.85 |

The rheometer curves corresponding to these values are presented in Appendices A and B. It can be pointed out, that the baseline compound A/0 was not ideal. The cross-link density was quite low, which can be seen from the MH value 5.40 dNm. When this is compared to values given by the compounds A/4, A/5, A/9 and A/10, it is clear that the original vulcanization system had not been optimized. The compounds A/4, A/5, A/9 and A/10 have much higher MH values than the other compounds measured and thus their cross-link density is also higher. This indicates that the results of other tests cannot be compared to the results of the control compound straightforwardly, as the values for the control compound were not optimal. The highest extents of vulcanization were given by the compounds, where Vultac TB710 was used as the replacement accelerator. The ML

values between the compounds vary only slightly, which indicates that the different vulcanization systems do not affect the flowing and processability of the rubber. It is not meaningful to compare the $t_{10}$ and $t_{90}$ times of the test compounds with the baseline compound, as the original compound is clearly not cross-linked to the extent desired. It can be noted however, that the rheometer results of the compounds A/4, A/5, A/9 and A/10 are relatively close to each other.

The tensile, tear resistance and hardness tests were done according to the methods described in sections 5.4.1, 5.4.2 and 5.4.3 and the results for compounds A/0-A/10 are presented in Table 11.

*Table 11.*     *The mechanical test results for compounds A/0-A/10.*

| Compound | Tensile strength (MPa) | Elonga-tion at break (%) | Modulus 100% (MPa) | Modulus 200% (MPa) | Modulus 300% (MPa) | Tear re-sistance (kN/m) | Hard-ness (ShA) |
|---|---|---|---|---|---|---|---|
| A/0 | 9.3 | 673 | 0.96 | 1,68 | 2.71 | 35.0 | 41 |
| A/1 | 8.8 | 643 | 1.02 | 1.82 | 2.92 | 36.8 | 38 |
| A/2 | 8.9 | 634 | 1.00 | 1.79 | 2.92 | 35.6 | 37 |
| A/3 | 9.1 | 656 | 1.01 | 1.79 | 2.87 | 35.8 | 38 |
| A/4 | 14.6 | 643 | 1.52 | 2.89 | 4.88 | 41.9 | 45 |
| A/5 | 14.9 | 654 | 1.53 | 2.97 | 5.00 | 42.4 | 46 |
| A/6 | 10.9 | 654 | 1.07 | 1.94 | 3.28 | 36.6 | 40 |
| A/7 | 10.2 | 651 | 1.09 | 1.93 | 3.18 | 35.3 | 40 |
| A/8 | 10.3 | 629 | 1.17 | 2.06 | 3.39 | 35.1 | 42 |
| A/9 | 14.0 | 584 | 1.59 | 3.10 | 5.31 | 48.0 | 49 |
| A/10 | 13.4 | 557 | 1.69 | 3.26 | 5.61 | 49.1 | 49 |

The same trend continues in the results of the mechanical tests as was noted in the rheometer tests. The baseline was poor and so the test results for all the compounds with thiuram accelerators have produced poor results. The compounds A/4, A/5, A/9 and A/10, which are the ones that had Vultac TB710 as the replacing accelerator, have functioned well and have the highest tensile strengths, tear resistances and hardness of the tested compounds. It was established in the beginning of chapter 4, that the maximum elongation and tensile strength are competing properties and a compromise must be found between these properties. In compound A the elongation at break is not a limiting property and the tensile strength is more important.

Reasons for these results for compounds A/1-A/3 and A/6-A/8 are probably wrong amounts of thiuram accelerator and sulfur in the compounds. The test amounts for TBzTD were based on the original vulcanization system, which was clearly not optimized for this compound. The levels of TBzTD should have probably been much higher and the levels of sulfur might have been too low also. This has resulted in a too low cross-link density and thus inferior mechanical properties. When the compounds A/1-A/3 are compared

with each other they give similar results in the rheometer test and for their mechanical properties. This is also valid for compounds A/6-A/8. This indicates that the level of accelerator is far too low, as tripling the amount does not bring notable changes.

It was mentioned in section 4.5.3 that Vultac TB710 may also function as a sulfur donor and according to these results this has been confirmed, as the compounds A/4, A/5, A/9 and A/10 have a much higher cross-link density than the other test compounds, while all the other parameters were kept the same.

The TR and ozone tests were not run for all the compounds. To save time and effort, only some of the samples were tested. The TR and ozone resistance tests were done according to the methods described in sections 5.4.4 and 5.4.5. The results for compounds A/0-A/10 are presented in Table 12.

***Table 12.*** *The TR and ozone resistance test results for compounds A/0-A/10.*

| Compound | Ozone resistance (% at 96 h) | TR 10 (°C) | TR 30 (°C) | TR 50 (°C) | TR 70 (°C) |
|---|---|---|---|---|---|
| A/0 | >80 | -53 | -45 | -34 | -17 |
| A/1 | - | - | - | - | - |
| A/2 | 40 | -53 | -44 | -34 | -18 |
| A/3 | - | - | - | - | - |
| A/4 | >80 | -54 | -47 | -40 | -28 |
| A/5 | >80 | -54 | -48 | -42 | -32 |
| A/6 | - | - | - | - | - |
| A/7 | >80 | -53 | -44 | -32 | -16 |
| A/8 | - | - | - | - | - |
| A/9 | 60 | -54 | -47 | -41 | -30 |
| A/10 | 60 | -54 | -48 | -41 | -31 |

At this point it was clear that the compounds A/4, A/5, A/9 and A/10 have the best performance, so the emphasis of the test was on them. The baseline A/0 was of course tested and A/2 and A/7 were chosen as decent representatives of the other thiuram compounds.

The ozone test results are given as the highest percentage elongation the samples could withstand for 96 hours in the ozone cabinet. The result >80% means that no defects were found in the 80% samples, which were the highest elongations used and thus the samples could have withstood even larger elongations. The results for A/9 and A/10 are slightly worse than those for A/5 and A/6, but they still performed well.

In general, all the tested compounds perform well enough in the TR test for this application, but the same compounds A/4, A/5, A/9 and A/10 have the best results, as they retract at lower temperatures than the other tested compounds. At TR10 and TR30 the differences are quite small, but at TR50 and TR70 they are already quite significant. These

results probably originate from the same reason, as the mechanical test results, which is the higher cross-link density.

The compounds with TBzTD did not give the expected results, but the compounds with Vultac TB710 exceeded expectations. The $t_{10}$ times were almost the same for all the tested compounds, so no scorch issues could be detected with Vultac TB710, although this was expressed as a possible concern in section 4.5.3.

A successful accelerator pair has been found and satisfactory results have been achieved for compound A. The compounds which performed the best in the tests were compounds A/4, A/5, A/9 and A/10. The compounds did not have significant differences in properties, except for the hardness. The compounds A/4 and A/5 are slightly too soft, whereas A/9 and A/10 have the required hardness for the end use of this compound.

The vulcanization system from compound A/9 is chosen as the compound for future research. A/9 has good overall results and there is no need to use excess ingredients, when the same can be achieved with less, and thus it is chosen over A/10. The most important properties for this compound are the tensile strength, hardness, ozone resistance and low temperature retraction, and compound A/9 is a good choice considering all of these. The development of compound A will continue, but not within this thesis. The aim is to make the compound overall safer for production and its downstream users.

## 6.2   Compound B

The results for compound B followed a more expected path than for compound A. The large variations in the accelerator concentrations also produced large variations in the results, which was to be expected. Promising results were also found, and the use of the CCD allowed to analyze the effect of varying the accelerator concentration on single properties. The purpose of CCD analysis is to gain varied results over the set measurement space and use these results to find the optimum. The specific analysis of the results of each individual compound is not meaningful here, as the point is to use the Design-Expert program to analyze the results and find optimal amounts of both accelerators. The rheometer tests were ran according to the method described in section 5.3 and the results, ML, MH, $t_{10}$ and $t_{90}$ for compounds B/0-B/11 are presented in Table 13.

