

## **DEVULCANISATION OF NR BASED LATEX PRODUCTS FOR TYRE APPLICATIONS**



The research described in this thesis was financially supported by the Dutch Organisation for International Co-operation in Higher Education (NUFFIC) within the framework of the Joint Financing Program for Co-operation in Higher Education (MHO).

Devulcanisation of NR based latex products for tyre applications

Comparative investigation of different devulcanisation agents in terms of efficiency and reaction mechanism

By Vipin Rajan

Ph.D Thesis, University of Twente, Enschede, The Netherlands, 2005

With references – With summary in English and Dutch

Copyright © Vipin Rajan, 2005

All rights reserved.

Cover design by Vipin Rajan and Steven Mookhoek

Front Cover illustration:

Top: The reaction of diphenyldisulphide with a sulphur vulcanisate in the opening of crosslinks or the scission of main-chains and their combination with a diphenyldisulphide radical, which prevents the recombination of the rubber polymer chains.

Bottom: The nucleophilic reaction of an amine with the sulphur crosslink.

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

ISBN 90 365 2257 9

**DEVULCANISATION OF NR BASED  
LATEX PRODUCTS FOR TYRE APPLICATIONS**

**COMPARATIVE INVESTIGATION OF DIFFERENT DEVULCANISATION  
AGENTS IN TERMS OF EFFICIENCY AND REACTION MECHANISM**

DISSERTATION

to obtain  
the doctor's degree at the University of Twente,  
on the authority of the rector magnificus,  
prof.dr. W.H.M. Zijm,  
on account of the decision of the graduation committee,  
to be publicly defended  
on Friday, 2 December 2005 at 13.15 hrs.

by

**Vipin Vattanattu Rajan**

born on 11 December 1975  
in Ernakulam, India

This dissertation has been approved by:

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

Assistant promoter : dr. dipl.-chem. W. K. Dierkes

---

# Table of contents

---

<b>Chapter 1</b>	Latex products reclamation, a brief introduction	1
<b>Chapter 2</b>	Science and technology of rubber reclamation: a review	7
<b>Chapter 3</b>	Mechanisms involved in the reclamation of NR based latex products with diphenyldisulphide	35
<b>Chapter 4</b>	Reclamation of NR based latex products: a comparative evaluation of amines and disulphides as reclaiming agents	49
<b>Chapter 5</b>	Model compound studies on the devulcanisation of natural rubber using 2,3-dimethyl-2-butene	65
<b>Chapter 6</b>	Effect of diphenyldisulphides with different substituents on the reclamation of NR based latex products	91
<b>Chapter 7</b>	Application of NR based latex reclaim: The link between structure and properties	119
<b>Chapter 8</b>	NR based cured latex material reclaimed with 2,2'-dibenzamidodiphenyldisulphide in a truck tyre tread compound	143
<b>Chapter 9</b>	Summary and final remarks	159
<b>Samenvatting en afsluitende opmerkingen</b>		165
<b>Symbols and Abbreviations</b>		171
<b>Bibliography</b>		175
<b>Curriculum Vitae</b>		177
<b>Acknowledgements</b>		179



# Chapter 1

---

## Latex products reclamation, a brief introduction

---

A concise introduction to the subject of this thesis and the objective of this work is given in this chapter. The history of rubber reclamation is briefly reviewed, and latex reclamation is discussed in terms of importance and driving force. An outline of the structure of this thesis is given at the end.

### 1.1 HISTORICAL REVIEW

Charles Goodyear invented the process of sulphur vulcanisation in 1839,<sup>1</sup> and as a result of his discovery the rubber industry expanded explosively. The first products manufactured from vulcanised rubber in the 1840's were footwear, but soon many different types of rubber goods, sheet rubber and hard rubber articles were produced. In those days, before the establishment of rubber plantations in India, all raw rubber was collected from the jungles of Brazil.<sup>2,3</sup> The demand for crude rubber soon overtook supply, with prices sky-rocketing. At that time there was a great economic incentive to spur the development of re-using scrap vulcanised rubber.

One method of recycling scrap rubber is to grind it as fine as possible and blend it with new rubber as an elastomeric filler. This was the first method of reclaiming and a patent was granted to Charles Goodyear<sup>4</sup> himself for this technique. This was suitable for compounding carriage springs, which were fairly large barrel-shaped moulded articles. However, most of the demand and growth in those days were in the footwear business and simply using ground rubber, quality wise these products were not acceptable for this application. Boots and shoes were the most important rubber products in the nineteenth century. They were formulated with a

fairly low level of sulphur in order to prevent unsightly sulphur bloom. As a result, they were lightly vulcanised and could easily be reclaimed. Such a material can be successfully devulcanised or partially replasticised by the action of steam alone at a higher temperature but for a substantially longer period of time than the original vulcanisation cycle. This is known as the heater process, patented by Hiram L. Hall in 1858.<sup>5</sup> The product of this reclaiming process was revulcanisable and could be blended with the new natural rubber at a higher percentage.

In order to make a high-quality reclaim, reinforcing fibres must be removed from the rubber scrap. In the early years this was done by the cottage industry in which women and children stripped the rubber from the fabric of old boots “by soaking the rubber in water, and then taking a small knife and starting to separate the rubber from the cloth and stripping it off”. Eugene H. Clapp<sup>2</sup> used an air-blast method of separating fibres and rubber after the scrap was ground. Clapp did not patent the technique but managed to keep it secret for several years. Although Clapp’s method is the early version of present day defibering equipment, it was not developed to the point that it could produce a raw material of more than mediocre quality. Better methods of producing large quantities of higher-quality reclaim were needed.

It had been common knowledge for many years that acid has a degrading effect on fabric and that rubber is resistant to acid. N. Chapman Mitchell<sup>2</sup> was a leader in the development of the acid process, and started the first company to produce reclaimed rubber by that method. Mitchell filed patents on the process in 1881, which were granted, but they were poorly drawn and were later on canceled. In the acid process, the ground scrap was boiled for several hours in a fairly strong solution of either sulphuric or formic acid to destroy the fabric; the rubber was washed and devulcanised with high-pressure steam in the so-called pan process; a two-step operation. Although the acid process was used quite successfully for a longer period of time, it had its shortcomings. One of the problems was the inability to process high-sulphur rubber scrap, such as bicycle tyre scrap. If the acid was not thoroughly washed, it could cause poor ageing characteristics. The high quantities of free sulphur in such types of rubber scrap tend to cause further vulcanisation during the process instead of devulcanisation.

A breakthrough was achieved in 1899 with the patent of Arthur H. Marks, which describes an invention that came to be known as the alkali digester process.<sup>6,7</sup> Ground rubber, fibre, and a dilute solution of caustic soda were cooked at high pressure for about 20 hours. This process caused de-fibering, desulphuring, and devulcanisation of the rubber scrap in one step. This technique could be used to reclaim any type of rubber scrap available at that time. A year later, in 1900, Marks obtained another patent on an improvement that involved steam jacketing the vessel and agitation of the mass. This is the method used by most reclaimers for more than fifty years.

Two other important developments occurring at the turn of the nineteenth century involved the introduction of new machines to greatly improve the quality of reclaimed rubber. One development was the refiner that is a special type of mill used to produce a much smoother and more homogeneous product. The other was the strainer, which is an extruder equipped with a screen for removal of foreign matters from the rubber. With the exception of invention of the Reclaimator in 1953,

developments in the reclaiming industry since the time of Marks have been mostly evolutionary rather than revolutionary.<sup>8</sup>

The Reclaimator process is the only commercially successful continuous technique for devulcanising rubber scrap; all the other techniques are batch processes. The Reclaimator is a special type of screw-extrusion machine. It is jacketed to provide several zones of controlled temperature using either hot oil or cooling water and the clearances between the screw and the chamber wall are close and adjustable. The rubber is subjected to a controlled amount of high shear and pressure in continuously moving equipment.

The latex industry has expanded over the years to meet the world demand for examination gloves, condoms, latex thread etc. Due to strict specifications for latex products, up to 15% of the products might be rejected. These rejects create a major disposal problem for the rubber industry. Since latex product waste represents a source of high quality rubber hydrocarbon it is a potential feedstock for reclaimed rubber of superior quality.

Probably the largest numbers of defects encountered in articles produced by latex dipping are pinholes, craters and blisters. These defects are caused by air bubbles entrapped in the latex compound, particles of dirt in the latex compound and on the former, and greasy areas of the former.<sup>9</sup> The former is the positive mould, which is dipped in the latex repeatedly, onto which the rubber remains as a film and is cured in an oven. The rubber article is later manually removed from the former. Problems arising from particles of dirt and dust settling on the former are especially critical in dry-coagulant dipping processes. This is because the coacervant film usually goes through a tacky stage as it dries.

Over the past 43 years, the world NR Latex (NRL) consumption has grown at an average of 4.2% per year, increasing to an estimated 925,000 tonnes in 2003. However, the growth was not smooth; NRL consumption had a slower growth period from 1960 to 1983, with an average growth rate of 2.1% per year and a faster growing period from 1984 to 2003, averaging 5.6% per year. In terms of actual tonnage the increase was 159,000 tonnes and 597,000 tonnes<sup>10</sup> for the respective periods. The main driving force of the faster growth rate of the latter period was and still is the AIDS-HIV threat and the consequent growing awareness of the need for protection, reflected in the rapid rise of demand for medical gloves, in particular, since the mid-1980s. Gloves were the main reason for the rising NRL uptake over the past 20 years; it was and still is playing the leading role in the latex world.<sup>11</sup> The product range of NRL is wide and varied, ranging from industrial to household over medical applications.

The main area of growth of latex consumption was Asia from 1984 to 2003, the average growth rate for the region was 9.2% a year, increasing its annual consumption from 144,000 tonnes to 692,000 tonnes. This is 5% above the world rate for the same period. As of 2003, the annual consumption level of the other five regions are: North America 101,000 tonnes, Latin America 33,000 tonnes, European Union 78,000 tonnes, other European countries 14,000 and Africa 4,000 tonnes.

## 1.2 AIM OF THIS THESIS

The aim of this thesis is two-fold. In an application oriented study the effect of material characteristics (feedstock), reclaiming agents and process conditions are investigated on the quality of reclaim made from different sulphur vulcanised latex products. Secondly in a fundamental study, the reaction mechanism and chemistry of the reclamation process using different reclaiming agents under different processing conditions are elucidated. Liquid chromatographic techniques and Model Compound (MC) studies will be employed to unveil the reaction steps during reclamation.

The analysis of the feedstock is important, because the crosslink scission in sulphur vulcanisates during reclamation depends on the type and amount of sulphidic linkages. It is well known that the bond energy of the monosulphidic crosslinks is higher than that of poly- or disulphidic crosslinks,<sup>12,13</sup> that implies that a sulphur vulcanisate with a lower percentage of monosulphidic crosslinks will reclaim easier. Different aliphatic amines and aromatic disulphides are used as reclaiming agent. The selection of the reclaiming agents is based on literature data and historically they have most prominently been used as devulcanisation agents for natural rubber.<sup>14,15</sup>

## 1.3 STRUCTURE OF THE THESIS

The work described in this thesis investigates the effect of feedstock characteristics, process conditions and reclaiming agents on the quality of reclaim from different latex products. A profound study on the mechanistic pathway of devulcanisation with amine and disulphide is done with model compounds. The thesis is divided into 8 chapters:

A concise introduction into different aspects of reclamation with special attention on latex reclamation is given in Chapter 2. Different types of reclaiming processes are described with special attention to processes, which selectively cleave the crosslinks in the vulcanised rubber. The state-of-the-art techniques in the reclamation process are mentioned thereafter. One section is dedicated to the model description of main-chain and crosslink scission during devulcanisation of a rubber vulcanisate.

In Chapter 3, an investigation is made using diphenyldisulphide as a reclaiming agent for sulphur vulcanised waste latex rubber in a thermo-mechanical reclaiming process. The parameters investigated are the concentration of the reclaiming agent, as well as reclaiming temperature and time required for proper reclamation of the feedstock.

Two reclaiming agents for waste latex rubber vulcanisates are compared in Chapter 4. Hexadecylamine and diphenyldisulphide were selected as reclaiming agents, because historically these two have most prominently been used as devulcanisation agents for natural rubber and they react according to different mechanisms: amines reclaim by a nucleophilic and disulphides by a radical

mechanism. Ideally, this study is to compare between the radical mechanism from disulphide and the nucleophilic mechanism from amine.

In Chapter 5, the mechanism of devulcanisation of sulphur vulcanised natural rubber with aromatic disulphides and aliphatic amines is studied using model compounds. Squalene and 2,3-dimethyl-2-butene is used as the low-molecular weight model compound. The kinetics and chemistry of the breakdown of the sulphur-bridges during devulcanisation are monitored at different temperatures and at different concentrations of devulcanisation agents.

In Chapter 6, the effect of different substituents on diphenyldisulphides on the efficiency of reclamation is investigated. The kinetics of the reclamation reaction with variation of different reclamation agents and feedstock are discussed. Reaction rates for different conditions are calculated and compared with theoretical values in order to get a better view on the correlation between the time-temperature profile of the reclaiming process and the degree of reclamation.

The application of NR latex reclaim, produced using diphenyldisulphide as the reclaiming agent, is discussed in Chapter 7. The usage of the reclaim in a truck tyre tread recipe by replacing the virgin polymer rubber is studied. A mechanistic approach is followed to explain the changes in properties after the addition of reclaim to the compound.

In Chapter 8, an alternative reclaiming agent is chosen due to its high reclaiming efficiency and low environmental impact. 2,2'-dibenzamido-diphenyldisulphide is selected as the reclaiming agent. The influence of the reclaim on the cure behaviour, mechanical and viscoelastic properties of the blend are investigated.

## 1.4 REFERENCES

1. C. Goodyear, US 3633 (June 15, 1844).
2. P. Schidrowitz, T. R. Dawson, *History of the Rubber Industry*, Institute of Rubber Industries, Eds., Heffer & Sons, Cambridge, (1952).
3. W. Hoffmann, *Rubber Technology Handbook*, Hanser Publishers, New York, (1994).
4. C. Goodyear, GB 2933 (December 16, 1853).
5. C. M. Blow and C. Hepburn (Eds.), *Rubber Technology and Manufacture*, Butterworth, London, (1982).
6. E. Sverdrup, *Encyclopedia of Polymer Chemistry and Technology*, **12**, (1970), 341.
7. R. N. Hader, D. S. L. Beau, *Ind. Eng. Chem.*, **43**, (1951), 250.
8. J. M. Ball, *Reclaimed Rubber*, Rubber Reclaimers Association, Inc., New York, (1947).
9. D. C. Blackley, *Polymer Latices – Science and Technology*, Chapman and Hall, London, (1997).
10. P. Jumpasut, paper presented at the Latex conference, Hamburg, Germany (2004).
11. R. H. D. Beswick, D. Dunn paper presented at the Latex conference Hamburg, Germany (2004).
12. T. H. Kuan, *Rubber World* **192**(5), (1985), 20.
13. C. M. Kok, V. H. Yee, *Eur. Polym. J.*, **22**, (1986), 341.
14. J. A. Beckman, G. Crane, E. L. Kay, J. R. Laman, *Rubber Chem. Technol.*, **47**, (1974), 597.
15. M. A. L. Verbruggen, L. van der Does, J. W. M. Noordermeer, M. van Duin, H. J. Manuel, *Rubber Chem. Technol.*, **72**, (1999), 731.

# Chapter 2

---

## Science and technology of rubber reclamation: a review

---

A comprehensive overview of reclamation of cured rubber with special emphasis on latex reclamation is depicted in this chapter. The role of the different components in the reclamation recipe is explained and the reaction mechanism and chemistry during reclamation are discussed in detail. Different types of reclaiming processes are described with special reference to processes, which selectively cleave the crosslinks in the vulcanised rubber. The state-of-the-art techniques of reclamation with special attention on latex treatment is reviewed. A model description of main-chain and crosslink scission during devulcanisation of a rubber vulcanisate is given.

### 2.1 INTRODUCTION

The rubber industry faces a major challenge in finding a satisfactory way to deal with the increasing quantities of rubber goods, which reach the end of a useful life and are rejected from the factories as scrap. The main source of waste rubber is discarded rubber products, such as tyres, rubber hoses, belts, shoes and flash. Recycling of waste rubber has important implications, such as:<sup>1</sup>

- Protection of the environment: the environmental pollution caused by waste rubber is getting more and more serious. Piles of discarded tyres are good breeding places for mosquitoes and disease. They spread infections such as encephalitis and malaria. Tyre dumps catch fire, they are difficult to extinguish.
- Conservation of energy: raw materials for rubber industry are based on oil to a large extent, especially in countries where natural rubber resources are

very scarce. More than 70% of the raw materials for the synthetic rubber are made from oil. Moreover, waste rubber is a high-value fuel, with a calorific value of approximately  $3.3 \times 10^4$  kJ/kg,<sup>2</sup> which is the highest value in the industrial waste sector, and is similar to that of coal.

- Use as industrial raw material: regenerated rubber and powdered rubber are raw materials not only for the rubber industry.
- Reducing the costs and improving the processing behaviour of rubber compounds.

For the reasons mentioned above, recycling of waste rubber has received much attention in recent years worldwide.<sup>2</sup>

This chapter is a summary of many previous review articles on different aspects of reclamation. Important references on disposal problems are Crane, Elefritz, Kay and Laman<sup>3</sup> as well as Beckman.<sup>4</sup> Smith,<sup>5</sup> Klingensmith,<sup>6</sup> and recently Myhre<sup>7</sup> did a lot of work on recycling. Excellent overviews are provided by Manuel and Dierkes,<sup>8</sup> Dunn<sup>9</sup> and LeBeau.<sup>10</sup> A comprehensive review on the chemistry of reclamation is provided by Warner<sup>11</sup> and Yamashita.<sup>12</sup>

## **2.2 ROLE OF RECLAIMING AGENTS, OILS AND CATALYSTS**

Reclaim can be defined as “the product resulting from the treatment of vulcanised scrap rubber, tyres, tubes and miscellaneous waste rubber articles by the application of heat, mechanical energy and chemical agents whereby regeneration of a rubber compound to its original plastic state is effected, thus permitting the product to be processed, compounded and vulcanised.”<sup>13</sup> Regeneration can occur either by breaking the existing crosslinks in the vulcanised polymer or by promoting scission of the main-chain of the polymer or a combination of both processes.

A definition of reclaiming agents, catalysts and reclaiming oils depends on their reaction and function within the process. Yamashita<sup>12</sup> published a review on the different reactions that might occur during reclaiming. The auto-oxidation accelerated degradation reactions are described and these reactions occur particularly in reclaiming processes that involve shearing actions. Without the addition of reclaiming agents, auto-oxidation reactions will progress through hydroperoxides formed by the attack of oxygen, which is always present in the rubber. Utilisation of reclaiming agents speeds up and introduces new pathways for the reclamation reactions. Reclaiming catalysts are chemical compounds, which are effective in only small amounts during reclamation.

Reclaiming oil has several roles apart from raising the plasticity of reclaimed rubber, such as an accelerating action on the oxidation of the rubber<sup>14</sup> and a gel preventing action by acting as a radical acceptor. It also facilitates the dispersion of the reclaiming agent into the rubber matrix. Hence reclaiming oil with a high compatibility with the rubber should be used. The reclaiming oils often have active double bonds or methylene groups in the molecules, through which they are more easily oxidised than the rubber molecule. It is assumed that these activated

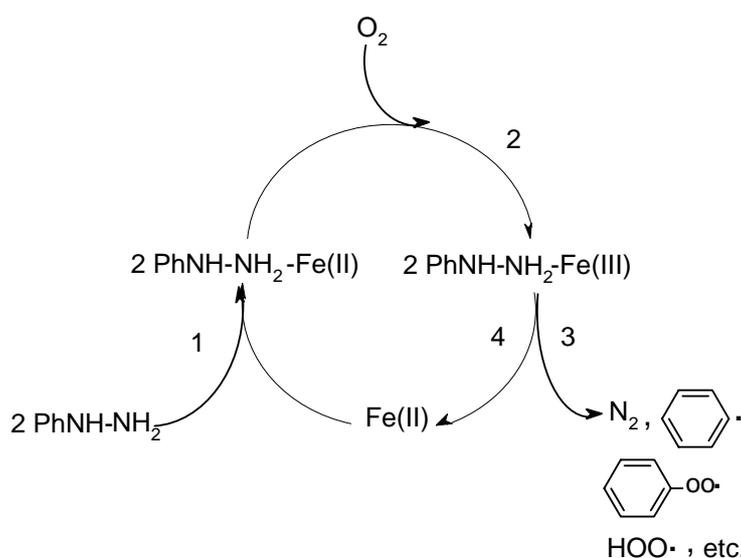
molecules formed by the auto-oxidation reaction, accelerate the oxidation of the rubber.

## 2.3 REACTION MECHANISM DURING RECLAMATION OF VULCANISED RUBBER

The reaction mechanisms in reclaiming are complex and not well investigated. However, the following basic reactions can be formulated: Reclamation can occur by breaking the existing crosslinks in the vulcanised rubber (crosslink scission) or by promoting scission of the main-chain of the polymer (main-chain scission) or by both processes. All three possibilities are considered separately in the following sections.

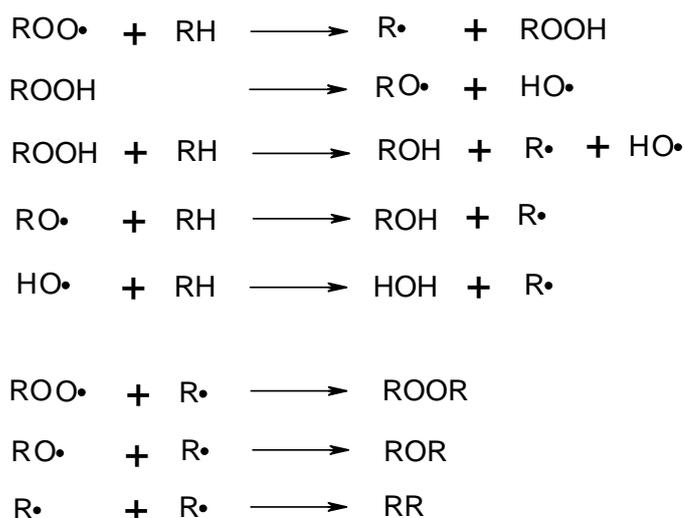
### 2.3.1 Main chain scission (Phenyl hydrazine-Iron chloride)

As an example of this mechanism, the phenyl hydrazine-Iron(II)chloride system (PH-FeCl<sub>2</sub>) is taken. This is very effective for the oxidative degradation of the rubber molecules at low temperatures. In the degradation reaction of polyisoprene rubber with the PH-FeCl<sub>2</sub> system in presence of air, the phenyl hydrazine is the main reagent and FeCl<sub>2</sub> acts as catalyst: the rate of degradation of the rubber is determined by the phenyl hydrazine concentration.<sup>15</sup> Phenyl hydrazine is itself easily degraded by oxygen and it is known that nitrogen gas is liberated in this reaction.<sup>16,17</sup> The rate of degradation is very high in the presence of a metal salt. The initial oxidative degradation of rubber molecules with the PH-FeCl<sub>2</sub> system is outlined below: Figure 2.1



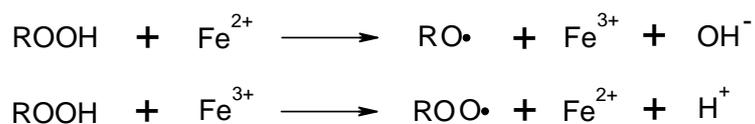
**Figure 2.1** Oxidation mechanism for the PH-FeCl<sub>2</sub> system<sup>18</sup>

If sufficient oxygen is present, the various radicals formed by this reaction degrade the rubber molecules as indicated in Figure 2.2



**Figure 2.2** Bolland oxidation mechanism (RH = rubber hydrocarbon) <sup>19</sup>

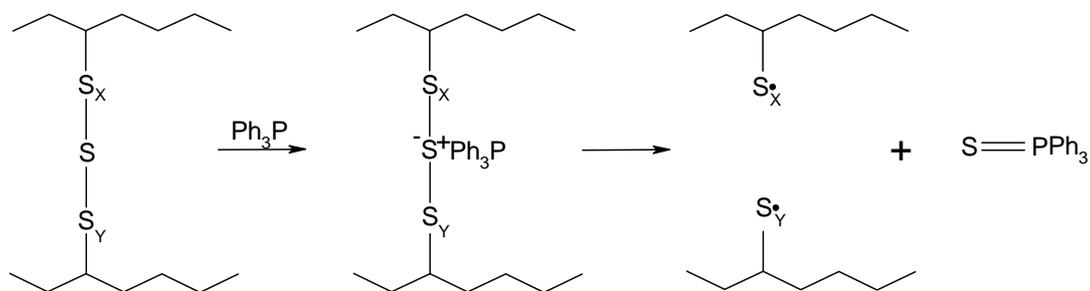
The hydroperoxide is decomposed in the presence of transition metals as shown in Figure 2.3



**Figure 2.3** Decomposition of peroxides by ions of metals (Redox mechanism)

### 2.3.2 Crosslink scission (Triphenyl phosphine)

Triphenyl phosphine is known to open the sulphur crosslinks by a nucleophilic reaction<sup>20</sup> as shown in Figure 2.4:

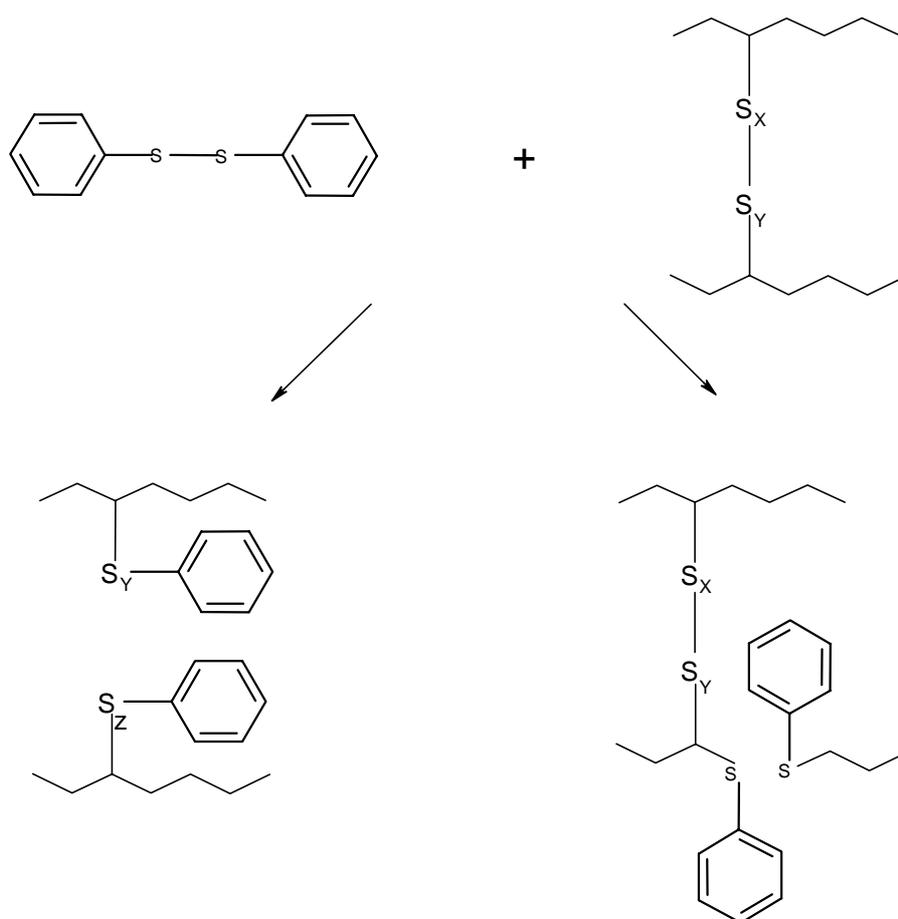


**Figure 2.4** Opening of sulphur crosslinks by triphenyl phosphine

The radicals can recombine, but a reaction with a double bond is also possible, with the net effect that the crosslink is broken.

### 2.3.3 Main chain and crosslink scission (Thiols and disulphides)

Thiols and disulphides interact with radicals formed during the degradation of the rubber network. It is assumed that they initiate an oxidative breakdown of sulphur crosslinks and a degradation of rubber vulcanisates<sup>21</sup> and inhibit gel formation by combination with the radicals. A vulcanisate that is recycled with thiols and disulphides shows a larger degree of network breakdown. In thermo-mechanical processes disulphides and thiols are equally reactive.<sup>22</sup> Aliphatic thiols are found to be less active than aromatic thiols. The efficiency of aromatic compounds seems to increase when alkyl groups or halogens are substituted on the benzene ring. A mechanism that is often proposed for the reaction of disulphides with sulphur vulcanisates is the opening of crosslinks or the scission of chains by heat and shearing forces and their reaction with disulphides, which prevents recombination (Figure 2.5). Atmospheric oxygen is also said to prevent recombination by stabilising the radical sites.<sup>23,24</sup> The result is a drop in molecular weight of the polymer. During the thermal degradation hydrogen sulphide and thiols are produced.



**Figure 2.5** Proposed reaction mechanism of crosslink and main-chain scission with disulphides

## 2.4 OPENING OF SULPHUR CROSSLINKS

Various chemical probes are already used in crosslink structure analysis for opening the sulphur crosslinks.<sup>25</sup> The reaction described in Figures 2.6 - 2.10 have been proposed as typical methods for rupturing the sulphur crosslinks of rubbers.<sup>26-28</sup>

### 2.4.1 Opening by oxidation

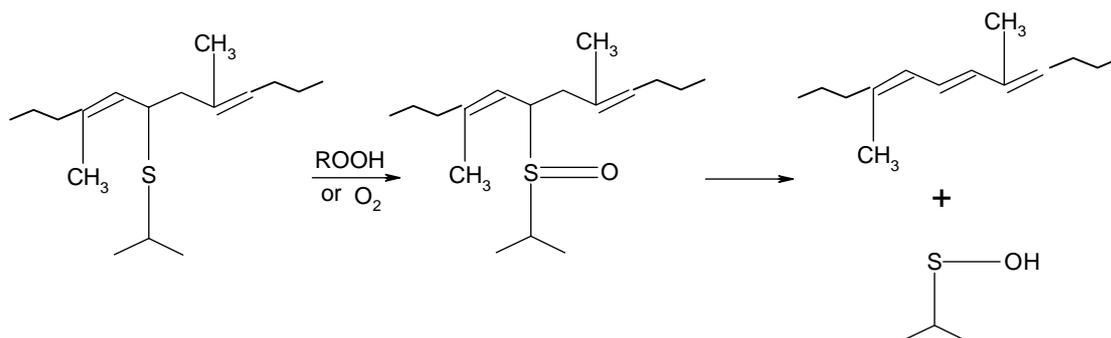


Figure 2.6 Opening of sulphur crosslinks by oxidation (ROOH = Organic hydroperoxide)

### 2.4.2 Opening by heat or shear

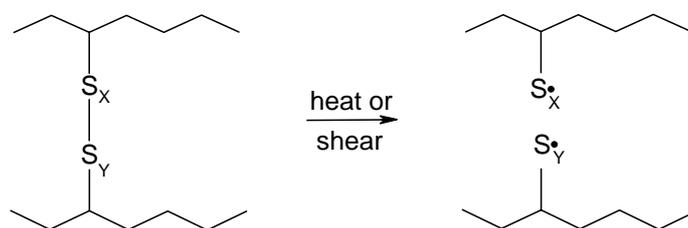


Figure 2.7 Opening of sulphur crosslinks by heat or shear

### 2.4.3 Opening with nucleophilic reagents

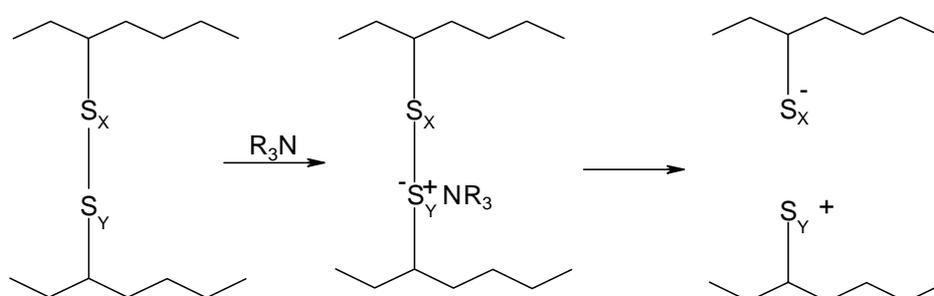
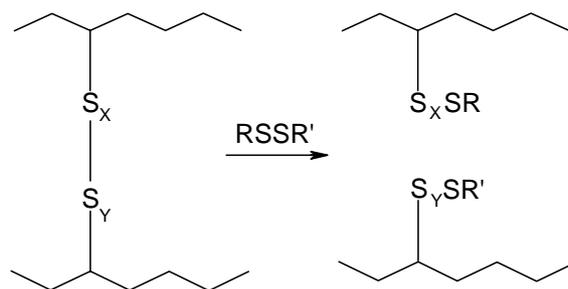


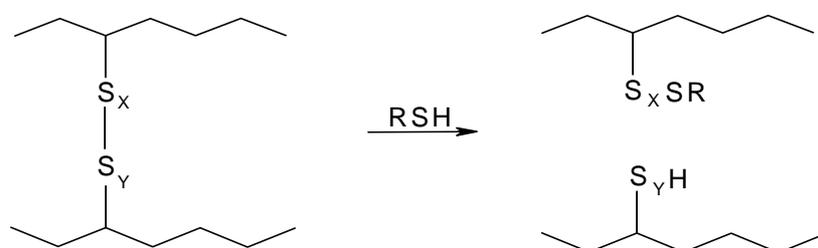
Figure 2.8 Opening of sulphur crosslinks by nucleophilic reagents

### 2.4.4 Opening by rearrangement



**Figure 2.9** Opening of sulphur crosslinks by rearrangement

### 2.4.5 Opening by substitution



**Figure 2.10** Opening of sulphur crosslinks by substitution

These reactions take place under the given reaction conditions, but the complete reaction is not as simple as shown. Hydrogen addition and reduction reactions are also possible but these are to be avoided from the point of view of reclaiming.

## 2.5 DIFFERENT TYPES OF RECLAIMING PROCESSES

There are basically four different levels of recycling: <sup>29</sup>

- Material recycling;
- Monomer recycling;
- Fuel recycling;
- Energy recycling.

In this study only material recycling will be taken into consideration.

The two principle methods to obtain a reusable recycled rubber material are:

- Grinding of the rubber and reusing it in the form of a granulate or surface activated powder;
- Treating the material in a reclaiming process to generate a viscoelastic reclaim.

Different processes are developed in order to reclaim vulcanised rubber.

### **2.5.1 Thermal processes**

In this section, reclaiming processes that make use of heat and possibly chemicals to plasticise the rubber scrap are summarised.<sup>8</sup>

#### **2.5.1.1 Heater or Pan process**

The heater or pan process is one of the oldest and most simple processes used in the rubber reclaim industry. In this process, finely ground, fibre-free rubber powder is mixed with oils and reclaiming agents and put into trays. The trays are designed to help to spread the heat into the powdered mass by means of hollow metal pipes going through the bulk of the material. These trays are heated with steam inside the heater to the desired temperature, typically 180°C for 5-10 hours. Reclaiming chemicals are aromatic thiols, disulphides and aromatic oils. Their use allows lower temperatures and shorter reclaiming times and produces a product with superior mechanical properties.

#### **2.5.1.2 Digester process**

In this method the ground scrap material is mixed with fibre dissolving agents, water, plasticising oils and, if needed, reclaiming agents. This mix is then transferred to a large jacketed agitator-equipped autoclave. It is heated to 180-210°C for 5 - 24 hours by using steam. Afterwards the digester is emptied in a blow-down tank, the material is washed, dried and then ready for final refining and straining steps.

#### **2.5.1.3 Alkaline process**

The fibre in the scrap is digested by the use of sodium hydroxide in a high concentration (upto 7%).<sup>30</sup> the cellulose in the fibre containing scrap is hydrolysed. After recycling, a washing procedure is required to remove excess de-fibreising agent. The crumb is then dried and refined. The process is found to be detrimental to SBR containing rubber material, as hardening takes place.

#### **2.5.1.4 Neutral process**

An improvement to overcome the hardening problem was the development of the neutral process. In this process, zinc chloride and pine oil are used.<sup>8</sup> Calcium chloride or zinc chloride is added for the hydrolysis of the textile.

The heater, digester, alkaline and neutral processes use long reaction cycles are characterised by long recycling time.

### **2.5.1.5 High pressure steam process**

More recent developments aimed at shorter reaction times. In the high pressure steam process,<sup>30</sup> fibre-free, coarse ground rubber scrap is mixed with reclaiming agents and reclaimed in a high pressure autoclave at a temperature around 280 °C for 1-10 minutes.

### **2.5.1.6 Engelke process**

Another modification is the Engelke process,<sup>31</sup> in which coarse ground rubber scrap, mixed with plasticising oil and peptisers, is lowered in cages into a small autoclave. This mixture is heated to very high temperatures for 15 minutes, after which refining and straining takes place.

### **2.5.1.7 Continuous steam process**

A continuous steam process uses temperatures around 260 °C and high pressures in a hydraulic column. The rubber is ground and water is used as a carrying medium and to seal the material from extraneous oxygen, because otherwise heat and pressure would cause combustion. Heat and pressure combined with the injected chemical agents cause a substantial breakdown of the rubber in suspension.

## **2.5.2 Thermo-mechanical process**

During most mechanical processes a strong rise in temperature occurs that aids in degrading the rubber network. Thermo-mechanical recycling of rubber is assumed to be a combination of breaking of carbon-to-carbon bonds and sulphur crosslinks. This results in the formation of soluble branched structures called sol and fragments of gel. The modern material recycling processes all use thermo-mechanical regeneration methods. Recycling chemicals and oils are frequently used in addition to the thermal and mechanical breakdown: disulphides, thiols, amines and unsaturated compounds are the most common recycling chemicals. They are added in quantities of around 1wt%.<sup>30</sup> Softeners lower the thermal degradation resistance of a vulcanisate by weakening the interaction between filler and rubber chains.

### **2.5.2.1 High speed mixing**

A fast thermo-mechanical recycling process is the high speed mixing process. The rubber is stirred at a speed of 500 rpm and the temperature rises to 200 °C.<sup>12</sup> The process takes 15-20 minutes.

### **2.5.2.2 Reclaimator process**

The Reclaimator process, developed in the 1960's, is a single screw extrusion process. A flow diagram of the process is given in Figure 2.11.<sup>32</sup> Again, the rubber is quickly heated to 200 °C by shearing forces. As the extrusion time is around 3 minutes, this process is suitable for synthetic rubbers that show hardening during longer recycling times like SBR.

Another reclaiming process based on extrusion is the Ficker reclaiming method that uses an extruder with co-rotating screws. Temperatures of 240-280 °C are reached.

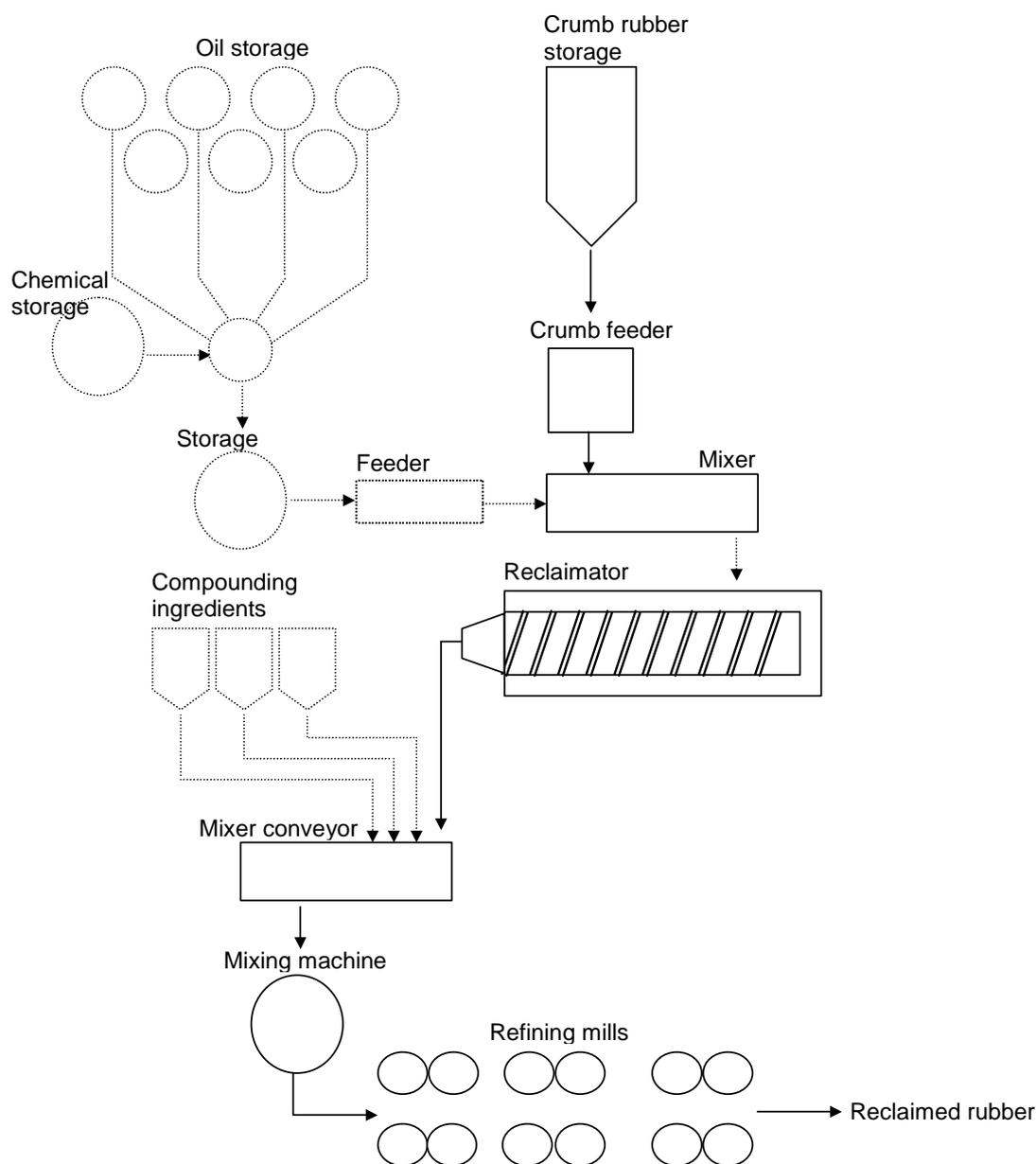


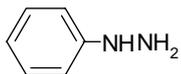
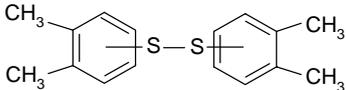
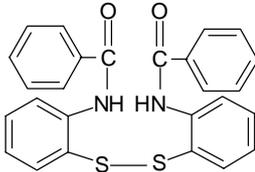
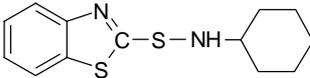
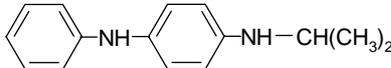
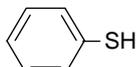
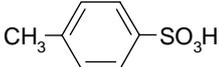
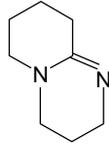
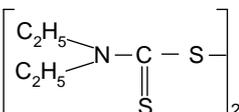
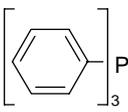
Figure 2.11 Flow diagram of the Reclaimator process<sup>32</sup>

### 2.5.3 Mechano-chemical methods

Plasticisation can be improved by using a reclaiming accelerator while applying a mechanical force to the rubber powder in the presence of air at room temperature. In general, at low temperatures a reclaiming catalyst, reclaiming oil and process oil are used jointly with the reclaiming agent. Typical agents are shown in the Table 2.1.<sup>12</sup>

Peroxide in combination with methyl halide (material 1) is a powerful radical initiator for a redox system. Phenyl hydrazine and ferrous chloride as well as tributylamine and cuprous chloride (materials 2 and 3) form a complex with each other. This complex is easily degraded by oxygen, under formation of the oxidation initiators. These systems degrade diene-based rubber in the presence of oxygen at room temperature. Dicylyldisulphide and 2,2'-dibenzamidodiphenyldisulphide (materials 4 and 5) are used as peptising agents. N-Cyclohexylbenzothiazole-2-sulphenamide (material 6) is commonly used as vulcanisation accelerator and N-isopropyl-N'-phenyl-p-phenylene diamine (material 7) is used as an antioxidant. Thiophenol and n-butylamine (material 8), toluene sulphonic acid and 1,8-diazabicyclo[5.4.0]undec-7-ene (material 9) as well as the rubber

**Table 2.1** Reclaiming agents used in mechano-chemical methods

No.	Chemical name/Abbreviation	Reclaiming accelerator	Reclaiming catalyst
1	Peroxide – Methyl halides	ROOR	Me <sub>n</sub> X <sub>m</sub>
2	Phenyl hydrazine – Ferrous chloride (PH-FeCl <sub>2</sub> )		FeCl <sub>2</sub> ·4H <sub>2</sub> O
3	Tributylamine – Cuprous chloride (TBA-CuCl)	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	Cu <sub>2</sub> Cl <sub>2</sub>
4	Dicylyldisulphide		
5	2,2'-dibenzamidodiphenyl disulphide		
6	N-Cyclohexylbenzothiazole-2-sulphenamide (CBS)		
7	N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD)		
8	Thiophenol – n-Butylamine (TP-BA)		n-BuNH <sub>2</sub>
9	Toluene sulphonic acid - 1,8-diazabicyclo[5.4.0]undec-7-ene (TS-DBU)		
10	Tetraethylthiuramdisulphide – Triphenyl phosphine (TETD – TPP)		

accelerators, tetraethylthiuram disulphide and triphenyl phosphine (material 10) were found to increase the plasticity of rubber reclaim. The fact that these reagents behave as reclaiming agents for rubber is explained by their function as a radical acceptor for the rubber radicals that are formed in the mechano-chemical reaction.

### **2.5.3.1 Trelleborg Cold Reclaiming process**

In the Trelleborg Cold Reclaiming (TCR) process, small quantities of recycling agents are mixed into cryogenically ground rubber powder. A short treatment is carried out in a powder mixer at room temperature or at a slightly higher temperature. Phenyl hydrazine-methyl halide or diphenyl guanidine is used to react with the vulcanisates.<sup>12</sup>

### **2.5.3.2 De-Link process**

The recycling of rubber crumb with vulcanisation accelerators and sulphur on a mill is used in the patented De-Link process. The process is not only suitable for NR, but also for EPDM. The rubber is processed on a two-roll mill for approximately 7 minutes at temperature below 50 °C. The added chemical mixture is prepared from the zinc salt of dimethyldithiocarbamate and mercaptobenzothiazole with stearic acid, sulphur and zinc oxide dispersed in diols.<sup>33</sup> Tetramethyl thiuram disulphide can also be used. It is assumed that the process is based on a proton transfer reaction. The process is more effective for conventional sulphur vulcanisates than semi-efficient and efficient sulphur vulcanisates, the number of crosslinks is decreased by a factor of 2. As the nip opening of the mill was found to have a significant effect on properties, the vulcanisate breakdown is probably caused by mechanical breakdown.

### **2.5.3.3 Swelling in benzene with a sulphoxide**

NR vulcanisates are attacked by swelling in benzene with a sulphoxide compound like dimethyl sulphoxide (DMSO), di-n-propyl sulphoxide (DPSO) or a mixture of these with thiophenol, methyl iodide or n-butyl amine in a mechano-chemical process on a mill.<sup>34,35</sup> A thiol and DMSO react to form a disulphide and a nucleophilic agent  $S(CH_3)_2$ . It is reported that these reagents cause selective scission of sulphur bonds. NR is completely degraded by the combination of DMSO and thiophenol, but SBR is much less reactive. Although the degree of swelling in an organic solvent increased, only 2% of sol fraction was formed. The low sol fraction and high swelling ratio is in agreement with the theory of selective crosslink scission.<sup>36</sup> A disadvantage of this process is that solvents like DMSO and methyl iodides are highly toxic.

## **2.5.4 Microwave recycling**

In this method, microwave electromagnetic energy is used to break the S-S or C-S bonds in the rubber powder.<sup>37,38</sup> By using microwaves, the temperature of the material increases very fast to reach finally 260 °C to 350 °C. A pre-condition to reach this temperature level for devulcanisation is that the vulcanisates should contain carbon black, making them suitable for this method. Carbon black containing rubber is susceptible to ultra high frequency in a microwave chamber due to interface or ion

polarisation: accumulation of free electrons at the interface of different phases with a different conductivity and dielectric constant. Microwave energy at 915 or 2450 MHz is sufficient to cleave crosslink bonds but insufficient to cleave polymer chains.

The properties of the reclaim are reported to be better than those of rubber obtained by other reclaiming methods: EPDM and IIR are particularly suitable for this process. The process is able to convert vulcanised waste such as EPDM (automotive coolant hoses) into a usable compound in just 5 minutes.<sup>39,40</sup> The process has the disadvantage that it is difficult to control.

### 2.5.5 Ultrasound recycling

Next to the microwave radiation, ultrasonic energy is used for the devulcanisation of crosslinked rubber. The first work with ultrasonic energy was reported by Pelofsky<sup>41</sup> in 1973. In this patented process, solid rubber articles are immersed into a liquid, then ultrasonic energy is applied whereby the bulk rubber effectively disintegrates and dissolves into the liquid. In this process ultrasonic radiation is in the range of about 20 kHz and at a power intensity of larger than 100 W was used. Ultrasonic reclaiming of a NR vulcanisate was also reported by Okuda and Hatano in 1987.<sup>42</sup> They subjected the NR vulcanisate to 50 kHz ultrasonic energy for 20 minutes to achieve devulcanisation. Mangaraj<sup>43</sup> indicated in his patent on vulcanisation of rubber by ultrasonic radiation a possibility of rubber degradation and devulcanisation by ultrasonic energy. Later Isayev and coworkers reported in a number of publications<sup>44-56</sup> the phenomenon of devulcanisation by ultrasonic energy.

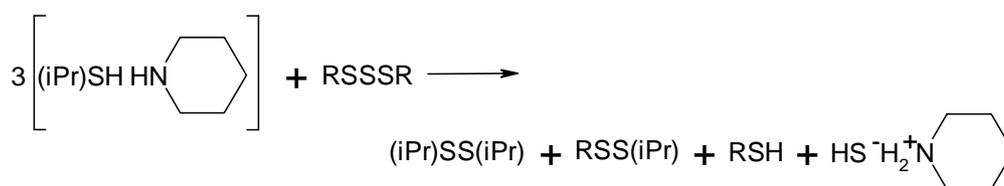
The devulcanisation process requires a high energy level to break C-S and S-S bonds,<sup>11</sup> which can be provided by an ultrasonic field creating high-frequency extension-contraction stresses. Isayev and his group at the University of Akron, Ohio, designed an ultrasonic reactor of a 38.1 mm rubber extruder with a length to diameter ratio of 11 and a co-axial cone shaped ultrasonic die attachment equipped with three temperature-controlled zones. The screw is heated electrically or cooled by water. The scrap rubber is fed into the extruder by a conveyor belt with adjustable output. A 3 kW ultrasonic power supply, an acoustic converter and a 76.2 mm cone-tipped horn are used. The horn vibrates longitudinally at a 20 kHz frequency and 5-10  $\mu\text{m}$  amplitude. The scrap rubber particles are transported within the extruder to the chamber with the ultrasound horn, and the recycled rubber can exit this chamber through a die. When SBR is recycled by ultrasound extrusion,<sup>57</sup> cleavages of intermolecular bonds such as C-S and S-S as well as C-C bonds in the main-chain take place. An increase in ultrasound amplitude is accompanied by significant decrease in molecular weight of the sol fraction and a decrease of the gel content. An increase in the extruder temperature also results in a higher sol fraction. Conventional sulphur vulcanisates are more susceptible to sol production. This process is characterised by substantial main-chain scission.

A continuous ultrasonic devulcanisation of unfilled EPDM rubber was also carried out,<sup>58</sup> and the mechanical properties of revulcanised EPDM rubber were measured. Gel fraction, crosslink density, and dynamic properties were also determined for the virgin vulcanisate, the ultrasonically devulcanised rubber, and the revulcanised rubber: The tensile strength of the revulcanised EPDM was much higher than that of the original vulcanisate with elongation at break values being

practically unchanged. It is proposed that the improvement in mechanical properties of revulcanised EPDM is mainly due to the extent of non-affine deformation of the bimodal network that possibly appears in the process of revulcanisation of ultrasonically devulcanised rubber. For dynamic viscoelastic properties, it is found that devulcanised EPDM is a more elastic material than uncured virgin EPDM and that revulcanised EPDM is less elastic material than the virgin EPDM vulcanisate at the same modulus level.

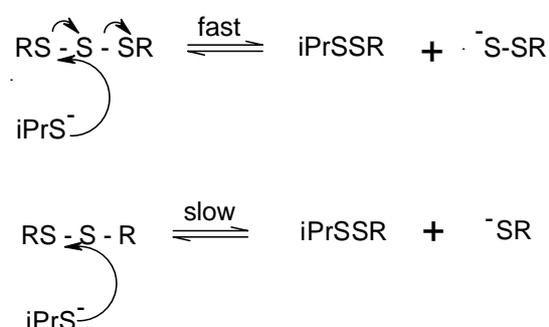
### 2.5.6 Selective scission of crosslinks by chemical probes

Some chemicals that cause selective scission of sulphur bonds are used as reagents to determine the relative amounts of mono-, di- and polysulphidic crosslinks. These reagents are called chemical probes. Thiols in combination with organic bases can selectively cleave sulphur crosslinks. Hexanethiol was found to cleave di- and polysulphidic crosslinks, while 2-propane thiol selectively cleaves polysulphidic crosslinks in a nucleophilic displacement reaction with piperidine as base.<sup>59,60</sup>



**Figure 2.12** Cleavage of polysulphide bonds by 2-propane thiol/piperidine probe (iPr = isopropyl and R = Rubber polymer)

The thiol-amine combination gives a complex, possibly a piperidinium propane-2-thiolate ion pair, in which the sulphur atom has enhanced nucleophilic properties, and is capable of cleaving organic trisulphides and higher polysulphides within 30 minutes at 20°C, according to a mechanism as shown in Figure 2.12.<sup>61,62</sup> Disulphides react at a rate, which is slower by a factor of one thousand. The



**Figure 2.13** Cleavage of polysulphide crosslinks and  $p_\pi - d_\pi$  delocalisation (iPrS<sup>-</sup> = nucleophilic thiol-amine associate)

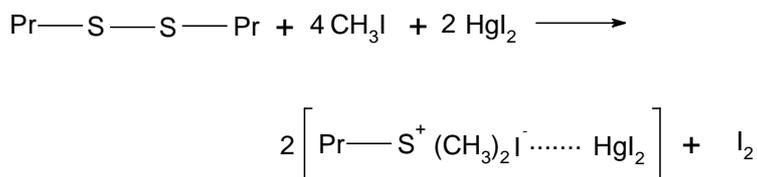
polysulphide cleavage is faster due to  $p_{\pi} - d_{\pi}$  delocalisation of the displaced  $\sigma$ -electron pair of  $\text{RSS}^-$  as outlined in Figure 2.13:

A rubber network can easily be swollen by methyl iodide which can be removed afterwards by heating under vacuum. Meyer and Hohenemser<sup>63</sup> introduced the use of methyl iodide to estimate monosulphide linkages in vulcanised natural rubber. The level of network bound iodine reflects the concentration of monosulphide groups since simple saturated monosulphide groups react as shown in Figure 2.14:



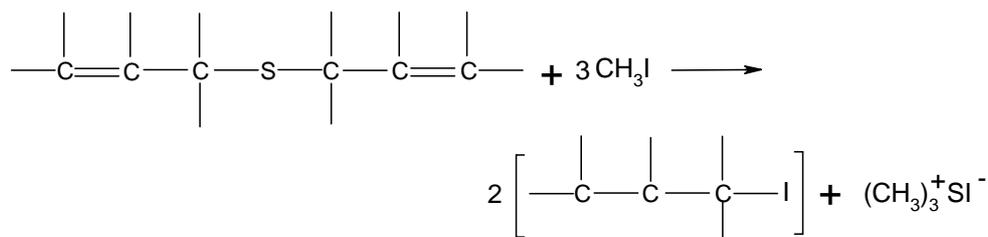
**Figure 2.14** Reaction of a monosulphide group with methyl iodide

Simple disulphides react very slowly with methyl iodide, but their reaction and those of monosulphides can be catalyzed by mercuric iodide.<sup>64</sup> Di-n-propyldisulphide reacts as shown in Figure 2.15:



**Figure 2.15** Reaction of disulphide with methyl iodide catalysed by mercuric iodide

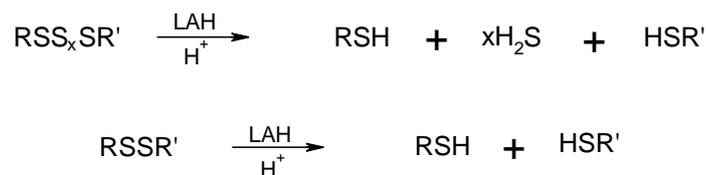
Only allylic sulphides breakdown easily to yield extractable trimethyl sulphonium salts, Figure 2.16:<sup>64</sup>



**Figure 2.16** Reaction of allylic sulphides with methyl iodide

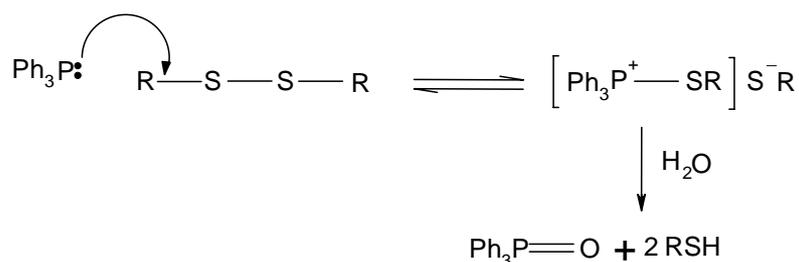
It is reported that not only sulphur crosslinks, but also cyclic monosulphidic structures in vulcanisates react with methyl iodide.<sup>66,67</sup> Nowadays this reagent is barely used anymore because it is carcinogenic.

Lithium aluminium hydride (LAH) can be used to convert organic poly- and disulphides into thiols. The liberated hydrogen sulphide gives an estimate of the amount of polysulphidic crosslinks, but again pendant accelerator and cyclic main chain modifications can also react (Figure 2.17).



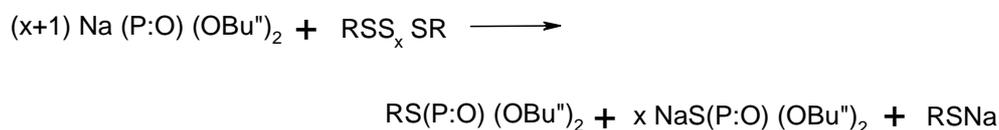
**Figure 2.17** Reaction of lithium aluminium hydride with polysulphides and disulphides (R = Rubber polymer)

Triphenyl phosphine<sup>68,69</sup> cleaves di- and polysulphidic bonds in the following manner (Figure 2.18):



**Figure 2.18** Cleavage of di- and polysulphidic bonds by triphenyl phosphine

Sodium dibutyl phosphite,<sup>70</sup> cleaves di- and polysulphidic crosslinks in NR vulcanisates: Figure 2.19



**Figure 2.19** Cleavage of di- and polysulphides by sodium dibutyl phosphite (X ≥ 0, Bu<sup>n</sup> = n-butyl, R = Rubber polymer)

Treatment of a polybutadiene vulcanisate with phenyl lithium in benzene cleaves the polysulphide and disulphide bonds.

