

REDUCED ZINC OXIDE LEVELS IN SULPHUR VULCANISATION OF RUBBER COMPOUNDS



The research described in this thesis was financially supported by the Ministry of Economic Affairs in the Netherlands in the framework of the Innovative Research Program (IOP): Environmental Technology / Heavy Metals.

Reduced zinc oxide levels in sulphur vulcanisation of rubber compounds;
mechanistic aspects of the role of activators and multifunctional additives

By G. Heideman

Ph.D. Thesis, University of Twente, Enschede, the Netherlands, 2004.
With references – With summary in English and Dutch

Copyright © G. Heideman, Enschede, 2004
All rights reserved.

Cover design by G. Heideman

Cover illustration: Diffuse emissions of zinc from products, such as the wear of tyres and run off from galvanised structures may enter the environment. Although zinc is generally considered one of the least harmful of the heavy metals, specifically soluble zinc compounds are classified as ecotoxic to aquatic organisms. If there is spillage into a watercourse, there might be an immediate localised toxic effect on algae in particular.

Printed by Print Partners Ipskamp, P.O. Box 333, 7500 AH, Enschede, the Netherlands

ISBN 90 365 2081 9

REDUCED ZINC OXIDE LEVELS IN SULPHUR VULCANISATION OF RUBBER COMPOUNDS

**MECHANISTIC ASPECTS OF THE ROLE OF ACTIVATORS
AND MULTIFUNCTIONAL ADDITIVES**

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof. dr. F.A. van Vught,
volgens het besluit van het College voor Promoties
in het openbaar te verdedigen
op vrijdag 15 oktober 2004 om 13.15 uur

door

Geert Heideman

geboren op 22 april 1976
te Dinxperlo

Dit proefschrift is goedgekeurd door:

Promotor : prof. dr. ir. J.W.M. Noordermeer

Assistent promotor : dr. R.N. Datta

'Who is as the wise? And who knows the explanation of things?'
Ecclesiastes 8:1

'A friend loves at all times, ...'
Proverbs 17:17

*Voor Judith
en voor mijn ouders*

Table of Contents

Chapter 1	Sulphur Vulcanisation and Zinc Oxide, a Concise Introduction	1
Chapter 2	Effect of Activators in Accelerated Sulphur Vulcanisation, a Review	7
Chapter 3	Optimisation of Zinc Oxide as Activator for Sulphur Vulcanisation in Various Rubbers	43
Chapter 4	A Study of the Influence of Zinc Oxide in Different Stages of Vulcanisation by MCV	59
Chapter 5	Effect of Zinc Complexes as Activator for Sulphur Vulcanisation in Various Rubbers	79
Chapter 6	Effect of Various Metal Oxides as Activator for Sulphur Vulcanisation in Various Rubbers	101
Chapter 7	Multifunctional Additives as Zinc-free Curatives for Sulphur Vulcanisation	125
Chapter 8	Zinc Loaded Clay as Activator in Sulphur Vulcanisation	153
Chapter 9	General Summary and Final Remarks	177
Samenvatting		185
Main Symbols and Abbreviations		189
Bibliography		191
Curriculum Vitae		193
Nawoord		195

Sulphur Vulcanisation and Zinc Oxide, a Concise Introduction

'The best way to become acquainted with a subject is to write a book about it.'
Benjamin Disraeli (1804 – 1881)

This introductory chapter provides a general outline of the topic of this thesis and gives some insight in the reasons to perform this research. The different approaches to reduce the potential harmful environmental impact caused by rubber compounds, with particular emphasis on activators, are shortly summarised.

1.1 HISTORICAL BACKGROUND

The famous vulcanisation process, or the process by which rubber is heated with sulphur to create a network of chemical crosslinks, was invented by Charles Goodyear already in 1839.¹ The vulcanised product is not sticky like raw rubber, does not harden with cold weather or soften much except at very high temperatures, is elastic, jumping back into shape when deformed instead of remaining deformed as unvulcanised rubber does and is highly resistant to abrasion. The process, a key advancement during its time, has been refined and improved since.^{2,3}

The rubber industry had to wait till the first decades of the 20th century before three discoveries greatly improved the quality and durability of rubber: organic accelerators, reinforcing carbon black filler and antioxidants.⁴ Inorganic activators/accelerators, like lead oxide, magnesium oxide and calcium oxide, were already added to reduce the vulcanisation time. The discovery of the first organic

accelerator by Oenslager in 1906, however, brought a really great improvement. This development was later on indicated as the greatest breakthrough since the beginning of the rubber industry.

The unaccelerated vulcanisation process utilised elemental sulphur at 8 parts per 100 parts of rubber (phr) and required a temperature of 142°C for 6 hours. By adding a few parts of organic accelerator, the vulcanisation time was reduced enormously.^{3,5} Further it was found that zinc oxide (ZnO) acts as a so-called activator, boosting the effect of most organic accelerators.

Table 1.1 Reduction of vulcanisation time obtained over 70 years

Year	1850	1880	1905	1920
Natural Rubber	100	100	100	100
Sulphur	8	8	6	3
Zinc oxide	-	5	5	5
Aniline	-	-	2	-
Stearic Acid	-	-	-	1
2-Mercaptobenzothiazole (MBT)	-	-	-	1
Optimal vulc. time at 142°C, min.	360	300	180	30

The use of accelerators in combination with zinc activators has a pronounced effect on the speed of vulcanisation and on the distribution of crosslinks formed. The advantage of organic accelerators lies not only in the shortening of the vulcanisation time, but also in lowering the temperature of vulcanisation and reducing of the amount of sulphur needed. Besides these, the durability of rubber articles as well as the physical properties, in particular the tensile strength, are very much improved by organic accelerators.

Another important discovery was the application of carbon black as a reinforcing filler in rubber articles. Reinforcement, signifying an increase in tensile strength, abrasion resistance and other ultimate properties as well as modulus, was reported in 1905, with ZnO as filler. Carbon black had been used as a colouring agent for a long time, but around 1904 experiments with carbon black as reinforcing agent indicated a strong increase in tyre tread wear resistance.⁶ Since 1912 the previously used ZnO was replaced in tyre treads by a high loading of carbon black to develop adequate physical properties. Nowadays, carbon blacks, and since the early nineteen forties also silicas are used for reinforcement and normally provide good physical properties for the cured rubber compound. A small amount of ZnO is still added because it plays an important role in the vulcanisation reactions.

Although sulphur vulcanisation is known since 1839, its exact mechanism is not completely understood and remains subject of research.⁷⁻¹⁰ The overall course of sulphur vulcanisation is generally accepted, but there is still no general agreement as to the nature of the active sulphurating agent and the mechanism of its reaction with the rubber molecule, in particular as to whether or not zinc is involved.^{11,12} Several mechanisms have been proposed, but fully elucidating the mechanisms remains difficult because of their complexity and the structural difficulties with analysis of vulcanisates.

In the past century much progress has been made in understanding the mechanism, especially by improving existing and developing new structural analysis methods. A major part of the knowledge of mechanisms and crosslink structures originates from the vulcanisation of a low molecular weight model as a substitute for the reactive unit of a rubber. This Model Compound Vulcanisation (MCV) method has become a vital tool to study the vulcanisation in detail.^{13,14}

Nowadays there is good evidence that zinc plays an important role in crosslinking, in particular in the efficiency of crosslinking. Although zinc is generally considered one of the least harmful of the heavy metals, the Dutch Ministry of the Environment decided, based on a very large number of studies, in 1985 to include zinc on a priority list of substances which were suspected to have negative environmental effects.¹⁵ Although zinc is defined as a heavy metal, the statement that zinc is dangerous for the environment per se is not correct. Zinc is natural, recyclable and inherently part of our environment. It is the 17th most common element in the earth's crust and an essential element for man, animals and plants,¹⁶ which is illustrated by the fact that for humans zinc deficiency can lead to adverse effects on growth, reproduction, cognition and immunity. Recently, the International Programme on Chemical Safety (IPCS) formed a Task Force on Zinc to establish Environmental Health Criteria for Zinc. Among its conclusions, the Task Force states: "Zinc is an essential element in the environment. The possibility exists for both a deficiency and excess of this metal. For this reason it is important that regulatory criteria for zinc, while protecting against toxicity, are not set so low as to drive zinc levels into the deficiency area."¹⁷

Small quantities of zinc enter the environment during manufacturing processes through point source emissions to air or wastewater from ZnO producers or user industries. In addition, diffuse emissions of zinc from products, such as the wear of tyres, run off from galvanised structures or roofing may enter the environment. Certain aquatic species have been shown to be sensitive to very low levels of zinc. Specifically soluble zinc compounds are therefore classified as ecotoxic to aquatic organisms. ZnO is also likely to be classified as such, which may lead to restrictions, in production or in applications of products in which it is contained. ZnO can be safely used in many applications as long as excess releases are controlled. However, if there is spillage into a watercourse then, as ZnO is in powder form, the dispersion rate is such that there would be an immediate localised toxic effect on algae in particular, because these are more sensitive to zinc than other organisms. Therefore, localised contamination sites, such as industrial plants, and diffuse sources require proper management.

Release of zinc into the environment from rubber occurs during production, during disposal and recycling of rubber products, for instance through leaching in land-fill sites. Also during service conditions, e.g. through wear of tires. In view of the upcoming legislations and ecolabelling requirements for vehicle tyres, for instance, it can be stated that it is desirable to keep the ZnO content in rubber compounds as low as possible, not only for environmental but also for economical reasons.¹⁸ The increased attitude of protecting the environment, gives rise to a demand for products that entail the least amount of environmental pollution impact.

1.2 AIM OF THIS THESIS

The aim of this thesis is to provide improved and new routes for reduction of the potential harmful environmental impact caused by rubber compounds, with particular emphasis on activators. The focus is on ZnO, zinc complexes and other metal oxides, because in rubber industry it is well-known that zinc species are the best activators for sulphur vulcanisation.

Complete elimination of zinc compounds would be rather ambitious. Nevertheless, alternative vulcanisation systems without any zinc or metal species will improve the knowledge regarding the role of activators and mechanisms involved in vulcanisation.

A large share of this research is directed to the development of a new activator, which does contain only traces of zinc, but demonstrates an effectivity comparable to conventional systems.

1.3 STRUCTURE OF THIS THESIS

The research described in this thesis encompasses different possible routes for reduction of ZnO in rubber compounds, an in-depth study of the role of activators in the vulcanisation process and provides an alternative for ZnO. This thesis is divided into 8 chapters, as outlined:

In **Chapter 2** of this thesis the background of the use of ZnO in rubber compounds and its effect is reviewed. It commences with an introduction of sulphur vulcanisation and a summary of the reaction mechanisms as described in literature, followed by the role of activators, particularly ZnO. The various possibilities to reduce ZnO levels in rubber compounding, that have been proposed in literature, are reviewed. Another paragraph is dedicated to the Multifunctional Additives (MFA) as zinc-free alternatives for conventional activator systems for sulphur vulcanisation. Furthermore, the Model Compound Vulcanisation (MCV) approach is described and an overview of MCV with respect to different models and activator/accelerator systems is given.

In **Chapter 3** reduction of ZnO by optimisation in two widely used different rubbers, *viz.* EPDM and s-SBR, is explored. Additionally, attention will be paid to special types of ZnO and one of the latest developments in this particular area: Nano ZnO.

In **Chapter 4**, subsequently the effects of ZnO in the different stages of the vulcanisation process are investigated *via* Model Compound Vulcanisation (MCV) experiments, so as to lay a base to study the basic principles and the effects of other activators later on. Therefore, particular emphasis is put on establishing reliable and accurate experimental procedures. The results are compared with the 'real' rubber results described in Chapter 3.

Another route for further reduction of the amount of ZnO in formulations would be the incorporation of zinc in a complexed, more chemically active form. This is the

subject of **Chapter 5**. Tests with several zinc complexes as activators in s-SBR and EPDM rubber are performed, as well as MCV studies to investigate the influence of zinc complexes in the different stages of vulcanisation.

Then, with the ultimate goal to develop a completely zinc-free vulcanisation system based on sulphur, in **Chapter 6** the application of a wide range of metal oxides as activator for sulphur vulcanisation is described. In addition to the s-SBR and EPDM rubber experiments, MCV is used to elucidate the influence of the metal oxide activators on the vulcanisation mechanisms.

Next, **Chapter 7** deals with a different type of zinc-free vulcanisation systems, mainly based on Multifunctional Additives (MFA), consisting of amines complexed with fatty acids. Several curing agents are synthesised with different functional groups. Parameters like basicity, steric hindrance and complexation strongly influence the vulcanisation process. It appears that the chemistry involved in the MFA systems is fundamentally different.

In **Chapter 8**, all information gained about ZnO as activator is used to develop a new activator for sulphur vulcanisation. The synthesis route as well as the effect on material properties is described. These systems with Zn²⁺-ions on a support, represent a new and novel route to reduce the zinc level, and therefore to minimise its environmental impact significantly.

The thesis is completed with a general evaluation of the described results as well as a brief outlook to future work: **Chapter 9**.

Parts of this thesis have been published,¹⁹⁻²¹ are in press,²²⁻²⁶ or still have to be submitted for publication.

1.4 REFERENCES

1. C.M. Blow, C. Hepburn, *Rubber Technology and Manufacture*, Butterworth Scientific, London (1981), 2nd Ed.
2. W. Hofmann, *Rubber Technology Handbook*, Hanser Publishers, New York (1994).
3. J.E. Mark, *Science and Technology of Rubber*, Academic Press, San Diego (1994), 2nd Ed.
4. J.v.d. Heijden, "The rise of the industry", *Natuurrubber* (2002).
5. G. Alliger, *Vulcanisation of Elastomers - Principles and Practice of Vulcanisation of Commercial Rubbers*, Reinhold Publishing, New York (1964).
6. S. Wolff, *Rubber Chem. Technol.*, **69**, (1996), 325.
7. L. Bateman, *The Chemistry and Physics of Rubber-like Substances*, MacLaren, London (1963).
8. M.R. Kresja, J.L. Koenig, *Rubber Chem. Technol.*, **66**, (1993), 376.
9. P.J. Nieuwenhuizen, *Rubber Chem. Technol.*, **70**, (1997), 106.
10. N.J. Morrison, M. Porter, "Crosslinking of rubbers", in *The synthesis, characterization, reactions and applications of polymers*, G. Allen, Ed., Pergamon press, (1984), 115.
11. P.J. Nieuwenhuizen, Thesis, University of Leiden, The Netherlands (1998).
12. M.M. Coleman, J.R. Shelton, J.L. Koenig, *Ind. Eng. Chem. Prod. Res. Develop.*, **13**, (1974), 154.
13. P. Versloot, *Rubber Chem. Technol.*, **65**, (1992), 343.
14. P.J. Nieuwenhuizen, J.G. Haasnoot, J. Reedijk, *Kautsch. Gummi Kunstst.*, **53**, (2000), 144.
15. A.V. Chapman, "Safe rubber chemicals: Reduction of zinc levels in rubber compounds", TARRC/MRPRA, (1997).
16. International Zinc Association (IZA), *Zinc in the Environment*, Brussels (1997), 2nd Ed.
17. World Health Organisation (WHO), *Environmental Health Criteria 221: Zinc*, Geneva (2001).
18. Internetpage, <http://europa.eu.int/comm/environment/ecolabel>.
19. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Kautsch. Gummi Kunstst.*, **56**, (2003), 650.
20. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Rubber Chem. Technol.*, **77**, (2004), 336.
21. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Rubber Chem. Technol.*, **77**, (2004), 512.
22. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Tire Technol. Intern.* 2004, In press.
23. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Rubber Chem. Technol.*, (2004), Submitted.
24. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *J. Appl. Polym. Sci.*, (2004), In press.
25. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Kautsch. Gummi Kunstst.*, **57**, (2004), In press.
26. G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Rubber Chem. Technol.*, (2004), Submitted.

Effect of Activators in Accelerated Sulphur Vulcanisation, a Review[#]

*'Since we cannot know all that there is to be known about anything,
we ought to know a little about everything.'*

Blaise Pascal (1623 – 1662)

This chapter provides relevant background information about the vulcanisation process, as well as the chemistry of thiuram- and sulphenamide-accelerated sulphur vulcanisation with emphasis on the role of activators, to lay a base for the research described in the following chapters. It commences with an introduction of sulphur vulcanisation and a summary of the reaction mechanisms as described in literature, followed by the role of activators, particularly ZnO. The various possibilities to reduce ZnO levels in rubber compounding, that have been proposed in literature, are reviewed. A totally different approach to reduce ZnO is described in the paragraphs about the various possible roles of multifunctional additives (MFA) in rubber vulcanisation. Another paragraph is dedicated to the role of amines in rubber vulcanisation, in order to provide some insight in the underlying chemical mechanisms of MFA systems. Furthermore, an overview of Model Compound Vulcanisation (MCV) with respect to different models and activator/accelerator systems is given. In the last part of this chapter the various functions of ZnO in rubber are summarised. It reveals clearly that the role of ZnO and zinc compounds is very complex and still deserves further clarification.

2.1 INTRODUCTION

Elastomers or rubbers play a very important role in modern technology. They constitute a class of materials, like metals, fibres, concrete, wood, plastics, or glass.

[#]This chapter has been published in Rubber Chemistry and Technology as a review article, Rubber Chem. Technol., **77**, (2004), 512.

The properties displayed by a particular rubber are determined by the compound composition, a mix of chemicals and additives, and the vulcanisation process. The latter process is one of the key factors in the technology of rubbers. It involves the conversion of raw rubber into a network through the formation of crosslinks. An essentially fluid material is transformed into a fully elastic rubbery product.¹ As more crosslinks are formed, the network becomes tighter and the forces necessary to achieve a given deformation increase.

Although sulphur vulcanisation is a very old large-scale industrial process, and a considerable research in studying this process was performed over the last several decades, a complete fundamental understanding of this complex chemical process remains a significant scientific challenge. A vigorous research effort continues today to unravel the mechanisms of the individual steps in the sulphur vulcanisation process. The difficulties encountered in this research field must be accredited to a combination of diversity, complexity and limitation. A wide range of chemical reactions takes place more or less simultaneously during the vulcanisation process, varying from reactions at the surface of metal oxides to radical chemistry. Superimposed, there are physicochemical aspects, such as dispersion and solubility of the chemicals in the rubber. Furthermore, standard analytical and chemical methods are not appropriate to analyse vulcanised rubber, because of the insolubility of the elastomer network, the low concentrations and the variety of crosslinked structures.

The objective of this chapter is to summarise and evaluate the work performed in the field of accelerated sulphur vulcanisation, with special emphasis on the role of activators in the curing process. Over the years, various accelerators, activators and retarders have been subsequently employed in order to better control the various aspects of the rate and extent of the vulcanisation process. This chapter treats the role of different activators in several vulcanisation systems, in particular zinc oxide (ZnO) as activator in thiuram- and sulphenamide-accelerated systems. Mechanistic details of sulphur vulcanisation are enclosed as an essential starting point for exploring new routes to reduce ZnO levels in rubber compounding. A new group of vulcanisation ingredients, which are referred to as Multifunctional Additives (MFA), should be regarded separately as they represent a fundamentally different approach. The last section of this chapter discusses and evaluates the work done in the field of Model Compound Vulcanisation (MCV) with respect to different models and activator/accelerator systems, to provide an overview of the work done and a proper background for interpreting the results obtained with the model studies.

This chapter has been compiled from many previous review articles on different aspects of vulcanisation published through the years. Important to mention are the early work of Bateman,² who provided a comprehensive review on the chemistry of sulphur vulcanisation, Scheele,³ Saville and Watson,⁴ who discussed network characterisation, and the Tun Abdul Razak Research Centre (TARRC) authors,^{2, 5, 6} reviewing the work on fundamental aspects of vulcanisation. More recently, Kresja and Koenig⁷ summarised details of the chemistry of accelerated and unaccelerated vulcanisation, while Nieuwenhuizen⁸ exhaustively reviewed the reaction mechanisms in thiuram- and dithiocarbamates-accelerated sulphur vulcanisation.

2.2 VULCANISATION AND THE ROLE OF ACTIVATORS AND ACCELERATORS

Vulcanisation agents are mostly based on sulphur or peroxide and sometimes other special agents or high energy radiation. Sulphur vulcanisation can only be applied to rubbers with unsaturation in the backbone or in rubbers with unsaturated side groups. The type of crosslinks formed in case of sulphur vulcanisation, largely depends on the vulcanisation system, *i.e.* vulcanisation chemicals which are added to the rubber. The crosslinks may be predominantly mono-, di-, or polysulphides. The rubber chains also become modified by cyclic sulphide groups and by accelerator-terminated pendant groups.⁹ The (polysulphidic) length distribution of these crosslinks is important, since it affects the thermal stability and the physical properties of a particular vulcanisate.¹⁰

The vulcanisation can be characterised relatively easily by measuring the evolution of crosslinks as a function of time, commonly called the cure curve, with an oscillating disc rheometer (ODR), moving die rheometer (MDR) or rubber process analyser (RPA). With these torsional (dynamic) rheometers the torque, or shear modulus, as a function of time at a certain temperature is measured. It is implicitly assumed that the modulus is proportional to the evolving concentration of crosslinks.

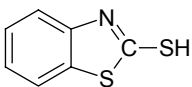
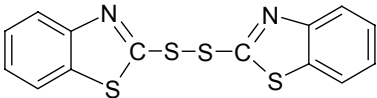
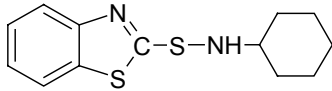
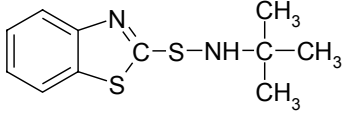
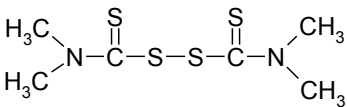
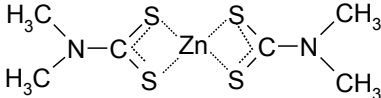
It is often desirable to increase the rate at which a rubber is vulcanised in order to reduce the time required to cure a rubber article. Increased vulcanisation rates accordingly lead to greater throughputs and decreased energy requirements in curing operations. Even a modest increase in vulcanisation rate can result in greatly increased productivity and substantial cost savings in the curing of rubber articles. Delbrück discovered around 1910 that piperidine and amines in general act as very potent and useful accelerators of vulcanisation, resulting in faster curing and improved properties of the vulcanisate.¹¹ Oenslager found that the addition of aniline to a rubber/sulphur formulation greatly increased the rate of vulcanisation and improved the final vulcanisate properties. These amines were the first accelerators for vulcanisation. Various derivatives of aniline were soon developed which were less toxic and possessed increased acceleration activity.¹²

Compounds which increase the rate at which rubbers vulcanise with sulphur are frequently referred to as primary accelerators. Some representative examples of compounds that can be utilised as primary accelerators include thiazoles and sulphenamides. In many cases the primary accelerators are used in conjunction with another accelerator, called a booster or secondary accelerator, which further increases the rate of sulphur vulcanisation.^{13, 14} Examples include dithiocarbamates and thiurams. A list of typical representatives of common accelerators is given in Table 2.1, where they have been categorised into benzothiazoles, benzothiazole-sulphenamides, thiurams, and dithiocarbamates. For an encyclopedic overview of all available accelerators and their characteristics the reader is referred to standard works such as by Hofmann¹ or Van Alphen.¹⁵ Although the chemical structures of the various accelerators presented in Table 2.1 are different, the basic features of the accelerators are similar; the accelerator is composed of one or two sulphur atoms between a pair of organic end groups. Structurally, all accelerators contain a common functionality, $N = C - S$.

Parallel to these developments runs the discovery of activators. It was reported in 1905 that ZnO acts as reinforcing filler for rubber compounds. Since 1912, however, the previously used ZnO was replaced in tyre treads by a high loading of carbon black to develop adequate physical properties. Inorganic activators/accelerators, like lead oxide, magnesium oxide and calcium oxide, were added to reduce the vulcanisation time. In the early 1920s the role of activators was discovered. It was found that ZnO, combined with stearic acid (SA), reduces the vulcanisation time and improves rubber properties, even in the case of unaccelerated vulcanisation. Fatty acids, like stearic acid, are used in addition to solubilise the zinc into the system and set zinc ions free to form complexes with accelerators.¹³ In special cases MgO and Ca(OH)₂ are used, as well as PbO in a number of specialty rubbers.

A subcategory of accelerated sulphur vulcanisation is sulphur-free systems, also referred to as sulphur-donor systems. In these systems the sulphur needed for network formation is supplied by the accelerator, which functions both as an accelerator and sulphur-donor. It should be noted that while unaccelerated sulphur systems are no longer of commercial significance, they are of interest as a starting point to understand accelerated sulphur vulcanisation systems.

Table 2.1 Common accelerators used in sulphur vulcanisation

Compound	Abbr.	Structure
Benzothiazoles		
2-Mercaptobenzothiazoles	MBT	
2,2'-Dithiobenzothiazole	MBTS	
Benzothiazolesulphenamides		
N-Cyclohexylbenzothiazole-2-sulphenamide	CBS	
N-tert-butylbenzothiazole-2-sulphenamide	TBBS	
Thiurams		
Tetramethylthiuram disulphide	TMTD	
Dithiocarbamates		
Zinc dimethyldithiocarbamate	ZDMC	

The aforementioned complexity of sulphur accelerated vulcanisation has given rise to many publications about the reaction mechanisms of the vulcanisation process. The situation is further complicated by the interaction of the accelerators and activators, each component influencing the reactivity of the other, and how these interactions affect the vulcanisation mechanism. Proposed mechanisms have ranged from radical to ionic. Several researchers have concluded that both radical and ionic mechanisms are operative.

Over the years, many researchers have proposed a division of the vulcanisation reactions into several sub-categories. In spite of all aforementioned differences, there seems to be a widespread agreement about the basic steps in accelerated sulphur vulcanisation, as illustrated in Figure 2.1, proposed by Morrison and Porter in 1984.¹⁶

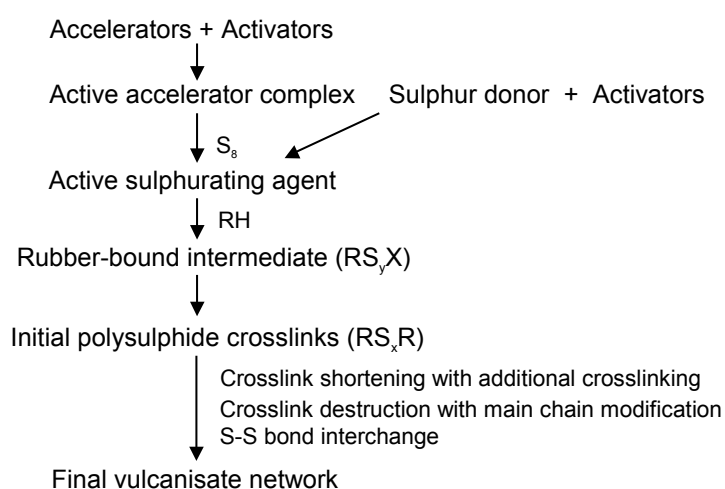


Figure 2.1 Outline reaction scheme for the sulphur vulcanisation of rubbers (R represents the rubber chain; X is the accelerator residue)

Another description of the vulcanisation process was reported by Ignatz-Hoover,¹⁷ suggesting four phases of sulphur vulcanisation for a sulphenamide-type accelerator:

- Initiation: a portion of the sulphenamide accelerator is decomposed. The MBT part of the accelerator can form an intermediate with zinc and the amine part can react with elemental sulphur.
- Induction: in this step sulphur exchange takes place. The polysulphidic accelerator is formed.
- Activation: the polysulphidic accelerator is transformed into (polysulphidic) MBTS.
- Sulphurisation and crosslinking: when all accelerator is consumed, sulphurisation and crosslinking takes place.

Ghosh *et al.*¹⁸ divided the vulcanisation reactions into three sub-categories: (i) *accelerator chemistry*, which involves the reactions leading to the formation of an active-sulphurating agent; (ii) *crosslinking chemistry*, which includes reactions leading to the formation of crosslinks; and (iii) *post-crosslinking chemistry*, which involves reactions that lead to crosslink shortening and crosslink degradation.

Although significant progress has been made in the last decades, the exact reaction mechanisms that occur in each of the discrete steps of the schemes are not completely unraveled yet. It is at least remarkable in view of the overwhelming number of vulcanisation studies that the statement of Bateman *et al.*,² made 30 to 40 years ago, is still true to a great extent: "Whilst it has long been appreciated, albeit intuitively, that sulphur vulcanisation is a very complex chemical process, the actual complexity (.....) is probably far in excess of what has ever been envisaged."

To judiciously reduce ZnO levels in rubber compounding, it is an absolute prerequisite to gain insight in the mechanistic details of sulphur vulcanisation. Paragraph 2.2.1 and 2.2.3 will deal with literature on mechanisms of accelerated sulphur vulcanisation in absence and presence of ZnO as activator, respectively, with special focus on thiuram- and benzothiazole-sulphenamide-accelerated vulcanisation. The generally accepted scheme, as depicted above in Figure 2.1, suggests the formation of an active accelerator complex via a reaction between the activator and the accelerator as a first step in the vulcanisation process. This complex interacts subsequently with molecular sulphur to produce a distribution of sulphurating species. These activated species then react with the allylic sites of the rubber chain and become intermediates or crosslink precursors, which are accelerator-terminated polysulphidic pendant groups attached to the rubber chain. These intermediates react with other intermediates or polymer chains resulting in polysulphidic crosslinks. These initial crosslinks contain a large number of sulphur atoms, but may eventually desulphurate over longer times to form shorter crosslinks, or degrade to cyclic sulphides or other main chain modifications.

2.2.1 Acceleration Mechanisms in Absence of an Activator

As a first step in sulphur vulcanisation, an active sulphurating species is formed, which is in a later stage transformed into a crosslink precursor. Gradwell proposed that polysulphidic accelerator and 2-Mercaptobenzothiazole-disulphide (MBTS) formation by interaction of the accelerator molecule with molecular sulphur in the absence of an activator, proceeds via a radical pathway as shown in Figure 2.2.¹⁹ The accelerator depicted in this figure is N-tert-butylbenzothiazole-2-sulphenamide (TBBS), as an example.

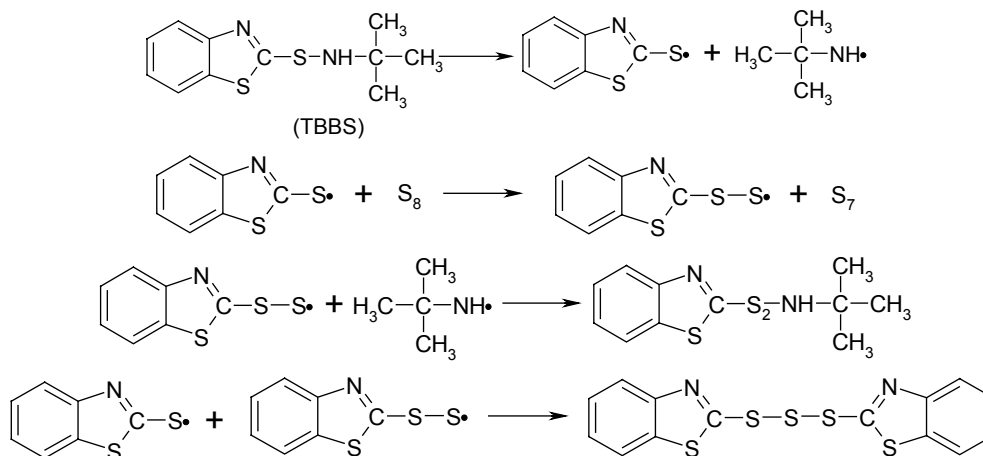


Figure 2.2 Reactional pathway for the accelerator and sulphur in the absence of an activator

Firstly, the S-N bond of the accelerator is cleaved resulting into two radical parts. The reason for this bond to break might be the stability of the mercapto radical due to stabilisation by resonance: Figure 2.3.

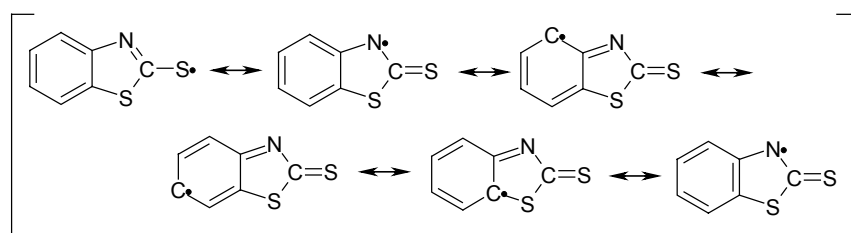


Figure 2.3 Resonance structure of radical formed from the accelerator mercaptobenzothiazole

The radical reacts with sulphur and results into a radical part with an extra sulphur atom. This new radical can react either with the amine radical to form a disulphidic TBBS molecule or with another mercapto radical, resulting in trisulphidic MBTS. The amine part can also react with sulphur according to the mechanism depicted in Figure 2.4.^{20, 21}

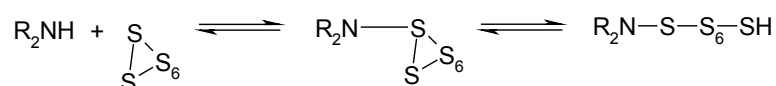


Figure 2.4 Reaction of amines with sulphur

Because the accelerator and the sulphur first react with each other, crosslinking does not immediately occur. This so-called delayed action improves the scorch time. Another contribution to the scorch time are the following reactions as depicted in Figure 2.5, in which the reaction rate K_C is lower than K_Q .

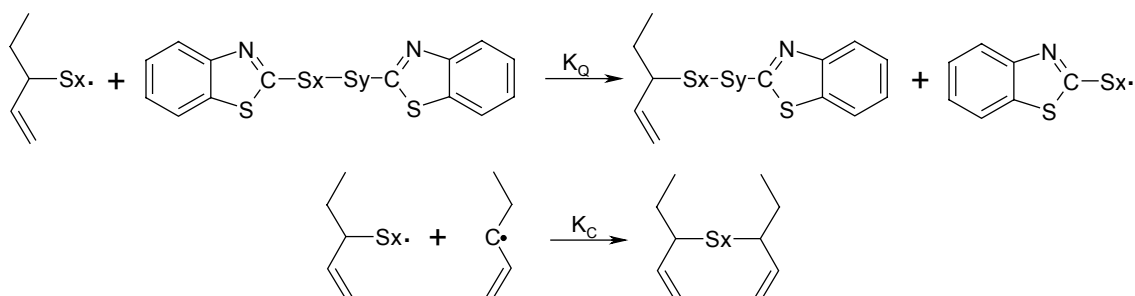


Figure 2.5 Crosslinking vs. crosslink precursor formation; $K_C < K_Q$

From this can be concluded that significant crosslinking occurs after the consumption of polysulphidic MBTS and transformation into 2-mercaptobenzothiazole (MBT) and a precursor according to the reactions depicted in Figure 2.6.

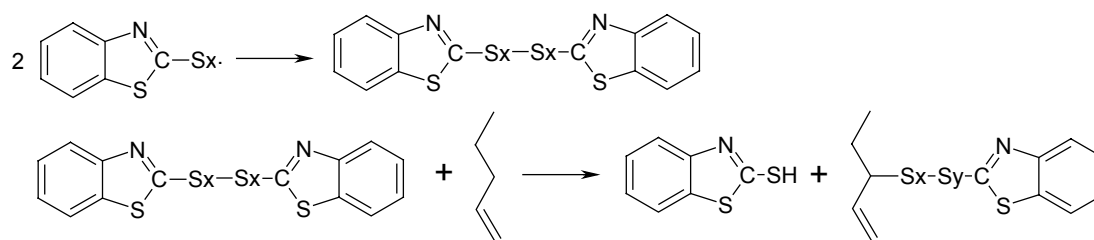


Figure 2.6 Crosslink precursor formation

This would explain the fact that in many model compound researches a lot of MBT is found, but hardly any (polysulphidic) MBTS. According to Gradwell²² crosslink precursors do not form crosslinks until all TBBS has been consumed. The polysulphidic TBBS is not detectable because of its instability.

The mechanisms shown are radical mechanisms.²³⁻²⁵ However, it is still unclear if the vulcanisation reactions occur via a radical or ionic pathway or even a combination, depending on the vulcanisation system. An ionic mechanism for the formation of crosslink precursors and crosslinks, shown in Figures 2.7 and 2.8 respectively, is proposed by Coran²⁶ and Bateman.²⁷

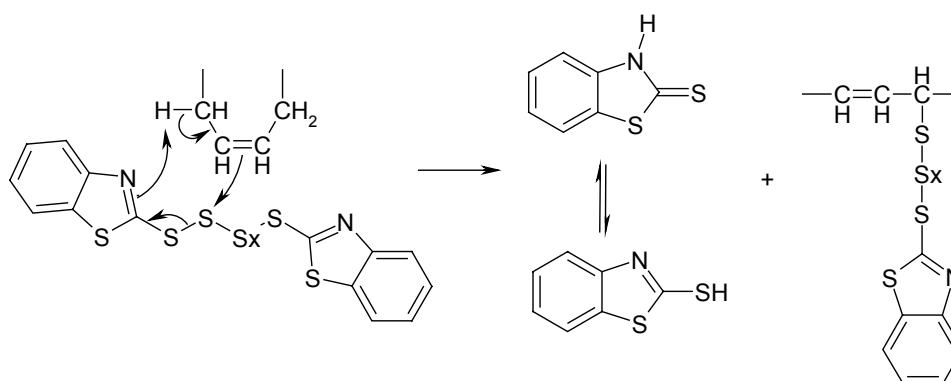


Figure 2.7 Ionic mechanism for the precursor formation²⁶

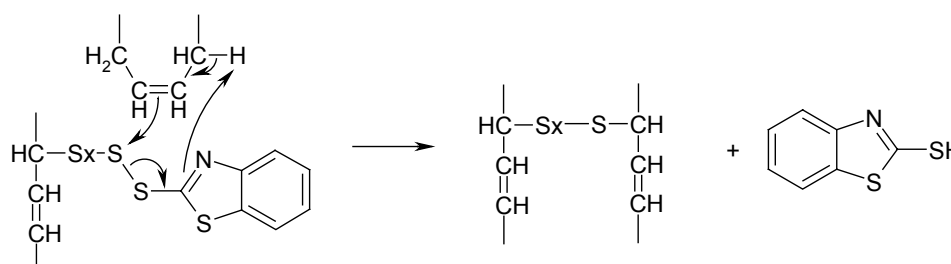


Figure 2.8 Ionic mechanism for the crosslink formation²⁶

It is generally assumed that the reactions occur via a mixture of radical and ionic mechanisms.¹³

2.2.2 ZnO as Activator for Sulphur Vulcanisation

ZnO is still generally known as the best activator for sulphur vulcanisation. As already mentioned in the previous chapter, there is an increasing concern regarding the potential environmental and health effects of release of zinc compounds into the environment from rubber products or rubber production.²⁸

A number of papers have been published on the effect of ZnO in the curing of rubber. ZnO is in many vulcanisation systems a precursor to zinc-derived accelerators.⁸ It reacts with most accelerators to form the highly active zinc salt.¹² Complex formation of the zinc ion with different accelerators is critical to get efficient curing. A preceding reaction with stearic acid forms the hydrocarbon-soluble zinc stearate and liberates water before the onset of crosslinking.²⁹ Adams and Johnson observed that the crosslink density increases with increasing zinc stearate concentration. The efficiency of crosslinking of natural rubber (NR) and polyisoprene rubber (IR) is largely increased when ZnO is present. Crosslink shortening is catalysed which leads to reduced reversion. ZnO appears to lead to a small increase in cure time and scorch safety.

In addition to its role as an activator for sulphur vulcanisation, there is also evidence that the inclusion of ZnO in a compound reduces heat-build-up and improves tyre abrasion resistance. ZnO acts as a 'heat sink', which accepts frictional energy without a large increase in internal temperature. It has also been found that ZnO improves heat resistance of the vulcanisates and their resistance to the action of dynamic loading.³⁰ The high thermal conductivity of ZnO helps to dissipate local heat concentrations that might otherwise affect the properties of rubber. The thermal properties of ZnO are particularly beneficial in applications such as rubber vibration mounts, where loading and cyclic stresses would otherwise generate heat and degrade the rubber. ZnO is also needed for bonding rubber to the steel cord of tyres and for bonding between metal and rubber in technical goods.

Besides improving the properties of vulcanised rubbers, ZnO also assists the processing of uncured rubbers. ZnO is added to rubber formulations to decrease shrinkage of moulded rubber products and maintain the cleanliness of moulds. This aids productivity by increasing the number of moulding cycles between cleaning. In earlier days zinc compounds were added as filler and to scavenge detrimental reaction products. Use of ZnO as filler is uneconomic due to its high cost, and hence it is normally replaced by other cheaper active fillers (carbon black or silicates).

In rubber formulations for other types of vulcanisation, e.g. peroxide, ZnO is also often present, although it does not activate peroxides. The role which ZnO can play in a peroxide-cured compound is as an acid acceptor in materials containing acid fillers or a polymer containing halogens. ZnO is also added to improve ageing resistance, possibly by reacting with the acidic by-products of the crosslinking reaction. It is also a crosslinking agent for polymers containing halogen as well as for those containing carboxyl groups.

2.2.3 Effects of ZnO as Activator of Accelerated Vulcanisation

Many mechanisms about the role of activators in sulphur vulcanisation have been proposed over the years.³¹ To get insight in the mechanism of ZnO in curing, low molecular weight compounds were used as representative models of elastomers.

Wolfe *et al.*³² studied the effects of ZnO on the mechanism of the reaction of cyclohexene with sulphur. The results showed a pronounced effect of ZnO on both rate and products of the reaction. The reaction rate was increased and the product distribution changed, which was an indication for a change in reaction mechanism. There seems to be a little doubt about the active role of the metal oxide in the formation of active sulphurating species. There is agreement, that accelerators and activators react to generate active accelerator complexes. The complexes interact with sulphur, a sulphur donor and other activators to generate the active sulphurating agent. It has been suggested in many different studies that Zn²⁺-ions form these active complexes with accelerators, which are more reactive than the free accelerator.^{13, 33} The active sulphurating agent then reacts at the allylic sites of the polymer unsaturations to form the rubber bound intermediate. This crosslink precursor can then react with another rubber bound intermediate or with another polymer chain to generate a crosslink. The exact activator role of ZnO is highly dependent on the type of accelerator present in the initial vulcanisation system.

In another mechanism it is assumed that ZnO is distributed in the form of crystal particles in rubber mixes. Molecules of accelerators, sulphur and fatty acids diffuse through the rubber matrix and are adsorbed on the ZnO with the formation of intermediate complexes. Nieuwenhuizen⁸ in his thesis proposed a mechanism in which the ZnO surface functions both as a reactant and as a catalytic reaction template, activating and bringing together reactants. The most important parameter here is the dispersion of the inorganic ZnO in the organic rubber polymer.

According to Coran²⁶ the addition of ZnO as an activator has a distinct effect on different stages of the vulcanisation process. It increases the rate of early (scorch) reactions that lead to formation of the crosslink precursors, increases the extent of crosslinking, but decreases the rate of the actual crosslink formation. Morgan *et al.*³⁴ suggested that ZnO increases the rate of different reactions in the accelerator chemistry by facilitating the opening of the sulphur ring leading to faster sulphuration of the active sulphurating species. In this section, the effect of ZnO on the formation of active sulphurating species, on the crosslink precursor and crosslink formation, and finally on the crosslink desulphuration and degradation will be discussed.

As mentioned in the previous paragraph, it is still unclear if the vulcanisation reactions in the absence of ZnO occur via a radical or ionic pathway. Manik and Banerjee³⁵, Shelton and McDonel³⁶ and Morita and Young³⁷ all concluded that in the presence of ZnO the reactions in sulphenamide-sulphur accelerated systems are mixed radical/ionic in nature.

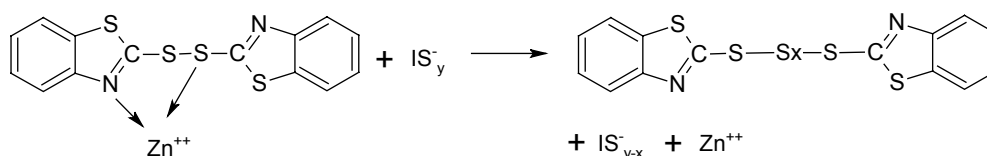


Figure 2.9 Formation of polysulphidic MBTS via a complex with zinc

When zinc or equivalently ZnO is present as an activator in the vulcanisation system, it catalyses the formation of macromolecular complexes. The rate of the

increase of the amount of sulphur atoms embedded in the accelerator, e.g. MBTS, is increased when ZnO is present, because of the interaction of Zn^{2+} with the accelerator. Due to the formation of the complex, sulphur insertion occurs more rapidly. A graphic representation is given in Figure 2.9, where IS_y^- represents an ionised form of linear sulphur. Several other structures of these macromolecular complexes have been suggested in literature. In Figure 2.10 the structure is shown in case zinc complexes with the accelerator polysulphides.

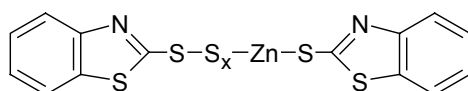


Figure 2.10 Complex with the zinc ion

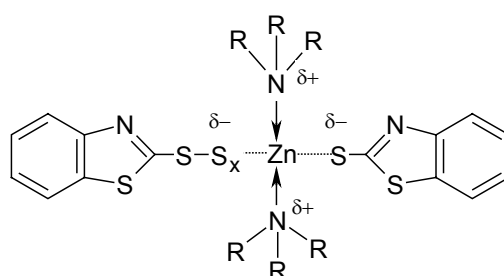


Figure 2.11 Complex with the zinc ion stabilised with ligands

If the zinc coordinates with an amine that is released from a sulphenamide or with carboxylate ligands, which are present in systems with stearic acid, the solubility and reactivity is strongly enhanced: Figure 2.11.

The two aforementioned structures implied that zinc is covalently bonded in the sulphidic chain of the accelerator. Another, perhaps more probable representation of the complex formation is shown in Figure 2.12.¹⁸

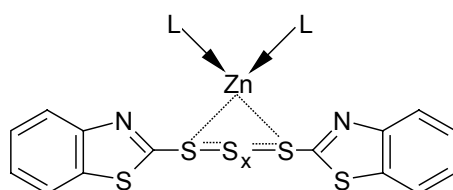


Figure 2.12 Complex with the zinc ion stabilised with ligands

These macromolecular complexes can be internally chelated, e.g. in dimethyl dithiocarbamate, or form a benzothiazole-zinc-complex.

A number of studies³⁸⁻⁴¹ on the effect of ZnO on the vulcanisation process have revealed that ZnO readily forms zinc-complexes with MBT upon heating, as shown in Figure 2.13. Although this reaction readily occurs, the formation of an insoluble layer of ZMBT on the surface of ZnO particles, however, might be the reason that the reaction of ZnO with MBT does not proceed to completion.^{39, 42} A similar reaction with MBTS and ZnO upon heating was not observed.

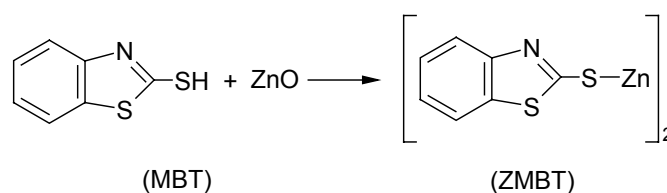


Figure 2.13 Reaction between MBT and ZnO

Gradwell and McGill⁴³ investigated the interaction of sulphenamide accelerators with sulphur, ZnO and stearic acid in the absence of rubber. They found that ZnO does not react with sulphenamide accelerators like CBS and TBBS. From this it can be concluded that the only way Zn-accelerator complexes like in Figure 2.10 can be formed, is via the reaction of MBT with ZnO to produce ZMBT, which eventually is converted into the active sulphurating complex.

MBT is initially formed by the thermal decomposition of the accelerator, as shown in Figure 2.14. With the MBT quickly converted into MBTS, it is likely that only small amounts of the zinc-accelerator complex are formed in that stage. The majority of the active sulphurating species are zinc-free structures. In the crosslinking stage, more MBT is formed and this leads probably to the formation of additional zinc-accelerator complexes.

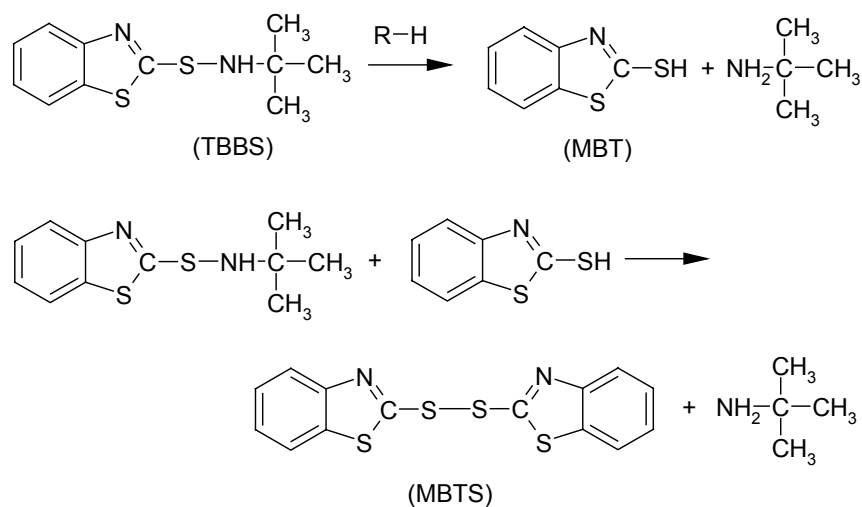


Figure 2.14 Thermal decomposition of TBBS and formation of MBTS
(R-H = Rubber hydrocarbon)

The formation of rubber bound intermediates, the so-called crosslink precursors, is a key stage in accelerated sulphur vulcanisation. As already shown in Figure 2.6, crosslink precursors are formed as a product of the reaction between accelerator polysulphides and the rubber chains. The resulting structure consist of an accelerator terminated polysulphidic group attached to a rubber chain. If zinc is complexed to the accelerator-polysulphide, the mechanism of crosslink-precursor

formation can be described as a concerted mechanism involving a six-membered ring in the transition state, with ZnS formed as a byproduct of this reaction.⁴⁴

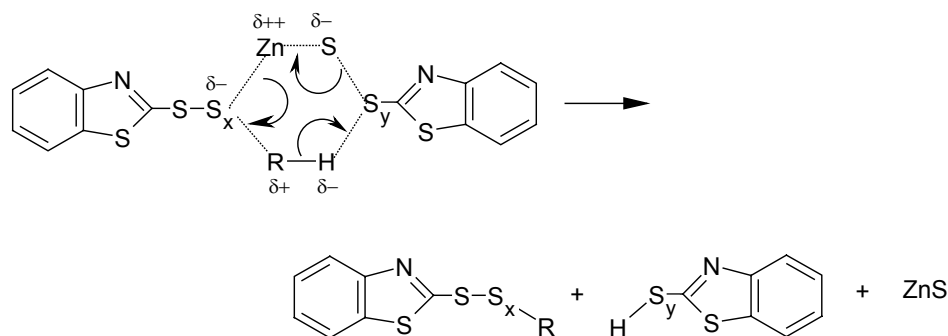


Figure 2.15 Crosslink precursor formation via a mechanism involving a six-membered ring in the transition state (R-H = Rubber hydrocarbon)

The sulphur attached to the zinc in the sulphurating complex has a nucleophilic character due to the presence of zinc. Amines further increase the nucleophilicity of the sulphur in the complex and thereby increase the rate of precursor formation.² The location of the scission of the zinc-accelerator complex depends upon the position where zinc is complexed on the sulphur chain, implying that different polysulphidic species can be formed. Only MBT, however, is thought to be stable, while the other species will undergo rapid reactions, like sulphur pick-up, attachment to allylic sites on the rubber chain and recombination to accelerator polysulphides.

Various mechanisms have been proposed for the conversion of crosslink precursors into crosslinks. Bateman² and Dogadkin *et al.*⁴⁵ have suggested a mechanism for the crosslink formation based upon the reaction between two precursor molecules, while subsequently a mechanism was proposed involving the reaction between a precursor molecule and the rubber chain. Although these reactions are basically catalysed by zinc-accelerator complexes, they can also occur in the absence of zinc, albeit at significantly lower reaction rates. Coran^{46, 47} proposed a mechanism for the formation of crosslinks by the direct reaction of the crosslink precursors with the rubber chain. In principle, any sulphur-sulphur bond in the crosslink precursor can break, but Coran *et al.*^{38, 46} have suggested that the weakest bond is the sulphur-sulphur bond adjacent to the benzothiazole group. Thus, without addition of ZnO, the bond indicated in Figure 2.16 would break.

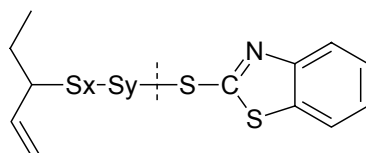


Figure 2.16 Crosslink precursor scission

However, in the presence of Zn^{2+} , the complex that is formed leads to a pathway, which changes the location of the split of the sulphur chain and decreases the rate of the actual crosslinking. The zinc chelation stabilises the other sulphur bonds and influences the position of the S-S bond most likely to break, as shown in Figure 2.17. Without addition of ZnO this bond is unlikely to break as it could not be stabilised by resonance.

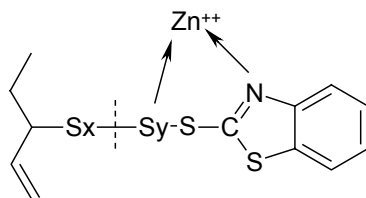


Figure 2.17 Crosslink precursor scission under influence of zinc

Another important characteristic of the vulcanisation process is the scorch delay. In literature two reasons for scorch delay have been suggested: the thermal stability of the accelerator and alternatively exchange reactions between accelerator polysulphides and other reaction intermediates. Although the thermal stability of the accelerator clearly affects the scorch delay, the exchange reactions involving the accelerator polysulphides are generally specified as the controlling mechanism.

The first mechanism was supported by the arguments of Bateman *et al.*² They proposed, that the crosslinking cannot start unless polysulphidic sulphurating species are formed, which depends on the initial formation of MBTS. MBTS cannot be formed, unless MBT reacts with the benzothiazolesulphenamide accelerator. Since MBT is formed from the accelerator by the thermal decomposition of the S-N bond, the scorch is delayed pending decomposition of this bond. Scheele *et al.*⁴⁸ suggested that an amine salt of MBT is the first product of sulphenamides, which then leads to the activation of elemental sulphur. In summary, the stability of the sulphenamides towards heat, hydrolysis and reduction determines the scorch delay.

Concerning the second mechanism, Gradwell and McGill⁴⁹ proposed a mechanism, based on their study of isoprene rubber vulcanisation with CBS, in which the scorch delay was attributed to exchange reactions between the accelerator and benzothiazole-terminated pendant groups to form amine-terminated pendant groups. These amine-terminated pendant groups convert slower to crosslinks as compared to benzothiazole-terminated pendant groups.

It is commonly known that the initial crosslinks are usually polysulphides with high sulphur rank, which subsequently can undergo rearrangement to form the more stable mono- and disulphidic crosslinks.^{10, 50-53} Since the S-S bonds are weaker when the crosslinks are longer, the reaction rate is higher for the longer length polysulphidic crosslinks. The sulphur removed, is used in the formation of new crosslinks, cyclic sulphides, pendant groups and the formation of ZnS .² $Zn(MBT)_2$ catalyses the shortening of the polysulphidic crosslinks and isoallylic transformation reactions by the formation of a complex between di- or polysulphides.⁵⁴ The reaction mechanism implies that desulphuration is a stepwise process, occurring atom by

atom: *i.e.* the trisulphide is reduced to disulphide, and eventually disulphide to monosulphide.

In the final vulcanised compound various forms of zinc ions can be present. A part can still be present as ZnO and zinc stearate. Also ZnS is formed after the breakdown of the zinc complex with the accelerator.

2.2.4 Effects of Level of ZnO

Traditionally, rubber formulations for sulphur curing contain 5 – 8 phr ZnO. The levels depend on particular applications and have been optimised based on performance requirements. Over the years lower levels have been tried and according to several researchers, it seems that ZnO levels can be reduced to a minimum of about 2 phr in tread compounds without serious detrimental effects on properties.^{28, 55-57} A small reduction in modulus can be compensated, by slightly increasing the level of accelerator. Higher levels of ZnO are usually used for EPDM.

Duchacek⁵⁵ investigated the effect of ZnO concentration on the course of tetramethylthiuram disulphide-accelerated (TMTD) sulphur vulcanisation of NR. He found an optimum ZnO content in the rubber mix of 2.5 phr. This value is in very good agreement with the optimum values of ZnO concentration found by Brajko⁵⁶ for both sulphenamide- and thiazole-accelerated sulphur cures. Reduction of ZnO loadings in several types of rubber compounds, *e.g.* NR, NR/BR, SBR and NBR, was also studied by Mukhitdinow *et al.*, Fel'dshstein, Schvarts and companies like Flexsys and Trelleborg, and accurately summarised in a state-of-the-art report.²⁸

Domka³⁰ reported that with no ZnO, vulcanisation of an unfilled NR compound did not occur at all. Morrison and coworkers used model compounds based on 2-methyl-2-pentene to analyse the behaviour of several accelerator systems.¹⁶ This work also concluded that ZnO plays a key role in sulphurisation and crosslink formation, as in the absence of zinc little sulphurisation and almost no crosslinking occurred. Rakhman and Fel'dshstein⁵⁸ observed increased reversion and decreased scorch delay with 1 phr or less ZnO.

A parameter which is quoted to affect the activity of ZnO is the specific surface area. In the so-called highly active zinc oxides the mean particle size is decreased and the specific surface area increased, which results in a easier and better dispersion and a higher reactivity.³⁰ 'Active' zinc oxides are normally prepared with BET specific surfaces ranging from 30 to 70 m²/g, compared to ~6 m²/g for conventional red seal ZnO. The higher activity is probably due to the increased accessibility of Zn²⁺-ions at the surface compared to the conventional particle sizes. One of the latest and probably most promising developments in this field, is the use of so-called Nano ZnO. Wei⁵⁹ investigated the effect of nano sized ZnO on the physical properties of NR/BR compounds. It was found that with Nano ZnO the physical properties are significantly improved, especially the abrasion resistance, H pull-out force and tear strength.

Another route for further reducing the amount of ZnO in formulations is to provide interaction between the accelerators, stearic acid, and ZnO before they are added in the rubber matrix.⁶⁰ Results already indicated the possibility of a considerable reduction of ZnO levels with retention of the properties of the vulcanisates.

2.2.5 Synergistic Effects of Stearic Acid

The acceleration system often needs some proportion of fatty acid for cure activation. As mentioned earlier, it is assumed that stearic acid reacts with ZnO to form zinc stearate, which is an essential cure activator. Its function has been the subject of extensive research by Kruger and McGill.⁴¹ Stearic acid also functions as an external lubricating agent for processing machinery and as a mould release agent. In addition, it acts as an internal lubricant between polymer chains. Morche *et al.*⁶¹ found that an ester/alcohol combination was superior to stearic acid as processing promoter, but not for vulcanisation activation purposes.

At the present time the range of available sulphur vulcanisation accelerators has stabilised, and further enhancement of the vulcanisation process is primarily associated with improving the activator system, which is commonly a ZnO/fatty acid combination. Several researchers found that the fatty acid can be adequately substituted by other species having surfactant properties (quaternary ammonium and phosphonium salts, oligomeric polyethers and other non-ionic surfactants). Romanova *et al.*⁶² hypothesised that the influence of these substances on sulphur vulcanisation is associated both with their surface properties and their participation in the inter-phase transfer reactions developing in the course of vulcanisation. There are indications that catalysts of inter-phase transfer, like combinations of quaternary ammonium salts and sodium hydroxide, take part in the degradation reactions of polysulphide units in the regeneration of sulphur vulcanisates. Romanova *et al.* studied the effectiveness of a system including cyclic or linear ethers and an inorganic base, *i.e.* calcium hydroxide, as sulphur vulcanisation activator in polybutadiene. It was shown that cyclic and linear oligomeric derivatives of ethylene oxide and their alkyl ethers are effective activators of sulphur vulcanisation. Their effectiveness depends strongly on the vulcanisation accelerator as well as on the chemical structure of the oligoester.

2.2.6 Other Metal Oxides

There have been a number of investigations comparing different metal oxides as vulcanisation activators, mostly with TMTD in NR, with variable results. Rakhman *et al.*⁵⁸ analysed the effect of various metal oxides on the extent of cure. Their work concluded that a variety of metal oxides can accelerate cure, but the degree of acceleration varies with the specific metal ion used. Duchacek⁶³ tested the effects of copper-, mercury-, nickel-, zinc-, cadmium-, indium-, magnesium-, and calcium-stearates on the course of CBS-accelerated sulphur vulcanisation of NR. Based on results and in accordance with Irving's and Williams' finding about the order of stability of metal complexes,⁶⁴ the following order for the stability of metal complexes with accelerator ligands was presented: Cu^{2+} , Hg^{2+} > Ni^{2+} , Zn^{2+} , Cd^{2+} , In^{2+} > Mg^{2+} , Ca^{2+} . They concluded that nickel, zinc, cadmium, and indium have a definite ability to form complexes, but they form significantly less strong coordination bonds, than, *e.g.* copper and mercury. This is why zinc and cadmium form active sulphurating vulcanisation intermediates. Magnesium and calcium have only a slight tendency to form complexes. This fact eliminates the possibility of formation of an active sulphur-containing complex. The alkaline character of magnesium- and calcium-stearates is

the reason for the acceleration of sulphur vulcanisation of rubber by an analogous way as in the cases of currently used basic accelerators. The greater basicity of calcium in comparison with that of magnesium is in good accordance with the larger vulcanisation rate found for calcium containing rubber compounds.⁶³

Lautenschlaeger⁶⁵ studied the effects of different metal oxides in accelerated sulphur vulcanisation with 2-methyl-2-pentene, as model olefin. The results of a comparison of ZnO, CdO, CaO, and a combination of ZnO and aniline indicated that cadmium oxide is the most effective oxide, resulting in a high yield in monosulphides and a relatively low production of byproducts.