***Table 13.*** *The rheometer results at 160 °C for compounds B/0-B/11. ML and MH values are given in dNm and $t_{10}$ and $t_{90}$ in minutes.*

| Compound | ML (dNm) | MH (dNm) | $t_{10}$ (min) | $t_{90}$ (min) |
|----------|----------|----------|----------------|----------------|
| B/0 | 0.95 | 10.33 | 1.46 | 4.25 |
| B/1 | 0.97 | 7.33 | 2.02 | 7.60 |
| B/2 | 0.97 | 8.76 | 2.33 | 6.84 |
| B/3 | 0.95 | 9.16 | 1.23 | 3.92 |
| B/4 | 0.95 | 11.27 | 1.47 | 3.94 |
| B/5 | 1.02 | 7.58 | 0.86 | 7.74 |
| B/6 | 0.96 | 10.63 | 1.74 | 4.49 |
| B/7 | 1.00 | 6.51 | 3.15 | 14.54 |
| B/8 | 0.96 | 10.69 | 1.40 | 3.75 |
| B/9 | 0.97 | 9.58 | 1.75 | 4.66 |
| B/10 | 0.98 | 9.59 | 1.75 | 4.63 |
| B/11 | 1.00 | 9.57 | 1.75 | 4.59 |

The rheometer curves corresponding to these values are presented in Appendices C and D. The rheometer test gave promising results, as for example compounds B/4 and B/8 both have higher MH values and faster $t_{90}$ times than the baseline compound B/0. This suggested that a compound with similar properties and a faster vulcanization rate could be achieved. The compounds B/9-B/11 have almost identical rheometer values, which is expected as they have the same recipe.

The rheometer results also confirm that an addition of sulfur is not necessary here, as MH values similar to B/0 can be achieved. The tensile, tear resistance and hardness tests were done according to the methods described in sections 5.4.1, 5.4.2 and 5.4.3 and the results for compounds B/0-B/11 are presented in Table 14.

***Table 14.***     *The mechanical test results for compounds B/0-B/11.*

| Compound | Tensile strength (MPa) | Elonga-tion at break (%) | Modulus 100% (MPa) | Modulus 200% (MPa) | Modulus 300% (MPa) | Tear re-sistance (kN/m) | Hard-ness (ShA) |
|---|---|---|---|---|---|---|---|
| B/0 | 10.1 | 471 | 1.71 | 3.97 | 6.38 | 27.9 | 49 |
| B/1 | 11.7 | 734 | 1.28 | 2.77 | 4.61 | 48.8 | 43 |
| B/2 | 13.4 | 668 | 1.51 | 3.34 | 5.54 | 41.5 | 45 |
| B/3 | 11.9 | 578 | 1.59 | 3.54 | 5.83 | 34.2 | 47 |
| B/4 | 11.7 | 472 | 1.91 | 4.45 | 7.24 | 30.5 | 50 |
| B/5 | 11.6 | 675 | 1.35 | 2.90 | 4.82 | 34.6 | 45 |
| B/6 | 12.1 | 511 | 1.81 | 4.24 | 6.94 | 35.0 | 49 |
| B/7 | 10.5 | 777 | 1.20 | 2.37 | 3.84 | 38.6 | 42 |
| B/8 | 11.9 | 506 | 1.82 | 4.17 | 6.79 | 32.3 | 49 |
| B/9 | 13.2 | 600 | 1.63 | 3.72 | 6.13 | 36.3 | 47 |
| B/10 | 12.7 | 580 | 1.65 | 3.69 | 6.12 | 33.0 | 47 |
| B/11 | 11.8 | 539 | 1.67 | 3.77 | 6.19 | 34.2 | 47 |

These results are in line with the rheometer results and again compounds B/4 and B/8 give better results than the control compound in tensile strength, elongation and tear resistance. The variation in the test results between different batches can be seen from compounds B/9-B/11. Although these should be the same compound, the measurement results can differ. This fluctuation is natural and can be caused by a variety of different reasons such as changes in ingredient dispersion or different quality in the rubber plates and test samples. It is important to notice that the other samples as well can have such fluctuations, although they cannot be observed as only one batch of each compound has been made. This variation is important when the results are analyzed, and the CCD method calculations are made. The variation tells how accurate and reliable the predictions are when the optimal accelerator concentrations are calculated using the CCD method.

Only some of the test compounds were chosen for the ozone resistance and De Mattia tests, as was done previously with compound A. The compounds chosen for the ozone and De Mattia tests were B/0, B/3, B/4, B/8 and B/9. The emphasis was put on the compounds, which had a shorter $t_{90}$ time, than that of the baseline. In addition to the compounds with a short $t_{90}$ time, the control compound B/0 and a center point compound B/9 were chosen for these tests. The ozone resistance and De Mattia tests were done according to the methods described in sections 5.4.4 and 5.4.6 and the results for compounds B/0-B/11 are presented in Table 15.

***Table 15.*** *The ozone resistance and De Mattia test results for compounds B/0-B/11.*

| Compound | Ozone resistance (at 96 h) | L+2 mm (×1000 cycles) | L+6 mm (×1000 cycles) | L+10 mm (×1000 cycles) |
|---|---|---|---|---|
| B/0 | 60 % | 2.50 | 70.5 | 325 |
| B/1 | - | - | - | - |
| B/2 | - | - | - | - |
| B/3 | 60 % | 15.5 | 500 | >600 |
| B/4 | 60 % | 2.25 | 35.0 | 240 |
| B/5 | - | - | - | - |
| B/6 | - | - | - | - |
| B/7 | - | - | - | - |
| B/8 | 60 % | 7.25 | 97.5 | 237.5 |
| B/9 | 60 % | 3.50 | 65.0 | 550 |
| B/10 | - | - | - | - |
| B/11 | - | - | - | - |

The ozone test results are the same for all the compounds. This means that varying the vulcanization system does not affect the ozone resistance of the compound. The De Mattia test results have some differences, but they cannot be considered reliable. Photos of example De Mattia test samples are presented in Figure 30.
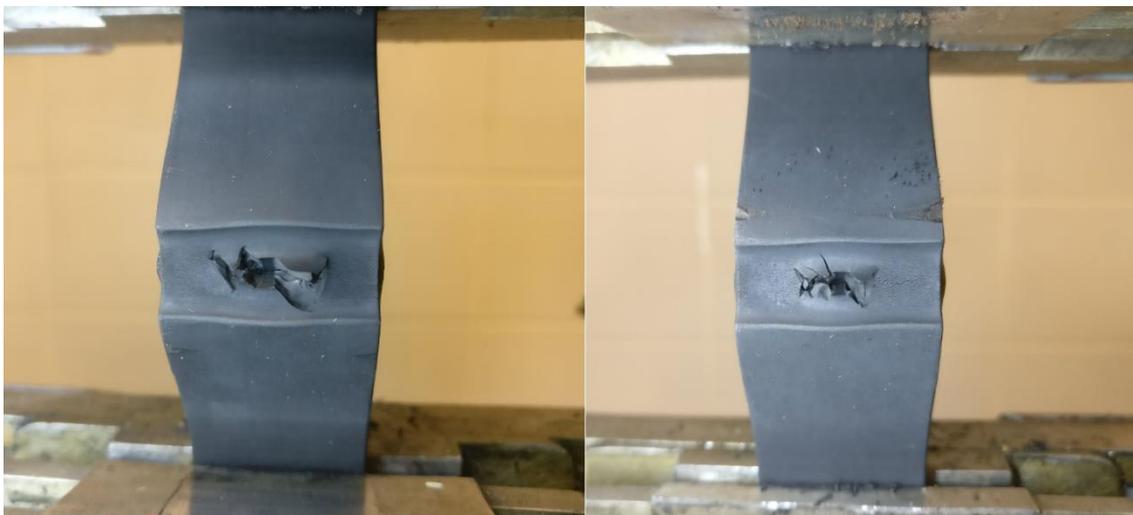


***Figure 30.*** *Examples of De Mattia test samples after testing.*

The samples presented here have not fractured in an ideal way. When studying the crack growth, the crack should grow in the original direction, which is perpendicular to the long edge of the sample. Here the cracks have started to propagate in various directions, which makes the analysis of the results difficult. With this kind of crack formation, the measured length is more random than regular, and it would take many tests to determine reliable differences between the compounds. This kind of cracking happened with all the test samples, so it seems to be characteristic to this type of rubber compound. Thus, the results of these De Mattia tests is not taken into larger consideration. All the test compounds had

similar values for tensile strength and hardness and better tear resistance than the control compound, so the new compounds should perform as well as or better than the original, when stressed or torn.