### 2.5.6.1 Comparison of chemical probes and reclaiming

Some of the chemicals for reclaiming mentioned in the literature are comparable with those used as probes. Katrenick<sup>71</sup> and Gregg<sup>72</sup> mentioned the use of phenyl lithium, similar to the use of a solution of sodium-aniline as a method for removing combined sulphur described by Miller<sup>73</sup> in 1937. Le Beau<sup>10</sup> mentioned phenol alkyl sulphides and disulphides, aliphatic and aromatic mercaptans, amino compounds and unsaturated compounds as active reclaiming agents. Some of these bear a similarity to the thiol-amine reagents described by Campbell.<sup>59</sup>

### 2.5.7 Other chemical methods

A phase transfer catalyst has been used for transporting hydroxide ions from water into rubber particles to cleave polysulphide, di- and monosulphide crosslinks with little main chain scission.<sup>74,75</sup> The transfer of an anion from water into the organic phase (finely divided rubber) was made possible by means of a quaternary ammonium chloride catalyst having a large hydrocarbon radical attached to the nitrogen. Hydroxide ions transported by onium ions, positively charged higher valency ions of the nonmetallic elements, from water rapidly break polysulphide crosslinks with little or no main chain scission. The advantage of this method is the possibility of working in an aqueous medium, but the slow rates of diffusion and residual traces of accelerators are disadvantages of this method.

Orthodichlorobenzene (ODCB) dissolves a variety of vulcanisates including hydrocarbon, nitrile and chloroprene rubbers.<sup>76</sup> The procedure involves cutting the vulcanisate into small pieces, refluxing at 180°C, centrifuging the carbon black, and casting a film. The final film acts like a piece of unvulcanised rubber. In the reference it is stated that most or all of the poly-, di- and monosulphidic crosslinks originally present were cleaved, without excessive degradation.

### 2.5.8 Biotechnological processes for reclaiming of rubber

A biotechnological approach of devulcanisation of rubber was reported in a patent by utilising chemolithiotrope bacteria in an aqueous suspension. The process was developed by Straube et al.<sup>77</sup> for the devulcanisation of scrap rubber, by holding the material in a bacterial suspension with a supply of air until elemental sulphur or sulphuric acid is formed.

Biodegradation of the cis-1,4-polyisoprene main-chain was achieved<sup>78-80</sup> using a bacteria that belongs to the genus *Nocardia* and led to considerable molecular weight loss of different soft types of NR vulcanisates. In a typical process, rubber powder, was treated with different species of *Thiobacillus* (*T. ferrooxidans*, *T. thiooxidans*, *T. thioparus*). The total sulphur in the rubber powder was oxidised to sulphate within 40 days.<sup>81</sup> The efficiency of the sulphur oxidation depends to a large extent on the particle size.

### 2.5.9 Devulcanisation in supercritical carbon dioxide

A new devulcanisation process was developed in which supercritical carbon dioxide (scCO<sub>2</sub>) was used along with devulcanising reagents.<sup>82</sup> Unfilled polyisoprene rubber vulcanisates with different crosslink distributions were prepared by controlling the cure time and the amount of curatives. Each of the vulcanisates was subjected to Soxhlet extraction using azeotropic acetone/chloroform to remove residual curatives. The devulcanisation was performed at various temperatures (140-200°C) in the presence of scCO<sub>2</sub> for 60 minutes. The product was fractionated into sol and gel components, and the molecular weight of the sol component and the crosslink density of the gel component were determined. The thiol-amine reagent was found to be the most effective one among several devulcanising reagents; the molecular weight of the resultant sol component was determined and the crosslink density of the gel component decreased substantially from the initial ones. The yield of the sol

component increased with increase in CO<sub>2</sub> pressure. In the supercritical fluid state of CO<sub>2</sub>, the vulcanisate was more efficiently devulcanised than in an ordinary gaseous state of CO<sub>2</sub>. The sol fraction depended considerably on the crosslink distribution in the vulcanisate. These results suggest that the devulcanising reagents penetrate and diffuse better into the vulcanisate in the presence of scCO<sub>2</sub>.

## 2.6 CHEMICAL STRUCTURE OF THE RUBBER AND THE METHOD OF DEGRADATION

Different polymers stock require different reclaiming processes and conditions. In the oxidative degradation of rubber at 30°C with a Ph-FeCl<sub>2</sub> system degradation occurs with increasing ease in the following order



Furthermore, polymers such as IIR and polyether based synthetic rubbers, where β- scission occurs easily, degrade on heating without air or in the presence of an organic peroxide. Polyurethane and silicone rubbers can be reclaimed by hydrolysis. High purity polyol and toluenediamine are obtained at 190-220°C from polyurethane foam.<sup>84</sup> It is reported<sup>85</sup> that it is possible to reclaim urethane foam scrap at 100-150°C with tin, lead and cobalt chlorides and thallium oxide. In this method a low molecular weight diol is used as the reclaiming medium. The degraded liquid can be recovered in the form of a glycol which can be used as a raw material for urethane foam.

With silicone rubber, reclamation is possible by hydrolysis with steam<sup>86</sup> at low temperatures and using a base. The aminolysis of crosslinked polysiloxane using 2-pyridone at room temperature is reported.<sup>87</sup>

## 2.7 LATEX PRODUCTS RECLAIMING

The latex industry expanded over the years to meet the world demand for examination gloves, condoms, latex thread etc. Due to strict specifications for latex products, as much as 15% of the products are sometimes rejected, and these rejects create a major disposal problem for the rubber industry. At the same time, the local authorities prohibit open burning of this waste due to environmental pollution. Since latex product waste represents a source of high quality rubber hydrocarbon it is a good candidate for generating reclaimed rubber of superior quality.

The Rubber Research Institute of India (RRII) reported a method for reclaiming latex products.<sup>88</sup> In this process, waste condoms were powdered initially by passing them through a hot two roll mill at 80-90°C to a size of about 40 mesh. The powdered material was admixed with 10 phr of naphthenic oil and 1 phr of pentachlorothiophenol (PCTP) on a cold mill. The resulting compound was heated in

an air oven at 140 °C for 30 minutes. The reclaimed rubber obtained by this process was found to form a smooth band on the mill and contain about 82% of rubber hydrocarbon. However, it was found that only a small amount of this reclaim could be added to raw rubber without adversely affecting the mechanical properties. The addition of 25% reclaimed rubber to filled NR caused a decrease in tensile strength, elongation at break, resilience, tear strength and abrasion resistance. The compression set of the raw rubber was not much affected, but an increase in heat built-up and hardness was observed. A compound containing this reclaim showed better processing characteristics.

Probably the largest number of defects encountered in articles produced by latex dipping are due to pinholes, craters and blisters, caused by air bubbles entrapped in the latex compound,<sup>89</sup> particles of dirt in the latex compound and on the former, and greasy areas of the former. Problems arising from particles of dirt and dust settling on the former are aggravated in dry-coagulant dipping processes.

From the foregoing it is clear that the utilisation of reclaimed rubber is at present limited to the preparation of elastomer blends. Reclaim is added only in a very small percentage of the raw rubber in high quality products or in high percentages in low quality products. This is mainly due to the degradation of the rubber hydrocarbon during the reclaiming process.

The utilisation of crosslinked waste latex rubber as a potential filler in epoxidised natural rubber (ENR) deserves much attention.<sup>90</sup> The crosslinked waste latex rubber was powdered and screened into different fractions. The ground vulcanisate preparation was done on a fast-rotating corrugated mill. The particle size distribution of the powder rubber was found to be polydisperse. With increasing filler content in a blend with virgin compound, curing characteristics like optimum cure time, scorch time and induction time decreased. The cure-activating nature of the filler is obvious from the increase in the rate constant values. The filler helps in reducing the sticky nature of the ENR compound during mixing. These observations are advantageous as far as processability and productivity are concerned. When the vulcanisation system is a conventional one, the finest size filler shows superior mechanical performance while the order of performance is reversed when the vulcanisation mode changes to efficient. As far as tear strength is concerned, a particle size of 0.3 to 0.5 mm was found to be the best. In every case, the properties degrade at a loading of 40 phr. The swelling index values register a constant increase with an increasing loading of the filler, and this increase is lowest for fine fillers. In addition to this, the reduction in crosslink density with increasing filler loading is also lowest for smaller particle size filler. The scanning electron micrographs of the fractured surfaces clearly support the good particle–matrix adhesion in the case of fine fillers. The phase-separated nature of the coarse filler particles in the ENR matrix classifies these materials as a filled ENR composite, rather than a blend system.

## 2.8 MODEL DESCRIPTION OF MAIN-CHAIN SCISSION AND CROSSLINK SCISSION

Relations between the degree of crosslinking and gel fraction in a polymer have been derived by several authors.<sup>91,92</sup> An important parameter in these relations is the crosslinking index,  $\gamma$ , the average number of crosslinks to which one original polymer molecule is linked. Vulcanised rubbers are an example of a three-dimensional polymer network in which the branching units or cross-link sites are commonly taken as tetra-functional.<sup>93</sup> The relations have been applied to the determination of the degree of crosslinking in linear polymers, but they can be used as well to calculate the soluble fraction of the network in a crosslinked polymer that has been subjected to a degradation process. The analysis of the amount of soluble polymeric material generated during the degradation process, sol-gel analysis, can be used to investigate the ratio of main-chain to crosslink scission during devulcanisation.

### 2.8.1 Chain scission at random

In case of a random main-chain destruction it is commonly assumed that a Poisson type molecular size distribution of fragments is formed. The Poisson distribution is defined as a special case of the Schultz-Flory distribution:

$$N_x = N\beta(1-\beta)^{x-1} \approx \frac{N\beta e^{-\beta x}}{(1-\beta)} \approx N\beta e^{-\beta x} \text{ for } \beta \ll 1 \quad 2.1$$

Where  $N$  is the total number of polymer molecules in the distribution,  $x$  is the number of monomer units in a fragment,  $N_x$  is the number of fragments with length  $x$ , and  $1/\beta$  is the number – average length of fragments.

On the basis of this distribution the following relationship for the sol fraction  $s$  and gel fraction  $g$  is derived by Charlesby:<sup>91</sup>

$$s = 1 - g = \frac{1}{(1 + \gamma - \gamma s)^2} \quad 2.2$$

An implicit equation for  $s$ , which can be made explicit to read

$$s = \frac{\left[ (2 + \gamma) - (\gamma^2 + 4\gamma)^{1/2} \right]}{2\gamma} \quad 2.3$$

in which  $\gamma$  is the crosslinking index of the whole polymer defined as the average number of crosslinked units per original length (of average length  $1/\beta$ ). It can also be

shown, that the number-average molecular weight  $M_{gel}$  of the primary molecule, incorporated in the gel, is given by:

$$M_{gel} = M_0 \frac{[(1 + \gamma - \gamma s)]}{\gamma} \quad 2.4$$

with  $M_{gel}$  being the number-average molecular weight for all primary molecules. The crosslinking index of the gel fraction equal to:

$$\gamma_{gel} = (1 + s)(1 + \gamma - \gamma s) \text{ for } \gamma > 0.5 \quad 2.5$$

$\nu_0$  is defined as the number of elastically effective polymer network chains per unit volume of network and represents a measure of the crosslink density, as commonly employed for gel measurements. For the sake of easiness, in the following the term elastically effective polymer network chain per unit volume will be used interchangeably with the term crosslink density. The latter is related to the former by a constant determined by the crosslink functionality.

$$\gamma = \frac{\nu_0}{N} \quad 2.6$$

It follows from equation 2.4 that the number of primary molecules per gram of network is given by:

$$N_{gel} = \frac{\gamma N}{(1 + \gamma - \gamma s)} = \frac{\nu_0}{(1 + \gamma - \gamma s)} \quad 2.7$$

By combining equations 2.5, and 2.7 it follows that the number of chains in the network can be calculated as follows:

$$\nu_{0, gel} = \gamma_{gel} N_{gel} = \nu_0 (1 + s) \quad 2.8$$

Horikx assumed, that the number of network chains  $\nu_0$  is only given by chains, which are chemically crosslinked. Using equations 2.2 and 2.7, the following relation is obtained:

$$N_{gel} = \nu_0 s^{1/2} \quad 2.9$$

According to Flory,<sup>94</sup> the number of elastically effective polymer chains in the network,  $\nu$ , as determined by mechanical measurements and swelling measurements, requires a correction on  $\nu_0$  to account for dangling chain-ends:

$$\nu = \nu_0 - 2N \quad 2.10$$

for tetra-functional crosslinks.  $\nu$  is determined by swelling experiments using the well known Flory-Rehner equation:

$$\nu = \frac{-[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2]}{V_s(\nu_r^{1/3} - 0.5\nu_r)} \quad 2.11$$

where  $\nu_r$  is the volume fraction of the polymer in the vulcanisate swollen to equilibrium,  $\chi$  is the polymer-solvent interaction parameter,  $\nu$  is the number of elastically active network chains per unit volume and  $V_s$  is the solvent molar volume.

The number of elastically effective chains per unit volume of network is then given by combining 2.8, 2.9 and 2.10

$$\nu_{gel} = \nu_{0,gel} - 2N_{gel} = \nu_0(1+s) - 2\nu_0s^{1/2} \quad 2.12$$

$$\nu_{gel} = \nu_0 \left(1 - s^{1/2}\right)^2 \quad 2.13$$

During the random scission process the number of crosslinks  $\nu_0$  remains constant and soluble matter is created by randomly detaching small molecular fragments out of the network. By virtue of equation 2.6,  $\gamma$  decreases as much as  $N$  increases. If equation 2.13 is formulated before and after the network scission and the ratio of both is taken as the relative decrease in cross-link density,  $\nu_0$  disappears from the equation and the remaining can be expressed as a function of the soluble fractions before and after scission of the sample:

$$1 - \left(\frac{\nu_f}{\nu_i}\right) = 1 - \left[ \frac{\left(1 - s_f^{1/2}\right)^2}{\left(1 - s_i^{1/2}\right)^2} \right] \quad 2.14$$

With  $s_i$  the soluble fraction of the still untreated vulcanisate,  $\nu_i$  the number of elastically effective network chains of the still untreated vulcanisate, and  $s_f$  and  $\nu_f$  correspond to the situation after the treatment.

### 2.8.2 Crosslink scission

To determine the soluble fraction in the case of crosslink scission,  $N$  is taken as a constant and  $\gamma$  decreases. In this case,  $\nu_0$  remains in the equation. The relative decrease in crosslink density is now dependent on the cross-link index  $\gamma$ .

$$v_{gel} = v_{0,gel} - 2N_{gel} = v_0 \left(1 - s^{1/2}\right)^2 = N\gamma \left(1 - s^{1/2}\right)^2 \quad 2.15$$

The relation between the effective number of network chains before and after treatment reads now:

$$1 - \left(\frac{v_f}{v_i}\right) = 1 - \left[ \frac{\gamma_f \left(1 - s_f^{1/2}\right)^2}{\gamma_i \left(1 - s_i^{1/2}\right)^2} \right] \quad 2.16$$

with  $\gamma_i$  the crosslinking index before treatment, and  $\gamma_f$  the crosslinking index after treatment.

Horikx used the measurement of the network chain density in the gel by equilibrium swelling together with the value measured for  $M_n$  with GPC to calculate  $\gamma_i$

$$\gamma_i = \frac{v_i M_n}{\rho} \quad 2.17$$

Another way to determine  $\gamma_i$  is by measuring the residual sol content immediately after vulcanisation and then making use of equation 2.3.

### 2.8.3 Intermediate stages between crosslink scission and main-chain scission

The disadvantage of the Horikx treatment is that it explains only the two limiting cases: crosslink scission or main-chain scission. For intermediate cases, Yashin and Isayev<sup>95</sup> used the model of Dobson and Gordon to describe the sol-gel formation of devulcanised rubber. On the basis of simulations of branched polymers, Dobson and Gordon<sup>96-98</sup> developed a model for a rubber network. This network is represented by a tree, starting from a primary chain or first generation—the stem—to which chains of second generation—the branches—are attached followed by further branches of the third generation, etc. Crosslinks connect pairs of chains of succeeding generations.

Yashin and Isayev state that under random chain scission conditions, a Poisson distribution of chain fragments is generated, and for the parameters  $p$  and  $q$  they propose an exponential decay as given by:

$$1 - p(t) = (1 - p_0) e^{-k_p t} \quad 2.18$$

$$q(t) = q_0 e^{-k_q t} \quad 2.19$$

where  $p$  is the probability of breaking a given bond linking two monomers in the infinite chain, constituting the crosslinked network,  $q$  is the probability of creating a bond or crosslink between two polymers.  $k_p$  and  $k_q$  are the scission rate constants for

chain scission and crosslink scission, respectively. In the same way as Horikx did, Yashin and Isayev normalised  $v$  to the network chain density for the still fully vulcanised sample and they did the same with the gel fraction  $g = (1-s)$ . By simulating network degradation in time and adjusting the ratio of the scission constants, the same type of curves can be constructed as those of Horikx. When  $k_p/k_q$  approaches  $\infty$ , only rubber chains are broken and when  $k_p/k_q$  approaches 0, only crosslinks are broken.

## **2.9 ADVANTAGES OF RECLAIMED RUBBER**

Although reclaimed rubber is a product of discarded rubber articles it has gained much importance as additive in various rubber article formulations. It is true that mechanical properties like tensile strength, modulus, tear strength, storage modulus and other properties are influenced with increasing amounts of reclaim rubber in virgin rubber formulations. But at the same time the reclaim rubber provides many advantages:

### **2.9.1 Easy breakdown and reduced mixing time**

During the reclamation process the material is plasticised due to a large amount of mechanical energy input. Therefore, it mixes faster than pure virgin rubber with less heat generation. In addition to the reduced mixing time there is a sizable reduction in power consumption during mixing.

### **2.9.2 Easy calendering and extrusion**

Reclaimed rubber provides faster processing during extrusion and calendering. When the vulcanised rubber is reclaimed, it is softened by scission of the crosslinks and main chains in the polymer network. The result is a system of crosslinked fragments that is more three-dimensional in nature than the original polymer. The three-dimensional structure gives dimensional stability to the compound. Extruder die swell and calender shrinkage are reduced due to the lower nerve of the blend containing reclaimed rubber.

### **2.9.3 Influence on ageing properties**

During vulcanisation, reclaimed rubber containing compounds show less tendency to reversion indicating better ageing resistance. Ball and Randall, as well as Dierkes<sup>99</sup> observed anti-ageing characteristics of reclaimed rubber. Ball and Randall explained the improved ageing resistance by the severe treatment of oxidation, heating, digestion and mechanical shearing during the reclaiming process to stabilises the hydrocarbon chains against further changes.

## 2.10 USES OF RECLAIMED RUBBER

Reclaim can be used in many different applications. Where cost is a primary consideration and quality requirements are not particularly demanding, reclaim can be the sole source of polymer. Examples of such products are mats and massive tyres. In other cases, reclaim is blended with virgin synthetic and natural rubber. The virgin polymer adds strength and the reclaim contributes to improved processing and better mixing. Such applications include most of the constituent parts of both passenger and truck tyres, bias and radial ply.

Formulating with reclaim is comparable to formulating with virgin rubber, except for its influence on the curing characteristics. The optimum cure system of virgin compound has to be adjusted when reclaim is added. The material, mixing, and energy consumption savings associated with reclaimed rubber are but a part of the total benefit of its use. These savings are substantial and significant, but there are further positive aspects to the use of reclaim, which accrue to our society as a whole. They include the employments of hundreds of people in the reclaim industry and the alleviation of solid-waste-disposal problems, as well as the conservation of petrochemical raw materials and of the energy required to convert the petrochemicals into synthetic rubber.

The major uses of reclaimed rubber are

- Carcass, sidewall and under-tread of passenger, light-truck and off-the-road tyres;
- Tubeless passenger tyre innerliner;
- Inner tubes;
- Semipneumatic tyres;
- Automotive floor mats;
- Mechanical goods;
- Adhesive, sealing and tape compounds;
- Rubberised asphalt.

## 2.11 REFERENCES

1. J. Scheirs, *Polymer Recycling: Science, Technology and Applications*, John Wiley & Sons, London (1998).
2. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, *Encyclopedia of Polymer Science and Engineering*, H. F. Mark, Ed. John Wiley & Sons, New York, **14**, (1988).
3. G. Crane, R. A. Elefritz, E. L. Kay, J. R. Laman, *Rubber Chem. Technol.*, **51**, (1978), 577.
4. J. A. Beckman, G. Crane, E. L. Kay, J. R. Laman, *Rubber Chem. Technol.*, **47**, (1974), 597.
5. D. R. Smith, *Rubber World*, **179**, (1978), 46.
6. B. Klingensmith, *Rubber World*, **203**, (1991), 16.
7. M. J. Myhre, D. A. MacKillop, *Rubber Chem. Technol.*, **75**, (2002), 429.
8. H. J. Manuel, W. Dierkes, *Rapra Review Reports*, **9**(3), 1997.
9. J. R. Dunn, paper presented at Recycle '93, Davos, March 1993.
10. D. S. Le Beau, *Rubber Chem. Technol.*, **40**, (1967), 217
11. W. C. Warner, *Rubber Chem. Technol.*, **67**, (1994), 559.
12. S. Yamashita, *Int. Polym. Sci. Technol.*, **8**(12), (1981), T/77.
13. R. Singleton, *Rubber J.*, **146**, (1964), 46.
14. Kawasaki et al., Ordinary Overall Research Publication Meeting of the Jap. Rubber Soc., Lecture Reprints, **36**, (1979), 37.
15. N. Kawabata et al., *Bull. Chem. Soc., Japan*, **5**, (1978), 625.
16. F. D. Chattaway, *J. Chem. Soc.*, **91**, (1907), 1323.
17. F. R. Mayo, J. Heller, R. L. Walrath, K. C. Irwin, *Rubber Chem. Technol.*, **41**, (1968), 289.
18. S. Yamashita et al, 34<sup>th</sup> Annual Autumn Meeting of the Jap. Chem. Soc., Lecture Reprints, (1976), 923.
19. J. L. Bolland, *Quart. Rev., Chem. Soc.*, **3**, (1949), 1.
20. A. C. Poshkus, J. E. Herweb, *J. Am. Chem. Soc.*, **79**, (1957), 4245.
21. V. M. Makarov, V. F. Drozdovskii, *Reprocessing of tyres and rubber waste: Recycling from the rubber products industry*, E. Horwood, Ed., Prentice Hall, New York (1991).
22. J. Paul, *Encyclopedia of Polymer Science and Engineering*, H. F. Mark, Ed., Wiley & Sons, New York, **14**, (1988).
23. K. Knorr, *Kautsch. Gummi. Kunstst.*, **47**, (1994), 54.
24. Y. Furukawa et al., *Nippon Gomu Kyosaishi*, **53**, (1980), 490.
25. S. Yamashita, *Nippon Gomu Kyokaishi*, **48**, (1975), 609.
26. S. Yamashita, *Nippon Gomu Kyokaishi*, **41**, (1968), 380.
27. S. Yamashita, *Nippon Gomu Kyokaishi*, **44**, (1971), 881.
28. S. Yamashita, *Nippon Gomu Kyokaishi*, **42**, (1969), 661.
29. Y. Saeki, *Proceeding of the International Rubber Conference*, (1995), 594.
30. E. Sverdrup, *Encyclopedia of Polymer Chemistry and Technology*, John Wiley & Sons, New York, **12**, (1970), 341.
31. R. N. Hader, D.S. LeBeau, *Ind. Eng. Chem.*, **43**, (1951), 250.
32. C. M. Blow and C. Hepburn (Eds.), *Rubber Technology and Manufacture*, Butterworth, London, (1982).
33. B.C. Sekhar, A. Subramaniam (to STI-K Polymers SDN BDH), EP 0748837 A1 (December 18, 1996)
34. R. Kohler, J.O. Neill, paper presented at the ACS Rubber Division Meeting,

- October 1996, Louisville, KY, USA.
35. Y. Onouchi, S. Inagaki, H. Okamoto, J. Furukawa, *Int. Pol. Sci. Techn.*, **55**, (1982), T/58.
  36. M. M. Horikx, *J. Polym. Sci.*, **19**, (1956), 445.
  37. K. A. Tyler, G. L. Cerny (to Goodyear Tire and Rubber) US 4459450 (July 10, 1984).
  38. D. S. Novotny, R. L. Marsh, F.C. Masters, D.N. Tally (to Goodyear Tire and Rubber) AU 2072376 (June 22, 1978).
  39. S. R. Fix, *Elastomerics*, **112**(6), (1980), 38.
  40. S. R. Fix, *Proceedings of the International Institute of Synthetic Rubber Producers* (1980)
  41. A. H. Pelofsky (to Cities Service Oil Co.), US 3725314 (April 3, 1973).
  42. M. Okuda, Y. Hatano (to Yokohama Rubber Co. Ltd.) JP 62121741 (June 3, 1987).
  43. D. Mangaraj, N. Senapathi (to Battelle Memorial Institute), US 4599711 (October 22, 1986).
  44. V. Y. Levin, S. H. Kim, A. I. Isayev, *Rubber Chem. Technol.*, **69**, (1996), 104.
  45. V. Y. Levin, S. H. Kim and A. I. Isayev, *Rubber Chem. Technol.*, **70**, (1997), 120.
  46. A. I. Isayev, J. Chen and A. Tukachinsky, *Rubber Chem. Technol.*, **68**, (1995), 267.
  47. V. V. Yashin and A. I. Isayev, *Rubber Chem. Technol.*, **72**, (1999), 741.
  48. A. I. Isayev, S. P. Yushnov, J. Chen, *J. Appl. Polym. Sci.*, **69**, (1996), 803.
  49. A. I. Isayev, S. P. Yushnov, J. Chen, *J. Appl. Polym. Sci.*, **69**, (1996), 815.
  50. A. I. Isayev, S. H. Kim, V. Y. Levin, *Rubber Chem. Technol.*, **70**, (1997), 194.
  51. S. T. Johnston, J. Massey, E. v. Meerwall, S. H. Kim, V. Y. Levin, A. I. Isayev, *Rubber Chem. Technol.*, **70**, (1997), 183.
  52. A. I. Isayev, J. Chen, A. Tukachinsky, *Rubber Chem. Technol.*, **68**, (1995), 267.
  53. A. Tukachinsky, D. Schworm, A. I. Isayev, *Rubber Chem. Technol.*, **69**, (1996), 92.
  54. R. Diao, A. I. Isayev, V.Y. Levin, *Rubber Chem. Technol.*, **72**, (1999), 152.
  55. S. P. Yushanov, A. I. Isayev, S. H. Kim, *Rubber Chem. Technol.*, **71**, (1998), 168.
  56. A. Tukachinsky, D. Schworm, A. I. Isayev, *Rubber Chem. Technol.*, **69**, (1996), 92.
  57. C. K. Hong, A. I. Isayev, *Rubber Chem. Technol.*, **75**, (2002), 133.
  58. J. Yun, A. I. Isayev, *Rubber Chem. Technol.*, **76**, (2003), 253.
  59. D. S. Campbell, B. Saville, *Proceeding of the International Rubber Conference*, Brighton, UK (1967).
  60. D. S. Campbell, *J. Appl. Polym. Sci.*, **13**, (1969), 1201.
  61. D. Kiroski, J. Sims, D. E. Packham, A. L. Gregory, *Kautsch.Gummi Kunstst*, **50**, (1997), 716.
  62. B. Saville, A. A. Watson, *Rubber Chem. Technol.* **40**, (1967), 100.
  63. K. H. Meyer, W. Hohenemser, *Rubber Chem. Technol.* **9**, (1936), 201.
  64. T. P. Hilditch, S. Smiles, *J. Chem. Soc.* 91, (1907), 1394.
  65. M. L. Selker, A. R. Kemp, *Ind. Eng. Chem.*, **36**, (1944), 16.
  66. R. F. Naylor, *J. Chem. Soc.*, (1947), 1106.
  67. C. G. Moore, *J. Polym. Sci.*, **32**, (1958), 503.
  68. R. E. Humphey, J. M. Hawkins, *Anal. Chem.*, **36**, (1964), 1812.
  69. R. E. Humphey, J. L. Potter, *Anal. Chem.*, **37**, (1965), 164.
  70. C. G. Moore, B. R. Trego, *J. Appl. Polym. Sci.*, **8**, (1964), 1957.
  71. E. C. Gregg, Jr., S. E. Katrenick, *Rubber Chem. Technol.* **43**, (1970), 549.
  72. E. C. Gregg Jr., *Rubber Chem. Technol.*, **42**, (1969), 1136.
  73. G. W. Miller, *The Chemistry and Technology of Rubber*, C.C. Davis and J. T. Blaker Eds., Reinhold Publishing corporation, NewYork, (1937).
  74. P. P. Nicholas, *Rubber Chem. Technol.* **55**, (1981), 1499.
  75. P. P. Nicholas (to the B.F. Goodrich company), US 4161464 (July 17, 1979).

76. H. L. Dinsmore, D. C. Smith, *Anal. Chem.*, **20**, (1948), 18.
77. G. Straube, E. Straube, W. Neumann, H. Ruckaet , R. Forkmann, M. Loffler (to Hoelzemann Metallverarbeitung), US 5275948 (January 4, 1994).
78. A . Tsuchii, T .Suzuki, K. Takeda, *Appl. Environ. Microbiol.*, **50**, (1985), 965.
79. A . Tsuchii, K . Takeda, Y. Tokiwa, *Biodegradation*, **7**, (1997), 405.
80. A. Tsuchii, K . Takeda, Y Tokiwa, *Appl. Environ. Microbiol.*, **56**, (1990), 269.
81. M. Loffler, G. Straube, E. Straube, *Biohydrometall Technol. Proc. Int.* **2**, (1993), 673.
82. M. Kojima, K. Ogawa, H. Mizoshima, M. Tosaka, S. Kohjiya, Y. Ikeda, *Rubber Chem. Technol.*, **76**, (2003), 957.
83. N. Kawabata et al., *Nippon Gomu Kyokaishi*, **53**, (1980), 768.
84. J. L. Gerlock et al., *J. Polym. Sci.*, (1980), 541.
85. Okamoto et al., *Kasen Koenshu*, **37**, (1980), 35.
86. W. E. Stafford, G. Meller, *Trans. Inst. Rubber Ind.*, **40**, (1964), 163.
87. S. P. Pappas, R. L. Just, *J. Polym. Sci.*, **18**, (1980), 527.
88. K. T. Thomas, N.M. Claramma, B. Kuriakose, E.V. Thomas, Paper presented at the International Conference on Rubber and Rubber-like Materials, November 1986, Jamshedpur, India.
89. D. C. Blackley, *Polymer Latices – Science and Technology*, Chapman and Hall, London, (1997).
90. G. Mathew, R. P. Singh, N. R. Nair, S. Thomas, *Polymer* **42**, (2001), 2137.
91. A. Charlesby, *J. Polym. Sci.*, **11**, (1953), 513.
92. A. Charlesby, *Proc. Roy.Soc.(London)*, **A222**, (1954), 542.
93. P. J. Flory, *J. Am. Chem. Soc.*, **63**, (1941), 3096.
94. P. J. Flory, J. Rehner, Jr., *J. Chem. Phys.* **18**, (1950) 108.
95. V. V. Yashin, A.. I. Isayev, *Rubber Chem. Technol.*, **73**, (2000), 325.
96. M. Gordon, *Proc. Roy. Soc. London*, **A268**, (1962), 240.
97. G. R. Dobson, M. Gordon, *J. Chem. Phys.*, **41**, (1964), 2389.
98. G. R. Dobson, M. Gordon, *J. Chem. Phys.*, **43**, (1965), 705.
99. W. Dierkes, *Eur. Rubber J.*, **169**, (1996), 36.

# Chapter 3

---

## Mechanisms involved in the reclamation of NR based latex products with diphenyldisulphide<sup>#</sup>

---

Diphenyldisulphide (DPDS) is an effective and well-known reclaiming agent for natural rubber vulcanisates. This compound is used successfully for the reclaiming of non-latex production waste. In the present chapter an investigation is made using DPDS as a reclaiming agent for Waste Latex Rubber (WLR) vulcanisates in a thermo-mechanical reclaiming process. Parameters investigated are the concentration of the reclaiming agent, reclaiming temperature and time required for proper reclamation. The efficiency of the reclamation process is studied by measurement of the Mooney viscosity, sol-gel analysis and swelling experiments. The ratio of main-chain scission to crosslink scission is studied and the distribution of mono-, di-, and polysulphidic crosslinks analysed by thiol-amine reactions. DPDS is found to be an efficient reclaiming agent at temperatures of 170°C and 180°C: All poly- and disulphide crosslinks in the vulcanisate are broken during reclamation at the temperatures noted above. An almost complete breakdown of the crosslink network is obtained when 1wt.% of DPDS reacts with WLR vulcanisates at 180°C.

### 3.1 INTRODUCTION

Various review articles regarding the disposal problem of rubber waste and possible solutions have been published.<sup>1-3</sup> Considerable attention is paid to reclaiming of scrap rubber by physical and chemical processes.

---

<sup>#</sup>The work described in this chapter was presented at the Advances in Polymer Technology conference, APT '04, January 16 – 17, Cochin, India and has been accepted for publication in Rubber Chem. Technol.

Different types of reclaiming processes reported are based on mechanical, thermo-mechanical and cryo-mechanical breakdown. New methods for the devulcanisation of waste rubber have been studied: Ultrasonic methods,<sup>4,6</sup> biotechnological processes,<sup>7</sup> devulcanisation with supercritical carbondioxide<sup>8</sup> are only a few to mention. All the above work is mainly concentrated on tyre recycling and only limited information is available on the field of recycling of waste latex products.

The application of DPDS to rubber vulcanisate allows lower reclaiming temperatures and shorter times compared to thermal reclamation. These reclaiming conditions provide a better quality reclaim, due to the suppression of degradative reactions during the process. A mechanism that is often proposed for the reaction of DPDS with sulphur vulcanisates is the opening of crosslinks or the scission of chains by heat and shearing forces and their combination with disulphides, which prevents recombination. They initiate a radical breakdown of sulphur crosslinks and a degradation of rubber vulcanisates<sup>9</sup> and inhibit gel formation by combination with the radicals. Reclamation can occur by breaking crosslinks in the vulcanised rubber, by scission of the main-chain of the polymer or by a combination of both processes.

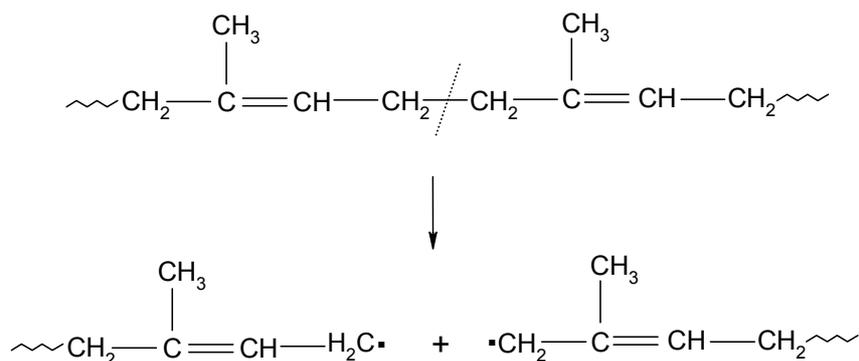
The mechanism of main-chain scission of the vulcanisate during reclamation can be compared to the mastication process of NR to reduce its viscosity through molecular weight reduction,<sup>10</sup> as shown in Figure 3.1. Long chain rubber polymers are split by the high shear force encountered in the mixing equipment, i.e., internal mixers or rubber mills. Chain fragments are formed with terminal free radicals. If they are not stabilised, they can recombine into long-chain molecules. If they are stabilised, short-chain molecules remain. In this case, the molecular weight of the rubber is lowered and consequently the plasticity is increased. Important factors for effective mastication of elastomers are:

- The presence of oxygen or radical acceptors;
- Composition of the elastomer;
- Mastication conditions.

The radicals formed by chain breakage during mastication are stabilised by the presence of oxygen or radical acceptors. The molecular weight decreases and consequently the viscosity is lowered. Mastication in a nitrogen atmosphere or other inert gases does not lead to depolymerisation of the rubber due to recombination of the chain fragments.

Synthetic rubbers behave differently during mastication. Criteria, which enhance mastication, are the following:

- The presence of double bonds;
- The reactivity of the allyl radicals;
- Stresses in the polymer during shearing.



**Figure 3.1** Cleavage of the polyisoprene chain

The energy of dissociation in a normal C-C bond is 343 kJ/mol and decreases by 80 kJ/mol in an allyl radical. In natural rubber, the splitting of the C-C bond, as shown in Figure 3.1, leads to two allyl radicals. The bonds in the polyisoprenyl chain of natural rubber have the lowest strength and therefore most likely undergo rupture at the -CH<sub>2</sub>-CH<sub>2</sub>- bonds as depicted in Figure 3.1. This is due to the fact that their dissociation energy is lower compared to the C-C bond in an isoprene monomer by the resonance energy of the mesomeric alkenyl radicals.<sup>11</sup>

Brusse<sup>12</sup> observed that the most essential factor in mastication is temperature. At low temperatures, mechanical chain breaking is predominant, whereas at high temperatures thermo-oxidative processes take place. Mastication at low temperatures largely depends on the mechanical characteristics of the mixing equipment. It cannot be influenced by the addition of a catalyst. Mastication at high temperatures is a chemical reaction. It can therefore be accelerated and controlled by temperature and the use of a catalyst. The catalysts for a thermo-oxidative breakdown are effective as radical acceptors at low temperatures in the absence of oxygen and as promoters of oxidative breakdown through formation of primary radicals. They also shift the start of the thermo-oxidative reaction to lower temperatures. The mastication effect in the mechanical process is highest in the beginning, when the molecular weight is high, the temperature is low and shear forces are high. In contrast, thermo-oxidative mastication continues to progress for the duration of the whole process.

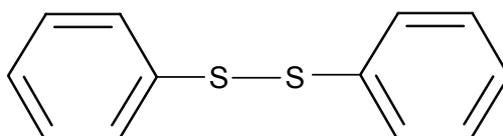
In this chapter DPDS as a reclaiming agent for WLR vulcanisates is described. DPDS is selected as reclaiming agent because this compound or its derivatives are the most prominent devulcanisation agents for natural rubber.<sup>13</sup>

## 3.2 EXPERIMENTAL

*Materials* - The waste latex rubber used in this investigation was gloves (WLR1) and condoms (WLR2). WLR1 was obtained from Primus Gloves Pvt. Ltd.,

Kochi, Kerala, India and WLR2 was obtained from Hindustan Latex Ltd., Thiruvananthapuram, Kerala, India. In WLR1 a mixture of Zincdiethyldithiocarbamate (ZDEC) and Zincmercaptobenzothiazole (ZMBT) was used as accelerators; the sulphur to accelerator ratio was less than 1. In WLR2 a mixture of different dithiocarbamates was used as accelerator and the sulphur to accelerator ratio was higher than 1.

The reclaiming agent investigated was diphenyldisulphide (Acros, 99%). The chemical structure of the reclaiming agent is given in Figure 3.2. Treated distillate aromatic extract, TDAE (BP Oil) was used as reclaiming oil.



**Figure 3.2** Chemical structure of diphenyldisulphide

*Reclamation experiments* - The feedstock was ground by passing it twice through a cold two-roll mill (Schwabenthan) with a nip size of 0.2 mm. The reclaim was prepared according to the recipe shown in Table 3.1 by a batch process in an internal mixer (Brabender Plasticorder PL-2000) having a mixing chamber volume of 50 cc and a cam-type rotor. The batch size was 30 grams. A constant rotor speed of 50 rpm was applied. The reclaiming temperature was 170°C, 180°C and 190°C and the reclaiming time was 5 minutes, 7.5 minutes and 10 minutes. TDAE was added prior to the addition of the reclaiming agent. After reclamation, the reclaimed material was passed twice through the cold two-roll mill with a nip size of 0.2 mm to form a sheet.

**Table 3.1** Reclaiming recipe

Ingredients	Amount (phr)
WLR	100
Diphenyldisulphide	0, 0.5, 1, 1.5, 2
Reclaiming oil	5

*Testing Procedures* - The Mooney viscosity - ML (1+4)100°C - of the reclaim was determined using a Mooney viscometer (MV2000 VS) according to ISO R289. Measurements were performed directly after reclamation.

After reclamation, the reclaim was extracted in a Soxhlet apparatus, first with acetone for 48 hours to extract the polar substances, and then with tetrahydrofuran

(THF) for 72 hours to extract debound polymers. During the extractions the samples were kept in the dark and under nitrogen atmosphere. The completion of the extraction was checked by drying the samples and determining the weight loss until no further significant amount of solubles (<0.1%) could be extracted. The sol fraction ( $S_r$ ) of reclaim was defined as the total soluble fraction (in acetone and THF) minus the amount of reclaiming agent and reclaiming oil added.

The elastically active network chain density was measured with equilibrium swelling in toluene for 72 hours. The data was analysed according to the Flory-Rehner equation, modified for tetra-functional networks by using swelling measurement data.<sup>14</sup> For the sake of easiness, in the following, the term elastically active network chain density will be used inter-changeably with the term crosslink density. The latter is related to the former by a constant determined by the crosslink functionality.

$$\nu = \frac{-\left[\ln(1-\nu_r) + \nu_r + \chi\nu_r^2\right]}{V_s(\nu_r^{1/3} - 0.5\nu_r)} \quad 3.1$$

where:  $\nu_r$  is the volume fraction of the polymer in the vulcanisate swollen to equilibrium,  $\chi$  is the polymer-solvent interaction parameter,  $\nu$  is the number of elastically active network chains per unit volume and  $V_s$  is the solvent molar volume.

The crosslink distribution of the feedstock and the reclaim were studied using thiol/amine chemical probes.<sup>15,16</sup> Samples with known overall crosslink densities were pre-swollen in toluene for 72 hours before adding the reagents to ensure unhindered diffusion. 2-propanethiol in combination with piperidine cleaves polysulphidic crosslinks in 2 hours and 1-hexanethiol with piperidine cleaves poly- and disulphidic crosslinks in 48 hours. Therefore, 2-propanethiol/piperidine treatment allows the determination of the amount of mono- plus disulphidic crosslinks, whereas 1-hexanethiol/piperidine treatment gives the amount of monosulphidic crosslinks. After the chemical probe treatment, the crosslink densities of the remaining samples were measured with equilibrium swelling in toluene for 72 hours, as mentioned in equation 3.1. Once, the amount of monosulphidic, mono- plus disulphidic, and overall crosslink density are estimated separately, a simple mathematical calculation allows the determination of mono-, di-, and polysulphidic crosslinks separately.

Molecular weight of the polymers were determined with gel permeation chromatography (GPC). Solutions of 5 mg/ml in tetrahydrofuran were filtered over 0.45  $\mu\text{m}$  filters (Schleicher & Schuell) and analysed with Waters styragel columns (pores  $10^5$ ,  $10^4$ ,  $10^3$ , and  $5 \times 10^2$  Å) with a flow rate of 1.47 ml/min. The intrinsic viscosity was determined with a Viscotek H502 viscometer equipped with a refractive index (RI) detector (Waters 410).

Gas Chromatography-Mass Spectroscopy (GC-MS) was used to elucidate the structure of the low molecular weight products formed during reclamation. The acetone extracts were analyzed on a Varian Saturn 3400 GC-MS, column (50m  $\times$  0.25mm ID  $\times$  0.12 $\mu\text{m}$  CP-Sil 5 CB-MS).

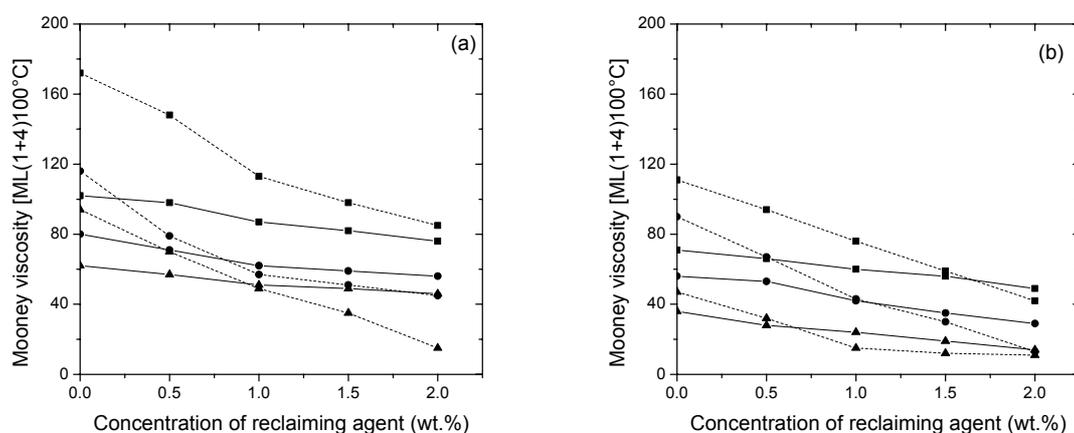
### 3.3 RESULTS OF THE RECLAMATION OF WLR1 AND WLR2 WITH DPDS

The crosslink density and the crosslink distribution of the feedstock are given in Table 3.2. These data are important, because the degree of crosslink scission during reclamation of sulphur vulcanisates depends on the type and amount of sulphidic bonds. It is well known that the bond energy of the monosulphidic crosslinks is higher than that of poly- or disulphidic crosslinks,<sup>17,18</sup> which means that a sulphur vulcanisate with a lower percentage of monosulphidic crosslinks will reclaim easier.

**Table 3.2** Distribution of different types of sulphur crosslinks in the vulcanisates

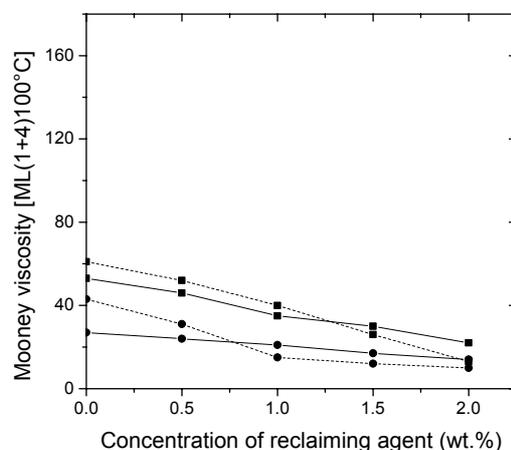
Feed stock	Overall crosslink density, $\nu$ ( $10^{-4}$ mol/cm <sup>3</sup> )	Mono sulphidic ( $10^{-4}$ mol/cm <sup>3</sup> )	Disulphidic ( $10^{-4}$ mol/cm <sup>3</sup> )	Polysulphidic ( $10^{-4}$ mol/cm <sup>3</sup> )
WLR1	1.5	0.24 (16%)	0.45 (30%)	0.81 (54%)
WLR2	1.8	0.20 (11%)	0.23 (13%)	1.37 (76%)

The Mooney viscosity of WLR1 and WLR2 at different reclamation times as a function of concentration of diphenyldisulphide at 170°C, 180°C and 190°C is depicted in Figures 3.3 and 3.4. The Mooney viscosity decreases with increasing concentration of diphenyldisulphide at all temperatures and the average level of viscosity is lower at higher reclaiming temperature. A strong decrease of viscosity is observed between 180°C and 190°C. Data for the reclaim obtained after 10 minutes of reclamation at 190°C are missing because the resulting product had a rather low viscosity and could not be analysed. The decrease in viscosity with increase in concentration of diphenyldisulphide is stronger for WLR2 than for WLR1. The lowest available viscosities are found at 170°C for WLR2 after 10 minutes of reclamation; at



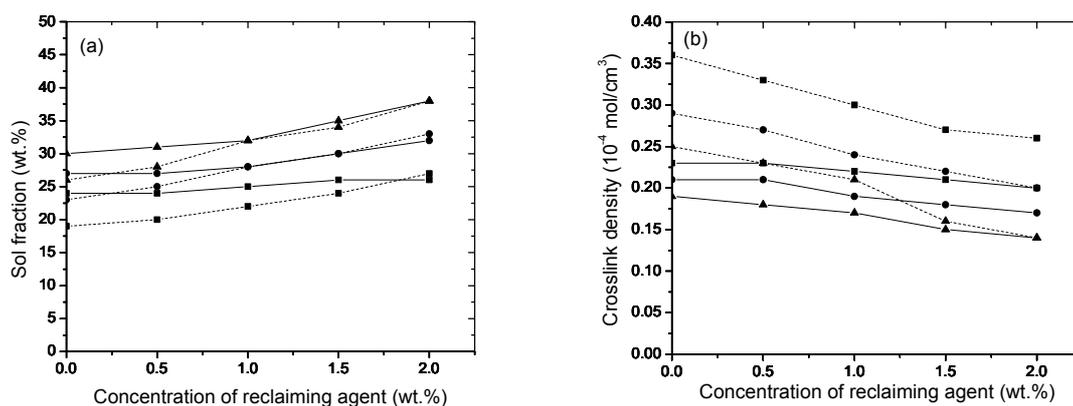
**Figure 3.3** Mooney viscosity as a function of concentration of diphenyldisulphide at various times for WLR1 (—) and WLR2 (-----) at 170°C (a); and 180°C (b); (■): 5min.; (●): 7.5 min.; (▲): 10 min.

180°C, both feedstocks are reclaimed as far as practically attainable. At 190°C the final level of viscosity is reached for both feedstocks already after 5 minutes.



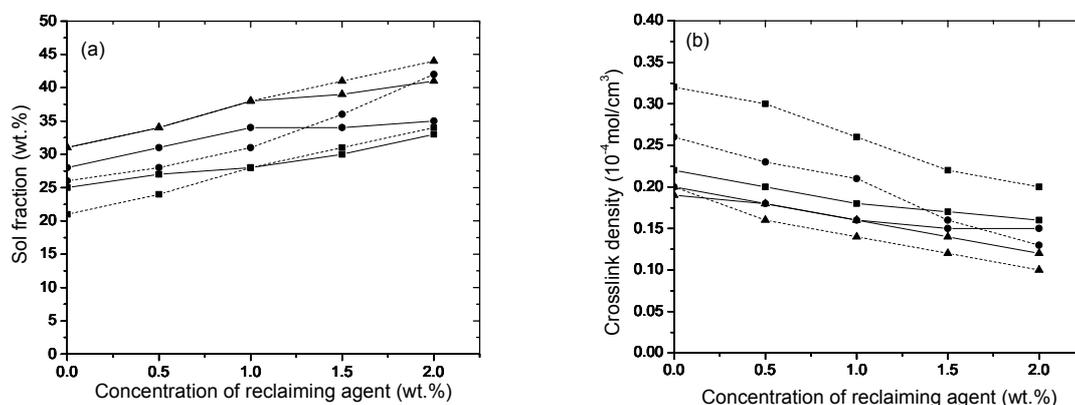
**Figure 3.4** Mooney viscosity as a function of concentration of diphenyldisulphide at various times for WLR1 (—) and WLR2 (-----) at 190°C; (■): 5min.; (●): 7.5 min.

Figure 3.5 shows the sol fraction and crosslink density of WLR1 and WLR2 at various times as a function of concentration of diphenyldisulphide at 170°C. The sol fraction increases and the crosslink density decreases with increase in concentration of diphenyldisulphide. An increase of the reclamation time results in an increase of the sol fraction and a decrease in crosslink density.

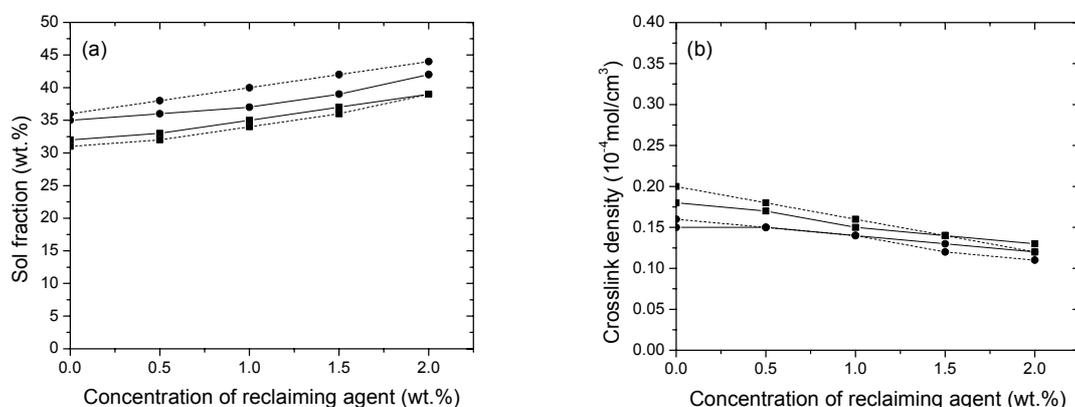


**Figure 3.5** Sol fraction (a) crosslink density (b) as a function of concentration of diphenyldisulphide at various times for WLR1 (—) and WLR2 (-----) at 170°C; (■): 5min.; (●): 7.5 min.; (▲): 10 min.

The sol fraction and crosslink density of WLR1 and WLR2 at various times as a function of the concentration of diphenyldisulphide at 180°C and 190°C are shown in Figures 3.6 and 3.7. The concentration of the reclaiming agent has the strongest influence at 180°C.



**Figure 3.6** Sol fraction (a) and crosslink density (b) as a function of the concentration of diphenyldisulphide at various times for WLR1 (—) and WLR2 (-----) at 180°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min



**Figure 3.7** Sol fraction (a) and crosslink density (b) as a function of the concentration of diphenyldisulphide at various times for WLR1 (—) and WLR2 (-----) at 190°C; (■): 5 min.; (●): 7.5 min

Horikx has developed a theoretical relationship between the soluble fraction after degradation of a network and the relative decrease in crosslink density as a result of either main-chain scission or crosslink scission.<sup>19</sup> When only main chain scission takes place, the relative decrease in crosslink density is given by equation 3.2:

$$1 - \left( \frac{\nu_f}{\nu_i} \right) = 1 - \left[ \frac{(1 - s_f^{1/2})^2}{(1 - s_i^{1/2})^2} \right] \quad 3.2$$

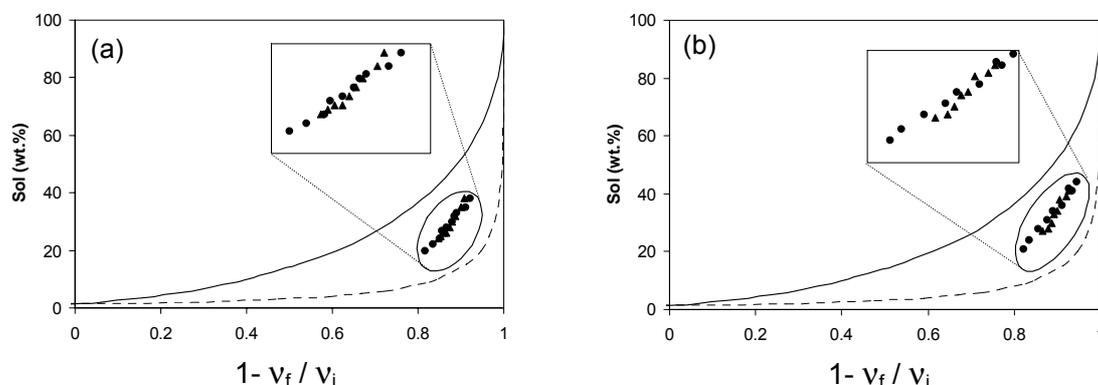
where  $s_i$  is the soluble fraction of the untreated vulcanisate,  $s_f$  is the soluble fraction of reclaimed vulcanisate,  $\nu_i$  is the crosslink density of the untreated vulcanisate and  $\nu_f$  the crosslink density of the reclaimed vulcanisate.

For crosslink scission, the soluble fraction is related to the relative decrease in crosslink density by equation 3.3:

$$1 - \left( \frac{\nu_f}{\nu_i} \right) = 1 - \left[ \frac{\gamma_f (1 - s_f^{1/2})^2}{\gamma_i (1 - s_i^{1/2})^2} \right] \quad 3.3$$

where the parameters  $\gamma_i$  and  $\gamma_f$  are the average number of crosslinks per chain in the remaining gel before and after reclamation, respectively. These numbers are calculated from the sol fraction via equation 2.3, Chapter 2.

Figure 3.8 shows the sol fraction of WLR1 and WLR2 as a function of the relative decrease in crosslink density at 170°C and 180°C and also gives a graphical presentation of equations 3.2 and 3.3. The curves in the figures correspond to the situation where only main chains are broken (solid curve) and where only crosslinks are broken (dotted curve). For crosslink scission almost no sol is produced until most of the crosslinks are broken; only then the long chains can be removed. In the case of main chain scission, sol is produced in an early stage because the random scission in the polymer network results in loose chain ends that can be removed. In Figure 3.7 the experimental data for WLR1 and WLR2 after reclamation with diphenyldisulphide are positioned in between the main-chain scission curve (equation 3.2) and crosslink scission curve (equation 3.3), showing that reclamation has mainly

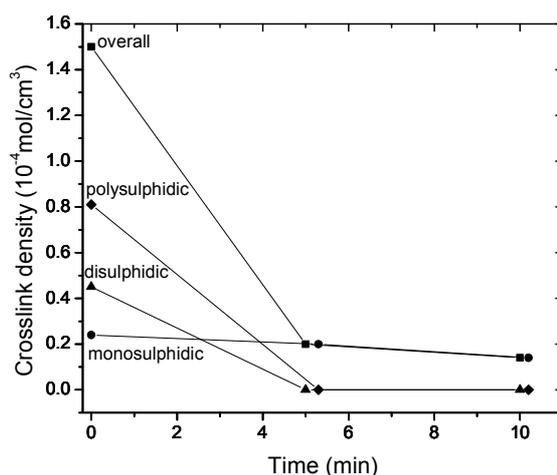


**Figure 3.8** Fraction of sol of WLR1 and WLR2 reclaimed with diphenyldisulphide against relative decrease in crosslink density at 170°C (a) and 180°C (b); (—): main-chain scission; (-----): crosslink scission; (▲): WLR1; (●): WLR2

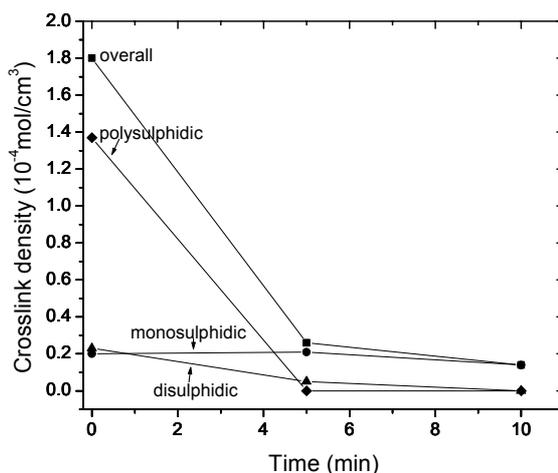
occurred through crosslink scission: As explained above, no sol is obtained until most of the crosslinks are broken.