In another research by Chapman,²⁸ it was found that of metal oxides other than ZnO, cadmium oxide on average appears to be best, followed by lead oxide and mercury oxide. However, in an investigation on the crosslinking of a model olefin by sulphur, tetraethylthiuram disulphide (TETD) and various metal oxides, cupric oxide was found to give higher yields than ZnO, and nickel oxide was also quite effective.⁶⁶

Some metal oxides behave synergistically with ZnO. Replacement of half of the ZnO by an equivalent amount of CdO, PbO, Bi₂O₃, CaO, HgO or CuO in an efficient vulcanisation (EV) system gave higher moduli. Other oxides gave moduli equal to or lower than with ZnO alone. Calcium oxide and magnesium oxide are apparently not so promising in conventional sulphur/sulphenamide cures, especially not in combination with ZnO. It has been reported that calcium oxide and magnesium oxide interfere with the efficient activation of ZnO.⁶⁵

2.3 THE VARIOUS POSSIBLE ROLES OF MULTIFUNCTIONAL ADDITIVES IN RUBBER VULCANISATION

A totally different and new approach to reduce ZnO in rubber compounding is based upon the research of Hepburn *et al.*^{67, 68} Because of the continuously increasing number and complexity of ingredients used in rubber compounds, a new ingredient with several functions was proposed in order to simplify the compound recipe. These so-called Multifunctional Additives (MFA) were reported to function in their own right as simultaneous activator and accelerator for sulphur vulcanisation, and therefore they might be promising alternatives for zinc-activated curing systems. Originally, for application as crosslinking agent in halogen containing rubbers, the term 'Amine Bridged Amides' (ABA) was used. It was found that this ingredient possesses several other functions and the term 'Surfactant-Accelerator Processing Aids' (SAPA) was introduced, later replaced by the term 'Multifunctional Additives'. The term MFA will be used throughout our discussions. The general structure of a MFA is $[R'NH_2(CH_2)_3NH_3]^{2+}2[C_{17}H_{33}COO]$. Several other types of compounding ingredients have been investigated but none have the versatility and combination of functions possessed by MFAs. These cationic surfactants impart to a rubber compound a combination of improved properties.

2.3.1 MFA as Crosslinking Agent

Kovacic⁶⁹ theorised that certain bifunctional diamines become crosslinks during vulcanisation of halogen containing rubbers such as polychloroprene (CR). The first crosslinking agents for fluorocarbon rubbers were diamine curatives. They are corrosive to mild steel moulds and have been replaced in many applications by bisphenol or other more recent cure systems.¹² Nevertheless, diamines are still used in zinc-free cures for halobutyl rubbers for pharmaceutical stoppers and for fluoroelastomers (FKM).

Hepburn^{67, 68} reported about a bifunctional diamine which functions even without the use of a metal oxide (ZnO or MgO) in contrast with conventional systems. These amines are able to react with CR and produce a well cured vulcanisate which possesses good physical properties. These MFAs function as multipurpose vulcanising agent and processing aids in polychloroprene rubbers. CR rubbers cured with MFA have long scorch times and therefore excellent processing safety.

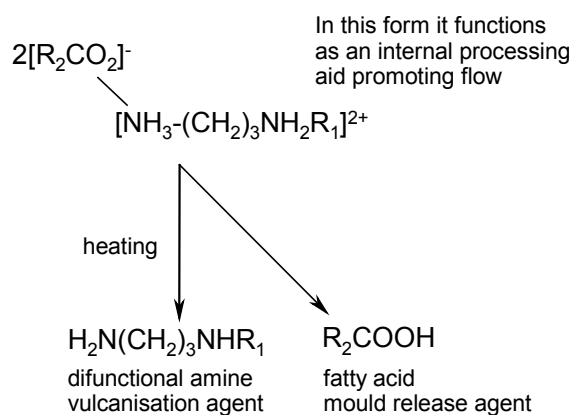


Figure 2.18 Proposed mechanism to account for the multiplicity of functions of MFA

Hepburn proposed a mechanism to account for the multiplicity of functions of an MFA, as shown in Figure 2.18. It is considered that the MFA on heating, dissociates into the diamine and a fatty acid. The diamine functions as a combined 'crosslinking agent – accelerator' and the fatty acid as a 'flow promotor – mould release agent'.

The difunctional amine produced during the heating of the rubber can function alone as a vulcanisation agent as shown in Figure 2.19.

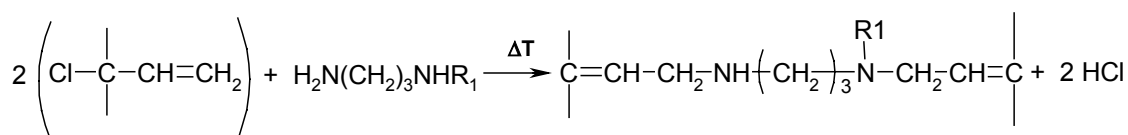


Figure 2.19 Crosslinking of CR with diamine

It is considered desirable to incorporate some metal oxide like MgO in the formulation of the halogen containing rubber to quench HCl or acidic byproducts to the level normally achieved in a conventional ethylene thiourea/ZnO system. The

reaction in Figure 2.20 would explain the increase in tensile strength, modulus, and hardness when MgO or ZnO is added to an MFA formulation.

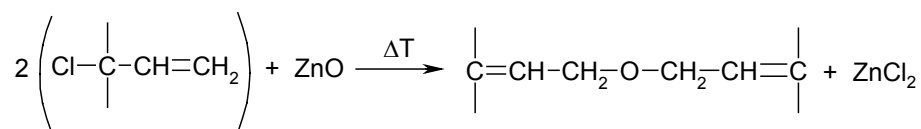


Figure 2.20 Crosslinking of CR when ZnO is present

2.3.2 MFA as Accelerator / Activator System

Hepburn *et al.*⁷⁰⁻⁷⁴ described the evaluation of different fatty acid diamine salts as rubber accelerator/activator ingredients in a NR/SBR base compound in the presence of ZnO, stearic acid and other additives. The results showed an increase in rate and state of cure and a reduction of scorch time in all cases. This reduction is considered to be due to the positively charged nitrogen group, which can act as an accelerator of cure. If an alkyl-propylenediamine alone is incorporated into the rubber compound, cure rate and state of cure enhancement again occurs. The availability of a positively charged nitrogen at the end of the molecule has a more pronounced effect on scorch and cure rate than the MFA with hydrophobic fatty acid anions attached to both the positively charged nitrogens. They found that the particular fatty acid residues present in alkyl propylene diamines, whether stearyl, oleyl, tallow, palmityl, or lauryl have little effect, relative to each other, on cure rate and state of cure.

The physical form of the cationic surfactant is important for factory storage and handling convenience. Stearic acid combined with propylenediamines produces wax-like solids which are preferred for rubber compounding. With oleic acid used as reactant a paste is produced.

It was anticipated that the chemical structure of MFA contains all the various chemical groups necessary to function both as activator and accelerator. Substitution of the conventional rubber activator/accelerator system of ZnO/stearic acid/CBS/S by MFA/S in a NR/SBR tyre sidewall type rubber formulation, revealed that MFA indeed can function as a cure activator and accelerator in its own right. It was not necessary to have ZnO and stearic acid present in the formulation.⁷⁰

As already mentioned before, it is considered that the MFA at vulcanisation temperatures decomposes into a primary amine, which functions as the accelerator of cure, and a fatty acid which acts as a release agent. Evidence to support this mechanism was found by the use of differential scanning calorimetry (DSC) and with infrared spectroscopy (IR). The DSC thermogram of MFA showed two distinctive endotherms. One corresponding to the melting of MFA and the other (between 130°C and 155°C) to the dissociation of MFA into an amine and a fatty acid. Further evidence was obtained with IR. As a result of the heating, new absorption bands at the wavelengths of -NH₂ and -COOH appeared, indicating the creation of primary amine and acid groups.

Good tensile strength, modulus, rebound resilience and hardness properties could be obtained using the MFA/S cure system. These properties were a little

increased by increasing the proportion of MFA from 1 to 3 phr. A level of 7 phr was obviously too much and a diluting and plasticising effect was observed. However, Ismail *et al.*⁷⁵ reported that the deterioration of properties is not associated with the internal lubrication (plasticisation), because results from gum compound for shear storage modulus G' vs MFA level showed that G' did not change significantly with increasing MFA level. If it acts as plasticiser a progressive decrease of the value of G' with increasing MFA level is expected.

2.3.3 Effect of ZnO in MFA Formulations

The dramatic reduction in scorch time as mentioned in the previous paragraph, is often a disadvantage in rubber processing. It was found that the inclusion of ZnO in a MFA containing recipe increases the scorch time drastically and eliminates cure reversion. Inclusion of 1 phr ZnO caused an increase in scorch time and the t_{90} values. Physical properties like tensile strength, modulus and resilience were found to decrease by further addition of higher quantities of ZnO.⁷⁰

Some indications for this cure retardation effect are found in literature. According to Kimishima,⁷⁶ the acceleration of aniline is reduced by the presence of ZnO. The proposed mechanism for aniline acceleration is outlined in Figure 2.21.

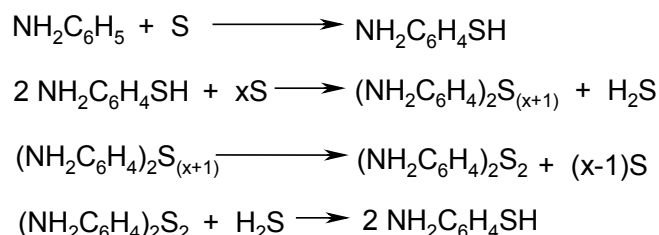


Figure 2.21 Aniline acceleration reactions

Kimishima believed that ZnO is capable of absorbing H_2S , thereby preventing the formation of the disulphide $(\text{NH}_2\text{C}_6\text{H}_4)_2\text{S}_2$. As a consequence, the formation of the active form of sulphur is retarded or prevented. Another explanation would be the formation of a rather stable sequestered complex of ZnO and MFA, thus delaying the onset of cure.

2.3.4 MFA as Processing Aid in Unfilled and Filled Rubbers

Most conventional processing aids are monofunctional, being added to control one specific property. Hepburn and Mahdi⁷⁰⁻⁷⁴ applied the new approach, whereby a single compounding ingredient would possess several functions for other rubber compounds as well. Recently a number of papers have been published on the effect of MFAs of different structure on several compounds, unfilled and filled with carbon black or silica, as explained in the following. The processing and vulcanisate properties of various synthetic rubbers, *i.e.* SBR, NBR and CR with MFA incorporated, were investigated. It was observed that in every case MFAs function as processing aid as well as mill roll and mould release agent, and that the vulcanisates

were free from moulding stresses. Increased tensile strength was observed with NR and SBR, but not with CR and NBR.

The combination of processing properties conveyed to a rubber mix by the inclusion of a cationic surfactant are shown hereafter:⁷⁷

1. Eliminate the use of a mould release agent;
2. Decrease viscosity and improve flow;
3. Promote wetting and dispersion of fillers;
4. Enhance tack or autohesion;
5. Lubricate to improve, for example: extrusion, calandering and moulding processability;
6. Reduce temperature, power consumption and time for filler incorporation during mixing.

Inclusion of MFA brings to the engineering process of rubber the feature of a compounding ingredient that eliminates mould fouling. Another feature is the ability to increase tensile strength and stiffness without any change in hardness (modulus).

It was observed that MFAs can also impart roll mill release properties and improved filler dispersion to the unvulcanised mix. Ismail⁷⁸ studied the modes of action of an MFA in carbon black filled NR. The results indicated an enhancement of the physical properties of vulcanised 50 phr N330 carbon black filled NR by MFA. The improvement of properties up to a level of 2 phr MFA was attributed to improved carbon black dispersion in the rubber compound. Abidin⁷⁹ found with respect to processability that the addition of MFA causes a higher rate of incorporation and lower power consumption at dispersion stage. It was postulated that MFA functions as a filler-rubber wetting agent which gives a more efficient disagglomeration of carbon black during mixing and therefore an improved dispersion. It was considered, that the presence of MFA reduces carbon black filler incorporation time and, if a constant mixing time is used, increases the time available for filler disagglomeration or dispersion.⁷⁷ Scorch time and cure time were reduced by the incorporation of MFA. Swelling tests showed very little change in solvent uptake with increasing MFA, indicating the small effect of MFA on crosslink density.⁷⁹ So this is not the primary mode of action of MFA causing property changes. Sheng⁸⁰ reported the effect of MFA on bound rubber in filled rubbers. With increasing MFA concentration the bound rubber on the carbon black decreased. This might imply that the interfacial interaction between carbon black and rubber molecules is weakened by MFA and thus the carbon black incorporation is improved. Alternatively, the decrease of bound rubber with the addition of MFA may be explained in terms of the release of the immobilised rubber which is fixed within the carbon black agglomerates. The amount of bound rubber also depends on the extent of disagglomeration. A more complete breakdown would be expected, due to the wetting effects of MFA.

In another study the influence of MFAs on silica filled NR (30 phr)^{57, 71, 73, 81} and on silica filled epoxidised NR compound was investigated.⁸² Great improvement was observed in processability for silica-reinforced NR mixes. Due to its action as cationic surfactant a MFA is especially effective in silica and silicate filler reinforced rubber formulations, giving them easy flow and fast cure rates. The time to t_{95} cure is reduced substantially and increasing the level of MFA to 5 phr was shown to have a further beneficial effect by increased cure rate. It shows that MFA is effective to

prevent the cure retardation of the accelerator CBS by silica. However, a level of 10 phr is too much as the compound becomes scorchy. Again, the mechanical properties were enhanced by the incorporation of MFA. The optimum mechanical properties occurred at a level of 5 – 7.5 phr. This might be due to the difference in molecular orientation of the MFA at the filler-rubber surface.⁸⁰ The improvement of mechanical properties was attributed to the improved silica dispersion in rubber and higher crosslink density. In contrast with carbon black filled rubbers, swelling tests indicated a substantial effect of MFAs on crosslink density.⁸¹ The weight of solvent uptake per gram of rubber was drastically reduced as the level of MFA increased. Rubber swelling is influenced by various factors, such as crosslink type and density, amount and type of filler and type of elastomer. As the swelling test has long been recognised as a criterion to give a true measure of adhesion between filler particles and rubber, it was concluded that increasing the level of MFA resulted in better crosslinking for silica filled rubber compounds. Increase of crosslink density implies a preferential absorption of MFA during mixing, before dissociation. There have been several reports to suggest that silica, by virtue of its acidity, has a preference to absorb amines.⁸¹ During the vulcanisation process, the dissociation of MFA will release an alkaline amine which is expected to strongly adsorb on the surface of silica. Lautenschlaeger⁶⁵ already reported that one of the effects of silica was a decrease in efficiency of the curing system, probably caused by adsorption of one or more curative components, most likely the accelerator.

Ismail⁵⁷ carried out some work to separate the contributions of the MFA in a silica-filled natural rubber. He found that silica dispersion showed a substantial improvement when the MFA level was increased from 0 to 3 phr. After this level, there was only a small further improvement. However, at MFA levels greater than 3 phr a higher crosslink density became the dominant factor for improvement in mechanical properties.

It is considered that the hydrophilic silica, which is relatively incompatible with rubber, becomes hydrophobic by surface modification with the MFA, thereby changing its compatibility. Addition of bis-(triethoxysilylpropyl)tetrasulphide (TESPT) coupling agent results in further improvement of mechanical properties and the effects are to some extent additive.⁸³ The improvement in mechanical properties, especially modulus, is probably attributable to higher crosslink density and greater coupling efficiency conferred by MFA and TESPT. MFA increases crosslink density and TESPT increases silica-rubber coupling, which effectively increases crosslink density using the filler aggregates as a crosslink. The results of swelling tests indicate that TESPT is more able to form chemical coupling with silica than the MFA.

Physical wetting by the incorporation of MFA improves dispersion and prevents formation of a secondary filler network. The consequence of this effect and the chemical bonding of the elastomer phase to the filler surface by TESPT, is to improve mechanical and dynamic properties by minimising the energy loss processes associated with the breakdown and reformation of a secondary filler network (low $\tan \delta$).⁸³

Sheng⁸⁰ also investigated the effect of MFA on bound rubber in silica filled compounds. No pronounced effects were observed of the addition of MFA to a silica filled NR compound. This might result from the combined effects of improved

dispersion (decreasing occluded rubber) and interaction enhancement (increasing bound rubber) at the silica-rubber interface, since the bound rubber test includes both immobilised and true bound rubber in the result.

2.3.5 Other Processing Additives

Stimulated by the work of Hepburn and other researchers on the MFA effect, Takino *et al.*⁸⁴ studied the use of functionally active synthetic waxes. They found that vinyl/acetate and acrylic acid wax were effective and appear to have some of the processing and vulcanisate property advantages of the MFAs, although their functionality is much lower than that of the MFAs. The general conclusion of this study was that, if the processing aid will disagglomerate the carbon black during mixing and wet or surface coat the carbon black due to its polarity, then many processing and vulcanisate properties of the rubber will be improved in a remarkable way.

2.4 THE ROLE OF AMINES IN RUBBER VULCANISATION

More insight in the underlying chemical mechanism of the accelerating function of MFAs might be obtained by studying the utilisation of amines in rubber vulcanisation. Several modes of action of amines in the vulcanisation process have been described already in previous paragraphs.

2.4.1 Amines as Accelerators

Guanidines were one of the first aniline-derivatives used as accelerators, Figure 2.22. Diphenylguanidine (DPG) has enjoyed a resurgence in demand as an activator for sulphenamides and as secondary accelerator in tire tread compounds, which employ silica fillers for low rolling resistance.¹² Guanidines and secondary amines in general, are rarely used as primary accelerator due to their weak accelerating effect. As activating secondary accelerators they often increase the vulcanisation rate and crosslink density of the primary accelerator. Amines like aniline and piperidine are slow acting accelerators and not used in practice anymore.¹

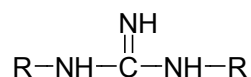


Figure 2.22 General formula of guanidine

Sandstrom⁸⁵ reported about the use of diamines as secondary accelerators. It has been determined that compounds having the following structural formula, have excellent properties as secondary accelerators:

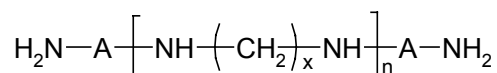


Figure 2.23 General formula of diamines

Wherein A represents an alkyl-group containing 2 to 5 carbon atoms, n is an integer between 1 and 4, and x is 2 or 3. For example it has been determined that 4,7-diazadecane-1,10-diamine is a particularly desirable secondary accelerator. These accelerators facilitate the cure of any sulphur vulcanisable rubber including natural and synthetic rubbers as well as mixtures thereof. Additionally, these amines have been reported not to be mutagenic, in contrast with tetramethylthiuram disulphide (TMTD) for example.

It was found that also secondary amines, belonging to the class of enamines (Figure 2.24), can be used as vulcanisation accelerators.⁸⁶ These compounds can be used in combination with other accelerators, but when they are used as the only accelerators, the results also indicate a decrease in vulcanisation time.

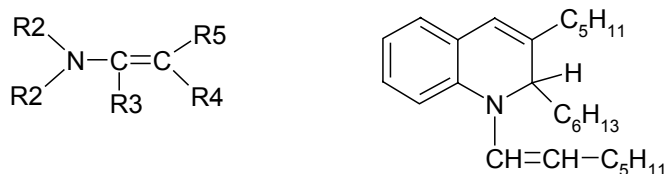


Figure 2.24 General formula of enamines; example of enamine useful as vulcanisation accelerator

The most studied amine is hydrofuramide, which was found to increase the percentage of cure, decrease the scorch time, and increase the vulcanisation rate.⁷ Other amides give similar results.

Krebs⁸⁷ postulated that the accelerating properties of amines are a function of their base strength. Although this supports the theory of an acid-base reaction, Raman-spectroscopic evidence was obtained for the existence of anionic amino polysulphides, which indicates a direct interaction of amines with sulphur.

The formation and use of secondary amines should be avoided for the reason that they react with NO_x and nitrites at high temperatures, forming carcinogenic nitrosoamines.⁸⁸⁻⁹⁰ It was found that aromatic secondary amines, e.g. dibenzylamine, have reduced carcinogenicity.⁹¹

2.4.2 Amines as Activators for Sulphur Vulcanisation

As mentioned before, it is necessary to use 'activators' to achieve the full potential of organic accelerators. The system rubber-sulphur-accelerator-ZnO is activated by the addition of inorganic activators, e.g. zinc stearate. It was observed that organic activators as dibutylamineoleate, 1,3-phenylguanidinephthalate and amines like mono-, dibutylamine (DBA), and dibenzylamine perform similar activity. Generally, it can be stated that increasing the pH leads to activation of the vulcanisation.¹

The reactivity and role of amines during the vulcanisation process is ascribed to their interaction with elemental sulphur and sulphur-containing species. Secondary and tertiary amines were thought to cause an ionic ring-opening reaction with elemental sulphur, as depicted in Figure 2.25.⁸ This reaction was considered the basis for the accelerating effect of amines in rubber vulcanisation.

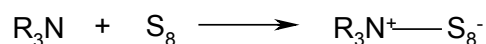


Figure 2.25 Assumed ring opening of elemental sulphur by tertiary amines

More recently, it was suggested that no direct reaction between amines and sulphur occurs, but with H_2S or sulphur dioxide, Figure 2.26. The formed highly thiophilic species, e.g. HS^- , subsequently give ionic cleavage of the sulphur ring.

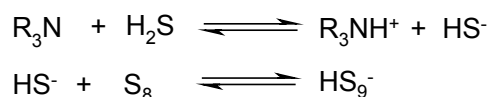


Figure 2.26 Ring opening of elemental sulphur by thiophilic species

The reactivity of amines is not restricted to elemental sulphur, but includes polysulphides as well. Secondary amines might destroy polysulphidic crosslinks, either by direct reaction, or by generation of HS^- .

2.4.3 Amines as Stabilisers of Accelerator Complexes

Several papers have focused on the nature of the accelerator complexes. The study of Milligan⁹² illustrated the importance of ligands in stabilising the zinc salt (ZMBT in his work). It was found that amines increase the activity of the complex, usually in conjunction with stearic acid or other fatty acids. Bravar *et al.*⁹³ found that the amines help to stabilise accelerator complexes, Figures 2.11 and 2.27, but components such as carbon black can preferentially absorb amines, limiting the stabilising power of these amines.

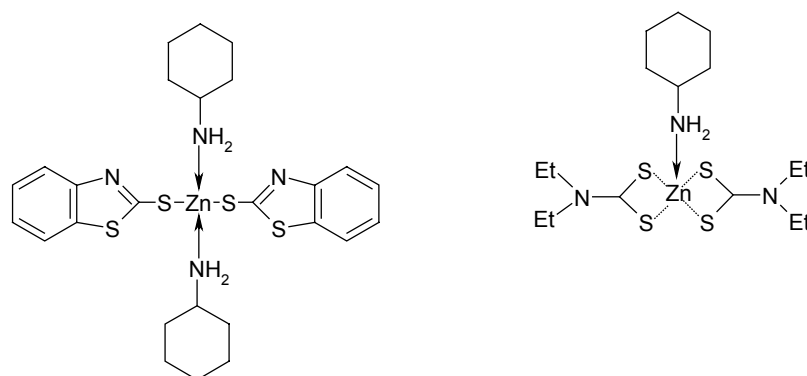


Figure 2.27 Stabilisation of Zn-complexes by amines

2.4.4 Amines as Antidegradants

Rubbers degrade when exposed to oxygen, UV-light, ozone etc. Early investigators found out that the degradation was related to reactions involving ozone and the unsaturation in the elastomeric polymer chain. Elastomers are also subject to atmospheric oxidation, even at moderate temperatures. Most degradation processes have a free radical character and therefore stabilisation by radical scavengers is possible. An important group of stabilisers consist of secondary aromatic and hydroaromatic amines and diamines and of aliphatic hindered amines (HAS) or (HALS).⁹⁴

Mostly, aromatic amines are used in the stabilisation of rubber vulcanisates. Aromatic amines are often substituted diphenylamines, N-phenyl-2-naphthylamines and N,N'-disubstituted 1,4-phenylenediamines. p-Phenylenediamines (PPD) constitute a special group of aromatic amines.^{95, 96} The use of PPD's in the tyre industry has become firmly established because they protect goods, not only from autoxidation but also from ozone cracking and mechanical fatigue. The substitution pattern of the PPD's covers alkyl-aryl-groups, bisalkylgroups and bisarylgroups. Hindered amines stabilisers (HAS) generally have structures of secondary and tertiary amines. Most HAS are derivatives of the heterocyclic 2,2,6,6-tetramethylpiperidine.

2.5 MODEL COMPOUND VULCANISATION

As stated before, standard analytical and chemical techniques are not appropriate to analyse vulcanised rubber, because of the insolubility of the elastomer network, the low concentrations and the variety of crosslinked structures. For that reason, the technique of Model Compound Vulcanisation is often called for help. The vulcanisation process is then simulated by reactions of monomeric olefins (models for rubber) with curatives. The low molecular weight products are more readily analysed than actual rubber. Model compound vulcanisation has been studied extensively, and has greatly contributed to the understanding of the vulcanisation process. Perhaps the first mention of it was by Meyer and Hohenemser⁹⁷ in 1935, who used cyclohexene to investigate unaccelerated sulphur vulcanisation.

The choice of a model compound for a specific experiment strongly depends on the aspects to be investigated. Squalene and geraniol are liquids with a relatively high boiling point, and therefore extremely suited for following the reaction. Squalene is a relatively low molecular weight material consisting of several isoprene units. Geraniol is an isoprene dimer with a terminal hydroxyl group. Main-chain modifications and crosslinks are rather difficult to study with these polyfunctional models and should be investigated with monofunctional models like 2,3-dimethyl-2-butene (TME). With TME valuable and realistic information can be obtained about the crosslink yield and factors which influence the formation and distribution of the crosslinks.

The choice of the structure of the model molecules needs to be based on the polymer material under investigation. But it is also strongly dependent on which

aspect of the vulcanisation process is considered. If the reaction between the polymer chain and the curatives is considered, the model should resemble the repeating unit of the polymer. Certain aspects must be taken into account:

- Position and configuration of the double bond;
- Number of double bonds;
- Additional functional groups;
- Availability of the model;
- Boiling point;
- Solubility.

On the other hand, if the reaction between only the curatives is considered and not the reaction with rubber, other properties of the model are important. Examples are dielectric constant, hydrophobicity, etc., in order to simulate the rubber-like environment. The presence of allylic hydrogen atoms (hydrogen atom next to a double bond) should then be prevented.⁹⁸

Two models are found in literature, which are used to simulate SBR rubber: *cis*-1-phenyl-3-heptene and polyoil 110, which contains 1,4-*cis*, 1,4-*trans* and 1,2-vinyl butadiene oligomer. The content of these three groups corresponds to the real value in (S)BR.⁹⁸ For EPDM, the model commonly used consists of ethylidene norbornane (ENBH),⁹⁹ since 5-ethylidene-2-norbornene is the most commonly used third monomer. Squalene and 2-methyl-2-pentene are commonly used to create a system similar to NR. The main difference between squalene and NR is the configuration of the double bond: *cis* in NR and *trans* in squalene. TME is not directly comparable with any specific rubber, but it is more a general model. It is used quite a lot because a clear picture of the structure of the vulcanised products can be obtained. It contains only equivalent allylic positions; therefore hardly any isomerisation takes place.

A disadvantage of using model compounds is the high concentration of end groups. An end group has a CH₃-configuration and in a macromolecular molecule CH₂ forms the major reactive group. By using larger molecules (*e.g.* squalene) this disadvantage can be partly overcome.

Many studies have been performed by means of model compound vulcanisation. A wide variety of model compounds has been used to study the different aspects of vulcanisation. Several approaches were chosen for the experiments: the curatives were varied as well as the amount of curatives, the reaction time and the reaction temperature. This section is therefore concerned with the research performed in MCV with special focus on the role of activators in accelerated sulphur vulcanisation.

2.5.1 Effects of ZnO as Activator as studied with MCV

Geyser and McGill¹⁰⁰⁻¹⁰² performed studies on the formation of products in the three stages of vulcanisation in the absence and presence of ZnO: formation of sulphurating agent (1), formation of crosslink precursors (2) and the formation of crosslinks (3). For product investigation of the first stage,¹⁰⁰ the system contained TMTD, ZnO and sulphur. Two mole ratios of sulphur were considered: 1 and 0.25. These measurements were taken at a constant temperature of 130°C. HPLC was used to determine the amount of products as a function of reaction time. For stage

(2),¹⁰¹ TME was added in this system. The reaction time was varied and HPLC was again used to investigate the products. The amount of formed TMTM, TMTD and crosslink precursors were given as a function of reaction time. The final crosslinked products (3)¹⁰² were studied again by means of HPLC. The amount of crosslinked products was given as a function of reaction time in comparison with the formation of crosslink precursors. In the presence of ZnO, the crosslink precursors react with other precursors as well as with the TME.

Reyneke-Barnard *et al.*^{103, 104} investigated the difference between two types of accelerators in a rubber and in a model compound, polyisoprene (IR) and TME respectively, in the absence¹⁰³ and presence¹⁰⁴ of ZnO. The accelerator was N,N'-pentamethylenethiuram disulphide and N,N'-pentamethylenethiuram hexasulphide. The curatives and the intermediates were analysed with HPLC. The reactants were analysed in every stage of the vulcanisation. In absence of ZnO, the formation of thiuram-polysulphide-terminated pendant groups as intermediates were confirmed. When dimethyldithiocarbamic acid (DMTC) was allowed to evaporate, the onset of vulcanisation was delayed and a low crosslink density was achieved. This study supports the mechanism of thiuram- and thiol-terminated pendant groups. The same model and accelerators were used in the presence of ZnO. The accelerator did not react with ZnO at vulcanisation temperature. The vulcanisation was initiated by an accelerator-polysulphide. Thiuram-terminated pendant groups were formed. Pentamethylene dithiocarbamic acid was released and trapped by ZnO. This made the crosslinking more rapid, because the acid could not attack the polysulphidic accelerator, thereby increasing the rate of formation of the pendant group.

Lautenschlaeger¹⁰⁵ used 2-methyl-2-pentene as a model compound to study the effects of sulphur, ZnO and accelerator. The compound contained ZnO, CBS, carbon black and stearic acid. One component was increased, the others remained at the same level. Gas-liquid chromatography (GLC) was used to identify the reaction products. Additionally, flame photometric detection (FPD) was used to determine which of the peaks of the GLC graph contained sulphur. The effect on the length of the sulphur bridges and the types of isomers were considered. The structure of the crosslinked products was investigated, both the length of the sulphur bridges and the types of isomers. Three types could be distinguished: dialkyl trisulphide, dialkyl disulphide and dialkyl monosulphide. There are different isomers possible for all three products which all have different retention times. The evolution of the different types of tri-, di- or monosulphidic bridges as a function of reaction time was charted for all systems.

Versloot¹⁰⁶ used TME for mechanistic studies. The reaction mixture consisted of TME, TMTD, sulphur and ZnO. The reaction time was one hour at a reaction temperature of 140°C. The products were *bis*(2,3-dimethyl-2-butenyl)sulphides: C₆H₁₁-S_n-C₆H₁₁ with the integer n varying. HPLC was used to determine the length of the sulphur bridges. ¹H-NMR was used to investigate the molecules with different length of sulphur bridges. It appeared that only a very small quantity of isomerised products were present, with a 1,3-shift of the double bond: Figure 2.28.

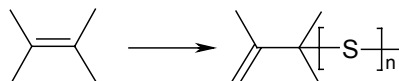


Figure 2.28 1,3-Shift of the double bond resulting in an isomer of the products, which reacted initially at the allylic positions

In another study Versloot¹⁰⁷ investigated different model molecules, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 1-decene, *trans*-2-hexene and *trans*-3-hexene. One of the major objectives of this research was to study isomerisation. With 1-decene complete isomerisation of the double bond occurred. For the hexenes, half of the products were isomers and for 2,3-dimethyl-1-butene 25% formed TME crosslinks. As mentioned before, the TME results showed hardly any isomers, except for vulcanisation at room temperature.

2.5.2 Effects of Zinc Complexes as Activator as studied with MCV

Nieuwenhuizen¹⁰⁸ performed a study on ZnO and zinc complexes. Two types of studies were carried out: MCV and Reaction Stage Modelling (RSM). RSM is defined as the study of a low molecular weight model for a particular stage of vulcanisation. The existence of zinc accelerator complexes was experimentally proven by the use of matrix assisted laser-desorption ionisation (MALDI). Nieuwenhuizen also investigated the reaction step after the formation of the crosslink precursor. It was unknown whether the crosslink precursor reacts with another crosslink precursor or with another allylic hydrogen atom. Model precursors were synthesised. In the absence of zinc complexes, these models were unreactive with each other, but when ZMBT was added, disulphidic crosslinks were formed immediately.

2.5.3 Effects of other Metal Oxides as Activator as studied with MCV

Borros, Rodriguez and Garreta¹⁰⁹⁻¹¹² have studied the effect of the activator during the scorch time and during the curing time in squalene as a model for NR. ZnO, MgO, CaO and CdO were compared as activators of cure. The length of the scorch time was, amongst others, dependent on the ease of cleavage of the accelerator. To compare the amount of intermediates formed, the reactions were carried out in squalene and squalane. Squalane does not have any double bonds and cannot react further, so there must be an accumulation of the intermediates. To determine the amount of CBS, HPLC was used. These reactions were first analysed by measuring the amount of accelerator (CBS) as a function of time. If the activators work properly, the amount of accelerator should decrease. After a certain reaction time, the mixture was quenched: the reaction stopped and the composition could be determined. CaO and CdO were found to be poor activators. MgO and ZnO were capable of 'breaking' the accelerator quite well. Gel permeation chromatography (GPC) was used to investigate crosslinked squalene concentration, since crosslinking increases the molecular weight of the reactants. The concentration of crosslinked squalene could be followed as a function of reaction time. ZnO performs better during the curing stage than MgO.

Versloot⁶⁶ used several metal oxides and metal complexes in his study with TME as model compound and TMTD and TETD as the accelerators. In the presence of ZnO the crosslink density was high and relatively short crosslinks were obtained. Experiments with CdO, CuO, PbO and NiO resulted in low vulcanisation activity.

Lautenschlaeger⁶⁵ has studied the effect of different metal oxides as activators in 2-methyl-2-pentene. The yield and types of products were compared from several metal oxides, like ZnO, CdO and CaO. CdO was found to be the most effective oxide, it yielded the most monosulphidic products and hardly any byproducts were found. CaO was the worst activator. The effects of the activators were translated from the crosslink yield, the length of the sulphur bridges and the types of isomers.

2.6 SUMMARY AND CONCLUDING REMARKS

2.6.1 General Remarks

In this chapter we have reviewed the various possibilities to reduce ZnO levels in rubber compounding, that have been proposed in literature. Furthermore, the course of accelerated sulphur vulcanisation with special emphasis on the role of activators has been examined and evaluated. These mechanistic details are an absolute prerequisite for developing alternative activators in order to reduce ZnO levels. Besides the introduction of 'active' zinc oxides, there has not been much development in this field anymore. In view of the multiple action of ZnO, it will be difficult to substitute. The chances of finding a completely zinc-free curing system must be regarded rather small, and would involve a fundamental change in practice as well as chemistry of sulphur vulcanisation.

2.6.2 Various Functions of Zinc in Rubber

The complexity of the curing process became evident again in this section, when considering the role and action of activators. The various studies with 'real' rubber compounds have reported several effects of ZnO:

- Activator for sulphur vulcanisation:
 - increased vulcanisation rate;
 - increased crosslink efficiency;
- Filler and scavenger of detrimental reaction products;
- Vulcanisation agent for halogen containing rubbers, *e.g.* CR, Cl-IIR and Br-IIR, etc.;
- Processing aid in uncured rubber:
 - decreased shrinkage of moulded products;
 - decreased mould fouling.

Also a significant influence on some of the physical properties of rubber vulcanisates have been mentioned:

- Lower heat-build-up;
- Improved abrasion resistance;

- Improved dynamic properties;
- Improved ageing properties in peroxide cured EPDM and HNBR.

From a mechanistic point of view, several functions of ZnO in different stages of vulcanisation are to be discerned:

- The initial scorch reactions proceed faster:
 - Breakdown of the accelerator;
 - Sulphur insertion in the zinc complex with the accelerator parts;
 - Crosslink precursor formation;
- The crosslinking reactions proceed slower;
- Change in crosslink distribution: the crosslinks contain less sulphur atoms, but the number of crosslinks is higher.

The multifunctional activity of ZnO in the accelerated sulphur vulcanisation, as summarised above, clearly demonstrates the complexity of the problem. As a general conclusion, it seems that there is no general agreement about all the mechanism of ZnO in the vulcanisation process and the applicability of other metal oxides. It is believed that reduction of ZnO can be achieved through further appraisal of its role in the curing process and the development of new curing systems based on chemicals whose environmental impact is known to be more acceptable.

2.6.3 Implications for the Research described in this Thesis

Future research efforts in the field of ZnO reduction should be aimed at a fundamental understanding of the different reactions in vulcanisation with emphasis on the function of the activator. It is apparent that for purpose of understanding vulcanisation on a more detailed level, the different vulcanisation systems and rubbers should be studied separately. The vulcanisation systems are basically similar in reactivity, however, it is quite understandable that any change in reactivity of one of the chemicals will have an pronounced influence on the whole vulcanisation process. Therefore, the research described in this thesis will mainly focus on the use of various activators in two specific systems, *viz.* sulphenamide-accelerated vulcanisation of s-SBR compounds and thiuram-accelerated vulcanisation of EPDM compounds.

Styrene-butadiene rubber (SBR) is the most widely used rubber for passenger tyre applications. Many tonnes of tread rubber are worn away nowadays, containing a considerable amount of the total anthropogenic zinc emissions. SBR is very low in polarity and can practically be blended with all non-polar rubber over a wide range of blend compositions. Blends with BR or NR are of great importance in tyre applications. The largest share by far of SBR rubber is produced in emulsion, but solution SBR (s-SBR) is steadily gaining importance. Especially for the so-called 'green' tyre technology, s-SBR is an essential ingredient.

EPDM is commercially produced by terpolymerising ethylene, propylene and a small amount of a diene monomer, *e.g.* ENB.^{1, 113, 114} The saturated polymer backbone of EPDM is resistant to oxygen or ozone attack, and degradation by heat and UV radiation. Therefore, EPDM is used for high temperature and outdoor applications such as coolant tubes, automotive sealings, and window profiles. The unsaturation present in the side groups of the polymer chain is essential for sulphur vulcanisation of EPDM. EPDM rubber is also quite often used in foils for roofing and

water reservoirs. Emission of zinc through aqueous extraction from these products is taking place, particularly from the relatively thin foils. For these reasons there is great interest in the possibility of reducing the amount of ZnO in these rubbers.

Based on literature, several possibilities can be proposed for further reduction of zinc levels in rubber compounding:

- Reduced levels or optimisation of normal ZnO dosings. Domka³⁰ established a correlation between the physicochemical properties of various types of ZnO and the activation of NR vulcanisation. They found that ZnO used in quantities above 3% by mass of rubber loses its activation properties in the vulcanisation process, and is only present in the form of a filler for the rubber.
- Reduced levels of a more active ZnO. It was observed that an increase in the mean particle size and a decrease in the specific surface area of the ZnO decreases the mechanical properties of the vulcanisates.
- Replacement by other zinc compounds at lower zinc levels. The use of zinc stearate, zinc sulphide, or zinc accelerator complexes instead of ZnO and stearic acid to reduce the requirement for ZnO.
- Elimination of zinc from rubber compounds. Hewitt¹¹⁵ investigated and developed zinc-free cure systems based on the accelerators TBBS and dipentamethylenethiuram hexasulphide (DPTH). Hepburn^{67, 68, 70-73} described the use of multifunctional additives. Domka reported that it seems possible to eliminate the amount of ZnO if modifier 'RU' is present in filled mixes based on polyisoprene (modifier 'RU' is a molecular complex of hexamethylene tetramine and resorcinol).

A completely zinc-free vulcanisation system based on sulphur keeps on being intriguing, though it seems rather ambitious. The suggested MFA system showed some very positive results and it might give a handle towards the design of new ways to reduce ZnO in rubber compounding. A fundamental understanding of this alternative cure system, however, is still lacking. Additional experiments should be aimed at elucidating the exact mechanisms occurring in these MFA based cure systems.

In order to obtain better insight in the vulcanisation mechanisms, alternative experimental approaches have to be applied. In particular, MCV should be used to investigate the multiple reactions in vulcanisation and study the exact role and action of the activator in the reaction mechanisms. Although we are aware that it may raise more fundamental questions than it solves problems, we believe that it is the most appropriate path. It offers, when combined with chromatographic and spectroscopic methods, a vital tool for studying the reaction products and separate reaction mechanisms. The differences between high-molecular weight rubber and low-molecular weight model compounds should of course not be neglected when interpreting the results.

Clearly, one important point in rubber chemistry is to realise that for the complex and interlinked reactions lots of suggestive evidence has been obtained, but that definitive answers are still lacking in many cases. The literature shows many uncertainties and even contradictions. Even today, a clear notion of the exact mechanisms in accelerated sulphur vulcanisation is still absent and the role of zinc or zinc complexes is rather ill-understood. This fact along with the upcoming legislations

for the use of zinc compounds, makes the activators an attractive subject for further research.

2.7 REFERENCES

1. W. Hofmann, *Rubber Technology Handbook*, Hanser Publishers, New York (1994).
2. L. Bateman, *The Chemistry and Physics of Rubber-like Substances*, MacLaren, London (1963).
3. W. Scheele, *Rubber Chem. Technol.*, **34**, (1961), 1306.
4. B. Saville, A.A. Watson, *Rubber Chem. Technol.*, **40**, (1967), 100.
5. M. Porter, *Organic Chemistry of Sulfur*, S. Oae, Ed., Plenum Press, New York (1977).
6. M. Porter, *The Chemistry of Sulfides*, A.V. Tobolsky, Ed., John Wiley & Sons, New York (1968).
7. M.R. Kresja, J.L. Koenig, *Rubber Chem. Technol.*, **66**, (1993), 376.
8. P.J. Nieuwenhuizen, Thesis, University of Leiden, (1998).
9. J.E. Mark, *Science and Technology of Rubber*, Academic Press, San Diego (1994).
10. N.J. Morrison, M. Porter, *Rubber Chem. Technol.*, **57**, (1984), 63.
11. J.A. Brydson, *Rubber Chemistry*, Applied Science Publishers, London (1978).
12. R.F. Ohm, "Rubber Chemicals", in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York (1997), 460.
13. M.R. Kresja, J.L. Koenig, "The nature of sulfur vulcanisation", in *Elastomer Technology Handbook*, CRC press, New Jersey (1993), 475.
14. R.F. de Block, R.N. Datta, H.W. Hovius, (to AKZO Nobel), WO 95/34602 A1 (June 09, 1995).
15. J.v. Alphen, *Rubber chemicals*, D. Reidel Publishing Company, Dordrecht (1973).
16. N.J. Morrison, M. Porter, "Crosslinking of rubbers", in *The synthesis, characterization, reactions and applications of polymers*, G. Allen, Ed., Pergamon press, (1984), 115.
17. F. Ignatz-Hoover, *Rubber World*, **220**, (1999), 24.
18. P. Ghosh, S. Katare, P. Patkar, J.M. Caruthers, V. Venkatasubramanian, K.A. Walker, *Rubber Chem. Technol.*, **76**, (2003), 592.
19. M.H.S. Gradwell, M.J. vd Merwe, *Rubber Chem. Technol.*, **72**, (1999), 55.
20. D.J. Banks, P. Wiseman, *Tetrahedron*, **24**, (1968), 6791.
21. R. Mayer, *Organic Chemistry of Sulfur*, S. Oae, Ed., Plenum Press, New York (1977).
22. M.H.S. Gradwell, M.J. vd Merwe, *Rubber Chem. Technol.*, **72**, (1999), 65.
23. E.H. Framer, F.W. Shipley, *J. Appl. Polym. Sci.*, **1**, (1946), 293.
24. E.H. Framer, *J. Chem. Soc.*, (1947), 1519.
25. E.H. Framer, *J. Soc. Chem. Ind.*, **66**, (1947), 86.
26. A.Y. Coran, *Science and technology of rubber*, Academic Press, San Diego (1994).
27. L. Bateman, C.G. Moore, M. Porter, *J. Chem. Soc.*, (1958), 2866.
28. A.V. Chapman, "Safe rubber chemicals: Reduction of zinc levels in rubber compounds", TARRC/MRPRA, (1997).
29. A.B. Sullivan, C.J. Hann, G.H. Kuhls, Rubber Division Meeting, American Chemical Society, Toronto, Canada (1991).
30. L. Domka, Krysztafkiewicz, *Int. Pol. Sci. Techn.*, **7**, (1980), T/18.
31. A.Y. Coran, *J. Appl. Polym. Sci.*, **87**, (2003), 24.
32. J.R. Wolfe, T.L. Pugh, A.S. Killian, *Rubber Chem. Technol.*, **41**, (1968), 1329.
33. A.Y. Coran, "Vulcanization", in *Science and Technology of Rubber*, E.R. Eirich, Ed., Academic Press, San Diego (1978), 291.

34. B. Morgan, W.J. McGill, *J. Appl. Polym. Sci.*, **55**, (2000), 1405.
35. S.P. Manik, S. Banerjee, *Rubber Chem. Technol.*, **43**, (1970), 1311.
36. J.R. Shelton, E.T. McDonel, *Rubber Chem. Technol.*, **33**, (1960), 342.
37. E. Morita, E.J. Young, *Rubber Chem. Technol.*, **36**, (1963), 844.
38. A.Y. Coran, *Rubber Chem. Technol.*, **37**, (1964), 679.
39. M.H.S. Gradwell, W.J. McGill, *J. Appl. Polym. Sci.*, **58**, (1995), 2193.
40. F.W.H. Kruger, W.J. McGill, *J. Appl. Polym. Sci.*, **42**, (1991), 2643.
41. F.W.H. Kruger, W.J. McGill, *J. Appl. Polym. Sci.*, **42**, (1991), 2651.
42. M.H.S. Gradwell, W.J. McGill, *J. Appl. Polym. Sci.*, **61**, (1996), 1131.
43. M.H.S. Gradwell, W.J. McGill, *J. Appl. Polym. Sci.*, **51**, (1994), 177.
44. P.J. Nieuwenhuizen, *Rubber Chem. Technol.*, **70**, (1997), 368.
45. B. Dogadkin, L. Beniska, *Rubber Chem. Technol.*, **31**, (1958), 329.
46. A.Y. Coran, *Rubber Chem. Technol.*, **37**, (1964), 673.
47. A.Y. Coran, *Rubber Chem. Technol.*, **38**, (1965), 1.
48. W. Scheele, H.E. Toussaint, Y.K. Chai, *Rubber Chem. Technol.*, **34**, (1961), 334.
49. M.H.S. Gradwell, W.J. McGill, *J. Appl. Polym. Sci.*, **61**, (1996), 1515.
50. M. Andreis, J. Liu, J.L. Koenig, *J. Polym. Sci., Polym. Phys. Ed.*, **27**, (1989), 1389.
51. C.G. Moore, B.R. Trego, *J. Appl. Polym. Sci.*, **8**, (1964), 1957.
52. R.B. Layer, *Rubber Chem. Technol.*, **65**, (1992), 211.
53. R.B. Layer, *Rubber Chem. Technol.*, **65**, (1992), 822.
54. A.A. Watson, Thesis, University of London, (1965).
55. V. Duchacek, *J. Appl. Polym. Sci.*, **20**, (1976), 71.
56. V. Brajko, *Rubber Bulletin*, (1970), 38.
57. H. Ismail, P.K. Freakley, *Eur. Polym. J.*, **32**, (1996), 411.
58. M.Z. Rakhman, M.S. Fel'dshstein, *Soviet Rubber Technol.*, **27**, (1968), 17.
59. A. Wei, *Rubber Industry of China*, **48**, (2001), 1.
60. A.A. Mukhitdinov, *Int. Polym. Sci. Technol.*, **21**, (1994), 48.
61. K. Morche, H. Ehrend, *Kautsch. Gummi Kunstst.*, **42**, (1989), 1015.
62. T.V. Romanova, A.A. Dontsov, A.G. Fomin, *Int. Polym. Sci. Technol.*, **15**, (1988), T/6.
63. V. Duchacek, A. Kuta, P. Pribyl, *J. Appl. Polym. Sci.*, **47**, (1993), 743.
64. H. Irving, R.J.P. Williams, *J. Chem. Soc.*, (1953), 3192.
65. F.K. Lautenschlaeger, K. Edwards, *Rubber Chem. Technol.*, **53**, (1980), 27.
66. P. Versloot, *Rubber Chem. Technol.*, **67**, (1994), 263.
67. C. Hepburn, *Rubber Technol. Intern.*, **24**, (1985), 5.
68. C. Hepburn, M.S. Mahdi, *Kautsch. Gummi Kunstst.*, **39**, (1986), 629.
69. P. Kovacic, *Ind. Eng. Chem.*, **47**, (1955), 1090.
70. C. Hepburn, M.S. Mahdi, *Plastics and Rubber Processing and Applications*, **6**, (1986), 247.
71. C. Hepburn, M.S. Mahdi, *Plastics and Rubber Processing and Applications*, **6**, (1986), 257.
72. C. Hepburn, M.S. Mahdi, *Plastics and Rubber Processing and Applications*, **6**, (1986), 267.
73. C. Hepburn, M.H. Halim, M.S. Mahdi, *Kautsch. Gummi Kunstst.*, **43**, (1990), 794.
74. C. Hepburn, (to Loughborough Consultants Ltd.), *Eur. Pat. 0146579 B1* (May 16, 1984).
75. H. Ismail, P.K. Freakley, E. Sheng, *Eur. Polym. J.*, **31**, (1995), 1049.
76. T. Kimishima, *Rubber Chem. Technol.*, **1**, (1928), 307.
77. C. Hepburn, *Rubber Technol. Intern.*, **24**, (1985), 35.
78. H. Ismail, *Plastics, Rubber and Composites Processing and Applications*, **23**, (1995), 43.

79. M.Z. Abidin, *Rubber World*, **211**, (1994), 30.
80. E. Sheng, *Eur. Polym. J.*, **32**, (1996), 35.
81. H. Ismail, *Eur. Polym. J.*, **31**, (1995), 1109.
82. H. Ismail, H.H. Chia, *Eur. Polym. J.*, **34**, (1998), 1857.
83. H. Ismail, *Eur. Polym. J.*, **33**, (1997), 1.
84. H. Takino, *Rubber Chem. Technol.*, **70**, (1997), 15.
85. P.H. Sandstrom, (to Goodyear Tire & Rubber Company), US 4,824,914 (April 25, 1989).
86. F. Broussard, *Eur. Pat.* 0634448 A1 (1994).
87. H. Krebs, *Rubber Chem. Technol.*, **30**, (1957), 962.
88. D. Seeberger, G. Raabe, *Kautsch. Gummi Kunstst.*, **42**, (1989), 27.
89. D. Seeberger, *Kautsch. Gummi Kunstst.*, **42**, (1989), 875.
90. D. Seeberger, G. Raabe, *Kautsch. Gummi Kunstst.*, **48**, (1995), 364.
91. R.W. Layer, D.W. Chasar, *Rubber Chem. Technol.*, **67**, (1994), 299.
92. B. Milligan, *Rubber Chem. Technol.*, **39**, (1966), 1115.
93. M. Bravar, J. Jelencic, M. Dabetic, *Kautsch. Gummi Kunstst.*, **41**, (1988), 462.
94. J. Pospisil, *Adv. Polym. Sci.*, **124**, (1995), 87.
95. J. Pospisil, *Die Angewandte Makromolekulare Chemie*, **216**, (1994), 135.
96. N.M. Huntink, Thesis, University of Twente, (2003).
97. K.H. Meyer, W. Hohenemser, *Helv. Chim. Acta*, **18**, (1935), 1061.
98. P.J. Nieuwenhuizen, J.G. Haasnoot, J. Reedijk, *Kautsch. Gummi Kunstst.*, **53**, (2000), 144.
99. J.H.M. vd Berg, *Rubber Chem. Technol.*, **57**, (1984), 265.
100. M. Geyser, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 425.
101. M. Geyser, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 431.
102. M. Geyser, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 439.
103. C.P. Reyneke-Barnard, M.H.S. Gradwell, M.J. McGill, *J. Appl. Polym. Sci.*, **78**, (2000), 1100.
104. C.P. Reyneke-Barnard, M.H.S. Gradwell, M.J. McGill, *J. Appl. Polym. Sci.*, **78**, (2000), 1112.
105. F.K. Lautenschlaeger, *Rubber Chem. Technol.*, **52**, (1979), 213.
106. P. Versloot, *Rubber Chem. Technol.*, **65**, (1992), 343.
107. P. Versloot, *Rubber Chem. Technol.*, **70**, (1997), 106.
108. P.J. Nieuwenhuizen, *Applied Catalysis A*, **207**, (2001), 55.
109. S. Borros, N. Agullo, *Kautsch. Gummi Kunstst.*, **53**, (2000), 131.
110. S. Rodriguez, *Kautsch. Gummi Kunstst.*, **52**, (1999), 438.
111. S. Borros, E. Garreta, "*The role of the zinc oxide in the different steps of the vulcanisation process of natural rubber, using a sulfenamide accelerator (CBS)*", Institut Quimic de Sarria-Universitat Ramon Llull: Barcelona (1999), 55.
112. E. Garreta, N. Agullo, S. Borros, *Kautsch. Gummi Kunstst.*, **55**, (2002), 82.
113. *The Vanderbilt Rubber Handbook*, R.F. Ohm Ed., R.T.VanderBilt Company, Norwalk (1990).
114. J.A. Brydson, *Rubbery Materials and their Compounds*, Elsevier, London (1988).
115. N.L. Hewitt, *Rubber World*, (1992), 24.

Optimisation of Zinc Oxide as Activator for Sulphur Vulcanisation in Various Rubbers[#]

*'We should be taught not to wait for inspiration to start a thing.
Action always generates inspiration. Inspiration seldom generates action.'*
Frank Tibolt

The addition of Zinc Oxide (ZnO) as an activator for sulphur vulcanisation of rubbers enhances the vulcanisation efficiency and vulcanisate properties and reduces vulcanisation time. In typical recipes for sulphur vulcanisation, ZnO and a fatty acid constitute the activator system, where the zinc ion is made soluble by salt formation between the acid and oxide.

The objective of the present chapter was to optimise and thereby reduce the amount of ZnO. Two widely different rubbers, viz. s-SBR and EPDM have been selected in the present study. The influence of stearic acid on the activation system was studied as well. Results demonstrate that the level of conventional ZnO (Red Seal) can be reduced to 1 and 2 phr respectively, retaining the curing and physical properties of the rubber products. The average particle size of conventional ZnO (Red Seal) is usually $\sim 0.6 \mu\text{m}$ with a specific surface area of $\sim 5 \text{ m}^2/\text{g}$. In 'active' ZnO the average particle size is decreased and the specific surface area increased to $\sim 0.2 \mu\text{m}$ and $\sim 40 \text{ m}^2/\text{g}$, respectively. Neither Active ZnO nor a pure grade ZnO led to major improvements in cure or physical properties relative to conventional ZnO (Red Seal). Of particular interest is a so-called Nano ZnO characterised by a nano-scale particle distribution, which is one of the latest developments in this field. Nano ZnO has an average particle size of $\sim 30 \text{ nm}$ and a specific surface area of $\sim 30 \text{ m}^2/\text{g}$. The cure characteristics clearly indicated that with Nano ZnO a reduction of the zinc concentration with a factor 10 could be obtained.

[#]The work described in this chapter has been accepted for publication in Journal of Applied Polymer Science.

3.1 INTRODUCTION

It is well known that Zinc Oxide (ZnO) is added to rubber compounds to activate the sulphur vulcanisation and thereby reduce the vulcanisation time. As already mentioned in the previous chapter, besides its effect on the curing process, ZnO has also many beneficial effects on the physical properties of rubber.¹ Furthermore, ZnO assists in the processing of uncured rubber.² In view of the increased attitude of protecting the environment and the upcoming legislations regarding the use and application of ZnO and zinc containing compounds, however, it is considered desirable to study the possibilities to reduce the ZnO content in rubber products.

Release of zinc into the environment from rubber occurs during production, during disposal and recycling of rubber products, for instance through leaching in land-fill sites. Also during service conditions, e.g. through wear of tires or run off from roofing foils. It is therefore desirable to keep the ZnO content as low as possible, not only to obtain a lower pollution impact but also as an advantage from an economical point of view.

Another reason to search for possibilities to reduce the zinc content in rubber vulcanisates is associated with the problem related to mould fouling. Mould fouling causes a great deal of problems and must be removed from the mould surface at regular intervals in order to obtain defect-free rubber articles. It is reported that Zinc Sulphide (ZnS) dictates the process of mould fouling.³ ZnS is considered to be a product of the vulcanisation reactions. In some rubbers like NR and EPDM, there is evidence that a considerable amount of ZnO is consumed and transformed into ZnS.³⁻⁵ Therefore, in order to reduce the problems with mould fouling it is strongly desirable to decrease the ZnO usage in rubber.

In order to judiciously reduce ZnO levels in rubber compounding, it is important to gain additional insight into the mechanistic details of sulphur vulcanisation. It is commonly quoted, that ZnO as activator forms a type of soluble complex with accelerator moieties and therefore plays an important role in accelerated sulphur vulcanisation of diene rubbers. Although the exact mechanisms about the role of activators in sulphur vulcanisation are still rather poorly understood, there seems to be an agreement that accelerators and activators react to generate active accelerator complexes. The complexes then interact with sulphur, a sulphur donor and other activators to generate the active sulphurating agent. The active sulphurating agent then reacts at the allylic sites of the polymer unsaturations to form the rubber bound intermediate or crosslink precursor. This crosslink precursor can then react with another rubber bound intermediate or with another polymer chain to generate a crosslink. The exact activator role of ZnO, however, is highly dependent on the type of accelerator present in the initial vulcanisation system.

The physical and chemical properties of ZnO are largely determined by the manufacturing method. The ZnO used nowadays in rubber compounds, is produced either by the 'direct' American Process, or the 'indirect' French Process. The American process was developed by treating oxidised ores or sulphide concentrates. In the French process the zinc metal is vapourised and then oxidised in a combustion

zone. A third method of production involves precipitation of zinc carbonate or hydroxide, which is then dried and calcined to remove water and/or carbon dioxide. This method, so-called 'Wet Process', produces more fine particles size ZnO. More recently, a new method was introduced by Nanophase Technologies Corporation, who patented a physical vapor synthesis process for the production of nanoparticle size ZnO.⁶ These particles are non-porous and free of contamination. Most of the grades of ZnO contain more than 99% of ZnO, up to more than 99.99% of ZnO for the purest grades of ZnO from the French Process. The purity is an essential parameter in many applications, because ZnO is a photochemically active material and impurities may severely affect its properties. One of the essential mechanisms is for example the prevention of product discoloration by the formation of zinc sulphides.

ZnO is a dense material that tends to compact and disperse with difficulty. Therefore, it is distributed in the form of crystal particles in rubber mixes.⁷ Nieuwenhuizen⁸ in his thesis proposed a mechanism in which the ZnO surface functions both as a reactant and as a catalytic reaction template, activating and bringing together reactants. Molecules of accelerators, sulphur and fatty acids diffuse through the rubber matrix and are adsorbed on the ZnO with the formation of intermediate complexes. An important parameter in this mechanism is an uniform dispersion of the inorganic ZnO throughout the organic polymer matrix. For optimum dispersion it is most commonly added early in the mixing stage and some grades of ZnO are surface modified, usually by the deposition of 0.2 – 0.4% of stearic acid, propionic acid, or light oil, which coatings facilitate mixing.

The efficiency of ZnO during vulcanisation can be enhanced by maximising contact between ZnO particles and the accelerators in the rubber formulation. This contact is dependent on the size of the particles, their shape and specific surface area. In the so-called (highly) active zinc oxides the mean particle size is decreased and the specific surface area increased. The average particles size of conventional ZnO (Red Seal) is usually in the range 0.3 – 1.0 μm , and its specific surface area is correspondingly in a range from 4 – 6 m^2/g . In the so-called highly active ZnO the mean particle size is decreased and the specific area increased, which results in an easier and better dispersion and a higher reactivity.⁹ Active ZnO is normally prepared with an average particle size of 0.1 – 0.4 μm , and with a substantially higher BET specific surface ranging from 30 up to 50 m^2/g . The high surface area is due to the small particle size, as ZnO has little porosity. The higher activity of this Active ZnO is probably due to the increased availability of Zn^{2+} -ions at the surface compared to the conventional particles.

One of the latest and probably most promising developments in this field, is the Nano ZnO.^{10, 11} It presents high activity due to its ultra-small size and large surface area. Nano ZnO has an average particle size of ~ 20 – 40 nm and a specific surface area of 15 – 45 m^2/g ; depending on the preparation method higher specific surface areas can be obtained, even up to 70 – 110 m^2/g .^{6, 12} The specific surface area of the Nano ZnO is only slightly higher as compared to Active ZnO and does not correlate directly with the decrease in the average particle size, which can be due to several reasons. The preparation conditions notoriously determine the final

properties of the Nano ZnO, e.g. chemical activity and morphology. Nanometer ZnO powders are commonly produced by using a high-temperature furnace to pyrolyse the precursor powders. The particle size, however, is larger than that prepared by plasma pyrolysis technology and the particles agglomerate easily, which might lead to a lower specific surface area. With the plasma pyrolysis technique the agglomeration of the particles is significantly reduced. Furthermore, the apparent (bulk) density of ZnO (Red Seal) and Active ZnO is about 0.4 – 0.6 g/cm³, while for Nano ZnO apparent density values of ~ 0.2 g/cm³ are reported. The lower apparent density implies a more voluminous material and thus a relatively lower specific surface area. In addition, the morphology of the ZnO powders varies considerably: from predominantly nearly spherical for the conventional preparation methods, to elliptical or even needle-shaped particles for the more special nano-sized ZnO, thereby influencing the specific surface area.

It has been reported that equivalent replacement of conventional ZnO (Red Seal) by Nano ZnO leads to an improvement of the properties of the rubber compound, especially the abrasion resistance, H pull-out force (a measure for rubber-cord adhesion) and tear strength.¹⁰ This might be due to the fact that the higher specific surface area and therefore, a relatively higher amount of Zn is accessible compared to conventional ZnO. For this reason, Nano ZnO is believed to offer possibilities to greatly reduce the ZnO content in rubber compounds.

