POST-CONSUMER TIRES BACK INTO NEW TIRES

DE-VULCANIZATION AND RE-UTILIZATION OF PASSENGER CAR TIRES

Sitisaiyidah Saiwari

POST-CONSUMER TIRES BACK INTO NEW TIRES

DE-VULCANIZATION AND RE-UTILIZATION OF PASSENGER CAR TIRES

The research described in this thesis was financially supported by RecyBem B.V., the Netherlands.

Graduation committee

Chairman:	Prof. Dr. F. Eising	University of Twente, CTW
Secretary:	Prof. Dr. F. Eising	
Promoter:	Prof. Dr. Ir. J.W.M. Noordermeer	University of Twente, CTW
Asst. Promoter:	Dr. Ir. W.K. Dierkes	University of Twente, CTW
Members:	Prof. Dr. Ir. M.M.C.G. Warmoeskerken	University of Twente, CTW
	Prof. Dr. Ir. S.R.A. Kersten	University of Twente, TNW
	Prof. Dr. F. Picchioni	University of Groningen
	Prof. Dr. N. Vennemann	University of Applied Sciences Osnabrück, Germany
Referee:	Dr. Ir. L.-Ph.A.E.M. Reuvekamp	Apollo Tyres Global R&D, BV

Post-consumer tires back into new tires, de-vulcanization and re-utilization of passenger car tires

By Sitisaiyidah Saiwari

Ph.D. Thesis, University of Twente, Enschede, the Netherlands, 2013.
With references – With summary in English, Dutch and Thai

Cover design by Panut Kanong & Nara Samran, Yala, Thailand
Printed at Wöhrmann Print Service, Postbus 92, 7200 AB Zutphen, the Netherlands.

ISBN : 978-90-365-3541-0
DOI: 10.3990/1.9789036535410
URL: http://dx.doi.org/10.3990/1.9789036535410

POST-CONSUMER TIRES BACK INTO NEW TIRES

DE-VULCANIZATION AND RE-UTILIZATION OF PASSENGER CAR TIRES

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
Prof. Dr. H. Brinksma,
on account of the decision of the graduation committee,
to be publicly defended
on Thursday, May 23rd, 2013 at 16:45

by

Sitisaiyidah Saiwari

born on April 1st, 1979
in Mecca, Saudi-Arabia

This dissertation has been approved by :

Promoter	: Prof. Dr. Ir. J.W.M. Noordermeer
Assistant Promoter	: Dr. Ir. W.K. Dierkes

"Read in the name of your Lord Who created.
He created man from a clot.
Read and your Lord is Most Honorable.
Who taught (to write) with the pen.
Taught man what he knew not.
Nay! man is most surely inordinate.
Because he sees himself free from want.
Surely to your Lord is the return."

Al-Alaq:1-8

To my son

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION

A general introduction into rubber recycling are given in this chapter. The aim of this research and the structure of the thesis are stated.

1.1 THE CHALLENGE OF RUBBER DE-VULCANIZATION

Recycling of rubber is worldwide of growing importance due to increasing raw material costs, diminishing resources and growing awareness of environmental issues and sustainability. The labeling of tires, which ranks them in terms of fuel efficiency, noise and safety, is an expression of this growing awareness. This system was introduced in the EU in 2012[1]. In addition, many countries pay more and more attention to extended utilization of used rubber in order to achieve the goals of protecting the environment and saving resources. As an example, the European Union passed a directive that banned disposal of whole tires by 2003 and of shredded tires by 2006. Since then, the quantity of landfilled tires decreased significantly in the European countries[2]. Furthermore, the 'End of life vehicles' EU regulation required that from 2006 on not more than 15% of the weight of an end-of-life vehicle may be disposed, and this amount has to decrease to less than 5% till 2015. It is clear that the consequence of these regulations is to find new and better ways for recycling and new outlets for recycled rubber. The currently available routes for rubber recycling are:

Re-use: application of whole tires e.g. as fenders or in agriculture

Material recycling: re-use of powder or reclaimed material in rubber, but also for e.g. road construction or floorings

Back-to-feedstock recycling: recuperating carbon black, oil and gas in e.g a pyrolysis process

Energy recovery: Incineration of tires and other rubber waste with recovery of the energy

The technologies currently used for recuperating rubber are not very sophisticated: mainly ground or reclaimed rubber is used, both having a low quality compared to the original material[3,4]. Therefore, the material is mainly 'downcycled': it is used for low quality applications, for which the property requirements are not too high. This limits the application of recycled rubber; the demands for recycled rubber for street furniture, floorings, bumpers etc. are a lot lower than the quantity of available rubber waste. Consequently, material recycling in the sense of using recuperated rubber in products equal in quality to that of the original material is the most efficient way of recycling. However, the obstacle here is that the concentration of recycled rubber in high quality rubber products is rather limited. This in general is attributed to the relatively poor mechanical properties of recycled rubber compared to new material; in the case of reclaimed material due to structural changes that occur during the treatment process[5,6,7].

In the reclaiming process, two types of rubber network breakdown simultaneously occur: reclamation and de-vulcanization, as shown in Figure 1.1.

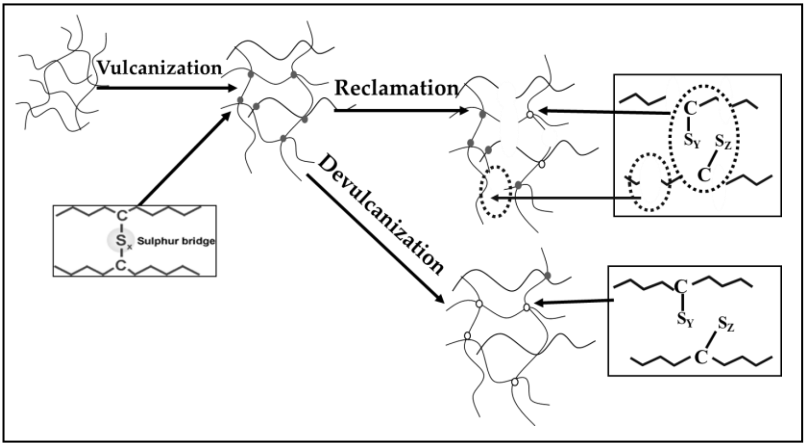


Figure 1.1 Simplified scheme of the 2 reactions occurring during rubber recycling processes: reclamation and de-vulcanization.

De-vulcanization is the process of cleaving the monosulfidic (C-S-C), disulfidic (C-S-S-C) and polysulfidic ($C-S_x-C$) crosslinks of vulcanized rubber. Actually, de-vulcanization should literally be the reverse process of vulcanization. In sulfur vulcanization, formation of both carbon-sulfur bonds (C–S) and sulfur-sulfur bonds (S–S) takes place and therefore only these bonds should be broken during de-vulcanization. In contrast to this, reclamation is different from de-vulcanization due to the scission of the carbon-carbon bonds of the polymeric chains. In view of these arguments, the conversion of used rubber into a re-processable and re-usable form by the currently used physical/chemical processes should be called reclamation rather than de-vulcanization. The broken polymer chains generated in the reclaiming processes influence the properties and reduce the quality of the recycled material. If the rubber is de-vulcanized, ideally only sulfur crosslinks are broken while the polymer chains remain intact. Consequently, the de-vulcanizate resembles the original material in structure and quality. An improvement of the properties of recycled rubber by developing a more selective breakdown process is an important issue and a global challenge.

The application of post-consumer tire material in new tire compounds is a necessity, but this implies that the properties of the material should not suffer by blending it with recycled rubber. The most promising way to achieve this is *de-vulcanization*, a process which aims to reverse vulcanization as far as possible without damaging the polymer.