The results presented in Table 13 and Table 14 were entered into the Design-Expert 11 program and analyzed using the CCD response surface method. The program was used to draw one factor graphs, contour plots and 3D surface graphs to model how varying the phr of MBTS and ZBEC affects the properties of the compound. The ozone and De Mattia test results were not used in this analysis, as these tests were done for only some of the samples. The purpose of these tests was only to determine if the properties will remain satisfactory when the vulcanization system is modified. The contour plot for $t_{10}$ is presented in Figure 31.
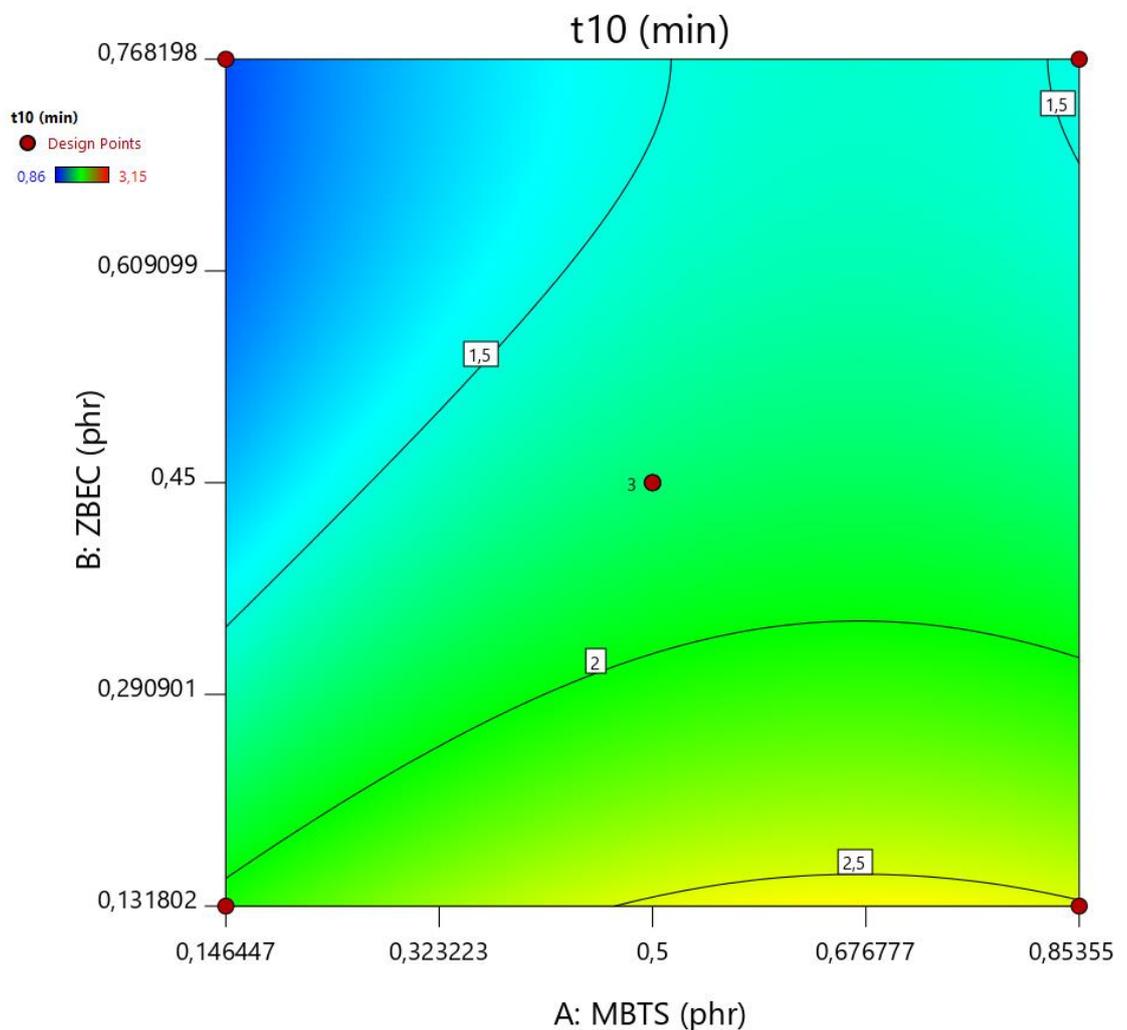


***Figure 31.*** *The contour plot for $t_{10}$ as a factor of MBTS (phr) and ZBEC (phr).*

The colors show the change of $t_{10}$ in the modeled area. For ideal vulcanization the $t_{10}$ should be as long as possible to prevent scorch and at the same time the $t_{90}$ should be as short as possible. However, these cases are rarely achieved simultaneously and thus the

optimization must be done by reviewing multiple properties. As expected, the longest $t_{10}$ times are achieved with high amounts of MBTS and low amounts of ZBEC. This is due to the fast acceleration of ZBEC and the slow initiation produced by MBTS, as presented in sections 4.3.1 and 4.3.3. According to the model, the $t_{10}$ is affected by the concentration of both MBTS and ZBEC and their quadratic components. The next modeled property is $t_{90}$ and its one factor graph is presented in Figure 32.
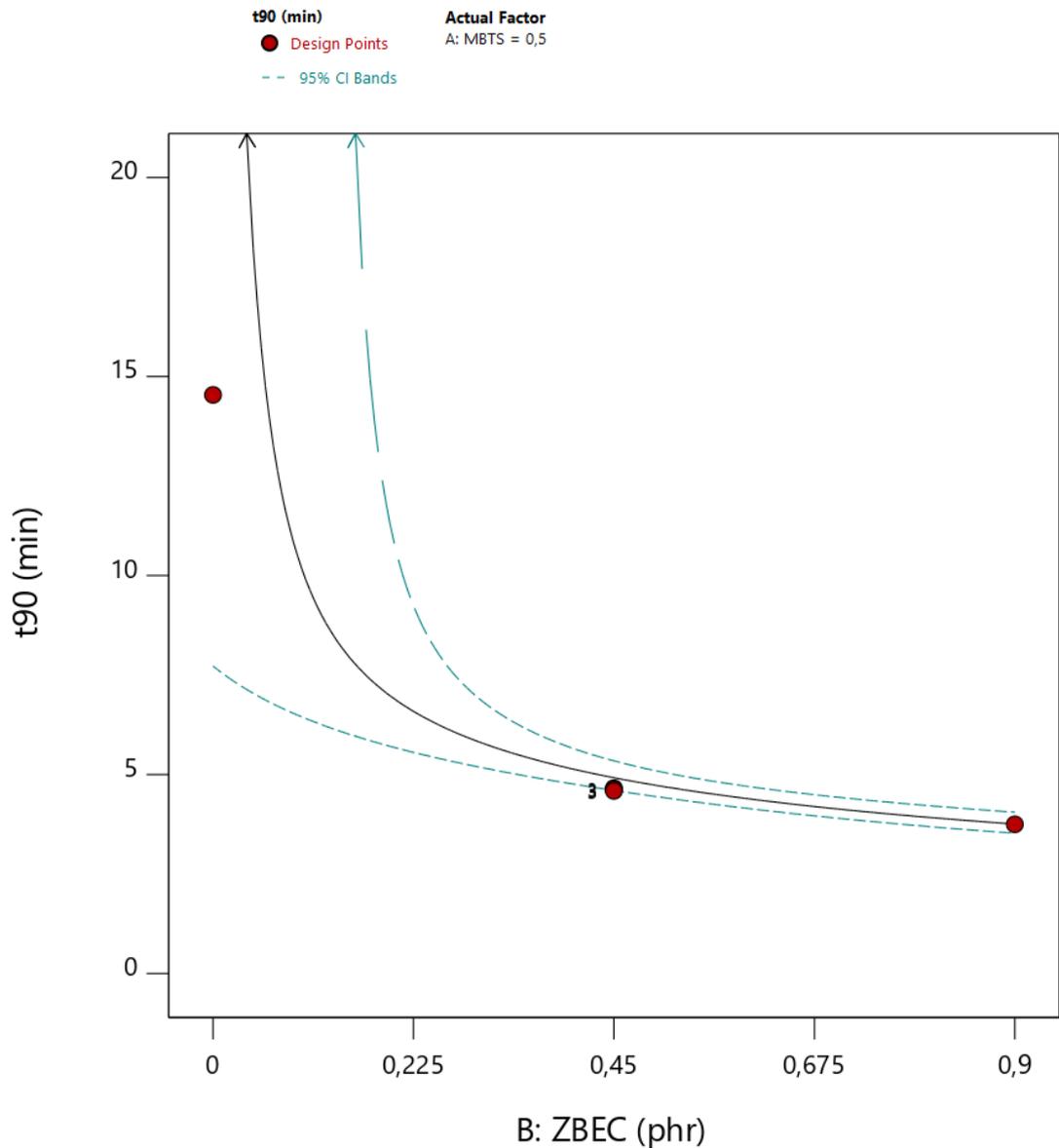