In order to further investigate main-chain scission during reclamation, the molecular weight of the sol was determined by GPC measurements for WLR1 and WLR2. The number average molecular weight ( $M_n$ ) detected for the non-devulcanised material was  $2.6 \times 10^5$  g/mol. A recent review article of Tanaka<sup>20</sup> shows that NR consists of two fractions with different molecular weight: a high molecular weight ( $M_n$ ) of  $2 - 3 \times 10^6$  g/mol and a low molecular weight fraction ( $M_n$ ) of approximately  $1 \times 10^5$  g/mol. Most probably the average molecular weight of  $2.6 \times 10^5$  g/mol belongs to the low  $M_n$  fraction. During reclamation, the low molecular weight fraction will preferentially be released from the network because it contains less crosslinks, and after reclamation these low molecular weight components will preferentially end up in the sol. After reclamation with 1wt.% of DPDS at  $180^\circ\text{C}$ , a  $M_n$  value of  $5.4 \times 10^4$  g/mol was measured for WLR 1 and  $3.4 \times 10^4$  g/mol for WLR2 but it cannot directly be compared to the original molecular weight of the feed stock. Further research is necessary to understand the main-chain scission during reclamation.

The crosslink distributions of WLR1 and WLR2 reclaimed with diphenyl-disulphide as a function of reclaiming time at  $170^\circ\text{C}$  and  $180^\circ\text{C}$  are depicted in Figures 3.9 and 3.10. In both cases the total amount of crosslinks as well as the fraction of the poly- and disulphidic crosslinks decreases, whereas the monosulphidic crosslinks remain constant in time. The overall crosslink density decreases only to the level of the monosulphidic crosslinks: This indicates that after reclamation the crosslinks still present in WLR1 and WLR2 are mainly monosulphidic ones.



**Figure 3.9** Crosslink distribution of WLR 1 reclaimed with diphenyldisulphide as a function of reclaiming times at  $170^\circ\text{C}$ ;  
 (■): overall crosslink density; (◆): polysulphidic; (▲): disulphidic; (●): monosulphidic



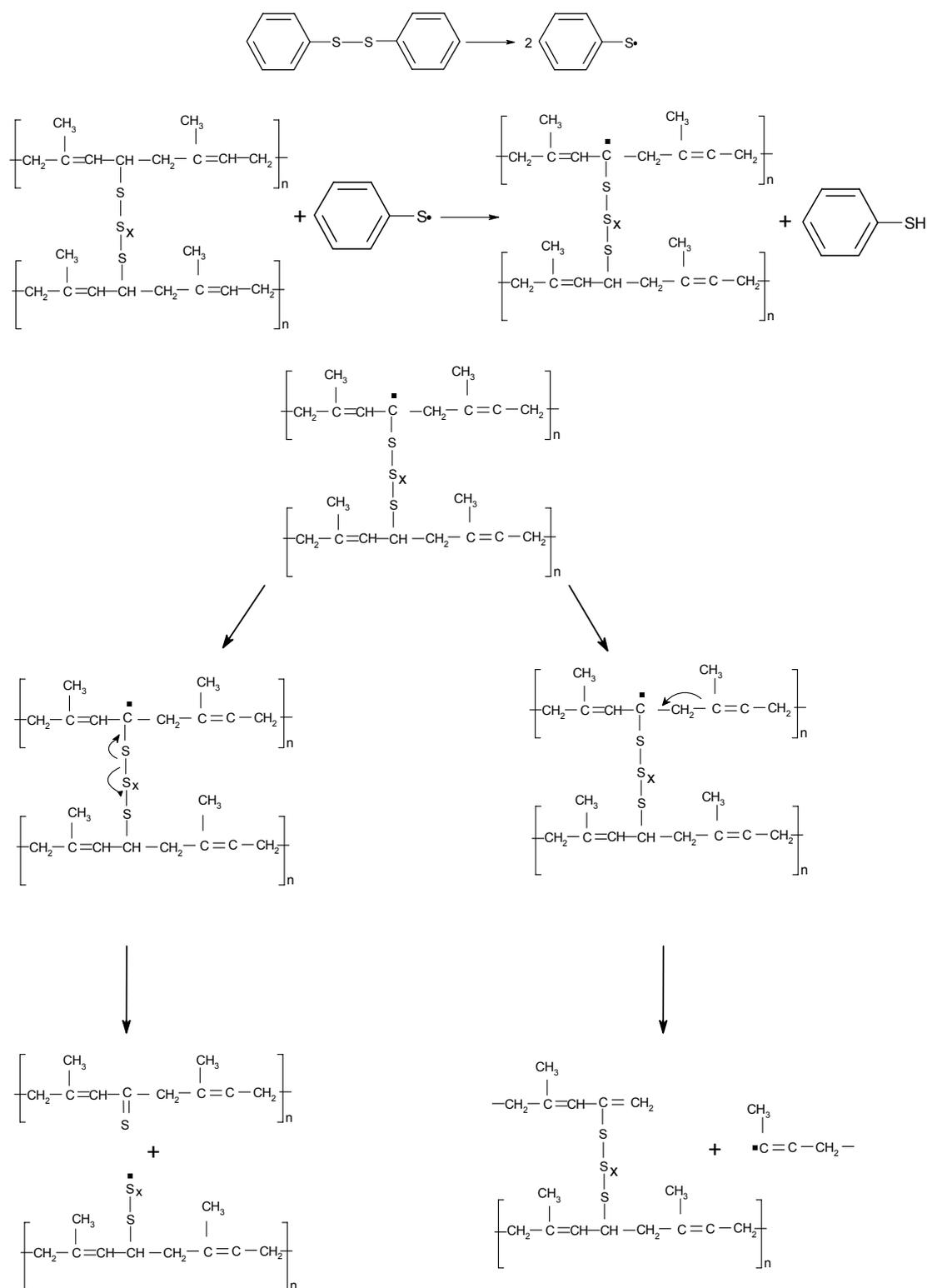
**Figure 3.10** Crosslink distribution of WLR 2 reclaimed with diphenyldisulphide as a function of reclaiming times at 180°C; (■): overall crosslink density; (◆): polysulphidic; (▲): disulphidic; (●): monosulphidic

### 3.4 DISCUSSION

The Mooney viscosity, sol fraction and crosslink density measurements show that DPDS is efficiently reclaiming WLR1 and WLR2. However, the main reclaiming effect comes from temperature plus mechanical action and the reclaiming agent helps in preventing the broken rubber polymer to recombine each other. This is seen from the crosslink density values at 0 wt.% concentration from the Figures 3.5 (b) – 3.7 (b) and Table 3.2.

At all reclaiming temperatures and at low and medium concentrations of DPDS it was noticed that DPDS reclaims WLR2 more effectively than WLR1. However, at high concentrations of DPDS, it reclaims both, WLR1 and WLR2, equally effective: Figures 3.1 - 3.7. There is a high percentage of polysulphidic crosslinks in WLR2, which is easily breakable (Table 3.2) and makes it more sensitive to reclamation. At high concentrations, DPDS more effectively breaks the poly- and disulphides present in WLR1 and WLR2, leaving the monosulphides in both systems intact and making DPDS equally reactive for WLR1 and WLR2.

A strong influence of DPDS on the reclamation of WLR1 and WLR2 at 180°C compared to 170°C was observed: Figures 3.5 - 3.7. The sol fraction increases and the crosslink density decreases faster at this temperature. The rate of main-chain scission of natural rubber depends both on the concentration of the reclaiming agent and the temperature of the process. The radical moieties of the chains can quickly recombine, unless a diphenyldisulphide molecule is present to act as a radical scavenger. At high temperatures chain scission occurs more readily, because the activation energy is overcome at more sites in the polymer matrix. In addition to



**Figure 3.11** Simplified reaction scheme proposed for the reclamation of natural rubber by diphenyldisulphide

this, the diffusion speed of the disulphide into the polymer matrix increases at high temperatures, enhancing the chance of combination with a rubber radical.

A simplified reaction scheme proposed for the reclamation of natural rubber with diphenyldisulphide is given in Figure 3.11. The radicals formed by scission of the disulphide are capable of hydrogen abstraction or addition to the double bonds in natural rubber.<sup>21</sup> Hydrogen abstraction is relatively easy because the protons in an allylic position are activated by the double bond (the resulting carbon radical is resonance-stabilised). The benzene-sulphide radical, therefore, abstracts the allylic hydrogen from the natural rubber vulcanisate to form benzenethiol and a natural rubber vulcanisate radical. The presence of benzenethiol in the acetone extract of natural rubber reclaimed with diphenyldisulphide detected by Gas Chromatography Mass Spectrum (GC-MS), supports the above reaction mechanism. The polymer radical can now undergo main-chain scission and/or crosslink scission.

The crosslink distribution study of WLR1 and WLR2 reclaimed with DPDS at 170°C and 180°C (Figures 3.9 and 3.10) shows that the monosulphidic crosslinks are stable. All poly- and disulphidic bonds are cleaved during the thermo-mechanical reclamation process with DPDS. Monosulphides are left behind because of the higher bond energy of the monosulphidic crosslinks compared to the bond energies of poly- or disulphidic crosslinks.

### 3.5 CONCLUSIONS

Diphenyldisulphide is found to be an effective chemical agent for the reclamation of WLR in a thermo-mechanical process. A stronger reduction of the crosslink density is observed with increasing temperature from 170°C - 190°C. In the present study all poly- and disulphidic crosslinks are broken during reclaiming with disulphide at the temperatures used for the reclamation, indicating that after reclamation the crosslinks remaining in WLR are mainly the monosulphides. Main-chain scission to crosslink scission studies showed that reclamation has mainly occurred through the scission of crosslinks rather than by main-chain scission.

### 3.6 REFERENCES

1. W. C. Warner, *Rubber Chem. Technol.*, **67**, (1994), 559.
2. S. Yamashita, *Int. Polym. Sci. Technol.*, **8**(12), (1981), T/77 – T/93.
3. B. Adhikari, D. De, S. Maiti, *Prog. Polym. Sci.*, **25**, (2000), 909.
4. A. I. Isayev, J. Chen, A. Tukachinsky, *Rubber Chem. Technol.*, **68**, (1995), 267.
5. V. Y. Levin, S. H. Kim, A. I. Isayev, *Rubber Chem. Technol.*, **69**, (1996), 104.
6. A. Tukachinsky, D. Schworm, A. I. Isayev, *Rubber Chem. Technol.*, **69**, (1996), 92.
7. A. Linos, A. Steinbuchel, *Kautsch. Gummi Kunstst.* **51**, (1998), 496.
8. M. Kojima, K. Ogawa, H. Mizushima, M. Tosaka, S. Kohjiya, Y. Ikeda, *Rubber Chem. Technol.*, **76**, (2003), 957.
9. M. A. L. Verbruggen, L. van der Does, J. W. M. Noordermeer, M. van Duin, H. J. Manuel, *Rubber Chem. Technol.*, **72**, (1999), 731.
10. H. Fries, R. R. Pandit, *Rubber Chem. Technol.*, **55**, (1982), 309.
11. L. Bateman, *The Chemistry and Physics of Rubber-like substances*, Maclaren, London, (1963).
12. W. F. Busse, *Proc. 2nd Rub.Tech.Conference*, London (1939) 288.
13. J. A. Beckman, G. Crane, E. L. Kay, J. R. Laman, *Rubber Chem. Technol.*, **47**, (1974), 597.
14. P. J. Flory, J. Rehner, Jr., *J. Chem. Phys.* **18**, (1950) 108.
15. D. S. Campbell, *J. Appl. Polym. Sci.* **13**, (1969), 1201.
16. D. S. Campbell, B. Saville, in "Proceedings of the International Rubber Conference", Brighton (1967).
17. T. H. Kuan, *Rubber World* **192**(5), (1985), 20.
18. C. M. Kok, V. H. Yee, *Eur. Polym. J.*, **22**, (1986), 341.
19. M. M. Horikx, *J. Polym. Sci.*, **19**, (1956), 445.
20. Y. Tanaka, *Rubber Chem. Technol.*, **74**, (2001), 335.
21. A. Z. Kuzmiski, *Developments in polymer stabilization*, G. Scott, Ed., Applied Science Publishers, London, (1981).

# Chapter 4

---

## Reclamation of NR based latex products: a comparative evaluation of amines and disulphides as reclaiming agents<sup>#</sup>

---

In this chapter two reclaiming agents for Waste Latex Rubber (WLR) vulcanisates are compared. Two WLR vulcanisates with different amounts of polysulphidic crosslinks are selected as feedstock. Diphenyldisulphide and hexadecylamine are used as reclaiming agents because they react according to different mechanisms: disulphides react by a radical and amines by a nucleophilic mechanism. The goal of this study is to investigate the influence of the two reclaiming agents on the process conditions and the properties of the reclaim. Diphenyldisulphide proves itself to be very effective as reclaiming agent, while amines result in the formation of new crosslinks during the reclaiming process compared to thermo-mechanical reclaiming with no reclaiming agent: The viscosity of the final reclaim is higher for hexadecylamine as reclaiming agent and some polysulphidic crosslinks remain in the reclaim. Of the two WLR types, the one with a higher amount of polysulphides shows a better performance in the reclaiming process.

### 4.1 INTRODUCTION

In the present investigation two reclaiming agents for WLR vulcanisates are studied. Hexadecylamine and diphenyldisulphide are selected as reclaiming agents because historically these two have most prominently been used as devulcanisation agents for natural rubber,<sup>1,2</sup> and they react according to different mechanisms: amines react by a nucleophilic and disulphide by a radical mechanism.<sup>3</sup>

---

<sup>#</sup>The work described in this chapter was presented at the India Rubber Tech. Expo IRI '04, February 13 – 14, Mysore, India and has been accepted for publication in Rubber Chem. Technol.

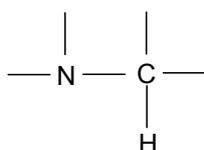
Basically, a comparative study on the nucleophilic and radical reaction mechanisms of the breakdown of crosslinks of NR latex vulcanisates will be discussed in this chapter. The mechanism of the reaction of diphenyldisulphide with NR was discussed in detail in chapter 3 while the reclamation mechanism of vulcanised rubbers by amines is discussed herewith.

Various aliphatic amines and their derivatives were applied in reclaiming synthetic rubbers basically since the time of the second world war<sup>4</sup> making use of the fact that primary and secondary amines can cleave cyclic octasulphur. The use of amines in reclaiming of synthetic rubber in general and of SBR in particular was reported. Dasher used various hydroxylamines, aliphatic amines and their mercapto derivatives in his research.<sup>5-7</sup> In another study, long-chain aliphatic amines and cyclohexylamines were used. Next to the ability of cleaving crosslinks, some specific amines act as accelerators in the formation of sulphur bonds. This finally results in an equilibrium of crosslink formation and scission for these compounds. The important factors that can influence the selection of amines are therefore:

- Type of amines (primary, secondary or tertiary);
- Steric hindrance;
- Boiling point;
- Basicity;
- The presence of  $\alpha$ -H in the amine.

Tertiary amines have the drawback of the nucleophilic nitrogen being sterically hindered by the groups present around them. Secondary amines were not selected for reclamation because these can react with the nitrous oxide present in the atmosphere to form N-nitrosoamines, considered to belong to the most carcinogenic substances known these days. So the final choice are primary amines and amongst them long chain amines were selected due to two reasons. Firstly, the increased nucleophilicity of the nitrogen by the inductive effect of the carbon backbone and secondly, the higher boiling point compared to the short chain aliphatic amines. This is advantageous when using high temperatures for the reclamation process because the evaporation of the reclaiming agent can be avoided.

It is reported that the most important parameter is the presence of an  $\alpha$ -hydrogen (Figure 4.1). Other aspects like basicity and steric hindrance were reported to be of minor influence on the efficiency of the amines.<sup>8</sup>

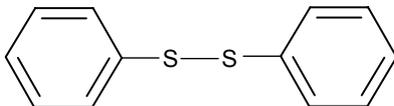


**Figure 4.1** General structure of an amine having  $\alpha$ -H

## 4.2 EXPERIMENTAL

*Materials* - The WLR types used in this investigation were gloves (WLR1) and condoms (WLR2), see Table 3.2, Chapter 3 for detailed description. The reclaiming additives investigated were hexadecylamine (Merck-Schuchardt, 92%), and diphenyldisulphide (Acros, 99%). The chemical name and structure of the reclaiming agents are given in Table 4.1. Treated distillate aromatic extract, TDAE (BP Oil), was used as reclaiming oil.

**Table 4.1:** Chemical names and structures of reclaiming agents investigated

Chemical name	Chemical structure
Diphenyldisulphide, DPDS (218.34 g/mol)	
Hexadecylamine, HDA (241.46 g/mol)	$\text{CH}_3\text{---}(\text{CH}_2)_{15}\text{---NH}_2$

*Reclamation experiments* - The reclaim was prepared according to the recipe shown in Table 4.2 by a batch process in an internal mixer (Brabender Plasticorder PL-2000) having a mixing chamber volume of 50 cc and a cam-type rotor. The batch size was 30 grams. A constant rotor speed of 50 rpm was applied. The reclaiming temperature was 170°C, 180°C and 190°C and the reclaiming times were 5 minutes, 7.5 minutes and 10 minutes.

**Table 4.2:** Reclaiming recipe

Material	Amount (phr)
WLR	100
Reclaiming agent	0, 0.5, 1, 1.5, 2
Reclaiming oil	5

*Testing procedures* - The Mooney viscosity - ML(1+4)100°C - of the reclaim was determined using a Mooney viscometer (MV2000 VS) according to ISO R289.

After reclamation, the reclaim was extracted in a Soxhlet apparatus, first with acetone for 48 hours to extract the polar substances, and then with tetrahydrofuran (THF) for 72 hours to extract debound polymers. The elastically active network chain density was measured with equilibrium swelling in toluene for 72 hours. The data were analysed according to the Flory-Rehner equation, modified for tetra-functional networks by using swelling measurement data.<sup>9</sup> The crosslink distribution of the feedstock and the reclaim were studied using thiol/amine chemical probes.<sup>10,11</sup> For details see Chapter 3.

The free sulphur content of the feedstock was determined according to ASTM D 297-72A. This method is based on the reaction of free sulphur with sodium sulphite

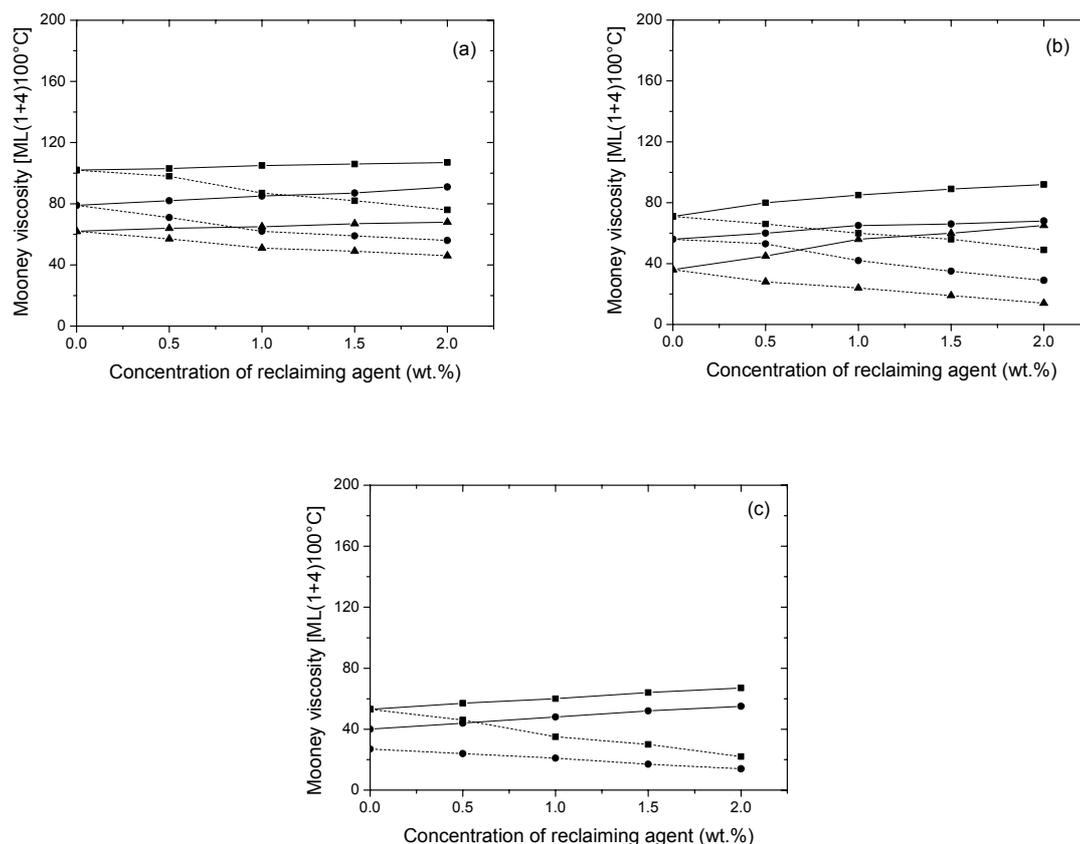
to give sodium thiosulphate, which is finally titrated against a standard iodine solution.

The molecular weight of the polymers was determined with gel permeation chromatography (GPC). Gas Chromatography-Mass Spectrometry (GC-MS) was used to elucidate the structure of the low molecular weight products formed during reclamation.

## 4.3 RESULTS

### 4.3.1 Reclamation of WLR1 with diphenyldisulphide and hexadecylamine

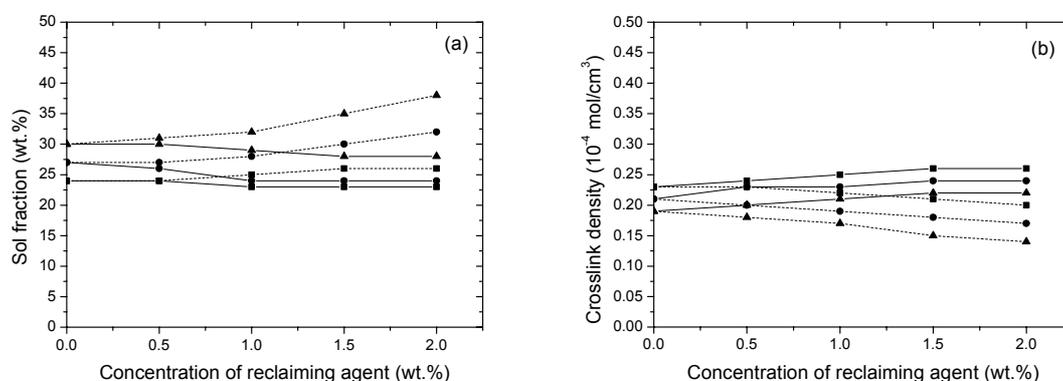
The Mooney viscosities of WLR1 after reclamation at various times against the concentration of diphenyldisulphide and hexadecylamine at 170°C, 180°C and 190°C are given in Figure 4.2. The viscosity at 0 wt.% concentration corresponds to the condition when no reclaiming agent is used for the reclamation. The most prominent result of this comparative investigation is that the Mooney viscosity



**Figure 4.2** Mooney viscosity of WLR 1 reclaimed with diphenyldisulphide (-----) and hexadecylamine (——) as a function of the concentration of the reclaiming agent at 170°C (a); 180°C (b); 190°C (c) (■): 5 min.; (●): 7.5 min.; (▲): 10 min

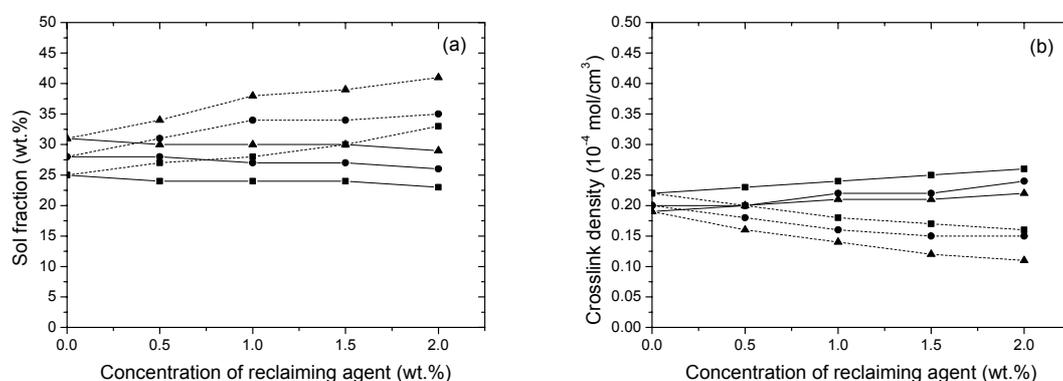
decreases with increase in concentration of diphenyldisulphide, but the viscosity increases with increase in concentration of hexadecylamine. The change in viscosity is generally linear with the concentration for both reclaiming agents.

Figure 4.3 shows the sol fraction and crosslink density of WLR1 at various times as a function of concentration of diphenyldisulphide and hexadecylamine at 170°C. The sol fraction increases and the crosslink density decreases with increase in concentration of diphenyldisulphide, but an opposite effect is seen with hexadecylamine: The sol fraction decreases and crosslink density increases with the increase in concentration of hexadecylamine compared to the values for thermal reclaiming without reclaiming agent. An increase of reclamation time results in an increase of the sol fraction and decrease in crosslink density for diphenyldisulphide as well as for hexadecylamine.



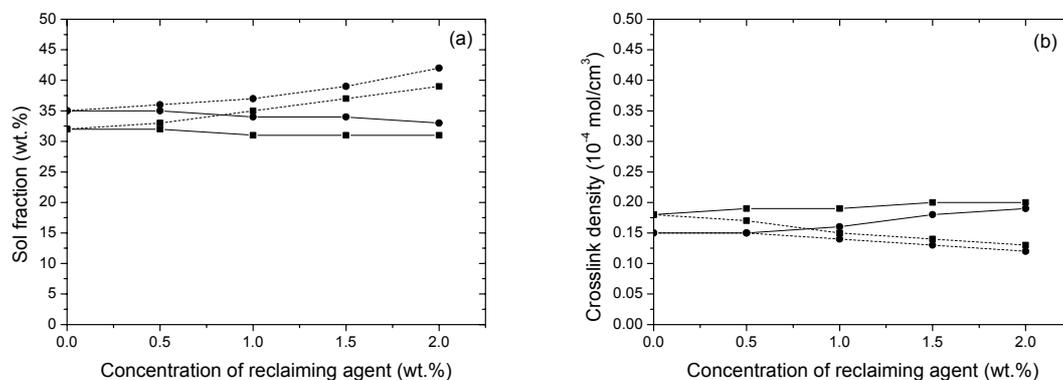
**Figure 4.3** Sol fraction (a) and crosslink density (b) as a function of the concentration of diphenyldisulphide (-----) and hexadecylamine (——) at various times for WLR1 at 170°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min

The sol fraction and crosslink density of WLR1 at various times as a function of concentration of diphenyldisulphide and hexadecylamine at 180°C and 190°C are shown in Figures 4.4 and 4.5. At these temperatures the concentration of the



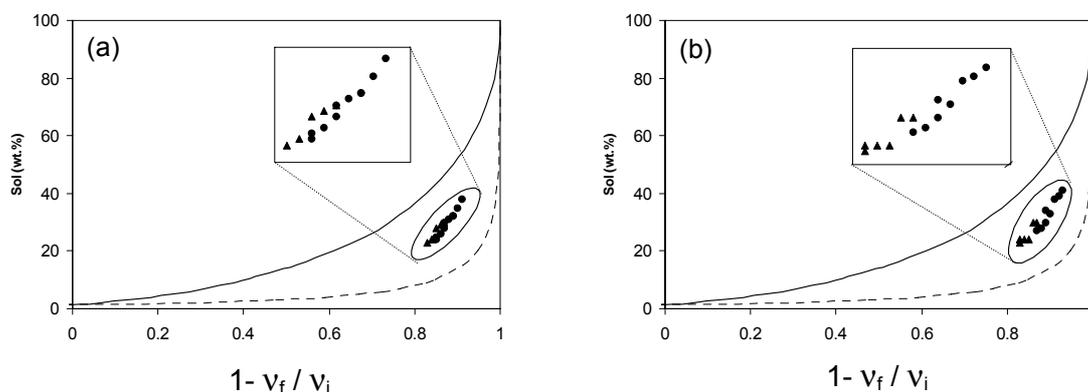
**Figure 4.4** Sol fraction (a) and crosslink density (b) as a function of the concentration of diphenyldisulphide (-----) and hexadecylamine (——) at various times for WLR1 at 180°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min

reclaiming agent has a stronger influence compared to reclaiming at 170°C: For diphenyldisulphide the sol fraction increases and the crosslink density decreases faster; the decrease in sol fraction and increase in crosslink density becomes more prominent for the hexadecylamine reclaimed material.



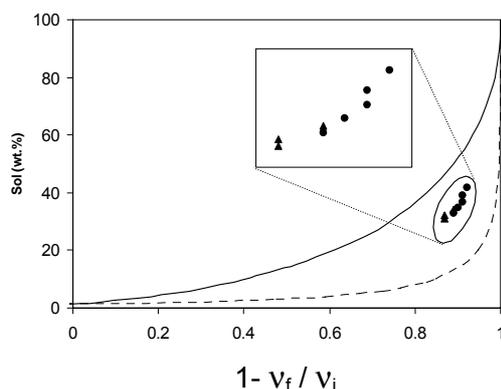
**Figure 4.5** Sol fraction (a) and crosslink density (b) as a function of the concentration of diphenyldisulphide (-----) and hexadecylamine (——) at various times for WLR1 at 190°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min

Figures 4.6 and 4.7 show the sol fraction of WLR1 as a function of the relative decrease in crosslink density ( $1 - v_f / v_i$ ) at 170°C, 180°C and 190°C. There are two extreme curves in the figures, calculated theoretically: One of them corresponds to the situation where only main-chains are broken (solid curve), and the other one corresponds to breaking of crosslinks (dotted curve). For details see Chapter 3. The experimental data for WLR1 reclaimed with diphenyldisulphide lie in between the main-chain scission curve and crosslink scission curve showing that reclamation has



**Figure 4.6** Fraction of sol of WLR1 reclaimed with diphenyldisulphide and hexadecylamine against relative decrease in crosslink density at 170°C (a); 180°C (b); (——): main-chain scission; (-----): crosslink scission; (▲): Hexadecylamine; (●): Diphenyldisulphide

mainly occurred through crosslink scission: No sol is obtained until most of the crosslinks are broken. Only a high amount of sol would indicate that the reclamation occurs mainly through crosslink scission. The experimental data for hexadecylamine are also given in Figures 4.6 and 4.7. As seen from the lower values of sol, hexadecylamine is less effective as a reclaiming agent for WLR1 compared to diphenyldisulphide.

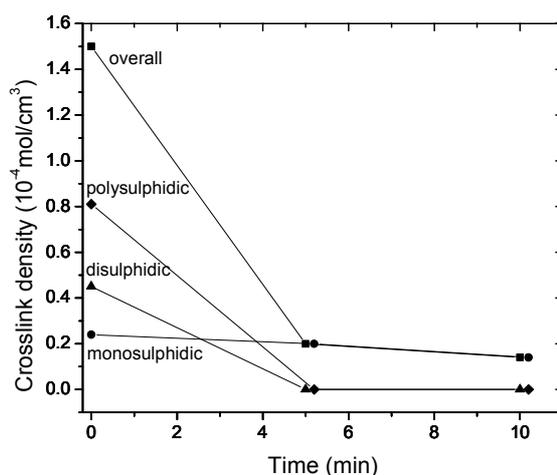


**Figure 4.7** Fraction of sol of WLR1 reclaimed with diphenyldisulphide and hexadecylamine against the relative decrease in crosslink density at 190°C; (—): main-chain scission; (-----): crosslink scission; (▲): Hexadecylamine; (●): Diphenyldisulphide

Again, the experimental data for hexadecylamine reclamation in Figure 4.6 and 4.7 suggest, that the breakdown of the structure is occurring mainly through crosslink scission.

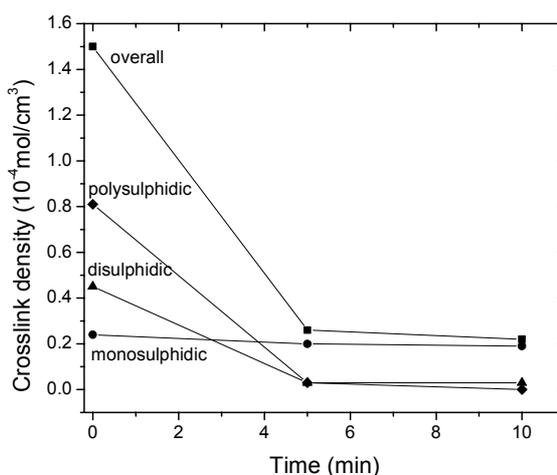
The molecular weight of the sol was determined by GPC measurements. The number average molecular weight ( $M_n$ ) of WLR1 decreased from  $2.6 \times 10^5$  g/mol to  $5.4 \times 10^4$  g/mol after reclamation with diphenyldisulphide and  $5.5 \times 10^4$  g/mol with hexadecylamine at 180°C.

The crosslink distribution of WLR1 reclaimed with 2 phr of diphenyldisulphide at 170°C as a function of reclaiming time is depicted in Figure 4.8. The total amount of crosslinks as well as the fraction of the poly- and disulphidic crosslinks decreases, whereas the concentration of monosulphidic crosslinks remain constant with reclamation time. The polysulphidic and disulphidic crosslinks diminish but interestingly the overall crosslink density decreases only to the level of the monosulphidic crosslinks: This indicates that after reclamation the crosslinks present in WLR1 are mainly monosulphidic.



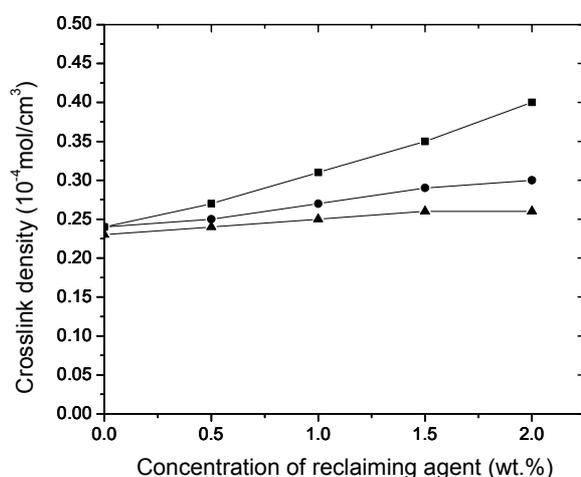
**Figure 4.8** Crosslink distribution of WLR1 reclaimed with diphenyldisulphide (2 phr) as a function of reclamation time at 170°C; (■): overall crosslink density; (◆): polysulphidic; (▲): disulphidic; (●): monosulphidic.

The crosslink distribution of WLR1 treated with 2 phr of hexadecylamine as a function of the reclaiming time at 170°C is depicted in Figure 4.9. The number of all crosslinks, of polysulphidic and of disulphidic crosslinks decreases whereas the amount of monosulphidic crosslinks remains constant within the reclaiming time. It is interesting, that some of the polysulphidic crosslinks remain intact in the sample after treatment with hexadecylamine whereas no polysulphidic crosslinks remain in the samples treated with diphenyldisulphide (Figure 4.8). This again confirms the fact that diphenyldisulphide more effectively breaks the polysulphide crosslinks in the latex vulcanisate compared to hexadecylamine.



**Figure 4.9** Crosslink distribution of WLR1 reclaimed with hexadecylamine (2 phr) as a function of reclaiming time at 170°C; (■): overall crosslink density; (◆): polysulphidic; (▲): disulphidic; (●): monosulphidic.

In order to investigate the formation rather than scission of crosslinks with hexadecylamine as reclaiming agent, experiments were conducted by extracting the WLR1 vulcanisates in a Soxhlet apparatus for 48 hours with acetone to remove residues of the vulcanisation ingredients and other non-polymeric materials, followed by an extraction for 72 hours with tetrahydrofuran to remove the uncrosslinked polymer. The crosslink density of extracted and unextracted samples of WLR1 after reclaiming at 170°C against the concentration of hexadecylamine (2 phr) is shown in Figure 4.10. The crosslink density of the sample obtained after treatment with hexadecylamine (2 phr) and sulphur (0.75 phr) increases much faster compared to the samples treated with hexadecylamine alone or to those of unextracted samples.



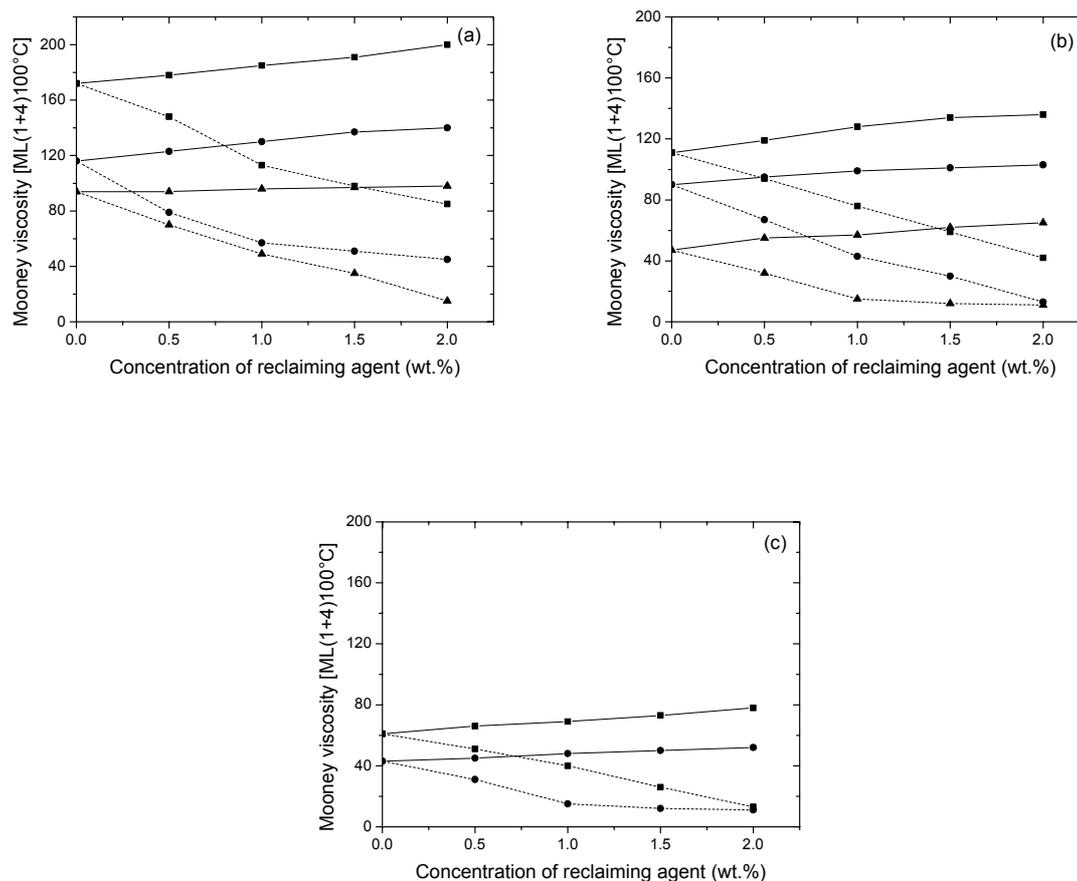
**Figure 4.10** The crosslink density of extracted and unextracted samples of WLR1 at 170°C against the concentration of hexadecylamine; (■): extracted and treated with hexadecylamine (2 phr) and sulphur (0.75 phr); (●): extracted and treated with hexadecylamine (2 phr) alone; (▲): unextracted and treated with hexadecylamine (2 phr).

The crosslink density of unextracted samples is the lowest of the three experiments and the value levels off for higher concentrations of hexadecylamine. The experiment of hexadecylamine with sulphur shows that the amine is capable of forming crosslinks in the rubber matrix if sulphur is available. The experiment with hexadecylamine in the absence of elemental sulphur also shows an increase in crosslink density, even though marginally. This proves that during the reclamation reaction sulphur in the poly- sulphidic crosslinks undergoes maturation or crosslink shortening,<sup>12</sup> and that this sulphur is able to form new crosslinks in presence of an amine.

#### 4.3.2 Reclamation of WLR2 with diphenyldisulphide and hexadecylamine

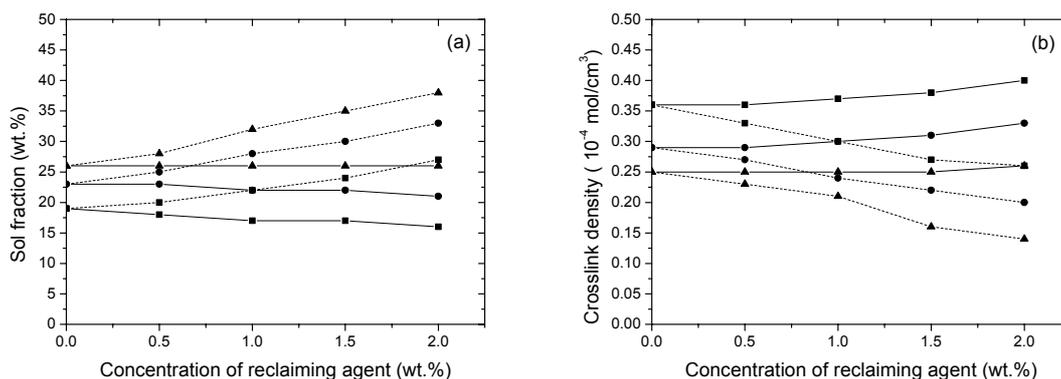
The Mooney viscosity of WLR2 at various times against the concentration of diphenyldisulphide and hexadecylamine at 170°C, 180°C and 190°C are given in

Figure 4.11. The Mooney viscosity decreases with increase in concentration of diphenyldisulphide, but the viscosity increases with increase in concentration of hexadecylamine, as already seen for WLR1. However, WLR2 shows a stronger decrease and increase in viscosity against diphenyldisulphide and hexadecylamine, respectively, compared to WLR1. The change in viscosity is almost linear with the concentration of diphenyldisulphide and hexadecylamine.



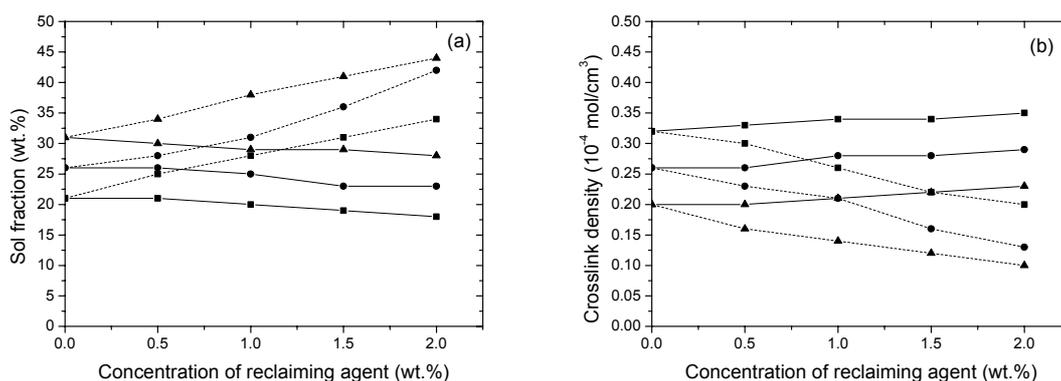
**Figure 4.11** Mooney viscosity of WLR2 as a function of diphenyldisulphide (-----) and hexadecylamine (——) at 170°C (a); 180°C (b); and 190°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min

Figure 4.12 shows the sol fraction and crosslink density of WLR2 at various times as a function of concentration of diphenyldisulphide and hexadecylamine at 170°C. The sol fraction increases and the crosslink density decreases with increase in concentration of diphenyldisulphide, but, as seen with the WLR1, the sol fraction decreases and crosslink density increases with the hexadecylamine concentration for WLR2. A sizable difference in sol fraction and crosslink density is noted with an increase of reclamation time.

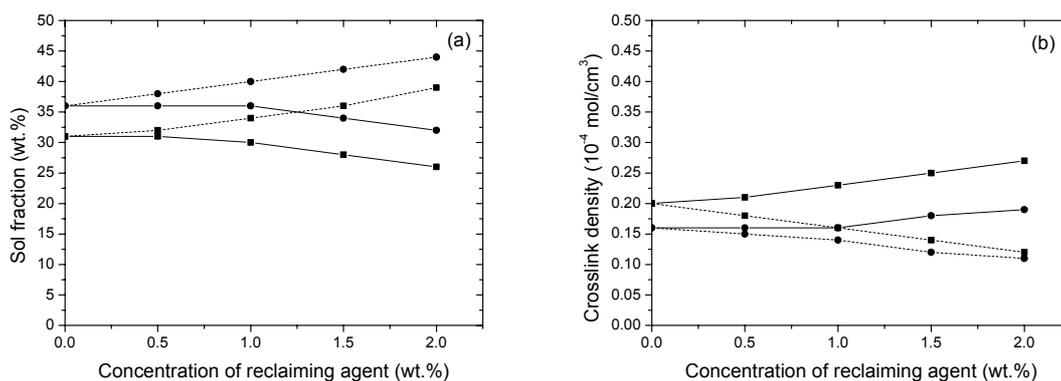


**Figure 4.12** Sol fraction (a) and crosslink density (b) as a function of concentration of diphenyldisulphide (-----) and hexadecylamine (——) at various times for WLR2 at 170°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min

Figures 4.13 and 4.14 present the sol fraction and crosslink density of WLR2 at various times as a function of concentration of hexadecylamine at 180°C and 190°C. Again, using diphenyldisulphide as reclaiming agent increases the sol fraction and the crosslink density decreases, whereas hexadecylamine works in the reverse manner. Increase of temperature does not change the behaviour of both reclaiming agents towards the latex product. These results again point to the fact that hexadecylamine is not effective compared to diphenyldisulphide or thermal reclaiming.

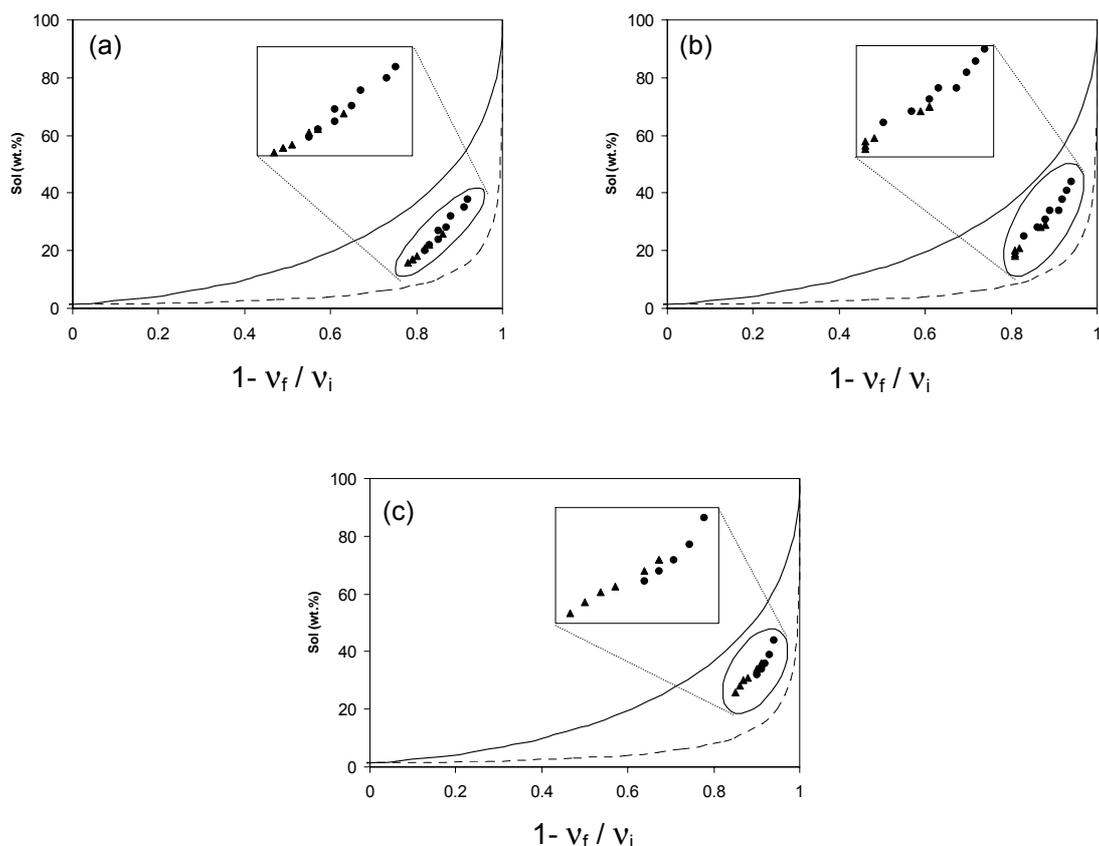


**Figure 4.13** Sol fraction (a) and crosslink density (b) as a function of concentration of diphenyldisulphide (-----) and hexadecylamine (——) at various times for WLR2 at 180°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min



**Figure 4.14** Sol fraction (a) and crosslink density (b) as a function of concentration of diphenyldisulphide (-----) and hexadecylamine (——) at various times for WLR2 at 190°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min

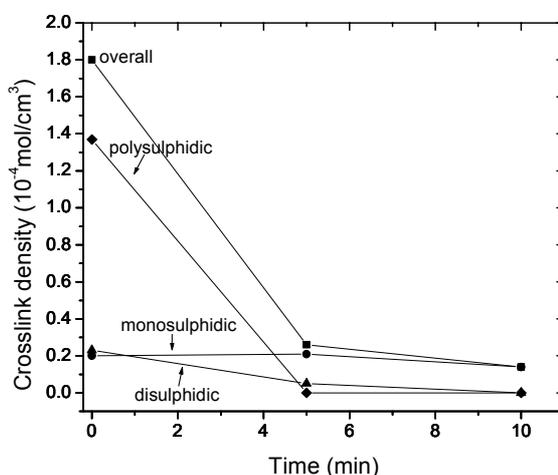
Figure 4.15 shows the sol fraction of WLR2 as a function of the relative decrease in crosslink density at 170°C, 180°C and 190°C. In this figure the experimental data for WLR2 with diphenyldisulphide and hexadecylamine are located



**Figure 4.15** Fraction of sol of WLR2 reclaimed with diphenyldisulphide and hexadecylamine against relative decrease in crosslink density at 170°C (a); 180°C (b); and 190°C (c); (——): main-chain scission; (-----): crosslink scission; (▲): Hexadecylamine; (●): Diphenyldisulphide

in between the main-chain scission curve (solid curve) and crosslink scission curve (dotted curve) showing that reclamation has mainly occurred through crosslink scission. The sol-gel analysis of WLR2 reclaimed with hexadecylamine proves that hexadecylamine is less effective for WLR2. Another result is that the experimental data are slightly closer to the main-chain scission curve at higher temperatures. This indicates indeed that at higher temperatures more chain scission is occurring for natural rubber vulcanisates.

The crosslink distribution of WLR2 reclaimed with diphenyldisulphide against the reclaiming time at 180 °C is presented in Figure 4.16. The cumulative crosslinks, the polysulphidic and the disulphidic crosslinks decrease whereas the amount of monosulphidic crosslinks remains constant with the reclamation time. The polysulphidic crosslinks decrease only to the level of monosulphidic crosslinks initially present in the system.



**Figure 4.16** Crosslink density of WLR2 reclaimed with diphenyldisulphide as a function of reclamation time at 180 °C; (■): overall crosslink density; (◆): polysulphidic; (▲): disulphidic; (●): monosulphidic.

#### 4.4 DISCUSSION

The results obtained from the diphenyldisulphide and hexadecylamine reclaimed WLR1 and WLR2 indicate that the two reclaiming agents have different effects on the reclaiming efficiency. This is a consequence of the fact that both reclaiming agents react with the natural rubber vulcanisate according to different mechanisms.

Diphenyldisulphide is effective as reclaiming agent for natural rubber based latex vulcanisates. Figures 4.2 – 4.4 and 4.11 - 4.14 show that diphenyldisulphide starts to aid the thermal rupture of the three-dimensional structured vulcanisate already at 170 °C.<sup>18</sup> A strong influence of the concentration of diphenyldisulphide is

found at temperatures of 180°C and 190°C: Figures 4.2(b), 4.2(c), 4.5 - 4.6, 4.11(b) 4.11(c) and 4.12 - 4.14. A simplified reaction scheme proposed for the reclamation of natural rubber with diphenyldisulphide is given in the section 3.3.1. The mechanism is based on splitting of diphenyldisulphide to radicals under the influence of temperature and followed by hydrogen abstraction or addition to the double bonds in natural rubber.<sup>13</sup>

Although diphenyldisulphide reclaims the latex vulcanisate quite efficiently, it is unable to break the monosulphidic crosslinks present in the latex vulcanisate. Figures 4.8 and 4.16 show that the diphenyldisulphide reclaimed samples of WLR1 and WLR2 contain almost the same amount of monosulphides initially present in the feed stock. This is caused by the higher bonding energy of monosulphidic crosslinks compared to the bonding energies of poly- or disulphidic crosslinks.<sup>14,15</sup>

The results obtained from Figures 4.2 – 4.5 and 4.11 – 4.14 show that hexadecylamine is not working as a reclaiming agent for natural rubber based latex products compared to diphenyldisulphide. Instead of decreasing the viscosity and crosslink density of the samples, it increases both properties relative to the thermal treatment, where no reclaiming agent is used.

In the case of a random network destruction, by assuming that a Poisson type molecular size distribution of fragments is formed, the sol fraction ( $s$ ) and crosslinking index ( $\gamma$ ), the average number of crosslinks in the gel molecule,<sup>16</sup> are correlated as follows:

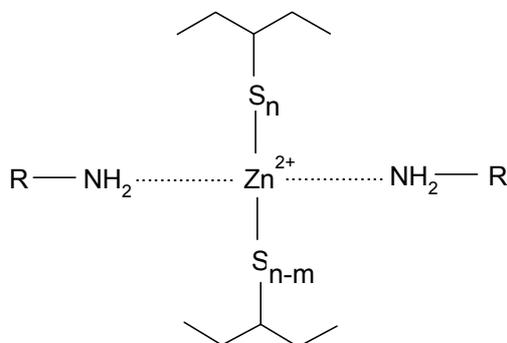
$$s = \frac{\left[ (2 + \gamma) - (\gamma^2 + 4\gamma)^{1/2} \right]}{2\gamma} \quad 4.1$$

The above relation shows that the sol fraction is related to the crosslinking index. A decrease in sol fraction is the result of formation of crosslinks in the matrix. The results for WLR1 and WLR2 indicate the formation of additional crosslinks thereby reducing the rate of crosslink breaking when hexadecylamine is used for the reclamation process.

An explanation for the formation of additional crosslinks when hexadecylamine is used as reclaiming agent relative to thermal treatment is given by Porter:<sup>12</sup> Alkaline nitrogen complexes are reported to be able to open a cyclo-octasulphur ( $S_8$ ) ring. Cleavage of  $S_8$  by primary and secondary amines occurs quite rapidly even at room temperature and forms polysulphide ions and sometimes free radicals. These polysulphide species are a crucial intermediate involved in the formation of the crosslinks.<sup>17</sup> Thus, the presence of free sulphur in a rubber vulcanisate may negatively influence the reclamation process when an amine is used as reclaiming agent: Figure 4.10. The free sulphur content in WLR1 was measured: 14% of the total sulphur used for the vulcanisation was still present in the form of free sulphur.

The crosslink distribution study of WLR1 reclaimed with hexadecylamine (Figure 4.9) shows that some of the polysulphidic crosslinks remain in the sample whereas no polysulphidic crosslinks remained in the sample treated with

diphenyldisulphide. A possible explanation is the formation of a complex between zinc-ions present in the reclaim and the crosslinks, as reported for the sulphur vulcanisation reaction and depicted in Figure 17. This complex can be stabilised by amines, thereby reducing the rate of crosslink scission.<sup>18</sup>



**Figure 4.17** Hypothetical complex stabilised by amines

## 4.5 CONCLUSIONS

Diphenyldisulphide is found to be effective for the reclamation of WLR in a thermo-mechanical process. A stronger reduction of the crosslink density is observed at temperatures of 170°C and 180°C when reclaimed with diphenyldisulphide compared to hexadecylamine. In the present study all poly- and disulphidic crosslinks are broken during reclaiming with disulphide at the temperatures mentioned above, indicating that after reclamation the crosslinks present in WLR are only monosulphidic. Main-chain scission versus crosslink scission studies showed that reclamation has mainly occurred through the scission of crosslinks rather than by main-chain scission.

On the other hand, hexadecylamine is found to be not effective as reclaiming agent, because it results in the formation of additional crosslinks compared to the thermo-mechanical reclamation without reclaiming agent. The crosslink distribution studies showed that some of the polysulphidic crosslinks remain in the sample after treatment with hexadecylamine whereas no polysulphides were found in the samples treated with diphenyldisulphide. This again proves the fact that diphenyldisulphide most effectively breaks the polysulphidic crosslinks in latex vulcanisates compared to hexadecylamine.

## 4.6 REFERENCES

1. J. A. Beckman, G. Crane, E. L. Kay, J. R. Laman, *Rubber Chem. Technol.* **47**, (1974), 597.
2. M. A. L. Verbruggen, L. van der Does, J. W. M. Noordermeer, M. van Duin, H. J. Manuel, *Rubber Chem. Technol.*, **72**, (1999), 731.
3. S. Yamashita, *Int. Polym. Sci. Technol.*, **8**(12), (1981), T/77 – T/93.
4. P. J. Dasher (to Goodrich Co. BF), US 2304548 (December 8, 1942).
5. P. J. Dasher (to Goodrich Co. BF), US 2304549 (December 8, 1942).
6. P. J. Dasher (to Goodrich Co. BF), US 2304550 (December 8, 1942).
7. P. J. Dasher (to Goodrich Co. BF), US 2304551 (December 8, 1942).
8. M. van Duin, J. W. M. Noordermeer, M. A. L. Verbruggen, L. van der Does (to DSM IP ASSETS BV), WO0123465 (December 16, 2004).
9. P. J. Flory, J. Rehner, Jr., *J. Chem. Phys.* **18**, (1950), 108.
10. D. S. Campbell, *J. Appl. Polym. Sci.*, **13**, (1969), 1201.
11. D. S. Campbell, B. Saville, in "Proceedings of the International Rubber Conference", Brighton (1967).
12. M. Porter, *Organic Chemistry of Sulphur*, S. Oae, Ed., Plenum Press, New York, 1977.
13. A. Z. Kuzmiski, *Developments in polymer stabilization*, G. Scott, Ed., Applied Science Publishers, London, **4**, 1981.
14. T. H. Kuan, *Rubber World* **192**(5), (1985), 20.
15. C. M. Kok, V. H. Yee, *Eur. Polym. J.*, **22**, (1986), 341.
16. A. Charlesby, *J. Polymer Sci.*, **11**, (1953), 513.
17. A. Y. Coran, *Science and Technology of Rubber*, F. R. Eirich, Ed., Academic Press, New York, 1978.
18. G. Heideman, PhD thesis, University of Twente, (2004). ISBN 90 365 2081 9.