1.2 AIM OF THIS THESIS

This research is a joint project with the University of Groningen. The objective of the project is to elaborate a de-vulcanization process for used whole passenger car tire rubber with the main constituent SBR, and to upscale this process to pilot scale. The research described in this thesis is focused on the influence of material composition on the de-vulcanization efficiency[8] and material properties, on choosing an appropriate de-vulcanization aid, on optimizing the de-vulcanization process conditions, and finally on an application study. The research topic of the University of Groningen within this project is the development of the continuous de-vulcanization process based on the de-vulcanization parameters elaborated within this part of the project.

The final aim of this study is to develop a de-vulcanization process for passenger car tire rubber, as sensitive to tire compound compositions. Passenger car tires consist of several types of rubber. The challenge of this work is the presence of SBR as the main elastomer in passenger car tires, which makes this material difficult to break-down due to the tendency of the rubber chain fragments to re-combine[9]. Polymer chain scission mainly occurs during physical treatment[10], therefore a shift of the balance between physical and chemical breakdown in a *thermo-chemical de-vulcanization process* will lead to a higher ratio of crosslink scission to polymer chain breakage, the precondition for efficient de-vulcanization. The first objective within this study is to define the pathway for the most efficient de-vulcanization process of SBR. Secondly, a best compromise for the de-vulcanization process conditions for all tire rubbers needs to be found. Finally, the intention is to investigate the productivity of the process for whole passenger car tire material and its properties in new tire products.

1.3 STUCTURE OF THIS THESIS

In the introduction in Chapter 1, the essential terms of rubber network breakdown are defined: *Reclamation and De-vulcanization*. A literature review about "End-of-life tires" and numerous reclaiming and de-vulcanization processes is given in Chapter 2.

This thesis further encompasses 6 experimental chapters.
Chapter 3: The focus within this chapter is on de-vulcanization of SBR as it is the main component in passenger car tires, and as its breakdown behavior is so far not well documented. A preliminary study of sulfur-cured SBR de-vulcanization by thermal treatment is performed. The de-vulcanization process is investigated under various conditions: The temperature range for the de-vulcanization is varied from 180°C to 300°C, and the treatments are done in air and under oxygen exclusion with nitrogen. Correlations between the process conditions and the ratio of polymer chain to crosslink scission are elaborated.

Chapter 4: The combination of a chemical and a thermal de-vulcanization step is one of the alternatives to reach efficient de-vulcanization. The use of small amounts of a "de-vulcanization aid" during the thermochemical treatment is investigated in this chapter. Special attention is given to the choice of the best de-vulcanization aid for SBR vulcanizates. Three different types of disulfides are investigated concerning their performance as de-vulcanization aid: diphenyldisulfide (DPDS), dibutyldisulfide (DBDS) and di(2-aminophenyl)disulfide (APDS). The best de-vulcanization conditions for SBR are elaborated, and the mechanisms behind the different breakdown processes are discussed.

Chapter 5. A further study regarding the inter- and intra-molecular rearrangements of chain fragments of butadiene moieties in SBR from uncontrolled degradation and oxidation effects is done. Oxidation stabilizers are added to the DPDS de-vulcanization to reduce the degradation and interrupt the oxidation cycles. The results are interpreted in terms of mechanisms of main chain and sulfur bridge scissions and the degradative cycles triggered by the presence of oxygen.

Chapter 6. The optimal process conditions for a high ratio of de-vulcanization to polymer degradation are investigated for tire rubbers: SBR, BR, NR and CIIR. The de-vulcanization mechanism of each of the rubbers is discussed, and the best de-vulcanization compromise for whole passenger car tire material is elaborated.

Chapter 7. The Ground whole Tire Rubber (GTR) from post-consumer passenger car tires is de-vulcanized using the optimal conditions elaborated in Chapter 6, which are the best compromise for all single types of rubber used in a passenger car tire. The de-vulcanization conditions for GTR are further optimized, and a study concerning the de-vulcanization efficiency is performed. Furthermore, the mechanisms of the breakdown processes of GTR are discussed.