Another route for reducing the amount of ZnO in formulations is to provide interaction between the accelerators, stearic acid, and the metal oxide before they are added to the rubber matrix.¹³ Results already indicated the possibility of a considerable reduction of ZnO levels with retention of the properties of the vulcanisates.

Many vulcanisation accelerator systems require additional activators, like fatty acids, or salts of fatty acids, in particular stearic acid, zinc soaps, or amine stearates. Although the addition of stearic acid as co-activator, appears to have no influence at all in Model Compound Vulcanisation (MCV), in the real rubber environment it might play an important role in solubilising various zinc-containing species. It has been reported that it increases the initial cure and decreases the level of polysulphidic crosslinks, thus effecting a more efficient use of sulphur.^{14, 15} It has also been suggested that both these effects are caused by stearic acid enabling a better dispersion of ZnO. Although the fatty acids and their salts are important as co-activators for vulcanisation, they can have a retarding effect on the scorch time as well. Depending on the mixing conditions, ZnO and stearic acid can already form zinc stearate during the compounding of the rubber. Kruger and McGill¹⁶ have performed DSC analysis of the interactions of sulphur with ZnO and stearic acid. Their results indicated the formation of zinc stearate and its subsequent reaction with sulphur. The sulphur-zinc stearate interaction helps to explain the activating role of ZnO in sulphur vulcanisation.

As an introductory study for this thesis the possibilities to reduce ZnO by optimising the amount of ZnO and by incorporating the zinc in a more chemically active form have been investigated. The first part of this chapter describes the effect of different amounts of standard ZnO (Red Seal) on the cure and physical properties.

The second part deals with special zinc oxides and with one of the latest developments in this particular area: Nano ZnO. In the last part the influence of stearic acid on the cure characteristics is demonstrated.

3.2 EXPERIMENTAL SECTION

Materials.— Solution butadiene-styrene rubber (Buna VSL 2525-0 M) was obtained from Bayer GmbH, Germany. Buna VSL 2525-0 M contains 25 wt % of 1,2-vinyl-butadiene and 25 wt % of styrene; it has a Mooney viscosity, ML (1+4) @ 100°C of 54. Ethylidene norbornene (ENB)-containing EPDM rubber (Keltan 4802) was obtained from DSM Elastomers B.V., the Netherlands. Keltan 4802 contains 52 wt % of ethylene units and 4.3 wt % of ENB; it has a relatively narrow molecular weight distribution and a typical Mooney viscosity, ML (1+4) @ 125°C of 77. As fillers were used: carbon black N-375 HAF, N-550 FEF and N-762 SRF (Cabot B.V.). Aromatic oil (Enerflex 75) was obtained from BP Oil Europe, paraffinic oil (Sunpar 2280) from Sun Petroleum Products Co., and stearic acid from J.T. Baker. Sulphur (J.T. Baker), N-tert-butyl-2-benzothiazolesulphenamide (Santocure TBBS, Flexsys B.V.), 2-Mercaptobenzothiazole (Perkacit MBT, Flexsys B.V.), and Tetramethylthiuram-disulphide (Perkacit TMTD, Flexsys B.V.), were also commercial grades and used as such. The various types of ZnO's are given in Table 3.1. The specific surface area of Nano ZnO is relatively low, which was explained in more detail in Paragraph 3.1.

Table 3.1 Types of ZnO investigated

Type	Specific surface area [m ² /g]	Average particle size [μm]	Supplier
ZnO (Red Seal)	3 – 5	0.3 – 1.0	Grillo GmbH
ZnO Pure Grade	4 – 6	0.3 – 1.0	Merck B.V.
Active ZnO	30 – 50	0.1 – 0.4	Silox Société Anonyme
Nano ZnO	15 – 45	0.02 – 0.04	Degussa AG

Rubber mixing.— A s-SBR- and an EPDM-masterbatch were prepared in an internal mixer (~ 50 kg) in order to get a homogeneous mixture and minimise the influence of mixing conditions. The vulcanisation systems, including the various ZnO's investigated, were added in a separate operation on a two roll mill at ~ 50°C. The compounds were sheeted off at a thickness of approximately 2 mm which was convenient for the subsequent preparation of test specimens. The compositions of the s-SBR and EPDM compounds with different levels of ZnO (Red Seal) are given in Table 3.2 and 3.3, respectively. The compounds with Nano ZnO are described in Table 3.4. Table 3.5 contains the compositions of the EPDM and s-SBR compounds with different levels of stearic acid.

Table 3.5 Composition of the s-SBR and EPDM compounds (phr) with different levels of stearic acid

Compound	S14	S15	S7	Compound	E8	E5	E9
s-SBR (Buna VSL 2525)	100	100	100	EPDM (Keltan 4802)	100	100	100
Carbon Black (N375HAF)	50	50	50	Carbon Black (N550 FEF)	70	70	70
Arom. Oil (Enerflex 75)	5	5	5	Carbon Black (N762 SRF)	40	40	40
-	-	-	-	Paraf. Oil (Sunpar 2280)	70	70	70
Stearic Acid	0	1	2	Stearic Acid	0	1	2
ZnO (Red Seal)	3	3	3	ZnO (Red Seal)	3	3	3
Accelerator (TBBS)	1.5	1.5	1.5	Accelerator (TMTD)	1.0	1.0	1.0
-	-	-	-	Accelerator (MBT)	0.5	0.5	0.5
Sulphur	1.75	1.75	1.75	Sulphur	1.5	1.5	1.5

Curing.— The cure characteristics of the different compounds were measured at 160°C with a Rubber Process Analyser RPA2000 (Alpha Technologies), a type of moving die rheometer. The optimal vulcanisation time (t_{90}) and scorch time (t_{02}) of the compounds were determined. The compounds were cured in a Wickert laboratory press WLP 1600/5*4/3 at 160°C and 100 bar, according to the t_{90} of the specific compounds.

Characterisation.— Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Ageing of the test specimens was carried out in a ventilated oven in the presence of air at 100°C for 3 days according to ISO 188. Tear strength was measured with trouser shaped specimens according to ISO 34. Compression set (CS) tests were performed at 23°C and 100°C for 72 hours according to DIN 53517. Hardness of the samples was measured with a Zwick Hardness-meter Shore A Type, according to DIN 53505. The fatigue-to-failure of the s-SBR compounds was measured with a Monsanto fatigue tester. Heat-build-up was determined using a Goodrich Flexometer (load 11 kg, stroke 0.445 cm, starting temperature 100°C, running time 2h) according to ASTM D623.

Swelling measurements were performed in order to obtain information about the crosslink density. The unextracted filled s-SBR samples were swollen until constant weight in toluene at room temperature. The EPDM samples were swollen in decahydronaphthalene at room temperature as well. The crosslink density was calculated according to the Flory-Rehner equation.^{15, 17} Although this equation as such is only valid for non-filled systems, the data obtained with these measurements do yet give an indication of the relative crosslink densities. The Flory-Huggins parameter χ for s-SBR-toluene networks was taken from literature: 0.21.¹⁸ For swollen EPDM-decahydronaphthalene networks the χ -parameter was calculated via the relationship $\chi = 0.121 + 0.278 * v_2$, reported by Dikland,¹⁹ with v_2 = polymer network volume fraction at equilibrium swelling.

3.3 RESULTS AND DISCUSSIONS

As mentioned before, the zinc ion is the central atom of the active complex in accelerated sulphur vulcanisation. In addition to its role as an activator for sulphur vulcanisation, there is also evidence that the inclusion of ZnO in a compound reduces heat-build-up and improves tire abrasion resistance. It has also been found that ZnO improves heat resistance of vulcanisates and their resistance to the action of dynamic loading. Traditionally, typical recipes for sulphur curing of SBR rubbers contain 5 phr ZnO. Over the years lower levels have been used and, according to several researchers,^{20, 21} it seems that ZnO levels can be reduced to a minimum of about 2 phr without serious detrimental effects on properties. A small reduction in modulus can be compensated by slightly increasing the level of accelerators. Higher levels of ZnO are normally used for EPDM.

3.3.1. ZnO Optimisation in s-SBR Compounds

The s-SBR masterbatch according to Table 3.2 was investigated over a range of ZnO (Red Seal) levels, evaluating vulcanisation behaviour and physical properties. Vulcanisation experiments without any ZnO as activator were performed in order to separate the activity of the acceleration system itself and the activator. Figure 3.1 shows the cure characteristics for the s-SBR compounds with the ZnO amount varied between 0 – 3 phr. As can be seen in this figure, the same cure rate and increase in torque was observed for compounds with 0.3 to 3 phr ZnO. Complete absence of ZnO leads to a decrease in cure rate and therefore much longer cure times. For the compounds with very low ZnO levels, in particular 0.3 phr ZnO, a slight decrease in torque or reversion is observed at longer vulcanisation times.

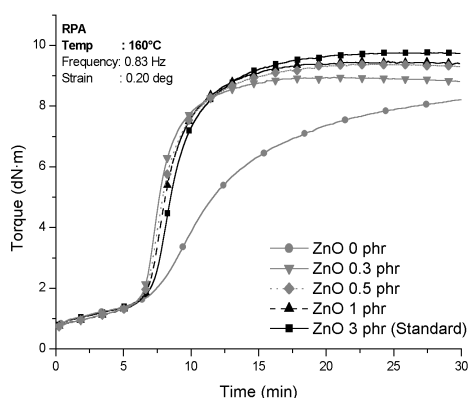


Figure 3.1 Cure characteristics of s-SBR compounds with different levels of ZnO (Red Seal)

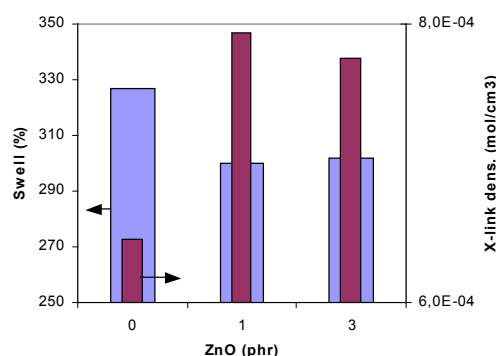


Figure 3.2 Swell and crosslink density of s-SBR compounds with different levels of ZnO (Red Seal)

The results of swelling experiments with different levels of ZnO (Red Seal) are presented in Figure 3.2. A higher swelling percentage corresponding to a lower crosslink density was found for the compound without ZnO, which is in accordance with the torque measurements.

The physical properties of the compounds with 0 and 1 – 5 phr ZnO are presented in Table 3.6. A lower value for elongation at break and higher compression set at 100°C for the compound without ZnO was found. This can be attributed to the lower crosslink density, as was already observed with the swelling and torque measurements. The influence of ZnO on heat-build-up, as suggested in literature, could not experimentally be corroborated. No major differences were observed between the compounds with 1 to 5 phr ZnO. Concerning the abrasion resistance no substantial increase with increasing ZnO level was detected either. As can be seen in Table 3.6, the fatigue-to-failure properties decrease at higher ZnO levels.

Table 3.6 Properties of s-SBR compounds with different ZnO (Red Seal) levels

Compound	S1	S2	S5	S6	S7	S8	S9
Hardness (Shore A)	65	64	64	65	65	65	65
M ₂₅ (MPa)	1.1	1.1	1.1	1.1	1.1	1.1	1.1
M ₅₀ (MPa)	1.7	1.6	1.6	1.6	1.6	1.6	1.5
M ₁₀₀ (MPa)	2.9	2.6	2.7	2.7	2.8	2.8	2.6
M ₃₀₀ (MPa)	14.4	12.8	12.9	13.3	14.5	13.6	12.7
Tensile strength (MPa)	16.1	15.6	22.2	20.6	24	23.6	23.1
Elongation at Break (%)	320	335	431	397	432	429	458
Tear strength (N/mm)	35.9	37	36.4	34.7	34	32.8	36.2
CS 72h/23°C (%)	6	9	8	8	10	8	8
CS 72h/100°C (%)	62	63	55	52	55	52	63
After 72 Hours / 100°C ageing:							
M ₂₅ (MPa)	1.4	1.4	1.6	1.7	1.7	1.7	1.6
M ₅₀ (MPa)	2.2	2	2.7	2.7	2.8	2.7	2.7
M ₁₀₀ (MPa)	4.2	4	5.7	5.9	5.8	5.8	5.7
M ₃₀₀ (MPa)	-	-	-	-	-	-	-
Tensile strength (MPa)	14.2	13.2	17.6	16.7	18.5	18.7	18.8
Elongation at Break (%)	216	220	213	190	215	210	213
Abrasion resistance (mm ³)	96	75	97	96	97	102	95
Fatigue-to-failure (kc)	29	34	50	49	53	42	34
Goodrich HBU							
Perm. set C (%)	9.9	11.2	12.4	11.8	11.8	11.2	12.1
Holder T (°C)	131.6	131.3	136.2	135.2	136.1	135.4	138
Needle T (°C)	155.6	156.5	165.5	161.9	165.5	163.8	164.7

In summary, the data shown in this paragraph reveals that a reduction to 1 phr of ZnO in s-SBR compounds seems to be possible without major effects on cure and physical properties.

3.3.2. ZnO Optimisation in EPDM Compounds

Also EPDM was investigated over a range of ZnO (Red Seal) levels, evaluating vulcanisation behaviour and physical properties according to the recipes in Table 3.3. Figure 3.3 shows, that the cure characteristics for EPDM with 3 – 10 phr ZnO (Red Seal) are comparable. The state of cure ($M_H - M_L$) of the compound with 1 phr ZnO is lower and the cure curves display a slight decrease or reversion. Swelling percentages and crosslink densities of the EPDM compounds are depicted in Figure 3.4. As already expected from the rheograms, a considerably higher swelling percentage was measured for the compound without ZnO, and a slightly higher swelling percentage for the compound with 1 phr of ZnO compared to the compounds with 3 – 10 phr.

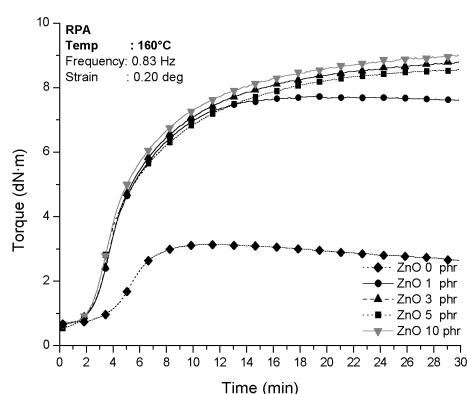


Figure 3.3 Cure characteristics of EPDM compounds with different levels of ZnO (Red Seal)

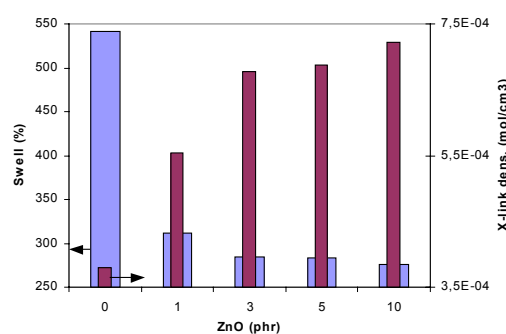


Figure 3.4 Swell and crosslink density of EPDM compounds with different levels of ZnO (Red Seal)

The mechanical properties of the cured compounds with different ZnO levels are listed in Table 3.7. When ZnO is omitted the crosslink density is considerably lower, resulting in notoriously inferior mechanical properties. Inclusion of only 1 phr of ZnO in the compound recipe leads to a significantly higher crosslink density. The crosslink density of the standard 5 phr ZnO compound, however, is still distinctly higher, as can be deduced from the values for the elongation at break and compression set.

Overall, a reduction to 2 phr ZnO (Red Seal) in EPDM compounds seems to be possible without noticeable effects on the cure and physical properties. Depending on the exact requirements for a specific compound, a further reduction might still be possible.

Table 3.7 Properties of EPDM compounds with different ZnO (Red Seal) levels

Compound	E1	E2	E3	E4	E5	E6	E7
Hardness (Shore A)	43	43	59	61	63	63	62
M ₂₅ (MPa)	0.6	0.6	0.9	0.95	1	1	1
M ₅₀ (MPa)	0.7	0.7	1.3	1.48	1.6	1.6	1.6
M ₁₀₀ (MPa)	0.9	0.9	2.4	2.82	3.1	3.2	3.1
M ₃₀₀ (MPa)	1.8	2	7.4	8.79	9.4	9.7	9.4
Tensile strength (MPa)	2.5	3.1	13.7	13	13	13	12.6
Elongation at Break (%)	655	661	563	450	413	406	407
Tear strength (N/mm)	17.4	24.1	40.6	36	34.5	36.5	34.3
CS 72h/23°C (%)	23	23	5	6	5	5	6
CS 72h/100°C (%)	99	94	81	68	65	61	66
After 72 Hours / 100°C ageing:							
M ₂₅ (MPa)	0.9	0.8	1.2	1.2	1.3	1.4	1.3
M ₅₀ (MPa)	1.2	1	2.2	2.2	2.3	2.3	2.3
M ₁₀₀ (MPa)	2.1	1.5	4.6	4.7	5.1	5.0	4.8
M ₃₀₀ (MPa)	6.1	4.3	12.5	-	-	-	-
Tensile strength (MPa)	13.3	9.3	12.3	12.4	12.1	12.4	12.6
Elongation at Break (%)	742	-	281	260	243	248	268

3.3.3. Other Zinc Oxides

When ZnO pure grade (99.5%, Merck) was used as activator in s-SBR and EPDM compounds instead of ZnO (Red Seal), no major differences were observed in cure and physical properties, as illustrated in Figures 3.5 and 3.6.

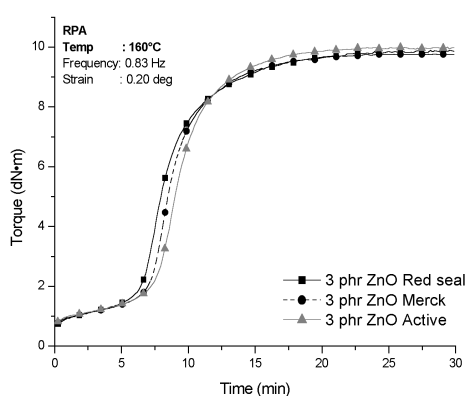


Figure 3.5 Comparative curing behaviour of s-SBR compounds containing ZnO, ZnO pure and Active ZnO

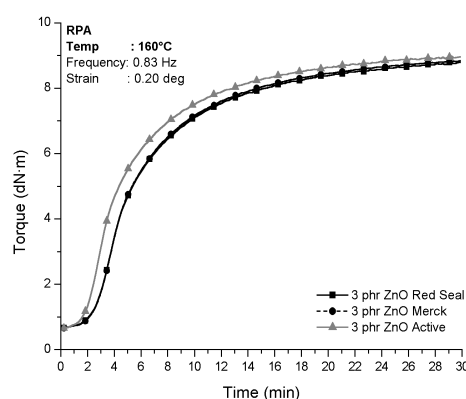


Figure 3.6 Comparative curing behaviour of EPDM compounds containing ZnO, ZnO pure and Active ZnO

Another parameter which is quoted to affect the activity of ZnO is the specific surface area. Substitution of 3 phr ZnO (Red Seal) by 3 phr Active ZnO leads in both rubbers to a slight, virtually insignificant, increase in delta torque, as shown in Figures 3.5 and 3.6. Also no major differences in physical properties are observed.

To study the effects of dispersion in greater detail, experiments were performed using Nano ZnO: Table 3.4. The cure characteristics of s-SBR compounds with different levels of Nano ZnO are presented in Table 3.8.

Table 3.8 Cure characteristics of s-SBR compounds with different Nano ZnO levels

Parameters Compound	Nano zinc				ZnO (Red Seal)	
	S10	S11	S12	S13	S2	S7
Phr	0.05	0.10	0.20	0.30	0	3
M_H-M_L (dN•m)	8.76	8.76	9.08	9.07	8.43	9.08
t_{02} (min)	4.48	4.44	4.21	4.44	4.48	4.48
t_{90} (min)	18.07	12.45	10.24	11.09	22.05	11.53

The cure characteristics indicate indeed, that with Nano ZnO as activator a pronounced reduction of ZnO content can be achieved. It seems to be possible to reduce the quantity of ZnO to 0.2 – 0.3 phr, without detrimental effects on the curing properties.

The water content of ZnO might affect the activity as well. As already mentioned in the introduction, Nieuwenhuizen⁸ in his thesis proposed a mechanism in which the ZnO surface functions both as a reactant and as a catalytic reaction template, activating and bringing together reactants. In this mechanism it is suggested, that water donates a proton to an oxygen ion, and coordinates as OH⁻ at a free zinc site. In the net reaction water, or actually a proton, may be regarded as a catalyst. Geysler *et al.*²² noted that water strongly influences the amount of ZDMC that is formed in ZnO/TMTD vulcanisation systems. Therefore it might be useful to examine the influence of water, adsorbed onto ZnO, on the vulcanisation. It is commonly known in the field of catalysis that at higher temperatures ZnO loses most of its coordinated water easily. However, testing of the effect of dried ZnO in rubber compounds is not very realistic because rubber compounds always contain a considerable amount of water. For that reason this sort of experiments have not been further pursued.

3.3.4. Synergistic Role of Stearic Acid with ZnO

With the objective to enhance the availability of Zn²⁺-ions in the presence of stearic acid, two different levels of stearic acid were included in this study. In this part the influence of stearic acid on the cure characteristics of s-SBR and EPDM compounds is demonstrated. The composition of the compounds with 3 phr ZnO (Red Seal) and different levels of stearic acid are listed in Table 3.5. The cure characteristics for s-SBR and EPDM compounds with different levels of stearic acid are presented in Figures 3.7 and 3.9, respectively. The accompanying swelling percentages and crosslink densities are given in Figures 3.8 and 3.10.

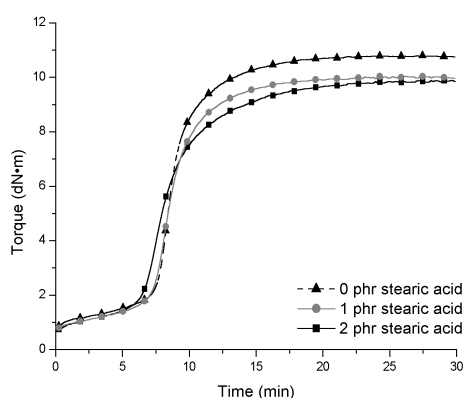


Figure 3.7 Cure characteristics of s-SBR compounds with different levels of stearic acid

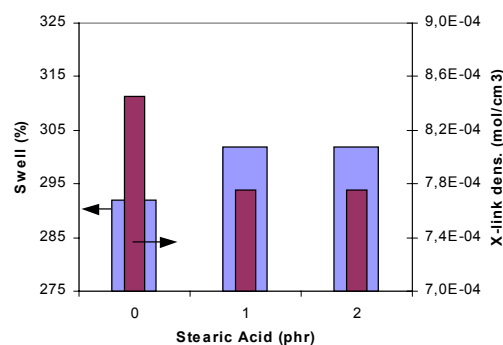


Figure 3.8 Swelling and crosslink density of s-SBR compounds with different levels of stearic acid

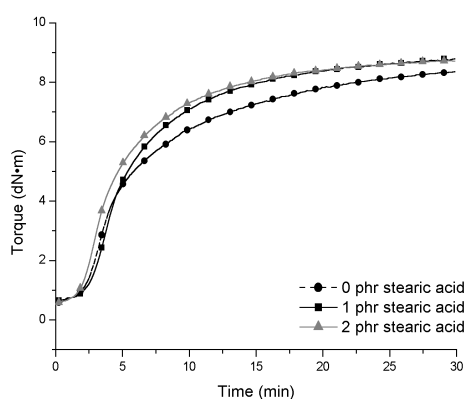


Figure 3.9 Cure characteristics of EPDM compounds with different levels of stearic acid

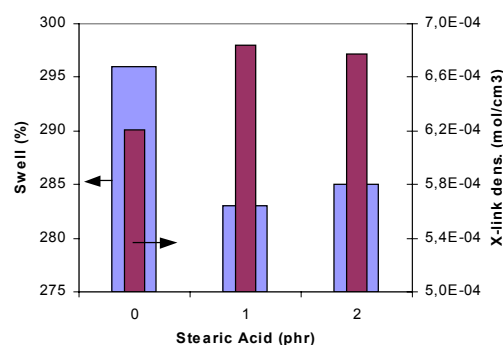


Figure 3.10 Swelling and crosslink density of EPDM compounds with different levels of stearic acid

The addition of ≥ 1 phr stearic acid in EPDM compounds indeed causes a small increase of torque level. The swelling experiments also reveal a decrease in swelling percentage or increase in crosslink density with addition of stearic acid. This might be the result of a better dispersion of ZnO in the EPDM rubber matrix when stearic acid is added or the result of a co-activating effect by stearic acid. While in EPDM a lower torque level is observed for the compound without stearic acid, in s-SBR the opposite effect was found: a higher torque level and correspondingly a higher crosslink density. The lower torque level of the compounds with stearic acid is not caused by a plasticising effect, because also lower values for the corresponding crosslink densities are obtained. The retarding effect of stearic acid on the scorch time, as suggested in literature, was neither observed in s-SBR nor in EPDM.

3.4 CONSIDERATIONS ON ZINC OXIDE LEVELS NEEDED FOR PROPER VULCANISATION

This chapter described the first investigations into the possibilities to optimise and reduce the amount of ZnO in two different rubbers, s-SBR and EPDM. It turned out, that it is possible to reduce the quantity of 3 – 5 phr ZnO traditionally used in rubber formulations, still resulting in acceptable properties. The cure characteristics and the physical properties (tensile strength, elongation at break, compression set and hardness) of s-SBR compounds with ZnO (Red Seal) as activator do not improve significantly anymore with levels higher than a minimum of 1 phr. Apparently, the effect of ZnO (Red Seal) in the TMTD/MBT accelerated vulcanisation system in EPDM is more conspicuous, than in the TBBS accelerated system in s-SBR. While in s-SBR the cure and mechanical properties of compounds with no ZnO or very low levels are somewhat inferior, in EPDM these properties are seriously affected. As a result, EPDM compounds require higher amounts of ZnO (Red Seal), *i.e.* 2 phr at least, to obtain properties comparable with standard compounds containing 3 – 5 phr ZnO. In general, the above-described results have demonstrated the possibility to optimise and reduce the amount of ZnO (Red Seal), yet at the same time pointed out that no general conclusions can be drawn, but that every application requires its own specific optimisation.

A parameter of paramount importance in the activation of sulphur vulcanisation, is the accessibility of Zn. Although the more active, higher specific surface ZnO did not result in a significant improvement, experiments with Nano ZnO have proven that it is possible to reduce the quantity of ZnO with a factor of 10, retaining the curing properties of the rubber products. The Nano ZnO represents a new route to reduce ZnO levels in rubber compounds. The main disadvantage of Nano ZnO is its high price compared to conventional ZnO, mainly due to the current small scale production.

The results of the experiments with stearic acid have shown that it certainly has an influence on the effectivity of ZnO as activator. However, the exact role of stearic acid cannot be inferred from these results. The presence of stearic acid seems to have a different influence on the accelerator system for s-SBR vs. the one for EPDM.

3.5 CONCLUSIONS

It is concluded from the experiments described in this chapter that for the sulphur vulcanisation of rubbers in the presence of accelerators, an activator like ZnO is an essential ingredient. It enhances the vulcanisation efficiency and vulcanisate properties and reduces vulcanisation time. The cure characteristics and the physical properties (tensile strength, elongation at break, compression set and hardness) of the compounds with conventional ZnO (Red Seal) do not change

significantly with levels ≥ 1 phr in s-SBR and ≥ 2 phr in EPDM. So, it is possible to reduce the quantity of ZnO used traditionally in rubber formulations: 3 – 5 phr.

The dispersion, particle size and specific surface area are parameters of paramount importance for the activity of ZnO. Active ZnO with a somewhat larger specific surface area than conventional ZnO (Red Seal), apparently has a negligible influence on the cure characteristics and physical properties. Nano zinc on the other hand, as a newcomer, represents a new dimension for activation of sulphur curing. When compared with conventional ZnO, only one tenth of the amount of Nano ZnO is necessary to achieve the same cure characteristics. This might be associated with the ultra-small average particle size combined with the high specific area of Nano ZnO.

Stearic acid definitely has an influence on the cure characteristics, albeit different for the sulphenamide and benzothiazole/thiuram accelerator system used for s-SBR and EPDM, respectively.

The overall conclusion is that, to achieve a pronounced reduction of zinc levels in rubbers, small particles and a high surface area are predominant parameters. A better accessibility of the zinc ions is most probably the key factor to achieve a higher chemical activity.

3.6 REFERENCES

1. W. Hofmann, *Rubber Technology Handbook*, Hanser Publishers, New York (1994).
2. *Invisible Partner Zinc keeps the Bounce in Rubber*, International Zinc Association (IZA), Brussels (2000).
3. M.F. Bukhina, Y.L. Morozov, P.M. van den Ven, J.W.M. Noordermeer, *Kautsch. Gummi Kunstst.*, **56**, (2003), 172.
4. T.D. Skinner, *Rubber Chem. Technol.*, **45**, (1972), 182.
5. M. Porter, T.D. Skinner, M.A. Wheelans, *J. Appl. Polym. Sci.*, **11**, (1967), 2271.
6. G. Wypych, *Handbook of Fillers*, ChemTec Publishing, New York (1999).
7. R.F. Ohm, *Additives that affect mixing*, Chapman&Hall, London (1997).
8. P.J. Nieuwenhuizen, Thesis, University of Leiden, (1998).
9. L. Domka, A. Krysztafkiwicz, *Int. Polym. Sci. Technol.*, **7**, (1980), T/18.
10. A. Wei, *Rubber Industry of China*, **48**, (2001).
11. L. Cao, *Chem. J. Internet*, **4**, (2002), 45.
12. L. Yuanhua, T. Zilong, Z. Zhongtai, *J. Am. Ceram. Soc.*, **83**, (2000), 2869.
13. A.A. Mukhitdinov, *Intern. Polym. Sci. Technol.*, **21**, (1994), 48.
14. F.P. Baldwin, *Rubber Chem. Technol.*, **45**, (1972), 1348.
15. B. Saville, A.A. Watson, *Rubber Chem. Technol.*, **40**, (1967), 100.
16. F.W.H. Kruger, W.J. McGill, *J. Appl. Polym. Sci.*, **42**, (1991), 2651.
17. P.J. Flory, J. Rehner, *J. Chem. Phys.*, **11**, (1943), 521.
18. R.A. Hayes, *Rubber Chem. Technol.*, **59**, (1986), 138.
19. H.G. Dikland, Thesis, University of Twente, (1992).
20. A.V. Chapman, "*Safe rubber chemicals: Reduction of zinc levels in rubber compounds*", TARRC/MRPRA, (1997).
21. V. Duchacek, *J. Appl. Polym. Sci.*, **20**, (1976), 71.
22. M. Geysler, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 425.

A Study of the Influence of Zinc Oxide in Different Stages of Vulcanisation by MCV[#]

'You can know the name of a bird in all the languages of the world, but when you're finished, you'll know absolutely nothing whatever about the bird... So let's look at the bird and see what it's doing; that's what counts.'

Richard Feynman (1918 – 1988)

Although it has been firmly established that ZnO plays an important role as activator in sulphur vulcanisation, the exact mechanisms are still far from completely understood and the subject of ongoing scientific research.

In this chapter Model Compound Vulcanisation (MCV) is introduced to critically investigate the effects of ZnO in the different stages of the vulcanisation process that have been reported in literature. Standard analytical techniques can be applied to analyse these low molecular weight model systems. Experiments are described with two different models, squalene and TME, both with benzothiazolesulphenamide-accelerated vulcanisation systems. It is realised that the results obtained apply to model compounds and that these findings may not necessarily be extrapolated to real rubbers.

Results clearly demonstrate the influence of ZnO in the different stages of the vulcanisation process. In the squalene/CBS system the different effects are more pronounced than in TME/TBBS. With ZnO present in the system, a marked decrease is observed in the sulphur concentration in an early stage of the vulcanisation and a slight delay in the disappearance of the crosslink precursor. The crosslinked products distribution is influenced by the presence of ZnO as well.

[#]The work described in this chapter has been accepted for publication in Journal of Applied Polymer Science.

4.1 INTRODUCTION

ZnO is proven to be the best activator for sulphur vulcanisation and at present no viable alternative has been found to eliminate ZnO completely from rubber compounds without significantly jeopardising processing as well as performance characteristics. The nature of sulphur vulcanisation activation and acceleration has been subject of many studies, and several theories on the role of ZnO have been postulated. The complexity of the vulcanisation process has given rise to many uncertainties and contradictions in literature about the influence of ZnO in the different stages of the process and its exact mechanisms. It is evident that in order to judiciously reduce ZnO levels in rubber compounding additional insight in the mechanistic details should be obtained.

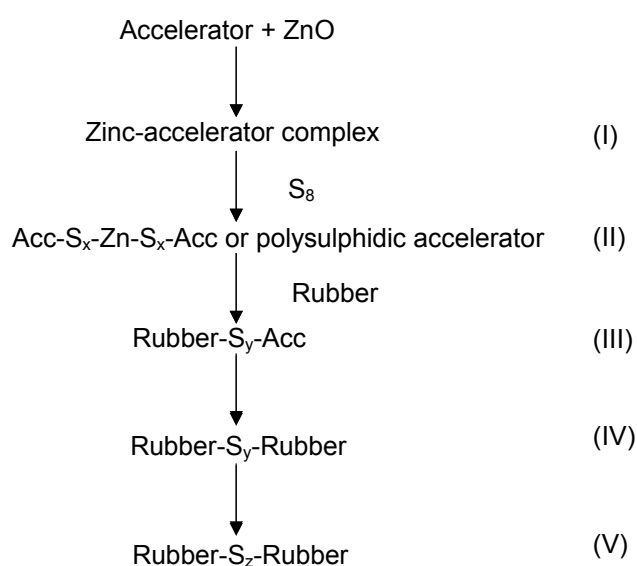


Figure 4.1 General scheme for sulphur vulcanisation^{1, 2}

Accelerated sulphur vulcanisation is generally accepted to take the course as visualised in Figure 4.1.^{1, 3, 4} As a first step in the vulcanisation process, accelerators and activators form an active accelerator complex (I) which subsequently interacts with sulphur to produce active sulphurating species (II). The actual composition depends of course on the accelerator system used. It has been suggested in many studies, that Zn²⁺-ions play an important role in the formation of this active sulphurating agent. This reactive species reacts with allylic hydrogen atoms of rubber unsaturations to form a rubber bound intermediate or preferentially designated as crosslink precursor (III). It is generally assumed that there is no major role for ZnO in the formation of crosslink precursors and that it first must be transformed into a zinc-accelerator complex (see also Figure 2.15) to participate. Layer⁵ suggested a mechanism for precursor formation via interaction of an olefin, ZnO and the polysulphidic accelerator tetramethylthiuram polysulphide (TMTP), Figure 4.2.

It is rather unlikely that three molecules at the same time engage in one transition state, but the reaction may take place on the surface of ZnO crystals.⁶

Geyser and McGill⁷ indeed observed an acceleration of precursor formation in the presence of ZnO, when TMTD, sulphur and a model olefin were heated. It is reported that it might take place via a weakening of the S-S bond in the polysulphidic accelerator, due to coordination to the ZnO surface.

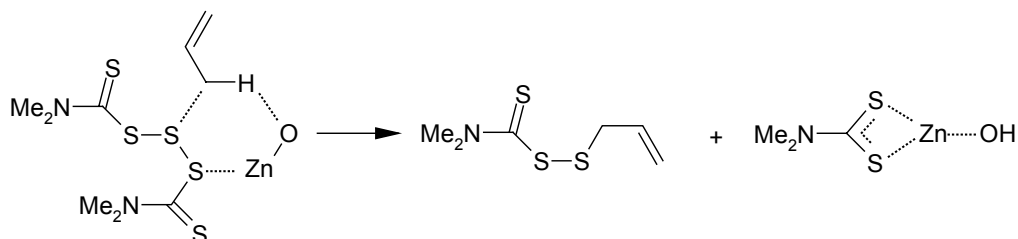


Figure 4.2 Precursor formation via interaction of an olefin, ZnO and TMTD as suggested by Layer⁵

Polysulphidic crosslinks (IV) are formed through the reaction of these intermediates with another intermediate moiety or through the reaction with polymer chains. Various mechanisms have been proposed for the conversion of crosslink precursors into crosslinks. Basically, these reactions are catalysed by zinc-accelerator complexes, although they can also occur in the absence of ZnO, albeit at significantly lower reaction rates. The initial crosslinks may eventually desulphurate to form shorter crosslinks (V) or degrade to cyclic sulphides. It has been reported that also in this stage of the vulcanisation process zinc ions play a role.⁸ The shortening of the polysulphidic crosslinks and isoallylic transformation reactions are catalysed by a zinc-accelerator complex, such as Zn(MBT)₂. From the above discussion, it is clear that the role of ZnO in sulphur vulcanisation is still subject of controversy. In order to nail down all the hypotheses, Model Compound Vulcanisation (MCV) was applied.

MCV is widely used to gain mechanistic insight in rubber vulcanisation, because of its alleged good agreement with real rubber systems and the possibility to use conventional analytical techniques. It remains a very useful method because, despite recent developments in the field of analytical techniques, rubbers are difficult to analyse using standard analytical and spectroscopic techniques. The model compound should be as much as possible representative for the reactive unit of the polymer. In particular, its chemical behaviour should be similar to the behaviour of the reactive unit of the polymer. Other factors, like the presence of additional functional groups, position and configuration of the double bond, occurrence of double bonds present in the model should be considered as well. An elementary disadvantage of these low-molecular-weight compounds is the high concentration of end-groups. The reactivity of these end-groups is considerably different from the methylene (—CH₂—) and methyne (—CH—) groups, which constitute the majority of the reactive groups in a polymer. Other differences not to be neglected are the solubility of the chemicals in rubbers and model systems, and the loss of volatiles from rubbers and open or closed model experiments.

Furthermore, the choice of a certain model compound should be determined by the purpose of the experiments. Squalene is the most used of the polyfunctional compounds as a model for natural rubber, due to its similarity to the real rubber

structure. Polyfunctional models display a reactivity more similar to rubbers, because of the presence of more than one double bond and relatively less end-groups. These models are very well suited to investigate the fate of reactants. Investigation of crosslinks and main-chain modifications, however, is very difficult and requires elaborate separative and analytic procedures. Therefore, despite its simplicity, the monofunctional model 2,3-dimethyl-2-butene (TME) is a good choice to investigate crosslinks and product distribution. The model contains only one type of allylic position and after vulcanisation hardly any isomerisation products are obtained. High temperature techniques, like Gas Chromatography (GC), should be avoided for analysis because of their profound effect on polysulphidic organic compounds. The conditions cause isomerisation and/or degradation of di- and polysulphidic products and possibly even of the monosulphides. HPLC separation at room temperature in combination with UV-detection has been applied successfully in MCV as analysis technique.⁹

In this chapter, as an introductory study, the influence of ZnO as activator on the different stages of the vulcanisation process will be dealt with. Although it has been studied already quite extensively, a detailed investigation was regarded as an important base to study the basic principles and the effects of other activators later on. Particular emphasis was put on establishing reliable and accurate experimental procedures. The first part of this chapter focuses on the influence of ZnO in a CBS-accelerated vulcanisation system with squalene as model olefin. In the second part, a more detailed study is described about the influence of ZnO in a TBBS-accelerated sulphur vulcanisation with TME as a model compound. In the latter experiments the reaction products could be analysed as a function of time as well. In the last part of this chapter the results are compared with the 'real' rubber results described in Chapter 3 in order to find explanations for the effects of ZnO on the physical properties, based on the insights obtained with the mechanistic studies.

4.2 EXPERIMENTAL SECTION

Materials.— The materials used in the model compound experiments are listed in Table 4.1. The compositions of the model compound samples are listed in Table 4.2. The experiments were divided into two parts: experiments with squalene as model compound and CBS as accelerator; and experiments with TME as model compound and TBBS as accelerator.

Table 4.1 Materials used for model compound vulcanisation

Material	Source
Squalene	Merck
2,3-dimethyl-2-butene (TME)	Aldrich
N-Cyclohexylbenzothiazole-2-sulphenamide (CBS)	Flexsys
N-tert-butylbenzothiazole-2-sulphenamide (TBBS)	Flexsys
Sulphur	Merck
Zinc Oxide	Merck
Stearic Acid	Merck

The squalene model systems were vulcanised with CBS as accelerator to compare with the results obtained by Borros.¹⁰ For the TME system TBBS was chosen in slightly different amounts, comparable to the real rubber systems, in particular s-SBR rubber, described in Chapter 3. In order to examine the influence of ZnO in the several stages of vulcanisation, samples with and without ZnO were prepared.

Table 4.2 Model compound systems

Squalene				TME			
	Mass (g)	(phr)	(mmole)		Mass (g)	(phr)	(mmole)
Squalene	0.5000	100	1.217	TME	0.5000	100	5.941
CBS	0.0060	1.2	0.023	TBBS	0.0075	1.5	0.025
Sulphur	0.0100	2	0.039	Sulphur	0.0088	1.75	0.034
ZnO	0.0250	5	0.307	ZnO	0.0250	5	0.307
Stearic acid	0.0100	2	0.035	Stearic acid	0.0100	2	0.035

Model compound vulcanisation.— The model compound vulcanisation experiments were carried out in a glass ampoule. The reaction mixture was weighed into this ampoule. In order to minimise the influence of oxygen in the reactions, the ampoule was fluxed with nitrogen and sealed off. The reaction was performed in a preheated thermostatic oil bath at 140°C for a fixed time. A magnetic stirrer was added to the mixture to provide adequate stirring during the reaction. After a definite period of time the reaction was arrested by taking the ampoule out of the oil bath and by immersion in liquid nitrogen. After cooling, the ampoule was covered with aluminium foil to avoid an UV influence, and stored in a refrigerator.

Analysis of the reaction products.— A small portion of the filtered sample (about 0.03 g) was weighed and dissolved in 2.5 ml of acetonitrile, containing an internal standard: dibutyldisulphide. The response factors for all the initial components in reference to the internal standard were measured with the HPLC at a wavelength of 254 nm. The internal standard was added after the vulcanisation as an extra component for quantitative analysis.

Table 4.3 HPLC conditions

Column	Nucleosil 100-5 C18 HD (reverse phase)
Length of column	250 mm
Internal diameter of the column	4.6 mm
Mobile phase	97 Acetonitrile : 3 Water (vol%)
Flow rate	1 ml/min
Temperature	23 °C
Detector	UV
Wavelength	254 nm
Injected Volume	20 µl

Before injecting in the HPLC, the sample was filtered twice over a 45 μm porous filter. About 20 μl of this diluted sample was injected onto the HPLC-column for analysis according to the conditions described in Table 4.3. The areas of the different peaks in the chromatogram were determined and converted into concentrations via the measured response factors for the several components. Reaction conversions as a function of reaction time were calculated by dividing the concentration of the component by the initial concentration and expressed in percentages.

Synthesis of the (mono)sulphidic crosslink.— One of the reaction products, a monosulphidic crosslink, was synthesised to determine the exact retention time and response factor in the chromatograms. The monosulphidic crosslink of TME was synthesised by a three step synthesis. The first step was to synthesise 1-bromo-2,3-dimethyl-2-butene, Figure 4.3, via 1,4 addition of HBr to 2,3-dimethyl-1,3-butadiene. HBr was obtained by a HBr-generator: tetralin was dried with magnesium sulphate and anhydrous calcium sulphate for several hours. The filtered tetralin was distilled under reduced pressure. Bromine was added dropwise to the tetralin to generate HBr. The HBr was added to the redistilled 2,3-dimethyl-1,3-butadiene under a dry nitrogen flow for 6 hours. The exothermic reaction was cooled in an ice bath. The product was purified by distillation and analysed by $^1\text{H-NMR}$: (CDCl_3): $\delta = 1.70$ (s, 3H), 1.77 (s, 6H), 4.07 (s, 2H).

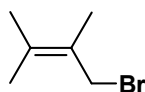


Figure 4.3 Structural formula of 1-bromo-2,3-dimethyl-2-butene

The second stage was the synthesis of 2,3-dimethyl-2-butene-1-thiol. In a nitrogen atmosphere, 26.47 g TME-Br and 15.77 g thiourea were dissolved in ethanol in a three necked flask with a condenser and an oil-lock on top. The solution was refluxed for three days. A rotavap was used to evaporate the solvent. A white solid remained which was dissolved in ultrasonically degassed distilled water together with 8.28 g NaOH. After refluxing for one hour, the product was extracted with methylene chloride, three times 50 ml. The methylene chloride was removed by rotavap distillation. The product was distilled in vacuo. The structure of the TME-SH is given in Figure 4.4. $^1\text{H-NMR}$: (CDCl_3): $\delta = 1.40$ (t, 1H), 1.66 (s, 3H), 1.72 (s, 3H), 1.80 (s, 3H), 3.18 (d, 2H).

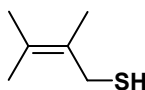


Figure 4.4 Structural formula of TME-SH

The final step was the synthesis of the monosulphidic crosslink, Figure 4.5. In a three necked flask with a condenser and an oil-lock, 0.4 g of solid sodium and 50 ml isopropylether was heated to 70 $^{\circ}\text{C}$. In 10 minutes, 2 g of TME-SH dissolved in 50

ml of diisopropylether was added dropwise. The solution was stirred for 2 hours until all sodium had reacted. After dropwise addition of 2.8 g TME-Br the solution was refluxed for 24 hours. A white suspension was obtained. The crystals were filtered out and the diisopropylether was evaporated under reduced pressure. A further purification was accomplished by vacuum distillation. The desired product was obtained as a colourless oil in quantitative yield.

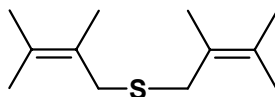


Figure 4.5 Structural formula of the monosulphidic crosslink

The product was analysed by ¹H-NMR (CDCl₃): δ = 1.73 (s, 3H), 1.75 (s, 3H), 1.80 (s, 3H), 3.20 (s, 2H). Although small impurities were detected, the major part was the desired product.

4.3 RESULTS

As an introductory study, a detailed investigation of the function of ZnO in the several stages of vulcanisation was carried out with the polyfunctional model squalene and the monofunctional model TME. The experiments with squalene were used to compare the results with literature; Borros^{10, 11} performed a similar study with squalene on the effect of the activator during the scorch and curing times. In an analogous manner, in the present study the changes in composition of the model compound samples as a function of time were studied. The development of the initial ingredients and the formation of MBT was characterised and quantified by HPLC-UV. To obtain more information about other stages of the vulcanisation, the monofunctional model TME was used. With this model compound, besides the development of the initial ingredients and the formation of MBT, the crosslinked products as well as the crosslink precursors could be characterised by HPLC at a wavelength of 254 nm.

4.3.1 Reactions in Squalene

Squalene was reacted for 5 – 60 minutes in the presence of sulphur and CBS, with and without ZnO according to the recipe given in Table 4.2. Stearic acid, used to solubilise the zinc into the rubber system, was added as well, while it might set zinc ions free to form complexes with accelerators. The vulcanisation reaction was carried out at 140°C, a representative temperature for NR vulcanisation, as chosen for the majority of MCV studies.¹²⁻¹⁵ At higher vulcanisation temperatures, e.g. 160°C, which is selected as vulcanisation temperature for many rubbers, the reactions would proceed much faster, particularly in model compound systems. In order to follow the development of the reactions more gradually, a lower reaction temperature was preferred.

The reactions were carried out for a definite time period and the reaction products analysed with HPLC. An example of a HPLC-chromatogram is given in Figure 4.6. The weight percentages for every component could be calculated via the internal standard. Based on the data for the various reaction times, the concentration development of the several components as function of reaction time could be plotted.

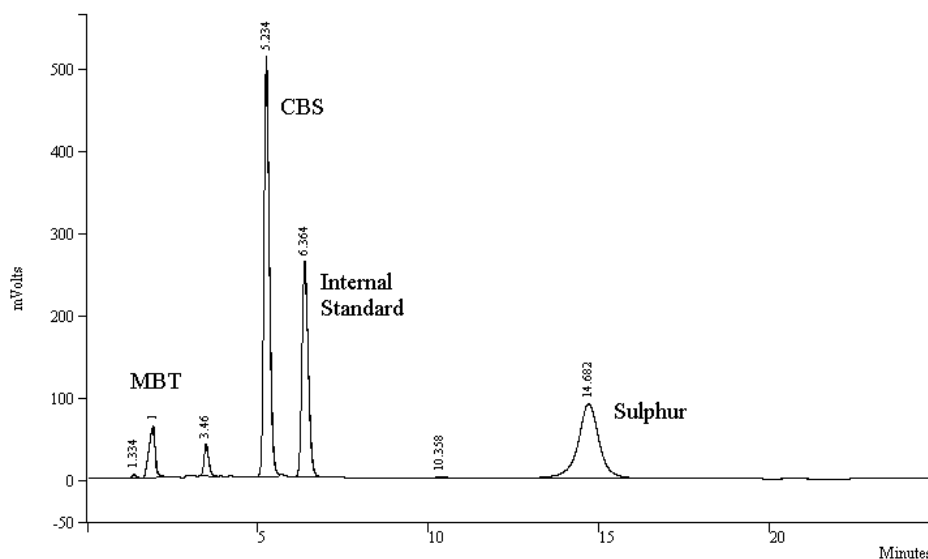


Figure 4.6 Example of a HPLC-chromatogram of the reaction products of a squalene sample without activator, after a reaction time of 25 minutes

Figure 4.7 shows the CBS concentration in the samples with (designated as ZnO) and without ZnO (designated as none) as a function of the reaction time, as analysed with HPLC-UV. Another material to be considered in the model system is elemental sulphur. The concentration development of elemental sulphur is depicted in Figure 4.8.

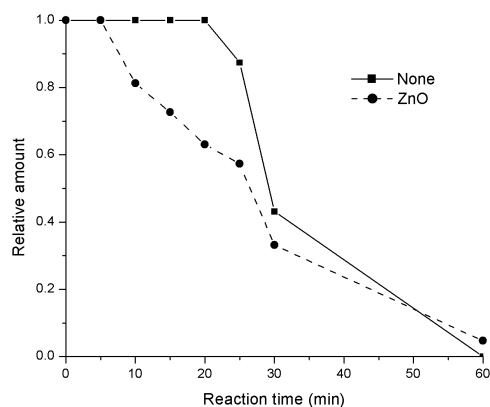


Figure 4.7 Decomposition of CBS in squalene as a function of reaction time, with and without ZnO as activator

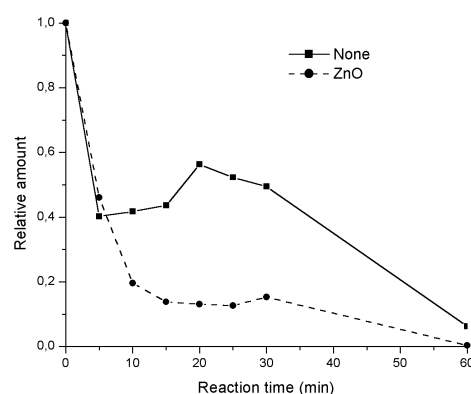


Figure 4.8 Sulphur concentration in squalene as a function of reaction time, with and without ZnO as activator

From Figure 4.7 it becomes evident, that the breakdown of the accelerator starts at shorter reaction times in the presence of ZnO. Therefore, ZnO activates the breakdown of CBS in squalene. After one hour, almost all the accelerator has been consumed in both systems. Concerning the sulphur concentration, a very fast decay is observed in the first five to ten minutes for both systems. Presumably, the sulphur is incorporated in the accelerator during the first 10 minutes to form polysulphidic species. In the presence of ZnO, however, much more sulphur is consumed in this initial stage of the reaction.

MBT is formed during the course of the reaction as decomposition product of the accelerator, or as a side product from the transformation of a crosslink precursor into a crosslink. The formation of MBT is shown in Figure 4.9. When ZnO is present in the reaction mixture, the MBT concentration remains at a low level, contrary to the case where no ZnO has been added: MBT tends to accumulate at longer reaction times. A possible explanation could be the formation of a complex between the zinc ions and MBT: ZnMBT. Although it has been proven by others, that MBTS is also formed very rapidly in the earlier stages of the vulcanisation, it reacts readily and remains at a negligible level.^{16, 17} This explains the fact that hardly any MBTS was detected in our experiments.

Unfortunately, it was very difficult to analyse the crosslinked products of the squalene samples with this HPLC-UV setup. It was found that other techniques, like Gel Permeation Chromatography, are suitable to study the crosslinking of 'high' molecular weight squalene.¹⁸ The resulting chromatograms, however, are not unequivocal and rather difficult to interpret. As mentioned earlier, in TME-model systems the crosslinked products as well as the crosslink precursors can be properly characterised. Therefore, it was decided to study the crosslinking reaction in detail in TME-model systems, rather than in squalene.

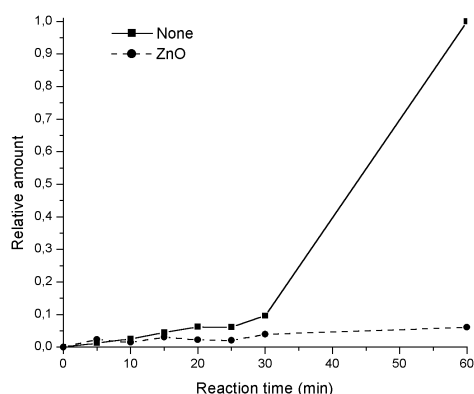


Figure 4.9 MBT concentration in squalene as a function of reaction time, with and without ZnO as activator

4.3.2 Reactions in TME

Although TME is less similar to rubbers, its simplicity, *viz.* monofunctionality and one type of allylic position, offers great advantages when studying the

vulcanisation reaction intermediates and products. With this model compound three different stages in the vulcanisation process were studied as a function of time: kinetics of curative formation and disappearance, crosslink precursor formation and disappearance, and the crosslinked products formation.

An example of a HPLC-chromatogram for a TME-model compound according to the recipe given in Table 4.2, with a vulcanisation time of 37.5 minutes is given in Figure 4.10. When the chromatograms of similar squalene and TME compounds are compared, Figure 4.6 vs. 4.10, it becomes clear that in the TME case several new peaks are appearing during the reaction period. These peaks strongly indicate the formation of reaction products.

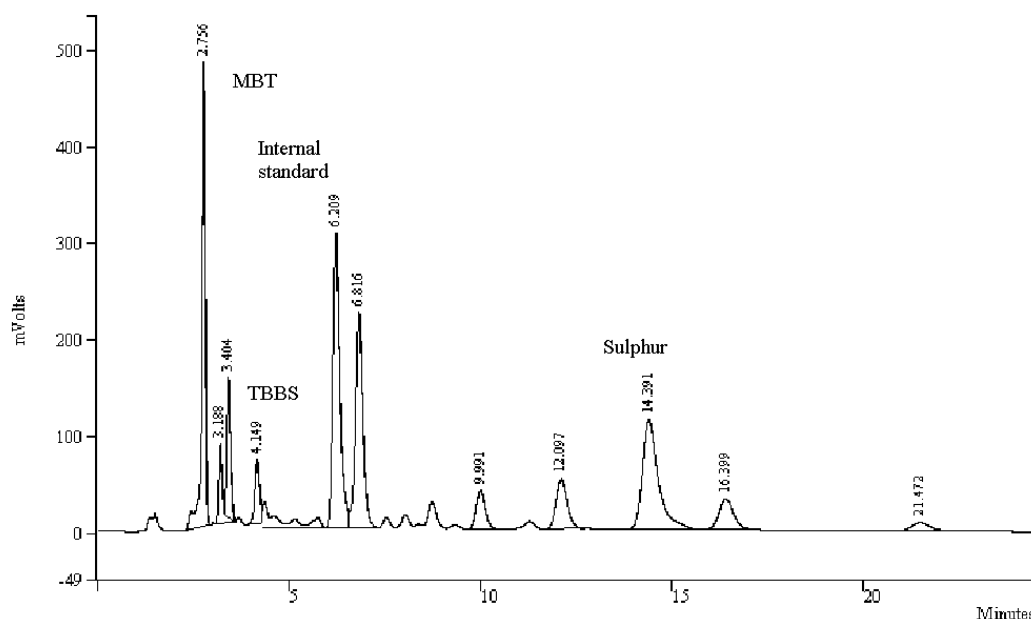


Figure 4.10 HPLC-chromatogram of a TME sample with ZnO after a reaction time of 37.5 minutes

The initial ingredients could be identified and characterised in this chromatogram. For instance, the TBBS elutes at a retention time of 4.2 minutes, the internal standard at 6.3 minutes and the sulphur at 14 minutes. Figure 4.11 and 4.12 show the decrease in amount of some of the initial vulcanisation ingredients, TBBS and sulphur respectively, for samples with and without ZnO. From Figure 4.11 it is evident that ZnO hardly has any influence on the decomposition of TBBS. In the TME samples a very fast decay of sulphur in the first five minutes is observed, comparable with the results obtained in squalene. It can clearly be seen in this figure, that the amount of sulphur remains highest in the case without ZnO relative to the sample with ZnO, at least up to about 35 minutes. Then sulphur starts to decrease very fast, till almost all the sulphur is consumed.

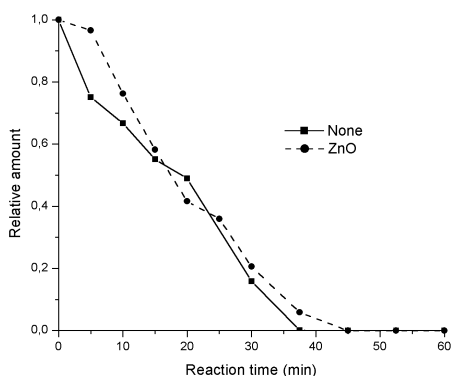


Figure 4.11 Decomposition of TBBS in TME as a function of reaction time, with and without ZnO as activator

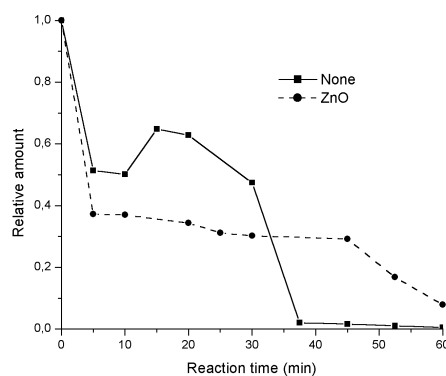


Figure 4.12 Sulphur concentration in TME as a function of reaction time, with and without ZnO as activator

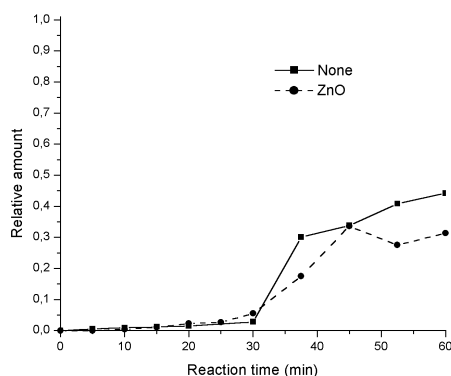


Figure 4.13 MBT concentration in TME as a function of reaction time, with and without ZnO as activator

The development of MBT with reaction time is plotted in Figure 4.13. For both systems, with and without ZnO, the formation of MBT starts around 30 minutes. A relative amount of 1 corresponds to the complete conversion of TBBS into MBT. After 40 minutes of reaction almost all the TBBS has reacted: Figure 4.11, while the relative amounts of MBT formed are only in the range of 0.2 – 0.4. This is a strong indication, that TBBS is also converted into other reaction products or intermediates. Possible reaction products which may be formed from TBBS are summarised in Figure 4.14.

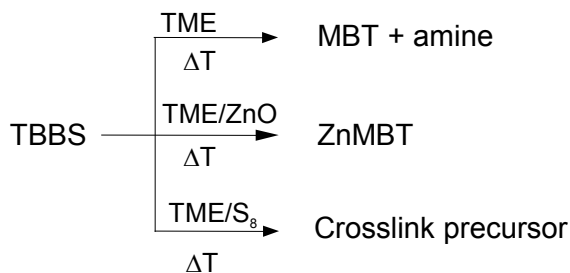


Figure 4.14 Reaction products of TBBS

As indicated in Figure 4.14, MBT may form a complex with zinc ions to form ZnMBT. ZnMBT precipitates in the reaction mixture and is therefore difficult to analyse with HPLC. In the systems without ZnO, however, this complex can not be formed. As indicated in the general scheme for sulphur vulcanisation (Figure 4.1), crosslink formation requires intermediate compounds, e.g. crosslink precursors, formed via accelerator scission prior to the crosslinked products formation. This precursors consist of the mercapto part of the accelerator, bonded to the allylic position of the model molecule via a polysulphidic bridge (rubber-S_y-acc). New peaks have appeared in Figure 4.10 at retention times of approximately 7, 10, 12 and 17 minutes. Although no direct identification of the crosslink precursor was possible, the peak that represents the crosslink precursor could be identified via the TBBS and the MBT graphs. If the relative amount of both TBBS and MBT are low, those groups can be attached to TME or formed into a complex with a zinc ion. The peak at 7 minutes clearly shows a maximum around a reaction time of 30 minutes. Furthermore, the peak at 7 minutes is the first peak appearing during the reaction. Therefore, it is logical to accept that the peak at 7 minutes represents the crosslink precursor. This is in accordance with the concept that the formation of crosslink precursors occurs before the formation of crosslinks. In Figure 4.15 the crosslink precursor development is plotted as a function of reaction time. The peak areas in the HPLC chromatograms are plotted as a function of reaction time. It is not possible to derive the relative amounts from these graphs, because the exact response factors were not known.