**Figure 32.**      *The one factor graph for $t_{90}$ as a factor of ZBEC (phr).*

The graph presents how the $t_{90}$ time varies as a factor of ZBEC at a fixed level of 0.5 phr of MBTS. According to the model, only the amount of ZBEC affects the $t_{90}$ at such a level that it can be detected. This case is not exactly true as MBTS also has some effect, but it is so minimal compared to ZBEC that it is left out. The effect caused by ZBEC is predictable as a higher loading causes a shorter $t_{90}$. The requirement was to find a compound,

which has a $t_{90}$, which is lower than or equal to the $t_{90}$ of the original, which was 4.25 minutes. Looking from the graph this means that a fairly high loading of ZBEC is required to achieve this $t_{90}$. The contour plot for the elongation at break is presented in Figure 33.
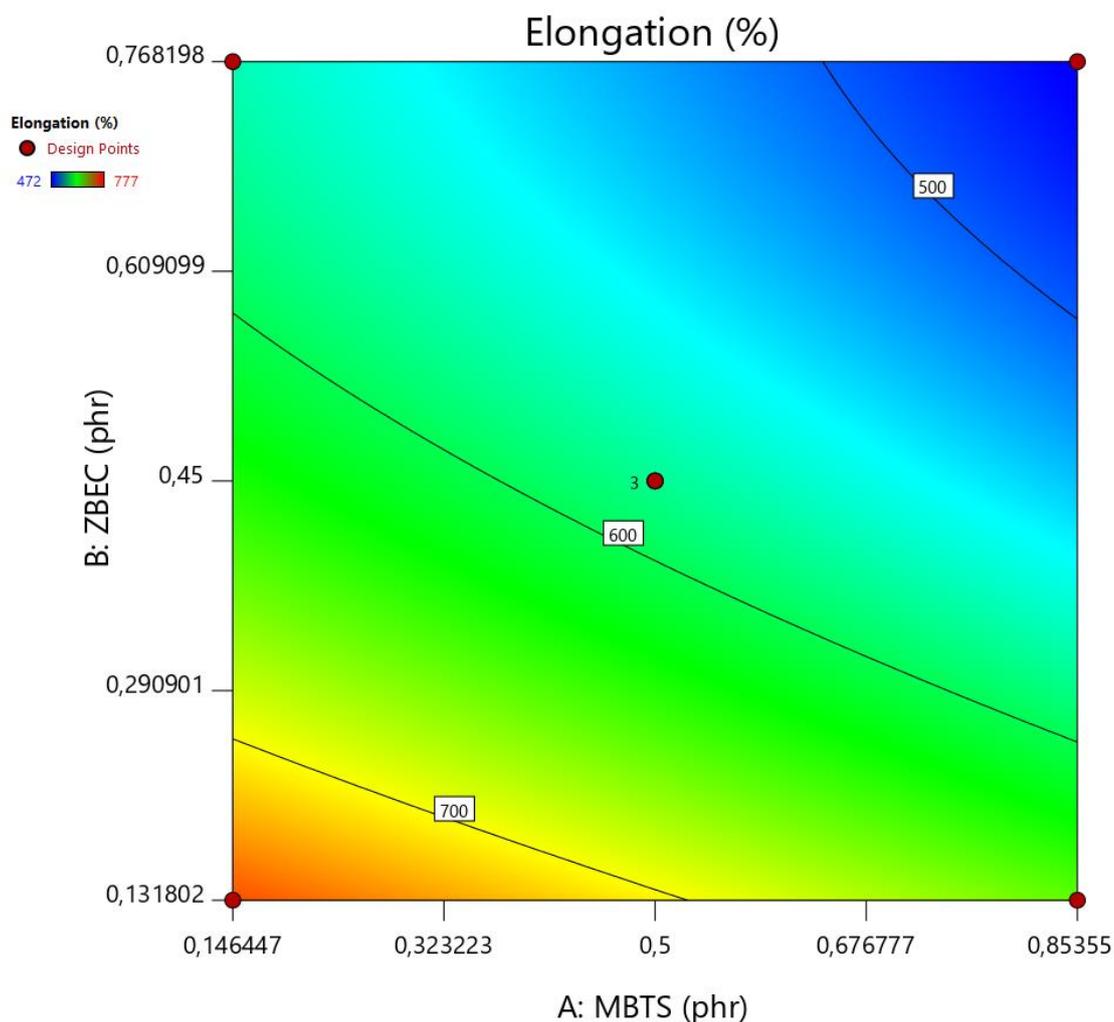