Chapter 8. An application study is performed using de-vulcanized ground tire rubber (D-GTR). In first instance, the fundamental properties of D-GTR: viscosity, cure behavior and mechanical properties are analyzed. Next, the D-GTR is blended with a virgin tire tread compound at a ratio of 50/50. The curative as well as the compounding recipe are adjusted in order to compensate for effects on the material from the first processing cycle and service life. The cure behavior and mechanical properties of the blend are measured and compared to original tire tread properties.

Finally, conclusions as well as suggestions for a further study are given in summary chapter.

1.4 REFFERENCES

1 www.ec.europa.eu

2 European Tire Recycling Association (ETRA), Introduction to Tyre Recycling, V.L. Shulman, Ed. (2008).

3 M. Myhre and D.A. Mackillop, *Rubber Chem. Technol.*, **75**, 429 (2002).

4 M. Myhre, S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, *Rubber Chem. Technol.*, **85**, 408 (2012).

5 V.V. Rajan, W.K. Dierkes, R. Joseph and J.W.M. Noordermeer, *J. Appl. Polym. Sci.*, **102**, 4194 (2006).

6 K.A.J. Dijkhuis, I. Babu, J.S. Lopulissa, J.W.M. Noordermeer and W.K. Dierkes, *Rubber Chem. Technol.*, **81**, 190 (2008).

7 J. Choi and A. I. Isayev, *Rubber Chem. Technol.*, **84**, 55 (2011).

8 M. M. Horikx, *J. Polym. Sci.*, **19**, 445 (1956).

9 R.N. Hader and D.S. le Beau, *Ind. Eng. Chem.*, **43**(2), 250 (1951).

10 S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, presented at the meeting of the Rubber Division, ACS, October 2011, Cleveland (USA).

CHAPTER 2

RECYCLING ROUTE FOR SULFUR-CURED RUBBER: A LITERATURE OVERVIEW

An extensive overview of rubber recycling routes with special emphasis on post-consumer tires recycling is depicted in this chapter. The history of tire production and the present tire composition are briefly described. Various outlets of post-consumer tire materials are comprehensive by reviewed. The most efficient rubber recycling route can be achieved by using a de-vulcanization process. Different types of de-vulcanization processes are described with special reference to the chemical processes, which selectively cleave the crosslinks in the vulcanized rubber. The reaction mechanism and chemistry during the de-vulcanization processes are discussed in detail.

2.1 TIRES AND THE END OF THEIR LIFE

With the discovery of vulcanization in 1839, the rubber industry started to grow exponentially. In 1888, John Boyd Dunlop introduced the pneumatic tire, giving birth to the tire industry[1]. Starting with the bicycle and moving to the growing automotive market, tire consumption exploded. In the late 19th century, primitive tire construction techniques and poor road conditions resulted in poor tire performance. A tire would typically last not more than 800 kilometres, and each car would wear out 37.5 tires per year on average, as reported by Zelibor[1]. The first significant improvement in the automotive tire technology was made with the introduction of reinforcing fabrics in 1893. Additional improvements were based on chemical accelerators which reduced cure times and provided greater rubber strength, introduced in 1910. The important innovations during the 1920s, such as the cylindrical drum building machines, pneumatic tires and anti-degradants (anti-oxidants and anti-ozonants) improved quality and reduced costs of tires. In 1938, synthetic rayon fibers were introduced as reinforcing material. From 1940 on, the

application of the synthetic rubber resulted in a higher consistency of rubber compounds and higher performance of the tires. Furthermore, it allowed a safer tire design. The commercial introduction of the radial tire in 1948 had the advantage of a lower rolling resistance of the tire, improved handling and longer service life. During the 1970s, the introduction of ultra-high performance, square shouldered, low profile, steel belted, radial tires provided further improvements in the dynamic performance of tire-car systems. Since 1980, the tire industry continued in improving rolling resistance and durability of tires. The truck tire market became increasingly dominated by the radial tire design, and truck tire retreading grew as tire casings became more durable. Tire design became increasingly vehicle- and application-specific, and tire complexity increased. Purcell[2] stated in 1978 that:
"As tires become more sophisticated and more durable, they are becoming less recyclable".