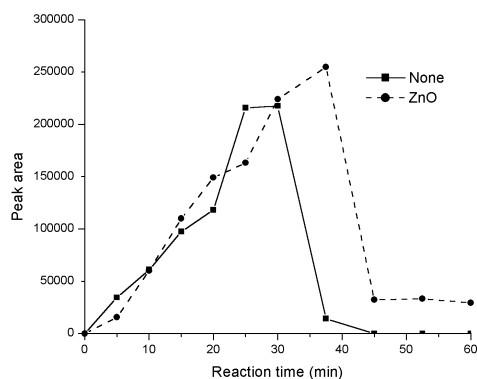


Figure 4.15 Crosslink precursor: TME-S_x-MBT, concentration as a function of reaction time, with and without ZnO as activator

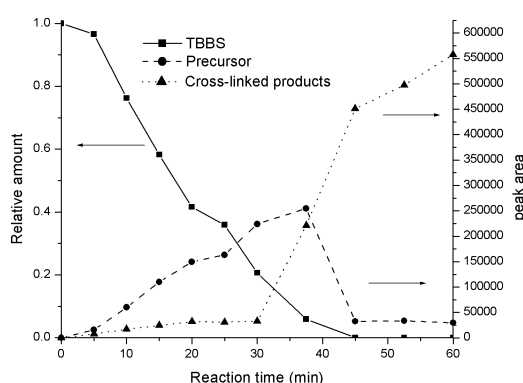


Figure 4.16 TBBS, crosslink precursor, and crosslinked products concentration as a function of reaction time with ZnO

Figure 4.15 shows no significant difference in rate of crosslink precursor formation in the two systems, which is in good agreement with the decomposition of the TBBS as summarised in Figure 4.16. A maximum concentration of crosslink precursor is observed around 30 minutes reaction time. In the samples with ZnO present, the breakdown of the crosslink precursor is delayed to some extent.

Contrary to the peak at 7 minutes, the peaks at 10, 12 and 17 minutes are most probably related to the crosslinked products. Versloot *et al.*¹⁹ have

demonstrated, that two molecules of TME react with sulphur to form a structure as shown in Figure 4.17. These crosslinked polysulphidic products are mainly formed without isomerisation, but some isomerisation might occur, leading to the formation of a product as depicted in Figure 4.18.¹²

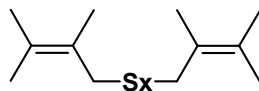


Figure 4.17 Structure of the reaction products of TME and sulphur

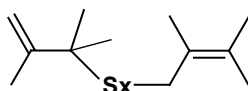


Figure 4.18 Structure of the reaction products of TME and sulphur when isomerisation takes place

The polarity of a compound in a common HPLC set-up determines the retention time in the chromatographic column. The column used in the experiments was a reverse phase column, for which the retention time is related to the non-polar part of the molecules. A higher retention time corresponds to a more non-polar molecule, e.g. a higher sulphur rank. Furthermore, Hann *et al.*²⁰ have reported a linear correlation between the sulphur rank and the logarithm of the retention time, with retention time increasing with longer sulphur bridge length. Based on this relation, even with no direct identification of the reaction products, it may be concluded that if the three peaks can be interpreted as reaction products with different sulphur chain lengths, the peak at ~17 minutes corresponds to the longest sulphur bridge.

It is interesting to analyse the peaks of the reaction products in more detail. Figures 4.19 and 4.20 show the development of three of the reaction products in time measured with HPLC. Figure 4.19 corresponds to the case without ZnO; whereas in Figure 4.20 a system with ZnO is shown. In these figures the peak areas as obtained from the chromatograms are plotted as a function of time. The different (poly)sulphidic crosslinked products cannot be compared absolutely while the response factors of these products were not all determined. Only the trends between the different systems can be compared.

It can be seen that the crosslinked products concentration increases rapidly around 30 minutes reaction, at the time the accelerator is almost completely dissociated, as was seen in Figure 4.11; respectively, the concentration of crosslink precursor started to decrease, as depicted in Figure 4.15. In both Figures 4.19 and 4.20 the reaction product with a retention time of approximately 12 minutes increases earlier and faster than the product that has a retention time of 10 minutes. The onset of the actual vulcanisation or crosslink formation is slightly delayed when ZnO is present. Furthermore, the distribution of the crosslinks is clearly influenced by ZnO. Based on literature, crosslink shortening at longer reaction times is expected.

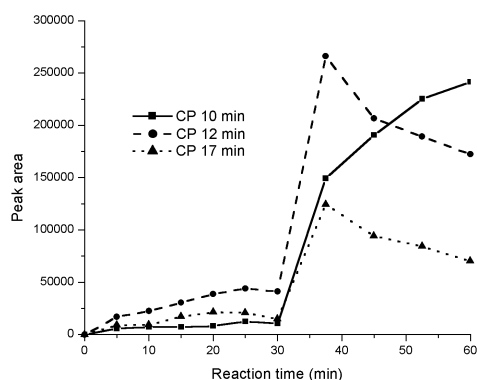


Figure 4.19 Crosslinked products development as a function of reaction time, without ZnO present

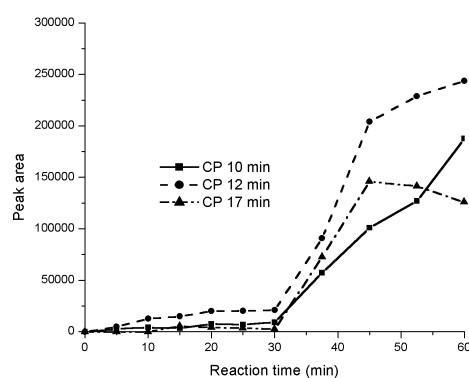


Figure 4.20 Crosslinked products development as a function of reaction time, with ZnO present

Identification of those peaks with LC-MS did not succeed to reveal the structure, mainly due to the complexity of the reaction mixture. Another approach to obtain evidence about the exact nature of crosslinked products and their position in the chromatogram, could be to inject these crosslinked products in their pure form. The monosulphidic crosslink was prepared according to the experimental procedure described in paragraph 4.2. A HPLC measurement was performed with this monosulphidic crosslinked product. The ingredients for the synthesis were injected separately in order to identify the peaks of the initial components in the chromatogram of the monosulphidic crosslink. The peak with a retention time of ~ 6 minutes represented the monosulphidic crosslink.

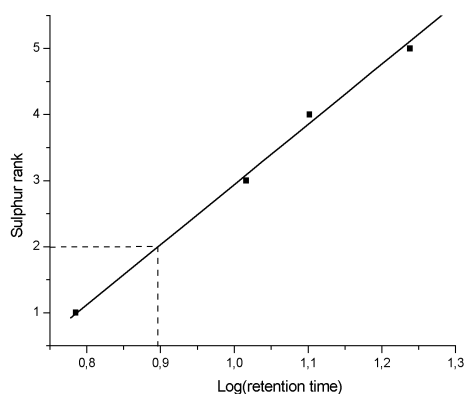


Figure 4.21 Sulphur rank vs. logarithm of retention time

The linear correlation between the sulphur rank and the logarithm of the retention time, as proposed by Hann, is graphically represented in Figure 4.21, by using the data of the unknown peaks and the synthesised monosulphidic crosslink. Based on this plot, it can be concluded that the peaks at 10, 12 and 17 minutes indeed correspond with S_{3^-} , S_{4^-} and S_{5^-} -TME-crosslinks. The disulphidic crosslink

should then be located in the chromatogram at a $\log(\text{retention time})$ of ~ 0.89 , corresponding with a retention time of 7.9 minutes. The mono- and disulphidic crosslink were not clearly observed in the reaction mixtures due to the low resolution in the chromatograms and the presence of interfering components, see e.g. Figure 4.10. Mono- and disulphidic crosslinks are generally assumed to be quite stable, although no direct indication about their stability could be obtained. The higher sulphur ranks, however, were found to be rather unstable, Figure 4.19 and 4.20, and tend to decrease, perhaps even degrade again with increasing reaction times.

4.3.3 Comparison of the MCV Studies with real Rubber Vulcanisation

It is to be noted that the results obtained so far apply to model compounds, *i.e.* squalene and TME, and that these findings may not necessarily be extrapolated to real rubbers such as EPDM and s-SBR. However, the general trend of the reactions is unlikely to be influenced by the particular allylic structures of the various rubbers involved.

As mentioned earlier, for sulphur vulcanisation of rubbers in the presence of accelerators, an activator like ZnO is an essential ingredient. It enhances the vulcanisation efficiency and vulcanisate properties and reduces vulcanisation time. The dispersion, particle size and specific surface area, which are parameters of paramount importance for the activity of ZnO in rubber compounds as discussed in the previous chapter, are much less important in model compound vulcanisation. Diffusion of the vulcanisation ingredients in these liquid model systems is much faster than in real rubbers. In addition, stearic acid was added to the model systems, because it has shown an influence on the cure characteristics in the benzothiazole accelerator system used for s-SBR, as discussed in the previous chapter. Stearic acid may set zinc ions free to form complexes with accelerators. In MCV studies stearic acid can also have an influence on the system via the pH.

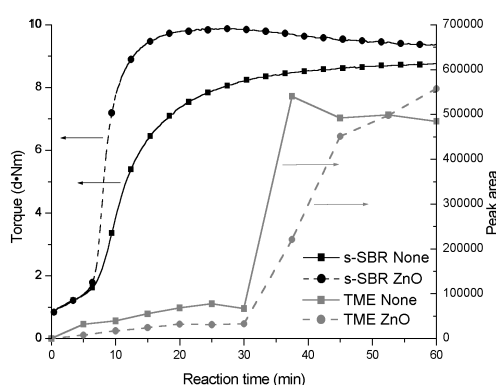


Figure 4.22 Comparison cure-torque of s-SBR compounds with total crosslinked products in MCV of TME as a function of reaction time

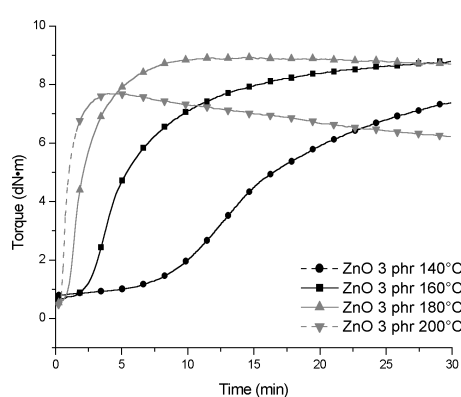


Figure 4.23 Comparison of curing characteristics at different temperatures in EPDM compounds

For MCV, the crosslinked reaction products, as evaluated with HPLC, can be added by summing all the peaks of the various sulphur chains, *i.e.* area of S_3 , + area

of S₄ etc. In Figure 4.22 the crosslink development obtained with the TME model compounds and the rheograms of s-SBR compounds, as shown before in Chapter 3, for systems with and without ZnO are combined in one graph.

At first sight, the MCV results are not at all in agreement with the s-SBR compounds, as described in Chapter 3 of this thesis. After 60 minutes of MCV the total peak area of the crosslinks in the sample with ZnO, is still increasing and reaches a higher final level than the sample without ZnO. This is in good agreement with the higher torque level observed in the s-SBR compound with ZnO present. The onset of vulcanisation, in particular, is delayed in the model compounds. This can be explained by the lower vulcanisation temperature, viz. 140°C instead of 160°C, utilised for the MCV studies. The influence of the vulcanisation temperature is illustrated with the cure behaviour of different rubber compound, viz. a standard EPDM compound, for four different temperatures, Figure 4.23. At lower temperatures the main increase in crosslinking, indicated by the increase in torque level, is clearly delayed and the vulcanisation rate decreased. The crosslink distribution might be influenced as well, as indicated by Van den Berg.^{9, 21} He studied the influence of temperature on the crosslink distribution in ENBH as a model molecule for EPDM at reaction temperatures of 120, 140, 160 and 180°C. It was found that a higher temperature leads to the formation of disulphidic bridges at the expense of higher sulphidic bridges.

4.4 DISCUSSION

An important characteristic of the vulcanisation process is the scorch delay. In literature, several reasons for scorch delay have been suggested: the thermal stability of the accelerator and, alternatively, exchange reactions between accelerator polysulphides and other reaction intermediates. The accelerator decomposes at the onset of the crosslink formation, Figure 4.16, suggesting that the cure delay period is caused by a more rapid reaction of the intermediate compounds, e.g. crosslink precursors, with the vulcanising agents rather than with the rubber hydrocarbons to yield crosslinks.

It has been reported, that MBT has a catalytic effect on the CBS decomposition.²² Other authors emphasise the role of ZnO in the decomposition of the accelerator. A third effect which has been mentioned in literature, is the influence of the presence of the model compound and the type of model molecule.¹⁰ The decomposition rate of the accelerator can be followed quite accurately via the decrease of the accelerator content in model compounds as a function of time. In squalene, CBS is broken down faster when ZnO is present. In TME, however, hardly any difference between the two systems was observed. Apparently, the role of ZnO in the decomposition of the accelerator is more pronounced in squalene, which can be due to the influence of the type of model olefin, or the fact that CBS was used instead of TBBS as with TME.

The sulphur insertion in the active sulphurating species is more difficult to evaluate because the zinc complexes are not detectable with the chosen method.

However, the sulphur content at short reaction times can be compared, while in that stage not all accelerator is consumed and complex formation is taking place for the system with ZnO. A smaller amount of sulphur for the ZnO system in comparison with the ZnO-free system can be considered as an indication that sulphur is inserted in the complex or in the accelerator. In squalene as well as in TME, the sulphur content at short reaction times is lower when ZnO is present in the samples.

It was also observed that hardly any difference is noted between the precursor developments for the ZnO-free and the ZnO-containing systems. Apparently, ZnO does not accelerate the reactions that occur before the actual crosslinking in the TME model compound. The rate of decomposition of the crosslink precursor is not lower but occurs at longer reaction times. The delay in decomposition might be caused by the interaction of zinc with the precursor, as earlier proposed by Coran, Figure 4.24.

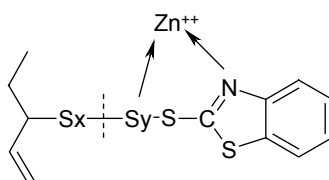


Figure 4.24 Interaction of zinc with the crosslink precursor²³

For the TME-model compounds the reaction products could also be monitored. It seemed that the actual crosslinking proceeds somewhat slower if ZnO is present. From the results for the ZnO-free and the ZnO systems, it can be concluded that ZnO favours the formation of crosslinks with a higher sulphur rank. The samples without ZnO produce a relatively large amount of shorter crosslinks. This seems to be in contrast with several studies that lead to the conclusion that crosslinks contain less sulphur atoms when ZnO is used.

Although the several steps in the vulcanisation reactions could be studied in detail by MCV, the results are not at all in agreement with the s-SBR rubber compounds. The effect of temperature has been mentioned already as an explanation for the difference in cure delay. Another fundamental difference between the model and the rubber, which plays an important role in this complex interplay of reactions, is the number of end-groups. The end-groups have a $-\text{CH}_3$ -configuration and in a macromolecular molecule $-\text{CH}_2$ forms the major reactive group. The position and configuration of the double bond are also important aspects. In the previous chapter s-SBR was used as the main polymer, for which the polybutadiene moiety consists for 25% out of the vinyl-configuration. A model which represents the vinyl-configuration very well is 3-methyl-1-pentene. Versloot *et al.*¹⁹ have already shown, that 3-methyl-1-pentene is more reactive towards elemental sulphur than TME. The higher reactivity of the vinyl-configuration, present in s-SBR, can also partly explain the observed delay in cure in the TME-model experiments.

The experimental studies reported in the current chapter have provided mechanistic insight concerning ZnO activated vulcanisation, albeit without complete conclusive evidence. However, the effects of ZnO in the different stages of

vulcanisation could be identified and an experimental base is laid for further investigations and development of activators.

4.5 CONCLUSIONS

The variety of aspects involved in sulphur vulcanisation remains an intriguing issue. As may be inferred from the above discussion, MCV, traditionally invoked as a technique to elucidate reaction mechanisms in real rubbers, does not always provide clear evidence. Many intermediates and products are formed with sulphur chemistry. Separation of all products formed and subsequent analysis is an extensive task and virtually impossible. Due to this complexity it is hardly possible to analyse the reaction steps under general conditions, applicable for all types of rubbers and vulcanisation systems. Therefore, the current conclusions can only be applied to the sulphur vulcanisation using benzothiazolesulphenamide accelerator type.

The several reactions steps could be studied in detail via MCV studies with squalene and TME as model compounds. In the squalene/CBS system the different effects were more pronounced than in TME/TBBS. The rapid decrease of the sulphur concentration in the first 5 – 10 minutes was assumed to be caused by incorporation in the active sulphurating species. In the presence of ZnO much more sulphur was consumed in this initial stage of the reaction. The MBT concentration remained at a low level when ZnO was present in the reaction mixture, caused by the formation of a complex between the zinc ions and MBT (ZnMBT). Although no conclusive evidence was obtained about the model-bound crosslink precursor, it can be stated that ZnO caused a slight delay in the disappearance of the crosslink precursor. The onset of the crosslinking reactions only started when the accelerator was almost completely dissociated and the concentration of the crosslink precursor started to decrease. At long reaction times, especially in the absence of ZnO, the sulphur bridges were shortening due to reversion reactions.

In contrast to the squalene experiments, in the TME experiments ZnO hardly had any influence on the several reactions rate constants. The role of ZnO, usually described as a catalyst for the vulcanisation, in particular for the decomposition of the accelerator, apparently depends on the type of accelerator and the type of model olefin. Overall, the results proved again the stunning versatility by which zinc or zinc compounds influence the different stages of the vulcanisation process.

4.6 REFERENCES

1. N.J. Morrison, M. Porter, *Rubber Chem. Technol.*, **57**, (1984), 63.
2. M.R. Kresja, J.L. Koenig, "*The nature of sulfur vulcanisation*", in *Elastomer Technology Handbook*, CRC press, New Jersey (1993), 475.
3. L. Bateman, *The Chemistry and Physics of Rubber-like Substances*, MacLaren, London (1963).
4. M. Porter, *The Chemistry of Sulfides*, A.V. Tobolsky, Ed., John Wiley & Sons, New York (1968).
5. R.W. Layer, *Rubber Chem. Technol.*, **66**, (1993), 510.
6. P.J. Nieuwenhuizen, Thesis, University of Leiden, (1998).
7. M. Geysler, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 431.
8. A.A. Watson, Thesis, University of London, (1965).
9. J.H.M. v.d. Berg, E.F.J. Duynstee, P.J.D. Maas, *Rubber Chem. Technol.*, **57**, (1984), 265.
10. S. Borros, N. Agullo, *Kautsch. Gummi Kunstst.*, **53**, (2000), 131.
11. S. Borros, E. Garreta, "*The role of the zinc oxide in the different steps of the vulcanisation process of natural rubber, using a sulfenamide accelerator (CBS)*", Institut Quimic de Sarria-Universitat Ramon Llull: Barcelona (1999), 55.
12. P. Versloot, *Rubber Chem. Technol.*, **65**, (1992), 343.
13. E. Garreta, N. Agullo, S. Borros, *Kautsch. Gummi Kunstst.*, **55**, (2002), 82.
14. P. Versloot, *Rubber Chem. Technol.*, **67**, (1994), 263.
15. M. Shumane, M.H.S. Gradwell, W.J. McGill, *J. Appl. Polym. Sci.*, **82**, (2001), 3074.
16. A. Mosch, presented at the DIK Kautschuk-Herbst-Kolloquium, Hannover, Germany November 2002.
17. A. Mosch, U. Giese, R.H. Schuster, *Kautsch. Gummi Kunstst.*, **56**, (2003), 184.
18. S. Rodriguez, *Kautsch. Gummi Kunstst.*, **52**, (1999), 438.
19. P. Versloot, *Rubber Chem. Technol.*, **70**, (1997), 106.
20. C.J. Hann, *Rubber Chem. Technol.*, **67**, (1994), 76.
21. J.H.M. v.d. Berg, E.F.J. Duynstee, P.J.D. Maas, *Rubber Chem. Technol.*, **57**, (1984), 725.
22. J.L. Craine, M. Raban, *Rubber Chem. Technol.*, **62**, (1989), 67.
23. A.Y. Coran, *Science and Technology of Rubber*, Academic Press, San Diego (1994).

Effect of Zinc Complexes as Activator for Sulphur Vulcanisation in Various Rubbers[#]

'We can have facts without thinking but we cannot have thinking without facts.'
John Dewey (1859 – 1952)

Because of environmental concerns, the zinc content in rubber compounds has come under scrutiny; therefore it is necessary to explore possibilities to reduce this zinc content. In this chapter the application of several zinc complexes as activator for sulphur vulcanisation is discussed, in order to find alternatives for the conventionally used ZnO and fatty acid activator system. The effects of different zinc complexes on the cure and physical properties of two widely different rubbers, *viz.* EPDM and s-SBR, are studied.

It can be concluded that zinc-m-glycerolate is a good substitute for ZnO as activator for sulphur vulcanisation, in EPDM as well as in s-SBR rubber, without detrimental effects on the cure and physical properties. Furthermore, the results indicate that, dependent on the intended applications, zinc-2-ethylhexanoate represents a substitute for the commonly used ZnO. Zinc stearate is considerably less active as activator in sulphur vulcanisation.

Additionally, Model Compound Vulcanisation studies with squalene and TME as model compounds are performed to investigate the influence of zinc complexes in the different stages of vulcanisation. With zinc-m-glycerolate present as activator, a higher crosslinked products yield is obtained, in accordance with the higher extent of cure and the ultimate properties observed in s-SBR compounds.

[#]Part of this work has been presented at the International Rubber Conference '02, July 01 – 04, in Prague (CZ); this chapter has been submitted for publication in Rubber Chemistry and Technology.

5.1 INTRODUCTION

As described in previous chapters, the zinc content in rubber products has come under increased scrutiny due to environmental concerns. The trend in rubber industry is therefore to reduce or even completely eliminate the zinc content, although to date no viable alternative for ZnO and zinc-containing species for vulcanisation purposes has been found. Also zinc-containing processing additives, e.g. zinc soaps of fatty acids, have not been matched in their improvement of processing properties, although recently a promising new zinc-free processing additive has been introduced.¹

There is general agreement, that zinc cations from ZnO and/or zinc compounds react with organic accelerators to give active zinc-accelerator complexes, which is one of the main steps in the vulcanisation scheme.² The complexes interact with sulphur, a sulphur donor and other activators to generate the active sulphurating agent. It has been suggested in many different studies that these active complexes of Zn²⁺-ions with accelerators are more reactive than the free accelerator.^{3, 4} This active sulphurating agent reacts at the allylic sites of the rubber polymer unsaturations to form a rubber bound intermediate, which reacts with another rubber bound intermediate or with another polymer chain to generate a crosslink. The exact activator role of ZnO is highly dependent on the type of accelerator present in the initial vulcanisation system.

The acceleration system often needs some proportion of fatty acid for cure activation. In general, fatty acids as co-activators in rubber vulcanisation increase the crosslink yield.⁵ As mentioned earlier, it is assumed that stearic acid reacts with ZnO to form zinc stearate, which is an essential cure activator. Its function has been the subject of extensive research by Kruger and McGill.⁶ The formation of zinc stearate from ZnO and stearic acid initiates already during compounding of the rubber. It is shown in ethylidene norbornane (ENBH) model compound vulcanisation (MCV) that a mix of ZnO and stearic acid is as effective as cure activator as pure zinc stearate. In some MCV studies the addition of stearic acid appeared to have no influence at all,⁷ but in real rubber compounds the solubilising effect of fatty acids for the various zinc species might be more relevant. In addition to the solubilisation of ZnO, these weak fatty acids can neutralise thiophilic reaction products like amines and HS⁻.⁸

In order to increase the activity of ZnO and thereby reduce the necessary amount, the availability of Zn²⁺-ions should be increased. In principle, all the zinc ions trapped in the ZnO crystal are wasted since it only functions as an expensive reinforcing filler. A reduction of the amount of ZnO needed in rubber formulations could then be realised when the accelerators, stearic acid, and the ZnO interact and form complexes before they are added to the rubber matrix.⁹

In this chapter the possibilities to reduce ZnO by incorporating more chemically active zinc in the form of reactive complexes will be investigated. It is anticipated that via zinc complexes a better dispersion of zinc into the system is achieved and a higher percentage of the zinc ions is free to form active accelerator complexes. In earlier work, described in Chapter 3 of this thesis, it was shown that the amount of conventional ZnO (Red Seal) could be reduced by optimisation to 1

and 2 phr for s-SBR and EPDM, respectively, retaining the curing and physical properties of the rubber products. In the present study, however, the main goal was to investigate the applicability of zinc complexes as activator for sulphur vulcanisation and therefore higher levels of zinc are included.

The first part of this chapter describes the effect of different zinc complexes on the cure and physical properties of EPDM and s-SBR rubbers. The second part is dedicated to the role of zinc complexes in different stages of the vulcanisation, studied by MCV in order to provide some insight in the underlying chemical mechanisms.

5.2 PRIOR LITERATURE ON THE ROLE OF ZINC COMPLEXES

Kruger and McGill⁶ have performed DSC analytical studies on the interactions of sulphur with ZnO and stearic acid. Their results indicated the formation of zinc stearate and its subsequent reaction with sulphur. The sulphur-zinc stearate interaction helps to explain the activating role of ZnO in sulphur vulcanisation. Fatty acids, like stearic acid, are used in addition to solubilise the zinc into the system and set zinc ions free to form complexes with accelerators.³

Just as with amines, carboxylates like stearic acid and zinc stearate are thought to coordinate with zinc dialkyldithiocarbamates, formed during thiuram-accelerated vulcanisation, resulting in increased solubility¹⁰ and also increased nucleophilicity of the zinc-sulphur bond and therefore enhanced reactivity. Kruger¹¹ observed no major differences in formation of dithiocarbamic acid in thiuram-accelerated vulcanisation when ZnO was substituted for zinc stearate, and concluded that ZnO and zinc stearate perform in a similar way. Dithiocarbamic acid can decompose in the corresponding secondary amine and CS₂. Kelm¹² found a significant decrease in the formation of amines in the presence of zinc stearate as compared to stearic acid and ZnO. It was suggested that this effect is due to a better dispersion of zinc species, which react with dithiocarbamic acid, thereby preventing decomposition.

The vulcanisation rate of a rubber compound is mainly influenced by the type of accelerator used, whereas the reaction by-products formed are determined by the absence or presence of zinc complexes. Desulphuration of prior formed crosslinks is effected by zinc complexes.¹³ It gives rise to crosslink shortening. The sulphur removed may yield additional crosslinks. Desulphuration is favoured by moderate vulcanisation temperatures and high concentrations of zinc-accelerator complexes. Morrison and Porter¹⁴ reported that zinc stearate inhibits zinc-promoted decomposition of monosulphidic crosslinks, though the mechanism is still unclear.

Four zinc complexes, currently used in the rubber technology, some for purposes other than activation of vulcanisation, are selected to study in detail as activator of cure: zinc stearate, zinc-2-ethylhexanoate, zinc borate and zinc-m-glycerolate.

Zinc soaps are the oldest of processing additives. They can greatly improve the processing properties for NR and synthetic rubbers, for example SBR and BR. Zinc stearate is commonly added as a zinc-containing processing additive. Zinc-2-ethylhexanoate is a rubber-soluble zinc soap sometimes used as an activator for NR. It is used instead of stearic acid and reduces stress relaxation and primary creep of NR-vulcanisates, especially in combination with EV-systems.

Zinc borate is a white, nontoxic, fine powder, extensively used in plastics, rubber, paints, ceramics, etc., especially used as flame retardant and after-glow suppressant. It is used successfully as an ingredient in flame retardant formulations containing halogens. In such formulations it is used either alone or in combination with antimony trioxide. It is used in many formulations to replace 30 – 60% of the antimony trioxide. Zinc borate·7H₂O dehydrates at about 160°C. The water of crystallisation in zinc borate·3.5H₂O is retained even till 260°C. Therefore, it can be used in processing at higher temperature. Zinc borate is regularly used for radial tyres.

Morche *et al.*¹⁵ found that an ester/alcohol combination was superior to stearic acid as processing promoter, but not for vulcanisation activation purposes. Zinc-m-glycerolate is glycerol (1,2,3-propanetriol) with one Zn²⁺-ion. Zinc-m-glycerolate has cosmetic and pharmaceutical as well as industrial applications, e.g. as a UV-shielding material and bonding agent in rubbers and plastics.

Table 5.1 Zinc containing activators

zinc stearate	$\text{H}_3\text{C}-(\text{CH}_2)_{16}-\text{C}\begin{matrix} \text{O} \\ \parallel \\ \text{O}^- \end{matrix} \quad \text{Zn}^{2+} \quad \text{O}^- \begin{matrix} \text{O} \\ \parallel \\ \text{C} \end{matrix} -(\text{CH}_2)_{16}-\text{CH}_3$
zinc-2-ethylhexanoate	$\begin{matrix} \text{H}_3\text{C} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}\begin{matrix} \text{O} \\ \parallel \\ \text{O}^- \end{matrix} \end{matrix} \quad \text{Zn}^{2+} \quad \begin{matrix} \text{O}^- \\ \parallel \\ \text{C} \end{matrix} -\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)-\text{CH}_2-\text{CH}_3$
zinc borate	$2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$
zinc-m-glycerolate	$\begin{matrix} \text{O}^- & & \text{Zn}^{2+} \\ & & \\ \text{O} & \text{---} & \text{O}^- \\ & & \\ \text{OH} & & \end{matrix}$

The four previously described zinc containing activators are listed in Table 5.1. The alternative types of zinc containing activators are different concerning the availability of the Zn²⁺-ions. The availability depends on the number of Zn²⁺-ions, the structure of the activator and the bond strength of the Zn²⁺-ions in the particular environment.

5.3 EXPERIMENTAL SECTION

Materials.— Solution butadiene-styrene rubber (Buna VSL 2525-0 M) was obtained from Bayer GmbH, Germany. Buna VSL 2525-0 M contains 25 wt % of 1,2-vinyl-butadiene and 25 wt % of styrene; it has a Mooney viscosity, ML (1+4) @ 100°C of 54. Ethylidene norbornene (ENB)-containing EPDM rubber (Keltan 4802) was obtained from DSM Elastomers B.V., the Netherlands. Keltan 4802 contains 52 wt % of ethylene units and 4.3 wt % of ENB; it has a relatively narrow molecular weight distribution and a typical Mooney viscosity, ML (1+4) @ 125°C of 77. The type of fillers used were: carbon black N-375 HAF, N-550 FEF and N-762 SRF (Cabot B.V.). Aromatic oil (Enerflex 75) was obtained from BP Oil Europe, paraffinic oil (Sunpar 2280) from Sun Petroleum Products Co., and stearic acid from J.T. Baker. Commercially available ZnO Red Seal (Grillo GmbH), zinc stearate (Aldrich), zinc-2-ethylhexanoate (Struktol ZEH, Schill + Seilacher AG) and zinc borate (Charmax ZB, Polymer Additives Group) were used as received. Sulphur (J.T. Baker) and N-tert-butyl-2-benzothiazolesulphenamide (Santocure TBBS, Flexsys B.V.), 2-Mercaptobenzothiazole (Perkacit MBT, Flexsys B.V.), and Tetramethylthiuram disulphide (Perkacit TMTD, Flexsys B.V.) were also commercial grades and used as such. The materials used in the model compound experiments are listed in Table 5.2.

Table 5.2 Materials used for model compound vulcanisation

Material	Source
Squalene	Merck
2,3-dimethyl-2-butene (TME)	Aldrich
TBBS	Flexsys
Sulphur	Merck
ZnO pure	Merck
Zinc stearate	Aldrich
Zinc-m-glycerolate	Lab sample (see below)
Stearic Acid	Merck

Synthesis of zinc-m-glycerolate.¹⁶— To synthesise zinc-m-glycerolate, glycerol (150 g), ZnO (25 g) and zinc acetate (2 g) were mixed for approximately 15 minutes to obtain a uniform slurry. The mixture was then heated to 105°C for 90 minutes under vigorous stirring. After cooling to approximately 40°C, isopropanol (75 g) was added and the slurry was mixed for 15 minutes before it was centrifuged. The washing and centrifuging procedure was repeated three times. The final centrifuge residue was dried in a hot air oven at 80°C for 8 hours. A white powder was obtained in good yield. The powder was confirmed to be zinc-m-glycerolate by both elemental analysis and IR spectroscopy and was substantially free of glycerol.

Rubber mixing.— Two masterbatches, *viz.* EPDM and s-SBR, were prepared in an internal mixer (~50 kg) in order to get a homogeneous mixture and to minimise the influence of mixing conditions. The vulcanisation systems were added in a

separate operation, on a two roll mill at 50°C. The compounds were sheeted off at a thickness of approximately 2 mm which was convenient for the subsequent preparation of test specimens. The compositions of the EPDM and s-SBR compounds with the various activators are given in Tables 5.3 and 5.4, respectively.

Table 5.3 Composition of the EPDM compounds (phr) with different activators

Compound	E1	E2	E3	E4	E5
EPDM (Keltan 4802)	100	100	100	100	100
Carbon Black (N550 FEF)	70	70	70	70	70
Carbon Black (N762 SRF)	40	40	40	40	40
Paraf. Oil (Sunpar 2280)	70	70	70	70	70
Stearic Acid	1	-	-	0.5	1
ZnO	3	-	-	0.5	-
Zinc stearate	-	10	20	6.11	-
Zinc-m-glycerolate	-	-	-	-	6
Accelerator (TMTD)	1.0	1.0	1.0	1.0	1.0
Accelerator (MBT)	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5

Table 5.4 Composition of the s-SBR compounds (phr) with different activators

Compound	S1	S2	S3	S4	S5	S6	S7	S8	S9
s-SBR (Buna VSL 2525)	100	100	100	100	100	100	100	100	100
Carbon Black (N375 HAF)	50	50	50	50	50	50	50	50	50
Arom. Oil (Enerflex 75)	5	5	5	5	5	5	5	5	5
Stearic Acid	2	-	2	-	-	0.33	-	2	2
ZnO	0.5	3	3	-	-	0.5	-	-	-
Zinc stearate	-	-	-	10	20	6.11	-	-	-
Zinc-m-glycerolate	-	-	-	-	-	-	6	-	-
Zinc-2-ethylhexanoate	-	-	-	-	-	-	-	4	-
Zinc borate	-	-	-	-	-	-	-	-	4.75
Accelerator (TBBS)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75

Curing.— The cure characteristics of the different compounds were measured at 160°C with a Rubber Process Analyser RPA2000 (Alpha Technologies), a type of moving die rheometer. The optimal vulcanisation time (t_{90}) and scorch time (t_{02}) of the compounds were determined. The compounds were cured in a Wickert laboratory press WLP 1600/5*4/3 at 160°C and 100 bar, according to the t_{90} of the specific compounds.

Characterisation.— Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Ageing of the test specimens was carried out in a ventilated oven in the presence of air at 100°C for 3 days according to ISO 188. Tear strength was measured with trouser shaped specimens according to ISO 34. Compression set (CS) tests were performed at 23°C and 100°C for 72 hours according to DIN 53517. Hardness of the samples was measured with a Zwick Hardness-meter Shore A Type, according to DIN 53505.

Swelling measurements were performed in order to obtain information about the crosslink density. The unextracted filled s-SBR samples were swollen until constant weight in toluene at room temperature. The EPDM samples were swollen in decahydronaphthalene at room temperature as well. The crosslink density was calculated according to the Flory-Rehner equation.^{5, 17} Although this equation as such is only valid for non-filled systems, the data obtained with these measurements do yet give an indication of the relative crosslink densities. The Flory-Huggins parameter χ for s-SBR-toluene networks was taken from literature: 0.21.¹⁸ For swollen EPDM-decahydronaphthalene networks the χ -parameter was calculated via the relationship $\chi = 0.121 + 0.278 * v_2$, reported by Dikland,¹⁹ with v_2 = the polymer network volume fraction at equilibrium swelling.

Table 5.5 Squalene model compound systems

	None		ZnO		Zinc stearate		Zinc-m-glycerolate	
	phr	mmole	phr	mmole	phr	mmole	phr	mmole
Squalene	100	1.217	100	1.217	100	1.217	100	1.217
CBS	1.2	0.023	1.2	0.023	1.2	0.023	1.2	0.023
Sulphur	2	0.039	2	0.039	2	0.039	2	0.039
Activator	-	-	5	0.307	10	0.068	5	0.199
Stearic Acid	2	0.035	2	0.035	2	0.035	2	0.035

Table 5.6 TME model compound systems

	None		ZnO		Zinc stearate		Zinc-m-glycerolate	
	phr	mmole	phr	mmole	phr	mmole	phr	mmole
TME	100	5.941	100	5.941	100	5.941	100	5.941
TBBS	1.5	0.025	1.5	0.025	1.5	0.025	1.5	0.025
Sulphur	1.75	0.034	1.75	0.034	1.75	0.034	1.75	0.034
Activator	-	-	5	0.307	10	0.068	5	0.199
Stearic Acid	2	0.035	2	0.035	2	0.035	2	0.035

Model compound vulcanisation.— Three zinc containing activators were studied with Model Compound Vulcanisation, *viz.* ZnO, zinc stearate and zinc-m-glycerolate, in two different model compounds: squalene and TME. Preparation of the samples and analysis of the reaction products were done according to the procedure described in Chapter 4. After obtaining the HPLC chromatogram of the reaction products, the areas of the different peaks were determined and converted into concentrations by using the measured response factors for the several

components. Reaction conversions as a function of reaction time were calculated by dividing the concentration of the component by the initial concentration, and expressed in percentages. The compositions of the squalene and TME reaction mixtures are listed in Tables 5.5 and 5.6, respectively.

5.4 RESULTS AND DISCUSSION I: RUBBER COMPOUNDS

The efficiency of the zinc complexes as compared to the conventional ZnO/stearic acid activator system has been studied in EPDM and s-SBR rubber, according to the recipes in Tables 5.3 and 5.4, respectively. The actual zinc contents and applied amounts of the various activators are listed in Table 5.7. The 10 phr of zinc stearate in recipe E2 and S4, and 4 phr of zinc-2-ethylhexanoate in recipe S8 correspond to a molar amount of Zn^{2+} -ions comparable with approximately 1 phr of ZnO. Zinc stearate and zinc-2-ethylhexanoate are very voluminous and, from a mixing point of view it is rather troublesome to add larger amounts. The molar amount of Zn^{2+} -ions in 6 phr of zinc-m-glycerolate is considerably higher, corresponding to approximately 3 phr of ZnO.

Table 5.7 Zinc content of applied zinc complexes in rubber compounds

Activator	Zn^{2+} -ions [mmole/g]	Amount of Act. [phr]	Zn^{2+} in comp [mmole/100g s-SBR]
ZnO	12.3	3	37
Zinc stearate	1.6	10	16
Zinc-2-ethylhexanoate	2.9	4	12
Zinc borate	4.0	4.75	19
Zinc-m-glycerolate	6.5	6	39

5.4.1 Zinc Complexes as Activators in EPDM Compounds

The cure characteristics of EPDM compounds E2 with zinc stearate and E5 with zinc-m-glycerolate as activator are plotted in Figure 5.1 in comparison with the ZnO/stearic acid reference compound E1. The corresponding results of swelling experiments are presented in Figure 5.2.

It can be seen that with zinc stearate present the state of cure is much lower compared to the compound containing ZnO and stearic acid as separate components. Explanations for this reduction could be threefold: the lower efficiency of zinc stearate as activator; or a plasticising effect due to the higher stearate content compared to the conventional system; or a lower zinc content with 10 phr of zinc stearate, corresponding with approximately 1 phr of ZnO. In order to clarify this, the crosslink density in the vulcanisates was determined by swelling measurements. From Figure 5.2 it is evident that the crosslink density is considerably lower for the zinc stearate, indicating that the lower state of cure is not caused by a plasticising effect of zinc stearate, but indeed by a lower activity towards vulcanisation. An

increase in the level of zinc stearate and thereby the amount of Zn^{2+} -ions, recipes E2 and E3 as depicted in Figure 5.3, adversely effects the rate and extent of cure. To study a synergistic effect of ZnO and zinc stearate, compound E4 with 0.5 phr ZnO in combination with 6.1 phr zinc stearate was prepared. The molar amount of Zn^{2+} -ions of these two activators together is comparable with 1 phr of conventional ZnO. The obtained results indicate similar cure characteristics to the case with only zinc stearate (10 phr) as activator present.

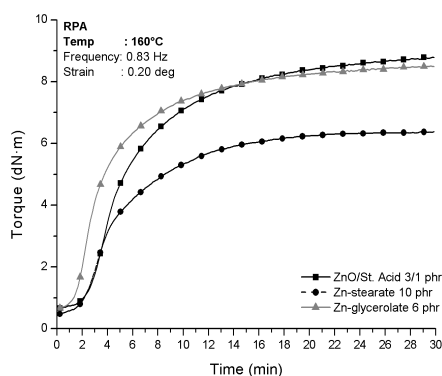


Figure 5.1 Cure characteristics of EPDM compounds E1, E2 and E5 with different zinc complexes as activator

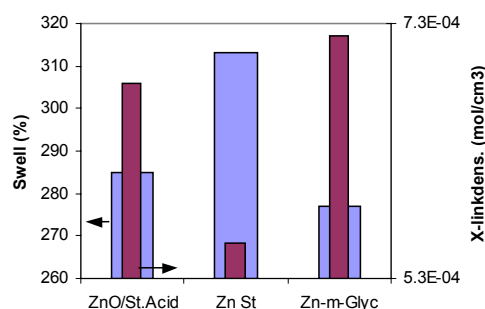


Figure 5.2 Swelling and crosslink density of EPDM compounds with different zinc complexes as activator

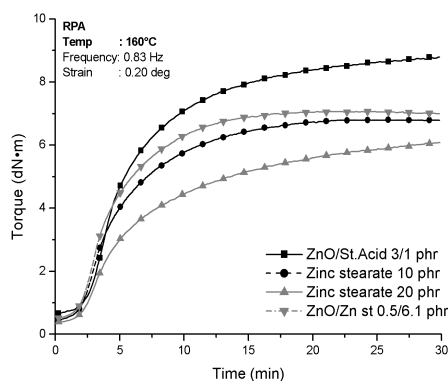


Figure 5.3 Cure characteristics of EPDM compounds E1 – E4 with zinc stearate as activator

While a considerably lower torque level was observed for the compounds with zinc stearate, with zinc-m-glycerolate, compound E5, a more positive effect is found: a grossly comparable rate and extent of cure albeit with a slightly shorter scorch delay. These observations are confirmed by the swelling experiments.

The physical properties of some relevant EPDM compounds with zinc complexes as activators are presented in Table 5.8. In accordance with the observed crosslink densities, the data in Table 5.8 demonstrates that zinc-m-glycerolate results in the best vulcanisate properties, comparable to the ZnO reference compound and

therefore can be considered as a good activator for sulphur vulcanisation of EPDM rubber. The value for elongation at break after 168 hours ageing at 100°C is even considerably higher as compared to the ZnO reference system, suggesting a major improvement in thermal behaviour due to the presence of zinc-m-glycerolate. With zinc stearate a lower cure rate and delta torque is reached than for the conventional ZnO system, which is also reflected in the vulcanisate properties.

Table 5.8 Properties of EPDM compounds with different zinc complexes

Compound	E1	E2	E5
Tensile strength (MPa)	13.3	12.3	13.8
Elongation at Break (%)	450	540	390
Tear strength (N/mm)	37	65	37
CS 72h/23°C (%)	6	16	6
CS 72h/100°C (%)	37	48	38
After 168 Hours / 100°C ageing:			
Tensile strength (MPa)	11.6	12.3	14.4
Elongation at Break (%)	180	249	313

The differences in activity of these zinc complexes might be related to the stability of the zinc complexes. In the more stable complexes the zinc-ions have a reduced availability and therefore a lower tendency to form intermediate active sulphurating vulcanisation compounds: the zinc-accelerator complexes.

5.4.2 Zinc Complexes as Activator in s-SBR Compounds

Having established the effect of zinc complexes in thiuram-accelerated sulphur vulcanisation of EPDM, next the activity of these complexes in benzothiazole-accelerated vulcanisation of s-SBR has been tested. In addition to the zinc complexes used in EPDM, for s-SBR also tests with zinc-2-ethylhexanoate as activator were performed. The cure developments of the compounds with zinc stearate are combined in Figure 5.4, while in Figure 5.5 the results of the swelling experiments are given.

The shape of the rheometer curve of a zinc stearate containing s-SBR compound differs significantly from conventional ZnO activated compounds, as earlier observed in EPDM compounds. Application of zinc stearate 10 phr results in a rather underdeveloped network, which is confirmed by the results of the swelling experiments. A higher amount of zinc stearate, compound S5 with 20 phr, affects the extent of cure as well as the crosslink density even more adversely. Addition of both ZnO and zinc stearate as activators in compound S6 is not advantageous either: a lower extent of crosslinking as compared with only ZnO as activator, implying that no synergistic effect of ZnO and zinc stearate is observed. The cure characteristics and swelling data of the compounds with the other zinc complexes are given in Figures 5.6 and 5.7, respectively.

From the curing properties it can be seen that zinc-2-ethylhexanoate leads to an increase in scorch time and a lower extent of crosslinking as compared to ZnO. With zinc-m-glycerolate present as activator the opposite effect is observed: a considerably higher crosslink density compared to the reference compound, but with a shorter scorch delay. Zinc borate demonstrates curing characteristics grossly comparable with the reference compound containing ZnO and stearic acid.

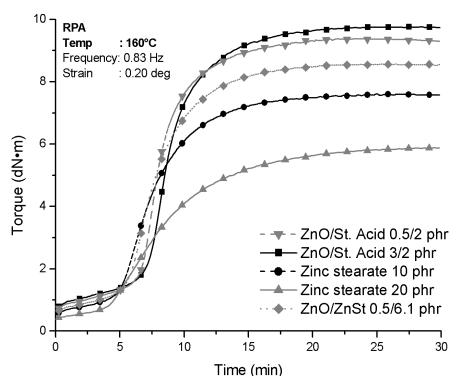


Figure 5.4 Cure characteristics of s-SBR compounds S1 and S3 – S6 with zinc stearate as activator

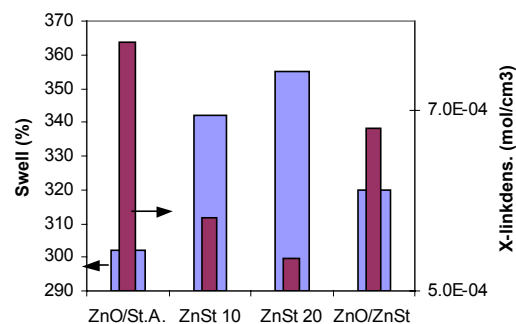


Figure 5.5 Swelling and crosslink density of s-SBR compounds S3 – S6 with zinc stearate as activator

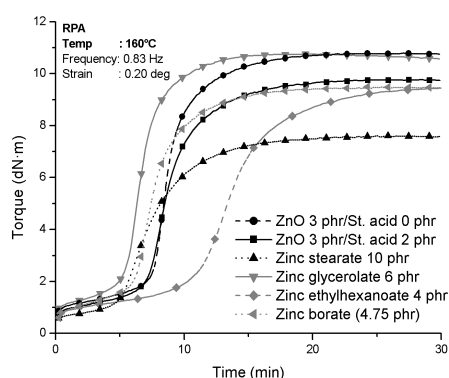


Figure 5.6 Cure characteristics of s-SBR compounds S2 – S4 and S7 – S9 with different zinc complexes as activator

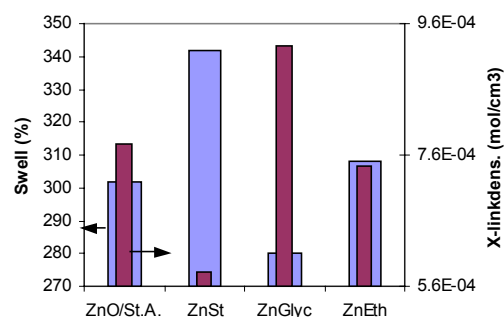


Figure 5.7 Swelling and crosslink density of s-SBR compounds S3, S4, S7 and S8 with different zinc complexes as activator

The physical properties of the compounds with zinc stearate (S4) and zinc-m-glycerolate (S7) are presented in Table 5.9, in comparison with the reference compound. The properties dependent on the cure state for the compound with zinc stearate are inferior to the properties of the reference compound: the moduli decrease and elongation at break and compression set increase. For the compound with zinc-m-glycerolate a lower value for elongation at break and lower compression set at 100°C are found. This can be attributed to the higher crosslink density, as was already observed with the swelling and torque measurements. The beneficial effect

of zinc-m-glycerolate on thermal stability, as previously observed in EPDM compounds, is not observed in these s-SBR compounds.

Table 5.9 Properties of s-SBR compounds with different zinc complexes

Compound	S3	S4	S7
Hardness (Shore A)	67	69	69
M ₂₅ (MPa)	1.2	1.2	1.4
M ₅₀ (MPa)	1.8	1.7	2.1
M ₁₀₀ (MPa)	3.4	2.8	3.9
M ₃₀₀ (MPa)	17.7	14.2	18.6
Tensile strength (MPa)	21.3	22.2	18.7
Elongation at Break (%)	345	412	300
Tear strength (N/mm)	37	36	33
CS 72h/23°C (%)	6	16	7
CS 72h/100°C (%)	35	34	31
After 168 Hours / 100°C ageing:			
M ₂₅ (MPa)	1.7	1.6	2
M ₅₀ (MPa)	2.8	2.5	3.3
M ₁₀₀ (MPa)	6.2	5	6.4
M ₃₀₀ (MPa)	-	-	-
Tensile strength (MPa)	16.6	13.1	12.4
Elongation at Break (%)	203	190	164

An explanation for the differences in scorch time can be found in the differences in the strength of the coordination bonds in the zinc complexes. Another explanation can be deduced from the general statement, that increasing the pH leads to activation of sulphur vulcanisation. Krebs²⁰ postulated that the accelerating properties of amines are related to their base strength. The alkaline character of zinc-m-glycerolate must be the reason for the acceleration of sulphur vulcanisation of rubber by an analogous way as in the cases of currently used basic accelerators. The greater basicity of glycerolate in comparison with that of stearate and hexanoate is in good accordance with the faster vulcanisation rate found for zinc-m-glycerolate and zinc-2-ethylhexanoate containing rubber compounds.

Overall, it can be concluded that particularly zinc-m-glycerolate is a good substitute for ZnO as activator for sulphur vulcanisation, in EPDM as well as s-SBR rubber, without detrimental effects on the cure and physical properties. Furthermore, the results indicate that dependent on the intended applications, also zinc-2-ethylhexanoate and zinc stearate might represent substitutes for the commonly used activator ZnO. Although not further investigated in the present research, it is anticipated that with proper zinc-containing complexes as substitutes for the conventional ZnO, a reduction of the zinc concentration in EPDM and s-SBR compounds can be achieved.

5.5 RESULTS AND DISCUSSION II: MODEL COMPOUND VULCANISATION

The outcome of the studies with zinc complexes in EPDM and s-SBR rubbers, encourages to further elucidate the role of zinc complexes in the vulcanisation reactions via the Model Compound Vulcanisation technique, as introduced in Chapter 4. Experiments are performed with zinc stearate and zinc-m-glycerolate as activator in two different model compounds, *viz.* squalene and TME.

The reactions are done as described in the experimental section and in Chapter 4 of this thesis, at 140°C in the presence of a vulcanisation system. The MCV compositions investigated are described in Table 5.5 and 5.6. The development of the initial ingredients, formation of 2-mercaptobenzothiazole (MBT) and other reaction products is characterised and quantified by HPLC-UV at room temperature. Squalene is used to study specifically the first stage in the vulcanisation process. In TME model studies three different stages in the vulcanisation process are studied as a function of reaction time: curatives development, crosslink precursor formation, and the crosslinked products development.

5.5.1 Squalene Model Compound Vulcanisation

As an introductory study, a detailed investigation of the function of zinc complexes in the initial stages of vulcanisation was carried out with the poly-functional model squalene. Squalene was reacted for 5 – 60 minutes in the presence of sulphur, CBS and the zinc-containing complexes according to the recipes given in Table 5.5. Stearic acid, used to solubilise the zinc into the rubber system, was added in all samples, even if the zinc ions are already supplied in a (pre)complexed form. The concentration profiles of the curatives can be calculated via the internal standard and the response factors belonging to the specific curatives, and plotted as a function of reaction time. The amounts of the curatives as represented in the graphs are related to their initial amounts.

Figure 5.8 shows the kinetics of decrease in CBS concentration in squalene as a function of reaction time for all three samples, with ZnO, with zinc stearate and with zinc-m-glycerolate as activator. It can be observed that the three zinc-containing activators induce a more or less comparable rate of dissociation of the accelerator CBS. With zinc-m-glycerolate present as activator the initiation of the decomposition of CBS occurs slightly faster. Scission of the labile bonds, such as –S–S– or –S–N–, present in an accelerator has been mentioned as a parameter which determines the length of the scorch time. After one hour, all the accelerator has been consumed in all systems.

The sulphur content is plotted as a function of reaction time for the three zinc-containing systems in Figure 5.9. A very fast decay of the sulphur content is observed in the first five minutes for all systems. In this stage the sulphur is incorporated in the accelerator during the first ten minutes to form polysulphidic species. In the presence of ZnO more sulphur is consumed in this initial stage of the reaction as compared to the other zinc-containing complexes. The sulphur content in the system with zinc-m-glycerolate is slightly higher, while for zinc stearate the profile

is comparable with the non-activated system. Apparently, in the presence of zinc stearate the rate of formation of active sulphurating species is lower and therefore a slower decay of sulphur is observed.

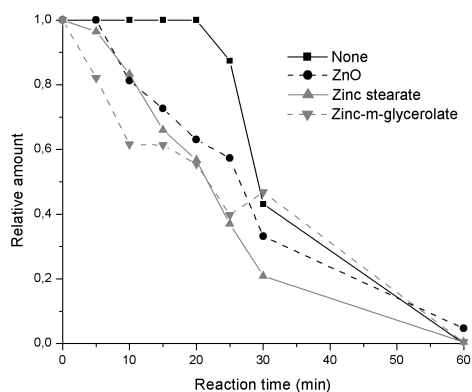


Figure 5.8 Decomposition of CBS with different zinc complexes as activators in squalene

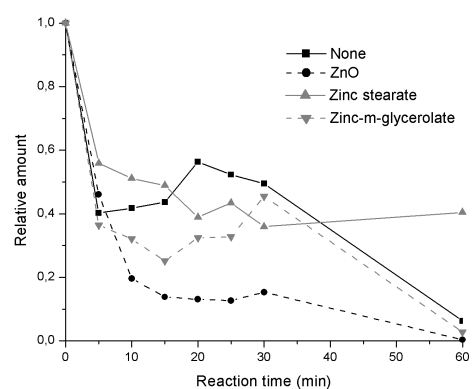


Figure 5.9 Decrease of sulphur content with different zinc complexes as activators in squalene

MBT is formed during the course of the reaction as decomposition product of the accelerator and as a side product from the transformation of a crosslink precursor into a crosslink. Since MBT is not present initially, the amounts are related to the maximum amount that can be formed if all CBS would transform into MBT. In the HPLC system used, MBT and MBTS have the same retention time. It is assumed that the peak at the retention time of 2 minutes in the HPLC chromatogram contains only MBT and the amount of MBTS is negligible, as earlier described in Chapter 4. The concentration profiles of MBT are shown in Figure 5.10.

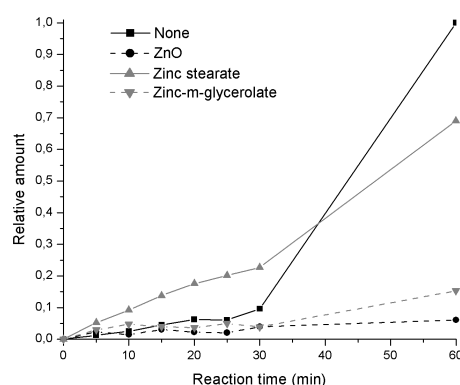


Figure 5.10 Increase of the MBT content with several zinc complexes as activators in squalene

The differences in accelerator decomposition in the ZnO, zinc stearate and zinc glycerolate systems are rather small. The MBT concentration profiles, however, are very different. In the presence of zinc-m-glycerolate hardly any MBT is formed,

similar to the ZnO-containing system. In the presence of zinc stearate, on the other hand, a considerable amount of MBT is formed, as in the non-activated system. Considering the fact that the MBT concentration in the sample without activator reached a relative amount of almost 1, it may be stated that the low MBT content in the sample with ZnO and zinc-m-glycerolate is due to a complex formation of MBT with Zn^{2+} . ZnMBT precipitates in the reaction mixture and is therefore difficult to analyse with HPLC. A higher MBT level is observed in the samples with zinc stearate. Due to the lower zinc content, as shown in Table 5.10, less complex formation between the zinc ions and MBT occurs. Apparently, the concentration of zinc-ions is too low to transform all MBT into ZnMBT complexes. Another explanation could be that the zinc stearate complexes have a high stability, thereby reducing the tendency of the zinc-ions to form active sulphurating complexes.

Table 5.10 Zinc content and amounts of applied zinc complexes

Activator	Zn ²⁺ -ions [mmole/g]	Amounts of activator [phr]
ZnO	12.3	5
Zinc stearate	1.6	10
Zinc-m-glycerolate	6.5	5

As already mentioned in Chapter 4, in general it can be stated that zinc containing activators accelerate the decomposition of CBS, since in the sample without activator no decay in CBS content is observed in the first 30 minutes reaction time. The incorporation of the sulphur in the accelerator in the initial stage in order to form polysulphidic species is also influenced by the presence and concentration of zinc-ions.

5.5.2 TME Model Compound Vulcanisation

To study the formation and decomposition of crosslink intermediates and crosslinking reaction in detail, additional experiments with zinc complexes as activator were performed in the monofunctional model TME. With this model compound, besides the decrease in concentration of the initial ingredients and the formation of MBT, the crosslinked products as well as the crosslink precursors can be characterised by HPLC-UV at a wavelength of 254 nm. The same activators are studied in TME MCV: none, ZnO, zinc stearate and zinc-m-glycerolate, according to the recipes given in Table 5.6. Figures 5.11 and 5.12 show the concentration profiles of the initial vulcanisation ingredients TBBS and sulphur, respectively.

From Figure 5.11 it is evident that, while ZnO hardly has any influence on the decomposition of TBBS, zinc-m-glycerolate and particularly zinc stearate seem to impose a slight accelerating effect on the rate of decomposition vs. 'none'. In the initial stage of the vulcanisation, a very fast decay of sulphur is observed in the TME samples, comparable with the results obtained in squalene. The ZnO systems again shows the lowest level of sulphur at short reaction times. The sulphur concentration profile with zinc-m-glycerolate present in the system takes an intermediate position,

while the profile of the zinc stearate containing sample is more similar to the non-activated system.

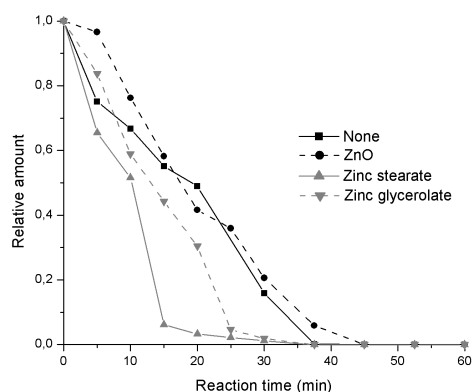


Figure 5.11 Decomposition of TBBS with different zinc complexes as activators in TME

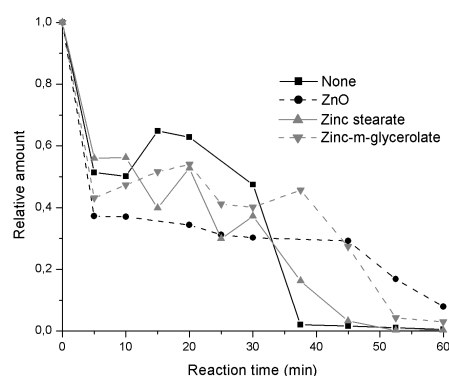


Figure 5.12 Decrease of sulphur content using different zinc complexes as activators in TME

The development of MBT with reaction time is plotted in Figure 5.13. For the samples with ZnO and zinc-m-glycerolate the formation of MBT starts around 30 minutes. In the presence of zinc stearate the formation of MBT starts at considerably shorter reaction times, which correlates with the faster dissociation of the accelerator. None of the TME systems shows a relative amount of MBT as high as 1, although in all systems after ca. 40 minutes all TBBS had reacted. A conversion of 100% is not achieved, due to the formation of crosslink precursors and the complex formation of MBT with Zn^{2+} .

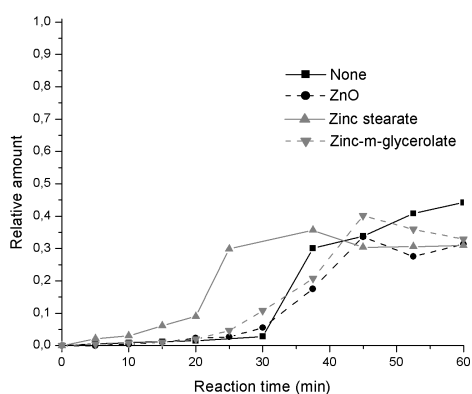


Figure 5.13 Increase of the MBT content with several zinc complexes as activators in TME

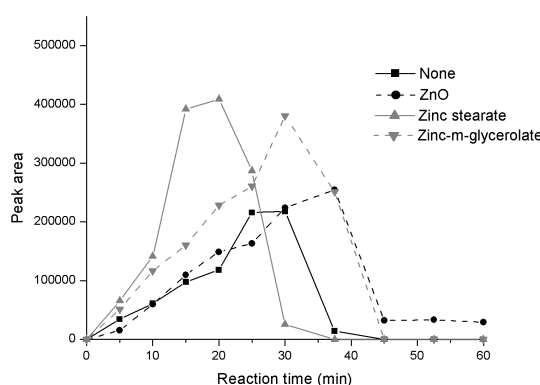


Figure 5.14 Development of the crosslink precursor with different zinc complexes as activators in TME

The next step is the formation of the so-called crosslink precursor, which consists of the mercapto part of the accelerator attached to the allylic position of the model via a sulphur bridge with a variable amount of sulphur atoms. These crosslink

precursor in the TME samples can be separated by the HPLC column and detected by UV light at a wavelength of 254 nm. The development of the precursors in the several systems as a function of reaction time is plotted in Figure 5.14. The formation as well as the decomposition of the precursor in the presence of zinc stearate proceeds much faster compared to the other systems. This is in good accordance with the faster decomposition of TBBS in the sample with zinc stearate as activator, as demonstrated in Figure 5.11. The maximum precursor concentration is reached at a reaction time of approximately 20 minutes. The presence of zinc-m-glycerolate results in a precursor concentration profile similar to the ZnO system, albeit with a higher maximum concentration of crosslink precursor.