***Figure 33.*** *The contour plot for elongation as a factor of MBTS (phr) and ZBEC (phr).*

The contour shows the change of elongation at break as factors of MBTS and ZBEC loadings. The change is quite straightforward, as higher amounts of both accelerators decrease the maximum elongation. This fits the general prediction, as the higher amounts of accelerators increase cross-link density of the vulcanizate, which in turn decreases the elongation at break. An elongation at break of 500% should be achievable for this compound by keeping the accelerator amounts below the maximum values of the set range. This elongation is enough for the application of the compound. The 3D graph of the compound hardness is presented in Figure 34.
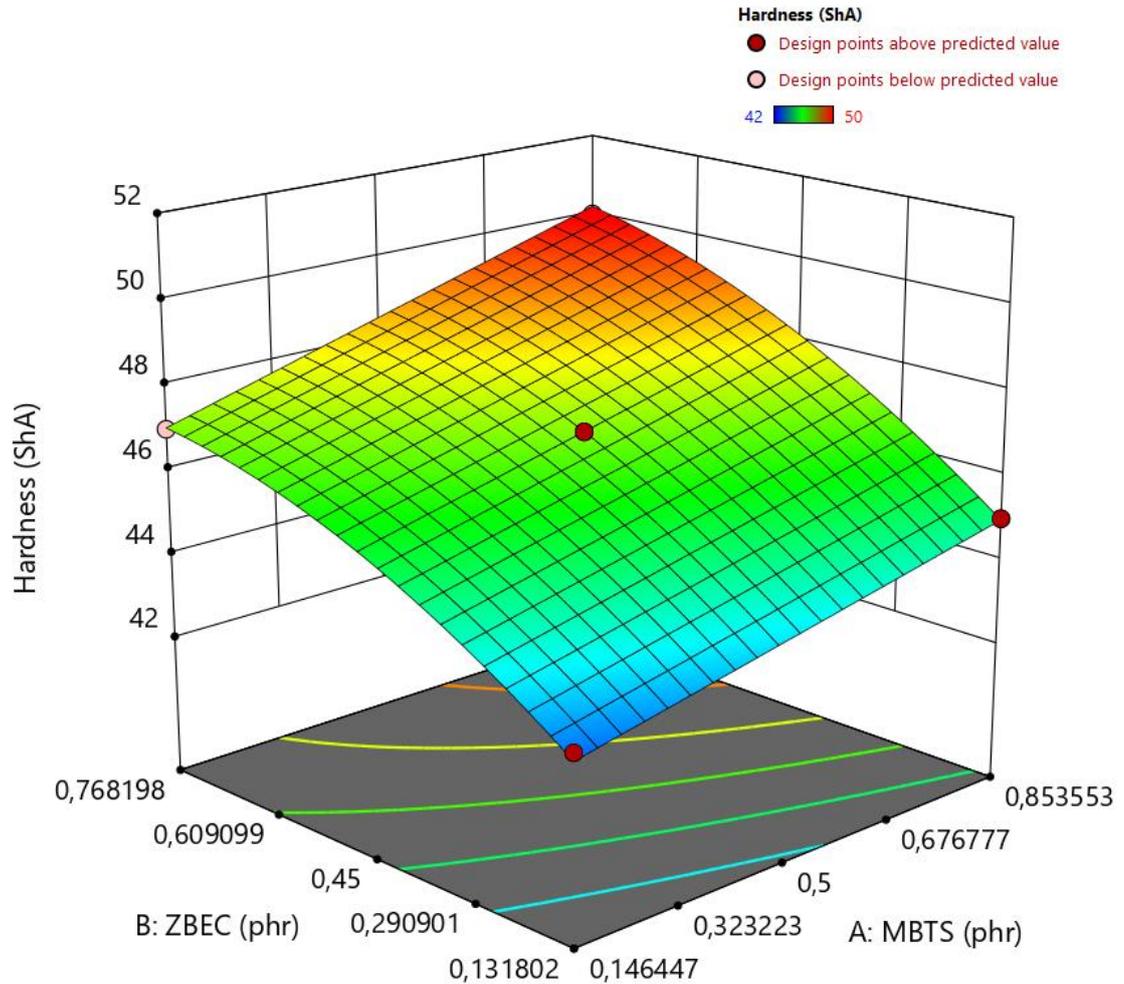
***Figure 34.*** *The 3D surface graph for hardness as a factor of MBTS (phr) and ZBEC (phr).*

The 3D surface graph is another version of showing similar information as the contour graph. Here the change in hardness is again modeled as a factor of the accelerator amounts. The dependence of hardness on the accelerator amounts is similar but inverse to elongation. Increasing the cross-link density increases the hardness of the compound. The hardness of the original compound was 49, so relatively high amounts of accelerator should be used, to achieve values close to it.

All these properties presented here in the graphs and plots make up the limitations which will be used to find the optimal vulcanization system for the compound. In addition to these properties, the 100% and 300% moduli are also important. These moduli have almost identical behavior compared to the hardness and thus their graphs are not presented here. The values naturally are different, and they will also be included in the optimization. In addition to the properties presented here, tensile strength and tear resistance of the compounds were also measured and modeled. The tensile strength values were so close to each other and random that an appropriate model could not be fitted into the data. The

tear resistance was only dependent on the amount of ZBEC, with the tear resistance decreasing as the amount of ZBEC increases. However, it was already noted in the context of the De Mattia results that these properties are satisfactory for all the compounds tested, so no problems should arise concerning them. The optimization limitations chosen for these properties arise from the properties of the baseline compound B/0 and the results presented by the other compounds. The limits were chosen so that they are fairly strict and the final choice for accelerator concentrations would be straightforward. The chosen limitations are presented in Table 16.

*Table 16.*     *Chosen limitations for the optimization of compound B.*

| Property | Desired result |
|---|---|
| $t_{10}$ (min) | > 1.5 |
| $t_{90}$ (min) | < 4.0 |
| Hardness (ShA) | > 49 |
| Elongation (%) | > 500 |
| Modulus 100% (MPa) | 1.5 – 1.9 |
| Modulus 300% (MPa) | 6.0 – 8.0 |

With these set properties, the new compound should perform as well as the original. The vulcanization times $t_{10}$ and $t_{90}$ were chosen so, that the new compound should be better than the original. It is also best to set the bar high as there will likely be fluctuation in the properties of the final compound. These property limits presented in Table 16 were entered into the Design-Expert graphical optimization tool and used to make an overlay plot. The lines in the plot represent the property limits as factors of the amounts of MBTS and ZBEC. These lines are the same which were presented in the previous plots and graphs. The overlay plot is presented in Figure 35.
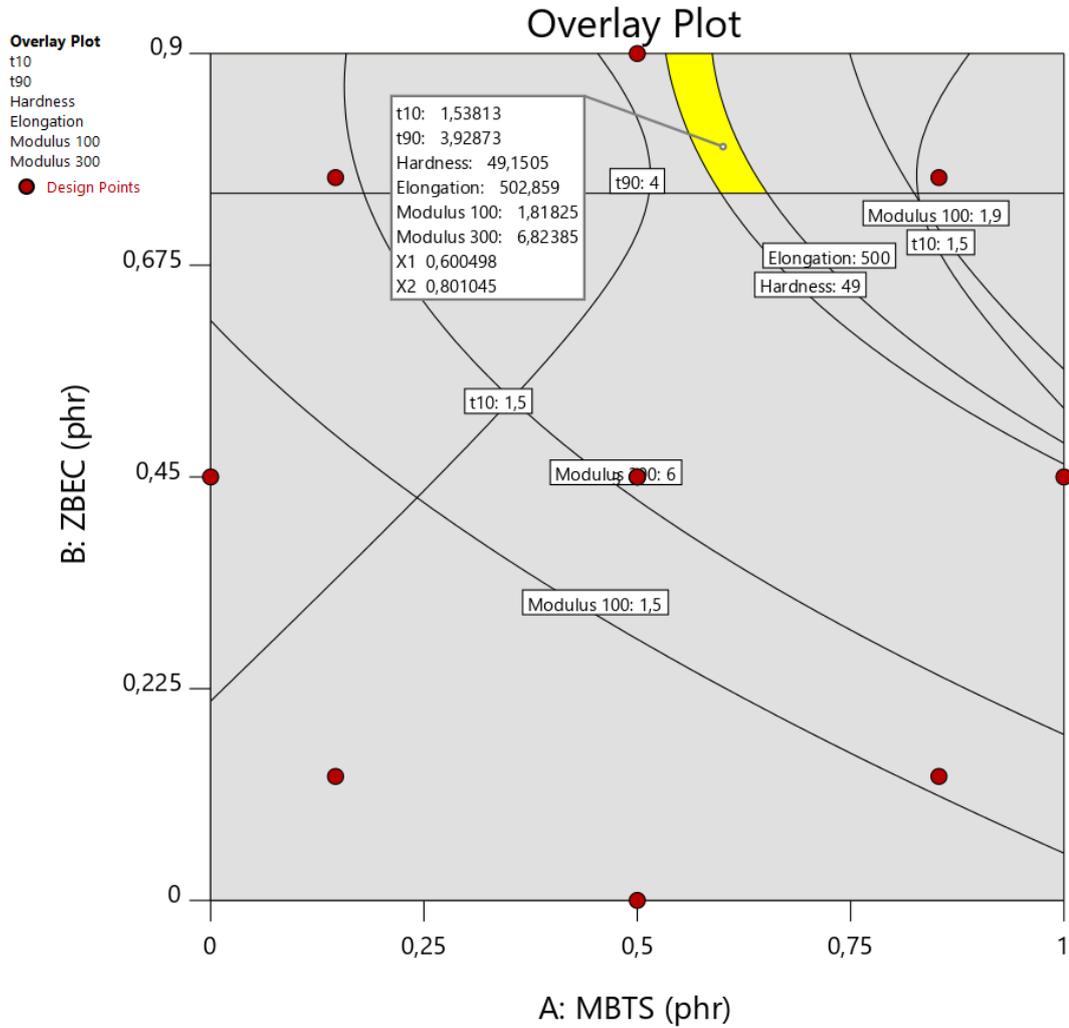
***Figure 35.*** *Overlay plot of the graphical optimization of compound B.*