# Chapter 5

---

## Model compound studies on the devulcanisation of natural rubber using 2,3-dimethyl-2-butene<sup>#</sup>

---

The mechanism of devulcanisation of sulphur vulcanised natural rubber with aromatic disulphides and aliphatic amines as reclaiming agents is studied using model compounds: Low-molecular-weight compounds are used as replacement of the reactive unit of the polymeric rubber. In the present study, 2,3-dimethyl-2-butene ( $C_6H_{12}$ ) is used as a low-molecular weight model alkene with only equivalent allylic positions.  $C_6H_{12}$  is first vulcanised with a mixture of sulphur, zinc stearate and N-cyclohexyl-2-benzothiazylsulphenamide (CBS) as accelerator at 140°C, resulting in a mixture of addition products of the general formula  $C_6H_{11}-S_x-C_6H_{11}$ . The compounds are isolated and identified by High Performance Liquid Chromatography (HPLC) with respect to their various sulphur ranks. In a second stage, the vulcanised products are devulcanised using the agents mentioned above at 200°C and 210°C. The kinetics and chemistry of the breakdown of the sulphur-bridges during devulcanisation are monitored at both temperatures. The devulcanisation efficiency depends on the distribution of the sulphur ranks: Higher ranks of the sulphide crosslinks are devulcanised quite easily whereas the lower trisulphidic and disulphidic ranks react slowly. The monosulphidic addition product is not devulcanised at all in the temperature range used in this study. Both devulcanisation agents decompose sulphidic vulcanisation products with sulphur ranks equal or higher than 3 quite effectively and with comparable speed at 200°C. Diphenyldisulphide as devulcanisation agent gives rise to a high amount of mono- and disulphidic compounds formed during the devulcanisation, while hexadecylamine as devulcanisation agent restrains these lower sulphur ranks from being formed at both the temperatures in the model reaction.

---

<sup>#</sup>A part of the work described in this chapter was presented at the 166<sup>th</sup> Technical meeting – Rubber Division, ACS, October 5 – 8, 2004 in Columbus, Ohio (paper no. 25) and is accepted for publication in Rubber Chem. Technol. Another part of the work in this chapter was presented at the International Rubber Conference IRC '05, June 6 – 9, in Maastricht, The Netherlands and is published in Kautsch. Gummi Kunstst., **58**, (2005), 312.

## 5.1 INTRODUCTION

Model compound (MC) studies in which a rubber polymer is replaced by a reactive low-molecular weight compound have been developed as a valuable method for the study of vulcanisation reactions. It remains a very useful method because rubbers are difficult to analyse using standard analytical and spectroscopic techniques despite recent developments in the field of analytical techniques. The low molecular weight compound used in MC studies needs to be chemically representative of the reactive unit of the polymer. Other factors like the presence of additional functional groups, position and configuration of the double bond and occurrence of double bonds present in the model should be considered as well. It is essential in sulphur MC study to have at least one allylic hydrogen atom in the model compound, since crosslink formation involves the substitution of an allylic hydrogen for a sulphur link. Other factors not to be neglected are the solubility of the chemicals in rubber compared to model systems and the loss of volatiles from the model compound in model experiments. Nieuwenhuizen, Haasnoot and Reedijk have given a comprehensive review of the technique of Model Compound Vulcanisation (MCV).<sup>1</sup>

An elementary disadvantage of low-molecular-weight model compounds such as the olefins used for sulphur MC vulcanisation is the high concentration of end-groups. These end-groups (i. e. methyl groups) have a reactivity that differs from the methylene (-CH<sub>2</sub>-) and methyne (-CH-) groups, which form the majority of groups in a rubber polymer. This disadvantage can partly be overcome by using larger models, such as squalene and pentadecene. It is also possible to use cyclic compounds, which do not contain any end-groups.<sup>2,3</sup>

Common model molecules, which are used for sulphur vulcanisation research, are squalene<sup>4-8</sup> and 2-methyl-2-pentene,<sup>9,10</sup> commonly used to create a system similar to NR. Two models are found in literature, which are used to simulate SBR rubber: *cis*-1-phenyl-3-heptene and a combination of 1,4-*cis*, 1,4-*trans* and 1,2-vinyl butadiene oligomers. The ratio of these three groups corresponds to the composition of SBR.<sup>1</sup> For EPDM, the model used consists of ethylidene norbornane (ENBH),<sup>11</sup> since 5-ethylidene-2-norbornene is the most commonly used termonomer. Cyclohexene seems to be an obvious monomeric model compound for BR, but when the three-dimensional configuration around the double bond is considered, it becomes apparent that the double bond in cyclohexene has a conformation which is completely different from the configuration of BR. Therefore, crosslink formation in cyclohexene occurs according to a different mechanism than crosslink formation in BR. In addition, the fact that the double bond is incorporated in a six-membered ring induces some ring strain in the molecule. In summary, the double bond environment in cyclohexene differs very much from the reactive units of BR. An alternative to cyclohexene may be 1,5-cyclooctadiene (COD).<sup>1</sup> In this compound both double bonds are in *cis*- configuration, which compares to BR. 5-chloro-4-methylene-2,2,8,8-tetramethylnonane was applied as a model to study the mechanism of ZnO-curing of the halobutyl rubbers CIIR and BIIR.<sup>12</sup>

In the present investigation a model compound study is used to elucidate the mechanism of devulcanisation of natural rubber with an aromatic disulphide and an

aliphatic amine. A model compound study instead of an in-rubber study is chosen, because it gives a more detailed picture of the devulcanisation characteristics of the various sulphur ranks of a vulcanisate. Model compound studies, in which the rubber polymer is replaced by a reactive low-molecular weight compound, have proven to be a suitable method for the study of vulcanisation reactions, and this technique has been extended in this chapter for the study of devulcanisation reactions as well.

Squalene is the most common polyfunctional compound used as a model for natural rubber due to its similarity to the real rubber structure. Polyfunctional models display a reactivity more similar to rubber, because of the presence of more than one double bond and a relatively low concentration of end-groups. Investigation of crosslinks and main-chain modifications, however, is very difficult and requires elaborate separative and analytical procedures. Therefore, despite its simplicity, the monofunctional model 2,3-dimethyl-2-butene (TME)<sup>1</sup> is used as a model molecule for natural rubber in the present study, as a clear picture of the structure of the vulcanised and devulcanised products can be obtained. This compound is a general model for different types of rubber and commonly used for model compound studies. The advantage of TME is that it has only one type of allylic moiety and therefore, the reaction products have only few isomers. Furthermore, the crosslinked products can be separated by HPLC from the crosslink precursors and the unreacted TME. High temperature techniques like Gas Chromatography (GC) should be avoided for analysis because of their strong effect on polysulphidic organic compounds. The conditions cause isomerisation and/or degradation of di- and polysulphidic products and possibly even of the monosulphides. The crosslink precursors and the products can be detected by a UV detector at a wavelength of 254 nanometers.

An aromatic disulphide and an aliphatic amine were chosen as devulcanisation agents for the present study, because historically these two have most prominently been used as devulcanisation agents for natural rubber.<sup>13</sup> A mechanism that is often proposed for the reaction of disulphides with sulphur vulcanisates is the opening of crosslinks or the scission of chains by heat and shearing forces and their recombination with disulphides which prevents recombination via a radical reaction. Amines cleave the sulphur crosslinks in the rubber vulcanisate by a nucleophilic reaction.<sup>14,15</sup>

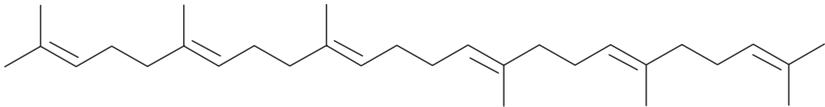
## 5.2 EXPERIMENTAL

*Materials* - The materials used in the model compound experiments are listed in Table 5.1. The experiments were divided into two parts: experiments with squalene as model compound and experiments with TME as model compound. The chemical structure of both model compounds are given in Table 5.2.

**Table 5.1** Materials used for model compound vulcanisation

Material	Source
Squalene	Merck
2,3-dimethyl-2-butene (TME)	Aldrich
N-Cyclohexyl-2-benzothiazylsulphenamide (CBS)	Flexsys
N-tert-butyl-2-benzothiazylsulphenamide (TBBS)	Flexsys
Sulphur	Merck
Zinc Stearate	Merck

**Table 5.2** Chemical structure of model compounds

Model	Chemical structure
Squalene (410.72 g/mol)	
2,3-dimethyl-2-butene (TME) (84.16 g/mol)	

*Model vulcanisation and devulcanisation* - The recipes for the vulcanisation and devulcanisation experiments are given in Tables 5.3 and 5.4. The reactions were carried out in thick-walled glass ampoules. Before closing the ampoule by melting the glass neck, a flow of nitrogen was passed through the ampoule to remove oxygen, because oxygen can oxidise the double bond in TME. The vulcanisation was done by placing the vessel in a thermostatic oil bath kept at 140°C and the devulcanisation was carried out at 200°C. The vulcanisation reactions were carried out for 2, 5, 10, 15, 20, 30, 40 and 60 minutes. For the devulcanisation reactions separate ampoules were used and the vulcanised products and the devulcanisation agents were added. During the reactions the model mixture was continuously stirred with a magnetic stirrer to assure its homogeneity. The devulcanisation reactions were done for 5, 10, 20 and 30 minutes. After the reactions the ampoules were quenched in an ice bath followed by a liquid nitrogen bath in order to stop the reaction.

**Table 5.3** Model compound vulcanisation recipe

Component	Mass (g)	Amount (phr)	Quantity (mmol)	Component	Mass (g)	Amount (phr)	Quantity (mmol)
Squalene	0.7500	100	1.826	TME	0.7500	100	8.912
S <sub>8</sub>	0.0173	2.3	0.540	S <sub>8</sub>	0.0173	2.3	0.540
CBS	0.0045	0.6	0.017	CBS	0.0045	0.6	0.017
Zn stearate	0.0375	5	0.059	Zn stearate	0.0375	5	0.059

**Table 5.4** Model compound devulcanisation recipe

Component	Amount (phr)
Vulcanisate	100
Devulcanisation agent	0, 1, 2

*Analysis of the reaction products* - The ampoules were opened and a small portion (roughly 0.03 g) of the sample was weighed and dissolved in 2.5 ml of acetonitrile already containing an internal standard. 20 µl of this sample was injected into the HPLC-column for analysis according to the conditions described in Table 5.5. Before injecting into the HPLC, this mixture was filtered twice over a 0.45 µm porous filter.

The internal standard is an extra component necessary for the quantitative analysis of the reaction mixture. It has a known response area with respect to the area of the other components. The internal standard used in this investigation is N-tert-butyl-2-benzothiazylsulphenamide (TBBS). TBBS is chosen because it has a retention time in the range of the retention times of the other components. Although it is a sulphur compound, it will not interfere with the sample, because it is added after vulcanisation at room temperature just before injecting the sample into the HPLC.

**Table 5.5** HPLC Measurements

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

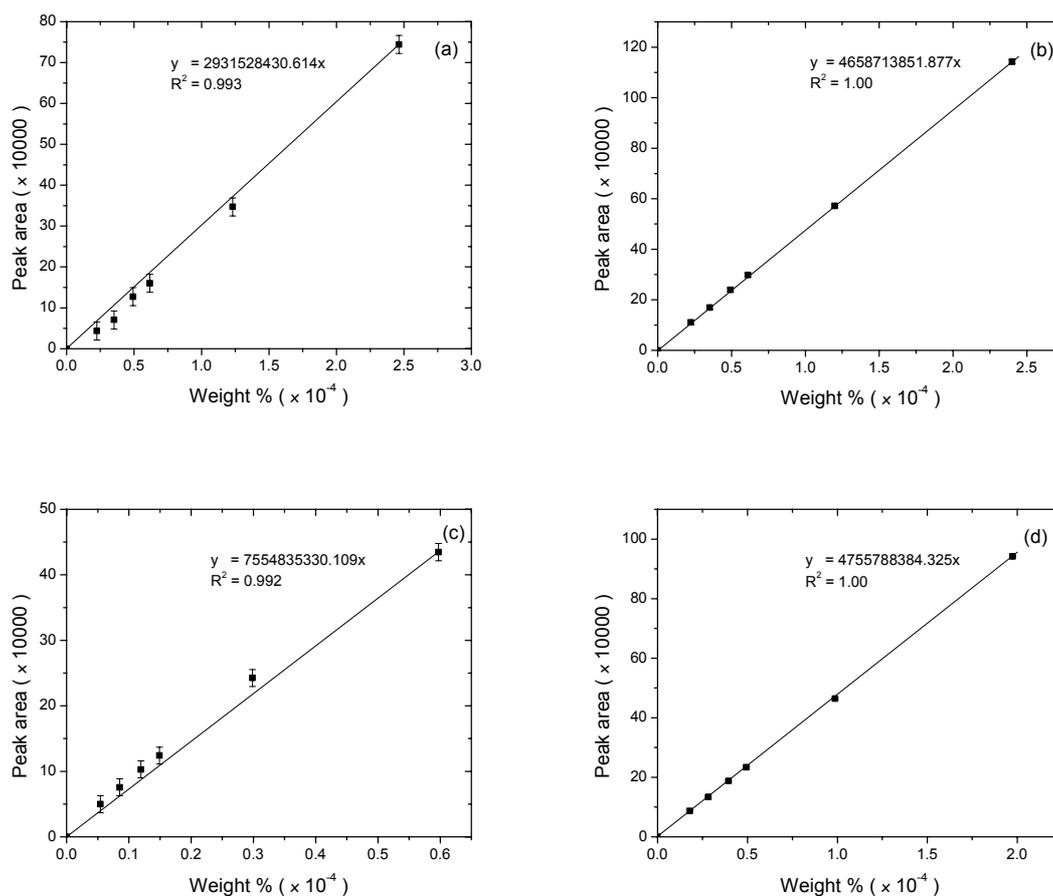
For determining the amount of components in the sample, calibration lines were measured (Figure 5.1) and response factors were calculated.

With use of the response factors the area of the HPLC chromatogram can be converted into concentrations. The response factor is calculated according to the following equation:<sup>16</sup>

$$R = \left( \frac{A_C}{A_{IS}} \right) \times \left( \frac{W_{IS}}{W_C} \right) \quad 5.1$$

with R representing the response factor,  $A_C$  being the area of the component,  $A_{IS}$  being the area of the internal standard,  $W_{IS}$  representing the weight percentage of the internal standard and  $W_C$  is weight percentage of the component. The slope of the

calibration line of a component, divided by the slope of the calibration line of TBBS (internal standard) results in the response factor. The response factors for the initial components measured at 254 nm are given in Table 5.6. Retention time and response factors of the pure ingredients were determined by injecting a solution of a single component into the HPLC device. TME cannot be detected by UV light with a wavelength of 254 nanometer therefore it does not have a retention time or a response factor.



**Figure 5.1** Calibration lines for sulphur (a), CBS (b), MBT (c) and TBBS (d) in terms of peak area vs. weight percentage

**Table 5.6** Retention times and response factors of the initial components

Component	Retention time (minutes)	Response factor
CBS	5.6	10.92
TBBS	4.2	1.00
MBT	2.5	34.73
S <sub>8</sub>	14.1	7.54

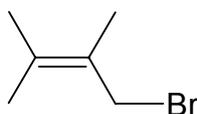
The response factors are then used to calculate the weight percentage of the component in the vulcanised sample using the following equation:<sup>16</sup>

$$m_c = \left( \frac{A_c}{A_{IS}} \right) \times \left( \frac{m_{IS}}{R} \right) \quad 5.2$$

with  $m_c$  being the mass of the component and  $m_{IS}$  the mass of the internal standard. Since the initial masses are known, relative amounts can be calculated.

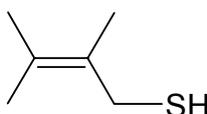
Whenever useful, <sup>1</sup>H-NMR spectroscopy (Bruker 300 MHz) was used to characterise the structure of the reaction products. The solvent used for these experiments was CDCl<sub>3</sub>.

*Synthesis of (mono)sulphidic crosslinks* – The monosulphidic crosslinks of TME were synthesised by a three step synthesis. The first step was the synthesis of 1-bromo-2,3-dimethyl-2-butene (Figure 5.2) 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 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 quenched in an ice bath. The product was purified by distillation and analysed by <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta = 1.70$  (s,3H), 1.77 (s,6H), 4.07 (s,2H).



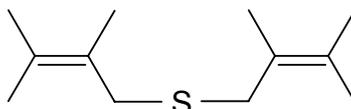
**Figure 5.2** Chemical structure of 1-bromo-2,3-dimethyl-2-butene

The second stage was the synthesis of 2,3-dimethyl-2-butene-1-thiol, Figure 5.3. In a nitrogen atmosphere, 26.47 g TME-Br and 15.77 g of 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. The rotavap was used to evaporate the solvent. The white solid was dissolved in ultrasonically degassed distilled water together with 8.28 g NaOH. After refluxing for one hour, the product was extracted three times with 50 ml of methyl- lene chloride. The methylene chloride was removed by rotavap distillation. The product was distilled in vacuo. The structure of the TME-SH is given in Figure 5.3. <sup>1</sup>H-NMR analysis gave the following signals (CDCl<sub>3</sub>):  $\delta = 1.40$  (t,1H), 1.66 (s,3H), 1.71 (s,3H), 1.74 (s,3H), 3.18 (d,2H).



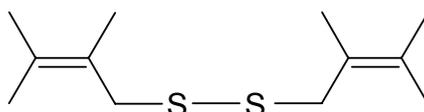
**Figure 5.3** Chemical structure of 2,3-dimethyl-2-butene-1-thiol

The final step was the synthesis of the monosulphidic crosslink, Figure 5.4. 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°C. 2 g of TME-SH dissolved in 50 ml of diisopropylether was added dropwise within 10 minutes. 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 a quantitative yield. The product was analysed by  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 1.73$  (s, 3H), 1.75 (s,3H), 1.80 (s,3H), 3.20 (s,3H).



**Figure 5.4** Chemical structure of the monosulphidic crosslink

*Synthesis of the (di)sulphidic crosslink* - To a stirred solution of 3.24 g of TME-SH in 70 ml pyridine, a solution of 3.54 g of iodine in 70 ml of pyridine was added over an hour. Pyridine was removed under reduced pressure and the residue was extracted three times with 50 ml of diethyl ether. Concentration in vacuo and purification by silica gel chromatography (petroleum ether 40-60) yielded TME-S-S-TME (Figure 5.5) in quantitative yield as a colourless oil.  $^1\text{H-NMR}$  signals were found at ( $\text{CDCl}_3$ ):  $\delta = 1.69$  (s,3H), 1.75 (s,3H), 1.77 (s,3H), 3.47 (s,2H).



**Figure 5.5** Chemical structure of the disulphidic crosslink

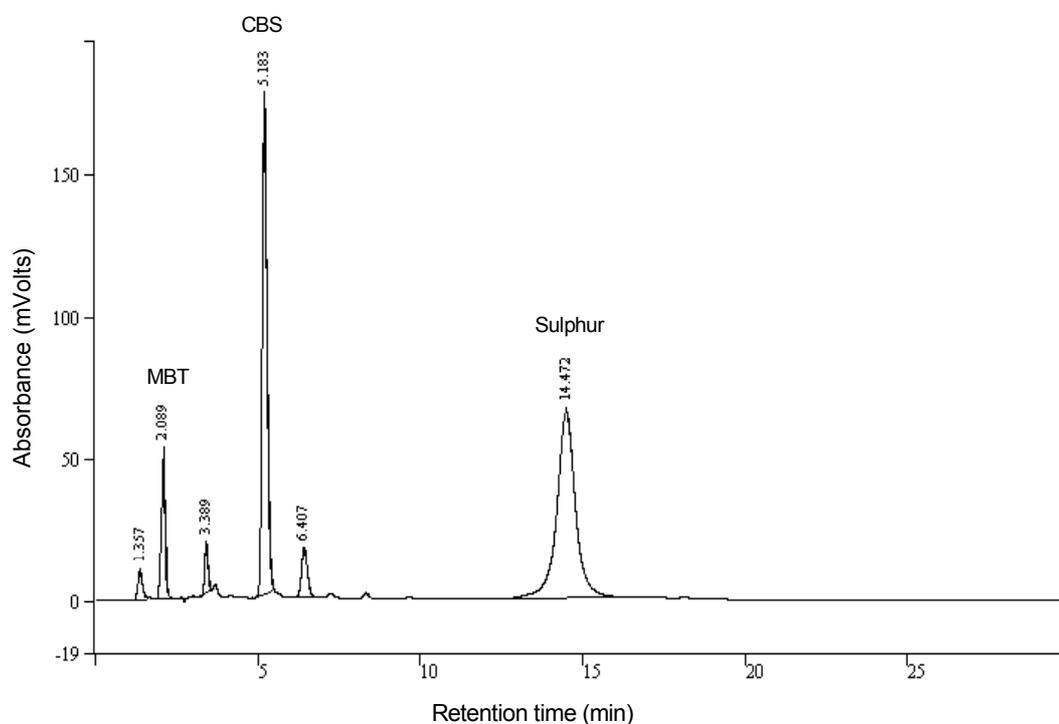
### 5.3 RESULTS

The model compound study is divided into two parts: In the first part, reactions were carried out with the polyfunctional model squalene. In the second stage the study was carried out with the monofunctional model TME.

### 5.3.1 Reaction with squalene

Squalene was reacted for 5-70 minutes in the presence of sulphur, CBS and zinc stearate as given in the recipe in Table 5.3. The vulcanisation reaction was carried out at 140°C, a representative temperature for NR vulcanisation as chosen for the majority of model compound studies.<sup>17,18</sup> At higher temperatures, in the range of typical curing temperatures for rubber, the reaction would proceed much faster, particularly in model compound systems. In order to be able to follow the development of the reactions more gradually, a low reaction temperature was preferred.

The reactions were carried out for a definite time period and the reaction products were analysed with HPLC. An example of a HPLC-chromatogram is given in Figure 5.6. One of the main objectives of this study is to closely analyse the distribution of mono-, di-, and polysulphidic crosslinks of the vulcanisate and the behaviour during the devulcanisation reaction with disulphides and amines. Unfortunately, it was very difficult to analyse the crosslinked products of squalene with this HPLC-UV setup. It was found that other techniques, like Gel Permeation Chromatography, are more suitable to study the crosslinking of 'high' molecular weight squalene.<sup>19</sup> The resulting chromatograms, however, do not show clearly the crosslinked products with different sulphur ranks. 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 5.6** Analytical HPLC chromatogram of the reaction mixture from the vulcanisation of Squalene with S<sub>8</sub> in the presence of zinc stearate and CBS at 140°C for 20 minutes

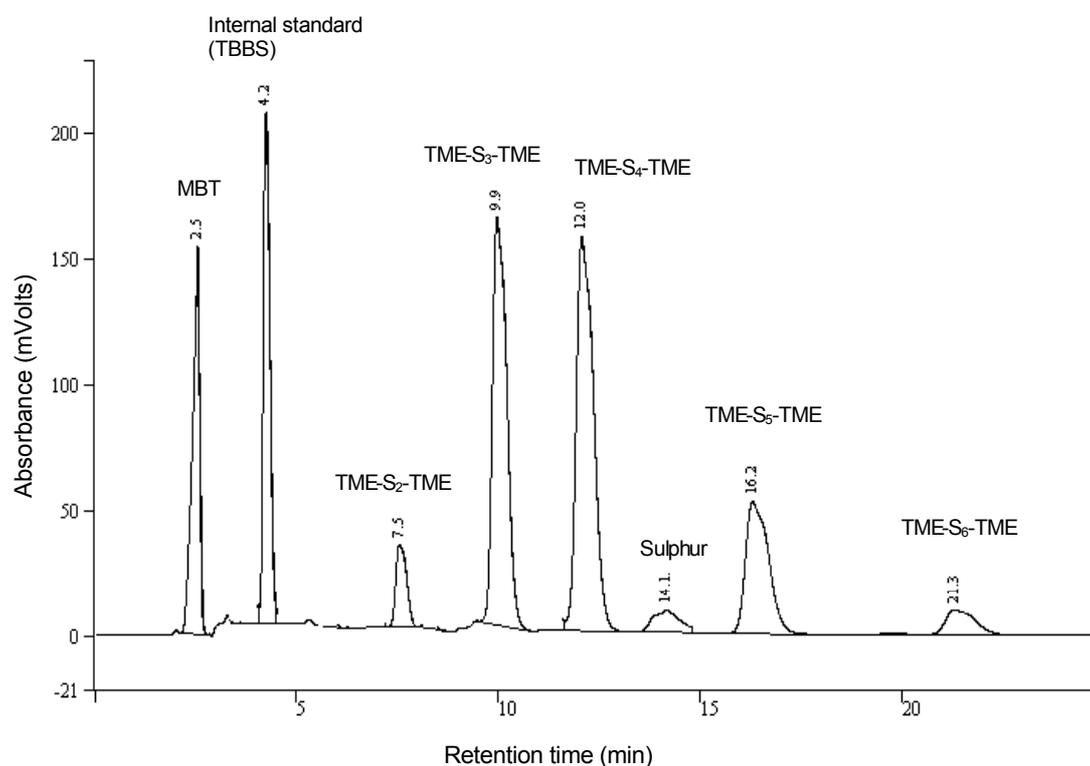
### 5.3.2 Reaction with TME

#### 5.3.2.1 Identification of the signals in the HPLC chromatogram

Although TME is chemically less similar to natural rubber compared to squalene, its simplicity, viz. monofunctionality and one type of allylic position, offers great advantages when studying the intermediates and final products of the vulcanisation and devulcanisation reactions. First, the optimum vulcanisation time for TME was determined and vulcanised TME was prepared. The second part covers the devulcanisation of the vulcanisate using the aromatic disulphide and aliphatic amine as devulcanisation agents.

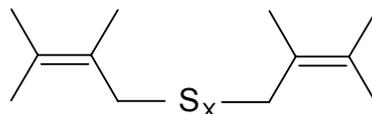
A HPLC chromatogram for the vulcanisation of TME with  $S_8$  in the presence of zinc stearate and CBS at a reaction time of 30 minutes is shown in Figure 5.7. Basically two types of peaks can be distinguished in the chromatogram at different retention times:

- The addition or crosslinked products with a general formula  $TME-S_x-TME$  ( $C_6H_{11}-S_x-C_6H_{11}$ ), but with a varying length of the sulphur chain ( $x = 1$  to 6);
- The starting materials and/or the decomposition products of the starting materials.



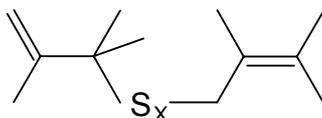
**Figure 5.7** Analytical HPLC chromatogram of the reaction mixture from the vulcanisation of TME with  $S_8$  in the presence of zinc stearate and CBS at 140°C for 30 minutes

From Table 5.6, in which the retention times of the starting materials are given, it can be concluded that the peaks with retention times of 2.5, 4.2 and 14.1 minutes correspond to MBT, the decomposition product of CBS, and TBBS (internal standard) as well as sulphur, respectively.<sup>20</sup> The so far unidentified peaks with retention times of 7.5, 9.9, 12.0, 16.2 and 21.3 minutes belong to the crosslinked products. Versloot et al.<sup>21</sup> have demonstrated, that two molecules of TME react with sulphur to form a structure as shown in Figure 5.8.



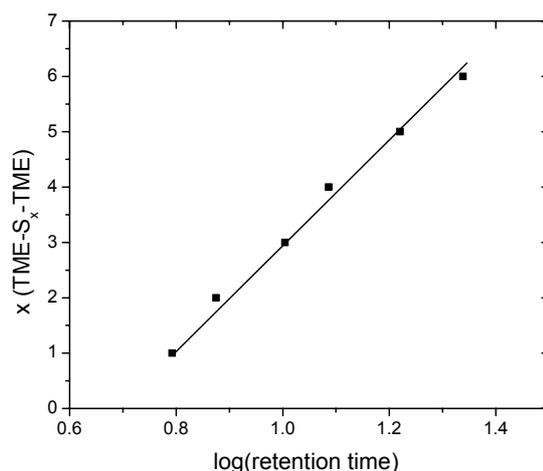
**Figure 5.8** Chemical structure of the reaction products of TME and sulphur

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 5.9.<sup>18</sup>



**Figure 5.9** Chemical structure of the reaction products of TME and sulphur when isomerisation takes place

The retention times of the mono- and disulphidic crosslinked products were determined by synthesising them and analysing them by chromatography. As the synthesis of some of the crosslinked products is not viable, only bis(2,3-dimethyl-2-butene-1-yl)monosulphide (TME-S<sub>1</sub>-TME) and bis(2,3-dimethyl-2-butene-1-yl)disulphide (TME-S<sub>2</sub>-TME) were synthesised and their structure was characterised by <sup>1</sup>H-NMR spectroscopy. The monosulphide TME-S<sub>1</sub>-TME has a retention time of 6.5 minutes and the disulphide TME-S<sub>2</sub>-TME has a retention time of 7.6 minutes. According to Hann et al. there is a linear correlation between the sulphur rank and the logarithm of the retention time.<sup>22</sup> Figure 5.10 presents the sulphur rank as a function of the logarithm of the retention time of various crosslinked products. Since the retention times of the mono- and disulphidic crosslinks are known, the sulphur rank of the other crosslinked products can be extrapolated from Figure 5.10. The peak with a retention time of 10.1 minutes is the trisulphide, the one with 12.2 minutes is the tetrasulphide, the one with 16.6 minutes is the pentasulphide and the peak with 21.8 minutes is the hexasulphide.



**Figure 5.10** Sulphur rank of various crosslinked products as a function of the logarithm of their retention time

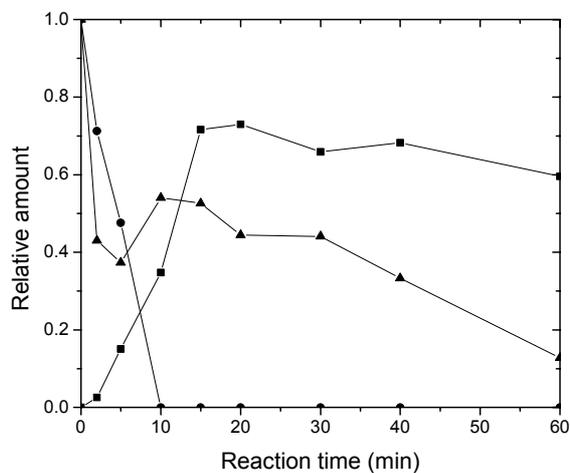
### 5.3.2.2 Determination of the optimum vulcanisation time

In Figure 5.11 the relative amounts of CBS, sulphur and MBT for the model vulcanisate are displayed as a function of reaction time. During vulcanisation at 140°C the amount of elemental sulphur decreases to 38% of the initial amount for a reaction time of 5 minutes. This is an indication that the sulphur is partly inserted into the zinc complex.<sup>23</sup> Since initially no MBT was present, the amount of MBT is related to the maximum that can be formed if all CBS would be transformed into MBT. CBS starts to decompose immediately after the start of the reaction, and at a reaction time of 10 minutes all CBS is decomposed. Correspondingly, the amount of MBT starts to increase from the very beginning of the reaction and levels off after a reaction time of 15 minutes.

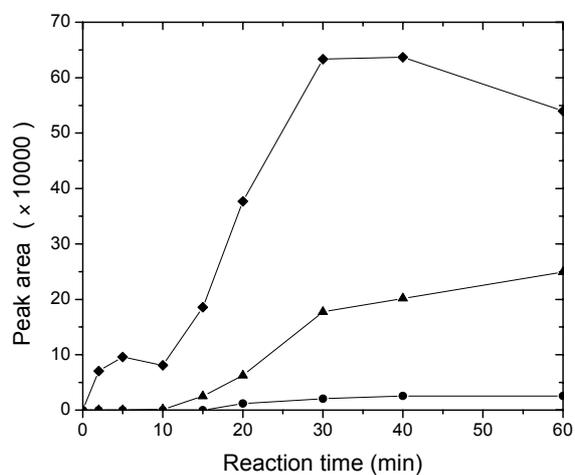
The peak areas of di-, tri- and polysulphidic crosslinks against the reaction time are given in Figure 5.12. For the crosslinked products it is not possible to plot relative amounts because the response factors cannot be determined. Therefore, the mono-, di-, tri- and polysulphidic crosslinked products cannot be compared in terms of absolute quantities; only the trends can be compared. The tetra-, penta- and hexasulphidic crosslinked products are all combined, as they react similarly.

The polysulphidic compounds increase up to a reaction time of 30 minutes and tend to decrease with further increasing reaction time. A slight initial decrease of the amount of polysulphidic compounds is found for a reaction time of 10 minutes, but the concentration rapidly increases again up to 30 minutes. The formation of di- and trisulphides starts only after the same reaction time of 10 minutes. The polysulphidic crosslinks act as precursors for the shorter tri- and di-sulphidic crosslinks.<sup>23</sup> The breakdown of this precursor boosts the formation of shorter crosslinks. Apparently, no monosulphidic products are formed in the reaction mixture due to the fact that a conventional curing recipe with a high sulphur to accelerator

ratio was used.<sup>20</sup> The amount of disulphides levels off after a reaction time of 30 minutes, whereas the trisulphides further increase with reaction time.



**Figure 5.11** Relative amount of major compounds as a function of reaction time during the vulcanisation of TME with  $S_8$  in the presence of zinc stearate and CBS at  $140^\circ\text{C}$ ; (▲): Sulphur ; (●): CBS ; (■): MBT



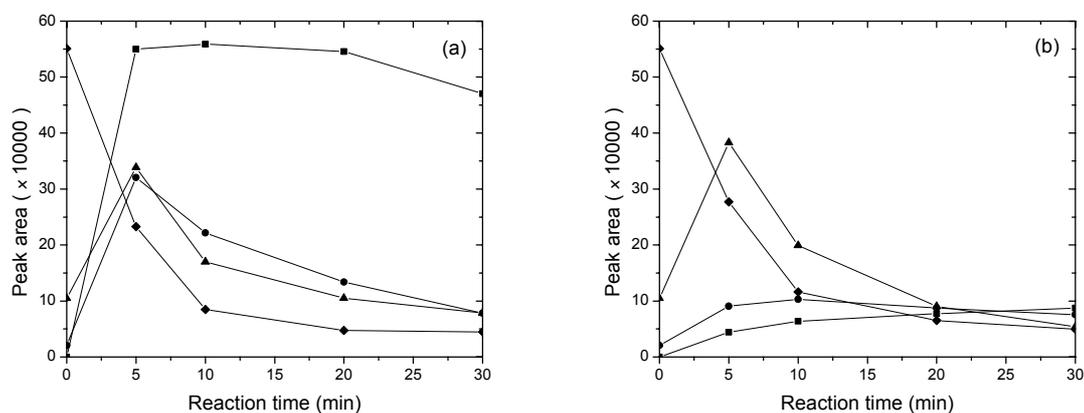
**Figure 5.12** Peak areas of the crosslinked products as a function of reaction time during the vulcanisation of TME with  $S_8$  in the presence of zinc stearate and CBS at  $140^\circ\text{C}$ ; (●): disulphide ; (▲): trisulphide ; (◆): polysulphide

In analogy with the definition of the curing time for the vulcanisation in real rubber systems, the time required for the formation of the maximum amount of

crosslinks was taken as the optimum vulcanisation time. Figure 5.12 shows that after approximately 30 minutes an optimum concentration of crosslinks is reached. This period was further chosen as the optimum vulcanisation time in this study. The devulcanisation experiments depicted in the following Figures 5.13 - 5.19 are preceded by a curing step under the above mentioned conditions. The starting crosslink distributions were measured in each case to define the system under investigation.

### 5.3.2.3 Devulcanisation of crosslinked products with disulphide and amine

Figure 5.13 shows the peak areas of mono-, di-, tri-, and polysulphidic crosslinks after devulcanisation with 1 phr of diphenyldisulphide and hexadecylamine at 200°C, respectively. The peak area at 0 minutes corresponds to the amount of sulphidic products originally present before devulcanisation. The amount of polysulphides decreases exponentially with reaction time. A small amount remains even after 30 minutes, for devulcanisation with diphenyldisulphide as well as with hexadecylamine. Both systems react similarly with respect to the decrease of polysulphides. The amount of trisulphides increases during the first 5 minutes and then decreases again with increasing reaction time, in a similar manner for both systems. The amount of disulphides first increases and then decreases for devulcanisation with diphenyldisulphide. Further, a large amount of monosulphides is formed right from the beginning of the devulcanisation with diphenyldisulphide. On the other hand, for the devulcanisation with hexadecylamine only minor amounts of di- and monosulphides are formed.

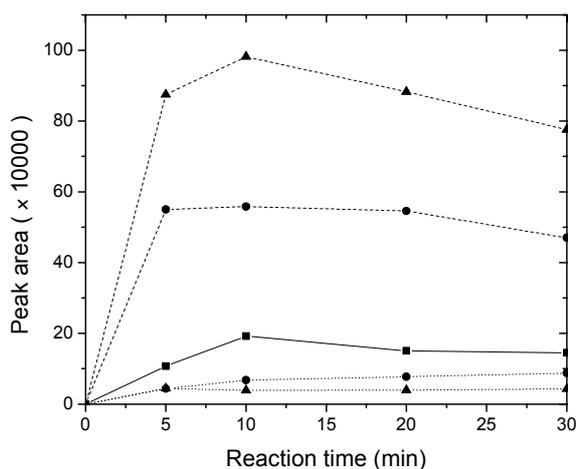


**Figure 5.13** Peak areas of the crosslinked products as a function of reaction time during the devulcanisation of the vulcanisate with 1 phr of diphenyldisulphide (a) and hexadecylamine (b) at 200°C; (■): monosulphide ; (●): disulphide ; (▲): trisulphide ; (◆): polysulphide

### 5.3.2.4 Effect of concentration of the devulcanisation agents

In Figure 5.14 the peak areas of the monosulphidic compounds are shown against the devulcanisation time at 200°C, for various concentrations of diphenyldisulphide and hexadecylamine, resp. after thermal devulcanisation. The

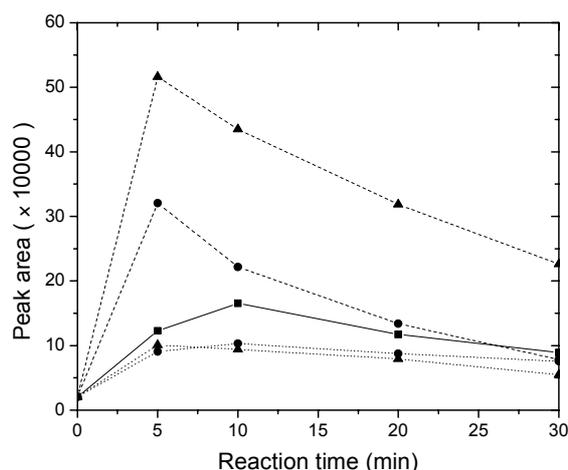
latter indicates the absence of devulcanisation agent. In all cases monosulphides are formed, but again the large difference between diphenyldisulphide and hexadecylamine is clear. The higher the amount of diphenyldisulphide added, the more monosulphidic compound is formed. For hexadecylamine the opposite applies: the more amine added, the less monosulphidic compound is formed. However, the difference between 1 phr and 2 phr of amine is less pronounced compared to the



**Figure 5.14** Peak areas of monosulphide crosslinks devulcanised with diphenyldisulphide(-----), hexadecylamine (.....) and thermally (——) at various concentrations of devulcanisation agents as a function of reaction time at 200°C; (■): 0 phr ; (●):1 phr; (▲): 2 phr

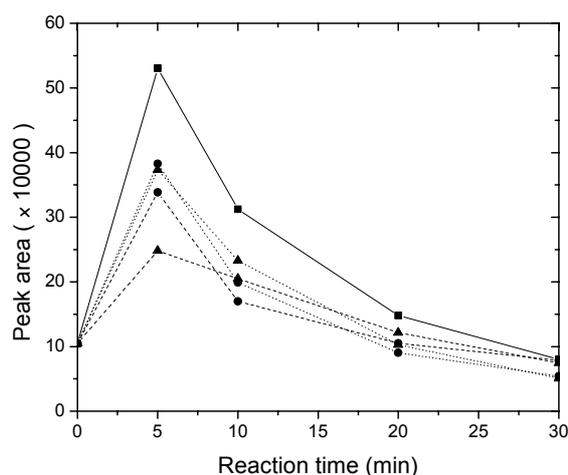
disulphides. The thermal treatment, without either of the two devulcanisation agents present, has an intermediate position. Once formed, there is little decrease of the monosulphidic crosslinks any more.

Figure 5.15 shows the peak areas of the disulphidic compound after the devulcanisation with diphenyldisulphide or hexadecylamine, respectively thermally at 200°C, for various concentrations of the devulcanisation agents. Again, large differences are seen between the use of diphenyldisulphide and hexadecylamine. For diphenyldisulphide the concentration of disulphidic crosslinks reaches a maximum after approximately 5 minutes and then decreases with time. During the whole reaction period the concentration is on a higher level than in the case of thermal devulcanisation. However, only a relatively small amount of disulphide compounds is formed for the amine as devulcanisation agent, more or less irrespective of its concentration, at a level below the thermal devulcanisation.



**Figure 5.15** Peak areas of disulphide crosslinks devulcanised with diphenyldisulphide (-----), hexadecylamine (.....) and thermally (——) at various concentrations of devulcanisation agents as a function of reaction time at 200°C; (■): 0 phr ; (●): 1 phr; (▲): 2 phr

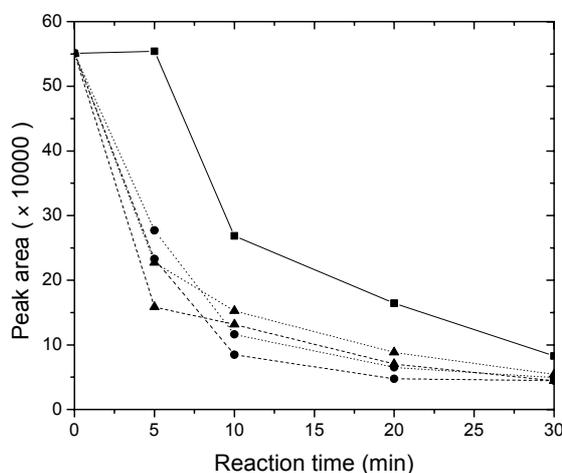
The peak areas of the trisulphidic compounds obtained for devulcanisation are shown in Figure 5.16. All curves now show the same trend of an initial increase, followed by a decrease in time. The curves for diphenyldisulphide as well as for hexadecylamine all fall below the line for thermal treatment. Diphenyldisulphide forms the least amount of trisulphides, and the amount decreases slightly with increasing concentration, whereas for hexadecylamine little effect of concentration is seen. Thermal devulcanisation leads to the maximum amount of trisulphides. There is not



**Figure 5.16** Peak areas of trisulphide crosslinks devulcanised with diphenyldisulphide (-----), hexadecylamine (.....) and thermally (——) at various concentrations of devulcanisation agents as a function of reaction time at 200°C; (■): 0 phr ; (●): 1 phr; (▲): 2 phr

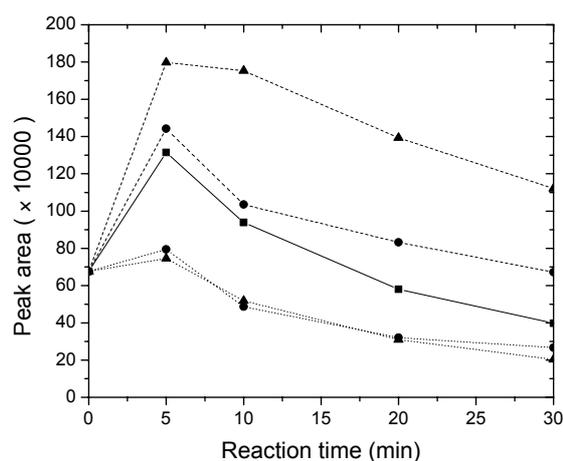
much difference in rate of decomposition of trisulphides after the initial increase, for both diphenyldisulphide and hexadecylamine.

Figure 5.17 shows the peak areas of the polysulphidic compounds against reaction time. The amount of polysulphides initially decreases faster with increasing concentration of both diphenyldisulphide and hexadecylamine, but the final concentration is comparable for both devulcanisation agents and concentrations. Both devulcanisation agents decompose the polysulphides in the same manner; both have a similar reactivity towards the polysulphide crosslinks. The decomposition of the polysulphide in the thermal treatment is much slower, particularly in the beginning.



**Figure 5.17** Peak areas of polysulphide crosslinks devulcanised with diphenyldisulphide(-----), hexadecylamine (.....) and thermally (——) at various concentrations of devulcanisation agents as a function of reaction time at 200°C; (■): 0 phr ; (●): 1 phr; (▲): 2 phr

The cumulative peak areas of all crosslinks of the compound as a function of the reaction time are presented in Figure 5.18. The cumulative areas representing the sum of all crosslinks increase in the initial 5 minutes of the reaction time and then decrease in all cases. Samples devulcanised with diphenyldisulphide show the highest values, with an increasing trend for higher concentrations of diphenyldisulphide. On the other hand, the hexadecylamine devulcanised products have lower values compared to thermally devulcanised material. No influence of the concentration of the amine is found.



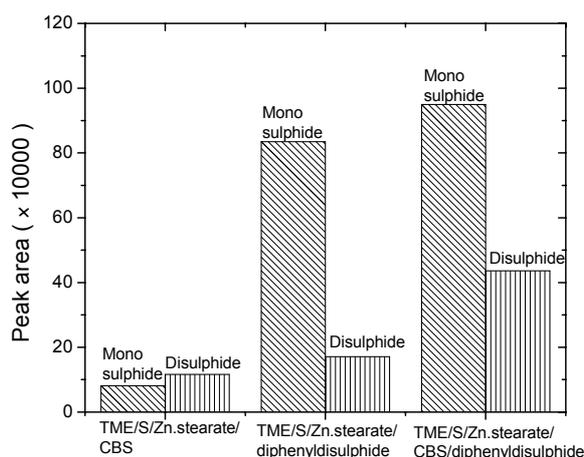
**Figure 5.18** Cumulative peak areas of all crosslinks devulcanised with diphenyldisulphide (-----), hexadecylamine (.....) and thermally (——) at various concentrations of devulcanisation agents as a function of reaction time at 200°C; (■): 0 phr ; (●): 1 phr; (▲): 2 phr.

In order to further investigate the interaction of diphenyldisulphide with the vulcanisation chemicals, experiments were conducted with the recipes A, B and C given in Table 5.7. The experiments were carried out at 200°C for a short incubation period of 5 minutes. In these recipes the accelerator CBS is replaced by diphenyldisulphide: recipe B; in recipe C, CBS and diphenyldisulphide are jointly added to the curing reaction mixture.

**Table 5.7** Curing recipes with different combination of CBS and diphenyldisulphide (phr)

Component	A	B	C
TME	100	100	100
S <sub>8</sub>	2.3	2.3	2.3
CBS	0.6	-	0.6
Zinc stearate	5	5	5
Diphenyldisulphide	-	0.6	2

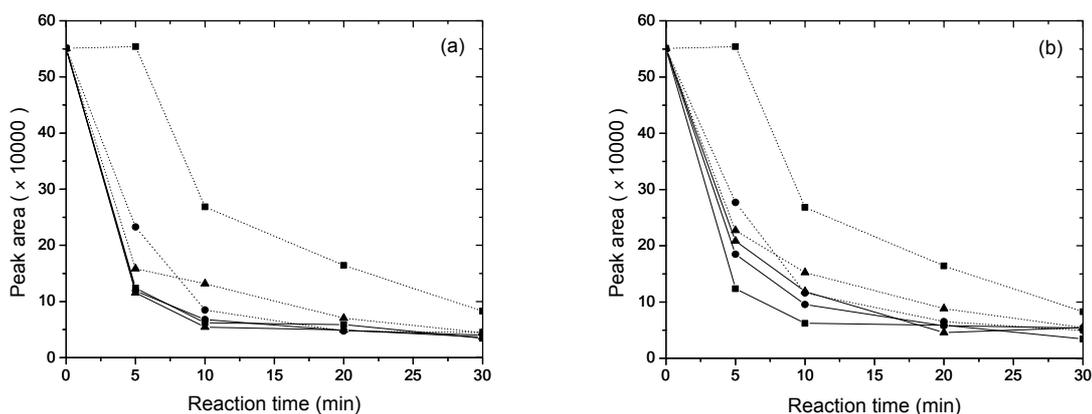
Peak areas of the mono- and disulphide crosslinked compounds are given in Figure 5.19. Large amounts of monosulphides and, to a lesser extent, disulphides are formed whenever diphenyldisulphide is used in the reaction, with or without CBS present.



**Figure 5.19** Peak areas of the mono- and disulphidic crosslinks as a function of different reaction mixtures at 200°C for 5 minutes

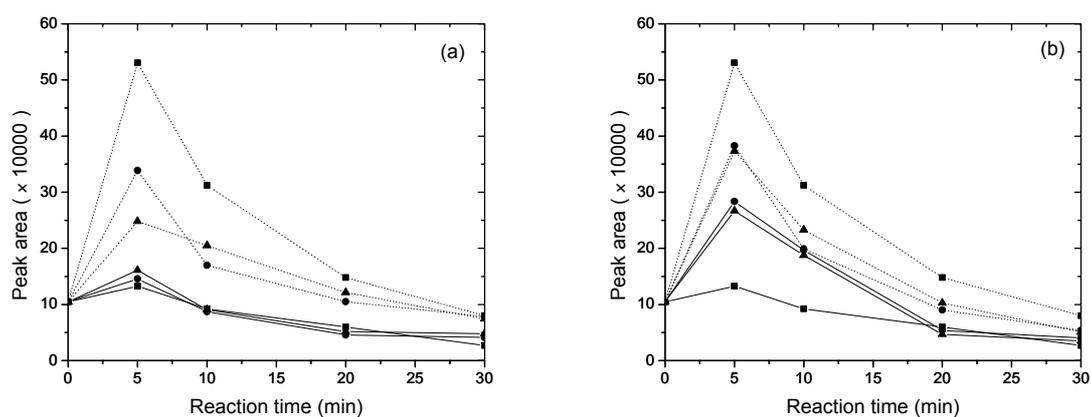
### 5.3.2.5 Devulcanisation with disulphide and amine at different temperatures

Figure 5.20 shows the peak areas of the polysulphidic crosslinks after devulcanisation with diphenyldisulphide and hexadecylamine, with the reaction parameters being temperature, concentration of the devulcanisation agent and reaction time. The amount of polysulphidic crosslinks decreases steeply up to a reaction time of 10 minutes and then levels off at a low concentration for both devulcanising agents. In general, the breakdown of polysulphides is faster the higher the temperature and the higher the concentration of the devulcanising agents. The influence of concentration is not clear except if there is no additive present.

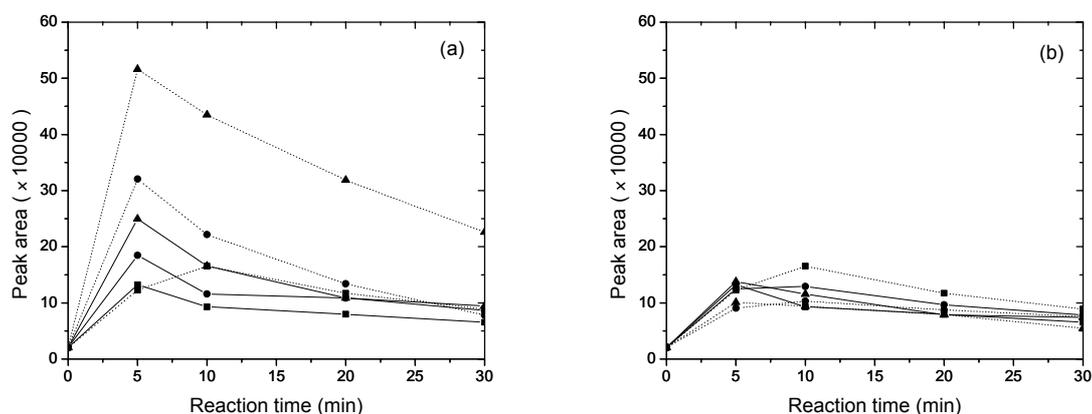


**Figure 5.20** Peak areas of polysulphidic crosslinks devulcanised with diphenyldisulphide (a) and hexadecylamine (b) at 200°C (.....) and 210°C (—) at various concentrations of the reclaiming agent against reaction time; (■): 0 phr ; (●): 1 phr ; (▲): 2 phr

The peak areas of the trisulphidic crosslinks at different temperatures and concentrations of devulcanisation agents are depicted in Figure 5.21. The concentration of the trisulphidic crosslinks shows a maximum at a devulcanisation time of 5 minutes. The devulcanisation with diphenyldisulphide at a temperature of 210°C results in less increase of the amount of trisulphidic crosslinks compared to the devulcanisation with amine. The influence of the concentration of the devulcanisation agent differs depending on the temperature. At 200°C the thermal devulcanisation results in the highest peak, whereas at a higher temperature it results in the lowest peak concentration of trisulphides.

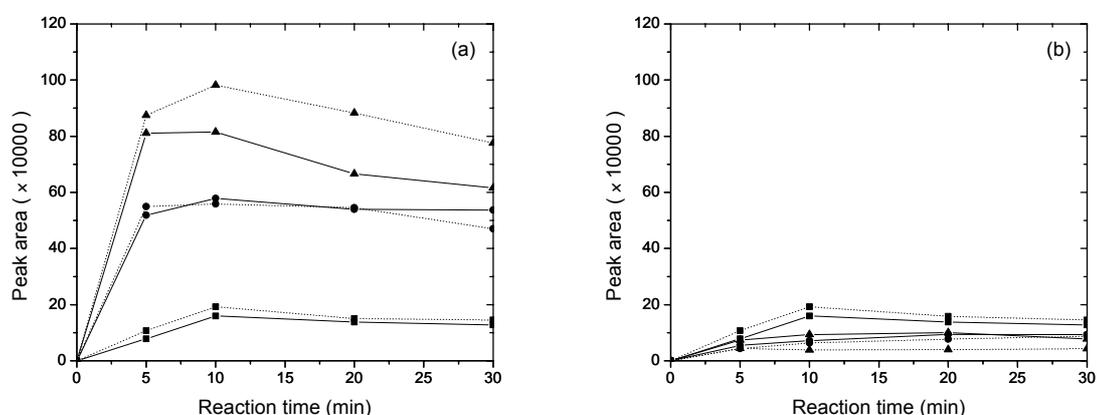


**Figure 5.21** Peak areas of trisulphidic crosslinks devulcanised with diphenyldisulphide (a) and hexadecylamine (b) at 200°C (.....) and 210°C (——) at various concentrations of reclaiming agents against reaction time; (■): 0 phr ; (●): 1 phr; (▲): 2 phr



**Figure 5.22** Peak area of disulphidic crosslinks devulcanised with diphenyldisulphide (a) and hexadecylamine (b) at 200°C (.....) and 210°C (——) at various concentrations of reclaiming agents against reaction time; (■): 0 phr ; (●): 1 phr; (▲): 2 phr

Figures 5.22 5.23 show the peak areas of the disulphidic and monosulphidic crosslinks after devulcanisation. The amount of disulphides shows a sharp maximum in the case of diphenyldisulphide as devulcanisation agent, whereas for hexadecylamine the concentration of the disulphidic crosslinks increases only slightly followed by a slow reduction of the concentration. The final concentration of the disulphides is comparable in both cases. The amount of monosulphidic crosslinks is significantly higher after devulcanisation with disulphide compared to amine and thermal devulcanisation. A higher concentration of diphenyldisulphide results in a higher level of monosulphidic crosslinks, whereas a higher concentration of hexadecylamine results in a slightly lower level of monosulphides.



**Figure 5.23** Peak areas of monosulphidic crosslinks devulcanised with diphenyldisulphide (a) and hexadecylamine (b) at 200°C (.....) and 210°C (——) at various concentrations of reclaiming agents against reaction time; (■): 0 phr ; (●): 1 phr; (▲): 2 phr

## 5.4 DISCUSSION

The well-known fact that the two reclaiming agents used in this study act according to different mechanisms is clearly proven by the results. For diphenyldisulphide as devulcanisation agent there is a clear increase in the amount of mono- and disulphides observed, compared to thermal devulcanisation, and the amount increases with increasing concentration of the diphenyldisulphide. For hexadecylamine, an increase in the concentration of the devulcanisation agent results in a decrease of the amount of mono- and disulphidic crosslinks relative to the case where no devulcanisation agent is present: The amine inhibits the formation of mono- and disulphides during the devulcanisation reaction.

The process of disulphidic crosslink formation already starts to a limited extent during the vulcanisation step: Figure 5.12. Bis-(2,3-dimethyl-2-butene-1-yl)-

polysulphide, TME-S<sub>x</sub>-TME, is known to undergo further reactions after formation, described as maturation of the vulcanisate.<sup>24</sup> The most important reactions in this context are:

- Disproportionation or S-S bond interchange reactions;
- Decomposition reactions; and
- Desulphuration reactions.

The disproportionation reactions may occur by a free radical mechanism<sup>24-27</sup> or by an ionic mechanism.<sup>28</sup> In polar media the reactions are unlikely to proceed rapidly. This reaction as such does not yield any new carbon-sulphur bonds and will therefore not change the total number of crosslinks. The decomposition of a polysulphide can lead to the liberation of elemental sulphur and to modification of the olefinic fragment. The de-sulphuration reactions are of a much greater influence on the product distribution than the other two reactions. In the presence of a zinc-accelerator complex the extracted sulphur can even be used for additional crosslink formation. The formation of these new crosslinks is then accompanied by a shortening of the average length of the sulphur bridges.<sup>29</sup> This may explain the initial decrease of the polysulphidic curve in Figure 5.12: the first polysulphides formed are quickly used for the formation of tri- and disulphides, after which the polysulphides start to become formed in large quantities. The initial decrease of polysulphides is also due to the breakdown of polysulphidic crosslink precursors, which are formed during the initial stage of the reaction. The vulcanisation step does not reach the point of monosulphidic crosslinks in the time-span allocated to the vulcanisation step.

The most conspicuous result is, that during the devulcanisation reaction with diphenyldisulphide large amounts of mono- and to a lesser extent disulphides are formed: Figures 5.13, 5.14 and 5.15. Crosslinked products with higher sulphur ranks decompose to a large extent into di- and monosulphides. The monosulphides do not disintegrate further under these circumstances due to the high bond energy of the carbon-sulphur bond.<sup>30,31</sup>

In the other case, with hexadecylamine present, the amount of di- and monosulphides is reduced relative to the thermal treatment where no devulcanisation agent is used: Figures 5.14 and 5.15. Hexadecylamine stabilizes the reaction mixture against these short sulphides formation.

The fundamentally different behavior between the two devulcanisation agents can be explained by side reactions, which diphenyldisulphide provokes by virtue of its sulphur-content. Besides the breakdown of diphenyldisulphide into sulphide radicals (thiyl radicals), it may liberate sulphur: it acts as a sulphur-donor. The sulphur can react with still unreacted TME to form mono- and disulphidic crosslinked products. Another mechanism is, that diphenyldisulfide exchanges its sulphur moiety via thiyl-radicals with polysulphidic crosslinks to preferably short crosslinks. The experiments in Table 5.7 and Figure 5.19 confirm the outcome of these reactions, but without

allowing a conclusion which one is the prevailing one. Further research is necessary to clear the mechanism.

Once monosulphides are formed, they are not broken anymore under the conditions of devulcanisation. The high bonding energy of monosulphidic crosslinks compared to the bonding energies of poly- or disulphidic crosslinks prevents this from happening. In that perspective, hexadecylamine and diphenyldisulphide perform equally well as devulcanisation agents for the higher sulphide ranks: 3 and more. But hexadecylamine is greatly preferred, because it prevents the formation of large amounts of di- and monosulphides, which eventually survive the devulcanisation and lowers the efficiency of the process.