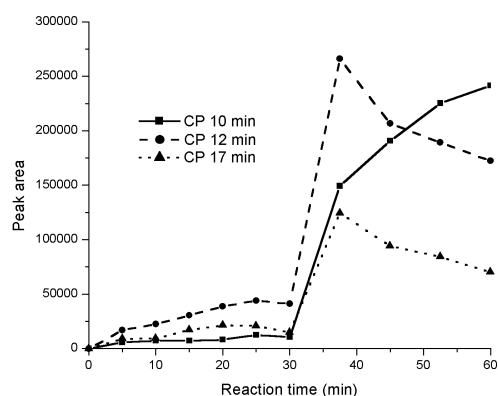


Figure 5.15 Development of the crosslinks without activator in TME

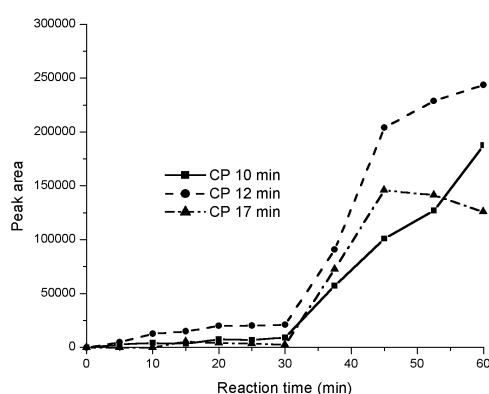


Figure 5.16 Development of the crosslinks with ZnO as an activator in TME

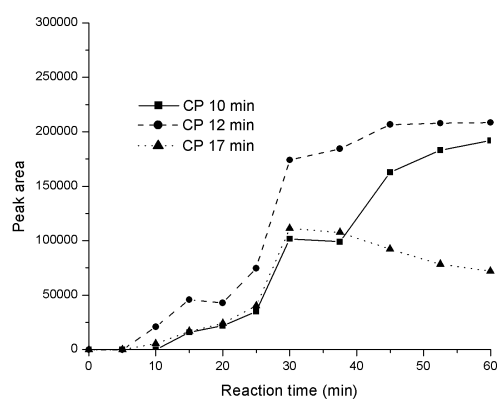


Figure 5.17 Development of the crosslinks with zinc stearate as an activator in TME

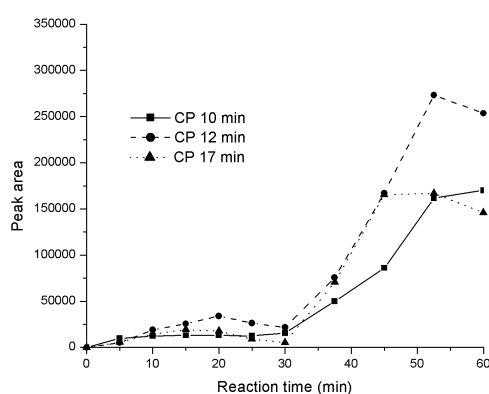


Figure 5.18 Development of the crosslinks with zinc-m-glycerolate as an activator in TME

As already mentioned before, the crosslinked products can be detected with HPLC measurements as well in the TME model compound systems. As mentioned in literature, the reaction products which are formed are mainly of the type: TME-S_x-TME. These polysulphidic crosslinks are formed by the reaction of the intermediates, crosslink precursors, with another intermediate moiety or via the reaction with

polymer chains. Figures 5.15 – 5.18 show the development of three of the reaction products, viz. the total of S₃-, S₄- and S₅-TME-crosslinks (see Chapter 4), with reaction time for the systems with different zinc complexes, measured with HPLC. The different (poly)sulphidic crosslinked products cannot be compared absolutely while the response factors of these products were not all determined. Therefore only the trends between the different systems can be compared. In accordance with the concept that the crosslink precursors convert into crosslinks, the formation of crosslinks begins slightly before the concentration of crosslink precursor starts to decrease. It is evident from these figures that the distribution of the crosslinked products is comparable in the zinc-containing samples. The highest concentration of crosslinked products is obtained in the presence of zinc-m-glycerolate, as illustrated later in Figure 5.21.

The final step of the schemes, presented in Chapter 4, is crosslink shortening. The initially formed polysulphidic bridges tend to reduce the sulphur chain length by releasing sulphur and by the formation of shorter tri-, di-, and monosulphidic crosslinks. To observe this particular phenomenon, the crosslinked products development for the different zinc complexes as a function of reaction time must be examined. Crosslink shortening is clearly observed in the non-activated system. The longer crosslinks decrease while the shortest sulphur bridges increase. In all systems the amount of the shortest crosslink keeps increasing with reaction time.

5.5.3 Comparison and Evaluation of Squalene and TME MCV Results

The effects of the zinc-containing activators in squalene and TME are grossly comparable from a mechanistic point of view. The order of the activators, regarding slight differences in the rate of decomposition of the accelerator in squalene, is as follows: zinc glycerolate > zinc stearate > ZnO > none. A different trend is observed in TME as compared to squalene: in the presence of zinc stearate the accelerator decomposes the fastest. In TME the observed order is: zinc stearate > zinc glycerolate > ZnO = none.

It has appeared that the sulphur concentration profiles in the two different model systems also show similar trends. In the presence of zinc stearate and zinc-m-glycerolate the sulphur level at short reaction times is higher as compared to the samples with conventional ZnO. When zinc stearate is present, the sulphur concentration profile is even comparable with the non-activated system. It may be concluded, that in the presence of zinc stearate less sulphur insertion in the active accelerator complex occurs. An explanation could be the very low zinc content of zinc stearate by the bulky stearate groups attached to the zinc ions, which prevent the formation of the active sulphurating species because of steric hindrance. This explanation corroborates the suggested mechanism of complex formation between the zinc cations and the accelerator parts.

Considerable differences in the concentration profiles of MBT are observed between the two model systems. In squalene the MBT concentration remains at a low level when ZnO or zinc-m-glycerolate are present in the reaction mixture, most likely due to the formation of a complex between the zinc ions and MBT (ZnMBT); in

TME the relative amounts of MBT formed are in the range of 0.2 – 0.4 in all systems. In both model systems, however, the formation of MBT in presence of zinc stearate starts at considerably shorter reaction times as compared to the conventional ZnO, in accordance with the previously observed faster decomposition of the accelerator in the presence of zinc stearate.

The formation of the crosslink precursor, as studied with TME model compounds, proceeds of all four systems the fastest for zinc stearate. The precursor development differs in extent of formation. In the presence of zinc stearate and zinc-m-glycerolate a higher concentration of precursors is generated. The rate of decomposition of the crosslink precursor is comparable, but occurs at different reaction times: fastest in the presence of zinc stearate. The delay in decomposition, caused by the interaction of zinc with the precursor, as shown in Figure 5.19 and previously described in Chapter 4, is illustrated by the difference in precursor concentration profiles in the zinc stearate and zinc-m-glycerolate containing samples. In the systems without ZnO or with a low concentration of zinc ions, *viz.* in the sample with zinc stearate, the breakdown of the precursors starts at short reaction times, while with a higher zinc concentration, in the samples with ZnO and zinc-m-glycerolate, apparently the breakdown is delayed.

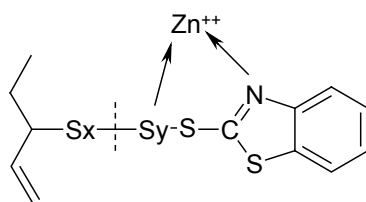


Figure 5.19 Interaction of zinc with the crosslink precursor²¹

In accordance with the reaction mechanisms in Chapter 4, suggesting that these vulcanisation intermediates convert into crosslinks, the concentration of crosslink precursors starts to decrease when the crosslinked products are formed. It is noted that in the presence of zinc stearate the formation of crosslinked products starts at considerably shorter reaction times, which is in accordance with earlier observations concerning the decomposition of the accelerator and formation and breakdown of the crosslink precursor. Apart from a slightly higher concentration of crosslinked products in the sample with zinc-m-glycerolate, no major differences in the formation, distribution and shortening of the crosslinked products are observed in the four TME-samples.

The main difference between the zinc complexes is the availability of the Zn^{2+} -ions. As already mentioned, the availability depends on the structure of the activator, the stability of the complexes or bond strength of the ion with the ligands and the amount of activator present. In the samples with ZnO and zinc-m-glycerolate the amount of zinc ions is quite high. In ZnO, however, the zinc ions are firmly embedded in a crystal structure and therefore strongly bonded. Furthermore, only a relatively small percentage of the ZnO is effective and actually undergoes reaction with the other compounding ingredients. In principle all the ZnO below the surface is

wasted since it only functions as a (expensive) little reinforcing filler. The complex stability of zinc stearate is probably higher than zinc-m-glycerolate due to the larger electronegativity of the acid functionality in zinc stearate in comparison with the alcohol functionality of zinc-m-glycerolate, giving the bond a more polar character. Zinc stearate has an additional advantage with respect to solubility and dispersion due to the long aliphatic apolar tail.

5.6 RESULTS AND DISCUSSION III: MUTUAL COMPARISON OF THE EFFECT OF ZINC COMPLEXES IN THE RUBBER COMPOUNDS AND MCV STUDIES

As stated before in Chapter 4, results obtained with model compounds, *i.e.* squalene and TME, may not necessarily be extrapolated to real rubbers such as EPDM and s-SBR. But the general trend of the reactions is unlikely to be influenced by the particular allylic structures of the various rubbers involved.

For MCV, the crosslinked reaction products, as evaluated with HPLC, can be added by summing all the peaks of the various sulphur chains, *i.e.* area of S₃, + area of S₄ *etc.* Although addition of peak areas is basically not correct, it provides a good idea of the development of crosslinking. The rheograms of s-SBR compounds and the crosslink development obtained with the TME model compounds for systems with ZnO, zinc stearate and zinc-m-glycerolate are shown in Figures 5.20 and 5.21, respectively. The rheometer data in Figure 5.20 and the crosslinked products development in Figure 5.21 from MCV correlate reasonably well. The enhancing effect of zinc-m-glycerolate on the crosslink density indicated by the higher delta torque level and reflected in the vulcanisate properties, as well as the lower extent of crosslinking in the presence of zinc stearate is proven with the MCV studies, in particular for the long reaction time. At first sight, the scorch times observed in MCV are not at all in agreement with the s-SBR compounds. However, there are many possible reasons for the difference in curing, as already indicated in Chapter 4.

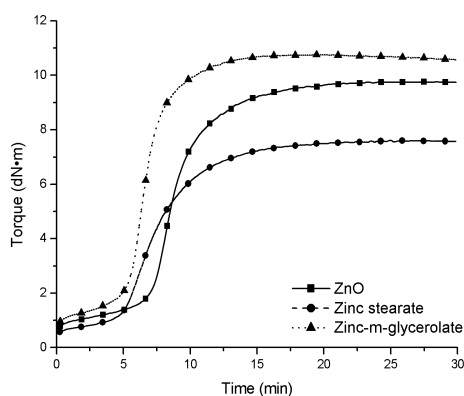


Figure 5.20 Cure development with zinc complexes as activator in s-SBR

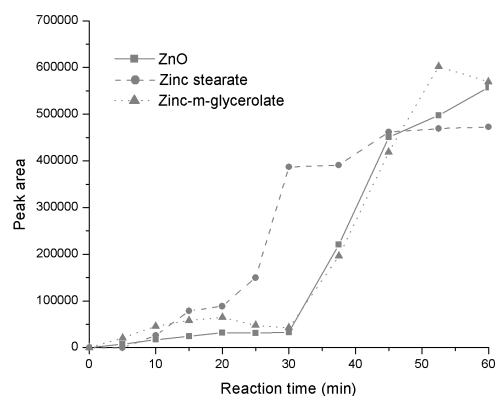


Figure 5.21 Crosslinked products development with zinc complexes as activator in TME

The experimental studies reported in the current chapter have provided mechanistic insight into zinc complex activated vulcanisation. The effects of zinc complexes in the different stages of vulcanisation could be identified, albeit without complete conclusive evidence. Overall, it can be concluded that particularly zinc-m-glycerolate is a good substitute for ZnO as activator for sulphur vulcanisation. Future work on zinc complexes should target on the characteristics of the complex ligands, e.g. alkalinity and steric hindrance, and the strength of the coordination bonds. It is therefore anticipated that a reduction of ZnO needed in EPDM and s-SBR compounds can be achieved by designing proper zinc-containing complexes.

5.7 CONCLUSIONS

In order to find routes to reduce ZnO levels in rubber compounds, this chapter describes a comprehensive study on the substitution of the conventional activator ZnO by zinc complexes. Real rubber and model compound systems are employed to investigate the effect of zinc complexes on the different stages of the vulcanisation process.

As a general conclusion, it appears that particularly zinc-m-glycerolate is a good substitute for ZnO as activator for sulphur vulcanisation, in EPDM as well as s-SBR rubber, without detrimental effects on the cure and physical properties. The properties after ageing suggest that the addition of zinc-m-glycerolate in EPDM compounds leads to a considerable improvement of the thermal stability. Furthermore, the results in s-SBR indicate that dependent on the intended applications, also zinc-2-ethylhexanoate and zinc stearate might represent substitutes for the commonly used activator ZnO, although zinc stearate is considerably less effective than ZnO *per se*.

By means of Model Compound Vulcanisation, additional information about the reactions and chemical mechanisms in real rubber vulcanisates has been obtained. From the results shown it has become clear that the reactions in the different stages of the vulcanisation process do not differ greatly for the various zinc complexes. Similar trends are observed in the squalene and TME model compound studies. The lower sulphur content at short reaction times for the systems with higher zinc content can be explained by sulphur insertion in a zinc-accelerator complex or in a polysulphidic accelerator. Experiments with zinc stearate as activator reveal a faster decomposition of the accelerator as compared to samples without or with ZnO as activator. Furthermore, a faster formation as well as decomposition of the crosslink precursor is observed in the presence of zinc stearate, resulting in a somewhat faster formation of reaction products or 'crosslinking'. The latter is not clearly observed in the s-SBR rubber compounds. The higher yield and minor differences in the distribution of the crosslinked products which are found in the model experiments with zinc-m-glycerolate, coincide with the cure and ultimate properties of real s-SBR rubber compounds.

The differences in activity of these zinc complexes may be related to the stability of the zinc complexes. The complexes with stronger coordination bonds may have a lower tendency to form intermediate, active sulphurating vulcanisation compounds: zinc-accelerator complexes. Furthermore, the activity of the zinc complexes can be affected by the basicity of the ligands or steric hindrance caused by the substituents. The higher activity of zinc-m-glycerolate compared to zinc stearate is in agreement with the concept that the accelerating properties of activators and accelerators are a function of their basicity.

Overall, it is anticipated that a significant reduction of zinc content can be achieved by optimisation of the zinc complex levels. Furthermore, additional research concerning the influence of the ligands in the zinc complex is considered worthwhile to possibly achieve even better systems.

5.8 REFERENCES

1. R. Galle-Gutbrecht, presented at the International Rubber Conference (IRC), Prague, Czech Republic, July 2002.
2. P.J. Nieuwenhuizen, Thesis, University of Leiden, (1998).
3. M.R. Kresja, J.L. Koenig, "*The nature of sulfur vulcanisation*", in *Elastomer Technology Handbook*, CRC press, New Jersey (1993), 475.
4. A.Y. Coran, "*Vulcanization*", in *Science and Technology of Rubber*, E.R. Eirich, Ed., Academic Press, San Diego (1978), 291.
5. B. Saville, A.A. Watson, *Rubber Chem. Technol.*, **40**, (1967), 100.
6. F.W.H. Kruger, W.J. McGill, *J. Appl. Polym. Sci.*, **42**, (1991), 2651.
7. P. Versloot, Thesis, University of Leiden, (1993).
8. F.W.H. Kruger, W.J. McGill, *J. Appl. Polym. Sci.*, **45**, (1992), 1491.
9. A.A. Mukhitdinov, *Int. Polym. Sci. Technol.*, **21**, (1994), 48.
10. P.W. Allen, D. Barnard, B. Saville, *Chem. in Britain*, **6**, (1970), 382.
11. F.W.H. Kruger, W.J. McGill, *J. Appl. Polym. Sci.*, **45**, (1992), 1545.
12. J. Kelm, L. Vogel, D. Gross, *Kautsch. Gummi Kunstst.*, **36**, (1983), 274.
13. M. Porter, *Organic Chemistry of Sulfur*, S. Oae, Ed., Plenum Press, New York (1977).
14. N.J. Morrison, M. Porter, *Rubber Chem. Technol.*, **57**, (1984), 63.
15. K. Morche, H. Ehrend, *Kautsch. Gummi Kunstst.*, **42**, (1989), 1015.
16. D.A. Matkin, D.C. Renshaw, A.R. Harrison, (to Pharmaserve Ltd.), WO 95/08524 (March 30, 1995).
17. P.J. Flory, J. Rehner, *J. Chem. Phys.*, **11**, (1943), 521.
18. R.A. Hayes, *Rubber Chem. Technol.*, **59**, (1986), 138.
19. H.G. Dikland, Thesis, University of Twente, (1992).
20. H. Krebs, *Rubber Chem. Technol.*, **30**, (1957), 962.
21. A.Y. Coran, *Science and Technology of Rubber*, Academic Press, San Diego (1994).

Effect of Various Metal Oxides as Activator for Sulphur Vulcanisation in Various Rubbers[#]

'Aim for success, not perfection. Never give up your right to be wrong, because then you will lose the ability to learn new things and move forward with your life.'

David M. Burns

A completely zinc-free vulcanisation system based on sulphur remains a challenging task. While ZnO is commonly used in the vulcanisation recipe, not much is known about the accelerating properties of other metal oxides. In this chapter the application of a wide range of metal oxides as activator for sulphur vulcanisation will be discussed.

Two widely different rubbers, viz. EPDM and s-SBR have been selected in the present study. The influence of the basicity, the crystal structure and the ability to form complexes of the metal oxides is studied. It has been observed that neither CdO, PbO, BaO, CaO, MgO and BeO are proper substitutes for ZnO as activator in thiuram-accelerated vulcanisation of EPDM, nor do they show a synergistic effect with ZnO. In s-SBR compounds, however, it is demonstrated that CaO and MgO can function as activator of cure for sulphur vulcanisation, retaining the curing and physical properties of the rubber vulcanisates.

Model Compound Vulcanisation has been used to elucidate the influence of the activators MgO and CaO on the vulcanisation mechanism. The influence of activator on the several reaction rate constants appeared to be different in squalene and TME Model compound experiments.

It can be concluded that depending on the exact requirements for a specific compound, certain metal oxides represent an alternative route to reduce the zinc level and therefore to minimise the environmental impact.

[#]Part of this work has been presented at the International Rubber Conference '02, July 01 – 04, in Prague (CZ); this chapter has been accepted for publication in *Kautschuk, Gummi und Kunststoffe*, **57**, (2004).

6.1 INTRODUCTION

It is generally known that for efficient vulcanisation of rubbers by elemental sulphur or by sulphur donors the presence of a metal activator is necessary.¹ ZnO is the most effective activator for sulphur vulcanisation. A great deal of attention has been paid to the problem of reducing the zinc content in rubber products. It has already been shown in Chapter 3 that the level of conventional ZnO (Red Seal) can be reduced by optimisation to 1 and 2 phr for s-SBR and EPDM, respectively, retaining the curing and physical properties of the rubber products. In another approach, described in Chapter 5, the zinc-ions are supplied in a complexed form, e.g. zinc stearate or zinc-m-glycerolate, in order to obtain a better dispersion of the activator in the rubber matrix and a more efficient use of the zinc-ions and thereby reducing the overall zinc content in the vulcanisates. The oxide variant, however, appeared to be more efficient than the zinc complexes or sulphides.

A completely zinc-free vulcanisation system based on sulphur keeps on being intriguing. There have been a number of investigations comparing different metal oxides as vulcanisation activators, mostly with tetramethylthiuram disulphide (TMTD) in NR, with variable results. It is concluded that a variety of metal oxides can accelerate cure, but the degree of acceleration varies with the specific metal ion used.² In a research by Chapman, it was found that of metal oxides other than ZnO, CdO on average appears to be best, followed by lead- and mercury-oxide.³ Lautenschlaeger *et al.* studied the effects of different metal oxides in accelerated sulphur vulcanisation with 2-methyl-2-pentene, as a model olefin.⁴ The results of a comparison of ZnO, CdO, CaO, and a combination of ZnO and aniline also indicated that CdO is the most effective oxide, resulting in a high yield in monosulphides and a relatively low production of by-products. In an investigation of the crosslinking of a model olefin with sulphur, tetraethylthiuram disulphide (TETD) and various metal oxides, cupric oxide was found to give higher yields than ZnO, and nickel oxide was also quite effective.⁵

Some metal oxides behave synergistically with ZnO. Replacement of half of the ZnO by an equivalent amount of CdO, PbO, Bi₂O₃, CaO, HgO or CuO in an efficient vulcanisation (EV) system gave higher moduli. Other oxides gave moduli equal to or lower than with ZnO alone. CaO and MgO are apparently not so promising in conventional sulphur/sulphenamide cures, especially not in combination with ZnO. It has been reported that CaO and MgO interfere with the efficient activation of ZnO.⁴

Where ZnO is commonly used in the vulcanisation recipe, not much is known about the accelerating properties of other metal oxides, so, a comprehensive study was considered worthwhile. In the first part of this chapter the sulphur vulcanisation of EPDM and s-SBR rubber with several alternative metal oxides as activators is described. The objective of the second part of this chapter is to gain additional insight into the mechanistic details of sulphur vulcanisation with other metal oxides as activator in order to judiciously reduce ZnO levels in rubber compounding.

6.2 OTHER METAL OXIDES IN COMPARISON WITH ZNO

It has been reported that the high activity of ZnO can be explained on the basis of the chemistry of complex formation. It is reported that a preceding reaction with stearic acid forms the rubber hydrocarbon-soluble zinc stearate and liberates water before the onset of crosslinking.⁶ Furthermore, ZnO is in many vulcanisation systems a precursor to zinc-derived accelerators.⁷ It has further been suggested in many different studies that Zn²⁺-ions form these active complexes with accelerators, which are more reactive than the free accelerator.⁸⁻¹⁰ Complex formation of the zinc-ion with different accelerators is critical to get efficient curing.

The Zn²⁺-ion functions as a Lewis acid in the complex formation and the cleaved accelerator as a Lewis base. The basicity of a metal ion is dependent on its size and the charge, according to equation 6.1.¹¹

$$\text{cation acidity} = \frac{k \cdot Z^2}{r} \quad \text{eq. 6.1}$$

where : k = constant
 Z = charge of the cation
 r = radius of the ion

Since for Ca²⁺, Zn²⁺ and Mg²⁺ the charges are equal, the size of the cation is the main factor that determines the difference in acidity between them. In Table 6.1, the sizes are given.

Table 6.1 Radii of Ca²⁺, Zn²⁺ and Mg²⁺

Cation	Radius (10 ⁻¹² m)
Ca ²⁺	94
Zn ²⁺	74
Mg ²⁺	65

From Table 6.1 can be concluded that the order of acidity from strongest acid to the weakest is Mg²⁺ > Zn²⁺ > Ca²⁺.

Duchacek *et al.*¹² tested the effects of copper-, mercury-, nickel-, zinc-, cadmium-, indium-, magnesium-, and calcium-stearates on the course of CBS-accelerated sulphur vulcanisation of NR. Based on results and in accordance with Irving's and Williams' finding about the order of stability of metal complexes,¹³ the following order for the stability of metal complexes with accelerator ligands was presented: Cu²⁺, Hg²⁺ > Ni²⁺, Zn²⁺, Cd²⁺, In²⁺ > Mg²⁺, Ca²⁺. They concluded that nickel, zinc, cadmium, and indium have a definite ability to form complexes, but they form significantly less strong coordination bonds, than, e.g. copper and mercury. This is why zinc and cadmium form active sulphurating vulcanisation species. Magnesium and calcium have only a slight tendency to form complexes. This fact eliminates the possibility of formation of an active sulphur-containing complex.

Generally, it is stated that increasing the pH leads to activation of the vulcanisation. Krebs¹⁴ postulated that the accelerating properties of amines are related to their base strength. The alkaline character of magnesium and calcium stearates is the reason for the acceleration of sulphur vulcanisation of rubber in an analogous way as in the cases of currently used basic accelerators. The greater basicity of calcium in comparison with that of magnesium is in good accordance with the larger vulcanisation rate found for calcium containing rubber compounds.¹²

In some of the vulcanisation mechanisms it is assumed that ZnO is distributed in the form of crystal particles in rubber mixes. Molecules of accelerators, sulphur and fatty acids diffuse through the rubber matrix and are adsorbed on the ZnO-surface with the formation of intermediate complexes. Nieuwenhuizen⁷ in his thesis proposed a mechanism in which the ZnO surface functions both as a reactant and as a catalytic reaction template, activating and bringing together reactants. The most important parameter here is the crystal structure of the ZnO. The most common crystal structure for ZnO is the zincite (wurtzite) structure. Zincite has a hexagonal structure, Figure 6.1, with each atom surrounded by a tetrahedron of atoms of the opposite type. The structure consists of a continuous network of interconnected tetrahedra. The only metal oxide isostructural with ZnO is BeO.

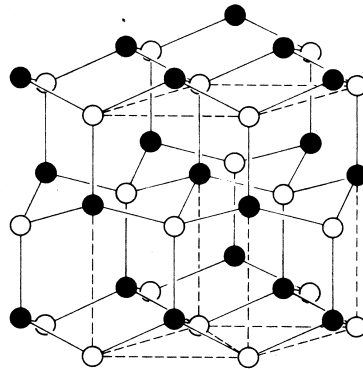


Figure 6.1 Zincite (ZnO) structure, isostructural with wurtzite; ● = Zn, ○ = O

In addition to its role as an activator for sulphur vulcanisation, there is also evidence that the inclusion of ZnO in a compound reduces heat-build-up and improves tyre abrasion resistance. ZnO acts as a 'heat sink', which accepts frictional energy without a large increase in internal temperature. It has also been found that ZnO improves the heat resistance of the vulcanisates and their resistance to the action of dynamic loading.¹⁵ The high thermal conductivity of ZnO helps to dissipate local heat concentrations that might otherwise affect the properties of rubber. Therefore, reduction of ZnO or complete elimination might influence these properties as well, although it is anticipated that other metal oxides also possess high thermal conductivities.

6.3 EXPERIMENTAL SECTION

Materials.— Solution butadiene-styrene rubber (Buna VSL 2525-0 M) was obtained from Bayer GmbH, Germany. Buna VSL 2525-0 M contains 25 wt % of 1,2-vinyl-butadiene and 25 wt % of styrene; it has a Mooney viscosity, ML (1+4) @ 100°C of 54. Ethylidene norbornene (ENB)-containing EPDM rubber (Keltan 4802) was obtained from DSM Elastomers B.V., the Netherlands. Keltan 4802 contains 52 wt % of ethylene units and 4.3 wt % of ENB; it has a relatively narrow molecular weight distribution and a typical Mooney viscosity, ML (1+4) @ 125°C of 77. As fillers were used: carbon black N-375 HAF, N-550 FEF and N-762 SRF (Cabot B.V.). Aromatic oil (Enerflex 75) was obtained from BP Oil Europe, paraffinic oil (Sunpar 2280) from Sun Petroleum Products Co., and stearic acid from J.T. Baker. Commercially available ZnO Red Seal (Grillo GmbH) and the different metal oxides (Aldrich) were used as received. Sulphur (J.T. Baker), N-tert-butyl-2-benzothiazolesulphenamide (Santocure TBBS, Flexsys B.V.), 2-Mercaptobenzothiazole (Perkacit MBT, Flexsys B.V.), and Tetramethylthiuram disulphide (Perkacit TMTD, Flexsys B.V.), were also commercial grades and used as such. The materials used in the model compound experiments are listed in Table 6.2.

Table 6.2 Materials used for model compound vulcanisation

Material	Source
Squalene	Merck
2,3-dimethyl-2-butene (TME)	Aldrich
TBBS	Flexsys
Sulphur	Merck
ZnO pure	Merck
MgO	Aldrich
CaO	Aldrich
Stearic Acid	J.T. Baker

Rubber mixing.— An EPDM and s-SBR masterbatch were prepared in an internal mixer (~50 kg) in order to get a homogeneous mixture and minimise the influence of mixing conditions. The vulcanisation systems including the various metal oxides investigated were added in a separate operation, on a two roll mill at 50°C. The compounds were sheeted off at a thickness of approximately 2 mm which was convenient for the subsequent preparation of test specimens. The compositions of the EPDM and s-SBR compounds with the different metal oxides are given in Tables 6.3 and 6.4, respectively.

Curing.— The cure characteristics of the different compounds were measured at 160°C with a Rubber Process Analyser RPA2000 (Alpha Technologies), a type of moving die rheometer. The optimal vulcanisation time (t_{90}) and scorch time (t_{02}) of the compounds were determined. The compounds were cured in a Wickert laboratory press WLP 1600/5*4/3 at 160°C and 100 bar, according to the t_{90} of the specific compounds.

Table 6.3 Composition of the EPDM compounds (phr) with different metal oxides

Compound	1	2	3	4	5	6	7	8	9	10
EPDM (Keltan 4802)	100	100	100	100	100	100	100	100	100	100
Carbon Black (N550 FEF)	70	70	70	70	70	70	70	70	70	70
Carbon Black (N762 SRF)	40	40	40	40	40	40	40	40	40	40
Paraf. Oil (Sunpar 2280)	70	70	70	70	70	70	70	70	70	70
Stearic Acid	1	1	1	1	1	1	1	1	1	1
ZnO	3	-	-	3	3	-	-	-	-	-
MgO	-	3	-	3	-	-	-	-	-	-
CaO	-	-	3	-	3	-	-	-	-	-
BaO	-	-	-	-	-	6	-	-	-	-
PbO	-	-	-	-	-	-	8	-	-	-
CdO	-	-	-	-	-	-	-	4.5	-	-
Cu(II)O	-	-	-	-	-	-	-	-	5	-
BeO	-	-	-	-	-	-	-	-	-	1
Accelerator (TMTD)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Accelerator (MBT)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 6.4 Composition of the s-SBR compounds (phr) with different metal oxides

Compound	1	2	3	4	5	6	7
s-SBR (Buna VSL 2525)	100	100	100	100	100	100	100
Carbon Black (N375 HAF)	50	50	50	50	50	50	50
Arom. Oil (Enerflex 75)	5	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2	2
ZnO	3	-	-	-	-	-	-
MgO	-	3	-	-	-	-	-
CaO	-	-	3	-	-	-	-
BaO	-	-	-	6	-	-	-
Cu(II)O	-	-	-	-	3	-	-
BeO	-	-	-	-	-	1	3
Accelerator (TBBS)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.75	1.75	1.75	1.75	1.75	1.75	1.75

Characterisation.— Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Ageing of the test specimens was carried out in a ventilated oven in the presence of air at 100°C for 3 days according to ISO 188. Compression set tests were performed at 23°C and 100°C for 72 hours according to DIN 53517. Hardness of the samples was measured with a Zwick Hardness-meter Shore A Type, according to DIN 53505.

Swelling measurements were performed in order to obtain information about the crosslink density. The unextracted filled s-SBR samples were swollen until constant weight in toluene at room temperature. The EPDM samples were swollen in decahydronaphthalene at room temperature as well. The crosslink density was calculated according to the Flory-Rehner equation.^{16, 17} Although this equation as such is only valid for non-filled systems, the data obtained with these measurements do yet give an indication of the relative crosslink densities. The Flory-Huggins parameter χ for s-SBR-toluene networks was taken from literature: 0.21.¹⁸ For swollen EPDM-decahydronaphthalene networks the χ -parameter was calculated via the relationship $\chi = 0.121 + 0.278 * v_2$, reported by Dikland,¹⁹ with v_2 = polymer network volume fraction at equilibrium swelling.

Model compound vulcanisation.— Three metal oxides were selected as activator, viz. ZnO, MgO and CaO, and investigated with model compound vulcanisation in two different model compounds: squalene and TME. Preparation of the samples and analysis of the reaction products were done according to the procedures described in Chapter 4. After obtaining the HPLC-chromatogram of the reaction products, the areas of the different peaks were determined and converted into concentrations by using the measured response factors for the several components. Reaction conversions as a function of reaction time were calculated by dividing the concentration of the component by the initial concentration and expressed in percentages. The compositions of the squalene and TME reaction mixtures are listed in Tables 6.5 and 6.6, respectively.

Table 6.5 Squalene model compound systems

	No activator		ZnO as activator		MgO as activator		CaO as activator	
	phr	mmole	phr	mmole	phr	mmole	phr	mmole
Squalene	100	1.217	100	1.217	100	1.217	100	1.217
CBS	1.2	0.023	1.2	0.023	1.2	0.023	1.2	0.023
Sulphur	2	0.039	2	0.039	2	0.039	2	0.039
Activator	-	-	5	0.307	5	0.620	5	0.448
Stearic Acid	2	0.035	2	0.035	2	0.035	2	0.035

Table 6.6 TME model compound systems

	No activator		ZnO as activator		MgO as activator		CaO as activator	
	phr	mmole	phr	mmole	phr	mmole	phr	mmole
TME	100	5.941	100	5.941	100	5.941	100	5.941
TBBS	1.5	0.025	1.5	0.025	1.5	0.025	1.5	0.025
Sulphur	1.75	0.034	1.75	0.034	1.75	0.034	1.75	0.034
Activator	-	-	5	0.307	5	0.620	5	0.448
Stearic Acid	2	0.035	2	0.035	2	0.035	2	0.035

6.4 RESULTS AND DISCUSSION I: EPDM AND S-SBR RUBBER COMPOUNDS

To obtain additional insight in the exact role of the activator in the vulcanisation mechanisms and to find routes to reduce the amount of ZnO in rubber compounds, experiments with metal oxides other than ZnO have been performed, evaluating vulcanisation behaviour and physical properties. Irrespective of the main goal of the present project, to reduce the amount of ZnO for its environmental impact as a heavy metal, in the current chapter not only the more 'eco-friendly' metal oxides, *viz.* MgO and CaO, but also other heavy metal oxides like CdO, CuO and PbO are investigated.

6.4.1 Several Metal Oxides as Activator in EPDM Rubber Compounds

Several metal oxides were investigated as activator in the EPDM masterbatch according to Table 6.3. Figure 6.2 shows the cure characteristics for the EPDM compounds with oxides from the group IIa of Mendelejev's periodic table as activator, *viz.* MgO, CaO and BaO. Compared to ZnO the scorch time increases, the rate and amount of cure decrease drastically. The presence of these oxides resulted in a poorly developed network, comparable with the results without any activator. The results of swelling experiments with different metal oxides are presented in Figure 6.3. A higher swelling percentage corresponding to a lower crosslink density was found for the compounds with MgO and CaO, which is in accordance with the torque measurements.

A combination of metal oxides as activator system has also been tested in EPDM to explore synergistic effects. As mentioned in the introduction, it has been reported that CaO and MgO interfere with the efficient activation by ZnO. The cure characteristics of the compounds with ZnO/MgO and ZnO/CaO as activator combinations are represented in Figure 6.4 and the corresponding results of the swelling experiments in Figure 6.3.

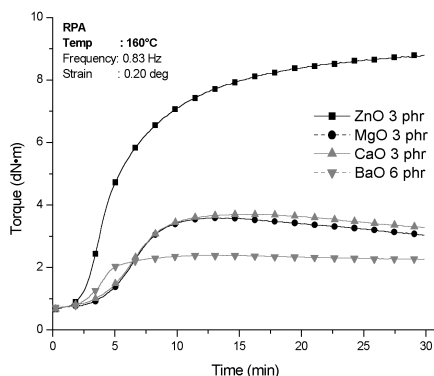


Figure 6.2 Cure characteristics of EPDM compounds with different metal oxides as activator

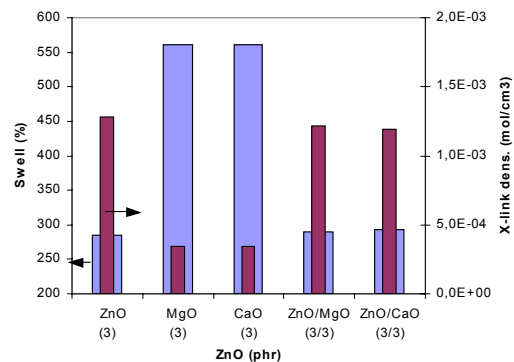


Figure 6.3 Swelling and crosslink density of EPDM compounds with different metal oxides as activator

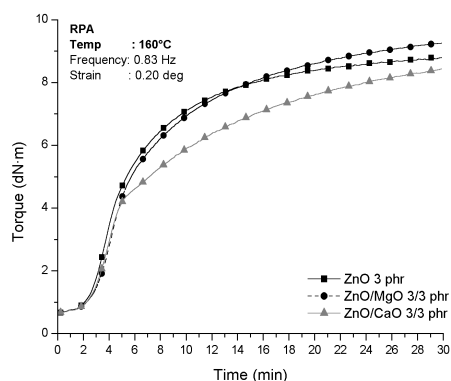


Figure 6.4 Cure characteristics of EPDM compounds with ZnO in combination with MgO and CaO as activator

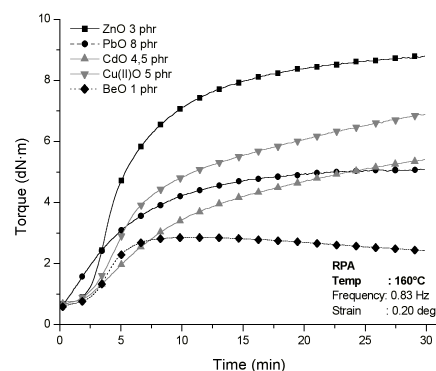


Figure 6.5 Cure characteristics of EPDM compounds with other metal oxides

The cure characteristics of the compounds with ZnO/MgO and ZnO/CaO as activator combinations indicate that only CaO slightly interferes in a negative way with the efficient activation by ZnO. The final states of cure and crosslink densities, as determined with the swelling experiments, are comparable with the reference compound with only ZnO.

Table 6.7 Properties of EPDM compounds with different metal oxides

Compound	1	2	3	4	5
Tensile strength (MPa)	13.3	3.0	4.4	12.2	13.3
Elongation at Break (%)	450	681	776	418	475
Tear strength (N/mm)	37	18	26	38	36
CS 72h/23°C (%)	6	28	25	4	7
CS 72h/100°C (%)	37	99	95	64	61
After 168 Hours / 100°C ageing:					
Tensile strength (MPa)	11.6	11.9	13.2	11.9	12.1
Elongation at Break (%)	180	449	466	232	220

The physical properties of the EPDM compounds with MgO, CaO and the combinations of these metal oxides are presented in Table 6.7. In accordance with the decreased extent of crosslinking, higher values for the elongation at break and compression set as well as lower tensile strength are observed in the compounds with MgO and CaO as activator. Examination of the data of the compounds with activator combinations reveals that neither the addition of MgO nor of CaO to the standard system with ZnO causes any major difference in vulcanisate properties, except for the compression set measured at 100°C. The compression set at elevated temperature is sometimes considered to provide a first indication about the thermal stability or ageing behaviour of the vulcanisates. The CS at 100°C is in both

compounds considerably higher. On the other hand, the values for elongation at break after 168 hours ageing at 100°C are only slightly higher as compared to the ZnO reference system, suggesting a similar high thermal stability, thereby contradicting the thermal behaviour indicated by the data of the compression set at 100°C. So, no conclusions can be drawn from these data.

Figure 6.5 summarises the cure behaviour of EPDM compounds with other (heavy) metal oxides, like PbO, CdO, Cu(II)O, and BeO. The compound with PbO displays a short scorch time and a substantially lower delta torque value compared with ZnO. CdO, which is a member of the zinc group, results in a lower rate of cure and an extent of cure comparable with PbO, albeit with a marching modulus. The latter contradicts earlier statements in literature, that CdO is a good activator for sulphur vulcanisation. Frenkel²⁰ hypothesised that CdO is an effective activator for mercaptobenzothiazole-accelerated vulcanisation, but not an activator for thiuram-accelerated vulcanisation, which is in accordance with the reduced effectivity of CdO in the current and earlier reported experimental results on thiuram/mercaptobenzothiazole-accelerated (TMTD/MBT) vulcanisation. The extent of crosslinking with Cu(II)O takes an intermediate position between CdO and ZnO concerning the rate and extent of crosslinking. Disadvantage of BeO is the extreme high toxicity by inhalation and ingestion, but it was tested anyway to check whether the wurtzite structure is the governing factor regarding the activity of ZnO. The compound with BeO as activator resulted in a considerably lower crosslink density than the reference compound, similar to the compound without activator. This provides evidence that the crystal structure of the metal oxide is not the main factor determining the activity. In view of the eco-toxicity of the majority of these metal oxides, further testing of the compounds was not considered worthwhile and not pursued in the present context.

Overall, close inspection of the data reveals that in EPDM rubber none of the chosen metal oxides is as active as ZnO. In the presence of CaO, MgO, BaO, BeO, and PbO, CdO, Cu(II)O the cure characteristics are inferior to the ZnO system and in some cases even perform the same as in an experiment without any activator, see Figure 3.3 in Chapter 3, indicating that there is less influence of these metal oxides on the reaction. See for example Figure 6.2 for the effect of CaO and MgO relative to ZnO, and Figure 6.5 for the effect of CdO. Though the results indicate that dependent on the intended applications, there exists the potential to replace ZnO by other metal oxides, like e.g. Cu(II)O, as activator in EPDM compounds, it does not constitute a very promising and realistic solution for the ZnO problem from an environmental point of view. It might appear that these alternative metal oxides exert (un)foreseen environmental implications even more problematic than the zinc-based systems.

6.4.2 Several Metal Oxides as Activator in s-SBR Rubber Compounds

The effect of metal oxides was investigated in s-SBR rubber as well, according to the recipes in Table 6.4. As already mentioned in the previous chapters, a TBBS-accelerated vulcanisation system is used in the s-SBR compounds. Figure 6.6 shows, that the scorch times for the s-SBR compounds with MgO, CaO and BaO are comparable with the reference compound with ZnO, but the rates of cure lower and mutually comparable. The extent of crosslinking ($M_H - M_L$) of the compounds is

slightly lower, in particular for the BaO-containing compound. Yet, in contrast with ZnO at longer vulcanisation times no decrease or reversion is observed.

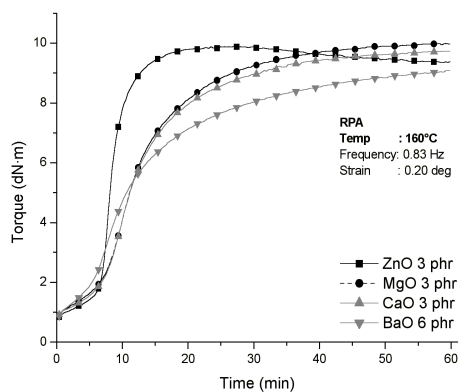


Figure 6.6 Cure characteristics of s-SBR compounds with different metal oxides as activator

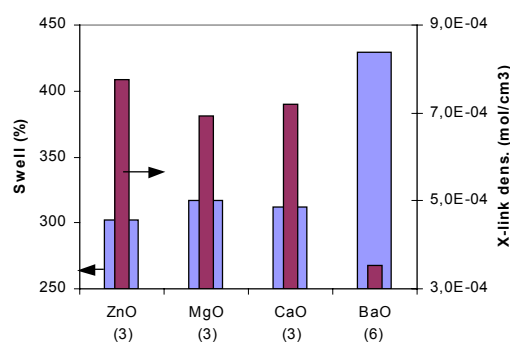


Figure 6.7 Swelling and crosslink density of s-SBR compounds with different metal oxides as activator

Table 6.8 Properties of s-SBR compounds with different metal oxides

Compound	1	2	3
Hardness (Shore A)	67	67	69
M ₂₅ (MPa)	1.2	1.2	1.3
M ₅₀ (MPa)	1.8	1.8	1.9
M ₁₀₀ (MPa)	3.4	3.3	3.4
M ₃₀₀ (MPa)	17.7	17.1	-
Tensile strength (MPa)	21.3	19.4	16.8
Elongation at Break (%)	345	329	296
Tear strength (N/mm)	37	34	34
CS 72h/23°C (%)	6	8	7
CS 72h/100°C (%)	35	35	37
After 168 Hours / 100°C ageing:			
M ₂₅ (MPa)	1.7	1.6	1.6
M ₅₀ (MPa)	2.8	2.6	2.6
M ₁₀₀ (MPa)	6.2	5.0	4.9
M ₃₀₀ (MPa)	-	-	-
Tensile strength (MPa)	16.6	15.6	13.1
Elongation at Break (%)	203	235	211

Swelling percentages and crosslink densities of the s-SBR compounds are depicted in Figure 6.7. The swelling experiments also reveal an increase in swelling

percentage or decrease in crosslink density for use of MgO, CaO and in particular BaO, relative to ZnO. While in EPDM a considerably lower torque level was observed for the compounds with these metal oxides, in s-SBR a more positive effect was found: a grossly comparable torque level and correspondingly a comparable crosslink density.

The physical properties of the s-SBR compounds with different metal oxides and the combinations of activators are presented in Table 6.8. It is evident from the data shown in Table 6.8, that MgO as well as CaO lead to vulcanisate properties, before as well as after ageing, comparable with the ZnO reference compound, and therefore can be considered as good activators for sulphur vulcanisation of s-SBR rubber.

Despite the high toxicity of BeO, the efficiency of BeO as activator of sulphur cure was investigated in s-SBR compounds as well, mainly to study the influence of the crystal structure of the metal oxides. The cure characteristics of compounds with different levels of BeO as activator are given in Figure 6.8. In the presence of BeO the results do not differ very much from the vulcanisates without activator, see Figure 3.1 in Chapter 3, indicating that BeO is not active as an activator in sulphur vulcanisation. It indicates again, that the wurtzite structure is not the governing factor for the activity of ZnO. In contrast with the observations in EPDM compounds, Cu(II)O demonstrated hardly any activating influence in the s-SBR compounds.

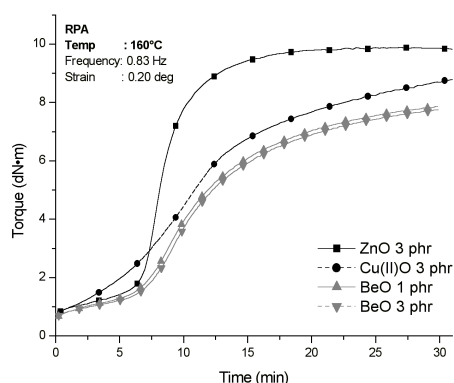


Figure 6.8 BeO and Cu(II)O as cure activator in s-SBR compounds

Overall, substitution of ZnO (Red Seal) in s-SBR compounds by MgO or CaO seems to be possible without large effects on the cure and physical properties, while the addition of Cu(II)O as activator leads to inferior cure characteristics. These findings contrast with the results in EPDM and imply that the activating influence of the metal oxides on the reactions in a benzothiazole- vs. a thiuram/mercaptobenzothiazole-accelerated vulcanisation system is different and less dominant. On the other hand, the difference in nature and reactivity of the rubbers can also (partially) cause the difference in activation induced by the various metal oxides.

6.5 RESULTS AND DISCUSSION II: MODEL COMPOUND VULCANISATION

In the previous paragraphs it was demonstrated, that the curing and physical properties of EPDM and s-SBR compounds with other metal oxides as activator, in most cases deviate considerably from the ones obtained with ZnO. As earlier introduced in Chapter 4, a more detailed knowledge of the effect of the activator on the reactions and mechanisms during the vulcanisation process can be obtained by studying the reactions of the curatives in a rubber-like model environment. In this section the results of Model Compound Vulcanisation experiments with four different metal oxides, *viz.* none, ZnO, MgO and CaO, in two different model compounds, *viz.* squalene and TME are described. The poly-functional compound squalene was used because of its similarity to the real rubber structure, *viz.* the presence of more than one double bond and relatively less end-groups. Squalene was used to specifically study the first stage in the vulcanisation process: curatives development. The mono-functional model 2,3-dimethyl-2-butene (TME) was selected to study three different stages in the vulcanisation process as a function of reaction time: curatives development, crosslink precursor formation, and the crosslinked products development.

The reactions were done as described in the experimental section and in Chapter 4 of this thesis, at 140°C in the presence of a vulcanisation system. Since the reactions were performed in inert atmosphere, the amount of products due to oxidation could be suppressed. The reaction products were analysed with the aid of HPLC at room temperature thereby preventing thermal decomposition of the products.

6.5.1 Squalene Model Compound Vulcanisation

The composition of the squalene samples as a function of reaction time was determined. For every reaction time a separate HPLC-chromatogram was obtained. The concentrations of the curatives can be calculated via the internal standard and the response factors, and can be plotted as a function of reaction time. Figures 6.9 depicts the concentration profile of the accelerator CBS for the four formulations. It can clearly be seen in Figure 6.9, that the various activators influence the decomposition of CBS differently. Without activator no decomposition of the accelerator CBS is observed in the first 20 minutes. MgO as activator causes a very fast decomposition of CBS: within 5 minutes all the accelerator is consumed. It is also evident from Figure 6.9 that CaO hardly has any influence on the decomposition of CBS. ZnO takes an intermediate position: a slower decomposition than MgO but faster than CaO. The results are in agreement with the earlier results obtained by Garreta,²¹ who performed similar measurements with ZnO, MgO, CaO and CdO as activator in squalene, Figure 6.10. Although the absolute values do not fully match, similar trends were observed: a very fast decay of CBS in the system with MgO, slightly slower with ZnO and hardly any influence of CaO on the decomposition of the accelerator.

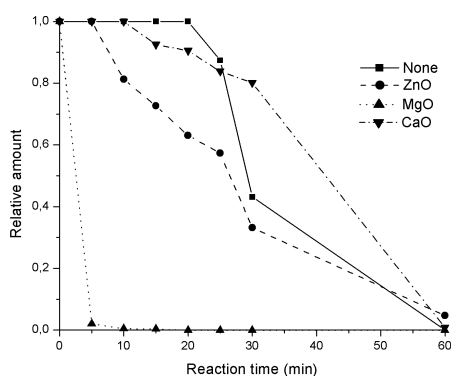


Figure 6.9 Decomposition of CBS in squalene as a function of reaction time, with ZnO, MgO, CaO as activator

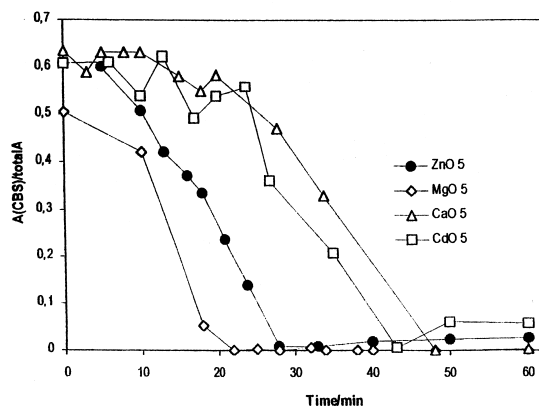


Figure 6.10 Decomposition of CBS in squalene as a function of reaction time with several metal oxides as reported by Garreta²¹

A very fast decay is observed in the sulphur concentration in the first five to ten minutes for all systems, Figure 6.11. In this stage the sulphur is incorporated in the accelerator during the first 10 minutes to form polysulphidic species. The sulphur content in the systems with ZnO and MgO shows similar incorporation behaviour, while with CaO the profile is comparable with the non-activated system. In the presence of CaO the rate of formation of active sulphurating species is lower, as indicated by the slower decomposition of the accelerator in Figure 6.9, and therefore a slower decay of sulphur is observed.

MBT is formed during the course of the reaction as decomposition product of the accelerator and as a side product from the transformation of a crosslink precursor into a crosslink. Since MBT is not present initially, the amounts are related to the maximum amount that can be formed if all CBS would transform into MBT. A relative amount of 0.5 suggests a 50% conversion of the CBS into MBT. Although in the HPLC system used, MBT and MBTS have the same retention time, it is assumed that the peak at the retention time of 2 minutes in the HPLC-chromatogram contains only MBT and that the amount of MBTS is negligible. This assumption is justified by several researches.^{21, 22} The concentration profile of MBT for the several metal oxides is shown in Figure 6.12. Only when ZnO is present in the reaction mixture, the MBT concentration remains at a low level, contrary to the case where no activator has been added: MBT tends to accumulate at longer reaction times. This can be explained by the formation of a complex between the zinc ions and MBT: ZnMBT. ZnMBT precipitates in the reaction mixture and is therefore difficult to analyse with HPLC. MgO leads to higher amounts of MBT at shorter reaction times. Presumably, less complex formation between the magnesium ions and MBT occurs, which corroborates the proposition that magnesium has only a slight tendency to form complexes. With CaO present, the MBT concentration follows again grossly the same profile as the non-activated system.

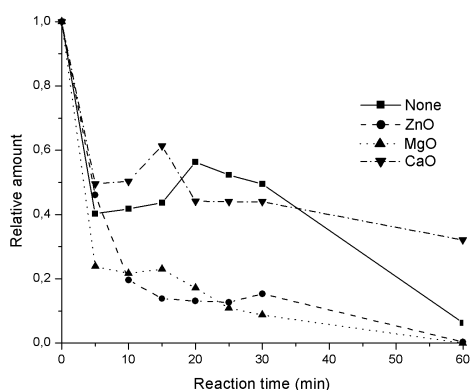


Figure 6.11 Sulphur concentration in squalene as a function of reaction time, without and with ZnO, MgO and CaO as activator

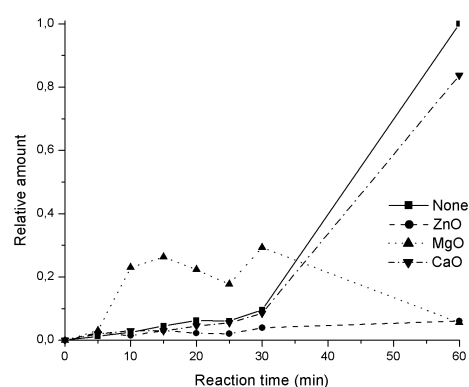


Figure 6.12 MBT concentration in squalene as a function of reaction time, without and with ZnO, MgO and CaO as activator

Overall, several steps in accelerated sulphur vulcanisation, generally accepted to take the course as visualised in Figure 6.13, could be investigated in the presence of metal oxides. The rate of accelerator decomposition is found to be strongly dependent on the metal oxide used, Figure 6.9. An active accelerating complex is formed which interacts with sulphur to generate the active sulphurating agent: a decrease of the sulphur content is observed, Figure 6.11.

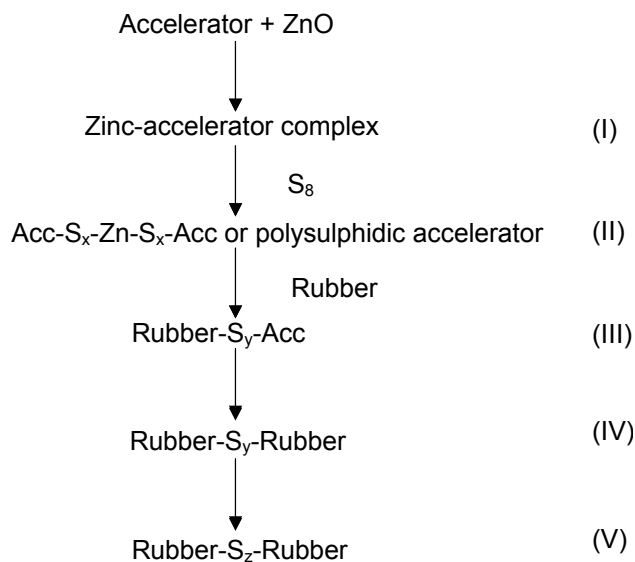


Figure 6.13 General scheme for sulphur vulcanisation²³

A part of the complex forms a (poly)sulphidic crosslink precursor, which is, for this particular model system, difficult to analyse with this HPLC-UV setup. Decomposition of the accelerator and transformation of the precursor into a crosslink yields a side product: MBT. Only in presence of ZnO, complexation between the metal ion and MBT is observed. In the presence of MgO, at a reaction time of 10

minutes the relative amount of MBT is about 25%, which is not exceeded within a reaction time of 60 minutes. It is suggested that MBT partly remains in a complex with the metal ion. CaO is apparently unable to remain bonded to the MBT. The accelerator decomposition and the MBT formation proceeds similar for CaO and in the absence of activator.

6.5.2 TME Model Compound Vulcanisation

To study the formation and decomposition of crosslink intermediates and crosslinking reactions in detail, additional experiments with MgO and CaO as activator were performed in TME-model systems. The same metal oxides as in the squalene system were studied in TME MCV: none, ZnO, MgO and CaO. Figures 6.14 and 6.15 show the concentration profiles of the initial vulcanisation ingredients, TBBS and sulphur, respectively, for samples without and with ZnO, MgO and CaO. In Chapter 4 it was already concluded that ZnO hardly has any influence on the decomposition of TBBS. In the initial stage, a more or less similar profile is observed in the non-activated system and the system with MgO, whereas after 15 minutes a faster decay of the accelerator is observed in the latter system. CaO, on the other hand, seems to impose a slightly delaying effect on the accelerator conversion.

In the TME samples a fast decay of sulphur in the first five minutes is observed, Figure 6.15, comparable with the results obtained in squalene. It is evident from this figure, that the amount of sulphur remains highest in the non-activated and CaO-containing systems. The sulphur concentration profile with MgO present in the system takes an intermediate position, as observed in the squalene samples.

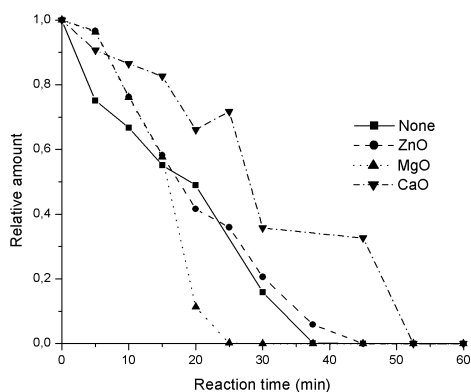


Figure 6.14 Breakdown of TBBS in TME as a function of reaction time, without and with ZnO, MgO and CaO as activator

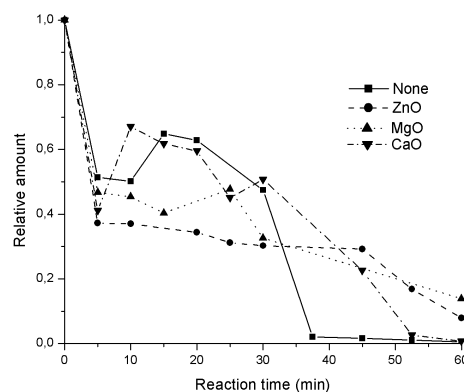


Figure 6.15 Sulphur concentration in TME as a function of reaction time, without and with ZnO, MgO and CaO as activator

Figure 6.16 represents the MBT-development as a function of reaction time. Except for the MgO-containing sample, the formation of MBT starts after a reaction time of approx. 30 minutes. In contrast with the results in squalene samples, a relative amount of 1 for the MBT content is not reached in any of the samples, though in all cases all TBBS has reacted after 40 minutes. As suggested before, the MBT

probably forms a complex with metal ions and precipitates in the reaction mixture or is present as crosslink precursor, bonded to the allylic position of the model molecule via a polysulphidic bridge (Rubber-S_y-Acc).

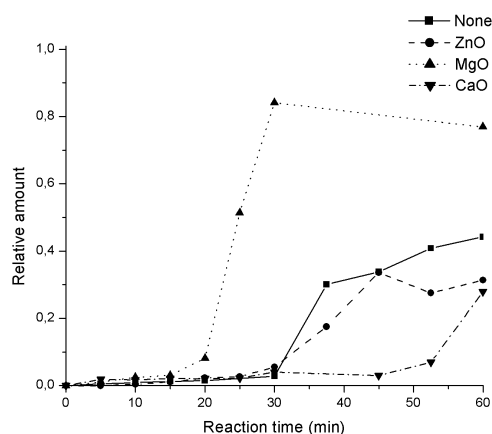


Figure 6.16 MBT concentration in TME as a function of reaction time, without and with ZnO, MgO and CaO as activator

The formation of this intermediate compound can be followed as a function of reaction time. The crosslink precursor development for the systems with different metal oxides as an activator are shown in Figure 6.17.

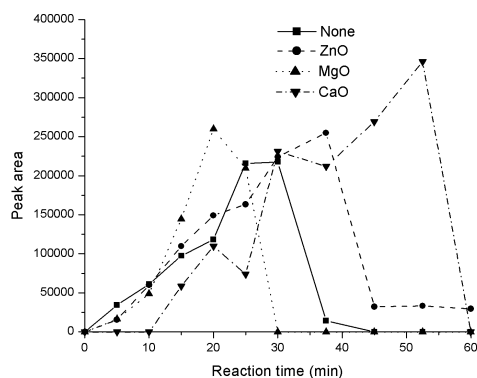


Figure 6.17 Crosslink precursor: TME-S_x-MBT, concentration as a function of reaction time, without and with ZnO, MgO and CaO as activator

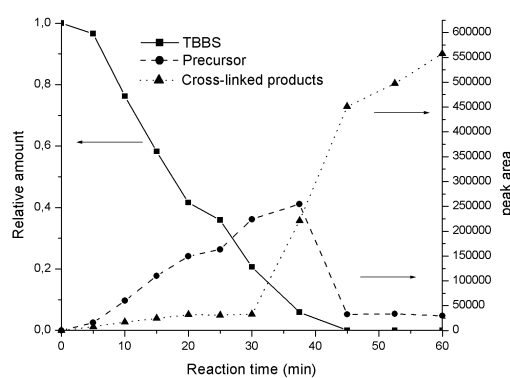


Figure 6.18 TBBS, crosslink precursor, and crosslinked products concentration as a function of reaction time with ZnO

Figure 6.17 indicates no significant differences in rate of crosslink precursor formation in the four systems, which is consistent with the decomposition profile of TBBS as summarised in Figure 6.14. In the non-activated system a maximum concentration of crosslink precursor is observed at approx. 30 minutes reaction time. In the samples with ZnO present, the breakdown of the crosslink precursor is delayed to some extent. In the presence of MgO crosslink precursors are formed slightly faster than with the other metal oxides. This coincides with the faster decomposition of the accelerator TBBS caused by MgO as shown in Figure 6.14. At a reaction time

of 20 minutes a maximum is reached and after 30 minutes the precursor is fully transformed again. With CaO the formation of crosslink precursors is delayed. During the first 10 minutes of reaction hardly any precursors are formed, neither any TBBS consumed. However, the formation of crosslink precursors occurs at a pace comparable to the other metal oxides. A maximum concentration of the crosslink precursor is observed at approx. 50 minutes. CaO apparently delays the formation as well as breakdown of precursors.