The small yellow area at the top of the plot is a graphical representation of accelerator combinations, which fulfill the set requirements. This area is bordered by three compound properties, which are $t_{90}$, hardness and elongation. The area where the set requirements are met is small, but still achievable. The flag set at approximately 0,6 phr MBTS and 0.8 phr ZBEC gives the prediction for compound properties at these accelerator amounts. These amounts of the accelerators were also chosen for the confirmation run. The Design-Expert program was used to calculate the predicted properties at this measurement point and then one more set of measurements were done to compare the predicted values with the actual measurements. This comparison is presented in Table 17.

***Table 17.*** *Predicted results and the confirmation run for compound B.*

| Response | Predicted Mean | Std Dev | SE Pred | 95% PI low | Confirma-tion Run | 95% PI high |
|---|---|---|---|---|---|---|
| $t_{10}$ | 1.54 | 0.16 | 0.18 | 1.09 | 1.42 | 1.98 |
| $t_{90}$ | 3.93 | 0.04 | N/A | 3.46 | 4.16 | 4.68 |
| Hardness | 49.15 | 0.16 | 0.18 | 48.69 | 49.00 | 49.60 |
| Tensile Strength | 12.05 | 0.81 | 0.84 | 10.17 | 12.40 | 13.93 |
| Elongation | 503.01 | 22.01 | 25.00 | 443.89 | 522.00 | 562.13 |
| Modulus 100 | 1.82 | 0.04 | 0.05 | 1.70 | 1.83 | 1.94 |
| Modulus 300 | 6.82 | 0.25 | 0.28 | 6.15 | 6.88 | 7.49 |
| Tear Strength | 31.53 | 3.55 | 3.96 | 22.57 | 35.60 | 40.49 |

The predictions are given as a mean value, with standard deviation and standard errors included. Also, the prediction intervals where 95% of the repeated measurements should fall, are included in Table 17. The errors in this table have been calculated based on the fluctuation in the center point tests. The errors are relevant as there is also fluctuation in the properties of rubber between different batches when rubber is produced at a large scale. These fluctuations can be caused by several different reasons, such as changes in the quality of ingredients, varying environment conditions and different storage times. The requirements for a specific rubber compound are set so that the compound should always meet the requirements and thus perform well enough as a product, despite fluctuations.

The confirmation run meets the predictions of the physical properties, but not the vulcanization characteristic times $t_{10}$ and $t_{90}$. Although the limits are not met, the times are still level with the results of the original control compound B/0. The chosen confirmation point is near the edge of the modeled area, which is best presented by the flag in Figure 35. The model accuracy at this point is not the best, but the confirmation run shows that desirable results can be achieved in practice. The accelerator combination chosen for the new recipe is 0.6 phr MBTS and 0.8 phr ZBEC.

## 6.3 Future development

The new, safer accelerator combinations were found for both studied compounds. The final accelerator combination for compound A is 1.5 phr TBBS and 1.5 phr Vultac TB710, which is the recipe of compound A/9 from the tests. For compound B, the final choice is 0.6 phr MBTS and 0.8 phr ZBEC, which was achieved by using the graphical optimization tool in Design Expert 11. The laboratory phase of the accelerator replacement is complete, which also meets the objective of this thesis. Next, the necessary actions must be taken to complete the compound development. The development is not complete until

the new compound properly functions in production and the products made with the new compound are accepted by the customer. As a conclusion, both new recipes are presented in Table 18.

***Table 18.*** *The new recipes for compounds A and B.*

| Compound A | | Compound B | |
|---|---|---|---|
| Ingredient | phr | Ingredient | phr |
| NR + BIIR | 100 | SBR + NBR | 100 |
| Fillers + Oils | 60 | Fillers + Plasticizers | 75 |
| ZnO + Stearic acid | 5 | ZnO + Stearic acid | 2 |
| Stabilizers | 5 | Stabilizers | 3 |
| Sulfur | 0.5 | Sulfur + Retarder | 2 |
| TBBS | 1.5 | MBTS | 0.6 |
| Vultac TB710 | 1.5 | ZBEC | 0.8 |

For compound A, the development will continue with replacing other ingredients to make the production even safer and the final product itself healthier and better for downstream users. The continued development will be done using the accelerator combination, which was chosen here. At the end, the vulcanization system might require optimization similar to what was done for compound B to achieve the best performance, like what was done with compound B. The important result is that satisfactory results can be achieved with the chosen accelerators, even with a poor baseline compound. The production tests can begin, when the required replacements have been made and the desired properties have been achieved.

The new recipe achieved for compound B is a proposition for a new production recipe and the large-scale tests will start soon. It was already mentioned in section 4.5.5 that the compound B is used for a product in food contact. This recipe change also requires new tests to confirm it meets the BfR requirements. Samples must be sent for migration tests to confirm that the compound is safe for food contact use. The manufacturing of new products can only begin after the compound has received the approval.

In general, after a proposition for a recipe change has been formulated in the laboratory, the first production tests must be made. A test batch of rubber will be made in production scale and test products will be made from this batch. First the manufacturer must approve the products and if these products are made for a certain customer, then the customer must also approve them. After all these tests, the large-scale production can begin with the new compound. The properties of compounds are often different when they are mixed in laboratory scale, compared to production scale. Also, the laboratory tests do not predict well enough how the compound will behave when the actual end products are manufactured. Therefore, all the steps are required, before a compound development project is complete.

# 7.  CONCLUSION

The purpose of this thesis was to improve the safety of rubber production and the end products by removing a nitrosamine producing vulcanization accelerator from use. The objective was to find suitable alternative accelerators for TMTD in two different rubber compounds. The hypothesis was that straight replacements would be found for TMTD in both studied compounds and new recipes could be created for these compounds with the use of other accelerators which do not produce regulated nitrosamines.

The formation of hazardous nitrosamines by certain vulcanization accelerators is a known issue in the rubber industry. Nitrosamines are potential carcinogens and they can be formed in the production, storage or the end use of the rubber. Thus, there is a common goal to get rid of nitrosamine producing compounds to improve the health and safety of both the workers and the downstream users of rubber products.

Two rubber compounds were studied in this thesis. Both compounds are currently used in production by Teknikum Group Ltd. Compound A was a mixture of natural rubber and bromobutyl rubber and compound B was a mixture of styrene butadiene rubber and acrylonitrile butadiene rubber. Eleven different test compounds were mixed from the masterbatch of compound A and twelve from the masterbatch of compound B. Laboratory tests on the vulcanization characteristics, tensile properties, tear resistance, hardness and ozone resistance were done on both compounds. In addition to these tests, the low temperature retraction of compound A was tested, and the flex crack growth of compound B was tested. The results obtained in all the tests of this work were compared with each other to determine how the changes in the vulcanization system affect the above-mentioned properties and to find suitable accelerator combinations to replace the potentially hazardous TMTD.