The devulcanisation mechanism at a temperature of 210°C differs from the mechanism at 200°C when diphenyldisulphide is used as devulcanisation agent: At the higher temperature the decomposed polysulphides are directly converted to di- and monosulphides without the intermediate step of the formation of trisulphidic bridges. Figure 5.21 shows a very low level of trisulphides at 210°C compared to the reaction at 200°C. The amount of di- and monosulphides increases faster and reaches a higher level compared to the devulcanisation with amine.

With hexadecylamine as devulcanisation agent, the devulcanisation mechanism follows the same pattern at both temperatures: The polysulphides are firstly converted to trisulphides, so their concentration shows a maximum followed by a decrease. The di- and monosulphides are formed at a lower rate and they reach their highest level at a later stage. The disulphides are again broken to a small extent, whereas the monosulphides are stable.

One reason for the difference in the kinetics between diphenyldisulphide and hexadecylamine depending on the temperature is the breakdown mechanism. Diphenyldisulphide, reacting mainly by a radical mechanism, has a higher reactivity at higher temperatures, whereas the hexadecylamine reacts according to a nucleophilic mechanism, which is less influenced by temperature.

In Figure 5.17 and 5.20 the amount of polysulphides for the thermally treated samples remain constant for the initial 5 minutes. A stepwise breakdown of polysulphide, mainly hexasulphidic crosslinks, to shorter penta- and tetrasulphide can occur in this period. As the hexa-, penta- and tetrasulphidic crosslinks are summed-up as polysulphides, a stepwise breakdown of hexa- to penta- or tetra was not separately analysed.

Even though in the model compound study, diphenyldisulphide is found to form a large amount of mono- and disulphide crosslinks, in the real rubber reclamation diphenyldisulphide proves to be more efficient than hexadecylamine. The main reasons for this difference between the results of the model compound study and the real rubber system are the following: In the model compound study TME was selected as low-molecular weight compound to mimic natural rubber. However TME is a general model for all sulphur vulcanisable rubber. Squalene is more appropriate for NR, but the analysis with squalene is more tedious (Figure 5.6), so the reactions with TME was chosen to understand the basic chemistry during devulcanisation. In the real rubber system more complex reactions are going on, such as main-chain scission, crosslink scission, main-chain modification and crosslink modifications. However, in the model compounds studies the main attention was given to the

reactions and modifications occurring to various ranks of sulphur bridges. The effect of amines and disulphides on the main-chain scission and the effect of shear could not be analysed by the model compound study, but in a thermo-mechanical reclamation process these factors also play an important role.

In a real rubber system a lot of competitive reactions are happening and the reclamation is the cumulative effect of all these reactions. But in the model compound study the attention is given to only one of the many reactions that are happening in real rubber. To explain all the reactions happening in the real rubber a more profound mechanistic study remains needed.

## **5.5 CONCLUSIONS**

Model compound studies in combination with HPLC measurements are an effective tool to study the reactions during the devulcanisation of sulphur vulcanised compounds. All crosslinked products with sulphur ranks from 1 to 6 can be identified in the HPLC chromatogram. Both devulcanisation agents, diphenyldisulphide and hexadecylamine, are effective agents in breaking polysulphidic and trisulphidic crosslinks at 200°C and 210°C. The rate of breakdown of the polysulphidic bonds increases with increasing concentration of the devulcanisation agents and temperature. Large amounts of mono- and disulphidic crosslinks are formed when diphenyldisulphide is used as devulcanisation agent and the amount of mono- and disulphides increases with increasing concentration of diphenyldisulphide. With increasing concentrations of hexadecylamine as devulcanisation agent the amount of mono- and disulphidic crosslinks formed is significantly reduced, relative to the case where no devulcanisation agent is used. Monosulphides formed during the devulcanisation reaction cannot be decomposed any further under the conditions of devulcanisation, neither by diphenyldisulphide nor by hexadecylamine, due to the high bonding energy of the monosulphidic crosslinks.

## 5.6 REFERENCES

1. P. J. Nieuwenhuizen, J. G. Haasnoot, J. Reedijk, *Kautsch. Gummi Kunstst.*, **53**, (2000), 144.
2. E. C. Gregg, S. E. Katrenick, *Rubber Chem. Technol.*, **43**, (1970), 549.
3. J. Hahn, M. Runk, M. Schollmeyer, U. Theimer, E. Walter, *Kautsch. Gummi Kunstst.*, **51**, (1998), 206.
4. G. F. Bloomfield, *J. Chem. Soc.*, **301**, (1947), 1546.
5. W. J. van Ooij, V. Rangarajan, *Rubber Chem. Technol.*, **61**, (1988), 595.
6. Y. M. Tsai, F. J. Boerio, W. J. van Ooij, D. K. Kim, *J. Adhesion* (1996).
7. R. N. Datta, M. S. Ivany, *Rubber World*, **212** (5), (1995), **24**.
8. N. Agulló, S. Borrós, *Kautsch. Gummi Kunstst.*, **53/3**, (2000), 131.
9. F. K. Lautenschlaeger, P. Zeeman, *Rubber Chem. Technol.*, **52**, (1979), 1030.
10. F. K. Lautenschlaeger, *Rubber Chem. Technol.*, **52**, (1979), 1043.
11. J. H. M. v. d. Berg, *Rubber Chem. Technol.*, **57**, (1984), 265.
12. R. Vukov, *Rubber Chem. Technol.*, **57**, (1984), 284.
13. J. A. Beckman, G. Crane, E. L. Kay, J. R. Laman, *Rubber Chem. Technol.*, **47**, (1974), 597.
14. W. C. Warner, *Rubber Chem. Technol.*, **67**, (1994), 559.
15. M. A. L. Verbruggen, L. van der Does, J. W. M. Noordermeer, M. van Duin, H. J. Manuel, *Rubber Chem. Technol.*, **72**, (1999), 731.
16. P. C. Sadek, *Troubleshooting HPLC systems*, Wiley-Interscience, New York, 1999.
17. E. Garreta, N. Agullo, S. Borros, *Kautsch. Gummi Kunstst.*, **55**, (2002), 82.
18. P. Versloot, *Rubber Chem. Technol.*, **65**, (1992), 343.
19. S. Rodriguez, *Kautsch. Gummi Kunstst.*, **52**, (1999), 438.
20. A. Y. Coran, *Science and Technology of Rubber*, F. R. Eirich, Ed., Academic Press, New York, 1978.
21. P. Versloot, *Rubber Chem. Technol.*, **70**, (1997), 106.
22. C. J. Hann, A. B. Sullivan, B. C. Host, G. H. Kuhls Jr., *Rubber Chem. Technol.*, **67**, (1994), 76.
23. P. J. Nieuwenhuizen, S. Timal, J. M. van Veen, J. G. Haasnoot, J. Reedijk, *Rubber Chem. Technol.*, **71**, (1998) 750.
24. M. Porter, *Organic Chemistry of Sulphur*, S. Oae, Ed., Plenum Press, New York, 1977.
25. I. Kende, T. L. Pickering, A. V. Tobolsky, *J. Am. Chem. Soc.*, **87**, (1965), 5582.
26. T. L. Pickering, K. J. Saunders, A. V. Tobolsky, *J. Am. Chem. Soc.*, **89**, (1967), 2364.
27. T. L. Pickering, K. J. Saunders, A. V. Tobolsky, *The Chemistry of Sulphides*, A. V. Tobolsky, Ed., Interscience Publishers, New York, 1968.
28. B. Milligan, *Rubber Chem. Technol.*, **39**, (1966), 1115.
29. M. Porter, *Stud. Org. Chem.*, **28**, (1987), 267.
30. C. M. Kok, V. H. Yee, *Eur. Polym. J.*, **22**, (1986), 341.
31. T. H. Kuan, *Rubber World*, **192** (5), (1985), 20.



# Chapter 6

---

## Effect of diphenyldisulphides with different substituents on the reclamation of NR based latex products<sup>#</sup>

---

Two types of Waste Latex Rubber (WLR) with different amounts of polysulphidic bridges are used in these experiments, which are performed with variation of the concentration of the reclaiming agents, the reclamation temperature and time. Diphenyldisulphide, 2-aminophenyldisulphide and 2,2'-dibenzamidodiphenyldisulphide are used as reclaiming agents, and the effect of diphenyldisulphides with different substituents on the reclamation efficiency of WLR is investigated. A kinetic study of the reclamation reaction with the three reclaiming agents is done. The reaction rates and activation energies are calculated and compared with literature values. The comparative study of the three different reclaiming agents shows that 2,2'-dibenzamidodiphenyldisulphide is able to break the crosslinks at temperature levels approximately 20°C below the temperature levels normally used. Another advantage of this reclaiming agent is the reduced smell during the reclamation process and of the final reclaims, one of the most important shortcomings of other disulphides used for this purpose.

### 6.1 INTRODUCTION

For both environmental and economic reasons, there is a growing interest in recycling of scrap rubber and development of improved recycling technologies. The focus of recent research is to apply processes free of hazardous by-products and that might be carried out directly in the product manufacturer's factory. The most important recycling process currently is to utilise scrap rubber as a very finely ground

---

<sup>#</sup>The work described in this chapter has been submitted for publication in J. Appl. Polym. Sci.

powder, produced either by ambient temperature mechanical grinding or by cryogenic shattering. In general, the powder rubber is combined with virgin elastomer compounds to reduce the costs with the additional advantage of an improvement of the processing behaviour. However, some loss in physical properties and performance is observed.

This factor has motivated the search for cost effective in-situ regeneration or devulcanisation of the scrap rubber to provide recycled material with superior properties. It is well known that direct material recycling and reshaping is difficult because of the irreversible three-dimensional crosslinking of rubber. Countless attempts have been proposed for material-sensitive recycling of rubber.<sup>1-5</sup> Most processes are based on mechanical shear, heat and energy input together with a combination of chemicals such as oils, accelerators, amines or disulphides to reduce the concentration of sulphur crosslinks in the vulcanised rubber.<sup>6</sup> An alternative to mechanical energy input and direct heating is microwave treatment.<sup>7-9</sup> Destruction of the main-chains accompanies all the high-temperature methods and thus leads to the partial loss of physical and mechanical properties of the reclaim.

The three dimensional network of sulphur-cured elastomers has the following types of chemical bonds:

- C-C, carbon-carbon bonds;
- C-S-C, sulphur-carbon bonds, and;
- C-S-S-C, C-S<sub>x</sub>-C ( $x \geq 3$ ), sulphur-sulphur bonds.

The bond dissociation energies of different bonds are given in Table 6.1. The devulcanisation is conducted by means of destruction of the inter-chain crossbonds such as C-S-C, C-S-S-C as well as C-S<sub>x</sub>-C ( $x \geq 3$ ) and / or by main-chain bonds in the elastomer.<sup>10</sup>

**Table 6.1** Bond strength of different bonds in rubber network

Type of bond	Bond dissociation energy (kJ/mol)
C-C	349
C-S-C	302
C-S-S-C	273
C-S <sub>x</sub> -C ( $x \geq 3$ )	256

Molecular weight reduction due to mechanical energy input results from the cleavage of polymer chains. Without chemical deactivation in a reaction with oxygen or other radical scavengers, the free radicals from the chain scission will predominately recombine. However, some chain transfer chemistry and disproportionation reactions will hasten the molecular weight reduction. As a consequence, chemical peptisers have served the rubber industry in the function of a host for radically reactive chemicals. For many years, mercaptans (especially pentachlorothiophenol) were the chemicals of choice as peptisers for natural rubber.

However, toxicity issues have shifted the market to the predominant use of dibenzamidodiphenyldisulphide and other softening agents.<sup>11</sup>

In chapter 3 it was concluded that diphenyldisulphide is effective as reclaiming agent for NR based latex products. In this chapter the study will be extended with different types of aromatic disulphides. It is commonly accepted that diphenyldisulphide gives rise to free radicals by thermal decomposition of the S-S bond. The dissociation energy of the S-S bond in diphenyldisulphide is 225 kJ/mol. The radicals generated are able to dehydrogenate substances and the process can be divided into three steps.

- The homolytic decomposition of disulphides into radicals;
- Hydrogen abstraction by the benzenesulphide radical from the polymer chain, resulting in the formation of polymer radicals;
- Combination of another disulphide radical with the polymer radical to stabilise the polymer chain.

The rate determining step of the overall reaction is the first step. The time necessary for reclamation is therefore dependent on the decomposition rate of the disulphide. The efficiency of the overall reaction mainly depends on the type of radicals formed after decomposition of the disulphide and of the substance.

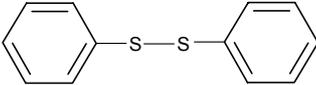
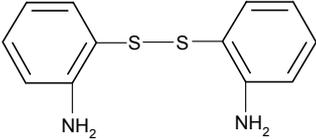
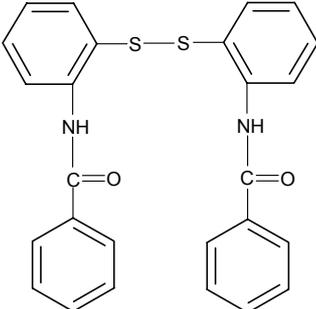
In this chapter the effect of different substituents on the o-position of diphenyldisulphide is investigated and their reactivity as reclaiming agent for NR based latex products is compared. This allows a view on the effect of the structure of aromatic disulphides on the efficiency of reclaiming. Three aromatic disulphides are selected: diphenyldisulphide (DPDS), 2-aminophenyldisulphide (APDS) and 2,2'-dibenz- amidodiphenyldisulphide (DBADPDS). DPDS is taken as the reference material. DBADPDS was selected, since this is used successfully as masticating agent for natural rubber, in analogy with DPDS. APDS was selected to study the effect of the  $-NH_2$  group. DBADPDS has an additional  $C_6H_5CO-$  substituent on the amino group. The sulphur content of DPDS is 29%; the sulphur content of APDS is 26% and the sulphur content of DBADPDS is 14% of its mass. This is an important characteristic because the amount of sulphur in the reclaiming agent influences the formation of mono- and disulphidic crosslinks during reclaiming. The higher the sulphur content in the reclaiming agent the higher is the probability of formation of mono- and disulphides.<sup>12</sup>

## 6.2 EXPERIMENTAL

*Materials* - The waste latex rubber used in this investigation was gloves (WLR1) and condoms (WLR2). For the characterisation of these materials see Chapter 3. The reclaiming additives investigated were diphenyldisulphide (Acros, 99%), 2-aminophenyldisulphide (Aldrich, 98%) and 2,2'-dibenzamidodiphenyldisulphide (Lancaster, 97%). The chemical name and structure

of the reclaiming agents are given in Table 6.2. Treated distillate aromatic extract, TDAE (BP Oil) was used as reclaiming oil.

**Table 6.2** Chemical name and structure of the different reclaiming agents

Chemical name	Chemical structure
Diphenyldisulphide, DPDS (218.34 g/mol)	
2-aminophenyldisulphide, APDS (248.37 g/mol)	
2,2'-dibenzamidodiphenyldisulphide, DBADPDS (456.57g/mol)	

*Reclamation experiments* - The reclaim was prepared according to the recipe shown in Table 6.3 by a batch process in an internal mixer (Brabender Plasticorder PL-2000) having a mixing chamber volume of 50 cc and a cam-type rotor. The batch size was 30 grams. A constant rotor speed of 50 rpm was applied. The reclaiming temperatures were 150°C, 160°C, 170°C and 180°C and reclaiming times were 5 minutes, 7.5 minutes and 10 minutes.

**Table 6.3** Reclaiming recipe

Material	Amount (phr)
WLR	100
Reclaiming agent	0, 0.5, 1, 1.5, 2
Reclaiming oil	5

*Testing Procedures* - The Mooney viscosity - ML (1+4)100°C - of the reclaim was determined using a Mooney viscometer (MV2000 VS) according to ISO R289. Measurements were performed directly after reclamation.

After reclamation, the reclaim was extracted in a Soxhlet apparatus, first with acetone for 48 hours to extract the polar substances, and then with tetrahydrofuran (THF) for 72 hours to extract debound polymers. The elastically active network chain density was measured by equilibrium swelling in toluene for 72 hours. The data were analysed according to the Flory-Rehner equation, modified for tetra-functional networks.<sup>13</sup>

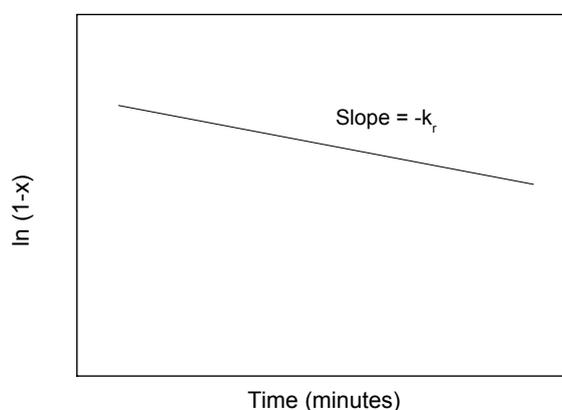
The crosslink distribution of the feedstock and the reclaim were studied using thiol/amine chemical probes.<sup>14,15</sup> The molecular weight of the polymers was determined with gel permeation chromatography (GPC).

The reaction rates and activation energy for the reclamation reaction were calculated using the Mooney viscosity data according to ISO 53529: The Mooney viscosity, MV, was measured as a function of reclamation time at different temperatures. The reaction constant for a first order reaction was calculated according to Equations 6.1 and 6.2.

The reaction variable  $x$  was calculated from the Mooney viscosity at time  $t$ ,  $MV(t)$ , the Mooney viscosity of the starting material  $MV_0$  and the Mooney viscosity for an optimally reclaimed sample  $MV_\infty$ . The reaction constant  $k_r$  is given by the slope of the line of the  $\ln(1-x)$  as a function of time, Figure 6.1.

$$k_r = \frac{\ln(1-x_1) - \ln(1-x_2)}{t_2 - t_1} \quad 6.1$$

$$x = \frac{MV_0 - MV(t)}{MV_0 - MV_\infty} \quad 6.2$$

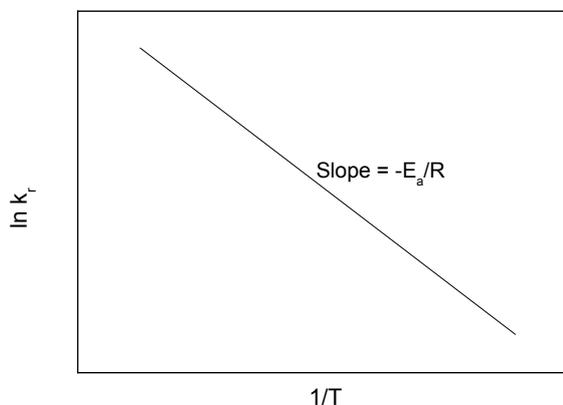


**Figure 6.1** Determination of the reaction constant.

The activation energy  $E_a$  was calculated from the reaction constants  $k_r$ , at different temperatures  $T$  using the Arrhenius equation, 6.3;

$$\ln k_r \propto -\frac{E_a}{RT} \quad 6.3$$

In a graph showing  $\ln k_r$  as a function of the reciprocal temperature, the slope of the line gives the value of the activation energy, as illustrated in Figure 6.2.



**Figure 6.2** The Arrhenius plot of  $\ln k_r$  against  $1/T$ .

## 6.3 RESULTS

The effect of DBADPDS, APDS and DPDS at four different temperatures, viz. 150°C, 160°C, 170°C and 180°C was studied. At 150°C and 160°C, a comparison can only be made between DBADPDS and APDS as DPDS was not reactive at this temperature. At 170°C a comparison is made for all three disulphides. At 180°C, DBADPDS was extremely reactive so that only APDS and DPDS are compared.

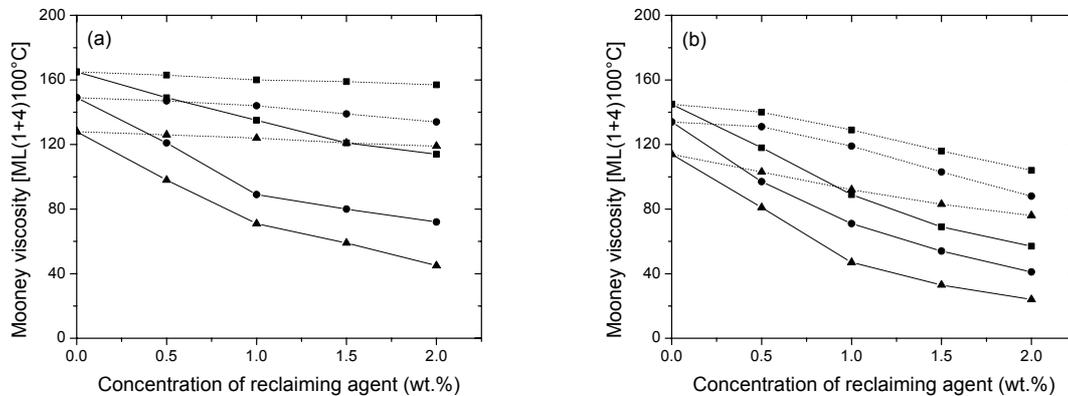
### 6.3.1 Reclamation of WLR1 with DBADPDS, APDS and DPDS

Figure 6.3 shows the Mooney viscosity of WLR1 at various times as a function of the concentration of DBADPDS and APDS at temperatures of 150°C and 160°C.

**DBADPDS:** The Mooney viscosity decreases for DBADPDS with increasing concentration of reclaiming agent and reclamation time at both temperatures. There is a strong decrease in Mooney viscosity up to a concentration of 1 wt.%; at higher concentrations the rate of viscosity decrease slows down. The decrease in viscosity shows the same trends for all temperature / time profiles. The viscosity level is in general lower than in the case of APDS as reclaiming agent.

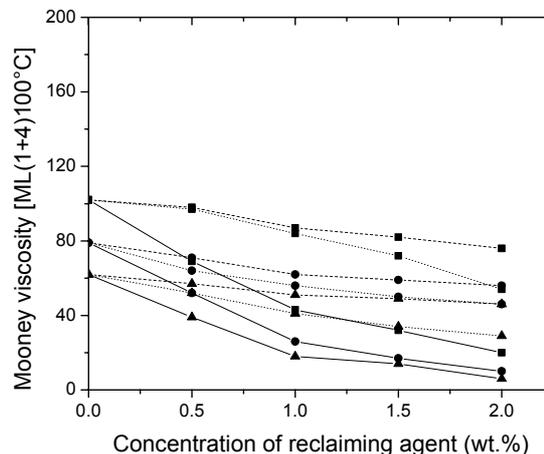
**APDS:** The increase in concentration of APDS has little effect on the Mooney viscosity of WLR1 after reclamation at 150°C and 160°C. With increasing reclamation time the Mooney viscosity of WLR1 decreases, probably due to mechanical breakdown of the vulcanisate rather than to the chemical influence of APDS. The

Mooney viscosity decreases less at 150°C compared to 160°C: At a higher temperature the decrease in viscosity due to the thermal effect is stronger.<sup>16</sup>



**Figure 6.3** Mooney viscosity as a function of the concentration of DBADPDS(—) and APDS(.....) at various times for WLR1 at 150°C (a) and 160°C (b); (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

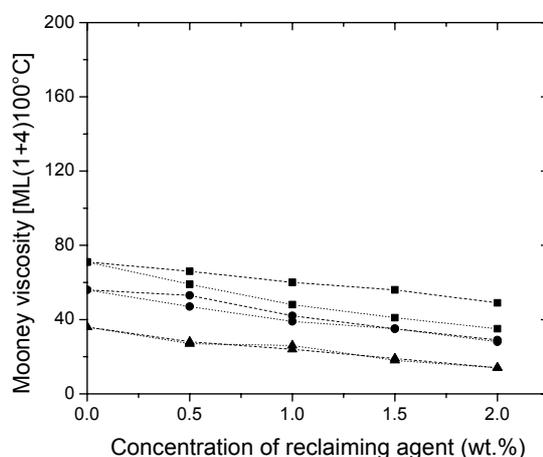
The Mooney viscosity of WLR1 at various times as a function of the concentration of DBADPDS, APDS and DPDS at 170°C is depicted in Figure 6.4. With DBADPDS as reclaiming agent the viscosity decreases much faster than with APDS and DPDS, but the decrease levels off for higher concentrations of DBADPDS. DPDS has the smallest effect on the viscosity of the vulcanisate.



**Figure 6.4** Mooney viscosity as a function of the concentration of DBADPDS(—), APDS (.....) and DPDS (-----) at various times for WLR1 170°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

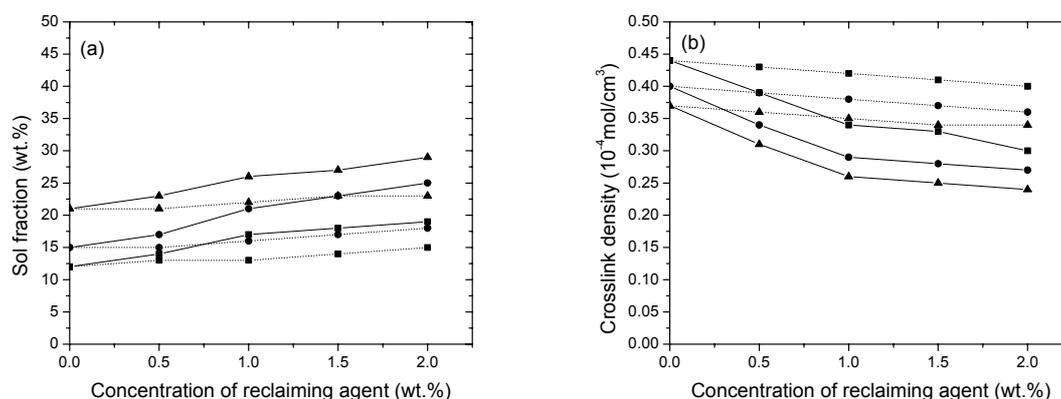
Figure 6.5 gives the Mooney viscosity of WLR1 at various times against the concentration of APDS and DPDS at 180°C. Both reclaiming agents cause a linear decrease of the viscosity of WLR1 with increasing concentration of the reclaiming

agent at this temperature. An increase in reclamation time also results in a decrease of the viscosity. Only small differences in the viscosity values are found for WLR1 treated with APDS compared to DPDS at 180°C.

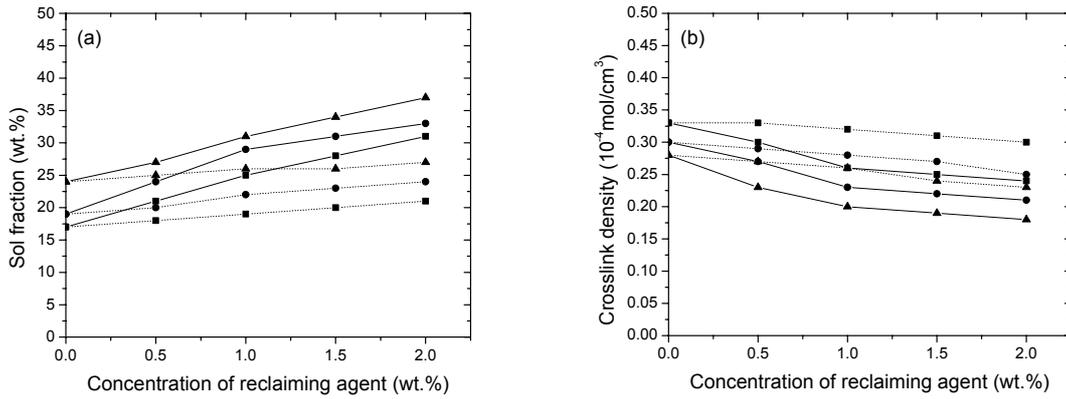


**Figure 6.5** Mooney viscosity as a function of the concentration of APDS (.....) and DPDS (-----) at various times for WLR1 at 180°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

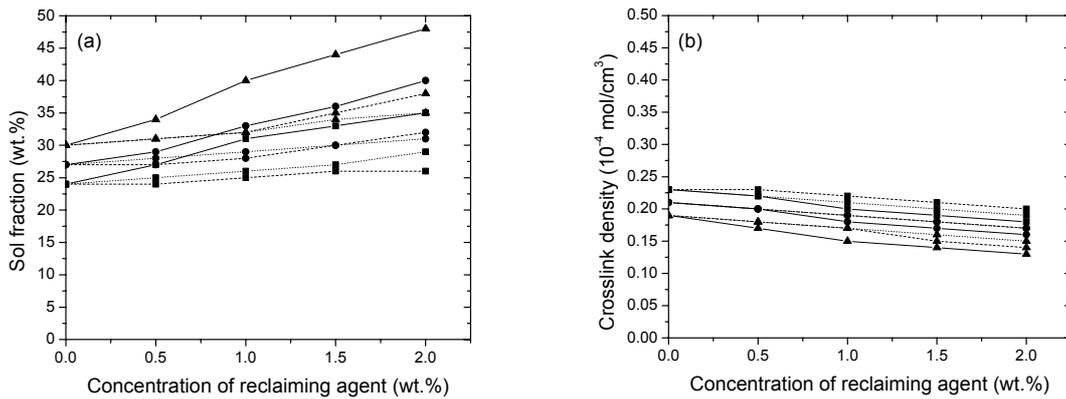
Figures 6.6 and 6.7 show the sol fraction and crosslink density for WLR1 at various times as a function of the concentration of DBADPDS and APDS at temperatures of 150°C and 160°C, respectively. The sol fraction increases and correspondingly the crosslink density decreases for DBADPDS. At 160°C a stronger increase in sol fraction and decrease in crosslink density is found due to the increase in reactivity of DBADPDS with increasing temperature. The increase in concentration of APDS has less influence on the sol fraction and crosslink density of the vulcanisate at these temperatures compared to DBADPDS as reclaiming agent.



**Figure 6.6** Sol fraction (a) and crosslink density (b) as a function of the concentration of DBADPDS (—) and APDS (.....) at various times for WLR1 at 150°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.



**Figure 6.7** Sol fraction (a) and crosslink density (b) as a function of the concentration of DBADPDS (—) and APDS (.....) at various times for WLR1 at 160°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

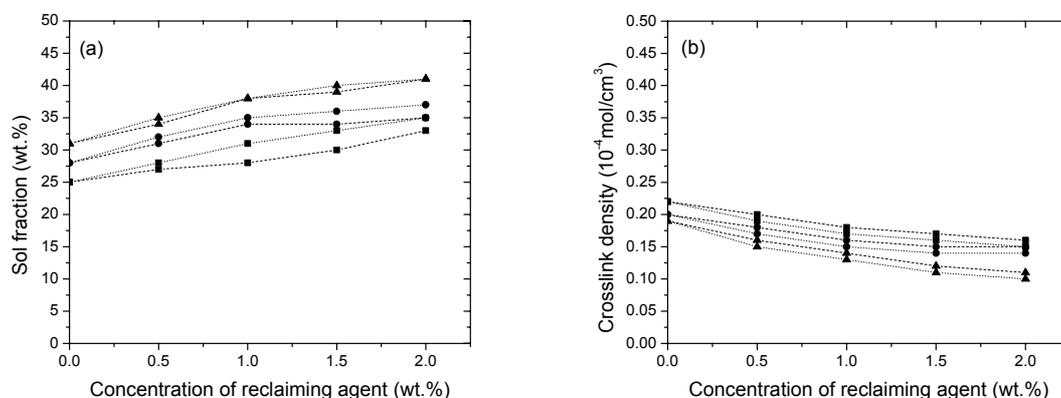


**Figure 6.8** Sol fraction (a) and crosslink density (b) as a function of the concentration of DBADPDS (—), APDS (.....) and DPDS (-----) at various times for WLR1 at 170°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

The sol fraction and crosslink density of WLR1 at various times as a function of concentration of the reclaiming agents at 170°C is given in Figure 6.8. Again, DBADPDS is more efficient than the other two reclaiming agents, and a significant increase in sol fraction and decrease in crosslink density is measured at this temperature.

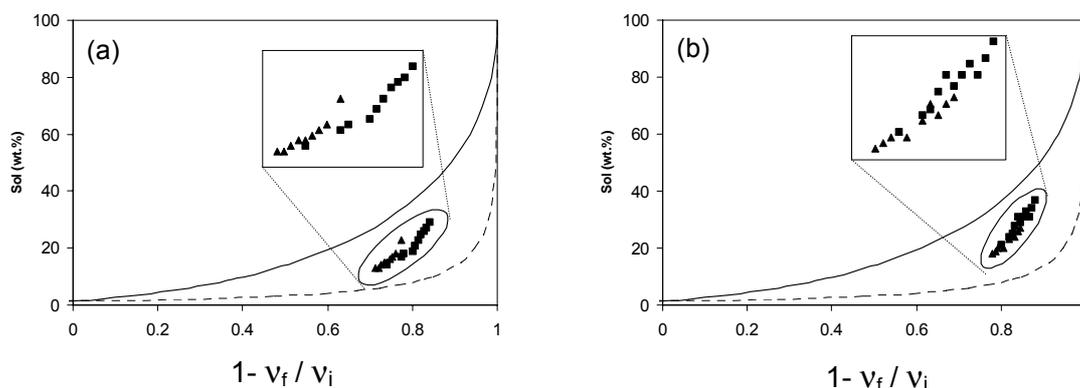
Figure 6.9 depicts the sol fraction and crosslink density of WLR1 as a function of the concentration of the reclaiming agents at 180°C. As expected, the sol fraction increases and crosslink density decreases with increase in concentration of both reclaiming agents, but at high degrees of reclamation the sol fraction and crosslink density level off. Only small differences are seen in the values of both

properties for the two reclaiming agents :their reactivity at this temperature is quite similar, as already seen in Figure 6.8 for lower temperature.



**Figure 6.9** Sol fraction (a) and crosslink density (b) as a function of the concentration of APDS (.....) and DPDS (-----) at various times for WLR1 at 180°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

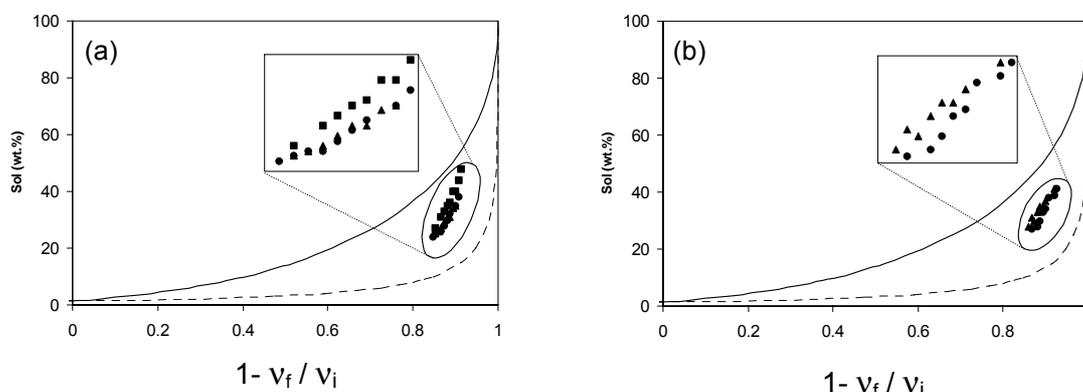
The sol fraction of WLR1 as a function of the relative decrease in crosslink density for DBADPDS and APDS at 150°C and 160°C is depicted in Figure 6.10. The curves in both figures show the two extreme cases: One corresponds to the situation where only main-chains are broken (solid curve), and the other corresponds to breaking of crosslinks (dotted curve). For crosslink scission almost no sol is formed until most of the crosslinks are broken, only then the long chains can be removed. In the case of main-chain scission, sol is produced in an early stage because the random scission of the polymer network results in loose chain fragments, which can easily be removed.<sup>17,18</sup> In Figure 6.10 the experimental data for breakdown of WLR1 with DBADPDS and APDS lie in-between the main-chain scission curve and



**Figure 6.10** Fraction of sol of WLR1 against relative decrease in crosslink density at 150°C (a) and 160°C (b); (—): main-chain scission; (.....): crosslink scission; (■): DBADPDS; (▲): APDS

crosslink scission curve. The sol fraction values of the experiments are significantly lower than the values predicted for main-chain scission. This indicates that the reclamation occurred mainly through crosslink scission.

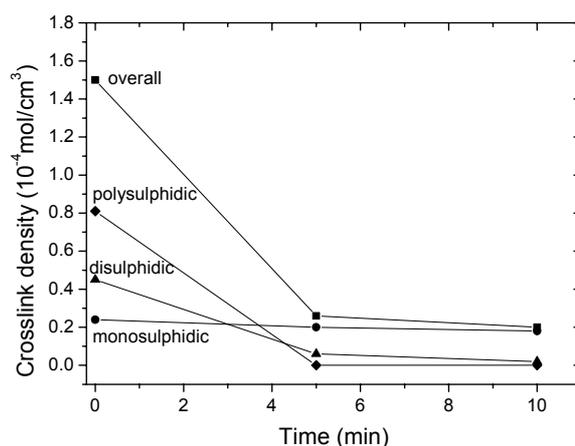
The sol fraction of WLR1 as a function of the relative decrease in crosslink density at 170°C and 180°C are depicted in Figure 6.11. Both reclaiming agents break the vulcanisate mainly by crosslink scission as described above. In Figure 6.11(a), the experimental data points for WLR1 reclaimed with DBADPDS are very close to the main-chain rupture curve (solid curve) showing a lot of main-chain scission occurring at this stage. On analysing the experimental condition for this particular case it becomes clear that these data belong to the extreme conditions of 170°C, 2 wt.% of reclaiming agent and 10 minutes of reclamation time: These conditions are apparently critical for the feed-stock and resulted in a significant breakage of main-chains.



**Figure 6.11** Fraction of sol of WLR1 against relative decrease in crosslink density at 170°C (a) and 180°C (b); (—): main-chain scission; (-----): crosslink scission; (■): DBADPDS; (▲): APDS; (●): DPDS

GPC measurements of the sol fraction of DBADPDS reclaimed samples showed that the number-average molecular weight ( $M_n$ ) of WLR1 decreased from  $2.6 \times 10^5$  g/mol to  $4.7 \times 10^4$  g/mol at 160°C and 1 wt.% of reclaiming agent. Increasing the concentration of DBADPDS from 1 wt.% to 2 wt.% did not result in a further decrease of the molecular weight of the polymer in the sol fraction.

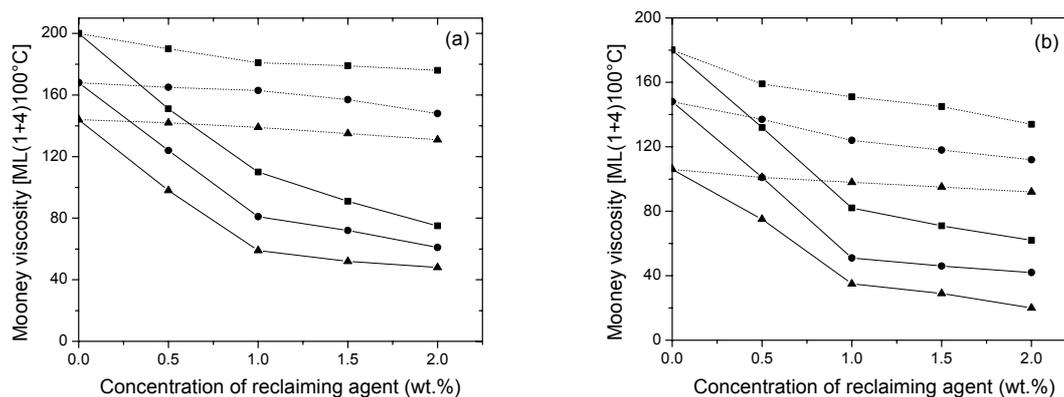
The crosslink densities of WLR1 reclaimed with DBADPDS as a function of the reclaiming time at 160°C are presented in Figure 6.12. The concentration of crosslinks as well as the fraction of poly- and disulphidic crosslinks decrease, whereas the concentration of monosulphidic crosslinks remains constant with reclamation time. The polysulphidic and disulphidic crosslinks diminish, but the overall crosslink density decreases to the level of the monosulphidic crosslinks: after reclamation the remaining crosslinks present in WLR1 are mainly monosulphidic. This is caused by the higher bonding energy of monosulphidic crosslinks compared to the bonding energies of poly- or disulphidic crosslinks.<sup>19,20</sup>



**Figure 6.12** Crosslink distribution of WLR1 reclaimed with DBADPDS as a function of reclaiming times at 160°C; (■): overall crosslink density; (◆): polysulphidic; (▲): disulphidic; (●): monosulphidic.

### 6.3.2 Reclamation of WLR2 with DBADPDS, APDS and DPDS

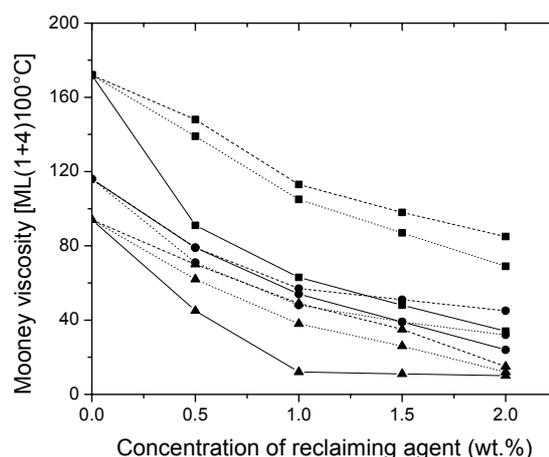
The Mooney viscosity of WLR2 as a function of the concentration of DBADPDS and APDS at temperatures of 150°C and 160°C at various times is presented in Figure 6.13. A significant decrease in viscosity for DBADPDS as reclaiming agent is observed at both temperatures and the decrease in viscosity is much faster for concentrations up to 1 wt.%; at higher concentrations it levels off. The decrease in Mooney viscosity observed with APDS at these temperatures is less pronounced.



**Figure 6.13** Mooney viscosity as a function of the concentration of DBADPDS (—) and APDS (.....) at various times for WLR2 at 150°C (a) and 160°C (b); (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

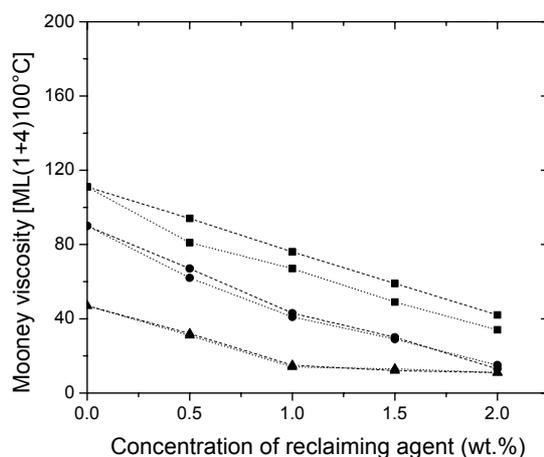
Figure 6.14 shows the Mooney viscosity of WLR2 at various times as a function of DBADPDS, APDS and DPDS at 170°C. The viscosity decreases with

increasing concentration for all reclaiming agents and for longer reclamation times. DBADPDS is the most effective reclaiming agent by far at medium concentrations. At short reclaiming periods the viscosity is drastically reduced by DBADPDS. DPDS and APDS also reduce the viscosity but they are less effective compared to DBADPDS. At longer reclamation times and at high concentrations of reclaiming agent, the viscosity values are comparable for all reclaiming agents.



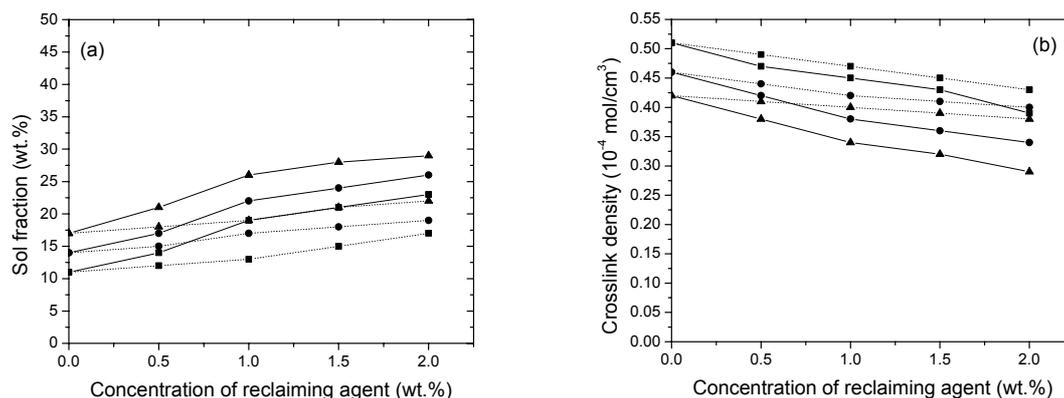
**Figure 6.14** Mooney viscosity as a function of the concentration of DBADPDS (—) and APDS (.....) and DPDS (-----) at various times for WLR2 at 170°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

The Mooney viscosity of WLR2 as a function of the concentration of APDS and DPDS at 180°C and at various times is given in Figure 6.15. The reactivity is similar for both reclaiming agents. For short reclamation times APDS is slightly more reactive than DPDS.

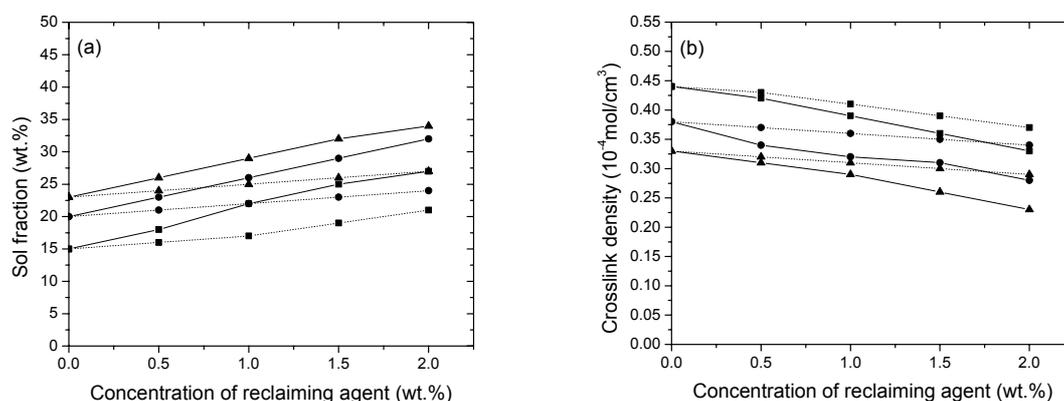


**Figure 6.15** Mooney viscosity as a function of the concentration of APDS (.....) and DPDS (-----) at various times for WLR2 at 180°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

The sol fraction and crosslink density of WLR2 as a function of the concentration of DBADPDS and APDS at 150°C and 160°C at various times is shown in Figures 6.16 and 6.17. The sol fraction and crosslink density of the DBADPDS reclaimed samples show a stronger change than those of APDS reclaimed samples at both temperatures. DBADPDS is breaking down the three dimensional structure of the vulcanised material more easily, through both crosslink scission and main-chain rupture.



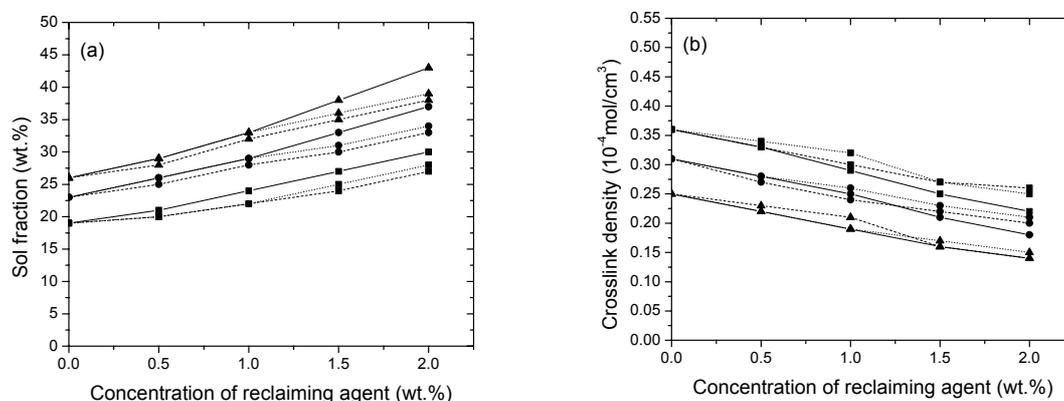
**Figure 6.16** Sol fraction (a) and crosslink density (b) as a function of the concentration of DBADPDS (—) and APDS (.....) at various times for WLR2 at 150°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.



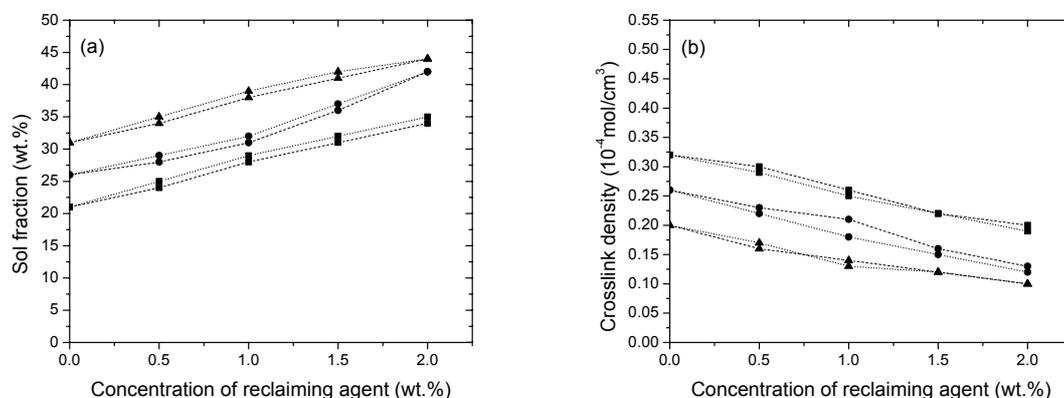
**Figure 6.17** Sol fraction (a) crosslink density (b) as a function of concentration of DBADPDS (—) and APDS (.....) at various times for WLR2 at 160°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

Figure 6.18 presents the sol fraction and crosslink density of WLR2 against the concentration of the three reclaiming agents at 170°C and Figure 6.19 shows the data at 180°C. The sol fraction increases and the crosslink density decreases linearly with increasing concentration of all reclaiming agents. The three reclaiming agents

are effective in reclaiming WLR2, and DBADPDS is slightly more effective than the other two reclaiming agents at 170°C. APDS and DPDS work better for WLR2 at 170°C and 180°C compared to their performance with WLR1 in breaking down the vulcanisate; compare Figures 6.8 and 6.9.



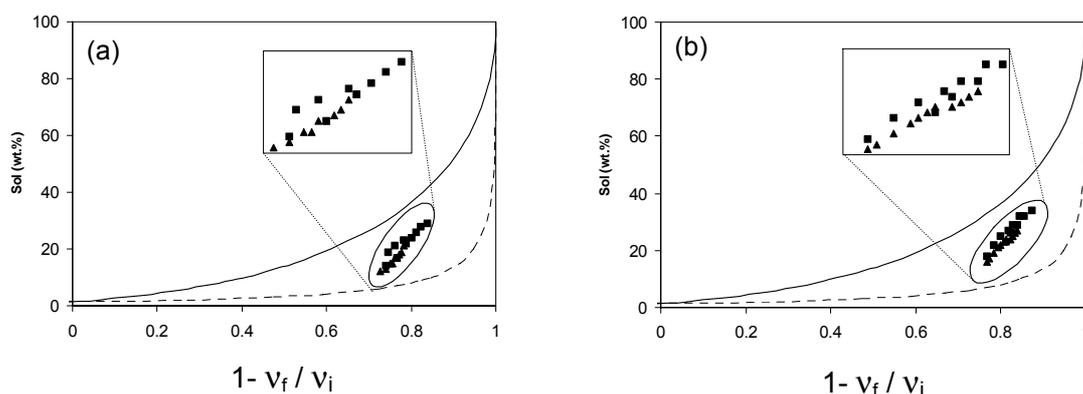
**Figure 6.18** Sol fraction (a) and crosslink density (b) as a function of the concentration of DBADPDS (—), APDS (.....) and DPDS (-----) at various times for WLR2 at 170°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.



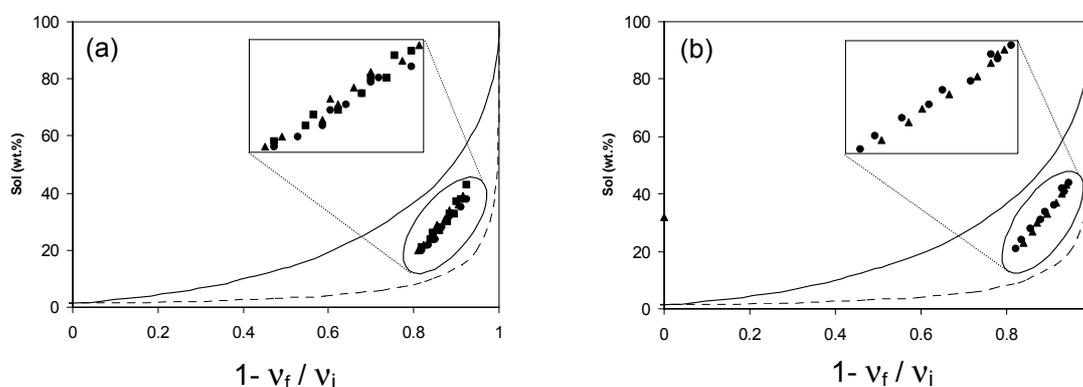
**Figure 6.19** Sol fraction (a) and crosslink density (b) as a function of the concentration of APDS (.....) and DPDS (-----) at various times for WLR2 at 180°C; (■): 5 min.; (●): 7.5 min.; (▲): 10 min.

Figure 6.20 shows the sol fraction of WLR2 as a function of the relative decrease in crosslink density for DBADPDS and APDS at 150°C and 160°C. As explained for Figure 6.10 the reclamation is mainly occurring through crosslink scission rather than by main chain scission, because the experimental data points are far from the main-chain scission curve (solid curve). The same result is observed in Figure 6.21, which depicts the sol fraction of WLR2 against the relative decrease in crosslink density for DBADPDS, APDS and DPDS at 170°C and 180°C, respectively.

In Figure 6.20 the experimental points with DBADPDS lie slightly closer to main-chain scission curve compared to APDS however, in other cases, Figure 6.21 no significant difference is observed between the behaviour of DBADPDS, APDS and DPDS. This observation is in contradiction to WLR1 (Figures 6.10 and 6.11), where DBADPDS is closer to main-chain scission in almost all cases compared to APDS.

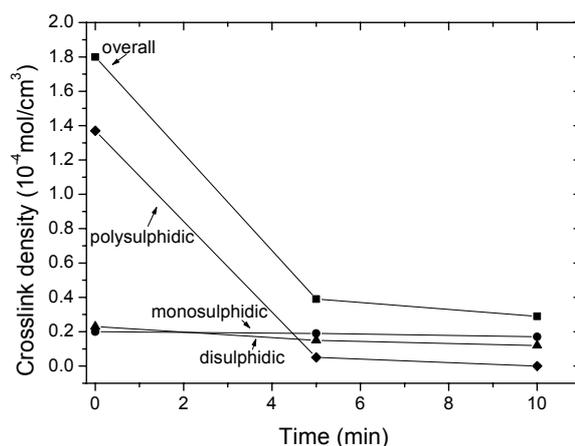


**Figure 6.20** Fraction of sol of WLR2 against relative decrease in crosslink density at 150°C (a) and 160°C (b); (—): main-chain scission; (-----): crosslink scission; (■): DBADPDS; (▲): APDS



**Figure 6.21** Fraction of sol of WLR2 against relative decrease in crosslink density at 170°C (a) and 180°C (b); (—): main-chain scission; (-----): crosslink scission; (■): DBADPDS; (▲): APDS; (●): DPDS

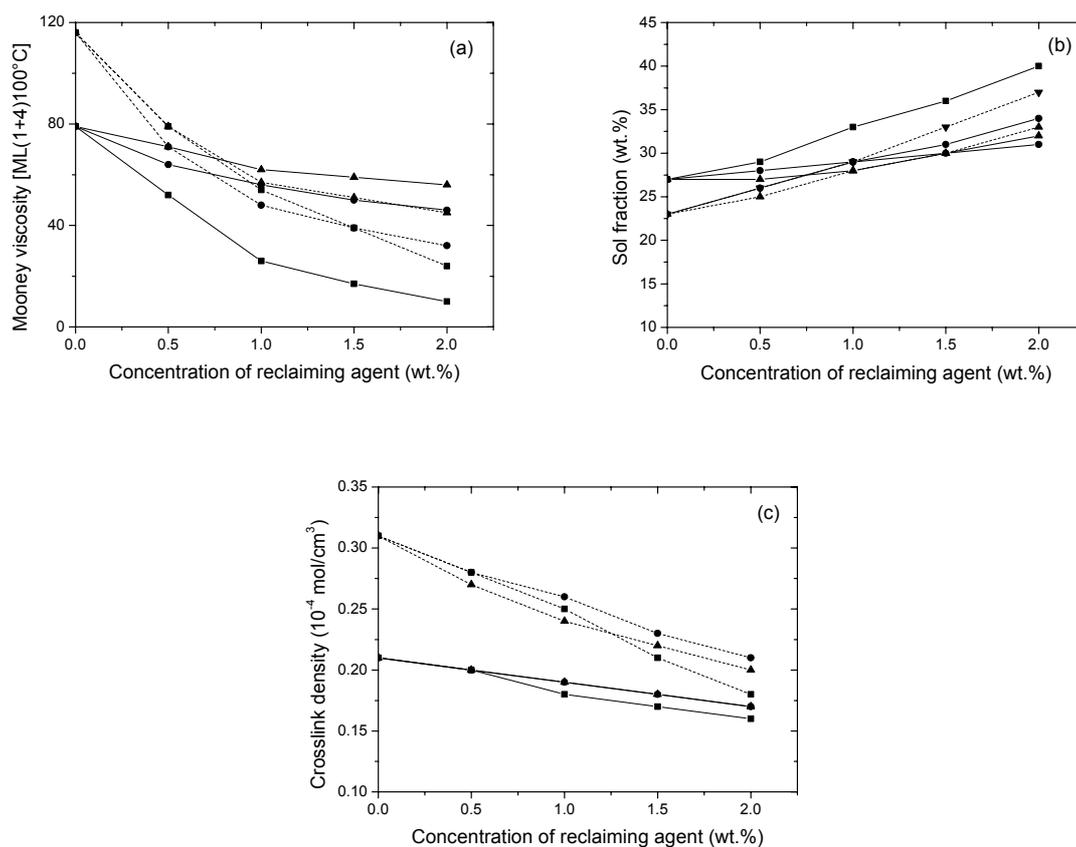
The crosslink densities of WLR2 reclaimed with DBADPDS as a function of reclaiming time at 160°C is depicted in Figure 6.22. The overall crosslink density and the concentration of poly- and disulphidic crosslinks decrease, whereas the monosulphidic crosslink density remains constant with reclamation time. This shows that DBADPDS is not able to break the monosulphides present in the rubber network, as seen for WLR1 in Figure 6.12.