Various mechanisms for the conversion of crosslink precursors into crosslinks have been discussed in Chapter 2. The reaction of the intermediate crosslink precursor with another intermediate moiety or through the reaction with polymer chains leads to the formation of polysulphidic crosslinks. For the system with ZnO as an activator, the concentration profiles of TBBS, crosslink precursor and crosslinked products are summarised in Figure 6.18. The symbols used in Figure 6.18 correspond with the symbols depicted in the general vulcanisation scheme, Figure 6.19. In accordance with the concept that the crosslink precursors convert into crosslinks, the formation of crosslinks begins slightly before the concentration of crosslink precursor decreases.

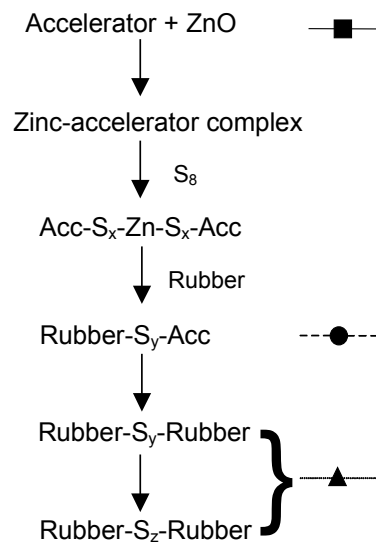


Figure 6.19 General vulcanisation scheme ($z < y$)

Figures 6.20 – 6.23 show the development in time of three of the reaction products, *viz.* S₃-, S₄- and S₅-TME-crosslinks, for the systems with different metal oxides, measured with HPLC. The different (poly)sulphidic crosslinked products cannot be compared absolutely while the response factors of these products were not all determined, therefore only the trends between the different systems can be compared. The peak areas of the crosslinked products for the samples without activator, with ZnO, MgO and CaO as activators are plotted versus reaction time in Figures 6.20, 6.21, 6.22 and 6.23, respectively.

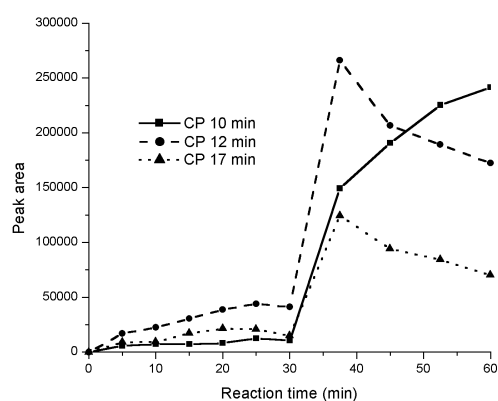


Figure 6.20 Crosslinked products (CP) concentration in TME samples without activator

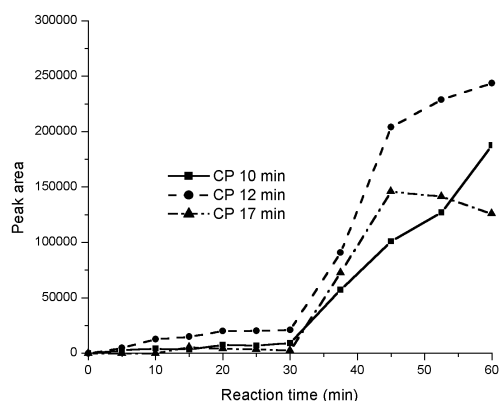


Figure 6.21 Crosslinked products (CP) concentration in TME samples with ZnO as activator

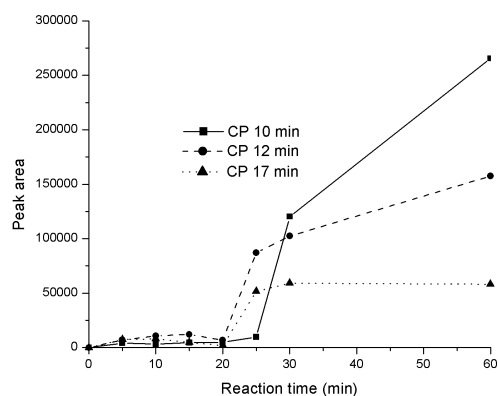


Figure 6.22 Crosslinked products (CP) concentration in TME samples with MgO as activator

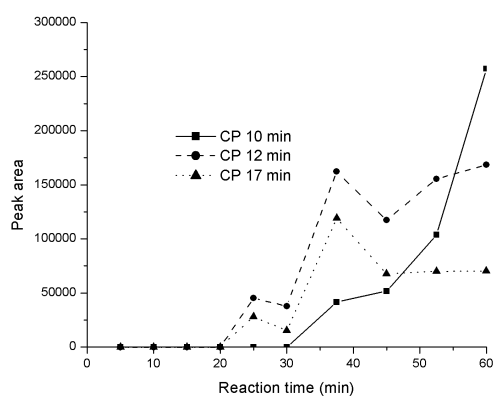


Figure 6.23 Crosslinked products (CP) concentration in TME samples with CaO as activator

The peak at 17 minutes corresponds to the longest sulphur bridge, S_5^- , while the peaks at 12 and 10 minutes represent the S_4^- and S_3^- -TME-crosslinks, respectively, in accordance with the linear correlation between the sulphur rank and the logarithm of the retention time reported by Hann *et al.*²⁴ It is evident from these graphs that the distribution of the crosslinked products is strongly affected by the applied metal oxides. It is noted that in the presence of MgO the formation of crosslinked products initiates at considerably shorter reaction times, which is in accordance with earlier observations on the decomposition of the accelerator and formation and breakdown of the crosslink precursor.

The final step of the scheme in Figure 6.19 is crosslink shortening. To observe this particular phenomenon, the crosslinked products development for the different metal oxides as a function of reaction time should be examined. Crosslink shortening is most clearly observed in the non-activated system: Figure 6.20. The longer crosslinks decrease while the shortest sulphur bridge increases. In all systems the amount of the shortest crosslinks increases with reaction time.

6.5.3 Comparison and Evaluation of Squalene and TME MCV Results

The rate of decomposition of the accelerator in the squalene model compound seems to depend strongly on the activator used. The order of the activators from the fastest to the slowest decomposition is: MgO > ZnO > CaO.

The differences between the rate of decomposition of the accelerator in the presence of metal oxides in TME is not as clear as in squalene. A similar trend is observed in TME as compared to squalene: in the presence of MgO the accelerator decomposes the fastest and in presence of CaO the slowest and even delayed. At short reaction times, however, considerably smaller differences between the activators are observed. Apparently, the accelerator TBBS used in the TME model compounds is more reactive, thereby decreasing the dependence on the activator.

The order of reactivity towards the accelerator is similar to the order of Lewis acidity of the cations. This corroborates the suggested mechanism of complex formation between the cations and the accelerator parts,⁸⁻¹⁰ as earlier described in Chapter 2.

It has appeared that the sulphur concentration profiles in the two model systems are influenced by the presence of metal oxides. The order of sulphur levels at short reaction times observed in squalene, starting with the highest sulphur level, is: CaO >> MgO = ZnO, whereas the order observed in TME is: CaO >> MgO > ZnO. When CaO is present, the sulphur concentration profile is comparable with the non-activated system. It can be concluded that in the presence of CaO hardly any sulphur insertion in the active accelerator complex occurs. On the other hand, in presence of MgO, sulphur is consumed much faster compared to the systems with ZnO present. Presumably, active sulphurating species are formed via sulphur insertion in the active accelerator complex.

The formation of the crosslink precursor, as studied with TME model compounds, proceeded fastest for MgO and slowest for CaO with respect to reaction time. The breakdown of the crosslink precursor as a function of reaction time follows a similar trend: MgO > ZnO > CaO. As mentioned before, it corresponds with the order of the Lewis acidities. It is an indication that the activators play a role in detaching the accelerator part (MBT) of the crosslink precursor via complex formation.

In conformance with the suggested reaction mechanisms, the concentration of crosslink precursors starts to decrease when the crosslinked products are formed. The initially formed polysulphidic bridges tend to reduce the sulphur chain length by releasing sulphur and the formation of shorter crosslinks. Apparently, the applied metal oxide also affects the final crosslink distribution in the model compound samples. With MgO present in the system, the formation of crosslinked products initiates at shorter reaction times and the dominating product appears to be the shortest crosslink, whereas in the ZnO-containing sample the longer crosslinks are formed to a higher extent. The overall product yield in presence of MgO, however, is considerably lower as compared to the ZnO-containing sample.

6.6 RESULTS AND DISCUSSION III: COMPARISON OF THE EFFECT OF METAL OXIDES AS ACTIVATOR IN MCV STUDIES AND RUBBER COMPOUNDS

The crosslinked products as studied with MCV can be evaluated by summing all the peaks of the various sulphur chains, *i.e.* area of S_3 , + area of S_4 etc. Although addition of peak areas is not totally correct, it provides a good idea of the crosslink development. Figure 6.24 shows in a combined graph the crosslink development obtained with the TME model compounds and the rheograms of s-SBR compounds for systems with ZnO, MgO and CaO.

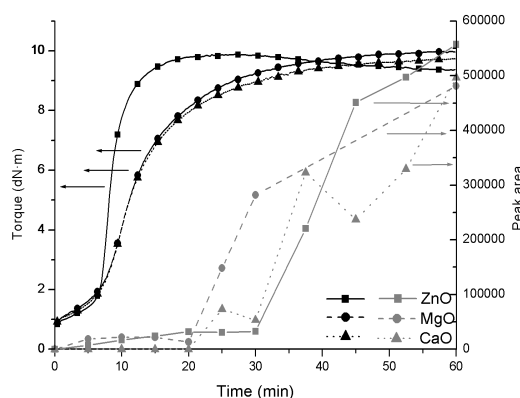


Figure 6.24 Comparison cure-torque of s-SBR compounds with total crosslinked products in MCV of TME as a function of reaction time

At first sight, the MCV results are not at all in agreement with the s-SBR compounds, probably due to many (fundamental) differences between the real rubber and model systems, as extensively described in Chapter 4.3.3 of this thesis. After 60 minutes of MCV the total peak area of the crosslinks in the sample with ZnO, is still increasing and reaches a higher final level than the samples with MgO and CaO, which is in good agreement with the higher torque level observed in the s-SBR compound with ZnO present. The effect of MgO on the onset of crosslinked products formation found in MCV experiments, is not observed however in the cure characteristics of s-SBR compounds. The lower final crosslink density and difference in crosslink distribution in the presence of CaO in particular, is also reflected in the physical properties presented in Table 6.8.

6.7 CONCLUSIONS

To explore possibilities to reduce ZnO levels in rubber compounds, this chapter describes a comprehensive study on the substitution of the conventional activator ZnO by other metal oxides. Both, real rubber and model compound systems are employed to investigate the effect of these metal oxides on the different stages of

the vulcanisation process. It has appeared that CdO, PbO, BaO, CaO, MgO and BeO do not perform as substitutes for ZnO as activator in thiuram-accelerated vulcanisation of EPDM neither show MgO and CaO any synergistic effect with ZnO. Interestingly, the results clearly demonstrate that in s-SBR compounds CaO and MgO are suitable as activator, as they show almost comparable physical properties, albeit with a slightly lower cure rate and state of cure. The addition of Cu(II)O as activator, however, leads to inferior cure characteristics, which contrasts with the results in EPDM. One may cautiously conclude that the activating influence of the metal oxides on the reactions in the benzothiazole-accelerated vulcanisation system is different and less dominant, albeit with the notion that the tested rubbers were also rather different in nature and reactivity.

The second part of the study described in this chapter elucidates the effect of the metal oxides on the different steps in the benzothiazole-accelerated vulcanisation process. In contrast to the squalene experiments, in the TME experiments the activator hardly had any influence on the several reactions rate constants. The role of the metal oxide, usually described as a catalyst for the vulcanisation, in particular for the decomposition of the accelerator, apparently also depends on the type of accelerator and the type of model olefin. Overall, the effectiveness of the metal oxides appears to be determined by its ability to form complexes with the accelerator-moieties.

6.8 REFERENCES

1. J.E. Mark, *Science and Technology of Rubber*, Academic Press, San Diego (1994).
2. M.Z. Rakhman, M.S. Fel'dshstein, *Soviet Rubber Technol.*, **27**, (1968), 17.
3. A.V. Chapman, "*Safe rubber chemicals: Reduction of zinc levels in rubber compounds*", TARRC/MRPRA, (1997).
4. F.K. Lautenschlaeger, K. Edwards, *Rubber Chem. Technol.*, **53**, (1980), 27.
5. P. Versloot, *Rubber Chem. Technol.*, **67**, (1994), 263.
6. A.B. Sullivan, C.J. Hann, G.H. Kuhls, Rubber Division Meeting, American Chemical Society, Toronto, Canada (1991).
7. P.J. Nieuwenhuizen, Thesis, University of Leiden, (1998).
8. R.F. Ohm, "*Rubber Chemicals*", in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York (1997), 460.
9. M.R. Kresja, J.L. Koenig, "*The nature of sulfur vulcanization*", in *Elastomer Technology Handbook*, CRC press, New Jersey (1993), 475.
10. A.Y. Coran, "*Vulcanization*", in *Science and Technology of Rubber*, E.R. Eirich, Ed., Academic Press, San Diego (1978), 291.
11. J.E. Huheey, E.A. Keiter, R.L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper-Collins, (1993).
12. V. Duchacek, A. Kuta, P. Pribyl, *J. Appl. Polym. Sci.*, **47**, (1993), 743.
13. H. Irving, R.J.P. Williams, *J. Chem. Soc.*, (1953), 3192.
14. H. Krebs, *Rubber Chem. Technol.*, **30**, (1957), 962.
15. L. Domka, Krysztafkiewicz, *Int. Polym. Sci. Technol.*, **7**, (1980), T/18.
16. P.J. Flory, J. Rehner, *J. Chem. Phys.*, **11**, (1943), 521.
17. B. Saville, A.A. Watson, *Rubber Chem. Technol.*, **40**, (1967), 100.
18. R.A. Hayes, *Rubber Chem. Technol.*, **59**, (1986), 138.
19. H.G. Dikland, Thesis, University of Twente, (1992).
20. R. Frenkel, V. Duchacek, *J. Polym. Sci.: Polym. Chem. Ed.*, **20**, (1982), 3005.
21. E. Garreta, N. Agullo, S. Borros, *Kautsch. Gummi Kunstst.*, **55**, (2002), 82.
22. A. Mosch, U. Giese, R.H. Schuster, *Kautsch. Gummi Kunstst.*, **56**, (2003) 184.
23. F.K. Lautenschlaeger, K. Edwards, *Rubber Chem. Technol.*, **52**, (1979), 1050.
24. C.J. Hann, *Rubber Chem. Technol.*, **67**, (1994), 76.

Multifunctional Additives as Zinc-free Curatives for Sulphur Vulcanisation[#]

'Curiosity is a delicate little plant which, aside from stimulation, stands mainly in need of freedom.'
Albert Einstein (1879 – 1955)

In previous chapters, alternative metal oxides and zinc complexes as activators for sulphur vulcanisation have been studied. At present, no viable alternative has been found to eliminate ZnO completely from rubber compounds, without significantly jeopardising processing as well as performance characteristics.

The present chapter reports about the application of MultiFunctional Additives (MFA), amines complexed with fatty acids, for sulphur vulcanisation of rubbers. MFAs were developed to function both as an activator and accelerator for sulphur vulcanisation. Good physical properties can be obtained in s-SBR compounds using the MFA/S cure system, albeit at the cost of a shortened scorch time as compared to a regular ZnO/stearic acid system. Inclusion of ZnO lengthens the scorch time, though it reduces the state of cure and ultimate properties. The introduction of metal oxides other than ZnO, *viz.* CaO and MgO, leads to an appreciable improvement in the state of cure. The physical properties are grossly comparable with those obtained with commonly employed vulcanisation ingredients.

Amines play a vital role in the vulcanisation process, hence various amine complexes have been synthesised and investigated as zinc-free curatives in s-SBR compounds. It is observed that the scorch time is related to the basicity of the amines.

The results of Model Compound Vulcanisation (MCV) studies with MFAs reveal a very fast decomposition of the accelerator TBBS and a fast formation as well as breakdown of the crosslink precursor. Furthermore, some major differences in the distribution of the crosslinked products are observed. The conclusion must be drawn, that the chemistry involved in the MFA systems is fundamentally different.

Overall, the results indicate that, dependent on the intended applications (e.g. tyres or roofing foils), there exists a potential to significantly or even completely reduce the need for ZnO with MFA-containing vulcanisation systems.

[#]The work described in this chapter has been submitted for publication in Rubber Chemistry and Technology.

7.1 INTRODUCTION

For sulphur vulcanisation, one of the key processes in the rubber technology, ZnO is generally known as the best activator. It reduces the vulcanisation time and improves vulcanisate properties. The classification of soluble zinc compounds as eco-toxic to aquatic organisms has led to an increasing interest to find potential substitutes. In view of the multiple action displayed by ZnO and zinc compounds, it is rather ambitious to eliminate ZnO completely and it would involve a fundamental change of the current technology of rubber vulcanisation.

In 1983 a new approach to decrease the number and complexity of ingredients used in rubber compounds was proposed by Hepburn and Mahdi.¹⁻⁵ A single compounding ingredient which possesses several functions was added to the formulation: a MultiFunctional Additive (MFA). These compounds were reported to function as simultaneous activator and accelerator for sulphur vulcanisation in their own right, and might therefore represent a promising alternative for zinc-activated curing systems. The general structure of a MFA is $[R'NH_2(CH_2)_3NH_3]^{2+}2[C_{17}H_{33}COO]^-$, a diamine complexed with stearic acid. The mechanism proposed for the multiplicity of functions is shown in Figure 7.1. Upon heating, the compound dissociates into the diamine and a fatty acid, which function as a combined crosslinking agent/accelerator and flow promoter – mould release agent, respectively. It was anticipated that the chemical structure of the MFA contains all the various functional groups necessary to act as activator and accelerator.

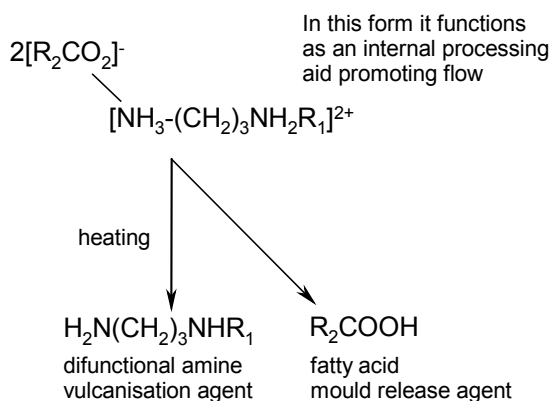


Figure 7.1 Proposed mechanism to account for the multiplicity of functions of a MFA

The evaluation of these different fatty diamine salts was described for a NR/SBR base compound in the presence of ZnO, stearic acid and other additives. It was found that a MFA/S system can substitute a conventional ZnO/stearic acid/CBS/S system, resulting in a combination of improved properties, such as good processability, good physical properties and good cure characteristics. However, the scorch time of these MFA mixtures turned out to be much shorter than these of conventional systems. A delayed-action acceleration system could be obtained by inclusion of ZnO as a scorch inhibitor.

The amount of ZnO used in the MFA formulations was considerably lower than in the conventional systems and therefore MFAs might represent a new route to reduce ZnO. Clearly, for applied and for fundamental reasons, more insight in the MFA systems is desirable. Since Hepburn *et al.* previously confirmed the accelerating and activating effect of MFAs only in NR/SBR compounds, the present research is directed to a detailed investigation of the several functions of MFAs in s-SBR and EPDM compounds. Additionally, the effects of inclusion of more 'eco-friendly' metal oxides on scorch time and cure rate are tested. Particular attention is given to the influence of the type and configuration of the amine-part of the MFA on the curing characteristics, in view of the interaction of amines with sulphur and sulphur containing species and the general notion that increasing the pH leads to activation of the vulcanisation. As it is anticipated that MFA-based cure systems differ fundamentally from the conventional systems, Model Compound Vulcanisation (MCV) studies are performed to elucidate the mechanistic aspects of the MFA-based curing systems.

In summary, there are basically three main objectives for the study described in the present chapter: the first is to show the several functions of MFAs in s-SBR and EPDM compounds; the second objective is to study the influence of the type and configuration of the amine-part of the MFA, by exploiting various amine-fatty acid complexes in s-SBR compounds; the third objective is to gain mechanistic insight in the MFA-based cure systems via MCV studies. Obviously, the general scope of this chapter is to find potential alternatives for the conventional ZnO-containing vulcanisation systems to eliminate ZnO partly or even completely from rubber compounds, without significantly jeopardising processing as well as performance characteristics.

7.2 ROLE OF AMINES IN SULPHUR VULCANISATION

Some background information about amines in the curing process is considered desirable, in order to gain insight in the underlying chemical mechanism of the several functions of MFAs. Several modes of action of amines in the vulcanisation process have been described in literature. Delbrück discovered around 1910 that piperidine and amines in general act as very potent and useful accelerators of vulcanisation, resulting in faster curing and improved properties of the vulcanisate.⁶ Oenslager found that the addition of aniline to a rubber/sulphur formulation greatly increased the rate of vulcanisation and improved the final vulcanisate properties. These amines were the first accelerators for vulcanisation. Apart from toxicity, amines like aniline and piperidine are slow acting accelerators and not used in practice anymore. Various derivatives of aniline were soon developed, which were less toxic and possessed increased acceleration activity.⁷

It was found that several types of (primary) diamines, e.g. amines shown in Figure 7.2, have excellent properties as secondary accelerators. Due to their weak accelerating effect these amines are rarely used as primary (main) accelerator. As

secondary accelerator these amines are used to increase the vulcanisation rate of the primary accelerator. These diamine accelerators facilitate the cure of any sulphur vulcanisable rubber including natural and synthetic rubbers.

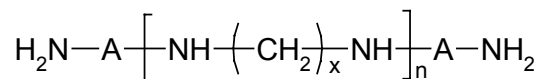


Figure 7.2 General formula of diamines; A represents an alkyl-group containing 2 – 5 carbon atoms, n is an integer between 1 – 4, and x is 2 or 3

7.2.1 Influence of Amines on Reaction Mechanism of Sulphur Vulcanisation

As mentioned before, it is necessary to use ‘activators’ to achieve the full potential of organic accelerators. The system rubber-sulphur-accelerator is activated by the addition of inorganic activators, e.g. ZnO. Organic activators like dibutylamineoleate, 1,3-phenylguanidinephthalate and amines like mono-, dibutylamine (DBA), and dibenzylamine perform a similar activity.

Krebs⁸ postulated that the accelerating properties of amines are related to their base strength. Generally, it was stated that increasing the pH led to activation of the vulcanisation.⁹ Although this would support the theory of an acid-base reaction, in other studies the existence of anionic amino polysulphides was proven, which would indicate direct interaction of amines with sulphur. The reactivity and role of amines during the vulcanisation process is ascribed to their interaction with elemental sulphur and sulphur-containing species. Secondary and tertiary amines are thought to cause an ionic ring-opening reaction with elemental sulphur, as depicted in Figure 7.3.¹⁰ This reaction was considered the basis for the accelerating effect of amines in rubber vulcanisation.

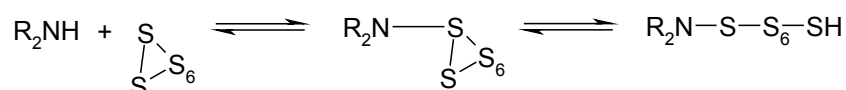


Figure 7.3 Assumed ring opening of elemental sulphur by secondary amines

More recently, it was suggested that no direct reaction between amines and sulphur occurs, but with H₂S or sulphur dioxide: Figure 7.4.¹¹ The highly thiophilic species formed, e.g. HS⁻, subsequently give ionic cleavage of the sulphur ring.¹²

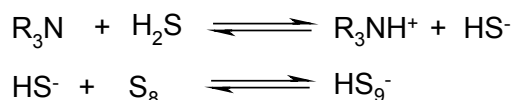


Figure 7.4 Ring opening of elemental sulphur by thiophilic species

In a recent study, the functionality of amines in dithiocarbamate accelerated vulcanisation systems has been proven.¹³ A mechanism is proposed which involves a

nucleophilic attack of an amine on the carbon atom of the thiocarboxy group of a zinc-accelerator complex, resulting in the formation of an amine-dithiocarbamic intermediate. Moreover, Geyser *et al.*¹⁴⁻¹⁶ reported in a series of articles that in TMTD/sulphur cure, in the absence of ZnO an unreactive thiol is formed, which is subsequently reactivated by a reaction with dimethylamine.

Gradwell and McGill¹⁷ suggest that amines cause a certain scorch delay. They propose a mechanism, based on their study of isoprene rubber vulcanisation with CBS, in which the scorch delay is attributed to exchange reactions between the accelerator and benzothiazole-terminated pendant groups to form amine-terminated pendant groups. These amine-terminated pendant groups convert slower to crosslinks as compared to benzothiazole-terminated pendant groups.

Furthermore, it was found that amines act as ligands to stabilise the accelerator complexes, as illustrated in Figure 7.5, usually in conjunction with a fatty acid. Components such as carbon black might limit the stabilising power of the amines by preferential absorption.

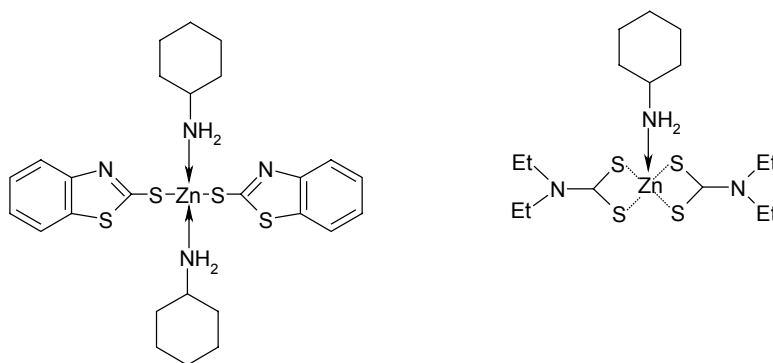


Figure 7.5 Stabilisation of Zn-complexes by amines

Although amines are proven to be cure activators, today there are limitations on the choice of particular amines because of the occurrence of *N*-nitrosamine formation, related to secondary amines and accelerators based on secondary amines.¹⁸⁻²⁰ Most of them are recognised as strong carcinogenic substances in tests on animals and therefore should be avoided.

7.2.2 Factors influencing Effectiveness of Amines

The primary physiochemical property of importance of the amino group is its basicity. The relative basicity of the amine functional group is a function of its ability to share its lone-pair of electrons on the nitrogen, which is a function of the compounds inductive, resonance and steric properties. The hybridisation state and bonding order of a nitrogen atom is an important determinant of basicity. Typical aliphatic amines are more basic than aromatic heterocyclic amines. Groups attached to the amine function influence the base strength as well. Electron-donating groups increase the base strength (increase pKa) while electron-withdrawing groups decrease the base strength (decrease pKa). A third factor which might influence the base strength of the amines is steric hindrance. Attachment of very bulky or multiple

substituents to the basic nitrogen of amines can hinder bond formation with a proton, thereby reducing the basicity. Amines with four hydrocarbon substituents are positively charged and exist as 'permanent cations' referred to as quaternary ammonium compounds. These compounds are stable and relatively unreactive.

Because of their basicity, amines react with acids to form salts. Salt forms of amines typically are solids and chemically more stable than the parent (free) amines. Salt formation results in formation of a cationic nitrogen centre. Both mineral acids and organic acids are commonly used to form amine salts.

In addition to the basicity, amines are capable of functioning as nucleophiles and participate in displacement reactions with electrophilic compounds.

7.3 EXPERIMENTAL SECTION

Materials.— Solution butadiene-styrene rubber (Buna VSL 2525-0 M) was obtained from Bayer GmbH, Germany. Buna VSL 2525-0 M contains 25 wt % of 1,2-vinyl-butadiene and 25 wt % of styrene; it has a Mooney viscosity, ML (1+4) @ 100°C of 54. Ethylidene norbornene (ENB)-containing EPDM rubber (Keltan 4802) was obtained from DSM Elastomers B.V., the Netherlands. Keltan 4802 contains 52 wt % of ethylene units and 4.3 wt % of ENB; it has a relatively narrow molecular weight distribution and a typical Mooney viscosity, ML (1+4) @ 125°C of 77. As fillers were used: carbon black N-375 HAF, N-550 FEF and N-762 SRF (Cabot B.V.). Aromatic oil (Enerflex 75) was obtained from BP Oil Europe, paraffinic oil (Sunpar 2280) from Sun Petroleum Products Co., and stearic acid from J.T. Baker. Commercially available ZnO Red Seal (Grillo GmbH), MgO (Aldrich) and CaO (Aldrich) was used as received. Sulphur (J.T. Baker) and N-tert-butyl-2-benzothiazolesulphenamide (Santocure TBBS, Flexsys B.V.), 2-Mercaptobenzothiazole (Perkacit MBT, Flexsys B.V.), and Tetramethylthiuram disulphide (Perkacit TMTD, Flexsys B.V.) were also commercial grades and used as such. As a reference MFA, n-tallow-1,3-propanediamine distearate (Duomeen TDO, AKZO Nobel B.V.) was used. The materials used in the model compound experiments are listed in Table 7.1.

Table 7.1 Materials used for model compound vulcanisation

Material	Source
2,3-dimethyl-2-butene (TME)	Aldrich
TBBS	Flexsys
Sulphur	Merck
ZnO pure	Merck
Duomeen TDO (MFA)	AKZO Nobel
MgO	Aldrich
CaO	Aldrich
Stearic Acid	Merck

Table 7.2B Composition of the s-SBR compounds with MFA-based cure systems and with various forms of zinc (phr)

	S3	S10	S11	S12
s-SBR (Buna VSL 2525)	100	100	100	100
Carbon Black (N375 HAF)	50	50	50	50
Arom. Oil (Enerflex 75)	5	5	5	5
Sulphur	1.75	1.75	1.75	1.75
Accelerator (TBBS)	1.5	1.5	-	-
Stearic Acid	2	2	-	-
ZnO (Red Seal)	3	-	-	-
ZnClay	-	5	5	5
CaO	-	3	-	3
MFA Duomeen TDO	-	-	3	3

Table 7.3 Composition of the EPDM compounds (phr) with MFAs

Compound	E1	E2	E3	E4	E5	E6
EPDM (Keltan 4802)	100	100	100	100	100	100
Carbon Black (N550 FEF)	70	70	70	70	70	70
Carbon Black (N762 SRF)	40	40	40	40	40	40
Paraf. Oil (Sunpar 2280)	70	70	70	70	70	70
Stearic Acid	1	-	1	-	-	-
ZnO	-	3	3	1	3	3
MFA	-	-	-	3	3	5
Accelerator (TMTD)	1.0	1.0	1.0	-	-	-
Accelerator (MBT)	0.5	0.5	0.5	-	-	-
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5

Characterisation.— Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Ageing of the test specimens was carried out in a ventilated oven in the presence of air at 100°C for 3 days according to ISO 188. Tear strength was measured with trouser shaped specimens according to ISO 34. Compression set (CS) tests were performed at 23°C and 100°C for 72 hours according to DIN 53517. Hardness of the samples was measured with a Zwick Hardness-meter Shore A type, according to DIN 53505.

Swelling measurements were performed in order to obtain information about the crosslink density. The unextracted filled s-SBR samples were swollen until constant weight in toluene at room temperature. The EPDM samples were swollen in decahydronaphthalene at room temperature. The crosslink density was calculated according to the Flory-Rehner equation.^{21, 22} Although this equation as such is only valid for non-filled systems, the data obtained with these measurements do yet give an indication of the relative crosslink densities. The Flory-Huggins parameter χ for s-SBR-toluene networks was taken from literature: 0.21.²³ For swollen EPDM-

decahydronaphthalene networks the χ -parameter was calculated via the relationship $\chi = 0.121 + 0.278 * v_2$, reported by Dikland,²⁴ with v_2 = polymer network volume fraction at equilibrium swelling.

Model compound vulcanisation (MCV).— The tests can be divided in three parts: experiments with model compound and MFA as a substitute for ZnO only; experiments with MFA as substitute for ZnO and TBBS; experiments with MFA as a substitute for TBBS in combination with different metal oxides. Preparation of the samples and analysis of the reaction products were done according to the procedure described in Chapter 4. After obtaining the HPLC-chromatogram of the reaction products, the areas of the different peaks were determined and converted into concentrations by using the measured response factors for the several components. Reaction conversions as a function of reaction time were calculated by dividing the concentration of the component by the initial concentration and expressed in percentages. The compositions of the TME reaction mixtures are listed in Table 7.4.

Table 7.4 Composition of the TME reaction mixtures (phr)

	M I	M II	M III	M IV	M V
TME	100	100	100	100	100
TBBS	1.2	-	-	-	-
Sulphur	1.75	1.75	1.75	1.75	1.75
MFA	3	3	3	3	3
ZnO	-	-	3	-	-
MgO	-	-	-	3	-
CaO	-	-	-	-	3

7.4 RESULTS AND DISCUSSION I: RUBBER COMPOUNDS

7.4.1 Effects of MFAs in s-SBR Compounds

The several functions of MFAs are investigated in s-SBR compounds and the results presented in this section. Figure 7.6 shows the cure characteristics of s-SBR compounds S3 – S7: with MFA as substitute for ZnO (activator) in combination with TBBS as accelerator; MFA as substitute for both the ZnO and TBBS (accelerator/activator); and MFA as substitute for TBBS (accelerator) in combination with ZnO. For a proper comparison of the data, a reference compound with ZnO as activator and TBBS as accelerator is included. The values of $t_{90} - t_{02}$, called the cure rate index, can be taken as an indication of rate of cure. Figure 7.7 shows the scorch time and cure rate indices for the different recipes. The results of swelling experiments and corresponding crosslink densities are presented in Figure 7.8.

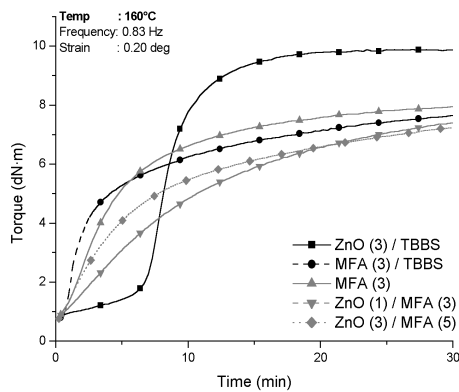


Figure 7.6 Cure characteristics of s-SBR compounds at 160°C with MFA-based cure systems

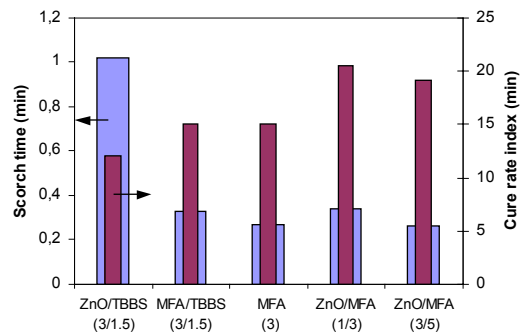


Figure 7.7 Cure rate indices of s-SBR compounds with MFA-based cure systems

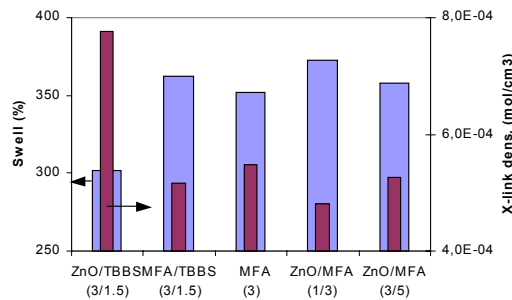


Figure 7.8 Swelling and crosslink density of s-SBR compounds with MFA-based cure systems

The rate of cure of the MFA systems without ZnO in s-SBR compounds is more or less comparable with the standard system, albeit with extremely short scorch times. The extent of crosslinking ($M_H - M_L$), however, is significantly lower than for the reference compound, Figure 7.6, as also shown by the swelling data and corresponding crosslink indices in Figure 7.8. In accordance with previous experiments of Hepburn, in Figures 7.6 and 7.7 the retarding influence of ZnO, S6 and S7, on the cure rate is clearly visible. The very short scorch times of these last compounds are grossly comparable with the MFA compounds S4 and S5, but a lower rate and state of cure is found, as also shown in Figure 7.8 demonstrated by the lower crosslink density. The physical properties of the s-SBR compounds with MFA-based vulcanisation systems are given in Table 7.5.

From the physical properties represented in Table 7.5, it can be deduced that the strength properties of all these compounds except S7, are grossly comparable with the reference compound. The properties dependent on the cure state are, however, slightly inferior to the properties of the reference compound: overall the moduli decreased and elongation at break and compression set increased, with the exception of compound S4 with MFA/TBBS, which resulted in lower compression set

values. No major differences with the reference compound were observed after ageing the compounds S4 and S6 for 72 hours at 100°C. For the compounds S5 and S7 after ageing decreased values for tensile strength and elongation at break were found.

Table 7.5 Physical properties of s-SBR compounds with MFA-based vulcanisation systems

Compound	S3	S4	S5	S6	S7
	ZnO/TBBS	MFA/TBBS	MFA	ZnO/MFA	ZnO/MFA
Hardness (Shore A)	67	63	62	62	60
M ₂₅ (MPa)	1.2	1	1.1	1	1
M ₅₀ (MPa)	1.8	1.4	1.6	1.5	1.4
M ₁₀₀ (MPa)	3.4	2.4	3	2.6	2.4
M ₃₀₀ (MPa)	17.7	13.7	15.4	14.1	12.3
Tensile strength (MPa)	21.3	22.3	23.2	23.3	15.8
Elongation at Break (%)	345	428	413	440	357
Tear strength (N/mm)	37	39	40	39	42
CS 72h/23°C (%)	6	4	8	8	10
CS 72h/100°C (%)	35	27	37	33	39
After 72 Hours / 100°C ageing:					
M ₂₅ (MPa)	1.7	1.3	1.5	1.5	1.4
M ₅₀ (MPa)	2.8	2.2	2.6	2.4	2.1
M ₁₀₀ (MPa)	6.2	4.8	6	5	4.3
M ₂₀₀ (MPa)	15.9	14.3	-	13.9	-
Tensile strength (MPa)	16.6	15.6	11.5	16.4	10.2
Elongation at Break (%)	203	212	155	229	185

Besides improving the properties of vulcanised rubbers, ZnO also assists in the processing of uncured rubbers. ZnO is added to rubber formulations to decrease shrinkage of moulded rubber products and maintain the cleanliness of moulds. This aids productivity by increasing the number of moulding cycles between cleaning. This aspect of ZnO-replacement by MFAs was not further pursued in the present context.

Some indications for the cure retardation effect as seen in this study are also found in literature. According to Kimishima,²⁵ the acceleration of aniline is reduced by the presence of ZnO. Kimishima believed that ZnO is capable of absorbing H₂S. As a consequence, the formation of a particular active form of sulphur is retarded or prevented. Another explanation would be the formation of a rather stable sequestered complex of ZnO and MFA, thus delaying the onset of cure.

7.4.2 Effects of MFAs in EPDM Compounds

The accelerator function of MFAs was studied in EPDM compounds as well, evaluating vulcanisation behaviour and physical properties. Due to the lower

reactivity of EPDM compounds, usually a highly reactive curing system is required: e.g. TMTD/MBT. Therefore, it is already anticipated that MFA is less efficient as accelerator in EPDM compared to s-SBR compounds. The compounds E3 – E6, as given in Table 7.3, were mixed according to the procedure described in the experimental section. The cure characteristics of the EPDM compounds with different levels of ZnO and MFA are depicted in Figure 7.9. In addition, Figure 7.10 displays the specific cure rate indices and scorch times. Swelling percentages and crosslink densities of these EPDM compounds are shown in Figure 7.11.

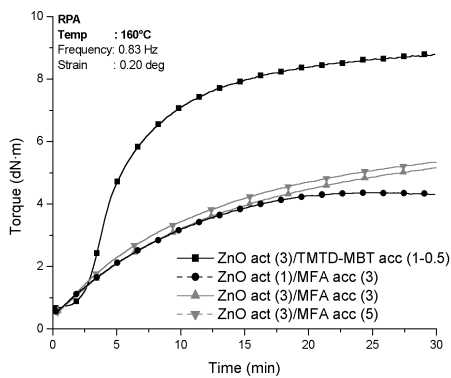


Figure 7.9 Cure characteristics of EPDM compounds at 160°C with different amounts of MFA

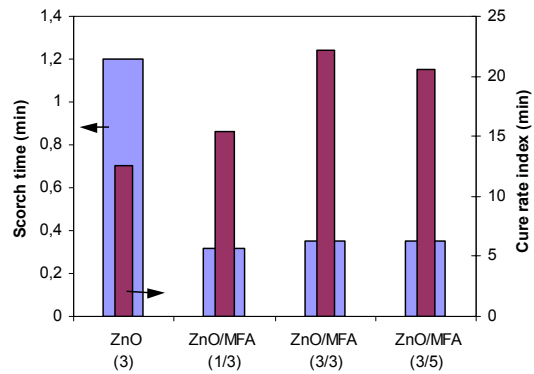


Figure 7.10 Cure rate indices for EPDM compounds with different amounts of MFA

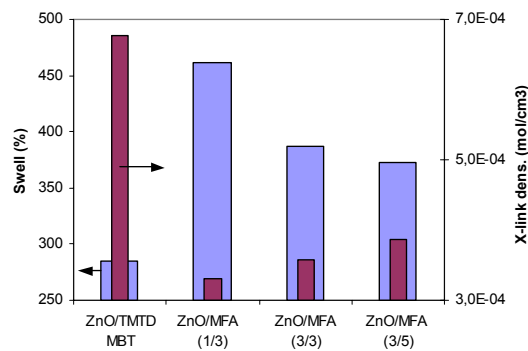


Figure 7.11 Swelling and crosslink density of EPDM compounds with different amounts of MFAs

Figures 7.9 and 7.11 indicate, that in EPDM the MFA is indeed much less active, resulting in a considerably lower state of cure than the reference compound E3. The cure characteristics of the compounds E5 and E6, with 3 phr ZnO in combination with MFA, are comparable. The extent of crosslinking ($M_H - M_L$) of the compound with 1 phr ZnO and 3 phr MFA is slightly lower and the cure curve displays a slight decrease or reversion. The scorch times of the MFA containing EPDM compounds are very short, Figure 7.10. As already expected from the rheograms, a considerably higher swelling percentage was measured for all the

compounds with MFAs. The physical properties of the EPDM compounds with MFA-based vulcanisation systems are given in Table 7.6.

Table 7.6 Physical properties of EPDM compounds with MFA-based vulcanisation systems

Compound	E3	E5	E6
	ZnO/TMTD-MBT (3/1-0.5 phr)	ZnO/MFA (3/3 phr)	ZnO/MFA (3/5 phr)
Hardness (Shore A)	66	57	57
Tensile strength (MPa)	13.3	14.8	14.5
Elongation at Break (%)	450	628	662
Tear strength (N/mm)	37	47	47
CS 72h/23°C (%)	6	11	9
CS 72h/100°C (%)	37	36	36
After 72 Hours / 100°C ageing:			
Tensile strength (MPa)	11.6	14.4	13.7
Elongation at Break (%)	180	505	539

As already expected from the cure characteristics, the elongation at break and the compression set increase significantly due to the lower crosslink density of the MFA-containing vulcanisates. After ageing, the tensile strength and elongation at break values remain higher as compared to the values of the reference compound E3. Therefore, it can be concluded that in EPDM compounds MFAs exert a stabilising influence on the physical properties. Although overall properties are inferior to the conventional compound properties, the results indicate that dependent on the intended requirements there exists a potential to apply MFAs, despite the scorch times are considerably shorter.

7.4.3 Effects of MFAs with several Metal Oxides in s-SBR Compounds

Different, more ecofriendly, metal oxides were evaluated as scorch inhibitors in the compounds containing MFA, according to the recipes S6 – S9 shown in Table 7.2A. For a proper comparison of the data, a reference compound with a conventional vulcanisation system was prepared as well: S3. The cure properties as measured with the RPA2000 are shown in Figure 7.12.

Comparing the cure curves for the several compounds, it becomes clear that in the presence of CaO and MgO as activator the extent of crosslink formation ($M_H - M_L$) is enhanced considerably relative to ZnO and MFA, comparable to the standard vulcanisation system. The higher the delta torque of the compound the more it constrains swelling and hence, the higher is the apparent value of crosslink density, as shown in Figure 7.14. The rates of cure are comparable or slightly lower than the reference compound, Figure 7.13. The torques increase fast at the beginning of cure and keep on increasing, resulting in a marching modulus. The extremely short scorch times are again found, irrespective of whether MFA is used in its role as activator or accelerator, paragraph 7.4.1. The physical properties of s-SBR compounds with

MFA-based cure systems in combination with different metal oxides are summarised in Table 7.7.

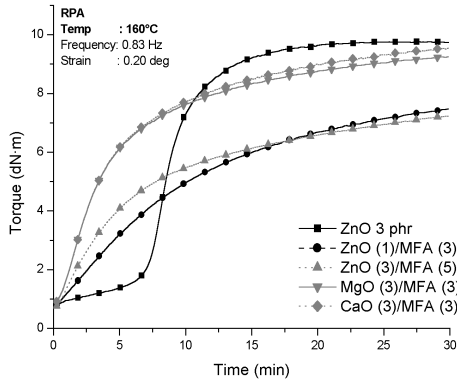


Figure 7.12 Cure characteristics of s-SBR compounds with different metal oxides in combination with MFAs

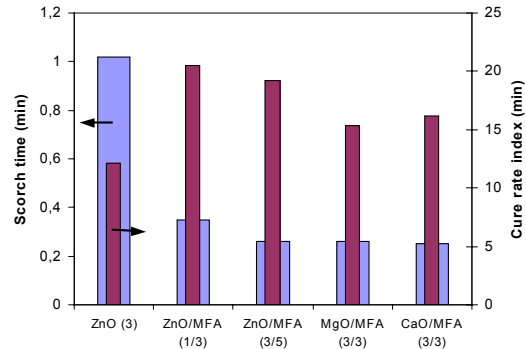


Figure 7.13 Cure rate indices for s-SBR compounds with different metal oxides in combination with MFAs

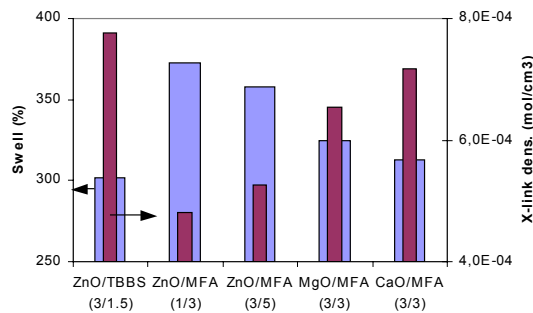


Figure 7.14 Swelling and crosslink density of s-SBR compounds with different metal oxides in combination with MFAs

The compounds with MgO and CaO show the highest delta torque values, in spite of their scorchiness. Furthermore, little difference is noticed between the various properties of these compounds and the reference compound. Ignoring the major drawback of the MFA-based cure systems: the scorchiness, it can be stated that the MFA in combination with CaO or MgO can properly function as accelerator for sulphur vulcanisation without noticeable effects on cure and physical properties.

Table 7.7 Physical properties of s-SBR compounds with MFA-based cure systems with different metal oxides (phr)

Compound	S3	S6	S7	S8	S9
	ZnO/TBBS	ZnO/MFA	ZnO/MFA	MgO/MFA	CaO/MFA
Hardness (Shore A)	67	62	60	65	67
M ₂₅ (MPa)	1.2	1	1	1.2	1.2
M ₅₀ (MPa)	1.8	1.5	1.4	1.8	1.8
M ₁₀₀ (MPa)	3.4	2.6	2.4	3.2	3.5
M ₃₀₀ (MPa)	17.7	14.1	12.3	15.7	16.8
Tensile strength (MPa)	21.3	23.3	15.8	17.6	17.2
Elongation at Break (%)	345	440	357	326	300
Tear strength (N/mm)	37	39	42	37	35
CS 72h/23°C (%)	6	8	10	8	8
CS 72h/100°C (%)	35	33	39	28	35
After 72 Hours / 100°C ageing:					
M ₂₅ (MPa)	1.7	1.5	1.4	1.5	1.5
M ₅₀ (MPa)	2.8	2.4	2.1	2.4	5.2
M ₁₀₀ (MPa)	6.2	5	4.3	4.9	5.2
M ₂₀₀ (MPa)	15.9	13.9		12.7	13.9
Tensile strength (MPa)	16.6	16.4	10.2	15	13.2
Elongation at Break (%)	203	229	185	226	189

7.4.4 Effects of MFAs with ZnClay in s-SBR Compounds

To examine the influence of a newly developed activator: ZnClay on the MFA-containing sulphur vulcanisation system, several compounds were prepared: Table 7.2B. The preparation and testing of this activator is subject of a separate chapter of this thesis: Chapter 8. In order to achieve a delayed action system, the activity of CaO in combination with ZnClay was also tested. After all, the MFA-containing compounds with CaO showed the highest delta torque values and good physical properties, comparable with the reference compound, whereas ZnO has a retarding effect on the cure rate, resulting in an increase in scorch time. The cure characteristics are shown in Figure 7.15.

The rate as well as state of cure of compound S11 with ZnClay and MFA is lower than of the reference compound S3. Addition of CaO leads to a considerable increase in state of cure, but the scorch time becomes even shorter and cure rate lower. The physical properties of the compounds with ZnClay are given in Table 7.8. The physical properties of compound S12 with ZnClay/CaO/MFA/S are grossly comparable with the reference compound S3. The higher value of the elongation at break and compression set are caused by a slightly lower crosslink density, which is in agreement with the lower delta torque values.

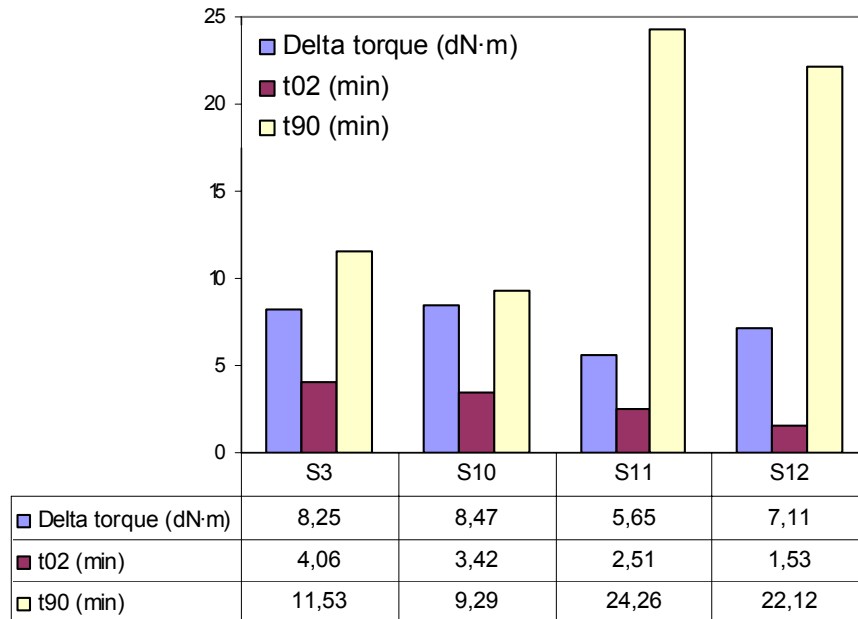


Figure 7.15 Cure characteristics t_{02} (min), t_{90} (min) and delta torque (dN-m) of s-SBR compounds with MFAs in combination with ZnClay

Table 7.8 Physical properties of s-SBR compounds with MFA-based cure systems with different metal oxides (phr)

Compound	S3	S10	S11	S12
	ZnO/TBBS	ZnClay/CaO/TBBS	ZnClay/MFA	ZnClay/CaO/MFA
Hardness (Shore A)	67	69	64	67
Tensile strength (MPa)	21.3	21.0	22.5	20.1
Elongation at Break (%)	345	435	535	450
Tear strength (N/mm)	37	34	42	39
CS 72h/23°C (%)	6	6	8	7
CS 24h/100°C (%)	42	52	49	46

In summary, the data shown in sections 7.4.1 till 7.4.4 reveal that dependent on the intended applications (e.g. tyres or roofing foils) there exists a potential to significantly or even completely reduce the need for ZnO, although in view of the extreme scorchiness of the MFA-based cure systems, additional research is considered essential to develop new MFA-systems having increased scorch times.

7.4.5 Other Amines as MFAs in s-SBR Compounds

The main problem encountered with MFAs so far, is their extreme scorchiness. In order to develop a new MFA, providing a proper balance between scorch time and state of cure and moreover, for a better understanding of the contribution of the amine-part of the MFA to the vulcanisation reactions, additional experiments have been designed and performed. In particular, the influence of three

characteristics of the amine-containing additive on scorch time and rate and state of cure were considered worthwhile to study in detail:

- Sterical hindrance (bulky groups);
- pKa values (basicity);
- Complex formation with a fatty acid, viz. stearic acid.

One of the factors which might influence the reactivity of the amines is steric hindrance. Attachment of very bulky or multiple substituents to the basic nitrogen of amines can hinder bond formation with a proton, thereby reducing the reactivity and increasing the scorch time. Furthermore, the accelerating properties of amines are related to their base strength. In general, curing with sulphur is a process that preferably takes place in an alkaline environment; hence an increase in pH leads to a shorter scorch time and an increase of the rate and state of cure. A higher acidity leads to a longer scorch time, a slower rate and lower state of cure. A third route to achieve some delayed action, or longer scorch time, in curing is to temporarily deactivate the active amine via complex formation. It is anticipated, that the strong cure activation and acceleration effects of the amine group are temporarily rendered ineffective by combination with another group, e.g. a fatty acid like stearic acid.

In line with the objectives of this chapter, to study the influence of the type and configuration of the amine-part of the MFA, two series of amines were selected and tested in s-SBR compounds: Tables 7.9A and B. The amine – fatty acid complexes were synthesised according to the preparation method described in the experimental section.

Table 7.9A Series of primary and secondary amines

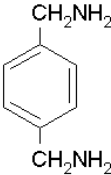
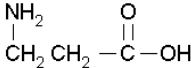
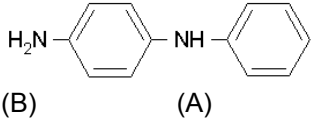
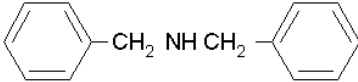
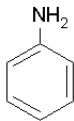
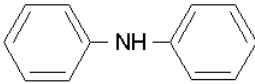
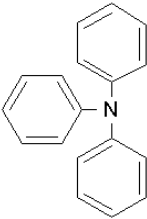
Type	Name	Structure image	pKa
	1,3-Diaminopropane 74.13 g/mol	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	10.94
Primary	p-Xylylenediamine 136.20 g/mol		~9.5
	β-Alanine 89.09 g/mol		2.35
Secondary	N-Phenyl-1,4-phenylenediamine 184.24 g/mol		~0,8-1,3 (A) ~4,6-5,0 (B)
	Dibenzylamine 197.28 g/mol		~6,5

Table 7.9B Series of amines with bulky groups

Type	Name	Structure image	pKa
Primary	Aniline 93.13 g/mol		4.63
Secondary	Diphenylamine 169.2 g/mol		0.79
Tertiary	Triphenylamine (N,N-diphenylaniline) 245.33 g/mol		

The same s-SBR masterbatch as described in Table 7.2, was used to explore the possibility of obtaining a proper delayed action cure system with the ZnO omitted. ZnO 1 phr was substituted by an equivalent amount of amine or amine-complex. The equivalent amounts of amines and amine-complexes were calculated based on fully complexed (di)amines, as represented in Table 7.10. Triphenylamine was used as such and not included in the series of complexed amines.

Table 7.10 Amounts of amines and amine-complexes used as substitution for ZnO in s-SBR compounds

Name	Code	Activator (Phr)	Activator Complex (Phr)
ZnO	A	1	-
1,3-Diaminopropane	B	0.91	7.90
<i>p</i> -Xylylenediamine	C	1.69	8.67
β -Alanine	D	2.19	9.18
<i>N</i> -Phenyl-1,4-phenylenediamine	E	2.26	9.26
Dibenzylamine	F	4.85	11.84
Aniline	G	2.29	9.82
Diphenylamine	H	4.16	11.15
Triphenylamine	I	6.03	-

The compounds were cured to optimum cure t_{90} at 160°C. As for cure behaviour, similar characteristics were observed for the compounds with amines and amines-fatty acid complexes, except for a slightly lower extent of crosslinking in the presence of amines-fatty acid complexes. The cure characteristics of the mixes with the amines-fatty acid complexes are considered representative for the compounds containing the amines as well, and given in Table 7.11. At first glance, it is already

clear from these data that the different amine-complexes behave differently with respect to delta torque as well as cure kinetics.

Table 7.11 Cure characteristics of s-SBR compounds with amine-complexes used as substitution for ZnO

Code	pKa	t ₀₂ (s)	t ₉₀ (s)	M _H -M _L (dN·m)
A	-	240	647	7.93
B	10.9 – 9.0	63	962	5.53
C	9.5	53	614	4.87
D	2.4	216	1021	4.98
E	4.8 – 1.0	146	1003	6.65
F	6.5	168	1017	6.27
G	4.6	225	1092	7.02
H	0.8	271	1172	5.90
I		291		

It is evident from the results that the inclusion of alkaline amines B and C reduces the scorch time drastically compared to the reference compound. The state of cure (M_H-M_L), however, also reduces which can be due to the lubricating effect of the amine-complexes. With increasing acidity, E and F, the scorch times increases, albeit at the cost of a considerably lower rate of cure. Furthermore, a certain improvement in the state of cure is observed. It is reported that strong acids interfere with the vulcanisation mechanism, leading to diminished crosslinking effects.^{26, 27}

The effect of the alkalinity of the amines and amine-complexes on scorch time is summarised in Figures 7.16 and 7.17, respectively. Although for a proper interpretation the rate and state of cure should be taken into account as well, it can be concluded that with increasing pKa the scorch time decreases. The consistency of this observation is evidence that the observed behaviour is a real phenomenon. It is in agreement with the concept as postulated by Krebs,⁸ that the accelerating properties of amines are a function of their base strength. Although this supports the theory of an acid-base reactions, Raman-spectroscopic evidence was obtained for the existence of anionic amino polysulphides, which indicates a direct interaction of amines with sulphur.

The temporarily deactivation of the active amine by complexation with a fatty acid does not seem to function. In general, the complexation of the amines with a fatty acid does not affect the scorch time. The slightly lower states of cure observed for the compounds with the amine-complexes as compared to the compounds with the amines can be attributed to the lubricating effect of the amine-complexes. It is noticed that the secondary amine-complexes tend to give a somewhat higher state of cure and a longer scorch time compared to primary amine-complexes.

Aromatic amines, e.g. N-phenyl-2-naphthylamines and N,N'-disubstituted 1,4-phenylenediamines, are used in the stabilisation of rubber vulcanisates. These antioxidants and antiozonants function as radical scavengers. Generally, it is assumed, see Chapter 2 of this thesis, that in absence of ZnO the vulcanisation is more radical in nature. Therefore, the increase in scorch time observed for the

compound with *N*-Phenyl-1,4-phenylenediamine could be due to a radical scavenging effect of this amine.

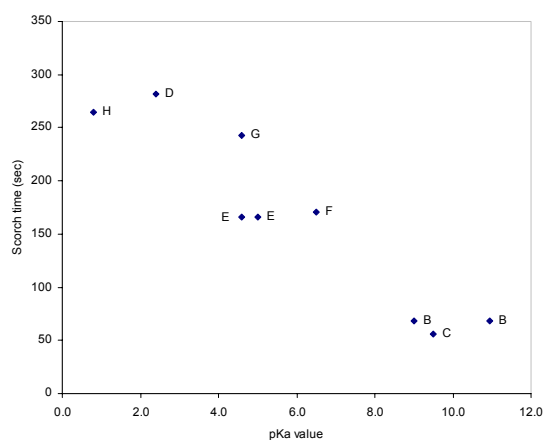


Figure 7.16 Cure characteristics of s-SBR compounds with different amines

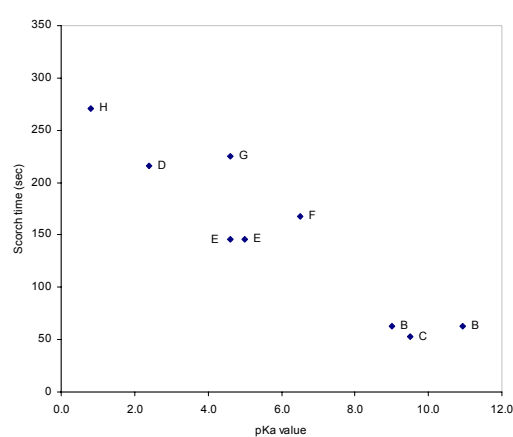


Figure 7.17 Cure characteristics of s-SBR compounds with different amine-complexes

In the second series, the compound with the aniline-complex exhibited the highest value in terms of state of cure. Although the scorch time is comparable with the reference compound, the rate of cure is somewhat lower. With increasing number of bulky substituents, and thereby the steric hindrance, the scorch time increased as well. It is important to stress for this series, that the difference in basicity also might affect the state of cure to a large extent.