The test accelerators chosen for compound A were TBzTD and Vultac TB710, which were combined with primary accelerators MBTS and TBBS. It became clear after the testing that the original control compound A/0 had not been optimized and this created problems in reliably comparing and analyzing the results of the test compounds. The expectation was that TBzTD would provide a straightforward replacement, as it is similar to TMTD in structure. This did not work out as planned, but fortunately Vultac TB710 functioned well and gave satisfying results in all the laboratory tests made. The cross-link density and thus many other properties of the thiuram compounds were poor. The compounds where the Vultac accelerator was used, had higher cross-link density and good tensile strength, hardness, ozone resistance and low temperature retraction. The final choice as the new accelerator system for compound A is a combination of TBBS and Vultac TB710.

The test accelerator chosen for compound B was ZBEC in combination with the original primary accelerator MBTS. The accelerator choice for compound B was more limited because this compound is used in a food contact application and it must pass the BfR regulations. The experimental setup for compound B was designed according to central composite design, and the test results were analyzed with a Design-Expert 11 program. The expectation was that a suitable combination of MBTS and ZBEC could be found within the chosen range of accelerator amounts. The results of the tests were entered into the program and the analysis tools were used to determine the dependence of properties on the amounts of accelerators. The property limits for the compound optimization for $t_{10}$, $t_{90}$, hardness, elongation at break, modulus at 100% and modulus at 300% were chosen based on the control compound and the overall performance of the test compounds. The CCD method proved successful in designing the experiment setup and a satisfying combination for the amounts of MBTS and ZBEC was found using the optimization tools in the Design-Expert 11 program.

The requirement for the development of the rubber compounds was that the properties must remain equal to the original compound or improve from them. In compound A, the properties improved substantially compared to the control compound, which was clearly not at an optimal level. In compound B the requirements of the vulcanization times were met and at the same time the tensile strength, elongation and tear resistance improved compared to the original compound. The hypothesis was confirmed for both compounds, as TMTD was successfully replaced with other secondary accelerators, which do not produce regulated nitrosamines.

The future goal following this thesis is to implement the recipe changes discovered in this thesis. The replacement of TMTD is part of a larger development process of compound A. Other ingredient replacements will follow to make both the production of this rubber compound and the final products safer. After these replacements are complete, the production tests and product approval can begin. Compound B will not be modified in other ways and the next step will be to produce a test batch of this compound in production scale and send tests samples of the compound for the appropriate BfR tests.

This thesis confirms that a nitrosamine producing accelerator such as TMTD can be replaced by a safer alternative without altering the compound in other ways. The replacement can also be done with an accelerator from a different class than the original one, which is proven by both test compounds in this thesis. Two different types of rubber compounds have been demonstrated and these examples propose a good basis to extend the replacement to other rubber compounds and other hazardous nitrosamine producing accelerators as well. The successful replacement of hazardous TMTD demonstrated in this thesis work will contribute to reducing the total exposure to hazardous nitrosamines for the production workers and the downstream users involved with the studied rubber compounds.

The general trend in the rubber industry is that the quantity and variety of hazardous substances will decrease over time. Increasingly more emphasis is put on the health and safety of the workers producing rubber and the downstream users of the products. The smaller availability of hazardous chemicals and the demands of customers will drive companies to search for better alternatives and bring health and work safety improvement on a large scale. Unfortunately, healthy alternatives often have inferior properties compared to traditionally used ingredients. This means that compromises must be made, and, in the end, the designated use of the end products will dictate the requirements. This type of development also creates challenges for compounding chemists to come up with new ideas to improve the rubber compounds using a smaller and more regulated selection of ingredients.