**Figure 6.22** Crosslink distribution of WLR1 reclaimed with DBADPDS as a function of reclaiming times at 160°C; (■): overall crosslink density; (◆): polysulphidic; (▲): disulphidic; (●): monosulphidic.

### 6.3.3 Comparison of reclamation of WLR1 and WLR2 with DBADPDS, APDS and DPDS

The change in Mooney viscosity, sol fraction and crosslink density of WLR1 and WLR2 with increasing concentration of DBADPDS, APDS and DPDS at 170°C and 7.5 minutes is presented in Figure 6.23. The Mooney viscosity and crosslink density of WLR1 and WLR2 decrease and consequently the sol fraction increases with increase in the concentration of the reclaiming agents. The initial viscosity and crosslink density of WLR1, when the concentration of the reclaiming agent is 0 wt.%, is lower than that of WLR2; but as the concentration of the reclaiming agents increases, WLR2 shows a more substantial reduction in viscosity and crosslink density compared to WLR1. The sol fraction values of WLR1 and WLR2 follow a similar trend. DBADPDS shows a different behaviour: The initial values of WLR1 follow the same pattern as the other reclaiming agents but at no stage of the reaction the viscosity or crosslink density is lower for WLR2 compared to WLR1. A possible explanation is a higher reactivity of DBADPDS at 170°C, breaking more main-chains under these extreme conditions. This is also visible in Figure 6.11(a), where the position of the points for DBADPDS indeed points to more main-chain scission relative to crosslink scission of WLR1 relative to the other two agents.



**Figure 6.23** Mooney viscosity (a), Sol fraction (b) and crosslink density (c) of WLR1 (—) and WLR2 (-----) as a function of concentration of the reclaiming agent at 170°C; (■): DBADPDS; (●): APDS; (▲): DPDS

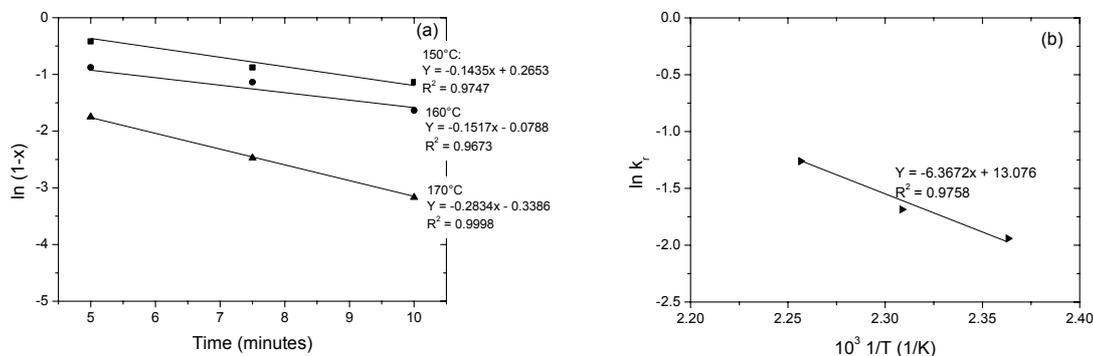
### 6.3.4 Kinetics of the reclamation reaction with DBADPDS, APDS and DPDS

Figures 6.24 through 6.29 and Tables 6.4 through 6.6 show the results of the kinetic study of different series of reclamation reactions carried out with different reclaiming agents and feed stocks. The temperature range of the reactions was from 150°C to 190°C and the reclamation times were 5, 7.5 and 10 minutes. The lowest achievable values of the Mooney viscosity for each reclaiming agent, necessary for the calculation of the reaction rate constants was measured for WLR1 and WLR2 after reclamation at 170°C and 10 minutes with DBADPDS, 180°C and 10 minutes with APDS, and 190°C and 7.5 minutes with DPDS. The initial Mooney viscosity was taken as the viscosity attainable with the mild reclamation conditions on the feedstocks and was measured as 200 MU.

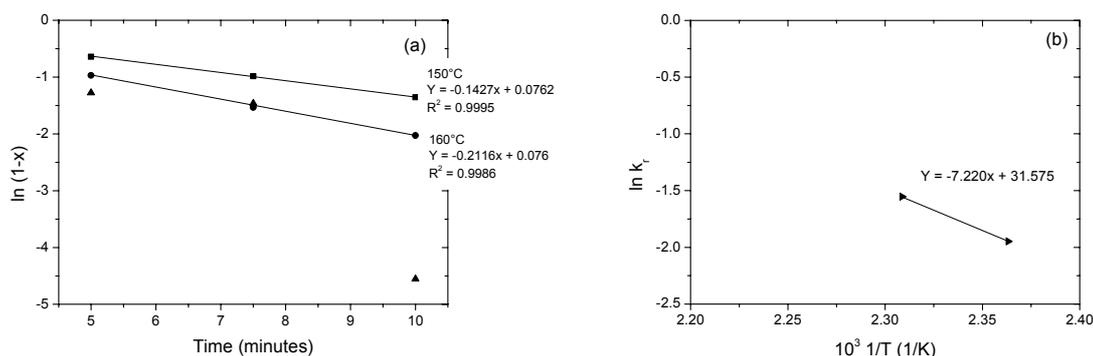
Figures 6.24 and 6.25 show graphical representations of the calculation of rate constant and activation energy for the reclamation of WLR1 and WLR2 at temperatures of 150°C, 160°C and 170°C with DBADPDS.

In Figure 6.25, the data points for the reclamation of WLR2 with DBADPDS at 170°C do not show a linear correlation with reclaiming time. This shows that this material reacts according to a different reaction mechanism at this temperature and therefore a different order for the reaction has to be assumed. 170°C is the highest

feasible experimental temperature with DBADPDS and this probably causes several side reactions to occur with WLR2.



**Figure 6.24** Determination of the rate constant (a) and activation energy of reclamation (b) for WLR1 with DBADPDS at different temperatures; (■): 150°C; (●):160°C; (▲):170°C



**Figure 6.25** Determination of the rate constant (a) and activation energy of reclamation (b) for WLR2 with DBADPDS at different temperatures; (■): 150°C ; (●):160°C; (▲):170°C

Table 6.4 shows the of rate constants at the different temperatures and activation energies for WLR1 and WLR2. At 150°C, WLR1 and WLR2 have comparable rate constants, but the rate constant of WLR2 is higher than the reaction rate of WLR1 at 160°C. At 170°C there is a significant increase in the rate constant for WLR1. The activation energies of both feedstocks were calculated for the temperature range given in Table 6.4: the activation energies are in the same order of magnitude, as can be seen in Table 6.4 and from the slope of the graph in Figures 6.24 (b) and 6.25 (b).

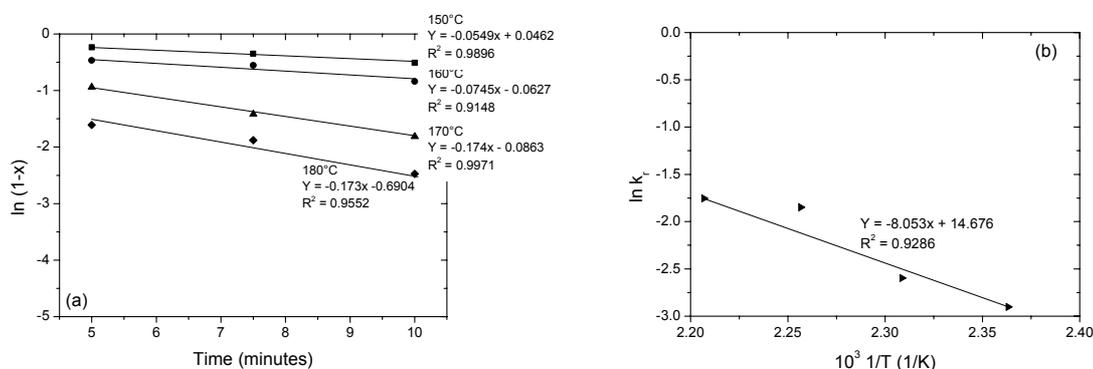
**Table 6.4** Kinetic data for the reclamation of WLR1 and WLR2 with DBADPDS

Rate of reclamation with DBADPDS		
Temperature (°C)	WLR1 $k_r$ (minute <sup>-1</sup> )	WLR2 $k_r$ (minute <sup>-1</sup> )
150	0.1435	0.1427
160	0.1517	0.2116
170	0.2834	-

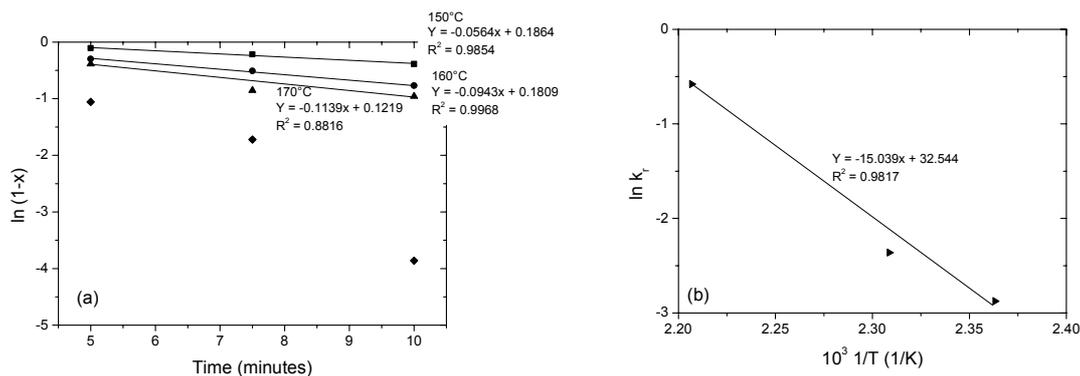
  

Activation energy, $E_a$		
	(kJ/mol)	(kJ/mol)
	53	60

Figures 6.26 and 6.27 show a graphical representation of the calculation of the rate constants and activation energies for the reclamation of WLR1 and WLR2 at temperatures of 150°C, 160°C, 170°C and 180°C with APDS. Table 6.5 gives the rate constants of the comparative investigation of the reclamation of WLR1 and WLR2 with APDS at temperatures of 150°C, 160°C, 170°C and 180°C. At 150°C and 160°C the rate constants do not vary significantly depending on the feedstock, the reaction rates for the reclamation with APDS are significantly lower compared to DBADPDS as reclaiming agent. Between 160°C and 170°C there is a large increase in the rate constant for WLR1. Surprisingly, at 180°C the rate constant of WLR1 differs not from the value at 170°C. The activation energies of both reclaiming materials show that WLR2 has a higher temperature dependence than WLR1, represented by a higher activation energy and the activation energy for the reclamation of WLR2 is higher for APDS compared to DBADPDS as reclaiming agent.



**Figure 6.26** Determination of the rate constant (a) and activation energy of reclamation (b) for WLR1 with APDS at different temperatures (■): 150°C; (●): 160°C; (▲): 170°C; (◆): 180°C.



**Figure 6.27** Determination of the rate constant (a) and activation energy of reclamation (b) for WLR2 with APDS at different temperatures (■): 150°C; (●): 160°C; (▲): 170°C; (◆): 180°C.

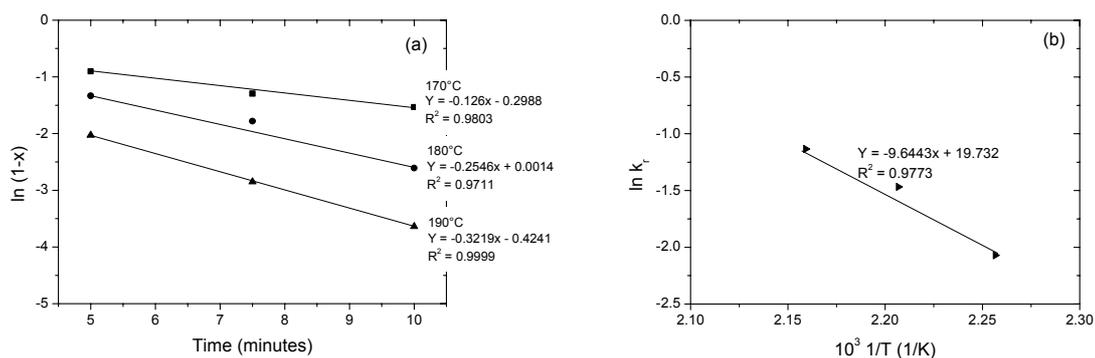
**Table 6.5** Kinetic data for the reclamation of WLR1 and WLR2 with APDS

Rate of reclamation with APDS		
Temperature (°C)	WLR1 $k_r$ (minute <sup>-1</sup> )	WLR2 $k_r$ (minute <sup>-1</sup> )
150	0.0549	0.0564
160	0.0745	0.0943
170	0.173	0.1139
180	0.174	-

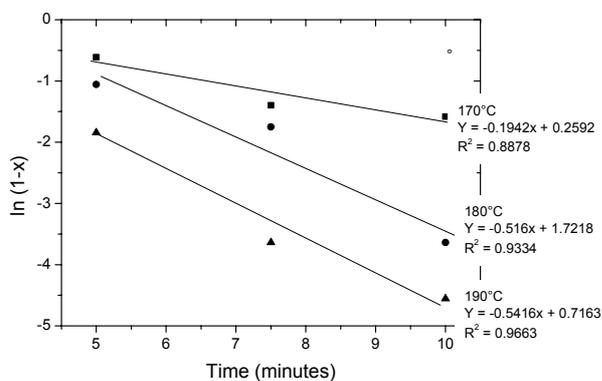
  

Activation energy, $E_a$	
(kJ/mol)	(kJ/mol)
67	125

Figures 6.28 and 6.29 is the graphical representation of the calculation of the rate constants and activation energies for the reclamation of WLR1 and WLR2 at temperatures of 170°C, 180°C and 190°C with DPDS. Table 6.6 gives the reaction rate constants and activation energy for DPDS reclaimed samples. An increase of the reaction rate for WLR1 is seen with increase in temperature. A large increase in the rate constant for WLR2 is found when the temperature is increased from 170°C to 180°C, with almost no further change of the rate constant when the temperature is increased to 190°C. The activation energy of the reclamation of WLR1 with DPDS is higher than the activation energy of the reaction with DBADPDS: the reaction with DPDS is more temperature-dependent. The activation energy of WLR2 could not be calculated because the correlation between  $\ln k_r$  and  $1/T$  is not linear, probably due to a change in the reaction mechanism within the temperature interval.



**Figure 6.28** Determination of the rate constant (a) and activation energy of reclamation (b) for WLR1 with DPDS at different temperatures (■): 170°C; (●): 180°C; (▲): 190°C



**Figure 6.29** Determination of the rate constant (a) and activation energy of reclamation (b) for WLR2 with DPDS at different temperatures; (■): 170°C; (●): 180°C; (▲): 190°C

**Table 6.6** Kinetic data for the reclamation of WLR1 and WLR2 with DPDS

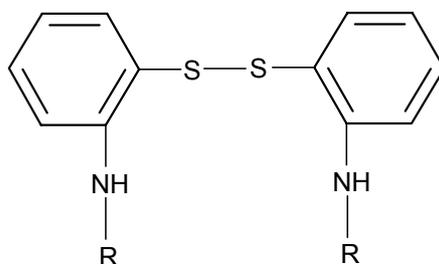
Rate of reclamation with DPDS		
Temperature (°C)	WLR1 $k_r$ (minute <sup>-1</sup> )	WLR2 $k_r$ (minute <sup>-1</sup> )
170	0.126	0.1942
180	0.2546	0.516
190	0.3219	0.5416
Activation energy, $E_a$		
(kJ/mol)		
	73	-

## 6.4 DISCUSSION

The results presented above comprehensibly point to the fact that DBADPDS reclaims a NR vulcanisate more efficiently than the other two reclaiming agents used in this investigation. The reactivity of reclaiming agents used shows the following trend:



All three reclaiming agents can in principle be represented as derivatives of one basic structure, as represented by Figure 6.30, where in the case of DPDS the -NH-R substituents are absent, in the case of APDS the -R group equals hydrogen, and in the case of DBADPDS, the -R group represents C<sub>6</sub>H<sub>5</sub>CO-.



**Figure 6.30** General representation of the reclaiming agents.

In an elementary study dating back to 1952, Imoto and Kiriya<sup>21</sup> have investigated the reactivity towards NR of several variants on the general structure in Figure 6.30, wherein they made the following variations, with the substituents in the ortho-, resp. in the para-position relative to the disulphide-bridge:

- R = -H                                    if in o-position = APDS
- R = -OC-CH<sub>3</sub>
- R = -OC-C<sub>6</sub>H<sub>5</sub>                        if in o-position = DBADPDS

Applying dilute amounts of these agents in a 0.85 wt.% solution of Smoked Sheet NR (SSNR) in toluene, they measured the decrease in viscosity of the solution in an Ostwald viscosimeter against time, at 40, 50 and 60°C. It was observed, that the agents with the substituents in the ortho-position were generally more active than those with the substituents in the para-position. Next, the order of reactivity found was:



This agrees well with the observations presented in this thesis.

Imoto and Kiriya further managed to calculate as sort of activation energy for the reaction of the reclaiming agents with the NR-solution using the equation:

$$\frac{1}{z} = ke^{-E/RT} \quad 6.4$$

where  $z$  was taken as the time necessary to achieve a (somewhat arbitrarily chosen) viscosity, which is proportional to the reaction velocity;  $k$  is an arbitrary constant,  $E$  is the activation energy for the viscosity decrease (in Calories),  $R$  the Gas constant and  $T$  the absolute temperature.

The activation energies for the decrease of the viscosity are given in Table 6.7, with the different groups to replace -R in Figure 6.30. The authors did not give the activation energies on a molar basis but only in absolute energy values. So, apart from the ranking of the values, a full comparison with the data obtained in the present work cannot be made. Clearly, the ranking of the activation energies confirm that substituents attached to the phenyl group lead to a decreasing efficiency as R-changes from ortho-C<sub>6</sub>H<sub>5</sub>CO- (=DBADPDS), over ortho-CH<sub>3</sub>CO- to ortho-H- (=APDS).<sup>22,23</sup>

**Table 6.7** Activation energies

-R group	Activation energy: Imoto et al. <sup>21</sup>	Activation energy : present work	
	SSNR (Calories)	WLR1 (kJ/mol)	WLR2 (kJ/mol)
DPDS	-	73	-
ortho: H- (APDS)	7000	67	125
para: H-	9400	-	-
ortho: CH <sub>3</sub> CO-	6300	-	-
ortho: C <sub>6</sub> H <sub>5</sub> CO- (DBADPDS)	5800	53	60

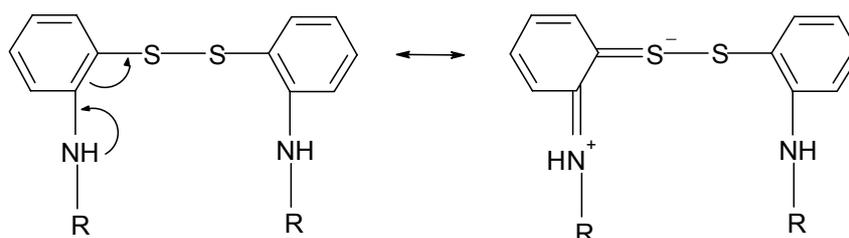
The activation energies for WLR1 and WLR2 reclaimed with DPDS, APDS and DBADPDS, as taken from Tables 6.4 – 6.6 are also inserted in Table 6.7. A full comparison with the results of Imoto et al. cannot be made, because they investigated partly different compounds in a completely different environment, for a significantly different temperature range of 40 – 60°C, vs. the present work: 150 – 180°C, and made use of another sort of Arrhenius-equation 6.4, relative to the Equation 6.3 in the present work. Still there is a reasonably good agreement between the two series of experiments, at least confirming the order of the reactivities found in the present work.

The viscosity decrease of the NR-solutions was claimed by Imoto et al. to be the result of main chain scission. Obviously, because in the solution there was no sulphur-based crosslink network present. The high reactivity of the agent with the C<sub>6</sub>H<sub>5</sub>CO-group in the o-position was then quoted to be the result of easy breakage of the S-S bond, resulting in a higher level of sulphidic radicals than with the other

agents. The dissociation energy of the S-S bonds in different diphenyldisulphide derivatives varies, as their environment influences their bonding strength. Walsh<sup>24</sup> pointed out the following four factors influencing the bond strength:

- Electronegative effects of the bonded groups;
- Resonance effect;
- Repulsion of filled atomic orbitals or steric effects;
- Overlap of atomic orbitals, dependent on co-planarity of the phenyl-rings, allowing for full resonance.

Particularly in the o-substituted amine-derivatives, the resonance effect is the most important factor for aromatic compounds. This effect is shown in Figure 6.31. The number of possible resonance structures becomes smaller as R changes from C<sub>6</sub>H<sub>5</sub>CO- over CH<sub>3</sub>CO- to H- to none. When a C<sub>6</sub>H<sub>5</sub>CO- group substitutes R- in Figure 6.31, it results in a large corresponding resonance hybrid, allowing for very many resonance structures. Correspondingly, the resonance energy gain of the radical has the largest value with C<sub>6</sub>H<sub>5</sub>CO- as substituent. When the substituent is -NH<sub>2</sub>, the number of possible resonating structures is less and the resonance energy is also lower.



**Figure 6.31** Resonance effect of amine o-substituents in general.

Steric hindrance and rotational strain may also have a serious effect on the strength of the disulphide bonds. If the substituent in an o-position is a bulky group, it is very unlikely that the molecule can take a co-planar configuration due to steric hindrance. The twisted molecule is stressed and therefore it breaks easier under formation of sulphidic radicals. C<sub>6</sub>H<sub>5</sub>CONH- is a bulkier group compared to -NH<sub>2</sub>, resulting in a stressed molecule, which releases the stress by making the molecule puckered and finally by breaking the -S-S- bond.

The results described in the Section 6.3.4, can now be interpreted as follows:

(i) The rate constant of reclaiming increases with increasing temperature, for WLR1 as well as for WLR2. This is due to the fact that with increasing temperature the reactivity of the reclaiming agents increases and the diffusion speed of the disulphide into the polymer matrix also rises, enhancing the chance of combination with a rubber radical. At higher temperatures, the polysulphides present in the rubber network are more easily broken.

(ii) The rate constants of the reaction of WLR2 are in general higher than the constants for WLR1. On the other hand, the activation energy values for WLR2 are higher than for WLR1. A high activation energy signifies that the rate constant depends strongly on temperature. The network characterisation of WLR1 and WLR2 was done and explained in detail in Chapter 3, Section 3.3. The crosslink distribution of WLR2 and WLR1 done with thiol-amine method showed that WLR2 has 76%, and that WLR1 has 54% of polysulphidic crosslinks of the total crosslinks present in the two systems. Polysulphidic crosslinks are more temperature sensitive because they have the lowest bond energy of all the crosslinks present in the rubber network, Table 6.1, and are easily broken. This explains the higher activation energy for WLR2.

A last point to mention is, that DBADPDS gives a significantly reduced smell during the reclamation process and of the final reclaim, relative to the other two agents, one of the most important shortcomings of the disulphides.

## 6.5 CONCLUSIONS

A comparative study of DBADPDS with APDS and DPDS shows that DBADPDS is most reactive for the reclamation of NR based latex products, compared to the other aromatic disulphides studied. This is due to resonance and steric effects originating from the bulky benzamido-substituents on the ortho-position of the phenyl-rings, relative to the disulphidic bridge. Consequently, the disulphidic bridge of DBADPDS is more easily broken, so that it is able to break the crosslinks at temperature-levels approximately 20°C below the temperature levels normally used in the reclamation process and necessary for the other two agents.

A main-chain to crosslink rupture study has shown, that all agents reclaim the vulcanisates mainly by crosslink scission. Analysis of the crosslink distribution using thiol-amine reagents has shown that all the poly- and disulphides are broken by DBADPDS. Monosulphides are not affected by neither of the aromatic disulphides chosen for the present study. The resonance energy of the radicals decrease in the order:  $C_6H_5CONH-$  >  $CH_3CONH-$  >  $NH_2-$ , corresponding to the ranking in reclamation efficiency of DBADPDS vs. APDS

## 6.6 REFERENCES

1. W. C. Warner, *Rubber Chem. Technol.* **67**, (1994), 559.
2. S. Yamashita, *Int. Polym. Sci. Technol.* **8**(12), (1981), T/77 – T/93.
3. B. Adhikari, D. De, S. Maiti, *Prog. Polym. Sci.*, **25**, (2000), 909.
4. A. I. Isayev, J. Chen, A. Tukachinsky, *Rubber Chem. Technol.*, **68**, (1995), 267.
5. V. Y. Levin, S. H. Kim, A. I. Isayev, *Rubber Chem. Technol.*, **69**, (1996), 104.
6. M. J. Myhre, D. A. MacKillop, *Rubber Chem. Technol.*, **75**, (2002), 429.
7. D. S. Novotny, R. L. Marsh, F. C. Masters, D. N. Tally (to Goodyear Tire and Co.), AU 2072376 (June 22, 1978)
8. S. R. Fix, *Elastomerics*, **112**(6), (1980), 38.
9. Y. Onouchi, S. Inagaki, H. Okamoto, J. Furukawa, *Int. Pol. Sci. Techn.* , **55**, (1982), T/58.
10. L. Bateman, *The Chemistry and Physics of Rubber-like Substances*, Maclaren, London, 1963.
11. F. I. Hoover, Paper presented at the meeting of the Rubber Division, American Chemical Society, Pittsburg, Oct. 8-11, 2002.
12. V. V. Rajan, W. K. Dierkes, R. Joseph, J.W.M. Noordermeer, Paper presented at the meeting of the Rubber Division, American Chemical Society, Ohio, Oct. 5-8, 2004 and *Rubber Chem. Technol.*, (2005), accepted for publication.
13. P. J. Flory, J. Rehner, Jr., *J. Chem. Phys.*, **18**, (1950), 108.
14. D. S. Campbell, *J. Appl. Polym. Sci.*, **13**, (1969), 1201.
15. D. S. Campbell, B. Saville, *Proceedings of the International Rubber Conference*, Brighton (1967).
16. W. E. Stafford, R. A. Wright, *Rubber Chem. Technol.*, **31**, (1958), 599.
17. V. V. Yashin, A. I. Isayev, *Rubber Chem. Technol.*, **72**, (1999), 741.
18. V. V. Yashin, C. K. Hong, A. I. Isayev, *Rubber Chem. Technol.*, **77**, (2004), 50.
19. T. H. Kuan, *Rubber World* **192**(5), (1985), 20.
20. C. M. Kok , V. H. Yee, *Eur. Polym. J.*, **22**, (1986), 341.
21. M. Imoto, S. Kiriyaama, *Rubber Chem. Technol.*, **25**, (1952), 91.
22. Swain, Stockmayer, Clarke, *J. Am. Chem. Soc.*, **72**, (1950), 5426.
23. Blomquist, Buselli, *J. Am. Chem. Soc.* **73**, (1951), 3883.
24. Walsh, *J. Chem. Soc.* (1948), 398.



# Chapter 7

---

## Application of NR based latex reclaim: The link between structure and properties<sup>#</sup>

---

The reclamation of natural rubber based waste latex rubber (WLR) is carried out by a thermo-mechanical process using diphenyldisulphide as reclaiming agent. Two types of WLR differing mainly in the amount of polysulphidic linkages are reclaimed and blended with a virgin rubber compound with and without adjustment of the curing system, the former in order to compensate for the extra input of sulphur and accelerators due to the addition of reclaim. The cure behaviour, final crosslink density and distribution, mechanical properties and dynamic viscoelastic properties of the blends with reclaimed WLR are compared to the property profile of the virgin material. The morphology of the blends as well as sulphur distribution between the matrix and the reclaim particle is analysed. With increasing concentrations of WLR reclaim, tensile strength, tear strength and elongation at break decrease, whereas modulus at 100% elongation, compression set and hardness show an increase. The storage modulus of the vulcanised rubber blends decreases with increasing WLR reclaim content in the blend. Swelling measurements show that the crosslink density is reduced for the adjusted cure system but increased for a fixed cure system. These influences of reclaimed WLR on the property profile of a virgin compound will be discussed fundamentally in terms of morphology and crosslink distribution.

### 7.1 INTRODUCTION

In almost all commercial applications, the reclaimed rubber is used in a blend with virgin rubber. Incorporation and dispersion of reclaim rubber into the virgin

---

<sup>#</sup>The work described in this chapter was presented at the 168<sup>th</sup> Technical meeting – Rubber Division, ACS, November 1 – 3, 2005 in Pittsburg, PA (paper no. 18) and has been submitted for publication in Rubber Chem. Technol.

rubber play important roles in product quality and production economy. Good and consistent dispersion is essential for optimum vulcanisate properties.

Myhre and MacKillop<sup>1</sup> describe a reclaiming process based on mixing of plasticisers, reactive chemicals that can break sulphur bonds and a catalyst to speed up the process with powdered rubber. Using this process, a material with moderate properties was produced. This process bears a close resemblance to another technique known as the Trelleborg Cold Reclaim (TCR) process.<sup>2</sup> In this process, cryogenically ground rubber is mixed in a stirred device with plasticisers and a reactive agent. A powder is produced, which compacts easily upon milling and has a Mooney viscosity of 50-80 MU. Phenylhydrazine metal oxide is mentioned as a possible reactive agent and diphenylguanidine as a less efficient but milder agent. Physical properties of compounds with either TCR powder or untreated crumb do not differ greatly up to 20%. At higher concentrations the TCR powder performs better. At higher levels of untreated crumb, processing becomes difficult due to the increased Mooney viscosity; with TCR the viscosity is not increased. The advantage of these two processes is that they are very energy-efficient.

Isayev and co-workers<sup>3-5</sup> studied the devulcanisation of different rubbers using an ultrasonic reactor at various temperatures. Gel fraction, crosslink density, mechanical properties and dynamic properties were also determined for the virgin vulcanisate, the ultrasonically devulcanised rubber, and the revulcanised rubber. Kohler<sup>6</sup> reported a technology for the devulcanisation of sulphur cured scrap elastomers using a material developed by Sekhar.<sup>7</sup> They did a comparative study of a fully virgin NR compound and the same compound containing 30% of devulcanised rubber. The Mooney viscosity and 300% modulus was higher whereas tensile strength, elongation at break and tear strength was lower for the reclaim blend. However, the influence of reclaim on the mechanical properties was not very strong.

In this chapter, the reclamation of natural rubber based waste latex rubber is carried out by using diphenyldisulphide as reclaiming agent. The waste latex rubber reclaim (WLRR) is then blended with a virgin rubber compound using two different compounding principles. In the first situation, the curing system of the compound is adjusted in order to compensate for the additional amount of sulphur and accelerators brought in by the addition of reclaim. In the second case the cure system is kept constant. The cure behaviour, final crosslink density and distribution, mechanical properties and dynamic viscoelastic properties of the blends with reclaimed WLR are measured and compared to the original property profile. The morphology of the blends, sulphur migration and final distribution is also analysed.

## **7.2 EXPERIMENTAL**

The research performed in this chapter was partly done at the Cochin University of Science and Technology (CUSAT), India, and the University of Twente (UT), The Netherlands.

*Materials* – The waste latex rubber used in this investigation was gloves (WLR1) and condoms (WLR2). At CUSAT, WLR1 and WLR2 were reclaimed and investigated in a blending study with a virgin compound. At the UT, only WLR1 was reclaimed and compounded with virgin material. In the following, WLR1 used at CUSAT and UT will be designated as WLR1C and WLR1T respectively to differentiate between these two feedstocks. The characterisation of these materials is described in Chapter 3. The materials used in the experiment and the source are listed in Table 7.1 and the instruments used are given in Table 7.2.

**Table 7.1** Materials used for the study

Component	Source CUSAT	Source UT
NR	Rubber Research Institute of India	-
BR	Indian Petrochemicals Corporation Ltd.	Korea Kumho Petrochemical Co. Ltd.
ZnO	Meta Zinc Ltd.	Merck
Stearic Acid	Godrej Soaps Pvt. Ltd.	Merck
HAF (N330 )	Carbon and Chemicals	Degussa AG
Aromatic Oil	HP Corporation Ltd.	BP Oil Europe
MBS	Flexsys B.V.	Flexsys B.V.
Sulphur	Standard Chemical Company	J.T. Baker
Antioxidant (TMQ)	Flexsys B.V.	Flexsys B.V.
Antioxidant (6PPD)	Flexsys B.V.	Flexsys B.V.

**Table 7.2** Different instruments used at CUSAT and UT

Instruments	CUSAT	UT
Tensile tester	Schimidzu	Zwick Z1.0
Rubber Process Analyzer (RPA 2000)	Alpha Technologies	Alpha Technologies
Hardness Tester	Zwick 3114	Zwick 2585
Two-roll mill	Santhosh	Schwabenthan
Press	Santhosh	Wickert
Internal mixer	Haake Rheomix	Brabender PL2000

*Reclamation experiments* - The reclaim was prepared according to the recipe shown in Table 7.3 by a batch process in an internal mixer. The reclaiming conditions and the properties of the reclaim are shown in Table 7.4.

**Table 7.3** Reclamation recipe

Ingredients	Amount (phr)
WLR	100
Diphenyldisulphide	1
Reclaiming oil	5

**Table 7.4** Reclaiming conditions and properties of the reclaim

Material	Temp. (°C)	Time (min)	Mooney viscosity (MU)	Sol fraction (wt.%)	Crosslink density (10 <sup>-4</sup> mol/cm <sup>3</sup> )	Relative decrease in crosslink density
WLRR1C (CUSAT)	170	10	54	28	0.20	0.87
WLRR1T (UT)	180	5	49	27	0.19	0.87
WLRR2	160	10	59	29	0.24	0.86

*Rubber mixing and compounding* – Mixing and homogenisation of rubbers and compounding ingredients were done on a laboratory size (15 × 33 cm) two roll mill at a friction ratio of 1:1.25 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. All experiments were carried out using a truck tyre tread composition as shown in Tables 7.5 and 7.6. In the compositions shown in Table 7.5, NR was progressively replaced by WLR reclaim. The amount of accelerator was decreased by 0.05 phr for each 10 phr of WLR reclaim. A series of experiments with different concentrations of reclaim and accelerator was performed in order to adjust for the extra input of accelerator by the addition of reclaim. In the other test series done, Table 7.6, the amount of accelerators was kept constant.

**Table 7.5** Composition of NR-BR-WLRR compounds with adjusted cure system

Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
NR (ISNR3)	70	65	60	55	50	45	40	30	20	0
WLRR	0	5	10	15	20	25	30	40	50	70
BR (Cisamer1220)					30					
ZnO					4.5					
Stearic Acid					2					
HAF Black (N330)					52					
Aromatic Oil					8.5					
Accelerator (MBS)	1	0.975	0.95	0.925	0.9	0.875	0.85	0.8	0.75	0.7
Sulphur					2.2					
Antioxidant (TMQ)					1					
Antioxidant (6PPD)					0.5					

*Curing* – The cure characteristics of the different compounds were determined with a Rubber Process Analyser RPA 2000, a sort of moving die rheometer from Alpha technologies. The measurement was done at 150°C, 0.833 Hz and 2.79% strain over a time period of 30 minutes. The optimum vulcanisation time ( $t_{90}$ ), initial torque and final torque of the compound were determined. The compounds were cured in a Santhosh laboratory press (CUSAT) having 46 × 46 cm platens at 150°C and 150 bar or a Wickert laboratory press (UT) 1600/5 × 4/3 at

150°C and 100 bar. The curing time was chosen as  $t_{90}$  of the respective compounds. The cured samples were 90 × 90 mm in area and 2mm thickness.

**Table 7.6** Composition of NR-BR-WLRR compounds with fixed cure system

Compound	T1	T2	T3	T4	T5
NR (SIR20)	70	60	45	30	0
WLRR	0	10	25	40	70
BR (Kosyn KBR 01)	_____	_____	30	_____	_____
ZnO	_____	_____	4.5	_____	_____
Stearic Acid	_____	_____	2	_____	_____
Carbon Black (N330 HAF)	_____	_____	52	_____	_____
Aromatic Oil (Enerflex 75)	_____	_____	8.5	_____	_____
Accelerator (MBS)	_____	_____	1	_____	_____
Sulphur	_____	_____	2.2	_____	_____
Antioxidant (TMQ)	_____	_____	1	_____	_____
Antioxidant (6PPD)	_____	_____	0.5	_____	_____

*Testing procedures* – Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Tear strength was measured with angle test pieces according to ISO 34. Compression set tests were done at 70°C for 22 hours according to ISO 815. Hardness of the samples was measured with a Zwick hardness-tester Shore A, according to ASTM D 2240. Abrasion loss of the samples was tested using a DIN abrader with a load of 10 N. The abrasion tests were performed according to ISO 4649. Accelerated ageing tests were carried out according to ISO 188 on dumb-bell shaped specimens after putting them at 100°C for 24 hours and 48 hours in an air-ageing oven without forced aeration.

Swelling measurements were done in order to obtain information on the crosslink density. Before swelling, the cured samples were extracted in a Soxhlet apparatus, first with acetone for 48 hours and then with tetrahydrofuran for 72 hours. The elastically active network chain density was measured by equilibrium swelling in toluene for 72 hours at room temperature. The crosslink density was calculated according to the Flory-Rehner equation<sup>8</sup> with the Kraus correction<sup>9</sup> for carbon black. The crosslink distribution of the compounds was studied using thiol/amine chemical probes.<sup>10,11</sup>

Dynamic measurements of the uncured and cured compounds were performed with the RPA 2000. Frequency sweeps of cured compounds were done to measure the  $\tan\delta$  at 60°C as a measure of the rolling resistance, an important property for tyre tread applications. For this measurement, an uncured sample was vulcanised for a time period corresponding to the optimum vulcanisation time,  $t_{90}$ . After vulcanisation the sample was cooled down to 60°C and  $\tan\delta$  was measured at different frequencies. The frequency was varied from 0.1 to 209 rad/s at 0.56% strain.

A frequency sweep was also conducted on uncured compounds to measure the storage modulus. The measurement was done at a temperature of 100°C and a strain of 14%. The frequency was varied from 0.1 to 209 rad/s.

Sulphur distribution was investigated by means of Scanning Electron Microscopy in combination with an Energy Dispersive X-ray spectrometer (SEM-EDX, LEO 1550 FEG, Thermo NORAN Instruments model Vantage). The samples were prepared by cutting a cross-section of the vulcanised material with a microtome (Leica EM FCS) at a temperature of -130°C; then an elemental analysis was performed with a resolution of 2  $\mu\text{m}^2$ . Prior to the analysis, the sample was coated with carbon. The accelerating voltage was 15 kV and the sample distance was 9 mm. On every composite a line scan was performed in threefold. In these measurements, an electron beam in the range of 10-20 keV strikes the surface of a conducting sample. This causes X-rays to be emitted from the material, whose energy depends on the material under examination. They are generated in a region of about 2 microns in depth, thus EDX is not limited to surface analysis.

## 7.3 RESULTS

In the following, the properties of a virgin compound as given in Tables 7.5 and 7.6 blended with reclaim based on WLR1C as well as WLR1T and WLR2 are discussed. As WLR1C, WLR1T and WLR2 reclaim differ in crosslink density after reclamation, it is expected that they behave differently during revulcanisation within a matrix of a virgin compound.

Two different compounding principles are used for WLR1: For the fixed cure system the curing recipe was not adjusted, resulting in different curing characteristics depending on the reclaim concentration in the blend. In the other case, the adjusted cure system, the concentration of the curing additives was compensated for the extra input of sulphur and accelerator by the reclaim. WLR2 was studied only for adjusted cure system. The adjusted cure system study was carried out at CUSAT whereas the fixed cure system study was done at UT.

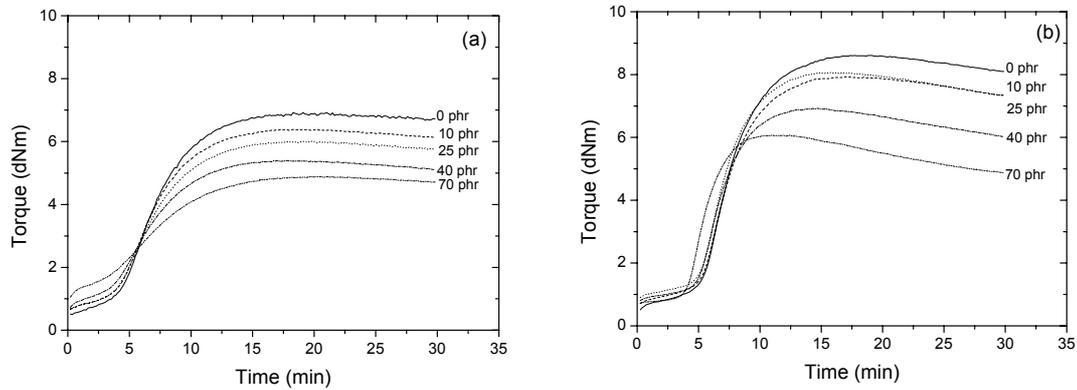
### 7.3.1 Cure behaviour

The rheograms of the compounds with adjusted and fixed curing systems containing WLR1C as well as WLR1T reclaim and with an adjusted cure system for WLR2 reclaim was studied.

#### 7.3.1.1 Compounds mixed with WLR1C and WLR1T reclaim

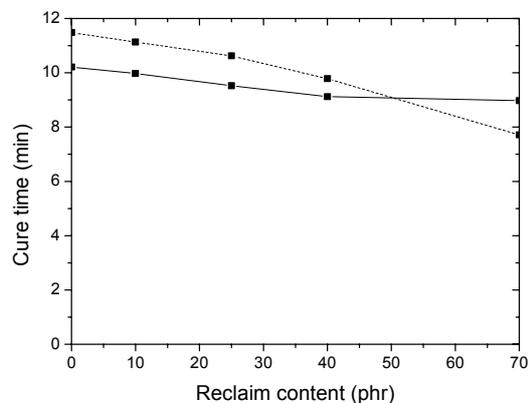
Figure 7.1 shows the rheogram for the virgin rubber compound and compounds containing various amounts of reclaim with an adjusted cure system and fixed cure system at 150°C. The maximum torque is decreasing and the initial torque is increasing with increasing amounts of reclaim in the compound when the curing

system is adjusted. In the case of a fixed curing system, the maximum torque is decreasing with increasing reclaim concentration, but the minimum torque is constant. The rate of vulcanisation slightly increases with increase in reclaim concentration for a fixed cure system.



**Figure 7.1** Rheogram of the compounds containing various amounts of WLR1 reclaim for the adjusted cure system (a) and fixed cure system (b);  
 (—): 0 phr; (— —): 10 phr; (- - -): 25 phr; (- · -): 40 phr; (- - · -): 70 phr.

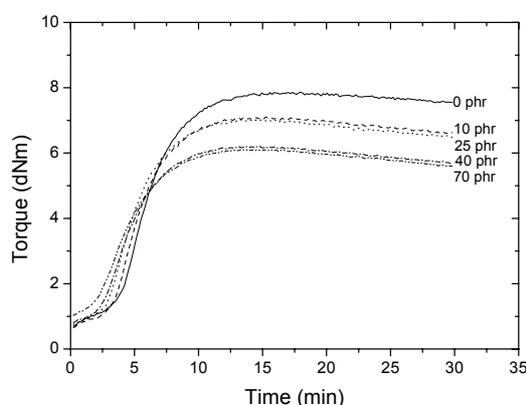
The optimum cure times for the fixed cure system compounds and adjusted cure system compounds at 150°C are given in the Figure 7.2. For the fixed cure system compounds the cure time decreases significantly. Only a very slight decrease in cure time with the increase in the reclaim content is observed for the adjusted cure system compounds.



**Figure 7.2** Optimum cure time of adjusted cure system (—) and fixed cure system compounds(- - -) as a function of WLR1 reclaim content at 150°C.

### 7.3.1.2 Compounds mixed with WLR2 reclaim

The cure curve for the virgin and the reclaim containing compounds with adjusted cure system at 150°C is shown in the Figure 7.3. For a better comparison the cure system was adjusted in the same way for both WLR1 reclaim and WLR2 reclaim containing compounds. A slight decrease in cure time for WLR2 reclaim containing compounds was found compared to WLR1. This might be due to the different compounding recipes used for the original WLR1 and WLR2 vulcanisates, for details see Chapter 3. The difference between final and initial torque decreases with increasing amount of reclaim in the compound. This is similar to the results found with WLR1 reclaim containing compounds (Figure 7.1). The cure time decreases with increasing reclaim content.



**Figure 7.3** Rheogram of the compounds containing various amounts of WLR2 reclaim with adjusted curing system;

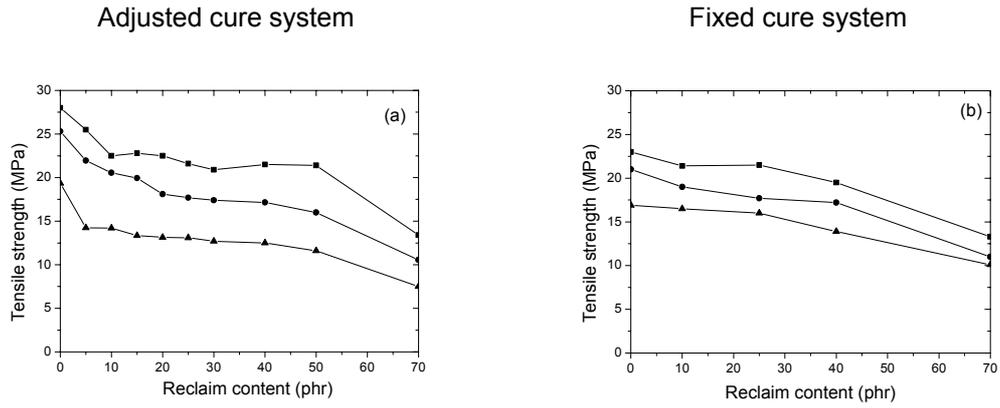
(——): 0 phr; (— —): 10 phr; (- - -): 25 phr; (— -): 40 phr; (— - -): 70 phr.

## 7.3.2 Mechanical properties

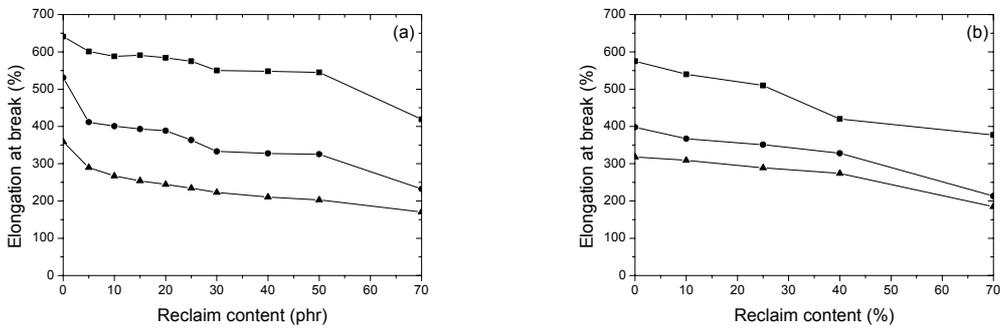
The mechanical properties of the WLR1C as well as WLR1T reclaim and WLR2 reclaim containing compounds were studied. Tensile strength, elongation at break, modulus at 100% and 300% elongation, tear strength, hardness and compression set were measured.

### 7.3.2.1 Compounds mixed with WLR1C and WLR1T reclaim

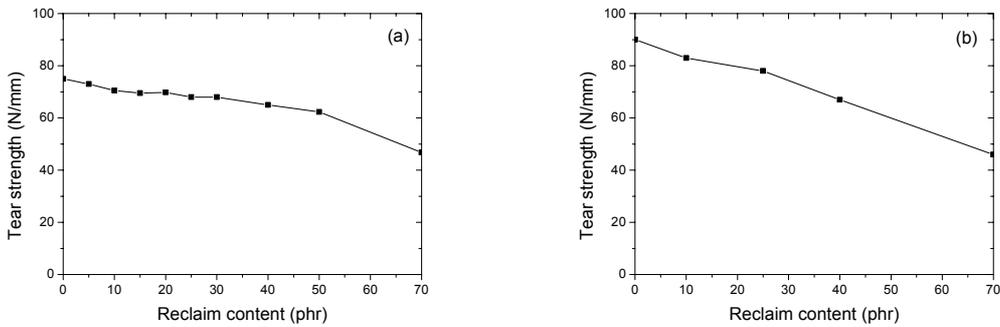
The tensile strength and the elongation at break of the unaged as well as aged samples of adjusted cure system compounds and fixed cure system compounds as a function of the reclaim content are depicted in Figure 7.4. The tensile strength decreases with increase in reclaim content. It also decreases after ageing, and an increase of ageing time results in a further decrease of the tensile strength as expected. For the adjusted cure system, a sharp decrease in tensile strength is found for the initial 10 phr of reclaim, then the tensile strength remains almost constant till 50 phr of reclaim and finally decreases significantly again when all of virgin NR is



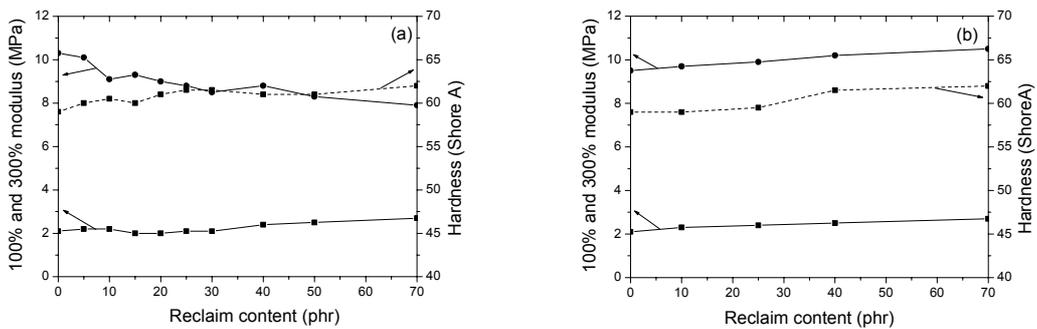
**Figure 7.4** Tensile strength as a function of WLR1 reclaim content; (■): unaged; (●): aged 24 hours at 100°C; (▲): 48 hours at 100°C.



**Figure 7.5** Elongation at break as a function of WLR1 reclaim content; (■): unaged; (●): aged 24 hours at 100°C; (▲): 48 hours at 100°C.



**Figure 7.6** Tear strength as a function of WLR1 reclaim content.



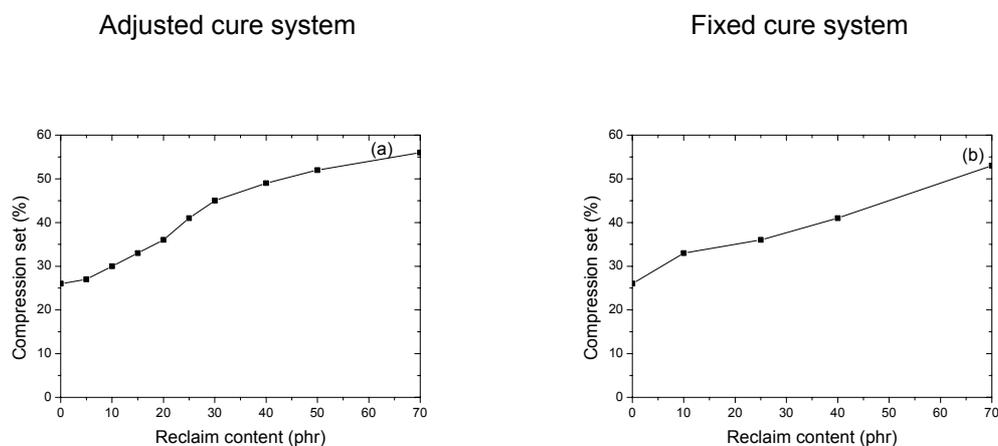
**Figure 7.7** Modulus (—) and hardness (- - -) as a function of WLR1 reclaim content; (■): 100% modulus; (●): 300% modulus.

replaced by WLR1C. The fixed cure system shows a different trend. A more or less linear decrease in tensile strength is observed with the increase in the amount of reclaim for unaged and aged compounds. Since the adjusted cure system and fixed cure system was compounded with different materials, the absolute values cannot be compared but the relative changes with increase in reclaim concentration can be compared. For the fixed curing system the decrease in tensile strength is less compared to the adjusted cure system with the increase in the reclaim content. Elongation at break decreases with an increasing amount of reclaim in the compound. It decreases in the same manner as tensile strength in both compounds. A sharp initial decrease followed by a plateau and a final decrease in the case of an adjusted cure system, and an approximately linear decrease in the case of a fixed cure system compounds.

The tear strength values for both cure systems against the reclaim content are given in Figure 7.6. The tear strength also decreases with an increasing amount of reclaim in the compound. The tear strength follows the same behaviour in both compounding principles: an almost linear decrease with increasing content of reclaim. However, the difference between the initial and final tear strength is larger for the fixed cure system than for the adjusted cure system compounds.

The modulus at 100% as well as 300% elongation and hardness against the reclaim content is plotted in Figure 7.7 for both compounds. There is a small increase in 100% modulus and hardness with increasing amount of reclaim for both cure system compounds. Interestingly the 300% modulus is decreasing for the adjusted cure system, whereas it increases in the fixed cure system compounds with increasing amounts of reclaim.

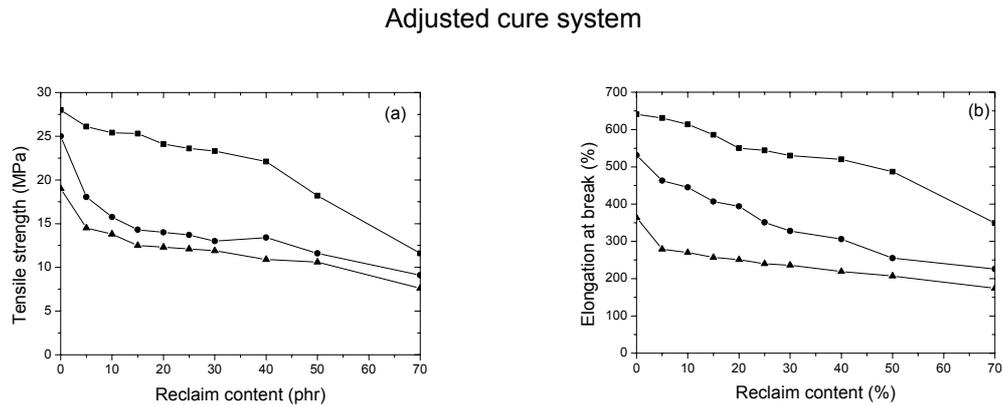
The compression set of the adjusted as well as fixed cure system compounds as a function of the reclaim content is depicted in Figure 7.8. Compression set increases with an increase of reclaim content for both cure system compounds. An almost linear increase of compression set is observed in both cases.



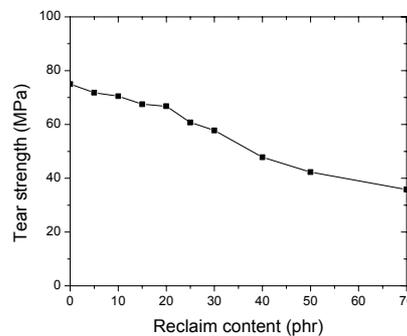
**Figure 7.8** Compression set as a function of WLR1 reclaim content.

### 7.3.2.2 Compounds mixed with WLR2 reclaim

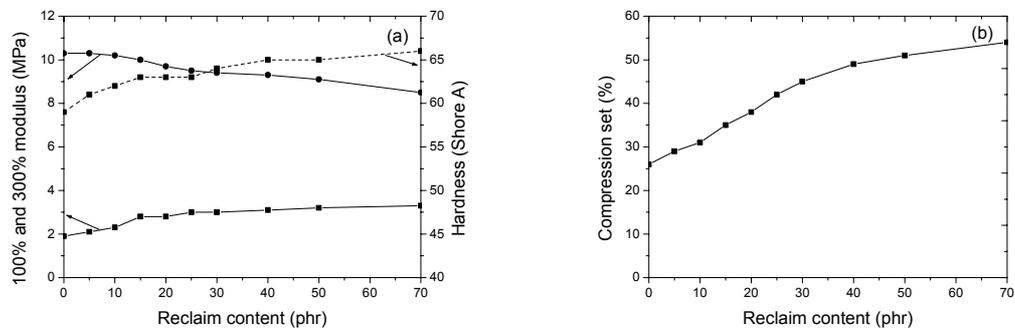
The tensile strength and elongation at break for unaged as well as for aged compounds are shown in Figure 7.9, and tear strength as a function of reclaim content with adjusted cure system is given in Figure 7.10. An approximately linear decrease of the tensile strength is found for the unaged compounds, whereas the aged compounds initially suffer a sharp decrease, which levels out for higher reclaim concentrations. The effect of ageing is less the higher the reclaim concentrations. Elongation at break for unaged compound decreases almost linearly with increasing



**Figure 7.9** Tensile strength (a) and elongation at break (b) as a function of WLR2 reclaim content; (■): unaged; (●): aged 24hours at 100°C; (▲): 48hours at 100°C.



**Figure 7.10** Tear strength as a function of WLR2 reclaim content.



**Figure 7.11** Modulus (—) hardness (- - -); (a) and compression set (b) as a function of WLR2 reclaim content; (■): 100% modulus; (●): 300% modulus.

amounts of reclaim, whereas for aged compound it follows the same trend as for tensile strength. Tear strength show a linear decrease with the increasing reclaim content.

Figure 7.11 shows the modulus at 100% as well as 300% elongation, hardness and compression set as a function of reclaim content for adjusted cure system compounds. The 100% modulus increases, but the 300% modulus decreases with increasing amount of reclaim. This is similar to the results found for WLR1 reclaim in compounds with an adjusted cure system (Figure 7.7). Hardness and compression set increase with an increasing amount of reclaim.

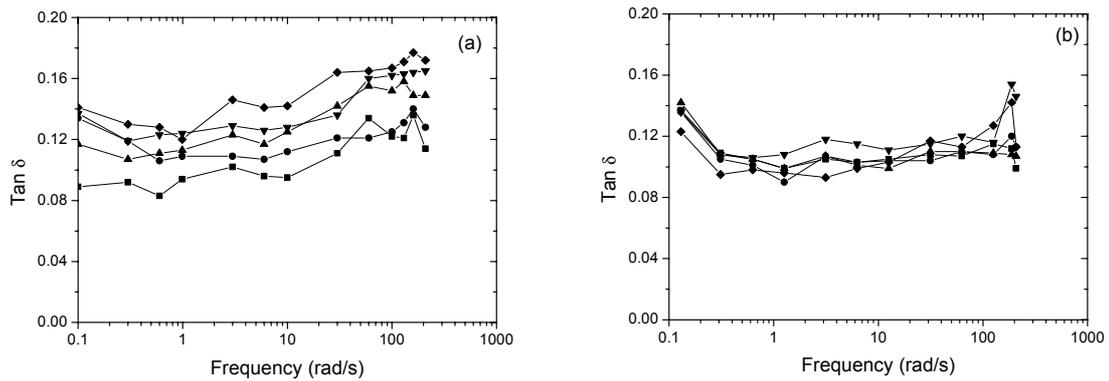
### 7.3.3 Dynamic viscoelastic measurements

From the viscoelastic property aspect, an ideal rubber which is able to meet the requirements for application in a high-performance tyre should give a low loss tangent ( $\tan\delta$ ) value at a temperature of 50-80°C in order to guarantee a low rolling resistance.<sup>12</sup> These measurements were done on the uncured reclaim/virgin blend and on their revulcanisates.