In general, the state of cure, representing the crosslink density, obtained with MFA-accelerated vulcanisation is lower than with the conventional system containing ZnO. An explanation could be, that the reactivity of amines is not only towards elemental sulphur, but includes all polysulphidic species. Therefore, the amines might destroy polysulphidic crosslinks as well. Unfortunately, it should be stated that none of the prepared amine – fatty acid complexes had the versatility and combination of functions possessed by the reference MFA, as far as examined. Furthermore, the data shown in paragraph 7.4 reveals, that with MFAs a reduction of ZnO in s-SBR compounds seems to be possible, depending on the exact requirements for a specific compound. At the same time the results pointed out that no general conclusions can be drawn, but that every application requires its own specific optimisation. In particular, attention should be paid to the extreme scorchiness of MFAs and additional research is considered essential for the development of new systems having a proper balance between scorch time and extent of cure.

7.5 RESULTS AND DISCUSSION II: MODEL COMPOUND VULCANISATION

Although valuable results were obtained in the previous studies, the variety of influences/mechanisms proposed make the data difficult to interpret. MCV studies have already shown to be particularly effective tools to elucidate the exact mechanism in curing. Therefore, several functions of MFAs were investigated with MCV and compared with the reference system containing ZnO. Particular attention was given to the influence of several metal oxides in combination with MFA, in view of their performance in s-SBR compounds. The MCV compositions investigated are described in Table 7.4. A typical HPLC-chromatogram of the reaction products of a MFA containing sample is shown in Figure 7.18. The chromatogram was obtained by heating a TME reaction mixture with MFA, TBBS and sulphur (M I, Table 7.4) for 5 minutes at 140°C.

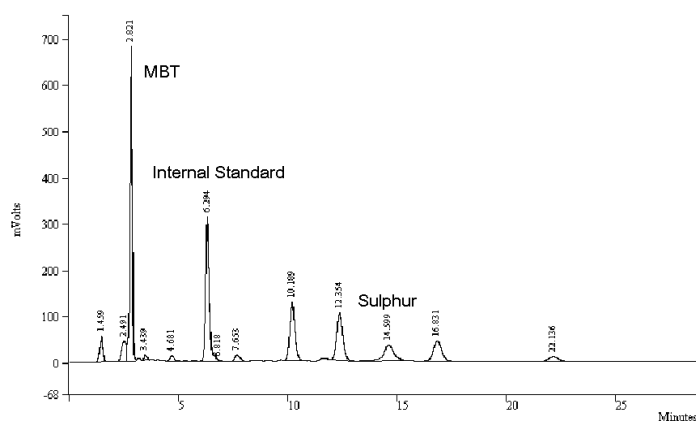


Figure 7.18 HPLC-chromatogram of a MFA sample with TBBS and sulphur after a reaction time of 5 minutes

The concentrations of the curatives can be calculated via the internal standard and the response factors, and can be plotted as a function of reaction time. At the retention time of sulphur, *viz.* 14 minutes, a small peak is observed in the chromatogram. So, the sulphur content can be monitored and plotted as a function of reaction time. This is done for all systems and the result is shown in Figure 7.19. The amounts of the sulphur as represented in the graph are related to their initial quantities.

From Figure 7.19 it can be seen that sulphur is consumed very fast in the presence of MFA. Except for the sample containing ZnO, in all other samples the sulphur is consumed within 20 minutes. With ZnO present in the system, a much slower decay of the sulphur content is observed: more than 30 minutes for complete disappearance. ZnO apparently decreases the rate of sulphur consumption.

Scission of the accelerator has been mentioned as a parameter which determines the length of the scorch time. As discussed in Chapter 4, TBBS has a retention time of 4.2 minutes. In Figure 7.18, no peak is observed at a retention time of 4.2 minutes, which indicates that after a reaction time of 5 minutes all TBBS is

already consumed. The crosslink precursor formation, which is related with the dissociation of the accelerator, and breakdown proceeded also faster under the influence of MFA than with the reference system and could not be detected. In the samples without TBBS completely different reaction mechanisms can be expected. In the present work no attempt was made to directly measure the specific intermediate and by-products of MFA-containing vulcanisation systems. The crosslinked products will be mainly focused on.

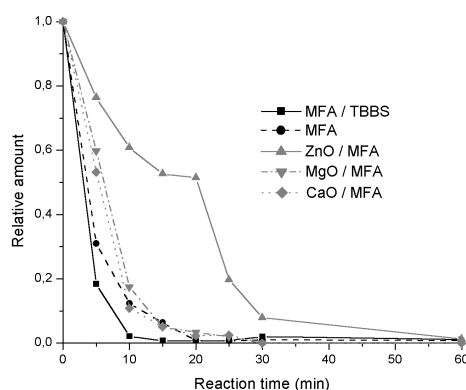


Figure 7.19 Decrease of sulphur in TME samples with MFA

As described before, the crosslinked products can be detected with HPLC measurements in the TME model compound systems. The reaction products which are formed are mainly of the type: TME-S_x-TME. Three new peaks were observed in the chromatograms at retention times of 10, 12, and 17 minutes, corresponding to the reaction products TME-S₃-TME, TME-S₄-TME and TME-S₅-TME, respectively, in accordance with the linear correlation between the sulphur rank and the logarithm of the retention time reported by Hann *et al.*²⁸ No relative or absolute amounts of the products can be plotted, but the trends between the three different systems can be compared. The peak areas of the crosslinked products for the samples with MFA/TBBS/S, MFA/S, MFA/ZnO/S, MFA/MgO/S and MFA/CaO/S as vulcanisation system are plotted versus reaction time in Figure 7.20, 7.21, 7.22, 7.23 and 7.24, respectively.

The Figures 7.20 and 7.21 clearly exhibit the scorchy behaviour of MFA containing systems as observed in rubber compounds. When MFA is used as a substitute for ZnO (activator) in combination with TBBS, within a reaction time of 10 minutes most of the reaction products are formed.

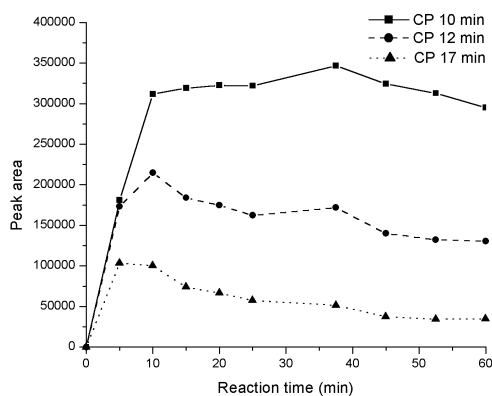


Figure 7.20 Crosslinked products development in a TME sample with MFA, TBBS and sulphur (M I)

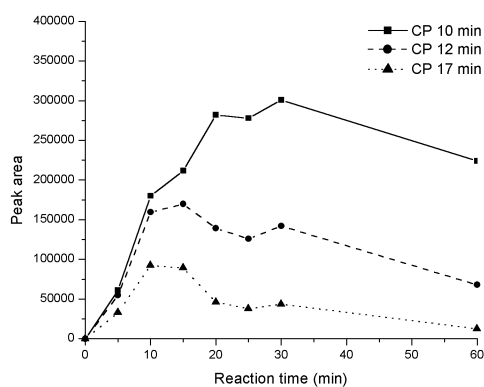


Figure 7.21 Crosslinked products development in a TME sample with MFA and sulphur (M II)

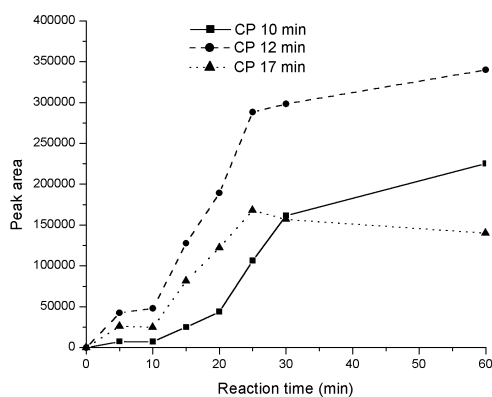


Figure 7.22 Crosslinked products development in a TME sample with MFA, sulphur and ZnO (M III)

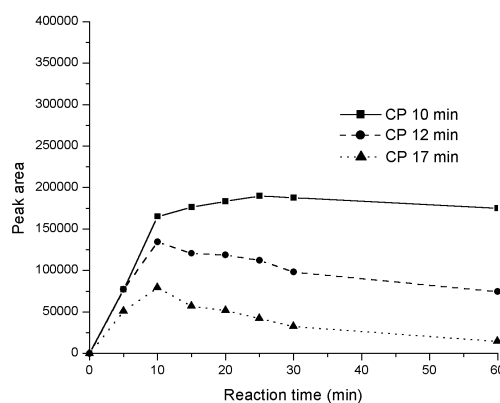


Figure 7.23 Crosslinked products development in a TME sample with MFA, sulphur and MgO (M IV)

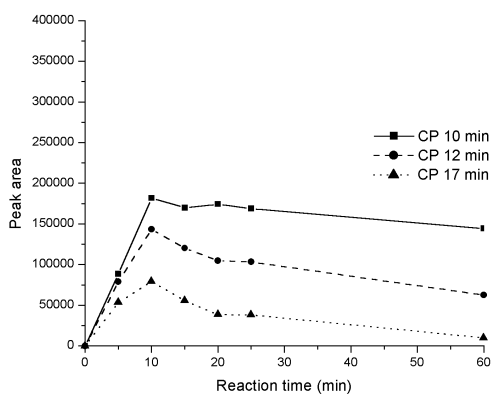


Figure 7.24 Crosslinked products development in a TME sample with MFA, sulphur and CaO (M V)

In accordance with previous experiments, see Figures 7.6 and 7.7, the retardation influence of ZnO on the cure rate is clearly visible in Figure 7.22. Further, the very fast decay of the sulphur content and formation of reaction products at very short reaction times reconfirms the scorchy behaviour of MFAs, as observed before in both s-SBR and EPDM compounds. After a reaction time of 30 minutes, the amounts of vulcanised products stabilise. After a reaction time of 10 minutes a slight tendency towards crosslink shortening is observed for all systems except for the system in which the MFA is used in combination with ZnO. In addition to the difference in scorch time and rate of vulcanisation, ZnO also affects the crosslinked products distribution. While in MFA systems without ZnO preferentially the shorter trisulphidic crosslinks are generated, in presence of ZnO the higher sulphur ranks prevail at the expense of the shorter crosslinks. An explanation although hypothetical, could be complex formation between the zinc-ion and the crosslink as depicted in Figure 7.25. This complex can be stabilised by the amines, thereby reducing the rate of crosslink shortening.

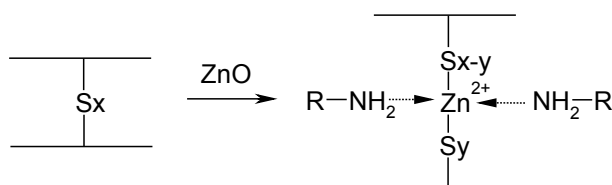


Figure 7.25 Hypothetical complex formation between ZnO and a polysulphidic crosslink

In summary, the use of ZnO in combination with MFA apparently has three consequences: a longer scorch time, a lower vulcanisation rate and a relatively larger amount of longer crosslinks.

When MgO and CaO are added as activator, the rate of product formation as well as the amount of reaction products turns out to be lower, as shown in Figure 7.23 and 7.24. Concerning the distribution of the crosslinked products no significant differences between the MFA systems without ZnO and these two systems are observed. In both systems the trisulphidic reaction product is preferentially formed, comparable with the MFA systems without ZnO.

7.6 RESULTS AND DISCUSSION III: MUTUAL COMPARISON OF THE EFFECT OF MFA IN THE RUBBER COMPOUNDS AND MCV STUDIES

The effectiveness of the MFAs varied considerably between the two rubbers. It was demonstrated, that MFAs might represent a route to reduce ZnO levels in s-SBR rubber compounds. Although the conventional vulcanisation system with ZnO overall still gave the best combination of cure characteristics and physical properties, MFAs assisted by CaO or MgO do provide physical properties, which come close to

those of the conventional system. Depending on specific requirements, in particular the demand for absence of ZnO, these combinations may be employed.

While for s-SBR rubbers the cure rate and physical properties of the MFA-compounds were grossly comparable with the conventional ZnO-compounds, application of MFA in EPDM resulted in a rather underdeveloped network. This can be due to the lower reactivity of EPDM, which usually requires a highly reactive curing system.

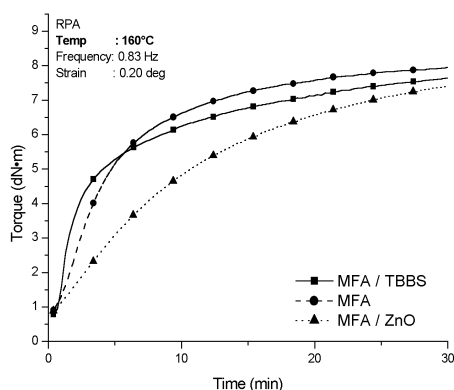


Figure 7.26 Cure characteristics of MFA containing s-SBR compounds with and without ZnO

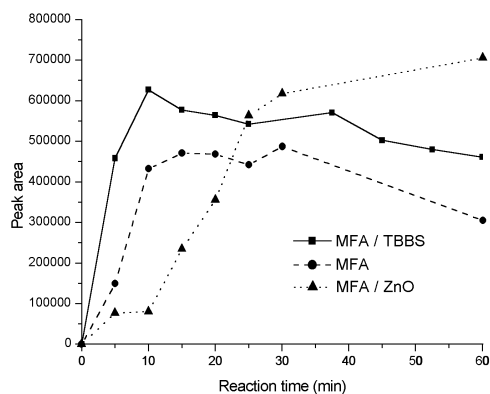


Figure 7.27 Crosslinked products development for MCV in TME samples with and without ZnO

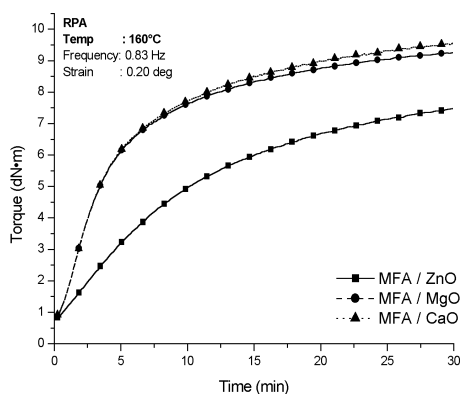


Figure 7.28 Cure characteristics of MFA containing s-SBR compounds with different metal oxides

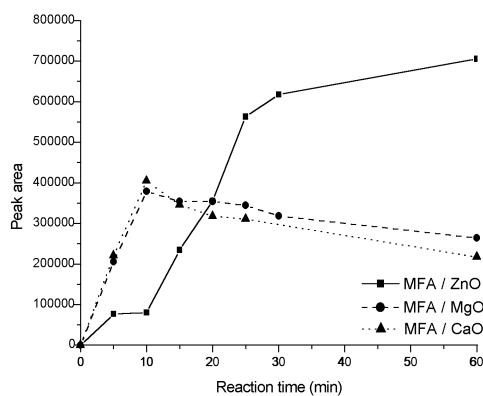


Figure 7.29 Crosslinked products development for MCV in TME samples with different metal oxides

An attempt to gain additional insight in the several effects of MFAs on the formation, distribution and shortening of crosslinks can be made by comparing the results of real rubber compounds with what has been observed in the MCV experiments. With MCV the crosslinked products can be evaluated with HPLC by summing all the peaks of the various sulphur chains, *i.e.* area of S_3 , + area of S_4 *etc.*, where the basic trends, not the absolute values, are meaningful. In Figure 7.26 the rheograms of s-SBR compounds with MFA/TBBS/S, MFA/S and MFA/ZnO/S as vulcanisation systems are depicted, and in Figure 7.27 the crosslinked products

development of the corresponding TME model compounds. The delta torque values and crosslinked products developments of the MFA in combination with various metal oxides are presented in Figures 7.28 and 7.29, respectively.

The rheometer data in Figures 7.26 and 7.28 and the crosslinked products development in Figures 7.27 and 7.29 from MCV correlate reasonably well. The short scorch times, the high cure rates and the retardation effect of ZnO are observed in rubber as well as in model compound studies. The enhancing effect of CaO and MgO on the crosslink density as observed in the rheograms could be proven with MCV studies as well, albeit not completely identical. There are many possible reasons for the difference in curing behaviour, as indicated in Chapter 4 and later in Chapter 8. In addition to these factors, the chemistry involved in the MFA systems is apparently fundamentally different. Other than the obvious difference in scorch delay and cure rate between the conventional and MFA systems, illustrated by the rheometer curves, the most striking analytical difference was the pattern of decomposition of TBBS. Whereas in the conventional system with ZnO a gradual disappearance of the accelerator was observed, see *e.g.* Figure 4.11 in Chapter 4, in these systems with MFA a very rapid disappearance occurs: all the accelerator dissociates within 5 minutes. Furthermore, crosslink precursor formation and breakdown could not be detected. Therefore, it can be concluded that the type and role of reaction intermediates as well as the crosslink formation are considerably different in both systems. Potentially, some fundamental different mechanisms occurring in the different stages of vulcanisation, *e.g.* crosslink formation and main chain modification can be caused by α -substitution, in certain systems accompanied by allylic rearrangement of the double bond, or addition to the double bond, which leads to crosslinks that differ in nature and in length of the sulphur bridge.²⁹

Future work on MFA-containing vulcanisation systems should target on intermediates and accelerator fate analysis. The reaction mechanisms in MFA systems should be studied in detail on a molecular level, which will be very difficult, though not impossible.

7.7 CONCLUSIONS

The application of Multifunctional Additives reported earlier for SBR vulcanisates,¹⁻⁵ is investigated and expanded in this work. Good physical properties can be obtained in s-SBR compounds using the MFA/S cure system, albeit at the cost of a very short scorch time in comparison with a regular ZnO/stearic acid system. These MFAs impart to a rubber compound a combination of improved properties. Inclusion of ZnO in the MFA-system lengthens the scorch time, though it reduces the state of cure and physical properties. The introduction of metal oxides other than ZnO, *viz.* CaO and MgO, leads to an appreciable improvement in the state of cure, but the scorch time is not lengthened. The physical properties are grossly comparable with those obtained with commonly employed vulcanisation ingredients. Experiments with EPDM are mainly focused on the accelerator function of MFAs.

Consistent with the lower reactivity of EPDM compounds, MFAs are, relative to the reference accelerators, much less efficient in EPDM as compared to s-SBR compounds, resulting in a considerably lower crosslink density and inferior vulcanisate properties. Similar extreme scorchiness has been encountered in both s-SBR and EPDM.

Several other types of amines and amine complexes were investigated. The synthesis of these amine–fatty acid complexes was a simple process. Using these amines and amine-complexes instead of the reference MFA, it was observed that with increasing pKa the scorch time decreases, in agreement with the concept that the accelerating properties of amines are a function of their base strength. An increase in the number of bulky substituents leads to a slight increase in scorch time. In general, the temporarily deactivation of the active amine by complexation with a fatty acid does not lengthen the scorch times. None of the pure amines and prepared amine–fatty acid complexes had the versatility and combination of functions possessed by the reference MFA.

By means of Model Compound Vulcanisation, additional information about the reactions and chemical mechanisms in real rubber vulcanisates was obtained. From the results it has become clear, that the reactions in the different stages of the vulcanisation process differ greatly for the conventional and MFA systems. The results reveal *inter alia* a decreased rate of sulphur consumption for the MFA/ZnO system compared to other MFA systems, which is in agreement with the retardation effect of ZnO. A major distinction is also the apparent fast accelerator decay, and fast formation as well as breakdown of the crosslink precursor throughout the vulcanisation process in the presence of MFA. Furthermore, major differences in the distribution of the crosslinked products are observed. Apparently, the chemistry involved in the MFA systems is fundamentally different. The higher delta torque values which are found in the real rubber compounds with MFA in presence of CaO and MgO, are clearly found back in a slightly different manner in the product yield and distribution of the crosslinked products in the MCV studies.

In summary, the results indicate that dependent on the intended applications (*e.g.* tyres or roofing foils) there exists a potential to significantly or even completely reduce the need for ZnO.

7.8 REFERENCES

1. C. Hepburn, M.S. Mahdi, *Plastics and Rubber Processing and Applications*, **6**, (1986), 247.
2. C. Hepburn, M.S. Mahdi, *Plastics and Rubber Processing and Applications*, **6**, (1986), 257.
3. C. Hepburn, M.S. Mahdi, *Plastics and Rubber Processing and Applications*, **6**, (1986), 267.
4. C. Hepburn, M.S. Mahdi, *Kautsch. Gummi Kunstst.*, **39**, (1986), 629.
5. C. Hepburn, M.H. Halim, M.S. Mahdi, *Kautsch. Gummi Kunstst.*, **43**, (1990), 794.
6. J.A. Brydson, *Rubber Chemistry*, Applied Science Publishers, London (1978).
7. R.F. Ohm, "Rubber Chemicals", in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, New York (1997), 460.
8. H. Krebs, *Rubber Chem. Technol.*, **30**, (1957), 962.
9. W. Hofmann, *Rubber Technology Handbook*, Hanser Publishers, New York (1994).
10. P.J. Nieuwenhuizen, Thesis, University of Leiden, (1998).
11. S. Oae, *Organic Sulfur Chemistry: Structure and Mechanism*, CRC Press, Boca Raton, FA (1991).
12. R.E. Davis, *Surv. Progr. Chem.*, **2b**, (1964), 189.
13. A. Dirksen, *J. Appl. Polym. Sci.*, **79**, (2001), 1074.
14. M. Geyser, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 431.
15. M. Geyser, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 439.
16. M. Geyser, M.J. McGill, *J. Appl. Polym. Sci.*, **60**, (1996), 449.
17. M.H.S. Gradwell, W.J. McGill, *J. Appl. Polym. Sci.*, **61**, (1996), 1515.
18. D. Seeberger, G. Raabe, *Kautsch. Gummi Kunstst.*, **42**, (1989), 27.
19. D. Seeberger, *Kautsch. Gummi Kunstst.*, **42**, (1989), 875.
20. D. Seeberger, G. Raabe, *Kautsch. Gummi Kunstst.*, **48**, (1995), 364.
21. P.J. Flory, J. Rehner, *J. Chem. Phys.*, **11**, (1943), 521.
22. B. Saville, A.A. Watson, *Rubber Chem. Technol.*, **40**, (1967), 100.
23. R.A. Hayes, *Rubber Chem. Technol.*, **59**, (1986), 138.
24. H.G. Dikland, Thesis, University of Twente, (1992).
25. T. Kimishima, *Rubber Chem. Technol.*, **1**, (1928), 307.
26. A.Y. Coran, *Rubber Chem. Technol.*, **68**, (1995), 351.
27. F. Ignatz-Hoover, *Rubber World*, **220**, (1999), 24.
28. C.J. Hann, *Rubber Chem. Technol.*, **67**, (1994), 76.
29. R. Seyger, Thesis, University of Twente, (1999).

Zinc Loaded Clay as Activator in Sulphur Vulcanisation[#]

*'The most exciting phrase to hear in science, the one that heralds new discoveries,
is not 'Eureka!' but 'That's funny ...'*
Isaac Asimov (1920 – 1992)

Concern about the release of eco-toxic zinc species from rubbers into the environment leads to an increasing interest in potential substitutes. Although alternative metal oxides and zinc compounds as activators for sulphur vulcanisation have been studied thoroughly, at present no viable alternative has been found to eliminate ZnO completely from rubber compounds, without significantly jeopardising processing as well as performance characteristics.

In this chapter the application of a new activator for sulphur vulcanisation will be discussed. This activator is developed based on the assumption that Zn-species act catalytically rather than being consumed during the sulphur vulcanisation. An increase in the accessibility of Zn²⁺-ions could allow for a considerable reduction of ZnO needed for vulcanisation of rubber compounds. A mineral clay, viz. Montmorillonite, was used as carrier material and loaded with Zn²⁺-ions via an ion-exchange process.

Application in a wide range of natural and synthetic rubbers has been explored. Results demonstrate that this ZnClay can substitute conventional ZnO, grossly retaining the curing and physical properties of the rubber products but reducing the zinc concentration with a factor 10 to 20. Model Compound Vulcanisation studies with squalene and TME as model compounds have been performed to gain an insight into the mechanism of this activator.

It can be concluded that systems with Zn²⁺-ions on a support represent a new and novel route to reduce the zinc level, and therefore to minimise its environmental impact significantly.

[#]Part of this work has been presented at the International Rubber Conference IRC '03, June 30 – July 3, in Nürnberg and has been published in *Kautsch. Gummi Kunstst.*, **56**, (2003), 650. The work described in this chapter has also been presented at the 164th Technical meeting - Rubber Division, ACS, October 14 – 17, in Cleveland (paper no. 22) and has been published in *Rubber Chem. Technol.*, **77**, (2004), 336.

8.1 INTRODUCTION

American and French process zinc oxides (ZnO) are well known additives for rubbers. In rubbers ZnO is primarily added for activating and accelerating sulphur vulcanisation. One of the problems inherent with the use of ZnO, however, is that only a relatively small percentage of the ZnO, is effective and actually undergoes reaction with the other compounding ingredients. If it is assumed that ZnO is distributed in the form of crystal particles in rubber mixes, in principle all the ZnO below the surface is wasted since it only functions as a (expensive) little reinforcing filler. Nieuwenhuizen¹ in his thesis proposed a mechanism in which the ZnO surface functions both as a reactant and as a catalytic reaction template, activating and bringing reactants together. Molecules of accelerators, sulphur and fatty acids diffuse through the rubber matrix and are adsorbed on the ZnO with the formation of intermediate complexes.

In order to increase the activity of ZnO and thereby reduce the necessary amount, the availability of Zn²⁺-ions at the surface of the crystals should be increased. In the so-called highly Active ZnO the mean particle size is decreased and the specific area increased. One of the latest and probably most promising developments in this field, is the so-called Nano ZnO.^{2, 3} Results already indicated the possibility of a considerable reduction of ZnO levels with retention of the properties of the vulcanisates: Chapter 3.3.2.

In the approach chosen for this study, the availability of Zn²⁺-ions is increased by loading a carrier with Zn²⁺-ions, like done in the field of catalysis. A cheap mineral as carrier to provide the bulk material, loaded with Zn²⁺-ions on the surface, to provide the activator function. It is assumed that the increased availability of the Zn²⁺-ions could lead to a considerable reduction of zinc concentrations in rubber compounds and costs.

Mineral fillers, especially clay and calcium carbonate, are widely used in the rubbers. They are used as low-cost additives and raise the modulus and stiffness, but are not generally considered to be reinforcing agents since the ultimate properties of mineral-filled rubber compounds are poor. Some improvement in reinforcement can be achieved by surface treatment so as to improve bonding with the elastomer.⁴ Certain minerals contain naturally exchangeable cations such as calcium, magnesium, potassium or sodium or mixtures thereof. These cations can relatively easily be exchanged with Zn²⁺-ions in order to prepare a zinc ion-saturated clay.

In the present chapter the preparation and utilisation of zinc ion-saturated clays as activator for sulphur vulcanisation is described. The objective is, that this new activator can substitute conventional ZnO, retaining the curing and physical properties of the rubber products and thereby significantly reducing the environmental impact. In the first part of this chapter, the new activator will be used in various rubbers. For these experiments a clay loaded with Zn²⁺-ions was prepared and mixed to evaluate its effectiveness as activator for sulphur vulcanisation.

The second part deals with a study of the reactions and reaction products obtained with this new activator. Besides the curing and physical properties,

additional information about the reactions and mechanisms taking place during rubber vulcanisation is desirable in order to understand the role and effectiveness of this activator for sulphur vulcanisation. Because of the insolubility of the rubber network, it is impossible to characterise the course of vulcanisation reactions in real rubber systems. Therefore, Model Compound Vulcanisation (MCV) has been selected to study the formation of reactive species. In this study 2,3-dimethyl-2-butene (TME) and squalene are used as models. Although TME is not directly comparable to a specific rubber, it is used quite a lot because it has only one type of allylic position and therefore the number of isomers of reaction products is limited. Furthermore, the crosslinked products as well as the crosslink precursors can be separated by HPLC and detected at a wavelength of 254 nm. Squalene is used as a model molecule for NR and simulates, due to its higher molecular weight, an environment more comparable with rubber.

8.2 CLAY MODIFICATION WITH ZINC

The main goal of the following experiments is to develop an activator with improved accessibility of the Zn^{2+} -ions. For that purpose, a clay was loaded with Zn^{2+} -ions. Clay minerals (layered silicates) are nowadays utilised for a wide variety of applications. There are many different types in existence. The most commonly used is Montmorillonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot x\text{H}_2\text{O}$), one of the major components of bentonite and Fuller's earth. A representation of the structure of a layered silicate is given in Figure 8.1.

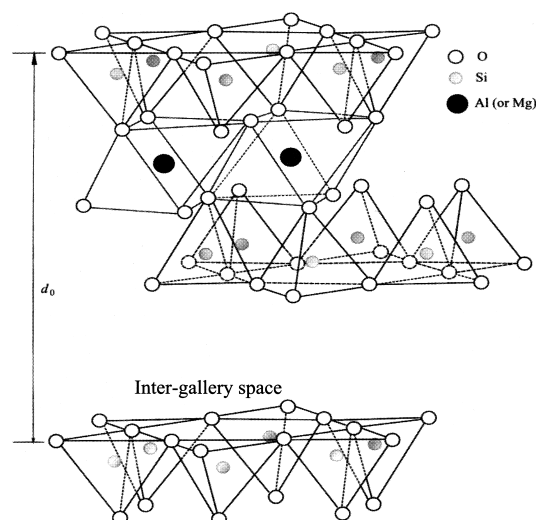


Figure 8.1 Crystalline structure of a 2:1 layered silicate

The Montmorillonite (MMT) crystals have a large net negative charge inside the crystal itself, which is caused by the substitution of Si^{4+} - by Al^{3+} -ions in tetrahedral positions (5–10% in natural MMT) and substitution of Al^{3+} - by Mg^{2+} -ions in octahedral positions. Therefore, it tends to attract any cations, such as calcium or sodium to its surface, in order to neutralise the charge. These metals are held or adsorbed by the

MMT in an ionic bonding and are readily exchangeable by other cations. This ion exchange property is of fundamental importance in most fields in which this clay is used. Extensive series of catalysts have been prepared by chemical treatment of montmorillonite. Characterised by high catalytic activity, these products have shown the ability to promote reactions that usually require Brønsted or Lewis acid catalysis.

All kind of exchange processes have been described in the literature. Brigatti⁵ found that the amount of the exchanged cations depends on the ionic strength of the solution. To further enhance the exchange capacity, the clays should be modified in various ways, such as treatment by inorganic and organic compounds, acid and bases. Acidic treatment of clays has been well known for many years.^{6, 7} In this method the clay material is first pre-treated with an excess of acid to displace the exchangeable cations of the clay with hydrogen ions and convert it to hydrogen clay. The common shortcoming of acidic treatment is the heavy loss of clay material (25 – 30%). In the next step of the process, a certain amount of a salt, in this case a zinc salt, is mixed with the hydrogen clay in order to prepare the zinc ion-saturated clay (ZnClay). When the salt is added to the system, the cations of the salt exchange with the adsorbed hydrogen ions of the hydrogen clay.

The utilisation of these cation-saturated clays, such as zinc-clays and iron-clays, as micronutrient supply for plants has been claimed before.⁸ The role of ZnClay as activator for sulphur vulcanisation has never been reported before.

8.3 EXPERIMENTAL SECTION

Materials.— Solution butadiene-styrene rubber (Buna VSL 2525-0 M) was obtained from Bayer GmbH, Germany. Buna VSL 2525-0 M contains 25 wt % of 1,2-vinyl-butadiene and 25 wt % of styrene; it has a Mooney viscosity, ML (1+4) @ 100°C of 54. Ethylidene norbornene (ENB)-containing EPDM rubber (Keltan 4802) was obtained from DSM Elastomers B.V., the Netherlands. Keltan 4802 contains 52 wt % of ethylene units and 4.3 wt % of ENB; it has a narrow molecular weight distribution and a typical Mooney viscosity, ML (1+4) @ 125°C of 77. As fillers were used: carbon black N-375 HAF, N-550 FEF and N-762 SRF (Cabot B.V.). Aromatic oil (Enerflex 75) was obtained from BP Oil Europe, paraffinic oil (Sunpar 2280) from Sun Petroleum Products Co., and stearic acid from J.T. Baker. Commercially available ZnO (Red Seal, Grillo GmbH) and ZnCl₂ (Aldrich) were used as received. Sulphur (J.T. Baker) and N-tert-butyl-2-benzothiazolesulphenamide (Santocure TBBS, Flexsys B.V.), 2-Mercaptobenzothiazole (Perkacit MBT, Flexsys B.V.), and Tetramethylthiuram disulphide (Perkacit TMTD, Flexsys B.V.) were also commercial grades and used as such. The clay mineral (Montmorillonite) was obtained from Aldrich. The natural montmorillonite has a surface area of 220 – 270 m²/g and a bulk density of 300 – 370 g/l. Clayzic, a MMT support loaded with ~0.35 mmol/g ZnCl₂, was obtained from Aldrich. Clayzic is commercially applied as a catalyst for Friedel-Crafts acylations and related alkylations of aromatic compounds. The materials used in the model compound experiments are listed in Table 8.1.

Table 8.3 Composition of the EPDM compounds (phr) with various activators

Compound	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10
EPDM (Keltan 4802)	100	100	100	100	100	100	100	100	100	100
Carbon Black (N550 FEF)	70	70	70	70	70	70	70	70	70	70
Carbon Black (N762 SRF)	40	40	40	40	40	40	40	40	40	40
Paraf. Oil (Sunpar 2280)	70	70	70	70	70	70	70	70	70	70
Stearic Acid	2	2	2	2	2	2	2	2	2	2
ZnO (Red Seal)	3	-	-	-	-	-	-	3	-	-
ZnCl ₂	-	5	-	-	-	-	-	-	-	-
Pure Clay (MMT K10)	-	-	5	-	-	-	-	-	-	-
Clayzic	-	-	-	7.75	-	-	-	-	-	-
ZnClay	-	-	-	-	2.5	5	15	-	5	10
Accelerator (TMTD)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	-	-	-
Accelerator (TBBS)	-	-	-	-	-	-	-	3	3	3
Accelerator (MBT)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	-	-	-
Sulphur	1.5	1.5	1.5	1.5	1.5	1.75	1.75	1.75	1.75	1.75

Characterisation.— Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Tear strength was measured with trouser shaped specimens according to ISO 34. Compression set (CS) tests were performed at 23°C and 100°C for 72 hours according to DIN 53517. Hardness of the samples was measured with a Zwick Hardness-meter Shore A Type, according to DIN 53505.

Swelling measurements were performed in order to obtain information about the crosslink density. The unextracted filled s-SBR samples were swollen until constant weight in toluene at room temperature. The EPDM samples were swollen in decahydronaphthalene at room temperature as well. The crosslink density was calculated according to the Flory-Rehner equation.^{9,10} Although this equation as such is only valid for non-filled systems, the data obtained with these measurements do yet give an indication of the relative crosslink densities. The Flory-Huggins parameter χ for s-SBR-toluene networks was taken from literature: 0.21.¹¹ For swollen EPDM-decahydronaphthalene networks the χ -parameter was calculated via the relationship $\chi = 0.121 + 0.278 * v_2$, reported by Dikland,¹² with v_2 = the polymer network volume fraction at equilibrium swelling.

Natural Rubber Latex Vulcanisation.— These samples were prepared with LA-TZ NR latex with a rubber content of 60 percent by mass. Commercially available ZnO (Red Seal, Grillo GmbH) was used as such; Active ZnO was obtained from Bayer GmbH, Germany; a ready-made ZnO dispersion with a ZnO content of approx. 50% from Rivièra, The Netherlands, was used as received. Darvan No. 1, sodium polynaphthalene sulfonate, was used to disperse the compounding ingredients and stabilise the latex (R.T. Vanderbilt Co. Inc.). The compositions of the four different activator dispersions are given in Table 8.4. A ready-made vulcanisation dispersion

from Rivièra, containing sulphur and accelerators, with a solid content of approx. 50% was used. The compositions of the NR Latex samples with the various activator dispersions are given in Table 8.5. Four series of films (thickness of ~ 2 mm) were casted and dried overnight. The films were vulcanised in hot air at 100°C for 60 minutes.

Table 8.4 Activator dispersions for NR latex compounds

Dispersion	1	2	3	4
ZnO (Red Seal)	60	-	-	-
ZnO Active	-	60	-	-
ZnClay	-	-	25	-
ZnO (Rivièra)	-	-	-	100
Demineralised water	37.4	200	73.2	-
Darvan No. 1	2.0	2.0	0.8	-
Aqueous ammonia 28%	0.6	1.2	1.0	-
Total	100	263.2	100	100

Table 8.5 NR latex compositions

Compound	NR I	NR II	NR III	NR IV
NR latex LATZ	167	167	167	167
Dispersion 1 (ZnO RS)	6	-	-	-
Dispersion 2 (ZnO Active)	-	7.9	-	-
Dispersion 3 (ZnClay)	-	-	14.4	-
Dispersion 4 (Rivièra)	-	-	-	6
Vulcanisation dispersion	4	4	4	4
Aqueous ammonia 28%	0.6	0.6	0.6	0.6
Total	177.6	179.5	186	177.6

The mechanical properties of the vulcanised NR latex cast films were investigated through stress-strain measurements. Dumb-bell shaped specimen with dimensions according to ISO 37, type 2 were cut from the vulcanised films. Stress-strain measurements were performed at ambient temperature.

Model compound vulcanisation.— Three types of model compound studies were done: experiments with model compound and no activator present; experiments with model compound and ZnO present as activator; experiments with model compound and ZnClay present as activator. The compositions of the squalene and TME reaction mixtures are listed in Tables 8.6 and 8.7, respectively.

Preparation of the samples and analysis of the reaction products were done according to the procedure described in Chapter 4. After obtaining the HPLC-chromatogram of the reaction products, the areas of the different peaks were determined and converted into concentrations by using the measured response factors for the several components. Reaction conversions as a function of reaction time were calculated by dividing the concentration of the component by the initial concentration and expressed in percentages.

Table 8.6 Composition of the squalene reaction mixtures

	No activator		ZnO as activator		ZnClay as activator	
	phr	mmole	phr	mmole	phr	mmole
Squalene	100	1.217	100	1.217	100	1.217
CBS	1.2	0.023	1.2	0.023	1.2	0.023
Sulphur	2.0	0.039	2.0	0.039	2.0	0.039
Activator	-	-	5	0.307	5	0.017 ^a
Stearic Acid	2	0.035	2	0.035	2	0.035

^a The value represents the actual Zn²⁺-content of the ZnClay

Table 8.7 Composition of the TME reaction mixtures

	No activator		ZnO as activator		ZnClay as activator	
	phr	mmole	phr	mmole	phr	mmole
TME	100	5.941	100	5.941	100	5.941
TBBS	1.5	0.025	1.5	0.025	1.5	0.025
Sulphur	1.75	0.034	1.75	0.034	1.75	0.034
Activator	-	-	5	0.307	5	0.017 ^a
Stearic Acid	2	0.035	2	0.035	2	0.035

^a The value represents the actual Zn²⁺-content of the ZnClay

8.4 RESULTS AND DISCUSSION I: ZNCLAY AND RUBBER COMPOUNDS

8.4.1 Preparation and Characterisation of ZnClay

The clay was boiled with 20% HCl solution in a round-bottom flask with a reflux condenser for 4h, the HCl content (as 100%) amounted to 50% of the clay mass. The mixture was diluted by demineralised water and, after separation of the liquid component by decantation, the suspension was neutralised with 25% NaOH solution till pH 6.7 – 7. The sediment was filtered, washed/dialysed in deionised water until excess Cl⁻ was totally eliminated (undetected by an AgNO₃-test), and dried at 65 – 70°C. The clay was saturated with zinc by shaking with a 1 M ZnCl₂-solution. Following the saturation treatment, again the sample was washed/dialysed with deionised water (Cl⁻-free) and dried in air.¹³

XRF measurements were performed to study the elemental surface composition of the natural and modified clays. The changes of the elemental compositions after the several treatment steps are shown in Table 8.8. In the first column the cation composition of the unmodified starting material is given. As seen, natural montmorillonite contains only very small traces of zinc.

The acidic treatment caused indeed dissolution of calcium, iron, potassium and magnesium, as can be seen in the second column. Although a substantial loss of material due to the acidic treatment is observed, the framework of the silicate stayed intact, as indicated by the slight decrease of Si and Al. After the subsequent exchange process of the hydrogen clay with ZnCl₂ the Mg, Ca and Fe concentrations have decreased slightly and the Zn concentration has increased to ~4 wt %. The uptake capacity for zinc of the hydrogen clay was found to be in the range of 4 – 6 wt %, depending on the treatment, in accordance with literature.⁵

Table 8.8 Chemical composition (wt %) of natural and modified Montmorillonite determined with XRF

Element	Starting material	After acidic treatment	ZnClay	Clayzic ^a
Al	10.03	9.70	9.65	10.23
Ca	0.24	0.16	0.06	0.16
Fe	3.79	3.20	3.08	2.36
K	1.49	0.01	1.32	1.14
Mg	1.14	0.97	0.63	0.72
Na	0.22	-	-	-
Si	34.61	34.53	33.33	35.22
Zn	0.01	0.01	4.33	2.60

^a Clayzic is loaded with ZnCl₂ but not washed/dialysed till Cl⁻-free, and therefore has a high Cl⁻-content

Generally, clay minerals offer two possible locations where metals can be adsorbed by ion-exchange: (1) structural and interlayer sites, and (2) external surfaces of the particles. The most preferred position for the Zn²⁺-ions to activate the sulphur vulcanisation, would be on the external surface. While XRF measurements mainly gave insight in the elemental surface composition, ICP-ES experiments provided additional information about the overall composition of the clay, *i.e.* the quantity and position of the Zn²⁺-ions. The overall weight percentage of zinc in the clay, found with ICP-ES, was 5.1 wt %, which is in reasonable accordance with the value obtained with XRF. This is an indication that the zinc ions are mainly located at the surface of the particles.

8.4.2 ZnClay as Activator in Various Rubbers

Properties of s-SBR compounds with ZnClay as activator.— To examine the effect of this new activator on the sulphur vulcanisation several compounds were prepared. The compounds were mixed according to the procedure described in the experimental section. The activity of the unmodified clay material was also tested, as it contains small traces of zinc as well: compound S2. Its cure characteristic is shown in Figure 8.2. Compared to the compound with 3 phr ZnO a much lower cure rate is observed, more or less comparable with non-activated vulcanisation, as shown in Figure 8.2 as well. The slightly earlier increase in torque might be due to a reinforcing effect of the clay.

An analogous commercially available activator Clayzic was included in the series as a reference. To investigate the effectiveness of this Clayzic, first the activating efficiency of pure ZnCl₂ and a ZnCl₂/clay blend were evaluated: compounds S3 and S4. Pure ZnCl₂ was found to be only slightly activating vulcanisation, and no improvement was observed when added in combination with clay. Addition of 7.75 phr Clayzic did not result in a vulcanisation behaviour comparable to the standard system of 3 phr ZnO and even higher amounts of Clayzic led to lower torque developments, as can be seen in Figure 8.3. Apparently, for sulphur vulcanisation of s-SBR, Clayzic is not suitable as an activator.

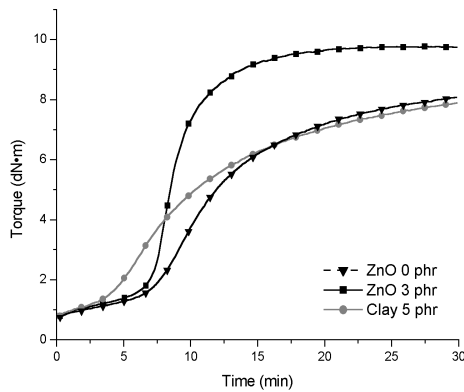


Figure 8.2 Cure characteristics of mixes with ZnO and pure Montmorillonite as activator in s-SBR

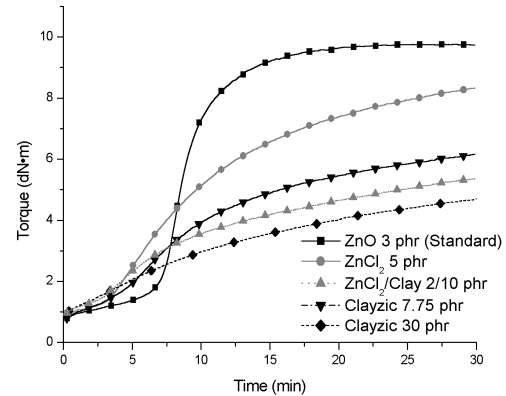


Figure 8.3 Cure characteristics of mixes with ZnCl₂ and Clayzic as activator in s-SBR

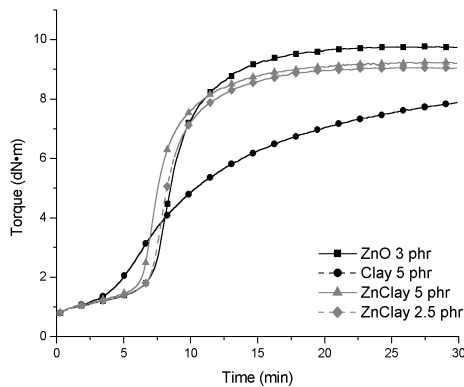


Figure 8.4 Cure characteristics of mixes with ZnClay as activator in s-SBR

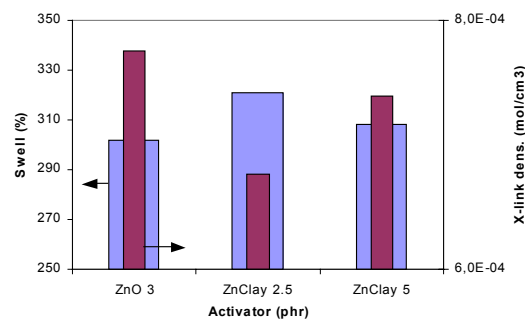


Figure 8.5 Swell and crosslink density of s-SBR compounds with ZnClay as activator

Addition of the newly developed ZnClay as activator leads to much better results. Figure 8.4 represents the cure behaviour of s-SBR compounds with ZnClay as activator. As can be seen from this figure, about 5 phr of ZnClay is sufficient to reach a cure rate and delta torque comparable to the conventional system of phr ZnO. The results of swelling experiments with ZnClay are presented in Figure 8.5. A slightly higher swelling percentage corresponding to a lower crosslink density was found for the compounds with ZnClay, which is in accordance with the torque measurements. The tensile properties of the compounds with ZnClay, S7 and S8 in Table 8.9, are grossly comparable with the standard compound S1. The higher values for the compression set and elongation at break are an indication of a slight undercuring of the test specimens.

Table 8.9 Properties of s-SBR compounds with ZnClay

Compound	S1	S7	S8
Hardness (Sh A)	67	65	68
M ₂₅ (MPa)	1.2	1.1	1.1
M ₅₀ (MPa)	1.8	1.6	1.7
M ₁₀₀ (MPa)	3.4	2.7	3.0
M ₃₀₀ (MPa)	17.7	13.0	13.1
Tensile strength (MPa)	21.3	21.9	21.8
Elongation at Break (%)	345	440	444
Tear strength (N/mm)	37	36	38
CS 72h/23°C	6	10	10

Overall, the cure and physical properties of the s-SBR compounds with the newly developed activator are grossly comparable with the ones obtained with the standard amount of 3 phr ZnO. The zinc content of ZnClay is around 5 wt %, as was shown in Table 8.8. It can be easily calculated that the zinc concentrations in the applied quantities of 5 and 2.5 phr ZnClay correspond with ~0.3 and ~0.15 phr ZnO, respectively. Thus a significant reduction of the zinc concentration with a factor 10 to 20 can be realised, retaining the curing and physical properties of the rubber products as far as examined.

Cure behaviour of EPDM compounds with ZnClay as activator.— The effectivity of the ZnClay as activator in EPDM compounds was studied as well. Due to the lower reactivity of EPDM compounds, a more reactive curing system was required: TMTD/MBT. The compound compositions are given in Table 8.3. The compounds were mixed according to the procedure described in the experimental paragraph. The activity of the unmodified clay was tested for reference, compound E3, as well as the activity of ZnCl₂ and the analogous commercially available activator Clayzic, compounds E2 and E4, respectively. The cure characteristics of these compounds are represented in Figure 8.6.

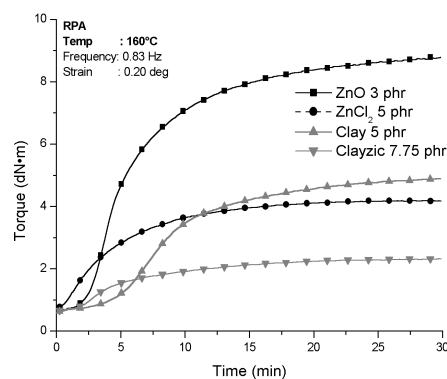


Figure 8.6 Cure characteristics of mixes with various forms of zinc as activators in EPDM

The unmodified clay material apparently activated the vulcanisation as well, albeit at a much lower pace and to a small extent. This can be due to the naturally occurring small traces of zinc on the untreated clay. Figure 8.6 also shows the different effects of ZnCl_2 , in free form or added on a clay: Clayzic. The free ZnCl_2 resulted in a very fast vulcanisation, almost without scorch delay but resulting in a low delta torque value. The cure behaviour of the Clayzic containing compound differed notably from the cure behaviour of the ZnCl_2 and ZnO reference compounds. The torque increased very slow and resulted in a poorly developed network. Compared to the cure behaviour of a compound without activator, shown in Figure 8.7, the vulcanisation even seems to be hindered by the presence of Clayzic.

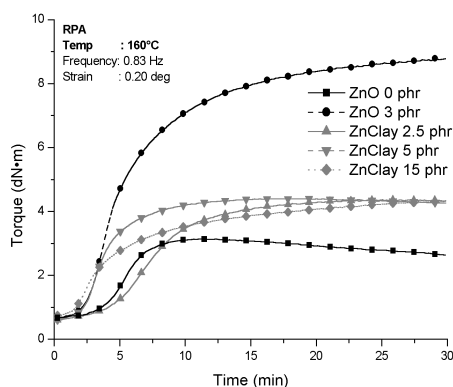


Figure 8.7 Cure characteristics of mixes with ZnClay as activator and TMTD/MBT as accelerators in EPDM

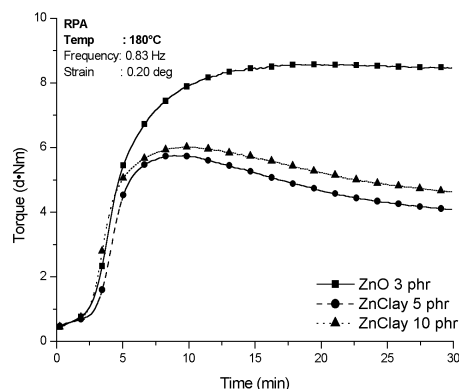


Figure 8.8 Cure characteristics of mixes with ZnClay as activator and TBBS as accelerator in EPDM

The cure characteristics of the compounds with various amounts of the newly developed ZnClay as activator are plotted in Figure 8.7. Comparing the cure curves for the 2.5, 5 and 15 phr ZnClay-containing compounds to the ZnO reference compound, it becomes clear that these compounds did not cure properly. In the first few minutes, the curing properties of the compounds with 5 and 15 phr ZnClay showed a behaviour similar to the ZnO reference compound. At a certain point, the vulcanisation rate clearly decreased and the cure curve levelled off. The absolute value of the torque increase was around 40 – 50% compared to the torque increase of the compound with 3 phr ZnO. The compound with 2.5 phr ZnClay showed a scorch time and vulcanisation rate comparable with the compound without an activator, although the maximum/final torque level was similar to the ones obtained with the compounds with higher levels of ZnClay.

The combination ZnClay as activator and TBBS as accelerator was found to be a suitable substitute for ZnO/TBBS in s-SBR compounds, as shown in the previous paragraph. In order to try to achieve a cure behaviour comparable with the conventional ones, an alternative vulcanisation system, viz. TBBS/S/activator, was applied in EPDM compounds. In Figure 8.8 the cure behaviour of the EPDM compounds with ZnO and ZnClay as activator and TBBS as accelerator is plotted. From these results it can be seen that a significant improvement in the delta torque

value was realised relative to the data shown in Figure 8.7. Apparently, the effectivity of the ZnClay and thereby the curing behaviour of the EPDM compounds depends on the type of accelerator applied.

Effect of ZnClay as activator in various rubbers.— In a similar manner as demonstrated in the previous paragraphs, application of ZnClay as activator has been explored further in a wide range of natural and synthetic rubbers and rubber blends. The main characteristics of the compounds, viz. accelerator type and cure behaviour, are summarised in Table 8.10. The delta torque values of the rubber compounds with ZnClay are expressed as a percentage of the corresponding values for a similar rubber compound with 3 phr ZnO.

Table 8.10 Effect of ZnClay as activator in various rubbers: (++) , very good; (+), good; (-), poor; (--), very poor

Rubber	Accelerator	Type	Cure	Cure Perc. after 30 min., [%]
s-SBR	TBBS	benzothiazolesulphenamide	++	90-95
s-SBR/BR	TBBS	benzothiazolesulphenamide	++	90
s-SBR/BR	MBS	benzothiazolesulphenamide	++	90
e-SBR/BR	MBS	benzothiazolesulphenamide	+	75
e-SBR/BR	TBBS	benzothiazolesulphenamide	+	75
e-SBR/BR	TBBS/MBTS	benzothiazolesulphenamide	+	85
EPDM	TMTD/MBT	thiuram/benzothiazole	--	50
EPDM	TBBS	benzothiazolesulphenamide	-	70
NR	CBS	benzothiazolesulphenamide	--	60
IR	CBS	benzothiazolesulphenamide	--	55
NR/BR	MBTS	benzothiazole	+	75
CR	ETU	thiourea	++	90
IIR	Resin	phenol formaldehyde	++	90
IIR	TMTD	thiuram	--	45
XIIR	MBTS	benzothiazole	+	85
NBR	TMTD/MBTS	thiuram/benzothiazole	+	80

It demonstrates, that an unequivocal comparison between all different rubbers is not possible, because of fundamental differences, e.g. in chemical nature of the rubber and curing systems. Addition of ZnClay as activator in a s-SBR/BR blend led to a torque level comparable with ZnO, confirming the observations in earlier experiments with s-SBR. In e-SBR/BR compounds a lower effectivity of ZnClay was observed. A small reduction in torque level could be compensated, by slightly increasing the level of accelerator or adding a secondary accelerator. In NR and IR compounds the addition of ZnClay as activator resulted in a much less developed network. The pH of the ZnClay might play a role, as sulphur vulcanisation of NR is usually considered to require a basic environment. Another possible factor can be the degree to which the zinc species are either acting catalytically or being consumed during the sulphur vulcanisation. NR and EPDM are known to be quite sensitive to reduction of the ZnO level, while other rubbers, in particular s-SBR, are less sensitive. In the case of NR, there is considerable evidence that much ZnO is

consumed during vulcanisation. In NR/BR blends ZnClay gave rise to a higher torque level, around 75% of the ZnO compound. This can be an indication that due to the presence of BR the vulcanisation mechanisms have slightly changed. In the ETU cured CR compound and the resin cured IIR compound the cure behaviour did not differ significantly between the compounds with ZnO and ZnClay as activator. The benzothiazole-cured XIIR and NBR compounds showed cure characteristics slightly inferior to those obtained with ZnO. Again it is anticipated that the small reduction in torque level could be compensated by increasing the level of accelerator.

Properties of NR latex compounds with ZnClay as activator.— One of the most commonly used accelerators in NR latex technology is zinc diethyldithiocarbamate (ZDEC) due to its beneficial effect on the properties of the corresponding vulcanisate. Besides the zinc salt of one of the various accelerators, also a type of ZnO-dispersion is usually added to the formulation. The substitution of these types of ZnO-dispersion by ZnClay was investigated and the results are presented in this paragraph. Four series of films were prepared with different types of ZnO dispersions according to the procedure described in the experimental section. The latex compositions are given in Table 8.5. The physical properties of the NR latex compounds are presented in Table 8.11.

Table 8.11 Physical properties of NR latex compounds

Compound	I	II	III	IV
Tensile properties (ISO 37)				
M ₁₀₀ (MPa)	0.8	0.8	0.8	0.8
M ₃₀₀ (MPa)	1.5	1.6	1.5	1.4
Tensile strength (MPa)	33.6	29.7	28.8	31.2
Elongation at Break (%)	820	765	810	830
Compression set (ISO 815)				
CS 25%, 24h/70°C (%)	36	37	34	35
CS 25%, 72h/23°C (%)	11	13	10	10

The physical properties of the compound with the ZnClay dispersion, compound III, are grossly comparable with the reference compounds I, II and IV with ZnO dispersions. The value of the tensile strength attained in the ZnClay compound is slightly lower. Films of all four series showed high values of elongation at break in the range of approximately 750 – 850%. The compression set results indicated that a proper degree of vulcanisation was reached within the applied vulcanisation conditions, 1 hour at 100°C.

In conclusion, the results showed that the ZnClay can be regarded as a proper substitute for the ZnO dispersions as far as good film properties are required, and moreover, can realise a significant reduction of the zinc concentration and thus the environmental impact. After all, with a zinc content on ZnClay of around 5 wt %, as was shown in Table 8.8, it can be easily calculated that the zinc concentration in the applied dispersion with ZnClay corresponds with ~0.18 phr. A point of major importance, although not touched upon in this investigation, is maintaining the desired physical properties during service. Oxidative and ozone degradation of NR

latex vulcanisates are complex processes that include a number of chemical reactions and might alter the properties of the vulcanisates drastically. It is known that zinc mercaptobenzothiazole transformation products (ZnMBT) could act as very powerful thermal antioxidants.^{14, 15} Therefore, the lower zinc content in a ZnClay vulcanisate might lead to a reduced thermal stability. This aspect of ZnO-replacement was not further pursued in the present context.

8.5 RESULTS AND DISCUSSION II: MODEL COMPOUND VULCANISATION

In paragraph 8.4.2 it was demonstrated, that the curing and physical properties of the s-SBR compounds with ZnClay as activator, are grossly comparable with the ones obtained with ZnO. However, a more detailed knowledge of the effect of ZnClay on the reactions and mechanisms during the vulcanisation process can be obtained by studying the reactions of the curatives in a rubber-like environment. In this section the results obtained with the three different activator systems, none, ZnO, and ZnClay, in Model Compound Vulcanisation experiments are described. The reactions were done as described in the experimental section and in Chapter 4 of this thesis at 140°C in the presence of a vulcanisation system. The reaction products were analysed with the aid of HPLC. Three different stages in the vulcanisation process were studied as a function of reaction time: curatives development, crosslink precursor formation, and the crosslinked products development.

8.5.1 Curatives

The composition of the samples as a function of reaction time was determined. For every reaction time a separate HPLC-chromatogram was obtained. In Figure 8.9 an example of such an HPLC-chromatogram is shown. The chromatogram was obtained by heating a TME reaction mixture without an activator (Table 8.7) for 15 minutes at 140°C.

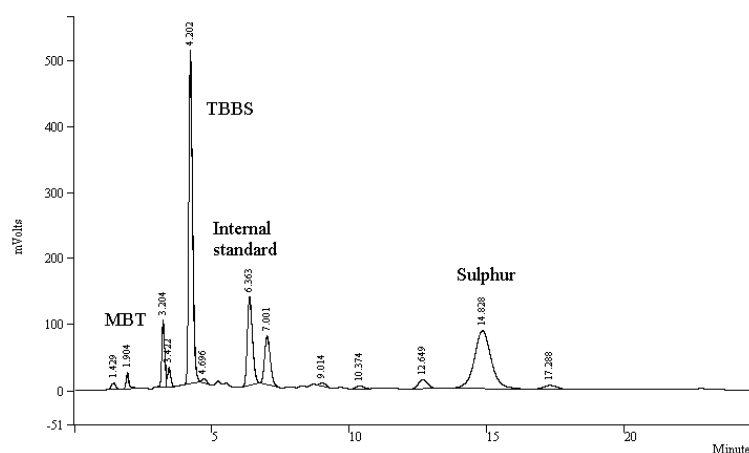


Figure 8.9 HPLC-chromatogram of a TME sample without activator with a reaction time of 15 minutes

The concentrations of the curatives can be calculated via the internal standard and the response factors, and can be plotted as a function of reaction time. Figure 8.10 shows an example of the curative concentrations in a TME reaction mixture as a function of time, as analysed with HPLC. The amounts of the curatives as represented in the graphs are related to their initial amounts. A steady decrease of TBBS can be observed. The formation of 2-Mercaptobenzothiazole (MBT) started at the moment that almost all TBBS was consumed. Since there is no initial amount of MBT, the amount is related to the maximum amount that can be formed if all TBBS is transformed into MBT.

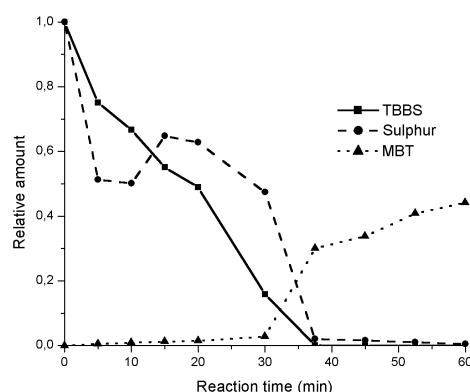


Figure 8.10 Sample composition as a function of reaction time for TME without activator

Scission of the accelerator has been mentioned as a parameter which determines the length of the scorch time. Figure 8.11 shows the kinetics of decrease in CBS concentration in squalene as a function of reaction time for all three samples, without activator, with ZnO, and with ZnClay.