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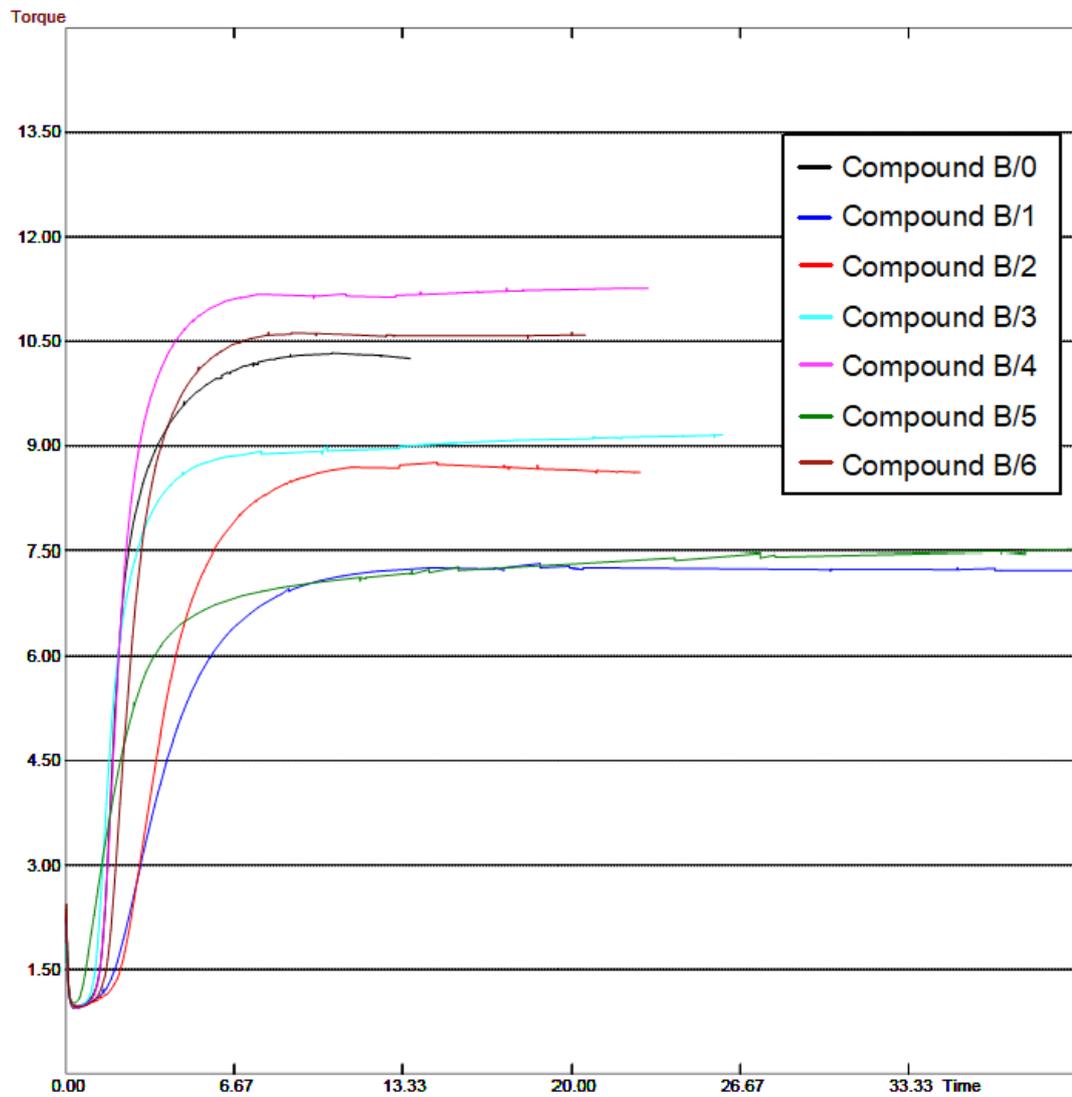
## APPENDIX A: RHEOMETER CURVES FOR RUBBER COMPOUNDS A/0-A/5
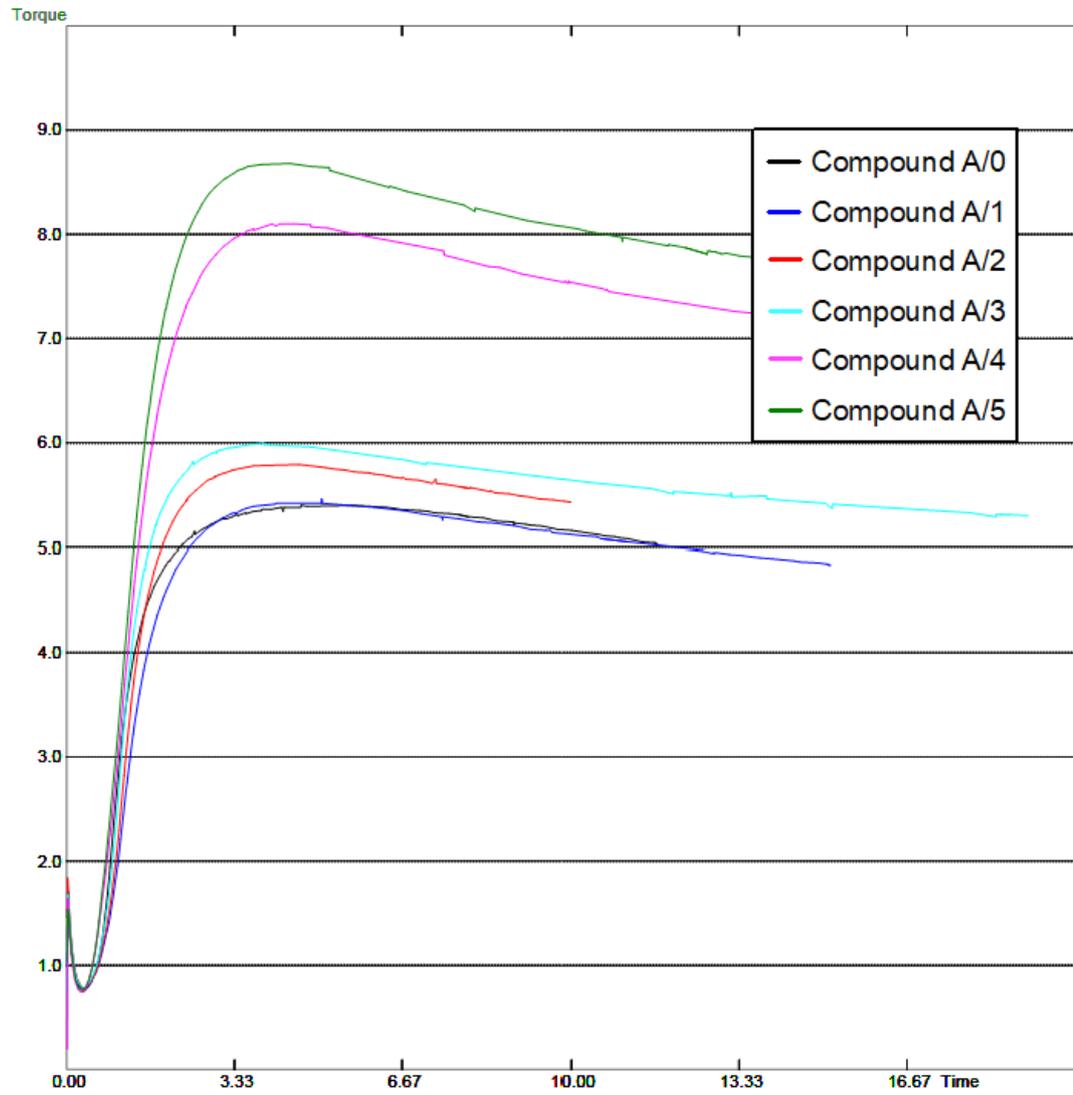
# APPENDIX B: RHEOMETER CURVES FOR RUBBER COMPOUNDS A/0, A/6-A/10
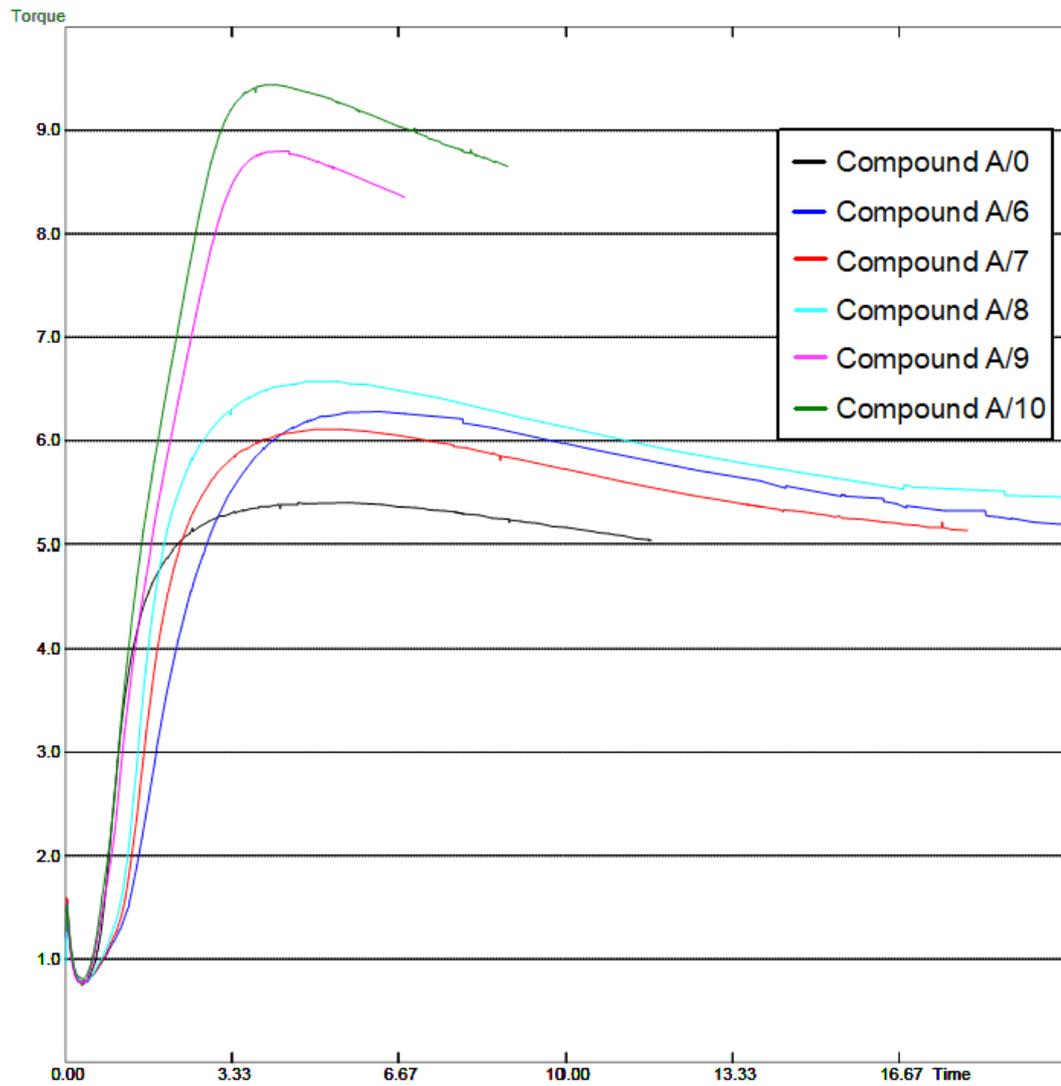
# APPENDIX C: RHEOMETER CURVES FOR RUBBER COMPOUNDS B/0-B/6

# APPENDIX D: RHEOMETER CURVES FOR RUBBER COM-
# POUNDS B/0, B/7-B/11