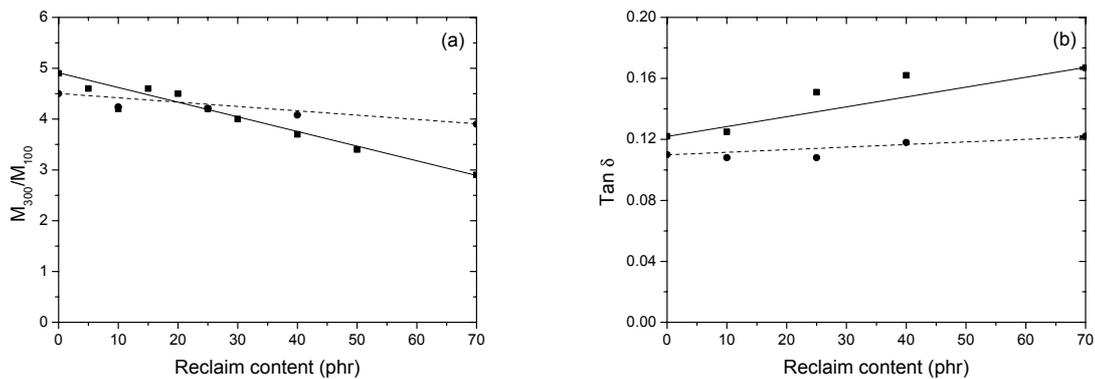
#### 7.3.3.1 Compounds mixed with WLR1C and WLR1T reclaim

The loss tangent is important due to the fact that the test compound is a typical truck tyre tread compound. The  $\tan\delta$  is defined as the ratio of the loss and the storage ( $G''/G'$ ) moduli.<sup>12</sup> While the storage modulus is representative of the dynamic stress that is in phase with the strain and a measure of the energy stored in the system, the viscous modulus is 90° out of phase and is related to the energy loss due to viscous dissipation. Therefore,  $\tan\delta$  is a ratio of the work converted into heat (or the work absorbed by the compound) and the recovered work. Figure 7.12 shows the  $\tan\delta$  values of the adjusted cure system and fixed cure system compounds against the frequency at 60°C for various cured compounds. The  $\tan\delta$  is generally increasing with increase in reclaim content over a frequency range of 0.1 to 209 rad/s for the adjusted cure system compounds. A large difference in  $\tan\delta$  is observed for the adjusted cure system when the amount of reclaim is increased from 0 phr to 70 phr; in contrast to this, the increase is marginal in the case of the fixed cure system.

Dividing the 300% modulus ( $M_{300}$ ) by the 100% modulus ( $M_{100}$ ) results in a measure for the rolling resistance: the higher the value, the lower the rolling resistance.<sup>13</sup> The  $\tan\delta$  values at 15 Hz and 60°C are also a measure of rolling resistance. The values of the two moduli are given in Figure 7.7. and the ratio of the two values is given in Figure 7.13, where the  $M_{300}/M_{100}$  values and  $\tan\delta$  at 15 Hz are plotted against the reclaim content for both the cure systems. The  $M_{300}/M_{100}$  values are decreasing stronger for the adjusted cured system compound compared to the fixed cured system compounds with increase in the reclaim content. The trends found for the  $M_{300}/M_{100}$  ratios match with the results found for the  $\tan\delta$  at 15 Hz for both cure systems: A stronger increase of  $\tan\delta$  correlating with a stronger decrease in  $M_{300}/M_{100}$  is found for the adjusted cure system compared to fixed cure system.



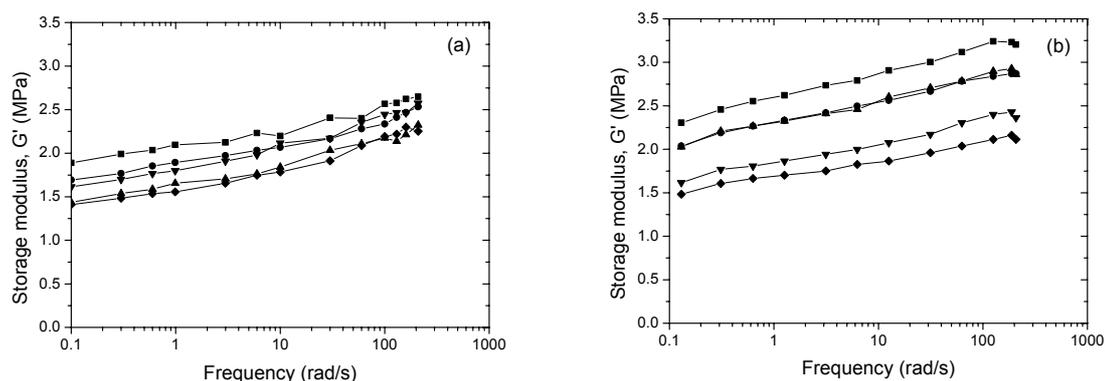
**Figure 7.12**  $\tan \delta$  of adjusted cure system (a) and fixed cure system compounds (b) with WLR1 reclaim as a function of frequency; (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr.



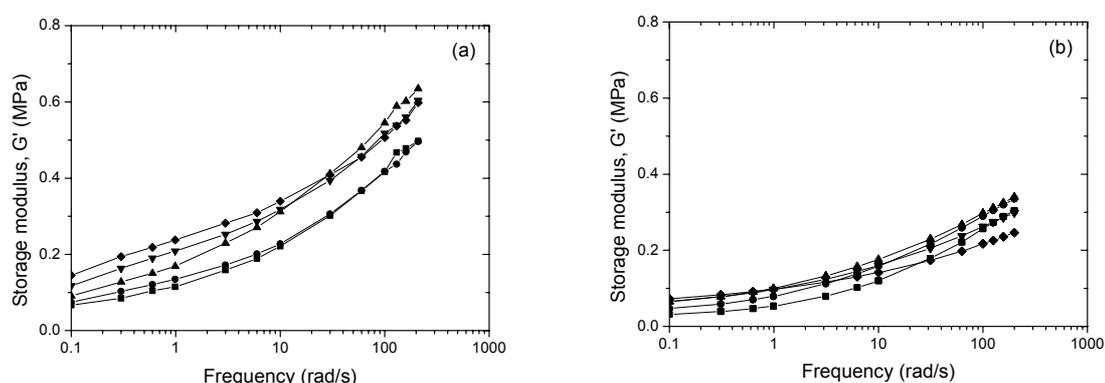
**Figure 7.13**  $M_{300}/M_{100}$  (a) and  $\tan \delta$  (b) for adjusted cure system (—) and fixed cure system compounds (- -) as a function of WLR1 reclaim content.

The storage modulus of both cure systems as a function of the frequency at 60°C and 0.56% strain for various cured compounds is illustrated in Figure 7.14. The storage modulus decreases with increasing amounts of reclaim for both cure systems, or in other words, the storage modulus of the virgin vulcanisate is higher than that of the reclaim/virgin blends. This is in accordance with the lower maximum torque of the reclaim containing compounds in the cure curves (Figure 7.1).

The storage moduli against the frequency at 100°C and at 14% strain for different uncured compounds are given in Figure 7.15. All compounds show an increase in storage modulus with increase of reclaim concentration. At lower frequencies the compound containing a higher reclaim concentration shows a higher modulus.



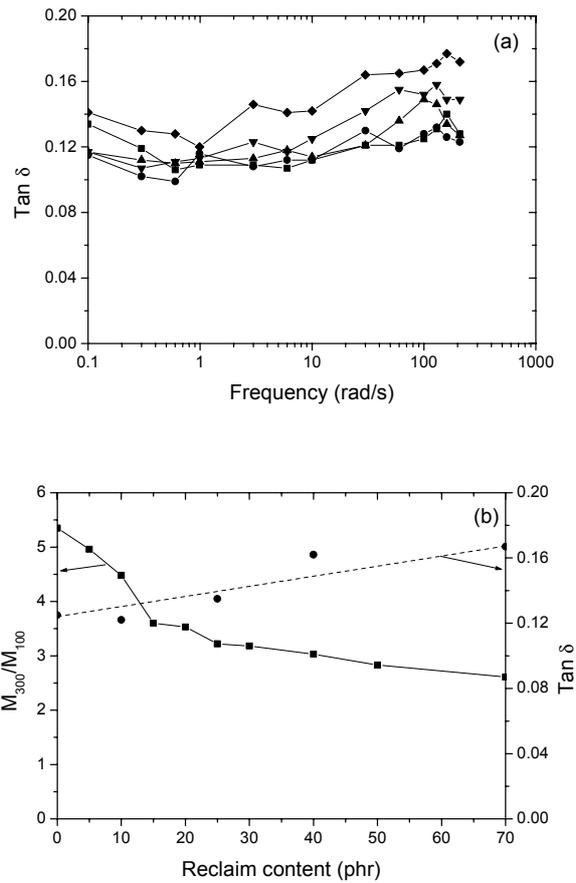
**Figure 7.14** Storage modulus of cured compounds for adjusted cure system (a) and fixed cure system compounds (b) with WLR1 reclaim as a function of frequency; (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr .



**Figure 7.15** Storage modulus of uncured compounds for adjusted cure system (a) and fixed cure system compounds (b) with WLR1 reclaim as a function of frequency; (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr .

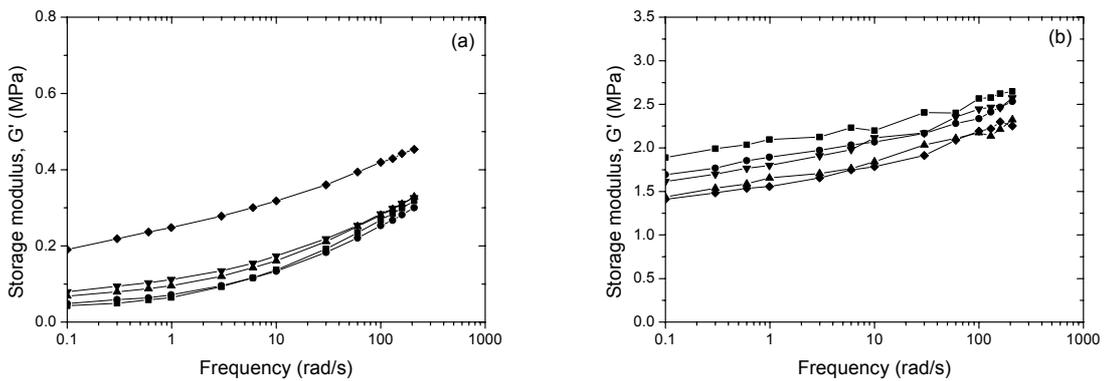
### 7.3.3.2 Compounds mixed with WLR2 reclaim

The  $\tan\delta$  measured at 60°C and at 0.56% strain and the  $M_{300}/M_{100}$  ratio of various reclaim containing compounds, which are cured at 150°C, are given in Figure 7.16. The  $\tan\delta$  values increase and the  $M_{300}/M_{100}$  values decrease with increase in the amount of reclaim in the compound. Both,  $\tan\delta$  and  $M_{300}/M_{100}$  represent the heat build-up and rolling resistance of the compound. Rolling resistance improves with decreasing  $\tan\delta$  and increasing  $M_{300}/M_{100}$ , so with increasing reclaim content a negative effect is found.



**Figure 7.16** Tan $\delta$  as a function of frequency (a) and  $M_{300}/M_{100}$  and tan $\delta$  as a function of WLR2 reclaim content (b); (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr.

The storage moduli of uncured and cured samples of reclaim containing compounds as a function of frequency are given in Figure 7.17. The storage modulus



**Figure 7.17** Storage modulus of uncured compounds (a) and vulcanised compounds (b) with WLR2 reclaim as a function of frequency; (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr.

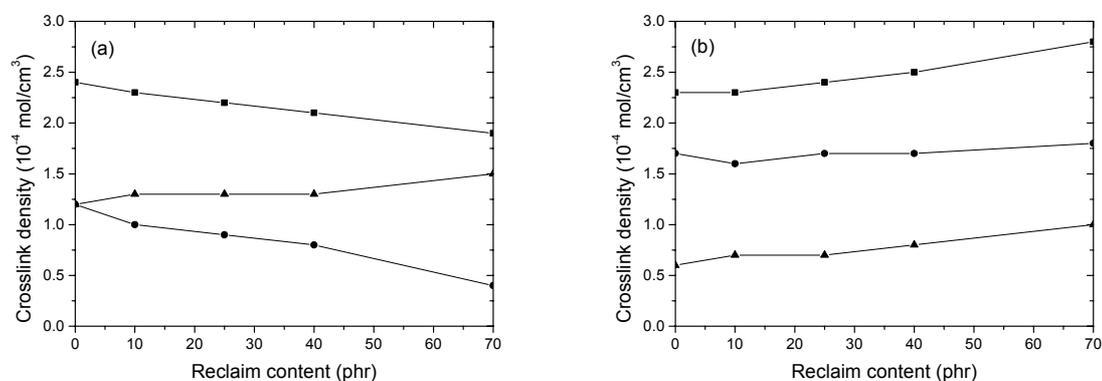
of the uncured compounds increases and the modulus of the cured compounds decreases with increasing amount of reclaim. The trends in the dynamic viscoelastic behaviour of the adjusted cure system compounds of WLR1 and WLR2 reclaim containing samples are comparable (Figures 7.12 – 7.15 and 7.16 – 7.17).

### 7.3.4 Crosslink density and distribution

The crosslink density and distribution measurements are important because the mechanical and dynamic viscoelastic properties depend to a large extent on the crosslink density as well as on the crosslink distribution. Mechanical and dynamic properties are influenced by the ratio of poly-, di- and monosulphidic crosslinks.

#### 7.3.4.1 Compounds mixed with WLR1C and WLR1T reclaim

The overall crosslink density and crosslink distribution of the adjusted cure system and fixed cure system compounds as a function of reclaim content are given in Figure 7.18. The overall crosslink density and the amount of polysulphidic crosslinks decrease, while the number of mono- and disulphidic crosslinks increases with increase of reclaim content in the compound for the adjusted cure system compound. Interestingly, for the fixed cure system compounds the overall crosslink density increases, whereas the polysulphidic crosslinks remain almost constant with increase of reclaim content.



**Figure 7.18** Crosslink distribution of for adjusted cure system (a) and fixed cure system compounds (b) as a function of WLR1 reclaim content;

(■): total number of crosslinks;

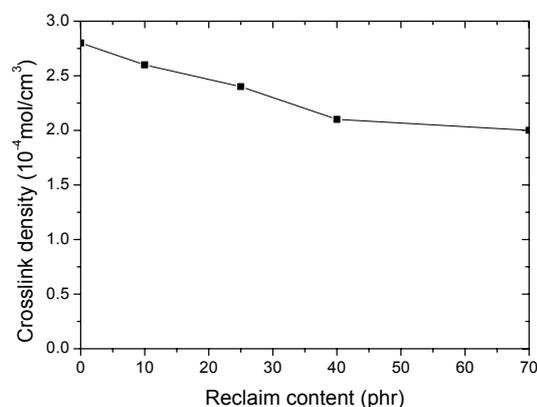
(●): polysulphidic crosslinks; (▲): mono- plus disulphidic crosslinks.

The amount of mono- and disulphidic crosslinks could not separately be calculated because of the phase inversion which occurred during the reaction with hexane-1-thiol and piperidine, where all the poly- and disulphidic crosslinks are broken. An extraction with acetone and tetrahydrofuran is preceded the crosslink density measurement. During extraction all the debound rubber polymer that is released during the thiol/amine reaction is removed from the network.

Considering the fact that out of the total weight of the sample 63 wt.% is rubber hydrocarbon, a weight loss calculation on the basis of the original rubber hydrocarbon was done. It was found that during the reaction with propane-2-thiol the rubber hydrocarbon content decreased from 63% to 60% and with hexane-1-thiol it decreased to 35 wt.%. As the weight of rubber hydrocarbon decreased, the weight of other ingredients in the sample increased relative to the rubber hydrocarbon. In regard to the crosslink density measurement, carbon black is the most important component that influences the measurement amongst the other ingredients. The weight of carbon black increases from 33 wt.% to 35 wt.% and to 55 wt.% during the reaction with propane-2-thiol and with hexane-1-thiol. The relative increase of carbon black concentration with propane-2-thiol is limited, but during the reaction with hexane-1-thiol it increases significantly. The sample that is treated with hexane-1-thiol contains more carbon black than rubber hydrocarbon. In the original sample, the ratio of polymer content to carbon black content is approximately 2. After hexane-1-thiol treatment, the ratio decreases to 0.63, indicating that a phase inversion occurs during this process. This high amount of carbon black inhibits the rubber chain to swell properly and results in an improper calculation of monosulphidic crosslink density values with these samples.

#### 7.3.4.2 Compounds mixed with WLR2 reclaim

The overall crosslink density of WLR2R containing compounds with adjusted cure system as a function of reclaim content is given in Figure 7.19. The crosslink density decreases with increasing amounts of reclaim.



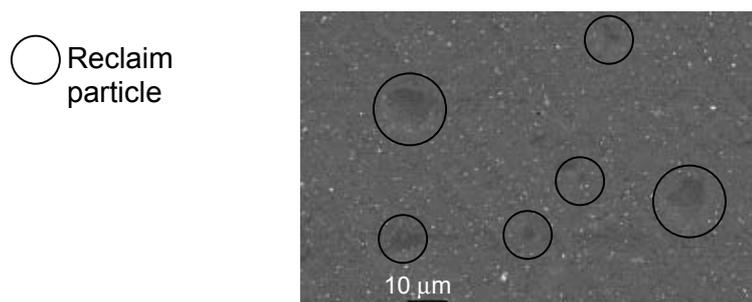
**Figure 7.19** Crosslink density as a function of WLR2 reclaim content.

#### 7.3.5 Morphology study : Scanning Electron Microscopy – Energy Dispersive X-ray spectrometry (SEM-EDX)

The morphology study was conducted to analyse the dispersion characteristics of reclaim in the blend and to investigate whether the reclaim particles are embedded in the rubber matrix or just acting as inert filler particles. The

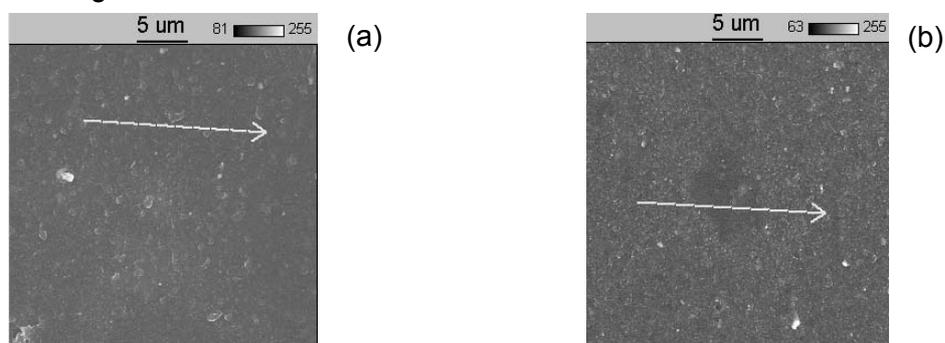
measurement also provides the size and shape of the particles. EDX measurements show the migration behaviour of sulphur in the reclaim and in the virgin rubber. The difference in the concentration level of sulphur between the reclaim phase and virgin phase affect the mechanical and viscoelastic properties.

Figure 7.20 shows the SEM picture of a cured compound loaded with 40 phr reclaim. The dark areas are the reclaim particles, which are dispersed in the NR/BR phase. The shape of the reclaim particles is basically circular. The size of the particles is not uniform and ranges from 1-8  $\mu\text{m}$ . The particle size distribution is quite broad. The particles seem to be embedded and attached to the matrix rather than just acting as inert filler particles.

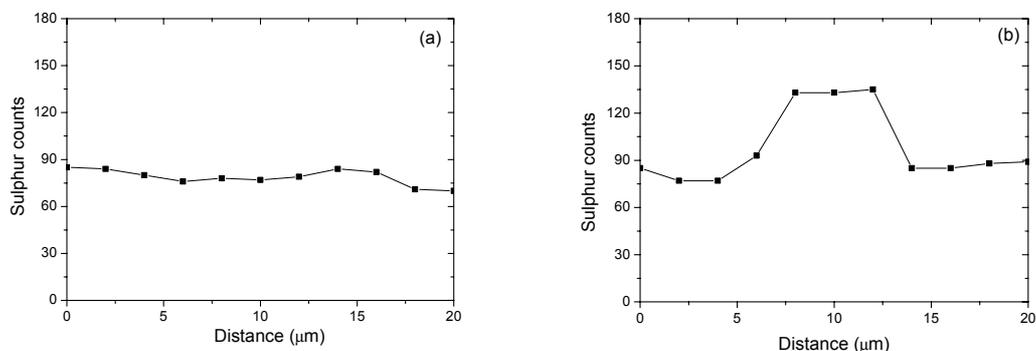


**Figure 7.20** SEM picture of the compound mixed with 40 phr of WLR1T reclaim.

The SEM-EDX measurements of samples containing 0 phr and 70 phr are shown in the Figures 7.21 and 7.22:



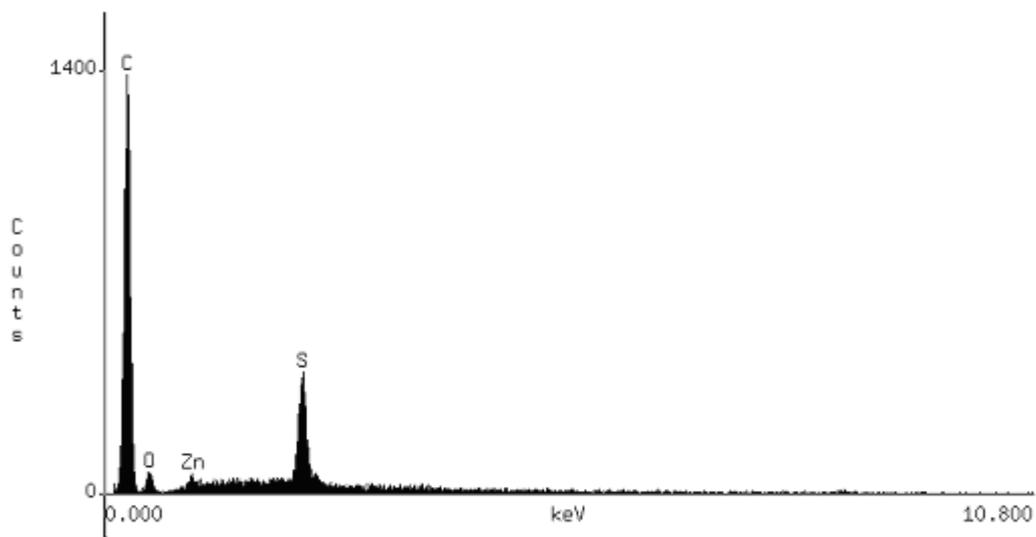
**Figure 7.21** SEM picture of the compound mixed with 0 phr (a) and 70 phr (b) of WLR1T reclaim.



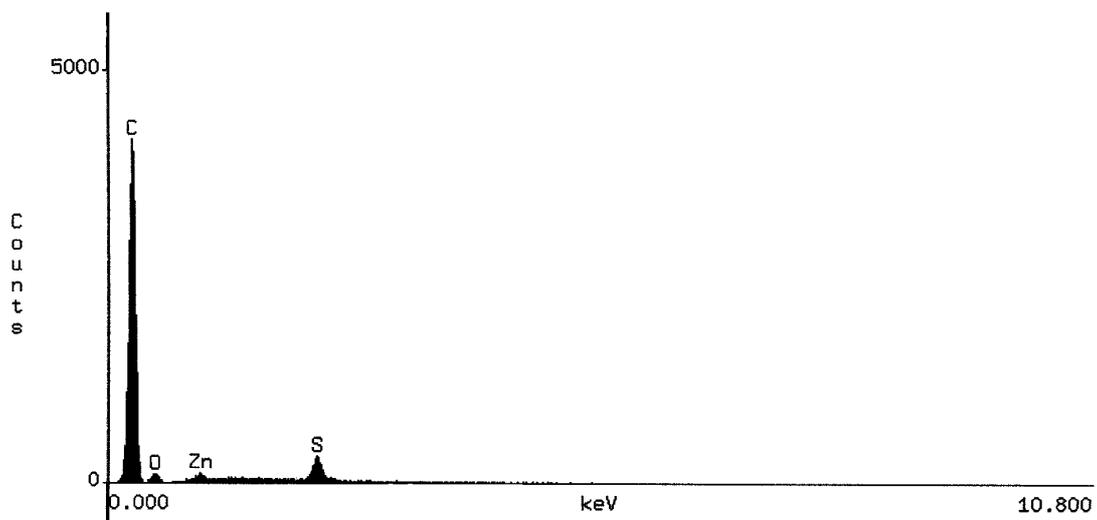
**Figure 7.22** Sulphur content of the compound mixed with 0 phr (a) and 70 phr (b) of WLR1T reclaim as a function of line scan distance.

A SEM picture is coupled with the EDX analysis of sulphur in the reclaim particle and in the matrix. A line scan was carried out to measure the difference in the amount of sulphur in the matrix and in the reclaim particle. In the virgin compound, Figure 7.21(a), a constant sulphur count is observed showing that the sulphur is uniformly distributed within the matrix. In Figure 7.21(b) where the sample contains 70 phr of reclaim, a difference in the amount of sulphur is observed as the line scan is performed through the matrix and reclaim particle.

To analyse the reclaim phase and the matrix more thoroughly, EDX spectra of the dark and the light phases are taken. The spectra are shown in Figures 7.23 and 7.24: A difference in the concentration of sulphur was observed between the matrix and reclaim particle as shown in the EDX spectra.



**Figures 7.23** EDX spectrum of the reclaim particle mixed with 70 phr of WLR1T reclaim.



**Figure 7.24** EDX spectrum of the matrix mixed with 70 phr of WLR1T reclaim.

## 7.4 DISCUSSION

In this chapter the influence of different amounts of reclaim on the properties of a virgin compound is discussed in terms of mechanical and dynamic viscoelastic properties, crosslink density and distribution, presence of gel and sulphur distribution between the matrix and the reclaim. The mechanical and viscoelastic properties are affected by the following factors:<sup>14,15</sup>

- Presence of gel in the reclaim;
- Adhesion of the reclaim to the matrix;
- Particle size of the reclaim;
- Sulphur distribution between the matrix and reclaim;
- Crosslink density and distribution.

The decrease in tensile strength with increasing concentrations of reclaim is reported by many researchers<sup>14-17</sup> with respect to the decrease in the molecular weight of the sol fraction in the reclaim and the presence of the crosslinked gel. The reclaim particle acts as an obstacle for stress transmission within a continuous matrix resulting in an initiation of failure expressed by lower tensile strength. This mismatch in properties can significantly reduce the strength of the material. The stress accumulates on the interface between the reclaimed particle and the matrix and fracture starts from this point. With increasing concentrations of reclaim, the concentration of weak spots increases and the tensile strength of the system decreases.

It is known that the tensile strength increases with increasing crosslink density, reaches a maximum value and then decreases again. It is also known that tensile strength increases with an increasing number of polysulphidic crosslinks and decreases with an increasing amount of mono- and disulphidic crosslinks. The improvement in tensile strength with an increasing number of polysulphidic crosslinks can be related to the greater flexibility and lability of the polysulphidic crosslinks: Under stress these crosslinks can cleave and recombine. This process permits the relief of stress which would otherwise accumulate and lead to the initiation of failure.<sup>18</sup> Viscoelastic dynamic properties are improved by polysulphidic crosslinks.

The initial decrease in tensile stress is higher for adjusted cure system than for fixed cure system compounds – Figure 7.4. The crosslink density measurements for both systems show that the crosslink density decreases for the adjusted cure system and increases for the fixed cure system: Figure 7.18. The crosslink distribution studies show that the amount of polysulphidic crosslinks decreases and that the cumulative number of mono- and disulphidic linkages is increased for the adjusted cure system. For the fixed cure system the number of polysulphidic crosslinks remains basically constant, and the number of mono- and disulphidic crosslinks increases: Figure 7.18. The sulphur contents in the matrix and in the reclaim particle show a difference: Figure 7.21 – 7.24. Due to the higher sulphur concentration of the reclaim particle compared to the matrix, these spots become

highly crosslinked during vulcanisation and over-cured. The tensile strength of these areas decreases and the tensile failure starts from these spots. The excess crosslinks in the reclaim particles and the increasing amount of mono- and disulphidic crosslinks explain the decrease in tensile strength for the fixed cure system compounds even though the overall crosslink density is increase with increasing reclaim content.

These are not the only factors which affect the mechanical properties of the compound. Factors like a decrease in chain length of the polymer during reclamation and the presence of crosslinked gel in the reclaim also influence the mechanical strength.<sup>19</sup>

Elongation at break is another property which depends mainly on the crosslink density and its distribution. The decrease in elongation at break for a fixed cure system and adjusted cure system can be explained similar to the reduction of the tensile strength: Figures 7.4 and 7.9.

The tear strength is influenced by the change in strain crystallisation of NR: This property might be disturbed by the addition of the reclaim which is still partly vulcanised and has a different structure: Figures 7.6 and 7.10.

The 300% modulus increases for the fixed cure system compounds but decreases for adjusted cure system compounds. This is a consequence of the increase and decrease of the polysulphidic crosslinks in both cure systems respectively. The increase in the 100% modulus in both cases, Figures 7.7 and 7.11(a), could be due to the increase of mono- and disulphidic crosslinks with increase in the amount of reclaim.

A comparative study between the adjusted cure system and fixed cure system compounds shows that the latter perform better on reclaim addition in terms of mechanical and dynamic viscoelastic properties. Within the concentration range of 10 – 50 phr the influence of reclaim on the properties of the virgin compound is less for the fixed cure system compound, Figures 7.4 – 7.8. The tensile strength values, tear strength and elongation at break follow the same trend. The WLR2 reclaim has more influence on tear strength and elongation at break compared to WLR1 reclaim, Figures 7.6 and 7.10. This might be due to the higher crosslink density of WLR2 reclaim (Table 7.4) making the material stiffer thereby increasing the difference in modulus between the two materials. The  $\tan\delta$  and  $M_{300}/M_{100}$  values (Figures 7.12 and 7.13) are improved for the fixed cure system compounds for higher reclaim concentrations. The improvement in properties for the fixed cure system compounds is due to the increase in the polysulphidic crosslinks compared to a decrease in the polysulphidic crosslinks for adjusted cure system (Figure 7.18).

The elasticity of the material decreases mainly due to the increase in the amount of mono- and disulphidic crosslinks with increasing reclaim content in the compound and due to the presence of gel in the reclaim. Both factors reduce the elastic nature of the compound, which is also the reason for the increased heat build-up, which is reflected in the  $\tan\delta$  values - Figures 7.12 and 7.16. The increased compression set values and hardness is also due to the presence of gel in the reclaim.

The storage modulus of the unvulcanised samples increases with the increase of reclaim concentration: Figures 7.15 and 7.17(a), again due to the

presence of an increased amount of gel in the compound. The three-dimensional gel imparts a certain elastic contribution to the unvulcanised sample causing the storage modulus to increase. However, in the vulcanised sample the storage modulus shows an inverse effect: Figures 7.14 and 7.17(b). As the sample is vulcanised, the gel particles also get attached to the matrix and crosslinked, hence the mobility and flexibility of the gel particle is lost. Therefore, these particles act as harder spheres with reduced elastic properties.

It is important to understand whether the difference in the sulphur level between the matrix and reclaimed particle is due to the migration of sulphur from the matrix to the reclaim particle or due to the initial distribution of sulphur between the two phases during mixing of the compound. A calculation based on the vulcanisation recipe of WLR1 and the amount sulphur in DPDS, which is added during the devulcanisation of WLR1 shows that WLR1 reclaim contains 1.36 wt.% of sulphur and that the virgin compound, T1 (Table 7.6), contains 1.43 wt.% of sulphur. The concentration of sulphur was also calculated from the sulphur counts during the EDX measurement and shows that the virgin compound (0 phr of WLR1 reclaim) contains 1.4 wt.% of sulphur and that the matrix of the 70 phr reclaim containing compound also has a sulphur level of 1.4 wt.%. The reclaim particle in the same sample contains 2.9 wt.% of sulphur. Considering the fact that 1.4 wt.% of sulphur was added during mixing of all compounds given in the Table 7.6, an additional 1.4 wt.% of sulphur is added to the reclaim particle. Together with the initial sulphur level of 1.36 wt.% this adds up to approximately 2.8 wt.%. This is the sulphur concentration found back during the EDX measurement, Figure 7.22(b). These calculations show that the difference in sulphur concentration between the matrix and the reclaim particle is not due to migration of sulphur between the matrix and the reclaim but due to a homogeneous distribution of sulphur throughout the matrix and reclaim during mixing of the compound. The sulphur stays in the matrix and in the reclaim and does no major migration during and after vulcanisation occurs.

## 7.5 CONCLUSIONS

Natural rubber based waste latex rubber with different amounts of polysulphidic linkages are reclaimed using diphenyldisulphide as reclaiming agent. The reclaimed rubber is blended with a virgin rubber compound. Two different compounding principles for the curing system are applied: adjustment of the amount of added curatives to compensate for the extra input of sulphur and accelerator by the reclaim addition, and a fixed cure system. The difference between initial and final torque decreases with the increase of reclaim content in both cases. The mechanical properties deteriorate with increasing reclaim concentration in the blend. Tensile strength, tear strength, and elongation at break decrease and modulus at 100% elongation, hardness and compression set increase with increasing amounts of reclaim. The modulus at 300% elongation decreases for the adjusted cure system, however it increases for a fixed cure system. Dynamic viscoelastic properties indicate that the reclaimed WLR is more elastic than an uncured virgin NR/BR blend

compound, while revulcanised WLR reclaim is less elastic than the virgin vulcanisate. The  $\tan\delta$  and  $E_{300}/E_{100}$  values of the compounds shows that the fixed cure system is having an improved rolling resistance compared to adjusted cure system compounds. A crosslink distribution study shows that the number of mono- and disulphidic crosslinks increases with increasing amount of reclaim. SEM-EDX measurements show a difference in the sulphur concentration between the reclaimed rubber phase and the virgin rubber phase in the compound: A higher concentration of sulphur is found in the reclaimed rubber phase compared to the virgin rubber phase. A comparative study between compounds with adjusted cure system and fixed cure system shows that up to a concentration level of 40 phr the fixed cure system is performing better than the adjusted cure system, and for higher reclaim concentrations the properties are similar for both systems. The final reclaims have the same characteristics independent from the feedstock under the condition that the reclaiming process was optimal.

## 7.6 REFERENCES

1. M. J. Myhre, D. A. MacKillop, *Rubber World*, **214**, (1996), 42.
2. Anonymous (Trelleborg AB) *Eur. Rubber J.*, **162**(7), (1980), 36.
3. A. I. Isayev, J. Chen, A. Tukachinsky, *Rubber Chem. Technol.*, **68**, (1995), 267.
4. A. Tukachinsky, D. Schworm, A. I. Isayev, *Rubber Chem. Technol.*, **69**, (1996), 92.
5. M. Tapale, A. I. Isayev, *J. Appl. Polym. Sci.*, **70**, (1998), 2007.
6. R. Kohler, J. O'Neill, *Rubber World*, **216**(2), (1997), 32.
7. B. C. Sekhar, A. Subramaniam (to STI-K Polymers SDN BDH), EP 0748837 A1 (December 18, 1996)
8. P. J. Flory, J. Rehner, Jr., *J. Chem. Phys.* **18**, (1950), 108.
9. G. Kraus, *J. Appl. Polym. Sci.*, **7**, (1963), 861.
10. D. S. Campbell, *J. Appl. Polym. Sci.* **13**, (1969), 1201.
11. D. S. Campbell, B. Saville, in "Proceedings of the International Rubber Conference", Brighton (1967).
12. M. J. Wang, *Rubber Chem. Technol.*, **71**, (1998), 520.
13. L. A. E. M. Reuvekamp, PhD thesis, University of Twente, (2003). ISBN 90 365 1856 3.
14. K. Fujimoto, T. Nishi, T. Okamoto, *Int. Polym. Sci. Technol.*, **8**(8), (1981), T/30.
15. M. Burgoyne, G. Leaker, Z. Krekic, *Rubber Chem. Technol.*, **49**, (1976), 375.
16. E. M. Fesus, R. W. Eggleton, *Rubber World*, **203**(6), (1991), 23.
17. K. Knorr, *Kautsch. Gummi Kunstst.*, **47**, (1994), 54.
18. A. Y. Coran, *Science and Technology of Rubber*, F. R. Eirich, Ed., Academic Press, New York, 1978.
19. A. I. Isayev, J. Jun, *Rubber Chem. Technol.*, **76**, (2003), 253.



# Chapter 8

---

## **NR based cured latex material reclaimed with 2,2'-dibenzamidodiphenyldisulphide in a truck tyre tread compound<sup>#</sup>**

---

2,2'-dibenzamidodiphenyldisulphide (DBADPDS) is used as a reclaiming agent for the reclamation of natural rubber based waste latex rubber (WLR). For progressive replacement of virgin natural rubber by the reclaim, two alternatives curing system were investigated. Adjustment or reduction of the curing system with increasing reclaim content, to compensate for the extra amount of curatives brought along by the reclaim, in order to keep the total sulphur in the compound constant; Fixed curing system, as if the reclaim were equivalent to virgin NR. The cure behavior, final crosslink density and distribution, mechanical properties and dynamic viscoelastic properties of the blends with reclaimed WLR are measured and compared with the virgin compound. The morphology of the blends, sulphur migration and final distribution are analysed. The amido substituted DBADPDS and the unsubstituted diphenyldisulphide (DPDS) are compared in terms of the property profile of the final product. The main differences are a higher tensile strength and a reduced smell of the DBADPDS reclaimed material. The mechanical and dynamic viscoelastic properties deteriorate for both curing systems but to a lesser extent for fixed curing system compared to adjusted curing system. Most important result with fixed cure system is the values obtained for  $\tan\delta$  and  $M_{300}/M_{100}$ , representative for the rolling resistance of tyres. With the fixed cure system both quantities indicated an improved performance with increasing amount of reclaim versus. adjusted cure system.

---

<sup>#</sup>The work described in this chapter has been submitted for publication in J. Appl. Polym. Sci.

## 8.1 INTRODUCTION

In this chapter, the reclamation of natural rubber based waste latex rubber is carried out by using 2,2'-dibenzamidodiphenyldisulphide as reclaiming agent. This material is compared to reclaim made with diphenyldisulphide, the standard reclaiming agent. The sulphur content in a reclaiming agent is an important characteristic because it influences the ratio of mono-, di- and polysulphidic crosslinks in the reclaimed rubber: The higher the sulphur content in the reclaiming agent, the higher the probability of formation of mono- and disulphides.<sup>1</sup> The sulphur content of DPDS is 29%; and the sulphur content of DBADPDS is 14% of its mass.

A detailed investigation of the efficiency of DBADPDS as reclaiming agent was done in Chapter 6, and the results of the study revealed that DBADPDS has a higher efficiency for the reclamation of NR-based latex products compared to the other aromatic disulphides used. A comparative study of DBADPDS with DPDS show that DBADPDS was able to cleave crosslinks and main-chains at temperature levels approximately 20°C below the temperature levels normally used in the reclamation process. Another advantage of the DBADPDS is the reduced smell during the reclamation process and of the final reclaims, one of the most important shortcomings of the disulphides.

The activation energies for the reclamation of WLR1 with DPDS and DBADPDS was calculated in Chapter 6 and found that the activation energy for DPDS is 73 kJ/mol and for DBADPDS is 53 kJ/mol. A lower activation energy for DBADPDS indicates that the reclamation reaction is less dependent on the temperature. Another important advantage of DBADPDS is its lower toxicity compared with mercaptans and other disulphides.<sup>2</sup>

After the reclamation of WLR1 with DBADPDS, the WLR1reclaim (WLRR1) is mixed with a virgin rubber compound using two different compounding principles. In the first case, the curing system of the compound is adjusted to compensate for the extra input of sulphur and accelerator by the reclaim. In the second case the cure system is kept constant: fixed curing system. The cure behaviour, final crosslink density and distribution, mechanical properties and dynamic viscoelastic properties of the blends with reclaimed WLR1 are measured and compared to the properties of the virgin compound without reclaim. The morphology of the blends and sulphur migration is also investigated.

## 8.2 EXPERIMENTAL

The research performed in this chapter is done partly at the Cochin University of Science and Technology (CUSAT), India, and partly at the University of Twente (UT), The Netherlands. The materials and instruments used in each research center are given in Chapter 7, Tables 7.1 and 7.2.

*Materials* – The waste latex rubber used in this investigation was gloves (WLR1). The materials used in the experiment and their suppliers are listed in the Chapter 7, Table 7.1. In the following, WLR1 used at CUSAT and UT will be designated as WLR1C and WLR1T, respectively, to differentiate between these two feedstocks. The characterisation of these materials is described in Chapter 3.

*Reclamation experiments* - The reclaim was prepared according to the recipe shown in Table 8.1 by a batch process in an internal mixer. The reclaiming conditions and the properties of the reclaim are shown in the Table 8.2.

**Table 8.1** Reclamation recipe

Ingredients	Amount (phr)
WLR1	100
2,2'-dibenzamidodiphenyldisulphide	1
Reclaiming oil	5

**Table 8.2** Reclaiming conditions and properties of the reclaim

Material	Temp. (°C)	Time (min)	Mooney viscosity (MU)	Sol fraction (wt.%)	Crosslink density (10 <sup>4</sup> mol/cm <sup>3</sup> )	Relative decrease in crosslink density
WLRR1 (CUSAT)	150	10	48	31	0.22	0.85
WLRR1 (UT)	160	7.5	55	29	0.24	0.84

*Rubber mixing and compounding* – Mixing and homogenisation of the polymers and compounding ingredients were done on a laboratory size (15 × 33 cm) two roll mill at a friction ratio of 1:1.25 at 50°C. All experiments were carried out using a truck tyre tread composition as shown in Tables 7.5 and 7.6, Chapter 7, in which NR was progressively replaced by WLR1 reclaim in both test series. The amount of accelerator was decreased by 0.05 phr for 10 phr replacement of NR by WLR1 reclaim in the adjusted cure system compound series. In the other test series the amount of accelerators was kept constant.

*Curing* – The cure characteristics of the different compounds were determined with a Rubber Process Analyser RPA 2000. The measurements were done at 150°C, 0.833 Hz and 2.79% strain over a time period of 30 minutes. The optimum vulcanisation time ( $t_{90}$ ), initial torque and final torque of the compound were determined. The compounds were cured in a Santhosh laboratory press having 46 × 46 cm platens at 150°C and 150 bar or a Wickert laboratory press 1600/5 × 4/3 at 150°C and 100 bar.

*Testing procedures* – Tensile tests were carried out on dumb-bell shaped specimens (Type 2) according to ISO 37. Tear strength was measured with angle test pieces according to ISO 34. Compression set tests were done at 70°C for 22 hrs

according to ISO 815. The hardness of the samples was measured with a Zwick hardness-tester Shore A, according to ASTM D 2240. Accelerated ageing tests were carried out according to ISO 188 on dumb-bell shaped specimens after putting them at 100°C for 24 hours and 48 hours in an air-ageing oven without forced aeration.

Swelling measurements were done in order to obtain information on the crosslink density. The elastically active network chain density was measured by equilibrium swelling in toluene for 72 hours at room temperature. The crosslink density was calculated according to the Flory-Rehner equation<sup>3</sup> with the Kraus correction<sup>4</sup> for carbon black. The crosslink distribution of the compounds was studied using thiol/amine chemical probes.<sup>5,6</sup>

Dynamic measurements of the uncured and cured compounds were performed with the RPA 2000. Frequency sweeps of cured compounds were done to measure the  $\tan\delta$  at 60°C as a measure of the rolling resistance of the tread compound. The frequency was varied from 0.1 to 209 rad/s at 0.56% strain.

A frequency sweep was also conducted on uncured compounds to measure the storage modulus. The measurement was done at a temperature of 100°C and a strain of 14%. The frequency was varied from 0.1 to 209 rad/s.

The curative migration was investigated by means of Scanning Electron Microscopy in combination with an Energy Dispersive X-ray spectrometer (SEM-EDX, LEO 1550 FEG, Thermo NORAN Instruments model Vantage). After cutting a cross-section of the vulcanised sample with a microtome (Leica EM FCS) at -130°C, elemental analysis was performed with a resolution of 2  $\mu\text{m}^2$ . Prior to the analysis, the sample was coated with carbon. The accelerating voltage was 15 kV and the sample distance was 9 mm. On every composite a line scan was performed in threefold.

## 8.3 RESULTS

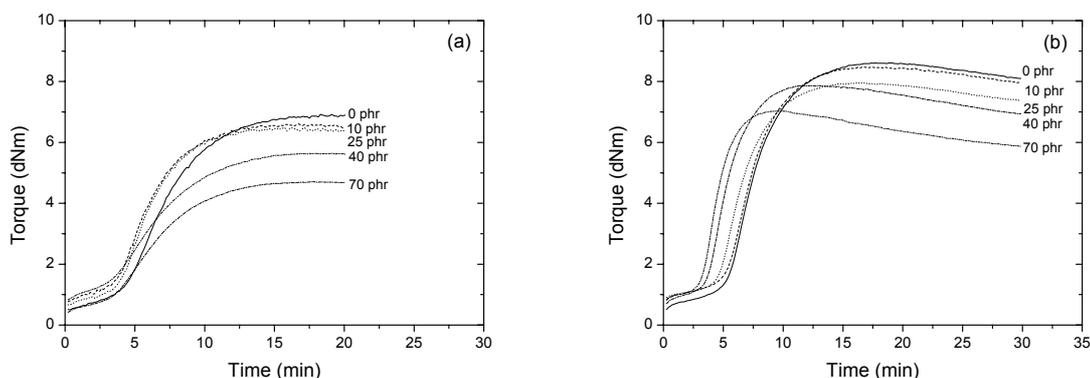
The effect of WLR1C and WLR1T reclaim, reclaimed with DBADPDS on the properties of a virgin compound is studied. The blends were compounded either with an adjusted curing system or with a fixed curing system. The results obtained with these two curing systems are compared. They are also compared to diphenyldisulphide reclaimed waste latex rubber in order to see the effect of the different reclaiming agents on the property profiles of the blended compounds. The adjusted cure system study was carried out at CUSAT whereas the fixed cure system study was done at UT.

### 8.3.1 Cure behaviour of the compounds mixed with WLR1C and WLR1T reclaim

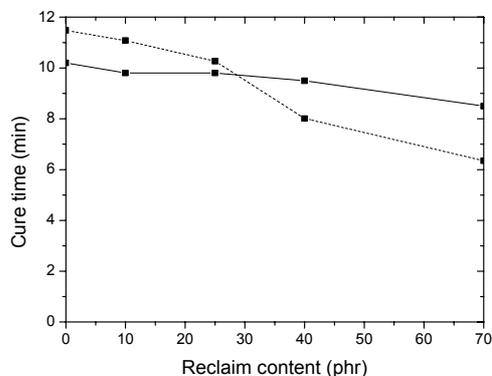
Figure 8.1 shows the rheogram of the virgin rubber compound and compounds containing various amounts of reclaim with an adjusted cure system and a fixed cure system at 150°C. The maximum torque as well as the difference between

final and initial torque are decreasing for both curing systems with an increase in the amount of reclaim in the compound. Another interesting point is that with a fixed curing system the reversion of the compound is higher than that for adjusted curing system. The same trends were found with WLR1 reclaimed with DPDS as shown in Figure 7.1, Chapter 7.

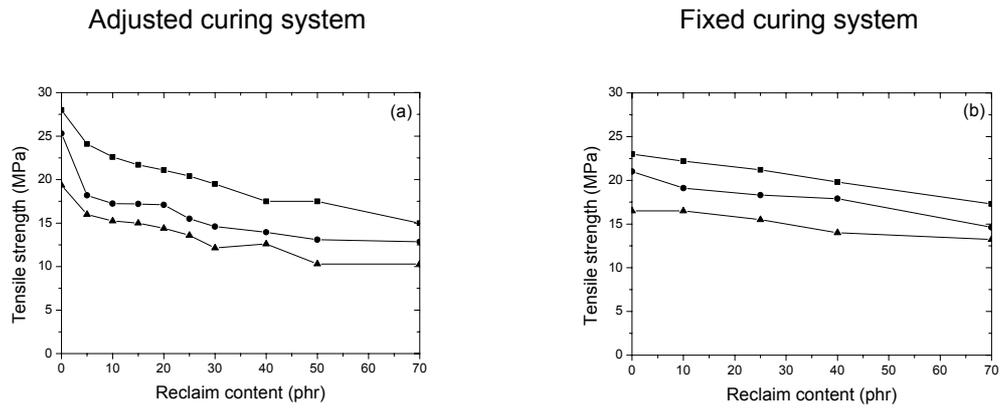
The optimum cure times,  $t_{90}$ , for the fixed cure system compounds and adjusted cure system compounds at 150°C are given in Figure 8.2. For the fixed cure system compounds, the cure time significantly decreases with increase in reclaim content. Only a very slight decrease in cure time is observed for the adjusted cure system compounds. The decrease in cure time as well as scorch time for the fixed curing system is also obvious from Figure 8.1 (b). The decrease in cure time for the fixed curing system compounds with DBADPDS reclaimed WLR1 is stronger than the decrease for compounds with DPDS reclaimed WLR1 (Figure 8.2 and Figure 7.2, Chapter 7).



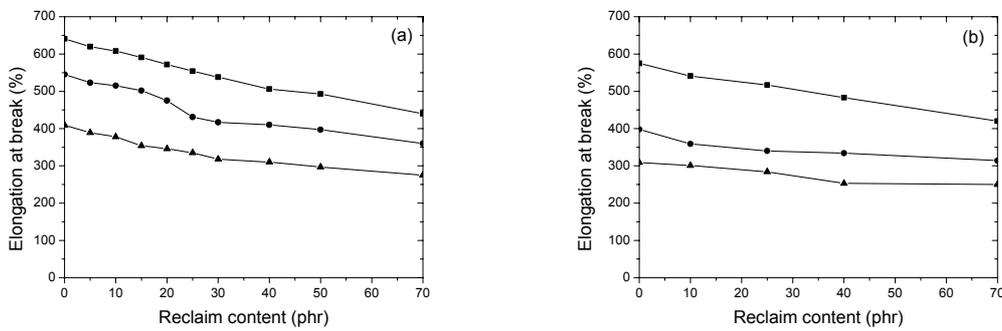
**Figure 8.1** Rheogram of the compounds containing various amounts of WLR1 reclaim for the adjusted cure system (a) and fixed cure system (b);  
(—): 0 phr; (— —): 10 phr; (- - -): 25 phr; (— -): 40 phr; (— - -): 70 phr.



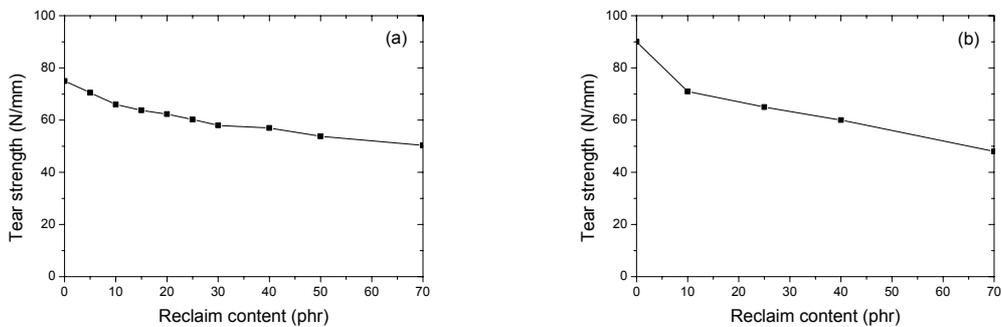
**Figure 8.2** Optimum cure time of adjusted cure system (—) and fixed cure system compounds (- - -) as a function of WLR1 reclaim content at 150°C.



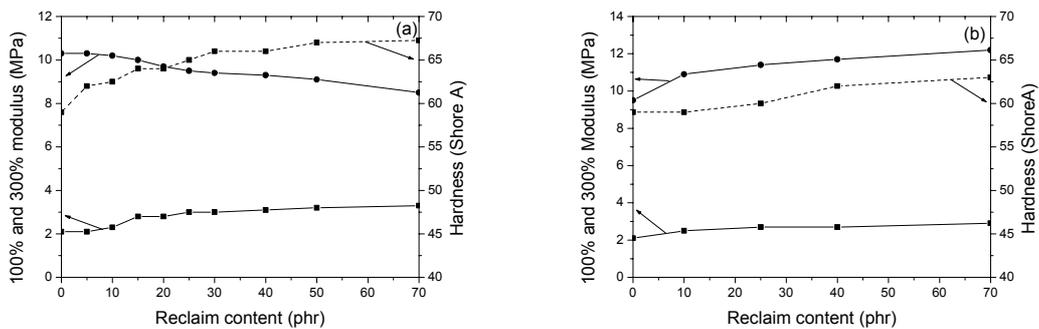
**Figure 8.3** Tensile strength as a function of WLR1 reclaim content; (■): unaged; (●): aged 24 hours at 100°C; (▲): 48 hours at 100°C.



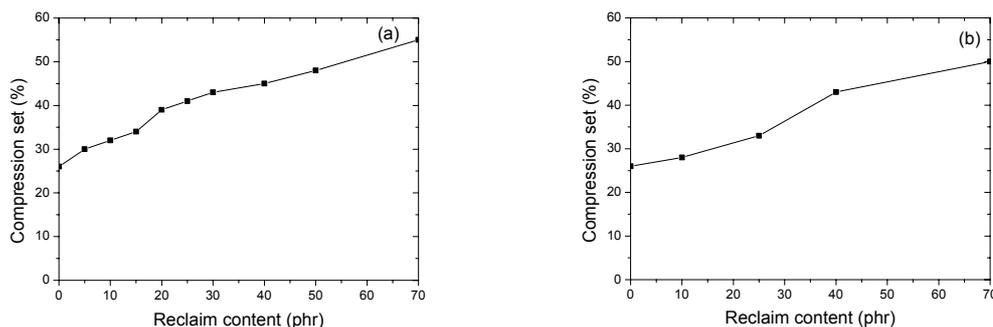
**Figure 8.4** Elongation at break as a function of WLR1 reclaim content; (■): unaged; (●): aged 24 hours at 100°C; (▲): 48 hours at 100°C.



**Figure 8.5** Tear strength as a function of WLR1 reclaim content



**Figure 8.6** Modulus (—) and hardness (- - -) as a function of WLR1 reclaim content; (■): 100% modulus; (●): 300% modulus.



**Figure 8.7** Compression set as a function of WLR1 reclaim content.

### 8.3.2 Mechanical Properties of the compounds mixed with WLR1C and WLR1T reclaim

In Figures 8.3 and 8.4 the tensile strength of the unaged as well as aged samples and elongation at break of the adjusted cure system compounds and fixed cure system compounds as a function of the reclaim content are given. The tensile strength decreases with increase of the reclaim content. An increase of ageing time results in a further decrease of the tensile strength. A sharp decrease in tensile strength is found for the adjusted curing system compounds with increasing reclaim contents. The tensile strength of aged samples decreases strongly with the first 10 phr of reclaim but then levels off. Fixed curing system compounds behave differently: A linear decrease in tensile strength is observed with increase in the amount of reclaim for unaged and aged compounds. Since the adjusted cure system and fixed cure system were compounded with different feedstock the absolute values cannot be compared, but the relative changes with increase of the reclaim can be compared. For the fixed curing system the decrease in tensile strength with the increase in the reclaim content is less compared to the adjusted cure system. At higher concentrations of reclaim the fixed cure system compounds containing DBADPDS reclaimed WLR1 show higher tensile strength values compared to DPDS reclaimed WLR1 compounds (Figure 7.4, Chapter 7). Elongation at break values are also decrease for both the cure system compounds with the increase in the amount of reclaim. A linear decrease in observed for both cases.

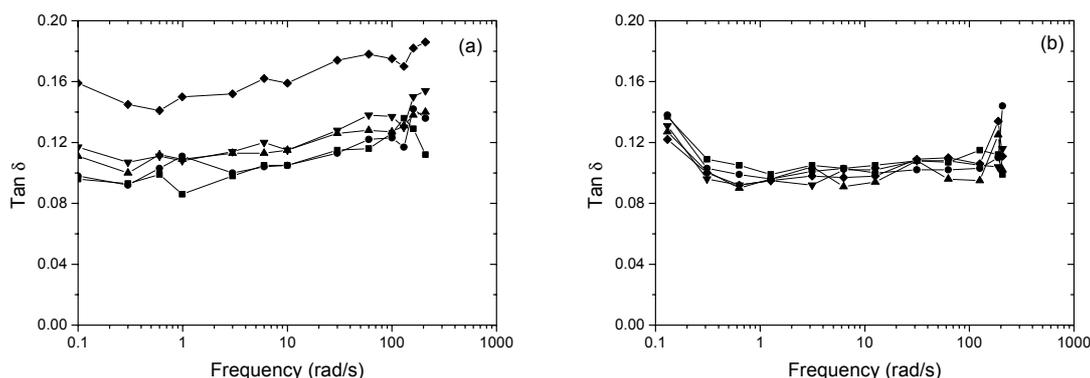
The tear strength values for both cure systems against reclaim content are given in Figure 8.5. Tear strength decreases with an increasing amount of reclaim in the compound. A strong decrease of tear strength is observed in the initial period and afterwards a linear decrease is observed with fixed curing system compounds, whereas a less strong decrease in tear strength is observed with adjusted curing system compounds.

Figure 8.6 shows the modulus at 100% as well as at 300% elongation and hardness against the reclaim content for both compounds. A small increase in 100% modulus and hardness with increasing amount of reclaim is found for both cure systems. The modulus at 300% elongation is decreasing for the adjusted cure system, whereas it is increasing in the fixed cure system compounds with increasing amounts of reclaim.

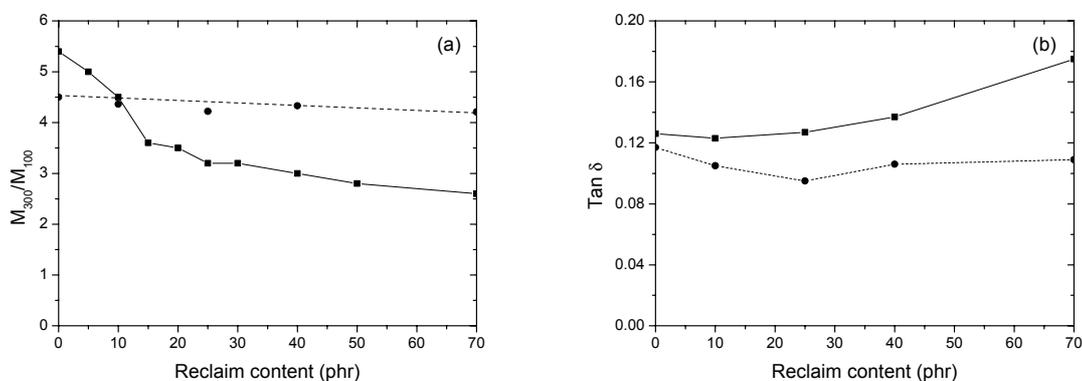
The compression set of the adjusted cure system compounds as well as the fixed cure system compounds as a function of the reclaim content is given in Figure 8.7. The compression set increases with an increase of the reclaim content.