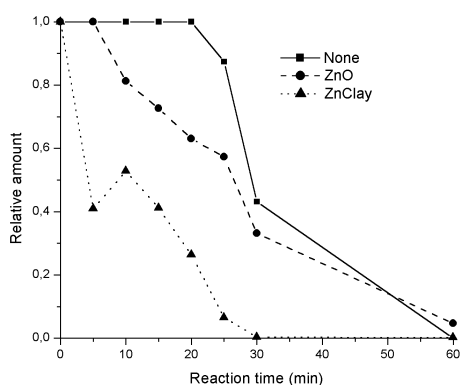


Figure 8.11 Decomposition of CBS with and without activator in squalene

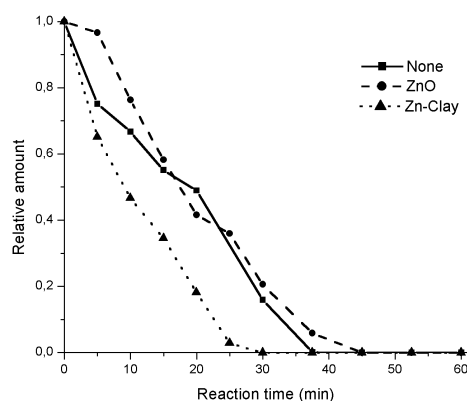


Figure 8.12 Decomposition of TBBS with and without activator in TME

It can be observed that CBS dissociated quite fast when using ZnO, while without activator a decrease in CBS concentration is seen only after 25 minutes. With

ZnClay present as activator the decomposition of CBS occurred very rapidly and after 30 minutes all the accelerator was dissociated. Figure 8.12 shows the results of similar experiments in TME systems with TBBS as accelerator. In TME no major difference is observed in the TBBS decrease for the samples with and without ZnO as activator. ZnClay, however, slightly accelerated the decomposition of TBBS. The sulphur content as a function of reaction time for the three systems in squalene and TME is plotted in Figures 8.13 and 8.14, respectively. The sulphur content decreased strongly in the first five minutes for all systems. Although the differences between the activators were more pronounced in squalene, similar trends were observed in the two model compound systems. After a reaction time of about 35 minutes no sulphur was left for the TME sample without activator. For the ZnClay system a longer time was observed. The ZnO systems showed the lowest level of sulphur at short reaction times in both model compounds.

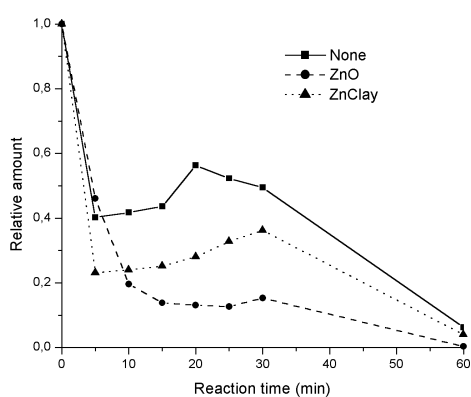


Figure 8.13 Decrease of the sulphur concentration with and without activator in squalene

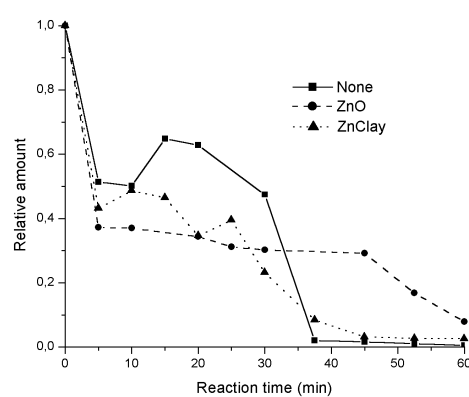


Figure 8.14 Decrease of the sulphur concentration with and without activator in TME

MBT must be formed as a dissociation product of the accelerators CBS and TBBS. Therefore, the change in the MBT concentration should correlate with the dissociation of these accelerators. The increase of the MBT concentration as a function of reaction time for the three systems in squalene and in TME is depicted in Figures 8.15 and 8.16, respectively.

Except for the squalene sample with ZnClay as activator, the formation of MBT started from a reaction time of 30 minutes. Although the differences in dissociation of the accelerator between the squalene samples with ZnO and ZnClay were relatively small, for the MBT formation major differences were observed. In the sample with ZnO present, hardly any MBT was formed. Considering the fact that the MBT concentration in the sample without activator reached a relative amount of almost 1, it can be stated that the low MBT content in the sample with ZnO was due to the complex formation of MBT with Zn^{2+} . As expected from the zinc content, shown in Table 8.6, an intermediate position regarding MBT level was observed in the samples with ZnClay.

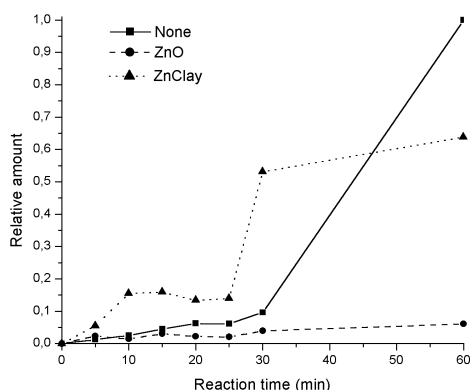


Figure 8.15 Increase of the MBT concentration with and without activator in squalene

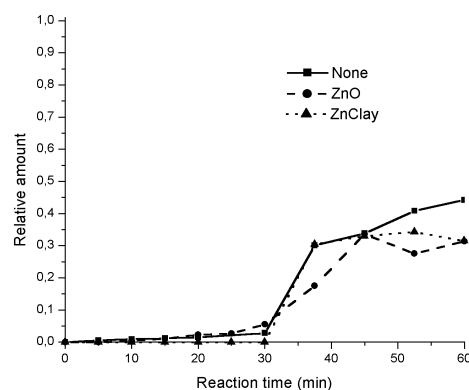


Figure 8.16 Increase of the MBT concentration with and without activator in TME

None of the TME systems showed a relative amount of MBT as high as 1, although after *ca.* 40 minutes all TBBS had reacted. A conversion of 100% was not achieved, probably due to the formation of crosslink precursors and the complex formation of MBT with Zn^{2+} .

8.5.2 Crosslink Precursor Formation

Generally accepted schemes for the chemistry of vulcanisation suggest the formation of intermediates (or crosslink precursors) prior to the formation of crosslinks. The intermediate reacts with another intermediate or polymer resulting in a crosslink. This so-called crosslink precursor consists of the mercapto part of the accelerator attached to the allylic position of the model via a sulphur bridge with a variable amount of sulphur atoms. The crosslink precursor in the TME samples can be separated by the HPLC column and detected by UV light at a wavelength of 254 nm. Therefore the development of the precursors in the systems as a function of time can be plotted as well. Figure 8.17 displays the crosslink precursor formation for the three systems.

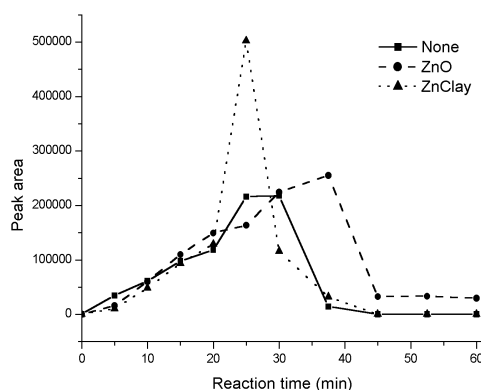


Figure 8.17 Crosslink precursor concentration with and without activator in TME

The formation as well as the breakdown of the precursor under the influence of ZnClay proceeded faster compared to the other systems. This is in good accordance with the faster decomposition of TBBS in the sample with ZnClay as activator, as demonstrated in Figure 8.12.

8.5.3 Crosslinked Products

As already mentioned before, the crosslinked products can be detected with HPLC measurements as well in the TME model compound systems. As mentioned in literature, the reaction products which are formed are mainly of the type: TME-S_x-TME. In order to calculate the response factors and to get a proof of the retention times of the several products, these components should be analysed in their pure form. However, these products are not commercially available, and must be synthesised. Although no direct identification of the reaction products was possible, an indication was obtained from the correlation between the breakdown of the crosslink precursors and the formation of the products. As the general vulcanisation scheme clearly shows, the crosslinked products originate from the reaction of an intermediate with a polymer molecule or between two intermediates. It is evident that the peaks appearing in the chromatogram when the signals of the crosslink precursors are decreasing, can be interpreted as crosslinked products. Besides the peaks for the starting materials and the crosslink precursor, three significantly new peaks were observed in the chromatograms at retention times of 10, 12, and 17 minutes, probably due to the fact that various sulphur chain lengths were formed. No relative or absolute amounts of the products can be plotted, but the trends between the three different systems can be compared. The peak areas of the crosslinked products for the samples without activator, ZnO and ZnClay as activator are plotted versus reaction time in Figures 8.18, 8.19 and 8.20 respectively.

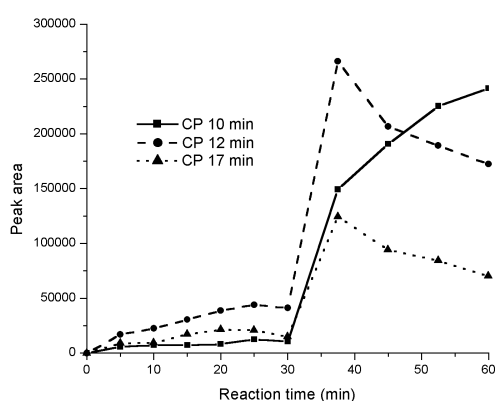


Figure 8.18 Crosslinked products (CP) concentration in TME samples without activator

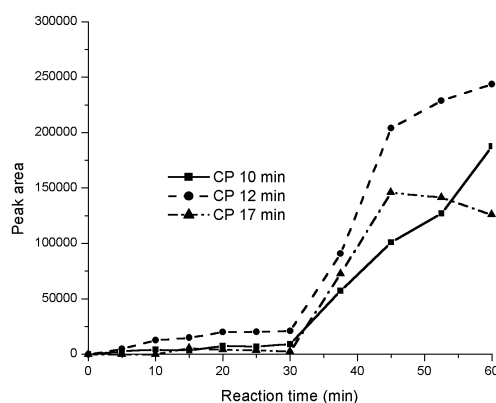


Figure 8.19 Crosslinked products (CP) concentration in TME samples with ZnO as activator

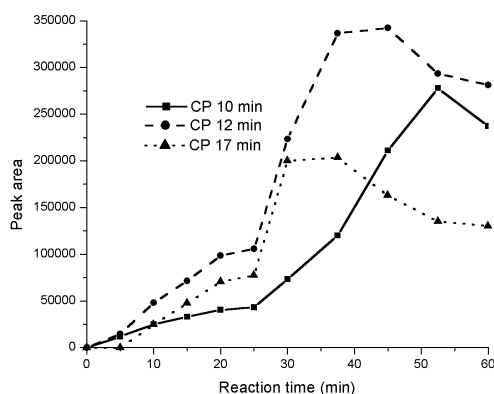


Figure 8.20 Crosslinked products (CP) concentration in TME samples with ZnClay as activator

It was concluded that the three peaks can be interpreted as reaction products with different sulphur chain lengths, with the peak at 17 minutes corresponding to the longest sulphur bridge, which is in accordance with the linear correlation between the sulphur rank and the logarithm of the retention time reported by Hann *et al.*¹⁶

As more often described in literature, another important stage in the vulcanisation process is the crosslink shortening. The initially formed polysulphidic bridges tend to reduce the sulphur chain length by releasing sulphur and the formation of shorter crosslinks, to tri-, di-, and monosulphidic crosslinks. Figure 8.18, representing the results of the sample without an activator, can be used to illustrate this phenomenon. The fast increase at approximately 30 minutes of the 12 and 17 minutes reaction products was immediately followed by a gradual decrease of both the lines while the graph for the 10 minutes product increased, clearly indicating the occurrence of crosslink shortening. When ZnO was added as activator, the rate of product formation as well as the amount of reaction products turned out to be lower and the distribution of the products was slightly different, as is shown in Figure 8.19. In both systems, however, the reaction product with a retention time of 10 minutes increased, whereas the others levelled off or decreased. The developments of the crosslinked products of the samples with ZnClay as activator are depicted in Figure 8.20. The amount of reaction products formed in these samples, was considerably higher than without any and with ZnO as activator, and the products were formed at shorter reaction times, which correlates with the faster breakdown of the crosslink precursor, as was shown in Figure 8.17. Concerning the distribution of the crosslinked products no significant differences between ZnClay and the two other systems was observed.

Summarising: the above-described results provide additional insight into the effect of ZnClay in different stages of the vulcanisation, yet at the same time also show that it remains a complicated system to investigate.

8.6 RESULTS AND DISCUSSION III: COMPARISON OF THE EFFECT OF ZNCLAY AS ACTIVATOR IN MCV STUDIES AND RUBBER COMPOUNDS

The relative number and the length of the sulphur crosslinks both have an influence on the physical properties of a vulcanised rubber. Monosulphidic crosslinks are regarded as being unable to exchange, rearrange, or break to relieve mechanical stresses without cleaving main chains. Polysulphidic crosslinks, on the other hand, are able to rearrange under stress, through breaking and reforming, which is partly associated with a high mechanical strength.¹⁷ The shorter mono- and disulphidic crosslinks contain thermally stronger bonds, which give rise to superior thermal and oxidative stability.

In view of these facts, additional insight in the effect of ZnClay as activator on crosslink formation, distribution and shortening is considered desirable, by comparing the results of real rubber compounds with those observed in the MCV experiments. With Model Compound Vulcanisation the crosslinked products can be evaluated with HPLC by summing all the peaks of the various sulphur chains, *i.e.* area of S₃, + area of S₄ *etc.* In Figure 8.21 the crosslink development obtained with the TME model compounds and the rheograms of s-SBR compounds for systems with ZnO and ZnClay are combined in one graph.

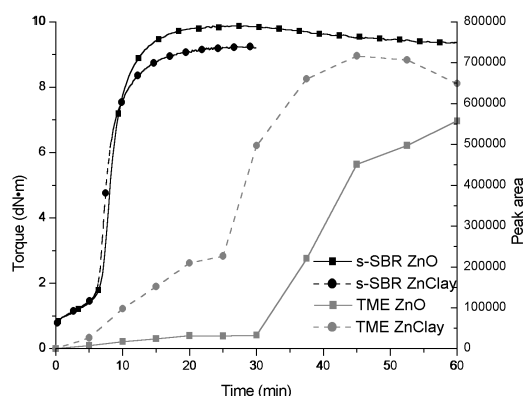


Figure 8.21 Comparison cure-torque of s-SBR compounds with total crosslinked products in MCV of TME as a function of reaction time

Again, at first sight, the MCV results are not at all in agreement with the s-SBR compounds. The MCV results, obtained with squalene and TME as model compounds, may not necessarily be extrapolated to real rubbers such as EPDM and s-SBR, due to some fundamental differences between the real rubber and model systems. However, the general trend of the reactions is unlikely to be influenced by the particular allylic structures involved. Further, the onset of the vulcanisation, in particular, is delayed in the model compound systems, but this is to a large extent due to the lower MCV vulcanisation temperature, 140 vs. 160°C in rubber compounds. Another major difference between the two types of experiments is the presence of carbon black in the rubber compounds. Carbon black appeared to

catalyse the formation of accelerator polysulphides, e.g. tetramethylthiuram polysulphide (TMTP), which explains part of the beneficial effect of carbon black in rubber vulcanisation.¹⁸

As discussed above, the effectiveness of the ZnClay as activator varied considerably between the different rubbers. While for s-SBR and e-SBR/BR rubbers the cure and physical properties of the compounds with ZnClay are grossly comparable with the conventional ZnO, for NR and EPDM application of ZnClay resulted in an impracticably underdeveloped network. A possible explanation can be the pH value of the ZnClay, which was prepared in an acidic environment. It is well known, that sulphur vulcanisation of NR requires a basic environment, and this will be negatively influenced by the acidic ZnClay. Another possible factor can be the degree to which the zinc species are acting either catalytically or being consumed during the sulphur vulcanisation. NR and EPDM are more sensitive towards reduced ZnO levels compared to other rubbers, e.g. s-SBR. It has been reported that in NR much ZnO is consumed and a considerable amount of ZnS formed during vulcanisation.^{19, 20} In polybutadiene (BR) rubber a much lower ZnS yield was measured.^{19, 21} This suggests that in BR the zinc species are acting more catalytically in the vulcanisation process. Not much has been published regarding the extent of formation of ZnS in EPDM vulcanisates. The formation of ZnS in EPDM vulcanisates was reported by Buhkina *et al.*²² In a direct reaction between ZnO and accelerator TMTD hardly any ZnS formation is observed.¹ Therefore, ZnS is assumed to be the product of crosslink precursor formation from a zinc-accelerator complex, viz. ZDMC, sulphur and rubber. Another explanation for the formation of ZnS was found in the reaction of ZnO with H₂S. Quantitative data on the formation of ZnS in EPDM vulcanisates, however, is not readily available. The lower effectiveness of ZnClay in EPDM therefore might be explained by a shortage of catalytic zinc species, due to consumption in one of the equilibrium reactions in the vulcanisation process.

8.7 CONCLUSIONS

As aimed for with the development of the new activator, a considerable reduction of the environmental impact can be achieved by providing a system with an increased availability of the Zn²⁺-ions. MMT Clay can be loaded as a carrier with around 5 wt % of zinc ions, via a relatively simple exchange process.

Experiments with the newly developed ZnClay have shown that with only 5 phr of ZnClay the cure and physical properties of s-SBR compounds are grossly comparable with the ones obtained with a standard amount of 3 phr ZnO. The zinc concentrations in the applied quantities of 5 and 2.5 phr ZnClay correspond to ~0.3 and ~0.15 phr ZnO, respectively. Thus a significant reduction of the zinc concentration with a factor 10 to 20 is possible, without significantly jeopardising the curing and physical properties of the rubber products as far as examined.

While in s-SBR rubber ZnClay performs surprisingly well as activator, results in rubbers other than s-SBR, have revealed that in some cases the properties of the

vulcanised products are inferior to those obtained with ZnO. This can potentially be related to the zinc species acting either catalytically or being consumed during the sulphur vulcanisation. NR and EPDM compounds, known to be quite sensitive to reduction of the ZnO level, demonstrate an inferior cure behaviour when using ZnClay as activator. In NR latex, on the other hand, physical properties are attained comparable with ZnO activated NR latex compounds.

It is anticipated that serious improvements might be achieved by the selection of a more suitable support clay and a further refining of the ZnClay preparation method. Furthermore, optimisation of the accelerator/ZnClay activator system is considered desirable as well.

Although no quantitative data is available yet, it can be assumed that the formation of ZnS is strongly reduced as well, because of the fact that less ZnO is available. Although no results are presented here, preliminary results have indeed shown a strong reduction of mould fouling when ZnO is replaced by ZnClay.²³

A commercially available Zn-loaded clay (Clayzic) has a decreased effectivity compared to standard ZnO and even shows some retardation of vulcanisation. This is most likely due to a high remaining Cl⁻-content which strongly interferes with the vulcanisation chemistry.

By means of Model Compound Vulcanisation additional information about the reactions and chemical mechanisms in real rubber vulcanisates is obtained, though it is sometimes difficult to reach clear conclusions because of the great many reactions and products involved in the sulphur chemistry. In this study squalene and TME were selected as model compounds. Although the differences between the various activators are more pronounced in squalene, similar trends are observed in the two model compound systems.

From the results shown it has become clear that the reactions in the different stages of the vulcanisation process do not differ greatly for ZnO and ZnClay. The lower sulphur content at short reaction times for the ZnO system compared to the system without activator can be explained by sulphur insertion in the zinc-accelerator complex or the polysulphidic accelerator and the formation of ZnS. The slightly lower sulphur content of the ZnO samples compared to the ZnClay samples might be an indication for more ZnS formation. Experiments with ZnClay as activator reveal a faster decomposition of the accelerator and therefore a faster formation as well as breakdown of the crosslink precursor, resulting in a somewhat faster formation of reaction products or 'crosslinking'. The latter is also observed to some extent in s-SBR rubber compounds, demonstrated by the slightly shorter scorch time, as shown in Figure 8.4. The higher product yield and minor differences in the distribution of the crosslinked products which are found in the model compounds, are not clearly found back in the properties of real vulcanised compounds.

Based on all the results, it can be concluded that systems with Zn²⁺-ions provided on a support can be regarded as potential substitutes for ZnO commonly used in rubber vulcanisation. As such, these new activator systems are worth further pursuing. They represent a new route to reduce the zinc level, and therefore to significantly minimise its environmental impact.

8.8 REFERENCES

1. P.J. Nieuwenhuizen, Thesis, University of Leiden, (1998).
2. G. Wypych, *Handbook of Fillers*, ChemTec Publishing, New York (1999).
3. A. Wei, *Rubber Industry of China*, **48**, (2001).
4. E.M. Dannenberg, *Rubber Chem. Technol.*, **55**, (1982), 860.
5. M.F. Brigatti, *Applied Clay Science*, **9**, (1995), 383.
6. A. Banin, (to Yissum Research Development Company of the Hebrew University of Jerusalem), US Patent 3,725,528 (February 18, 1971).
7. Z. Weiss, *Phys. Chem. Minerals*, **25**, (1998), 534.
8. A. Banin, (to Yissum Research Development Company of the Hebrew University of Jerusalem), US Patent 3,908,886 (August 2, 1971).
9. P.J. Flory, J. Rehner, *J. Chem. Phys.*, **11**, (1943), 521.
10. B. Saville, A.A. Watson, *Rubber Chem. Technol.*, **40**, (1967), 100.
11. R.A. Hayes, *Rubber Chem. Technol.*, **59**, (1986), 138.
12. H.G. Dikland, Thesis, University of Twente, (1992).
13. T. Vengris, R. Binkiene, A. Sveikauskaite, *Applied Clay Science*, **18**, (2001), 183.
14. J.K. Kurian, *J. Appl. Polym. Sci.*, **78**, (1999), 304.
15. J. Travas-Sejdic, *Eur. Polym. J.*, **32**, (1996), 1395.
16. C.J. Hann, A.B. Sullivan, *Rubber Chem. Technol.*, **67**, (1994), 76.
17. L. Bateman, *The Chemistry and Physics of Rubber-like Substances*, MacLaren, London (1963).
18. W.J. McGill, S.R. Shelver, *J. Appl. Polym. Sci.*, **58**, (1995), 1433.
19. T.D. Skinner, *Rubber Chem. Technol.*, **45**, (1972), 182.
20. M. Porter, T.D. Skinner, M.A. Wheelans, *J. Appl. Polym. Sci.*, **11**, (1967), 2271.
21. E.C. Gregg, S.E. Katrenick, *Rubber Chem. Technol.*, **43**, (1970), 549.
22. M.F. Bukhina, Y.L. Morozov, P.M. van den Ven, J.W.M. Noordermeer, *Kautsch. Gummi Kunstst.*, **56**, (2003), 172.
23. B. van Baarle, G. Heideman, *unpublished work*.

General Summary and Final Remarks

*'The vision must be followed by the venture. It is not enough to stare up the steps;
we must step up the stairs.'*
Vance Havner (1901 – 1986)

This chapter provides a general evaluation and some remarks with regard to the obtained results. The research approach that was utilised is discussed and critically evaluated. The chapter is completed with some suggestions for future research in this area.

9.1 MOTIVATION

The potential harmful environmental impact caused by the release of eco-toxic zinc species from rubbers leads to an increasing interest in potential substitutes. In the rubber field, however, it is well-known that zinc species are the best activators for sulphur vulcanisation. Although the activation of sulphur vulcanisation has been studied thoroughly, at present no viable alternative has been found to eliminate ZnO completely from rubber compounds, without significantly jeopardising processing as well as performance characteristics. The objective of the present research as described in this thesis was to provide improved and new routes to judiciously reduce ZnO and zinc complexes.

The first two chapters provide relevant background information and a review of the vulcanisation process, and of the chemistry of thiuram- and sulphenamide-accelerated sulphur vulcanisation with emphasis on the role of activators, to lay a base for the research described in the following six chapters. It encompasses different possible routes for reduction of ZnO in rubber compounds, an in-depth study

into the role of activators in the vulcanisation process and it provides an alternative for ZnO.

Chapter 2 presents a review of sulphur vulcanisation and the reaction mechanisms as described in literature, followed by the role of activators. In particular it outlines and describes the role of ZnO and the various possibilities that have been proposed in literature to reduce ZnO levels in rubber compounding. A totally different approach to reduce ZnO is described in the paragraphs covering the various possible roles of MultiFunctional Additives (MFA) in rubber vulcanisation. The chemical mechanisms involved in the MFA systems are evaluated in a separate part, dedicated to the role of amines in rubber vulcanisation. From a chemical point of view, vulcanisation is a very complicated process, difficult to analyse and with a complex interplay between the various reactions. Traditionally, essential information about the mechanisms of vulcanisation has been uncovered utilising Model Compound Vulcanisation (MCV) in combination with various forms of spectroscopy. An overview of MCV with respect to different models and activator/accelerator systems is given, with special focus on the role of activators in accelerated sulphur vulcanisation.

Examination of the literature has revealed, that the role of ZnO and zinc compounds is very complex and that a number of functions are in fact not well-understood at all. Nevertheless, on several occasions the literature clearly indicates an important role for zinc species in the vulcanisation. In the last part of Chapter 2 the various functions of ZnO in rubber, described in literature, are summarised.

9.2 SUMMARY OF THE RESULTS

The conducted literature survey rendered in Chapter 2 revealed that much information is available in literature about reduction, optimisation and substitution of ZnO, albeit fragmented over many different studies. Therefore, it was felt necessary to (re)investigate and perform a more in-depth study. In this thesis it is illustrated how rubber compounding experiments and MCV can be combined to judiciously reduce the zinc content and elucidate various important aspects concerning the role of the activator in sulphenamide-accelerated sulphur vulcanisation.

9.2.1 Introductory Studies

It is commonly known, that addition of ZnO as an activator for sulphur vulcanisation of rubbers enhances the vulcanisation efficiency and vulcanisate properties and reduces vulcanisation time. In typical recipes for sulphur vulcanisation, ZnO and a fatty acid constitute the activator system, where the zinc ion is assumed to be solubilised by salt formation between the acid and oxide. Chapter 3 describes the optimisation and thereby reduction of the amount of ZnO in two widely different rubbers, *viz.* s-SBR and EPDM. From the results it can be concluded that the level of conventional ZnO Red Seal can be reduced to 1 and 2 phr, respectively, retaining the curing and physical properties of the cured rubber products. The efficiency of ZnO

during vulcanisation can be enhanced by maximising the contact between ZnO particles and the accelerators in the rubber formulation. The contact is dependent on the size of the particles, their shape and specific surface area. The average particle size of conventional ZnO Red Seal is usually $\sim 0.6 \mu\text{m}$ with a specific surface area of $\sim 5 \text{ m}^2/\text{g}$. In 'active' ZnO the average particle size is decreased and the specific surface area increased to $\sim 0.2 \mu\text{m}$ and $\sim 40 \text{ m}^2/\text{g}$, respectively. Neither Active ZnO nor a pure grade ZnO led to major improvements in cure or physical properties relative to conventional ZnO Red Seal. One of the latest developments in this field and of particular interest is a so-called Nano ZnO characterised by a nano-scale particle distribution. The average particle size of Nano ZnO is $\sim 30 \text{ nm}$ and the specific surface area $\sim 30 \text{ m}^2/\text{g}$. The cure characteristics obtained with this ZnO species clearly indicated that a reduction of the zinc concentration with a factor of 10 could be obtained.

Although it has been firmly established that ZnO plays an important role as activator in sulphur vulcanisation, the exact mechanisms are still far from understood and the subject of ongoing scientific research. In Chapter 4 Model Compound Vulcanisation (MCV) is introduced to investigate the effects of ZnO in the different stages of the vulcanisation process that have been reported in literature. A major advantage of this technique is that standard analytical techniques can be applied to analyse these low molecular weight model systems. Experiments are performed with two different models, squalene and TME, both with benzothiazolesulphenamide-accelerated vulcanisation systems. It is realised that the results obtained apply to model compounds and that these findings may not necessarily be extrapolated to real rubbers. In the squalene/CBS system the influence of ZnO in the different stages of the vulcanisation process is more pronounced than in TME/TBBS. With ZnO present in the system, not only a marked decrease is observed in the sulphur concentration in an early stage of the vulcanisation and a slight delay in the disappearance of the crosslink precursor, but also the distribution of crosslinked products is influenced by the presence of ZnO.

9.2.2 Alternative Activators

Chapters 5 – 8 in this thesis deal with the investigation of alternatives for the conventionally used ZnO and fatty acid activator system. A similar combination of techniques is utilised in all these chapters. Apart from the cure characteristics and ultimate properties of rubber compounds, they describe an investigation of the fate of the initial vulcanisation ingredients, the formation of vulcanisation intermediates and crosslink formation/shortening.

In Chapter 5 the application of several zinc complexes as activators for sulphur vulcanisation in s-SBR and EPDM is studied. It can be concluded that zinc-m-glycerolate is a good substitute for ZnO as activator for sulphur vulcanisation in EPDM as well as in s-SBR rubber, without detrimental effects on the cure and physical properties. Dependent on the intended applications, zinc-2-ethylhexanoate as well as zinc-borate (might) represent a substitute for the commonly used ZnO. Zinc stearate is considerably less active as activator in sulphur vulcanisation. MCV

experiments with zinc-m-glycerolate as activator indicate a higher yield of crosslinked products, which corresponds with the higher extent of cure and ultimate properties observed in s-SBR compounds.

A completely zinc-free vulcanisation system based on sulphur remains a challenging task to cope with. In Chapter 6 the application of a wide range of metal oxides as activator for sulphur vulcanisation in s-SBR and EPDM are discussed. The influence of the basicity, the crystal structure and the ability to form complexes of the metal oxides are studied. It has been observed that neither CdO, PbO, BaO, CaO, MgO and BeO are proper substitutes for ZnO as activator in thiuram-accelerated vulcanisation of EPDM nor do they show a synergistic effect with ZnO. In benzothiazole-accelerated vulcanisation of s-SBR compounds, however, it is demonstrated that CaO and MgO can function as activator of cure for sulphur vulcanisation, retaining the curing and physical properties of the rubber vulcanisates. The influence of the metal oxides on the several reactions rate constants appears to be different in the squalene and TME model compound experiments. It is found that, depending on the exact requirements for specific compounds, certain metal oxides represent an alternative route to reduce the zinc level, and therefore to minimise the environmental impact.

Although many alternative metal oxides and zinc complexes as activators for sulphur vulcanisation have been studied, at present, no viable alternative has been found to eliminate ZnO completely from rubber compounds, without significantly damaging processing as well as performance characteristics. Chapter 7 reports about a fundamentally different approach: the application of MultiFunctional Additives (MFA). MFAs are amines complexed with fatty acids, developed to function both as activator and accelerator for sulphur vulcanisation. Good physical properties can be obtained in s-SBR compounds using the MFA/S cure system, albeit at the cost of a shortened scorch time as compared to a regular ZnO/stearic acid system. The scorch time can be lengthened by the inclusion of ZnO, though it reduces the state of cure and ultimate properties. The introduction of metal oxides other than ZnO, *viz.* CaO and MgO, leads to an appreciable improvement in the state of cure. The physical properties are grossly comparable with those obtained with commonly employed vulcanisation ingredients. Amines play a vital role in the vulcanisation process, hence various amine complexes have been synthesised and investigated as zinc-free curatives in s-SBR compounds. It is observed that the scorch time of the MFAs is related to the basicity of the amines used as components of the MFAs. The conclusion is drawn, that the chemistry involved in the MFA systems is fundamentally different, indicated by the very fast decomposition of the accelerator TBBS, fast formation as well as breakdown of the crosslink precursor and, above all, some major differences in the distribution of the crosslinked products. Overall, the results indicate that, dependent on the intended applications (*e.g.* tyres or roofing foils), there exists a potential to significantly or even completely reduce the need for ZnO with MFA-containing vulcanisation systems.

In the last chapter the application of a new activator for sulphur vulcanisation is discussed. This activator is developed with the knowledge obtained in the previous chapters and based on the assumption that zinc species act catalytically rather than

being consumed during the sulphur vulcanisation. An increase in the accessibility of Zn^{2+} -ions would allow for a considerable reduction of ZnO needed for vulcanisation of rubber compounds. A mineral clay, *viz.* Montmorillonite, is used as carrier material and loaded with Zn^{2+} -ions via an ion exchange process. Application in a wide range of natural and synthetic rubbers has been explored. It is demonstrated that this ZnClay can substitute conventional ZnO, grossly retaining the curing and physical properties of the rubber products, but reducing the zinc concentration with a factor 10 to 20. It is concluded that systems with Zn^{2+} -ions on a support represent a novel route to reduce the zinc level, and therefore to minimise its environmental impact significantly.

9.3 GENERAL CONSIDERATIONS

In this thesis evidence has been presented that several metal oxides, zinc complexes and MFAs, added as activators, participate in and facilitate to a certain extent the main reactions of the vulcanisation process. The catalytic action of these activators in each of these key steps and their implications are summarised in Table 9.1. They involve characteristics obtained from the rheograms, *viz.* scorch time and delta torque, as well as results obtained with the MCV studies, *viz.* fate of the initial ingredients, crosslink precursor formation and degradation, crosslink formation. The properties are all compared to the reference activator ZnO. The data show once more the versatile influence exerted by zinc-containing species and the difficulties to develop proper alternatives.

9.4 FINAL REMARKS

This thesis has been devoted to a great many different possibilities to reduce the level of ZnO in rubber compounds, with emphasis on the development of a new type of activator. It must be realised that vulcanisation is a complex process, whereby many ingredients and parameters play an important role. ZnO and zinc-containing species are considered indispensable for the vulcanisation process and certainly difficult to substitute. Long-term solutions for the reduction of emissions of zinc into the environment should be focused on the development of new and effective concepts for completely new zinc-free vulcanisation systems. Short-term strategies will be mainly concentrated on reduced dosages of zinc and a higher chemical activity, combined with an increased solubilisation. In this respect progress has been made by the development of the ZnClay. In summary, the research described in this thesis combines a pragmatic in-rubber investigation and a fundamental study of the chemistry all through the vulcanisation reactions cascade. It has contributed to a better understanding of the role of the activator in the sulphur vulcanisation process.

Table 9.1 Main characteristics of the zinc complexes, metal oxides and MFAs as activators for vulcanisation, compared with reference ZnO; the reaction characteristics are based on the results obtained with TME as a model compound

	scorch time*		delta torque*		accelerator decomposition**	precursor formation**		precursor breakdown**		crosslink formation**		
	s-SBR	EPDM	s-SBR	EPDM		rate	rate	reaction time	rate	reaction time	rate	reaction time
MgO	0	>	0	↓↓	↑	↑	<	0	<	↓	<	↓
CaO	0	>	0	↓↓	↓	↓	>	0	>>	↓↓	0	↓
BaO	0	>	↓	↓↓	-	-	-	-	-	-	-	-
Cu(II)O	<	0	↓	↓	-	-	-	-	-	-	-	-
BeO	0	0	↓	↓↓	-	-	-	-	-	-	-	-
PbO	-	<	-	↓↓	-	-	-	-	-	-	-	-
CdO	-	0	-	↓↓	-	-	-	-	-	-	-	-
Zn-stea	<	0	↓	↓	↑↑	↑↑	<	↑	<	↓	<	↓
ZEH	>	-	0	-	-	-	-	-	-	-	-	-
Zn-m-glyc	<	<	↑	0	↑	↑↑	0	0	0	0	0	↑
Zn-borate	<	-	0	-	-	-	-	-	-	-	-	-
ZnClay	0	0	0	↓↓	↑	↑	<	↑	<	↑	<	↑
MFA	<<	<	↓	↓	↑↑	-	-	-	-	↑↑	<<	↓

* >: longer; <: shorter; 0: equal; ↑: higher; ↓: lower, -: not measured;

** >: later; <: earlier; 0: equal; ↑: faster; ↓: slower, -: not measured;

Samenvatting

De toepassing van zink en zinkhoudende materialen in rubbers is door veranderingen in de milieuwetgeving een belangrijk aandachtspunt geworden. Ofschoon zink een essentieel element is voor vrijwel alle vormen van leven, wordt het gerekend tot de zware metalen en overmatige belasting van het milieu moet derhalve worden vermeden. In de afgelopen jaren is veel onderzoek gedaan naar de verspreiding van zinkverbindingen in het milieu en naar de mogelijkheden om eventuele schadelijke gevolgen aan het milieu te beperken of te voorkomen. Vanuit de rubberindustrie is een groeiende belangstelling getoond voor de mogelijkheden om het gebruik van zinkverbindingen in rubbers te reduceren.

Zinkverbindingen worden toegevoegd in rubbers als activator voor het proces van versnelde zwavelvulkanisatie en vormen daarmee een belangrijk onderdeel van het vulkanisatiesysteem. Tot dusver wordt zink zelfs beschouwd als zijnde onmisbaar. Hoewel de activering van zwavelvulkanisatie zeer grondig en veelvuldig bestudeerd is, is er tot op heden nog geen goed alternatief voorhanden om zinkoxide (ZnO) volledig te vervangen, zonder dat de verwerkbaarheid en eigenschappen danig beïnvloed worden. Het doel van het onderzoek beschreven in dit proefschrift, is om (nieuwe) methoden te ontwikkelen om het gebruik van ZnO en zinkverbindingen te reduceren, waarbij de verwerkbaarheid en eigenschappen niet fundamenteel aangetast worden.

Dit proefschrift beschrijft een aantal verschillende methoden om het gebruik van zink in rubbers te reduceren, waarbij de nadruk gelegd is op een nieuw type activator voor zwavelvulkanisatie. Hoofdstuk 1 begint met een beknopte introductie van het vulkanisatieproces van rubbers vanuit een historisch oogpunt, enkele algemene aspecten en toepassingen van rubbers en verder relevante

achtergrondinformatie omtrent het project. In hoofdstuk 2 wordt de stand van de wetenschap omtrent het vulkanisatieproces beschreven met een uitgebreide verhandeling over de chemie van thiuram- en sulfenamide-versnelde zwavelvulkanisatie. Speciale aandacht wordt geschonken aan de reactiemechanismen in dit proces en de rol van de activatoren, zoals die beschreven zijn in de literatuur, om een basis te leggen voor het onderzoek beschreven in de overige zes hoofdstukken. Hoofdstuk 2 wordt afgesloten met een samenvatting van de verschillende functies die ZnO in rubbers vervult en een overzicht van mogelijkheden die zijn beschreven in de literatuur om het gebruik van ZnO in rubbers terug te dringen.

Hoofdstuk 3 omvat een uitgebreid onderzoek naar de mogelijkheden om het gebruik van ZnO (Red Seal) in s-SBR en EPDM rubber te optimaliseren en daardoor zo mogelijk te reduceren. Er is aangetoond dat de hoeveelheid ZnO gereduceerd kan worden tot 1 respectievelijk 2 phr, zonder de vulkanisatiekarakteristieken en fysische eigenschappen van de vulkanisaten negatief te beïnvloeden. De efficiëntie van ZnO in het vulkanisatieproces is onder andere afhankelijk van het contactoppervlak tussen de ZnO-deeltjes en de versnellers in de rubber. Het contactoppervlak wordt bepaald door verschillende factoren, waaronder de deeltjesgrootte, de vorm van de deeltjes en het specifiek oppervlak. De gemiddelde deeltjesgrootte van conventioneel ZnO (Red Seal) is $\pm 0,6 \mu\text{m}$ met een specifiek oppervlak van $\pm 5 \text{ m}^2/\text{g}$. In 'actief' ZnO is de gemiddelde deeltjesgrootte verkleind en het specifiek oppervlak vergroot tot $\pm 0,2 \mu\text{m}$ respectievelijk $\pm 40 \text{ m}^2/\text{g}$. Een van de meest recente ontwikkelingen op dit gebied is de zogenaamde Nano ZnO, die een deeltjesgrootte karakteristiek heeft in de orde van nanometers. De gemiddelde deeltjesgrootte van Nano ZnO is $\pm 30 \text{ nm}$ en het specifiek oppervlak $\pm 30 \text{ m}^2/\text{g}$. Er is gebleken dat met Nano ZnO de zinkconcentratie gereduceerd kan worden met een factor 10.

In hoofdstuk 4 wordt een onderzoek met behulp van Model Compound Vulcanisation (MCV) naar de exacte rol van de activator (ZnO) en reactiemechanismen in de verschillende stadia van zwavelvulkanisatie beschreven. De MCV-methode maakt het mogelijk om diverse vulkanisatiereacties in modelsystemen te simuleren en met behulp van standaard technieken te analyseren. Veel van de relevante informatie omtrent de reactiemechanismen in het vulkanisatieproces is in het verleden verkregen via deze methode. In dit hoofdstuk worden experimenten behandeld met twee verschillende modelsystemen: squaleen en 2,3-dimethyl-2-buteen (TME), beide met een vulkanisatiesysteem gebaseerd op benzothiazolesulfenamide-versnellers. Door de resultaten van de experimenten met s-SBR en EPDM rubbers te combineren met de resultaten van modelexperimenten kon meer inzicht omtrent de exacte rol van de activator verkregen worden.

Met deze achtergrond wordt in de hoofdstukken 5 – 8 de invloed van alternatieve activatoren, zoals allerlei zinkverbindingen en diverse metaaloxiden, behandeld. Bovendien onderzoek naar de invloed van de diverse activatoren op het vulkanisatiegedrag en de fysische eigenschappen van de rubbervulkanisaten, wordt met behulp van MCV ook telkens aandacht besteed aan de invloed op het concentratieverloop van de initiële vulkanisatie-ingrediënten en de vorming van tussenproducten en crosslinks als functie van de reactietijd.

Hoofdstuk 5 beschrijft de toepassing van verschillende zinkcomplexen als activatoren voor zwavelvulkanisatie van s-SBR en EPDM rubber. Er is gebleken dat voor zowel s-SBR als EPDM zink-m-glycerolaat kan fungeren als activator voor zwavelvulkanisatie en een goed alternatief is voor ZnO. Voorts kan, afhankelijk van de toepassingen en gewenste eigenschappen, ook zink-2-ethylhexanoaat beschouwd worden als een goed alternatief voor ZnO. De MCV-studies bevestigen het hogere vulkanisatieniveau in het s-SBR compound met zink-mono-glycerolaat door een hogere opbrengst van gecrosslinkte producten.

In Hoofdstuk 6 wordt aandacht besteed aan volledig zinkvrije vulkanisatiesystemen. Een breed scala aan metaaloxiden is getest als activator in s-SBR en EPDM rubbers waarbij met name de invloed van basiciteit, kristalstructuur en complexvorming nader bestudeerd is. Geen van de geteste metaaloxiden bleek geschikt te zijn als vervanging voor ZnO in thiuram-versnelde zwavelvulkanisatie van EPDM rubber. In benzothiazole-versnelde zwavelvulkanisatie van s-SBR rubber echter, bleken zowel CaO als MgO prima te fungeren als activator voor vulkanisatie, resulterend in goede fysische eigenschappen.

Hoofdstuk 7 beschrijft een nieuwe benadering die tevens fundamenteel anders is: het gebruik van zogenaamde Multifunctionele Additieven (MFA) als alternatief voor de conventionele zinkoxide/stearinezuur/versneller systemen. Multifunctionele additieven zijn in dit verband amines die gecomplexeerd zijn met vetzuren, oorspronkelijk ontwikkeld om te fungeren als activator en tegelijkertijd als versneller van zwavelvulkanisatie. De fysische eigenschappen van de s-SBR compounds waarin het MFA/S-systeem toegepast is, zijn goed te noemen. Ten aanzien van de vulkanisatiekarakteristiek treedt er echter een beduidende verkorting van de scorchtijd op. Dit kan enigszins verlengd worden door toevoeging van een geringe hoeveelheid ZnO, maar hierdoor worden het vulkanisatieniveau en daarmee de eigenschappen negatief beïnvloed. Andere metaaloxiden, t.w. CaO en MgO, laten in combinatie met MFA/S in dit opzicht een gunstiger beeld zien: het vulkanisatieniveau ligt beduidend hoger en de fysische eigenschappen zijn zelfs vergelijkbaar met conventionele compounds. Een en ander betekent dat deze systemen, indien de scorchtijd op enigerlei wijze verlengd kan worden, voor specifieke doeleinden (bijv. banden en dakfolie) als zinkvrije vulkanisatiesystemen toegepast kunnen worden. Verder wordt ook de synthese en toepassing van een reeks van andere aminecomplexen in s-SBR rubber besproken. Er is een duidelijke samenhang gevonden tussen de scorchtijd en de basiciteit van de amine-component van de MFA. De chemie in de MFA-gebaseerde vulkanisatiesystemen is fundamenteel anders, hetgeen duidelijk naar voren komt in de MCV-experimenten. Met name de snellere afname van de versneller, de snelle vorming van de tussenproducten en bovenal de verdeling van de crosslinks illustreren dit afwijkende gedrag.

In Hoofdstuk 8 wordt tenslotte een nieuw type activator geïntroduceerd, die ontwikkeld is met de kennis opgedaan in het huidige onderzoek. Deze activator is ontwikkeld op basis van de aanname dat zinkverbindingen voornamelijk een katalytische functie hebben in het vulkanisatieproces. Door de beschikbaarheid van het zinkion te vergroten, kan mogelijk het gebruik van ZnO in rubbers gereduceerd

worden. Een kleimineraal, t.w. Montmorillonite, is geselecteerd als dragermateriaal en beladen met Zn^{2+} -ionen via een ionenwisselingsproces. De werking van deze nieuwe activator is getest in een reeks van natuurlijke en synthetische rubbers. Er is aangetoond dat deze ZnClay het conventionele ZnO kan vervangen, waarbij de vulkanisatiekarakteristieken en fysische eigenschappen vrijwel niet veranderen, terwijl de zinkconcentratie met een factor 10 tot 20 wordt teruggebracht. Concluderend kan gesteld worden dat met deze systemen, waarbij de Zn^{2+} -ionen worden aangeboden op een drager, een nieuwe en veelbelovende route geïntroduceerd is om het gebruik van zink te reduceren en daarmee de eventuele negatieve gevolgen ten aanzien van het milieu te minimaliseren.

In Hoofdstuk 9 worden tenslotte de verkregen resultaten samengevat en nabeschouwd, en wordt het proefschrift afgesloten met enkele algemene opmerkingen en overwegingen omtrent het gedane onderzoek.

Samenvattend, dit proefschrift behandelt verschillende mogelijkheden om het gebruik van ZnO in rubbers drastisch te reduceren. Het onderzoek omvat een enigszins pragmatische studie met s-SBR en EPDM rubber en een meer fundamenteel onderzoek met betrekking tot de reactiemechanismen die optreden in de verschillende stadia van het vulkanisatieproces. Opnieuw is de veelzijdige en gecompliceerde invloed van zinkverbindingen in zwavelvulkanisatie aangetoond, die vervanging of ontwikkeling van een alternatief tot een ingewikkeld probleem maakt. Met de kennis, verkregen in dit onderzoek, kunnen in de toekomst mogelijk meer activatoren ontwikkeld worden om ZnO op een gefundeerde wijze gedeeltelijk of geheel uit de formulering te verwijderen.

Main Symbols and Abbreviations

χ	polymer-solvent interaction parameter	[-]
E-modulus	Young's modulus for small strains of the stress-strain curve	[MPa]
M_{300}	stress at 300% strain	[MPa]
ML (1+4)	Mooney viscosity	[-]
S_{BET}	specific surface area	[m ²]
t_{02}	scorch time	[min]
t_{90}	optimum vulcanisation time	[min]
v_2	polymer network volume fraction at equilibrium swelling	[-]
ABA	amine bridged amides	
ASTM	american society for testing and materials	
BeO	beryllium oxide	
Bi_2O_3	bismuth oxide	
BR	butadiene rubber	
CaO	calcium oxide	
$Ca(OH)_2$	calcium hydroxide	
CBS	N-cyclohexyl-2-benzothiazolesulphenamide	
CdO	cadmium oxide	
CP	crosslinked products	
CR	polychloroprene rubber	
CS	compression set	
CuO	copper oxide	
DBA	dibutylamine	
DMA	dynamic mechanical analyser	
DPG	diphenylguanidine	
DPTH	dipentamethylene thiuram hexasulphide	
DSC	differential scanning calorimetry	
DMTC	dimethyldithiocarbamic acid	
ENB / ENBH	ethylidene norbornene / ethylidene norbornane	
EPDM	ethylene-propylene-diene rubber	
ETU	N,N'-ethylene thiourea	
EV	efficient vulcanisation	
FKM	fluorinated rubber	
FPD	flame photometric detection	
GC	gas chromatography	
GLC	gas-liquid chromatography	
GPC	gel permeation chromatography	
HALS / HAS	hindered amine light stabilisers / hindered amine stabilisers	
HgO	mercury oxide	
HNBR	hydrogenated nitrile rubber	
¹ H-NMR	proton nuclear magnetic resonance	
HPLC	high performance liquid chromatography	
HBU	heat-build-up	

ICP-ES	inductively coupled plasma-emission spectrometry
IIR	butyl rubber
IPCS	international programme on chemical safety
IR	infrared spectroscopy
IR	isoprene rubber
ISO	international organisation for standardisation
LC-MS	liquid chromatography – mass spectrometry
MALDI	matrix assisted laser-desorption ionisation
MBS	2-(morpholinothio)-benzothiazole
MBT	2-mercaptobenzothiazole
MBTS	2,2'-dithiobenzothiazole
MCV	model compound vulcanisation
MDR	moving die rheometer
MFA	multifunctional additives
MgO	magnesium oxide
MMT	montmorillonite
NBR	nitrile rubber
NiO	nickel oxide
NMR	nuclear magnetic resonance
NR	natural rubber
ODR	oscillating disc rheometer
PbO	lead oxide
phr	parts per hundred rubber
PPD	p-phenylenediamines
RPA/RPA2000	rubber process analyser
RS	red seal
RSM	reaction-stage modelling
S	sulphur
SA	stearic acid
SAPA	surfactant-accelerator processing aids
SBR / s-SBR	styrene-butadiene rubber / solution-styrene-butadiene rubber
TARRC	Tun Abdul Razak Research Centre
TBBS	N-tert-butylbenzothiazole-2-sulphenamide
TESPT	bis-(triethoxysilylpropyl)tetrasulphide
TETD	tetraethylthiuram disulphide
TLC	thin-layer chromatography
TME	2,3-dimethyl-2-butene, tetramethylene
TMTD	tetramethylthiuram disulphide
TMTM	tetramethylthiuram monosulphide
TMTP	tetramethylthiuram polysulphide
UV	ultraviolet
XIIR	halogenated butyl rubber
XRF	X-ray fluorescence spectroscopy
ZDEC	zinc diethyldithiocarbamate
ZDMC	bis(dimethyldithiocarbamate)zinc(II)
ZEH	zinc-2-ethylhexanoate
ZMBT/ZnMBT	zinc-2-mercaptobenzothiazole
Zn-m-glyc	zinc-mono-glycerolate
ZnO	zinc oxide
ZnS	zinc sulphide

Bibliography

JOURNAL PAPERS

- ◆ *Modified Clays as Activator in Sulphur Vulcanisation; A Novel Approach to Reduce Zinc Oxide Levels in Rubber Compounds*
G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, Kautsch. Gummi Kunstst., **56**, (2003), 650.
- ◆ *Zinc Loaded Clay as Activator in Sulfur Vulcanization: A New Route for Zinc Oxide Reduction in Rubber Compounds*
G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, Rubber Chem. Technol., **77**, (2004), 336.
- ◆ *Activators in Accelerated Sulfur Vulcanization, A Review*
G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, Rubber Chem. Technol., **77**, (2004), 512.
- ◆ *Various Routes for Reduction of Zinc Oxide Levels in Rubber Compounds*
G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, Tire Technol. Int., (2004), In press.
- ◆ *Influence of Zinc Oxide in Different Stages of Sulfur Vulcanization elucidated by Model Compound Studies*
G. Heideman, R.N. Datta, J.W.M. Noordermeer, B. van Baarle, J. Appl. Polym. Sci., (2004), In press.
- ◆ *Effect of Zinc Complexes as Activator for Sulfur Vulcanization in Various Rubbers*
G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, Rubber Chem. Technol., (2004), Submitted.
- ◆ *Effect of Metal Oxides as Activator for Sulphur Vulcanisation in Various Rubbers*
G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, Kautsch. Gummi Kunstst., **57**, (2004), In press.
- ◆ *Multifunctional Additives as Zinc-free Curatives for Sulphur Vulcanization*
G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, Rubber Chem. Technol., (2004), Submitted.

CONFERENCE PROCEEDINGS

- ◆ G. Heideman, J.W.M. Noordermeer, B. van Baarle, *Reduction of zinc oxide levels in rubber compounds*, Proceedings International Rubber Conference, July 2002, Prague, Czech Republic.
- ◆ G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Modified clays as activator in sulphur vulcanisation: A novel approach to reduce zinc oxide levels in rubber compounds*, Proceedings International Rubber Conference, July 2003, Nürnberg, Germany.

- ◆ G. Heideman, J.W.M. Noordermeer, R.N. Datta, B. van Baarle, *Zinc Loaded Clay as Activator in Sulfur Vulcanization: A New Route for Zinc Oxide Reduction in Rubber Compounds*, Paper no. 22, Proceedings 164th Technical meeting - Rubber Division, ACS, October 2003, Cleveland (OH), USA.
- ◆ G. Heideman, J.W.M. Noordermeer, B. van Baarle, *Various Routes for Reduction of Zinc Oxide Levels in Rubber Compounds*, Proceedings 6th Fall Rubber Colloquium, DIK, November 2004, Hannover, Germany.

EXTERNAL PRESENTATIONS

- ◆ G. Heideman, Meeting of the Dutch Society of Plastic and Rubber Technologists (VKRT), May 2001, Enschede.
- ◆ G. Heideman, International Rubber Conference, July 2002, Prague, Czech Republic.
- ◆ G. Heideman, International Rubber Conference, July 2003, Nürnberg, Germany.
- ◆ G. Heideman, 164th Technical meeting - Rubber Division, ACS, October 2003, Cleveland (OH), USA.
- ◆ G. Heideman, Annual meeting of the Swedish Institution of Rubber Technology, SGF, October 2003, Halmstad, Sweden.
- ◆ G. Heideman, Meeting of the Dutch Society of Plastic and Rubber Technologists (VKRT), December 2003, Eindhoven.

PATENT APPLICATIONS

- ◆ B. van Baarle, G. Heideman, J.W.M. Noordermeer, (to Nederlandse Organisatie voor Toegepast-Natuurwetenschappelijk Onderzoek TNO), WO2004/052981 A1 (December 11, 2003).

Curriculum Vitae

*'Whoso neglects learning in his youth,
loses the past and is dead for the future.'*
Euripides (480 BC – 406 BC)

Geert Heideman was born in Dinxperlo on 22nd of April, 1976. He attended high school at the Christelijk College 'Schaersvoorde' in Aalten. In 1994 he commenced his academic studies in chemical technology at the University of Twente in Enschede. He investigated amines as devulcanisation chemicals for EPDM rubber in the 'Rubber Technology' group of Prof. Dr. J.W.M. Noordermeer and graduated in December 1999. During his undergraduate period he did a research project at the National Starch & Chemical laboratories in Zutphen on solvent-borne adhesives.

From February 2000 until April 2004 the author worked as a Ph.D. student under the supervision of Prof. Dr. J.W.M. Noordermeer at the University of Twente (Faculty of Science and Technology) in a project in the framework of the Innovative Research Program (IOP): Environmental Technology / Heavy Metals. The results of this work are described in this thesis.

Nawoord

'A true friend is the greatest of all blessings, and that which we take the least care of all to acquire.'

Francois de La Rochefoucauld (1613 – 1680)

*'Some people come into our lives and quickly go.
Some stay a while and leave footprints on our hearts.
And we are never, ever the same.'*

Flavia Weedn

Het zal de lezer duidelijk zijn dat het eindresultaat van 4 jaar onderzoek dat nu in boekvorm voor u ligt, niet gerealiseerd zou zijn zonder de steun en enthousiaste inzet van velen. Derhalve is het een goed gebruik om enkele pagina's in het proefschrift te reserveren om allen die op enigerlei wijze bij de totstandkoming van het proefschrift betrokken zijn geweest te bedanken.

Als eerste wil ik mijn promotor, professor Noordermeer, bedanken voor de gelegenheid die hij mij geboden heeft om na het afstuderen verder te gaan met een promotie-onderzoek. De goede begeleiding en het enthousiasme met betrekking tot de onderzoeksresultaten heb ik altijd als zeer motiverend ervaren. Met name in de slotfase toen de resultaten op een goede manier aan het papier toevertrouwd moesten worden, heb ik enorm veel geleerd. Gelukkig was er naast het gebruikelijke wetenschappelijke contact ook vaak ruimte voor informele zaken.

Mijn assistent promotor, Rabin Datta, wil ik ook hartelijk bedanken voor de goede begeleiding, nuttige suggesties en de snelle correcties van diverse publicaties. De interessante discussies en gesprekken op de vrijdagen en de altijd aanwezige dosis humor heb ik bijzonder gewaardeerd.

Ook ben ik veel dank verschuldigd aan Ben van Baarle van TNO Industrial Technology, die als collega in het project betrokken is geweest. De brede kennis op het vakgebied en het grote netwerk zijn zaken die onontbeerlijk zijn geweest bij het openen van nieuwe wegen. De besprekingen van de resultaten, eerst in Delft en later in Eindhoven, heb ik altijd als nuttig en zeer plezierig ervaren.

De volgende leden van de IOP-begeleidingscommissie wil ik graag bedanken voor de tijd die ze vrijgemaakt hebben om de halfjaarlijkse bijeenkomsten bij te wonen en voor hun inzet en nuttige suggesties: prof. drs. J. Bussink, mw. dipl.-chem. W.K. Dierkes, dr. ir. M. van Duin, ing. O.A. Fokkinga, ir. N. Gevers, dr. A. de Hoog, dr. A.H.A. Tinnemans, W.H. van Rij LPRI en F.J. Baarslag. Ook een woord van dank voor mw. ir. Y.G.C. van Golstein Brouwers en mw. ir. B.C. Breimer van het secretariaat van het IOP Milieutechnologie/Zware Metalen, ondergebracht bij Senter, voor het soepel laten verlopen van het project en natuurlijk voor de getoonde belangstelling.

Een deel van het experimentele werk is uitgevoerd door Jan van Duijl. De vele adviezen en zijn talent om de meest bijzondere laboratoriumbenodigdheden overal vandaan te halen, waren een absoluut onmisbare bijdrage voor het onderzoek. Er moest natuurlijk veel routinewerk gebeuren, maar daarnaast hebben we ook veel leuke experimenten gedaan en in het laatste deel van het onderzoek een zekere bekendheid verworven met de zogenaamde dialyse-‘worsten’.

De HPLC experimenten zouden niet mogelijk zijn geweest zonder de hulp van Hennie Bevers. Met name de hulp bij het opstarten van de experimenten is van veel nut geweest voor het verdere verloop van het onderzoek. De resultaten van de LC-MS metingen zijn helaas niet opgenomen in het proefschrift. Toch wil ik de Chemical Analysis Group van prof. Karst en met name Suze van Leeuwen hartelijk bedanken voor de hulp bij het gebruik van de LC-MS en de bereidheid om mij wat kennis op dit vakgebied bij te brengen.

Een vakgroep kan natuurlijk niet goed functioneren zonder technische en administratieve ondersteuning. Daarom kan ik niet nalaten om John Kooiker en Zlata Rekenji te bedanken voor de technische ondersteuning en de zorg voor de benodigde materialen. Dankzij de inzet van Gerda, onze formidabele secretaresse, en niet te vergeten Karin en Geneviève, konden allerlei administratieve zaken op de juiste manier en op tijd afgehandeld worden. Dat er wel eens wat kritiek geuit werd over kleine onnauwkeurigheden of het aantal versies van een bepaald document betekent natuurlijk niet dat mijn dank minder groot is. Ook de collega's van het SGA hartelijk bedankt voor de absoluut onmisbare, snelle en adequate hulp op computergebied.

Mijn collega's van het eerste uur: Annemieke, Louis, Andries, Kinsuk en Pratip wil ik speciaal bedanken voor alle discussies en bijdragen aan de leuke sfeer in de groep. Het heeft er zeker toe bijgedragen dat ik kan terugzien op vier ontzettend leuke jaren. Ook de prettige samenwerking en discussies met de stafleden Wilma Dierkes en Auke Talma wil ik in dit verband memoreren. Omdat met name in de laatste fase van het promotie-onderzoek veel tijd achter de computer doorgebracht moet worden, is het hebben van behulpzame en leuke kamergenoten erg belangrijk. Daarom wil ik Marek, Montse, Kuno, Francesca, Kannika, Wilco, Tony en ook de collega's van het andere kantoor, Richard, Joost en Jan, bedanken voor hun medewerking en de gezelligheid. But of all roommates there is one who deserves a few extra lines. My direct neighbour in the office: Montse, who has introduced me in the world of Model Compound Vulcanisation and has often helped me out.

Ook alle andere collega's van de vakgroepen RBT, PBM, STEP en MTP wil ik bedanken voor de sociale inbreng tijdens de gezellige koffiepauzes, de befaamde RPK cursussen, borrels en filmavondjes. Heel speciaal wil ik nog noemen mijn mensmaatjes: Louis, Montse, Menno, Léon S. en Mark Ankoné. Hoewel het eten niet altijd even goed was, was het in ieder geval levendig en gezellig. Ook enkele oud-collega's wil ik nog met name noemen: Nico, Subhas, Nitu, Martijn H., Edgar, Judith, Marianne, Miechel en Kathrin. Alle collega's en oud-collega's bedankt voor de gezelligheid!

Nog een woord van dank aan allen die op welke wijze dan ook een bijdrage geleverd hebben aan de totstandkoming van dit proefschrift en misschien niet met name genoemd zijn. Allen hartelijk bedankt!

Tevens wil ik hier graag mijn twee paranimfen noemen. Louis wil ik bedanken voor de vele interessante discussies, hulp bij het project en natuurlijk de gezelligheid. Wilco wil ik speciaal bedanken voor de vele interessante resultaten die hij tijdens zijn afstudeerproject behaald heeft. Veel van zijn werk is daarom ook terug te vinden in dit proefschrift. De samenwerking tijdens de afstudeerperiode en later als collega's heb ikzelf als zeer plezierig ervaren. Voor beide paranimfen nog een woord van dank voor het snelle corrigeren van het proefschrift in de afgelopen maanden.

Mijn ouders, familie en vrienden wil ik bedanken voor de interesse die zij voor mijn promotie-onderzoek getoond hebben in de afgelopen jaren. Heel in het bijzonder wil ik mijn ouders bedanken voor de steun die ze mij, toen mijn wetenschappelijke ambities duidelijk werden, in alle opzichten hebben gegeven.

Tot slot wil ik nog degene noemen die een speciale plaats in mijn leven heeft ingenomen: Judith. Je steun en begrip tijdens deze periode heeft veel voor mij betekend... bedankt!

Geert