### 8.3.3 Dynamic viscoelastic properties of the compounds mixed with WLR1C and WLR1T reclaim

The loss tangent:  $\tan\delta$ ,<sup>7</sup> of this material is important, because  $\tan\delta$  values in the temperature range of 50–80°C are a measure of tyre rolling resistance. As the compound used in this investigation is a typical truck tyre tread compound, this is a prominent characteristic. The loss tangent is the ratio of the work converted into heat (or the work absorbed by the compound) and the work recovered for any given energy input. The  $\tan\delta$  values of the adjusted cure system and fixed cure system compounds against the frequency at 60°C for various cured compounds are depicted in Figure 8.8. The  $\tan\delta$  is increasing with an increase in reclaim content for a wide frequency range for the adjusted curing system compounds. When the cure system is fixed, the  $\tan\delta$  values remain all in the same range over a wide frequency range. A significant increase in  $\tan\delta$  is observed for the adjusted cure system compounds



**Figure 8.8**  $\tan\delta$  of the adjusted cure system (a) and fixed cure system compounds (b) with WLR1 reclaim as a function of frequency; (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr.



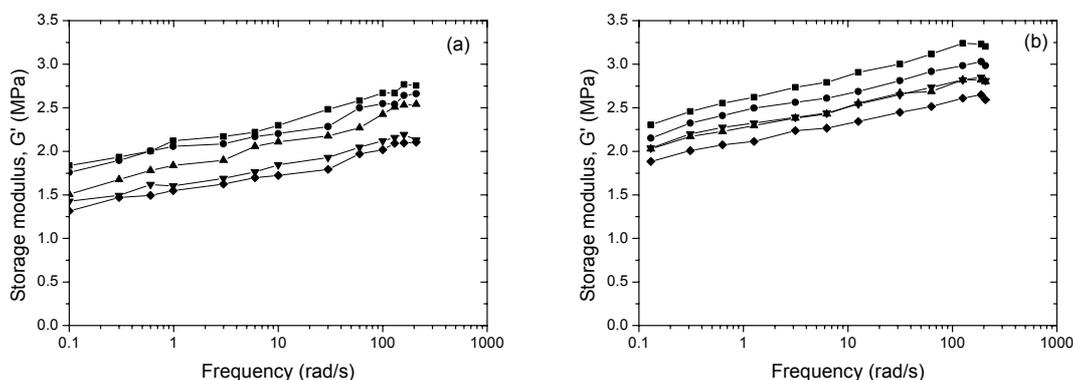
**Figure 8.9**  $E_{300}/E_{100}$  (a) and  $\tan\delta$  (b) for adjusted cure system (—) and fixed cure system (---) as a function of WLR1 reclaim content.

when the amount of reclaim is increased from 0 phr to 70 phr; in contrast to this, the increase is marginal in the case of the fixed cure system compounds. The  $\tan\delta$  results found with DPDS reclaimed WLR1 show the same trend as the DBADPDS reclaimed material (Figure 7.12, Chapter 7).

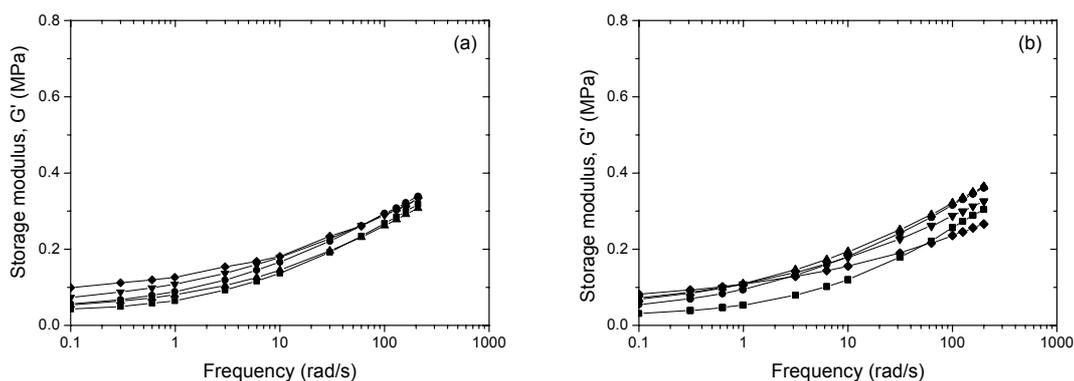
The  $M_{300}/M_{100}$  as well as  $\tan\delta$  values at 15 Hz and 60°C as a function of the reclaim content for cured compounds are given in Figure 8.9. The  $M_{300}/M_{100}$  values are decreasing and  $\tan\delta$  values are increasing stronger for the adjusted cure system compounds compared to the fixed cure system compounds. A smaller decrease in the  $M_{300}/M_{100}$  values and almost constant  $\tan\delta$  values are found for the fixed cure system compounds.

The storage modulus of the vulcanized compounds for both cure systems as a function of frequency at 60°C and 0.56% strain for various cured compounds is plotted in Figure 8.10. The storage modulus is found to decrease with increasing amount of reclaim for both cure systems. This indicates that the revulcanisates are not able to achieve the modulus values of the virgin vulcanisates: The elasticity of the revulcanised rubbers is lower than that of virgin vulcanisates.

The storage moduli of the unvulcanised compounds for the two cure system compounds against the frequency at 100°C and 14% strain for different uncured compounds are given in Figure 8.11. Both compounds show an increase in storage modulus with increase of reclaim concentration. This trend is very distinct at lower frequencies; at higher frequencies the trend is not very clear. No significant difference is found between adjusted and fixed curing system compounds.



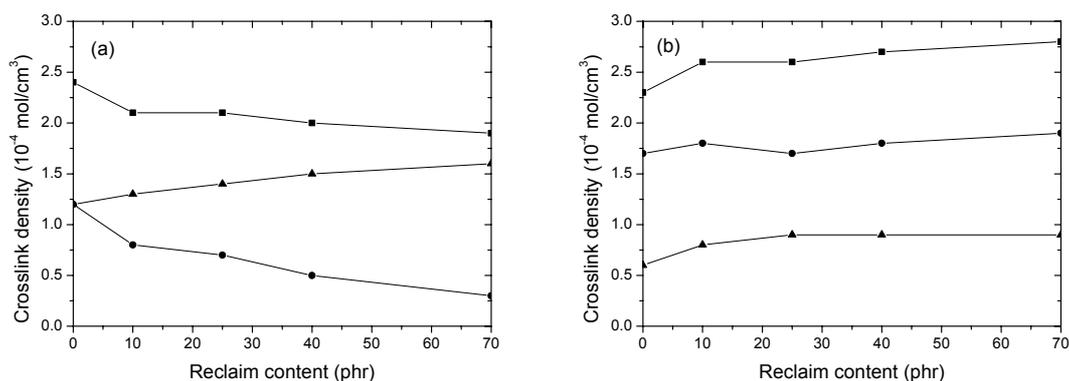
**Figure 8.10** Storage modulus of adjusted cure system (a) and fixed cure system compounds (b) after curing with WLR1 as a function of frequency; (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr.



**Figure 8.11** Storage modulus of adjusted cure system (a) and fixed cure system compounds (b) before curing with WLR1 reclaim as a function of frequency; (■): 0 phr; (●): 10 phr; (▲): 25 phr; (▼): 40 phr; (◆): 70 phr.

### 8.3.4 Crosslink density and distribution of the compounds mixed with WLR1C and WLR1T reclaim

In Figure 8.12 the overall crosslink density and crosslink distribution of the adjusted cure system and fixed cure system compounds as a function of reclaim content are depicted. For the adjusted cure system compounds the overall crosslink density and the amount of polysulphidic crosslinks decrease, while the number of mono- and disulphidic crosslinks increases with increase of reclaim content. For the fixed cure system compounds, the overall crosslink density, polysulphidic crosslinks as well as the mono- and disulphidic crosslinks increase with increase in reclaim content, in accordance with the results found in Chapter 7.



**Figure 8.12** Crosslink distribution for adjusted cure system (a) and fixed cure system compounds (b) as a function of WLR1 reclaim content; (■): overall; (●): polysulphidic; (▲): mono- plus disulphidic

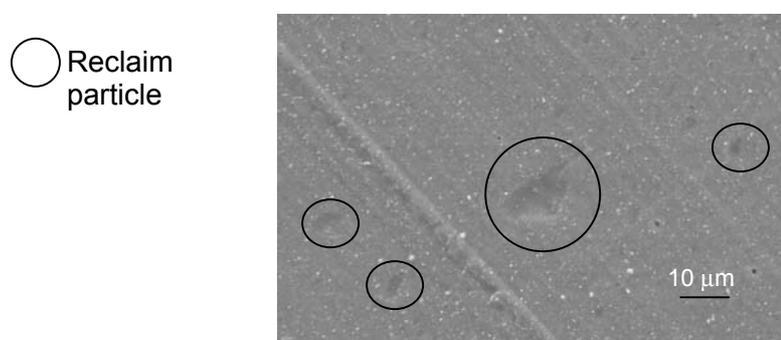
The amount of mono- and disulphidic crosslinks could not separately be calculated because of the phase inversion which occurred during the reaction with hexane-1-thiol and piperidine, where all the poly- and disulphidic crosslinks are broken. As a consequence, a very high number of monosulphidic crosslinks is observed for the hexane-1-thiol treated samples. This phenomenon is already explained in detail in Chapter 7.

### 8.3.5 Morphology study : Scanning Electron Microscopy – Energy Dispersive X-ray spectrometry (SEM-EDX)

It is important to point out that the morphology of the disperse rubber particles (size distribution and shape) will affect the mechanical properties of the polymer blend. The final morphology of an immiscible polymer blend is known to depend on several factors: the rheological properties of the components (viscosity, elasticity), the composition, the processing conditions (deformation rates, stresses and temperature) and the interfacial properties.<sup>8</sup>

An EDX study was performed to determine the sulphur concentration in the virgin matrix and the reclaimed particle. A concentration difference between these two phases can create a curing mismatch between the phases making the material susceptible to early failure.

Figure 8.13 shows the SEM photomicrographs of a cured compound loaded with 40 phr reclaim. The dark areas are the reclaim particles, which are dispersed in the NR/BR phase. These particles are generally circular, but irregular shapes are also observed.

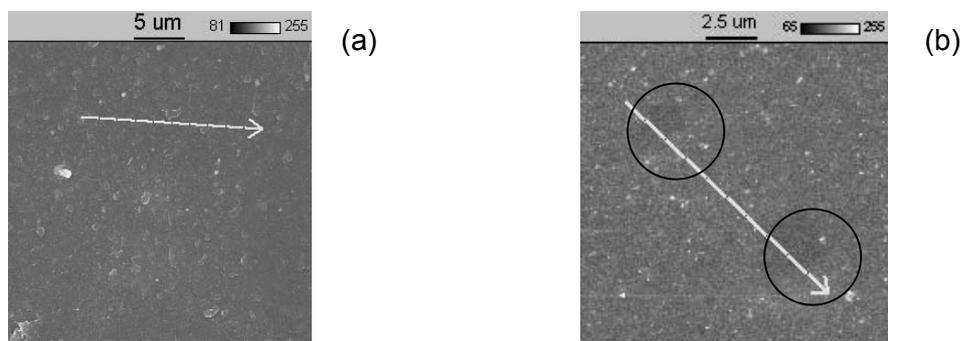


**Figure 8.13** SEM picture of a compound mixed with 40 phr WLR1T reclaim

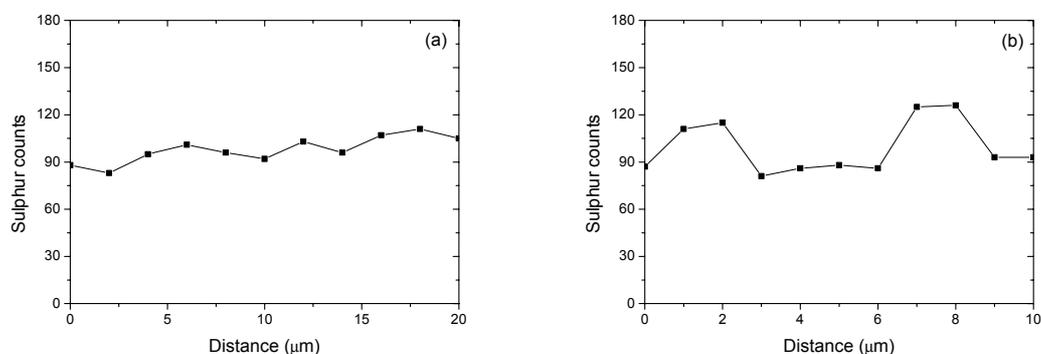
The SEM-EDX measurements of samples containing 0 phr and 70 phr are shown in Figures 8.14 and 8.15:

A SEM picture is coupled with the EDX analysis of the sulphur content in the reclaim particle and in the matrix. A line scan is carried out to measure the difference in the amount of sulphur in the matrix and in the reclaim particle. In the virgin compound, Figure 8.15(a), a constant sulphur count is observed showing that the sulphur is uniformly distributed within the matrix. In Figure 8.15(b), where the sample contains 70 phr of reclaim, a difference in the amount of sulphur is observed between the matrix and reclaim particle: A higher amount of sulphur is observed in the reclaim

particle. the matrix and reclaim particle: A higher amount of sulphur is observed in the reclaim particle.



**Figure 8.14** SEM picture of compounds containing 0 phr (a) and 70 phr (b) WLR1T reclaim



**Figure 8.15** Sulphur content of compounds mixed with 0 phr (a) and 70 phr (b) WLR1T reclaim as a function of line scan distance.

## 8.4 DISCUSSION

The cure behaviour, mechanical properties, dynamic viscoelastic properties, crosslink density, morphology and sulphur distribution were studied for WLR1 reclaim in a blend with a virgin compound: All properties were influenced by the addition of reclaim. A general discussion of the influence on the mechanical and dynamic viscoelastic properties on the basis of presence of gel, variation in crosslink density and distribution and the other factors was already done in Chapter 7. In the current chapter the discussion part will be restricted to the main differences found between the properties of compounds prepared by blending DPDS reclaimed and DBADPDS reclaimed WLR1 with the virgin compound. The differences found between the adjusted curing system and fixed curing system compounds of DBADPDS reclaimed WLR1 are comparable to DPDS reclaimed WLR1.

At higher concentrations of reclaim the cure time of the compounds with DBADPDS reclaimed WLR1 is shorter (Figure 8.2) compared to DPDS reclaimed WLR1 (Figure 7.2). This can be related to the difference in the chemical structure of the reclaiming agents: DPDS has the disulphide functionality (-S-S-) and DBADPDS has an additional amido (-NHCO-) group. Nitrogen-containing compounds in general accelerate the curing reaction, leading to a decrease in cure time with increase in reclaim content.

Slightly higher tensile values for both adjusted and fixed curing system compounds, are found when DBADPDS reclaimed WLR1 is used in comparison to DPDS reclaimed WLR1 at higher concentrations of reclaim - Figures 8.3 and 7.4. This could be due to the presence of some unreacted DPDS present in the reclaim which becomes reactive at the curing temperature and initiates some side reactions, lowering the tensile strength. The typical disulphide smell was noted when the DPDS reclaimed WLR1 containing compounds were revulcanised. DBADPDS by virtue of its high molecular weight (456.57 g/mol) compared to DPDS (218.34 g/mol) is present in a lower molar concentration and has a lower volatility and both factors are reducing the smell. Furthermore, the probability of the presence of unreacted DPDS is higher than the probability of having unreacted DBADPDS.

A comparison of the mechanical and dynamic properties of adjusted and fixed cure system compounds show that fixed cure system compounds have better properties compared to adjusted cure system compounds for the same amount of reclaim concentration, Figures 8.3 – 8.10. This is due to the difference in the sulphur crosslink distribution and crosslink density between adjusted cure system and fixed cure system: Figure 8.12. For adjusted cure system the overall crosslink level as well as polysulphidic level decreases and the mono- plus disulphidic crosslinks increases with increasing reclaim content in the compound. In the case of fixed cure system a different trend is observed. The overall as well as the polysulphidic crosslinks increases, also the mono- plus disulphides. But, most important is the amount of overall and polysulphide level which have an opposite behaviour for adjusted and fixed cure system: Both increases for fixed cure system, whereas both decreases for adjusted cure system. This explains the better mechanical and dynamical performance of fixed cure system compounds over adjusted cure system compounds.

EDX measurements show a different level of sulphur between the matrix and the reclaim particle. From Figure 8.15 the concentration of sulphur in the matrix and reclaim particle was calculated from the sulphur counts. The matrix contains 1.4 wt.% of sulphur and the reclaim particles contain 2.6 wt.% of sulphur, which is slightly lower than the level of sulphur measured with diphenyldisulphide reclaimed WLR1 vulcanisate, Figure 7.22. A theoretical calculation was done to estimate the amount of sulphur present in the DBADPDS reclaimed WLR1 vulcanisate: the reclaim particles contain 1.2 wt.% of sulphur. This is lower than the amount of sulphur detected for diphenyldisulphide reclaimed sample, which was 1.4 wt.%, for details see Chapter 7. This small difference is due to the difference in the sulphur content between the two reclaiming agents, DPDS and DBADPDS. The amount of sulphur measured in the matrix of the 70 phr reclaim added sample is the same as that measured in the 0 phr reclaim containing sample. This indicates that the added

curatives are homogeneously distributed within the matrix and the reclaim particle. The higher level of sulphur in the reclaim particle is due to the addition of sulphur which is already present in the reclaim particle (1.2 wt.%) and the amount obtained from the curative package (1.4 wt.%). Both sulphur contributions give a total of 2.6 wt.% of sulphur, which is exactly observed in the EDX measurement. No indication of sulphur migration between the virgin matrix and the reclaim phase is found, as this would lead to a smaller difference in sulphur concentration between the two phases.

## 8.5 CONCLUSIONS

Reclamation of natural rubber latex based rubber using 2,2'-dibenzamido-diphenyldisulphide as reclaiming agent, produces a valuable raw material to replace virgin natural rubber in a truck tyre tread composition. For progressive replacement of virgin natural rubber by the reclaim up till 70% by weight, two alternatives were investigated for the curing system: Adjustment or reduction of the curing system with increasing reclaim content, to compensate for the extra sulphur-amount brought along by the reclaim, in order to keep the total sulphur in the compound constant. Fixed curing system, as if the reclaim were equivalent to virgin natural rubber. In comparison with DPDS reclaimed WLR1, as dealt with in Chapter 7, the compounds with DBADPDS reclaimed WLR1 show shorter cure times for both curing systems. With the use of the adjusted cure package a significant decrease in properties is generally observed with increasing reclaim content. With the fixed cure system properties like tensile strength and compression set do still deteriorate, but to a lesser extent. Most conspicuous are the values obtained for  $\tan\delta$  and  $M_{300}/M_{100}$ , representative for the rolling resistance of tyres. With the fixed cure system both quantities indicate an improved rolling resistance with increasing amounts of reclaim vs. the virgin compound. With the adjusted cure system both quantities deteriorate. This is the consequence of the predominantly polysulphidic crosslink network obtained with the fixed cure system, well known to favour dynamic properties of rubber compounds, vs. the mainly mono- and disulphidic crosslink network obtained with the adjusted cure system.

## 8.6 REFERENCES

1. V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, Paper presented at the meeting of the Rubber Division, American Chemical Society Cleveland, Ohio, Oct. 5-8, 2004 and Rubber Chem. Technol, (2005), accepted for publication.
2. F. I. Hoover, Paper presented at the meeting of the Rubber Division, American Chemical Society, Pittsburg, Oct. 8-11, 2002.
3. P. J. Flory, J. Rehner, Jr., J. Chem. Phys. **18**, (1950), 108.
4. G. Kraus, J. Appl. Polym. Sci., **7**, (1963), 861.
5. D. S. Campbell, J. Appl. Polym. Sci. **13**, (1969), 1201.
6. D. S. Campbell, B. Saville, in "Proceedings of the International Rubber Conference", Brighton, UK (1967).
7. M. J. Wang, Rubber Chem. Technol., **71**, (1998), 520.
8. C. H. Scuracchio, R. E. S. Bretas, A. I. Isayev, J. of Elastomers and Plastics, **36**, (2004), 45.



# Chapter 9

---

## Summary and final remarks

---

A general summary of the complete work described in the previous chapters is given in this chapter. It commences with the objectives of the thesis, goes through the initial studies to define the system, describes the fundamental research, which is the core of this work, and ends with an application study. The chapter is completed with a final remark and suggestions for future research in this area.

### 9.1 MOTIVATION

The percentage of waste rubber products rejected from the latex industry is quite high because of defects such as pinholes, craters and blisters encountered in the articles due to entrapped air and dirt particles in the latex compound. Furthermore, the latex rubber waste contains about 95% of rubber hydrocarbon of very high quality, as it rarely contains fillers. Due to this reason the latex waste is a promising material for producing reclaimed rubber of higher quality compared to worn-out tyres and other rubber rejects. The main goal of this research is to study the most important factors influencing the quality of the reclaim and to identify the best reclaiming conditions to generate a high-quality recycling product. This investigation is done by studying the effect of feed stock characteristics, reclaiming agents and process conditions on the quality of reclaimed rubber. In a fundamental study with low molecular weight model compounds the reaction mechanism and chemistry of the reclamation of rubber with aliphatic amines and aromatic disulphides is elucidated.

## 9.2 GENERAL SUMMARY

In Chapter 2, an overview of the reclamation of sulphur vulcanised rubbers as described in the literature is given. The chapter discusses the chemistry of main-chain scission as well as crosslink scission in vulcanised rubber with different reclaiming agents. The relevance of temperature and shearing forces is emphasised in a separate section. A detailed description of the chemical probes, which selectively cleave the crosslinks in the vulcanised rubber, is given. The literature review unveils that, from a chemical point of view, reclamation is a complex process, it is difficult to analyse and is a complicated interplay between the various reactions. It also shows the limited fundamental knowledge in the field of rubber reclamation and the necessity to use modern techniques like model compound studies to understand the underlying principles of rubber reclamation.

From the literature survey it is revealed that the reclaiming agents for natural rubber are amines and disulphides. Especially the increasing usage of disulphides is reported. Therefore, the reclamation study of the natural rubber based latex waste products was started by using diphenyldisulphide as reclaiming agent: Chapter 3. This compound is commonly used for the reclamation of natural rubber based non-latex production waste. The efficiency of this compound was studied at different concentration levels, different reaction temperatures and times. A complete characterisation of the reclaimed rubber was done by viscosity measurements as well as a network characterisation through sol-gel analysis, crosslink density and crosslink distribution measurements. The ratio of main-chain scission of the rubber polymer and crosslink scission of the sulphur network during reclamation was also studied. The result of this study was that diphenyldisulphide is an efficient reclaiming agent in a temperature range of 170 – 190°C. This compound is capable of breaking all poly- and disulphide crosslinks in the vulcanisate during reclamation, but is unable to break the monosulphides present in the vulcanisate. Studies of the ratio of main-chain rupture to crosslink rupture showed that reclamation mainly occurred through rupture of crosslinks rather than by main-chain scission. The study of the reclamation chemistry of diphenyldisulphide with natural rubber vulcanisates revealed that the reaction is occurring through hydrogen abstraction. Another mechanism, which is commonly accepted, is a radical reaction.

A comparative study of amine and disulphide as reclamation agents is performed in Chapter 4. Hexadecylamine is selected as the amine reclamation agent because of the increased nucleophilicity of the nitrogen by the inductive effect of the carbon backbone and the higher boiling point of the long chain amine compared to the short chain aliphatic amines. The final results show that hexadecylamine is less effective as a reclaiming agent for sulphur vulcanised natural rubber latex product compared to diphenyldisulphide: Reclamation in the presence of hexadecylamine results additional crosslinks compared to thermo-mechanical reclamation without any reclaiming agent. The crosslink distribution studies showed that some polysulphidic crosslinks remain, when hexadecylamine is used, compared to no polysulphidic linkages in the reclaim treated with diphenyldisulphide. The formation of a complex

between zinc-ions and polysulphidic crosslinks that is stabilised by amines is proposed as a stable intermediate reducing the rate of crosslink scission.

In Chapter 5 the devulcanisation mechanism of natural rubber vulcanisates with amine and disulphide is studied by means of low molecular weight model compounds. Model compound studies are used extensively and have proven to be a suitable method for the study of vulcanisation reactions, and this technique was extended within the present work for the study of devulcanisation reactions. 2,3-dimethyl-2-butene ( $C_6H_{12}$ ) is used as a low-molecular weight model with only equivalent allylic positions.  $C_6H_{12}$  is firstly vulcanised with a mixture of sulphur, zinc stearate and N-cyclohexyl-2-benzothiazylsulphenamide as accelerator at  $140^\circ C$ , resulting in a mixture of addition products of the general formula  $C_6H_{11}-S_x-C_6H_{11}$ . The compounds are isolated and identified by High Performance Liquid Chromatography with respect to their various sulphur ranks. In a second stage, the vulcanised products are devulcanised using the agents mentioned above at  $200^\circ C$  and  $210^\circ C$ . The kinetics and chemistry of the breakdown of the sulphur-bridges during devulcanisation are monitored at both temperatures. The devulcanisation efficiency depends on the distribution of the sulphur ranks: Both devulcanisation agents, diphenyldisulphide and hexadecylamine, are effective agents in breaking polysulphidic and trisulphidic crosslinks at  $200^\circ C$  and  $210^\circ C$ . The rate of breakdown of the polysulphidic bonds increases with increasing concentration of the devulcanisation agents and increasing temperature. Large amounts of mono- and disulphidic crosslinks are formed when diphenyldisulphide is used as devulcanisation agent and the amount of mono- and disulphides increases with increasing concentration of diphenyldisulphide. With increasing concentrations of hexadecylamine as devulcanisation agent, the amount of mono- and disulphidic crosslinks is significantly reduced, relative to the case where no devulcanisation agent is used. The main difference in the reaction between amine and disulphide is explained by the presence of sulphur in diphenyldisulphide and hence the ability to act as a sulphur donor during the reactions.

The results obtained with the model compounds gave a new insight into the basic chemistry of devulcanisation, however they cannot directly be translated to the reclaiming mechanism for rubber as a very complex system. However, the effect of amines and disulphides on main-chain scission and the effect of shear could not be analysed by the model compound study.

Since diphenyldisulphide works effectively as a reclamation agent for a natural rubber vulcanisate, an in-depth study on various diphenyldisulphides was performed: Chapter 6. The effect of different substituents, an amino group and a benzamido group in ortho positions of the phenyl ring relative to the disulphidic bridge of the diphenylsulphides on the reclamation efficiency of natural rubber based latex products was studied. This comparative study shows that benzamido substituted diphenyldisulphides are able to reclaim the vulcanisate at a temperature level approximately  $20^\circ C$  below the temperature levels used in the production of reclaim. Another advantage of the benzamido substituted compound is the reduced smell during the reclamation process and of the final reclaim. The increased efficiency of a benzamido substituted diphenyldisulphide is due to the easy breakage of the S-S bond, caused by resonance and steric effects, resulting in a higher amount

of sulphidic radicals compared to the other agents. The higher molecular weight of this compound is one reason for the reduced smell of the reclaim.

The reclaimed rubber produced from natural rubber based latex waste is a valuable raw material to replace virgin rubber in any rubber products. The reclamation of the vulcanisate is performed with diphenyldisulphide, Chapter 7, and 2,2'-dibenzamidodiphenyldisulphide, Chapter 8, and both are used in a truck tyre tread compound by replacement of virgin natural rubber with reclaimed rubber. Two different compounding principles are used: Adjusted cure system - the concentration of the curing additives was adjusted to compensate for the extra input of sulphur and accelerators by the reclaim; and fixed cure system – without adjustment of the curing additives.

The study of the mechanical and dynamic properties, the crosslink density and distribution as well as sulphur distribution shows similar results for the diphenyldisulphide and 2,2'-dibenzamidodiphenyldisulphide reclaimed samples. In the case of the adjusted cure package a significant influence on the properties is generally observed at higher reclaim loadings. With the fixed cure system properties like tensile strength and compression set are still influenced, but to a lesser extent. Most conspicuous are the values obtained for  $\tan\delta$  and  $M_{300}/M_{100}$ , representative for the rolling resistance of tyres. With the fixed cure system both quantities indicate an improved rolling resistance with increasing amounts of reclaim versus the virgin compound. With the adjusted cure system both properties deteriorate. This is the consequence of the predominantly polysulphidic crosslink network obtained with the fixed cure system, well known to favour dynamic properties of rubber compounds versus the mainly mono- and disulphidic crosslink network obtained with the adjusted cure system.

In terms of processing behaviour the difference between the diphenyldisulphide and 2,2'-dibenzamidodiphenyldisulphide reclaimed samples was a shorter curing time of the latter compounds. This is due to the presence of the amido group (-NHCO-) in 2,2'-dibenzamidodiphenyldisulphide, since nitrogen containing compounds in general accelerate the curing reactions. An interesting general observation from the studies in Chapters 7 and 8 is, that the quality of the reclaim is independent from the feedstock under the condition that the reclaiming process for each feedstock is optimal. Combination of Scanning Electron Microscopy and Energy Dispersive X-ray spectrometry shows a difference in the sulphur concentration between the reclaimed rubber phase and the virgin rubber phase in the compound: A higher concentration of sulphur is found in the reclaimed rubber phase compared to the virgin matrix. This difference in sulphur concentration is not due to migration of sulphur between the matrix and the reclaim but is rather due to a homogeneous distribution of sulphur throughout the matrix and the reclaim particles during mixing of the compound.

### 9.3 FINAL REMARKS

In this research work an improved solution for the reclamation process of sulphur vulcanised natural rubber based latex waste, which is rich in rubber hydrocarbon, is developed. The processing window for the reclamation of latex waste is very narrow and temperature has a profound effect in the reclamation process. A small variation in temperature has a major influence on the breakdown of the final vulcanisate. Usage of reclaiming agent improves the quality of the final reclaim and determines the reclamation reaction mechanism. In this study an attempt is made to combine the science as well as technology of reclamation to produce a high quality reclaim that can be used in higher concentrations along with virgin rubber or can be used alone to manufacture rubber products from recycled material. Suggestions for the future research in this area include using a combination of hexadecylamine and diphenyldisulphide as reclaiming agent. This is similar to the usage of thiol-amine chemical probe to cleave the sulphur bonds in natural rubber vulcanisate. The model compound studies can be improved by using squalene as a low molecular weight compound, a better representative for natural rubber.



---

## Samenvatting en afsluitende opmerkingen

---

In dit hoofdstuk wordt een algemene samenvatting van het complete in de vorige hoofdstukken beschreven werk gegeven. Het begint met de doelstellingen van het proefschrift, doorloopt de initiële studies voor de definiëring van het systeem, beschrijft het fundamentele onderzoek, wat de kern is van dit werk en eindigt met een toepassingsstudie. Het hoofdstuk wordt gecompleteerd met een afsluitende opmerking en suggesties voor toekomstig onderzoek op dit gebied.

### 9.1 MOTIVATIE

Het percentage afval rubber producten, afgekeurd door de natuur-rubber latex industrie, is behoorlijk hoog. Dit komt door defecten, zoals gaatjes, kraters en blazen, die worden veroorzaakt door ingesloten lucht en vuildeeltjes in het latex mengsel. Echter, latex rubber afval bevat ongeveer 95% rubber koolwaterstof van zeer hoge kwaliteit, doordat het nauwelijks vulstoffen bevat. Om deze redenen is het latex afval een veelbelovend materiaal voor de productie van gereclaimed rubber, in vergelijking met versleten banden en andere afgekeurde rubber producten. Het hoofddoel van dit onderzoek is het bestuderen van de belangrijkste factoren, welke van invloed zijn op de kwaliteit van het reclaim en de identificering van de beste reclaim condities voor het regenereren van een hoog kwaliteits recycling produkt. Dit onderzoek is gedaan door het onderzoeken van het effect van de grondstof kenmerken, reclaiming hulpmiddelen en proces condities op de kwaliteit van het gereclaimde rubber. In een fundamenteel onderzoek met lage molecuulgewicht model verbindingen wordt het reactie-mechanisme en de chemie van de reclaiming van rubber met alifatische amines en aromatische disulfides toegelicht.

### 9.2 ALGEMENE SAMENVATTING

In hoofdstuk 2 wordt een overzicht gegeven van het reclaimen van met zwavel ge vulkaniseerde rubbers, zoals staat beschreven in de literatuur. Het hoofdstuk behandelt de chemie van hoofdketen-breuk alsmede van cross-link breuk

in ge vulkaniseerd rubber met verschillende reclaiming hulpmiddelen. De relevantie van temperatuur en frictiekrachten wordt in een apart gedeelte benadrukt. Een gedetailleerde beschrijving wordt gegeven van chemical probes, die selectief de cross-links in ge vulkaniseerd rubber verbreken. Het literatuur overzicht toont aan dat, vanuit een chemisch gezichtspunt, reclaimen een complex proces is, dat moeilijk te analyseren is en een complex samenspel is tussen verschillende reacties. Het toont ook de beperkte fundamentele kennis aan op het gebied van rubber reclaiming en de noodzaak van het gebruik van moderne technieken, zoals model compound studies, voor het begrijpen van de onderliggende principes van rubber reclaiming.

Uit het literatuur overzicht blijkt, dat de gebruikelijke reclaiming hulpmiddelen voor natuur rubber zijn: amines en disulfides. Vooral het toenemende gebruik van disulfides wordt vermeld. Vandaar dat de reclaiming studie van latex afval, gebaseerd op natuur rubber, werd begonnen met behulp van difenyldisulfide als reclaiming hulpmiddel: Hoofdstuk 3. Deze verbinding wordt veelvuldig gebruikt voor het reclaimen van op natuurrubber gebaseerd niet-latex productie-afval. De efficiëntie van deze verbinding is onderzocht bij verschillende concentraties, temperaturen en reactie-tijden. Een complete karakterisering van het reclaim is uitgevoerd aan de hand van viscositeits metingen. Netwerk karakterisering is uitgevoerd met behulp van sol-gel analyses, cross-link dichtheid bepalingen en cross-link verdeling metingen. De verhouding van hoofdketenbreuk van het rubber polymeer tot cross-link breuk van het zwavel netwerk is ook onderzocht. De uitkomst van dit onderzoek is, dat difenyldisulfide een efficiënt reclaiming hulpmiddel is in het temperatuur gebied van 170-190°C. Deze verbinding is in staat om alle poly- en disulfide bindingen in het vulkanisaat te verbreken tijdens het reclaimen, maar niet om de aanwezige monosulfide cross-links af te breken. Onderzoek naar de verhouding van hoofdketen breuk ten opzichte van cross-link breuk heeft aangetoond dat reclaiming voornamelijk plaatsvindt door verbreken van cross-links. De studie naar de reclaiming chemie van difenyldisulfide met natuur rubber vulkanisaten heeft aangetoond, dat de reactie plaatsvindt door waterstof abstraktie. Een ander mechanisme, dat algemeen wordt geaccepteerd, is een radicaal reactie.

Een vergelijkend onderzoek van amines en disulfide als reclaiming hulpmiddelen is uitgevoerd in hoofdstuk 4. Hexadecylamine is geselecteerd als amine reclaiming hulpmiddel, door de verhoogde nucleofiliteit van het stikstof door het inductieve effect van de koolstof hoofdketen. Tevens heeft hexadecylamine een hoog kookpunt ten gevolge van de lange keten, in vergelijking met korte keten alifatische amines. De resultaten tonen aan, dat hexadecylamine minder effectief is als reclaiming hulpmiddel in vergelijking met difenyldisulfide voor met zwavel ge vulkaniseerde natuur rubber latex producten. Reclaiming in de aanwezigheid van hexadecylamine resulteert in de vorming van additionele cross-links, vergeleken met thermisch-mechanische reclaiming zonder enig reclaiming hulpmiddel. Studies naar de lengte-verdeling van de cross-links laten zien, dat enkele polysulfide cross-links overblijven bij gebruik van hexadecylamine, terwijl er geen polysulfide bindingen overblijven in met difenyldisulfide behandelde reclaim. De vorming van een complex tussen zink-ionen en polysulfide cross-links, dat wordt gestabiliseerd door amines, wordt aangenomen als een stabiel intermediair, dat de snelheid van de cross-link breuk verlaagt.

In hoofdstuk 5 wordt het devulkanisatie mechanisme van natuur rubber vulkanisaten met amine en disulfide onderzocht met behulp van laag molecuulgewicht verbindingen. Dit soort studies worden veelvuldig gebruikt en hebben bewezen een geschikte methode te zijn voor de bestudering van vulkanisatie reacties. Deze techniek werd binnen dit onderzoek ook gebruikt voor de bestudering van devulkanisatie reacties. 2,3-dimethyl-2-buteen ( $C_6H_{12}$ ) is gebruikt als laag molecuul gewichts verbinding met slechts equivalente allylische posities.  $C_6H_{12}$  is allereerst gemengd met een mengsel van zwavel, zink stearaat en N-cyclohexyl-2-benzothiazylsulphenamide als versneller bij  $140^\circ C$ , hetgeen resulteerde in een mengsel van additie producten met de algemene formule  $C_6H_{11}-S_x-C_6H_{11}$ . Deze verbindingen zijn gescheiden met High Performance Liquid Chromatography, met betrekking tot hun verschillende lengtes van zwavel-bruggen. In een tweede stap zijn de gevulkaniseerde producten gedevulkaniseerd met gebruikmaking van bovengenoemde hulpmiddelen bij  $200^\circ C$  en  $210^\circ C$ . De kinetiek en chemie van de afbraak van zwavelbruggen gedurende de devulkanisatie zijn in beeld gebracht bij beide temperaturen. De devulkanisatie efficiëntie is afhankelijk van de verdeling van de zwavelbruggen: zowel difenyldisulfide als hexadecylamine zijn effectief in het verbreken van polysulfidische en trisulfidische cross-links bij  $200^\circ C$  en  $210^\circ C$ . De afbraaksnelheid van de polysulfide bindingen neemt toe met toenemende concentratie devulkanisatie hulpmiddelen en toenemende temperatuur. Grote hoeveelheden mono- en disulfide-cross-links worden gevormd bij gebruik van difenyldisulfide als devulkanisatie hulpmiddel en de hoeveelheid mono- en disulfides neemt toe met toenemende concentratie difenyldisulfide. Met toenemende concentraties hexadecylamine als devulkanisatie hulpmiddel neemt de concentratie mono- en disulfidische cross-links significant af, in vergelijking met de devulkanisatie zonder hulpmiddelen. Het belangrijkste verschil in de reactie tussen amine en disulfide wordt verklaard door de aanwezigheid van zwavel in difenyldisulfide en vandaar de mogelijkheid om als zwavel donor op te treden tijdens de reactie.

De resultaten verkregen met de model studie gaven nieuwe inzichten in de fundamentele vulkanisatiechemie. Deze kunnen echter niet direct vertaald worden naar het reclaim-mechanisme voor het complexe rubber. Het effect van de amines en disulfides op de hoofdketenbreuk en het effect van frictie kunnen niet onderzocht worden met een model compound studie.

Omdat difenyldisulfide werkt als een effectief reclaim hulpmiddel voor natuurrubber vulkanisaten is een nader onderzoek uitgevoerd naar verschillende difenyldisulfiden: Hoofdstuk 6. Het effect van verschillende substituenten op difenyldisulfiden op de reclaim-efficiëntie van op natuurrubber gebaseerde latex producten is onderzocht. Het effect van een amino-groep en een benzamido-groep in de ortho-posities van de fenyl ring ten opzichte van de disulfide brug van de difenyldisulfiden is onderzocht. Een vergelijkend onderzoek laat zien dat benzamido-gesubstitueerde difenyldisulfiden in staat zijn om het vulkanisaat te reclaimen bij een temperatuurniveau van ongeveer  $20^\circ C$  lager dan het gebruikelijke niveau. Een ander voordeel van de benzamido-gesubstitueerde verbinding is de verminderde geur tijdens het reclaim proces en van het verkregen reclaim. De verhoogde efficiëntie van een benzamido-gesubstitueerde difenyldisulfide wordt veroorzaakt door de makkelijk te breken S-S binding, resulterend in meer sulfidische radicalen door resonantie en

sterische effecten, vergeleken met andere hulpmiddelen.. Het hoger molekulgewicht van deze verbinding is een reden voor de verminderde geur.

Het gereclaimde rubber geproduceerd uit op natuurrubber gebaseerde latex afvalproducten is een waardevol materiaal voor de vervanging van maagdelijk rubber in een willekeurig rubber product. Reclaimen van het vulkanisaat is uitgevoerd met difenylsulfide, Hoofdstuk 7, en 2,2'-dibenzamidodiphenylsulfide, Hoofdstuk 8, en beide zijn gebruikt in het loopvlak van een vrachtwagenband door nieuw natuurrubber te vervangen door gereclaimde rubber. Twee verschillende compounding-principes zijn gebruikt: met aangepast vulkanisatiesysteem – de concentratie vulkanisatie-ingrediënten is aangepast om te compenseren voor de extra aanwezigheid van zwavel en versnellers door het reclaimen; en met onaangepast vulkanisatiesysteem – zonder aanpassing van vulkanisatie additieven.

Het onderzoek naar de mechanische en dynamische eigenschappen, de crosslink dichtheid en -distributie en ook de zwaveldistributie laat vergelijkbare resultaten zien voor de met difenylsulfide en met 2,2'-dibenzamidodiphenylsulfide gereclaimde monsters. Voor het aangepaste vulkanisatiesysteem wordt een significante afname van eigenschappen waargenomen met toenemend reclaimgehalte. Voor het onaangepaste vulkanisatiesysteem nemen eigenschappen als treksterkte en compressieset af, maar in mindere mate. Het meest opvallend zijn de verkregen waarden voor  $\tan\delta$  en  $M_{300}/M_{100}$ , die representatief zijn voor de rolweerstand van autobanden. Voor het onaangepaste vulkanisatiesysteem duiden beide waarden op een verbeterde rolweerstand bij toenemende hoeveelheid gereclaimde rubber, versus nieuw rubber. Voor het aangepaste vulkanisatiesysteem nemen beide eigenschappen af. Dit wordt veroorzaakt door het overwegend polysulfidisch netwerk dat verkregen wordt met een onaangepast vulkanisatiesysteem. Het is bekend, dat dit de dynamische eigenschappen van rubber compounds positief beïnvloedt, vergeleken met het overwegend mono- en disulfidische netwerk dat verkregen wordt met het aangepast vulkanisatiesysteem.

Wat verwerkingsgedrag betreft, vertonen met diphenylsulfide en 2,2'-dibenzamidodiphenylsulfide gereclaimde monsters een kortere vulkanisatietijd voor de laatste. Dit is een gevolg van de aanwezigheid van de amido-groep (-NHCO-) in 2,2'-dibenzamidodiphenylsulfide, daar stikstof-houdende verbindingen in het algemeen vulkanisatie-reacties versnellen. Een interessante algemene waarneming in de onderzoeken in Hoofdstukken 7 en 8 is, dat de kwaliteit van de reclaim onafhankelijk is van de soort grondstof, onder voorwaarde dat het reclaiming proces voor elk wordt geoptimaliseerd. Een combinatie van Scanning Electron Microscopy – Energy Dispersive X-ray' spectrometrie toont een verschil in zwavelconcentratie tussen de gereclaimde rubberfase en de nieuwe rubberfase in het compound: een hogere zwavelconcentratie in de gereclaimde fase wordt gevonden ten opzichte van de nieuwe fase. Dit verschil in zwavelconcentratie tussen de matrix en het reclaim-deeltje komt niet door migratie van zwavel tussen matrix en het deeltje, maar door de homogene distributie van zwavel door de matrix en het gereclaimde rubber tijdens het mengen van het compound.

### 9.3 AFSLUITENDE OPMERKINGEN

In dit onderzoek is een verbeterde oplossing ontwikkeld voor het reclaiming-proces voor zwavel-gevulkaniseerde, op natuurrubber latex gebaseerd afval dat rijk is aan koolwaterstoffen. Het procesvenster voor het reclaimen van latex afval is erg smal en temperatuur heeft een duidelijk effect op het reclaim-proces. Een kleine variatie in temperatuur heeft een enorme invloed op de afbraak van het uiteindelijke vulkanisaat. Het gebruik van reclaim-hulpstoffen verbetert de kwaliteit van het uiteindelijke reclaim en bepaalt het reclaim reactiemechanisme. In dit onderzoek is een poging ondernomen om de wetenschap en technologie van het reclaimen te combineren, om zo een reclaim te produceren van hoogstaande kwaliteit, dat gebruikt kan worden in hogere concentraties samen met nieuw rubber of los gebruikt kan worden om rubber producten te produceren van gerecycled materiaal. Aanbevelingen voor toekomstig onderzoek betreffen het gebruik van een combinatie van hexadecylamine en diphenyldisulfide als reclaiming hulpstoffen. Dit is vergelijkbaar met het gebruik van een thiol-amine chemical probe om de zwavelbruggen in een natuurrubber vulkanisaat te verbreken. De model studies kunnen verbeterd worden door gebruikmaking van squaleen als laag moleculaire verbinding, een betere vertegenwoordiger voor natuurrubber.



---

## Symbols and Abbreviations

---

$\gamma$	crosslinking index	[-]
$v$	number of elastically effective polymer network chains per unit volume	[moles/cm <sup>3</sup> ]
$\chi$	polymer-solvent interaction parameter	[-]
$v_f$	number of elastically effective polymer network chains per unit volume of the treated vulcanisate	[moles/cm <sup>3</sup> ]
$\gamma_f$	crosslinking index of the treated vulcanisate	[-]
$v_i$	number of elastically effective polymer network chains per unit volume of the untreated vulcanisate	[moles/cm <sup>3</sup> ]
$\gamma_i$	crosslinking index of the untreated vulcanisate	[-]
$v_r$	volume fraction of the polymer	[-]
$1/\beta$	number-average length of polymer fragments	[-]
$E_{100}$	stress at 100% strain	[MPa]
$E_{300}$	stress at 300% strain	[MPa]
$E_a, E$	activation energy	[J/mol]
$g$	gel fraction	[%]
$G'$	storage modulus	[MPa]
$G''$	loss modulus	[MPa]
$k_p$	scission rate constant for chain scission	[s <sup>-1</sup> ]
$k_q$	scission rate constant for crosslink scission	[s <sup>-1</sup> ]
$k_r$	reaction rate constant	[s <sup>-1</sup> ]
$M_{gel}$	number average molecular weight of primary molecule incorporated in the gel	[g/mol]
$M_n$	number average molecular weight	[g/mol]
$M_o$	number average molecular weight of all primary molecule	[g/mol]
MS	mass spectroscopy	
$MV(t)$	Mooney viscosity after a reaction time $t$	[-]
$MV_0$	initial Mooney viscosity	[-]
$MV_\infty$	lowest achievable Mooney viscosity	[-]
$N$	total number of polymer molecules	[-]
$N_{gel}$	number of primary molecules per gram of network	[-]
NR	natural rubber	
$N_x$	number of polymer fragments with length $x$	[-]
$R$	universal gas constant	[J]
$s$	sol fraction	[%]
$S_f$	sol fraction after the treatment of the vulcanisate	[%]
$S_i$	sol fraction before the treatment of the vulcanisate	[%]
$t_{02}$	scorch time	[min]
$t_{90}$	optimum vulcanisation time	[min]

$V_s$	solvent molar volume	[cm <sup>3</sup> /mol]
<sup>1</sup> HNMR	proton nuclear magnetic resonance	
6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine	
$A_c$	peak area of the component	
$A_{IS}$	peak area of the internal standard	
APDS	2-aminophenyldisulphide	
ASTM	American Society for Testing and Materials	
BA	n-butylamine	
BIIR	bromo isobutene isoprene rubber	
BR	butadiene rubber	
Bu"	n-butyl	
C	carbon	
CBS	N-cyclohexylbenzothiazyl-2-sulphenamide	
CIIR	chloro isobutene isoprene rubber	
COD	1, 5-cyclooctadiene	
CR	chloroprene rubber	
DBADPDS	2,2'-dibenzamidodiphenyldisulphide	
DBU	1,8-diazabicyclo[5.4.0] undec-7-ene	
DMSO	dimethyl sulphoxide	
DPDS	diphenyldisulphide	
DPSO	di-n-propyl sulphoxide	
EDX	energy dispersive X-ray	
ENBH	ethylidene norbornane	
ENR	epoxidised natural rubber	
EPDM	ethylene propylene diene rubber	
g	gram	
GC	gas chromatography	
GPC	gel permeation chromatography	
H	hydrogen	
HAF	high abrasion furnace	
HBr	hydrogen bromide	
HDA	hexadecyl amine	
HPLC	high performance liquid chromatography	
IIR	isobutene isoprene rubber	
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine	
iPr	isopropyl	
iPrS <sup>-</sup>	nucleophilic thiol-amine associate	
ISNR	indian standard natural rubber	
ISO	International Organization for Standardization	
LAH	lithium aluminium hydride	
MBS	2-(4-morpholiniothio)-benzothiazole	
MC	model compound	
$m_c$	mass of the component	
MCV	model compound vulcanisation	
MDR	moving die rheometer	

---

$m_{IS}$	mass of internal standard
ML(1+4)	Mooney viscosity
MU	Mooney units
N	nitrogen
O	oxygen
ODCB	orthodichlorobenzene
p	probability of breaking a bond in the polymer main-chain
PCTP	pentachlorothiophenol
Ph	phenyl hydrazine
phr	Per hundred rubber
q	probability of creating a crosslink between two polymers
R	rubber polymer
$R^2$	Correlation coefficient
RH	rubber hydrocarbon
RI	refractive index
ROOH	organic hydroperoxide
ROOR	peroxide
RPA	Rubber Process Analyzer
RRII	Rubber Research Institute of India
S	sulphur
SBR	styrene butadiene rubber
scCO <sub>2</sub>	supercritical carbondioxide
SEM	scanning electron microscopy
SSNR	smoked sheet natural rubber
tan $\delta$	loss tangent
TBA	tributylamine
TBBS	N-tert-butyl-2-benzothiazylsulphenamide
TCR	Trelleborg cold reclaiming
TDAE	treated distillate aromatic extract
TETD	tetraethyl thiuramdisulphide
THF	tetra hydro furan
TME	2,3-dimethyl-2-butene, tetra methyl ethylene
TME-Br	1-bromo-2,3-dimethyl-2-butene
TME-SH	2,3-dimethyl-2-butene-1-thiol
TMQ	polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
TP	thiophenol
TPP	triphenylphosphine
TS	toluene sulphonic acid
UV	ultra violet
$W_C$	weight percentage of the component
$W_{IS}$	weight percentage of the internal standard
WLR	waste latex rubber
WLR1	waste latex rubber1, gloves
WLR1C	waste latex rubber1 used at Cochin
WLR1T	waste latex rubber1 used at Twente

WLR2	waste latex rubber2, condoms
WLRR	waste latex rubber reclaim
z	time necessary to achieve a (arbitrarily chosen) viscosity
ZDEC	zincdiethyldithiocarbamate
ZMBT	zincmercaptobenzothiazole
ZnO	zinc oxide

---

## Bibliography

---

### JOURNAL PAPERS

- Model compound studies on the de-vulcanization of natural rubber using 2,3-dimethyl-2-butene at different temperatures  
W. K. Dierkes, V. V. Rajan, J. W. M. Noordermeer, *Kautsch. Gummi Kunstst.*, **58**, (2004), 312.
- Model compound studies on the de-vulcanization of natural rubber using 2,3-dimethyl-2-butene  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *Rubber Chem. Technol.* (2005), In press.
- Comparative investigation on the reclamation of NR based latex products with amines and disulphides  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *Rubber Chem. Technol.* (2005), In press.
- Application of NR based latex reclaim: The link between structure and properties  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *Rubber Chem. Technol.* (2005), Submitted.
- Effect of diphenyldisulphides with different substituents on the reclamation of NR based latex products  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *J. Appl. Polym. Sci.* (2005), Submitted.
- NR based cured latex material reclaimed with 2,2'-dibenzamido-diphenyldisulphide in a truck tyre tread compound.  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *J. Appl. Polym. Sci.* (2005), Submitted.
- Science and technology of rubber reclamation: a review  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *Progress in polymer science* (2005), Submitted.

### CONFERENCE PROCEEDINGS

- Model compound studies on the devulcanisation of natural rubber using 2,3-dimethyl-2-butene at different temperatures  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *Proceedings International Rubber Conference, Maastricht, The Netherlands. (6 - 9 June 2005)* and *Proceedings Kautschuk-Herbst-Kolloquium (KHK), Hannover, 10 – 13, November 2004.*

- Reclamation of sulphur cured NR vulcanisates by a novel reclaiming agent: A comparative evaluation with aromatic disulphide  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, Proceedings European Tyre Recycling Association Conference, Brussels, Belgium. (3 – 4 March 2005).
- Model compound studies on the devulcanisation of natural rubber using 2,3-dimethyl-2-butene  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, 166<sup>th</sup> Technical Meeting ACS Rubber Division, Ohio, U.S.A., Paper no. 25 ( 5-8 October 2004).
- Reclaiming of Natural Rubber based Latex Products: A mechanistic approach  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, India Rub. Tech. Expo , Mysore, India, 361-366, (13-14 February 2004).
- Reclaiming of Natural Rubber based Latex Products  
V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, Advances in Polymer Technology, Cochin, India) 326-332, (16-17 January 2004).

#### **EXTERNAL PRESENTATIONS**

- V. V. Rajan, International Rubber Conference (IRC), Maastricht, The Netherlands, June 2005.
- V. V. Rajan, European Tyre Recycling Association (ETRA) Conference, Brussels, Belgium, February 2005.
- V. V. Rajan, 166<sup>th</sup> Technical meeting - American Chemical Society (ACS), Rubber division, Ohio, United States, October 2004.
- V. V. Rajan, India Rub.Tech. Expo (IRI) Conference, Mysore, India, February 2004.
- V. V. Rajan, Advances in Polymer Technology (APT) Conference, Cochin, India, January 2004.

---

## Curriculum Vitae

---

Vipin V. Rajan was born in Ernakulam, India on December 11, 1975. He did his B.Sc (1996) and M.Sc.(2001) in Chemistry from Mahatma Gandhi University, Kottayam, India. He got his B.Tech (2000) degree in Rubber Technology from Cochin University of Science and Technology, Cochin, India. During his B.Tech he worked on a project "Study of various dipping conditions for Nylon-6 to improve Dip pick-up and adhesion level".

From November 2001 until October 2005 the author worked as a PhD student under the supervision of prof. dr. J.W.M. Noordermeer at the University of Twente, Faculty of Science and Technology. The PhD project was a part of the MHO programme, Joint Financing Programme for Co-operation in Higher Education, initiated by the Dutch government in co-operation with Nuffic, University of Eindhoven (TU/e), University of Twente (UT) and Cochin University of Science and Technology (CUSAT). The exchange nature of the PhD work allowed the author to work three years in University of Twente, The Netherlands and one year in Cochin University of Science and Technology, India.



---

## Acknowledgements

---

This PhD project is a part of the MHO programme, Joint Financing Programme for Co-operation in Higher Education, initiated by the Dutch government in co-operation with Nuffic, University of Eindhoven (TU/e), University of Twente (UT) and Cochin University of Science and Technology (CUSAT). The exchange nature of the PhD work allowed me to work three years in University of Twente, The Netherlands and one year in Cochin University of Science and Technology, India. I would like to thank all the personals and institutes involved in this project and their co-operation and collaboration, which makes the MHO project with CUSAT a big success.

First and foremost, I would like to express my sincere gratitude to prof. dr. Jacques W. M. Noordermeer for giving me an opportunity to carry out the research at the Rubber Technology group in the University of Twente. I have always appreciated your higher standards and quality for the work. Your coaching helped me to learn the skills of writing articles, critically analysing and interpreting the results as well as polishing my presentation skill. Thank you very much for being the promoter of my thesis.

Wilma, I wish to record my deep appreciation for the help and support you provided during the four years of my project. You always encouraged me with your active suggestions and constant support. When I was in India during my third year of work, you always kept in touch with me through emails and you always responded quickly and efficiently to my questions. I would also like to thank you for all the corrections that you did for my articles and chapters. I know that you really had a hard time to train me to write articles and chapters in proper way. Thank you very much for being the assistant promoter of my thesis.

I would like to express my profound regards to prof. dr. Rani Joseph and prof. dr. K.E. George for all the support and guidance they provided me during this period of research. I am thankful to prof. Rani Joseph for being my supervisor for the part of work I did in India and also for being one of my committee members during my defence. I am indebted to prof. K.E. George for selecting me from CUSAT to pursue my PhD studies in The Netherlands. Also, I would like to thank dr. Eby Thachil, dr. Philip Kurian, dr. Thomas Kurian, dr. Sunil Kutty, dr. Honey John, ms. Lity Alen Varghese and dr. Soney Varghese, the faculty members of PSRT for their best wishes.

I am thankful to dr. Rabin Datta and dr. Auke Talma for the suggestions, ideas and comments on my work.

I would like to thank my project co-ordinators Jan van Cranenbroek and his successor Patrick van Schijndel for the administrative and financial work of the project.

I acknowledge dr. Alan Roberts, prof. dr. Karst and prof. dr. Engbersen for being the committee members of my defence.

I am thankful to Gerda, Karin and Genevieve for all the administrative support during these years. I wish to appreciate the help and co-operation from Zlata regarding the lab work.

I wish to thank Jan for the contribution he gave with the model compound studies of my thesis. His skillful analytical techniques and enthusiastic support helped me to make the study a complete chapter of my thesis.

I would like to thank Hennie Bevers and Anita Poot for the help offered with the HPLC measurements and Clemens Padberg for the GPC measurements.

I always enjoyed the wonderful and lively atmosphere in the RBT group. I appreciate the multinational culture and cosmopolitan nature of the group. Annemieke, Louis, Kinsuk, Geert, Alexej , Pratip, Francesca, Montse, Richard , Kuno, Wilco, Marek, Mukund, Tony, Hongmei, Rui, Steven, Dorota, Jonnas, Indu, Joost, Dries, Jacob, Nitu , Subhas, Kannika, Anoma and Nico. I would like to extend my deep sense of gratitude to each and everyone for being friendly and supportive.

I would like to thank Kuno and Wilco for the Dutch translation of the summary of my thesis and Steven for helping with the designing of the cover page.

I want to thank all the members from PBM, STEP and MTP especially, Edwin, Debby, Arun, De, Priscilla, Christine, Bas, Menno, Miechel, Joost, Piet, Zheng, Feng, Edmondo, Sigggi, Sandra, Laura, Boon Hua, Zhiyuan, Fenghua, Ype, Ingrid, Mark, Piet, Wilco Z, Martijn, Nina, Douwe-Wiebe, Beata, Mark Ankone, Leon S, Monique, Ewa, Ferry and Alex for all the social activities and parties, especially triathlon, gluh wine party, movie evening etc. we had.

My special thanks to my paranimfen: Montse and Edwin, thank you very much for all the help you gave, which was utterly necessary for arranging the promotion ceremony.

I would also like to extend my gratitude to my friends outside the office hours: Vinay, Babu , Tony, Indu, Mercy, Denny, Soney, Suby, Merina, Shaji, Jijo, Arun, Prabhu, Sandeep, Prasanth, Aneesh for the nice time during the weekends. Also I would like to thank my friends in India during my one year time of PhD: Anoop, Thomas, Dhanya, Linu, Tigi, Bipin, Jayalatha, Sinto, Lovely teacher, Maya teacher, Mr.Joshy, Mr.Jude, Mr. Unnikrishnan and Mr. Benny.

Last but not least I would like to thank each and every members of my family for their love and affection towards me.

**Vipin**