Due to the increasing number of vehicles, the 'mountain' of used tires has grown dramatically during the last decades. Every year, approximately 800 million scrap tires are disposed of around the globe. Piled up, they would cover a distance of 200.000 km. This amount is expected to increase by approximately 2% each year[3].

TIRE PARTS AND THEIR COMPOSITION

Tires are made of vulcanized rubber and various reinforcing materials. The most commonly used rubber matrix is the co-polymer styrene-butadiene rubber (SBR) or a blend of natural rubber (NR) and SBR. In addition to the rubber compound, tires contain reinforcing fillers. Most widely used is carbon black; it reinforces the rubber and increases abrasion resistance. Carbon black in passenger car treads is more and more replaced by silica due to the better dynamic properties of the tire. It reduces rolling resistance without negatively influencing wear and wet grip. Reinforcing fibers, textile or steel, usually in the form of cords, are used to give dimensional stability and strength. Plasticizers such as petroleum oils are used to control viscosity, reduce internal friction during processing, and improve low temperature flexibility of the vulcanized material. Aromatic oils have been widely used in tire production. However, these oils which contain a high concentration of polycyclic aromatic hydrocarbons (PAHs) are identified as carcinogens. From January 2010 on, tires containing plasticizers with high concentrations of polyaromatic hydrocarbons are banned from the European market. These oils are replaced by Mild Extract Solvates (MES) or Treated Distillate Aromatic Extracts (TDAE).

A tire is an assembly of a series of parts, each of which has a specific function in the service and performance of the product. The various parts of a tire are shown in Figure 2.1.

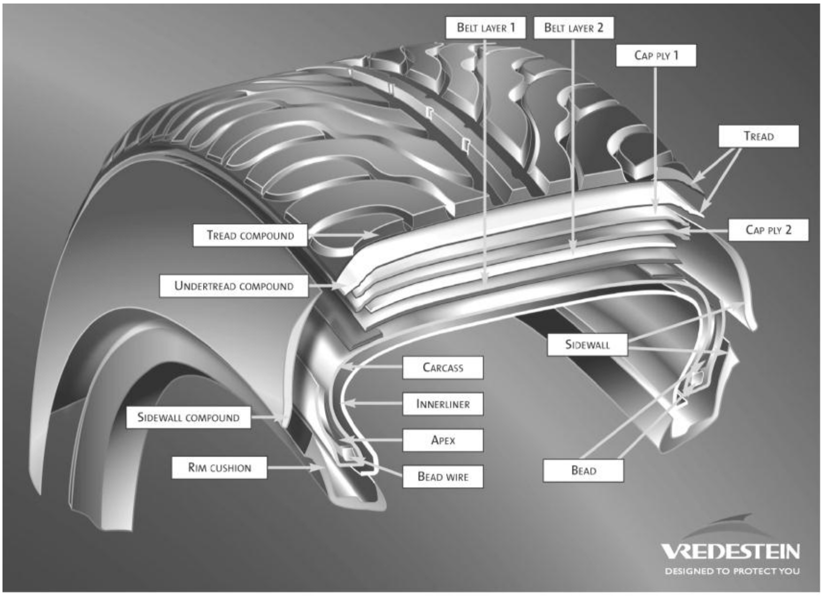


Figure 2.1 *Various components of a radial tire shown in cutaway view.*[4]

Each part of a tire has its own specific formulation with a variety of constituents. Tires contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cords, steel or fabric belts and steel-wire reinforcing beads. For passenger car tires, the most commonly used tire rubber is styrene-butadiene copolymer. Other rubbers used in tire manufacture include natural rubber, butyl rubber (isobutylene isoprene rubber, IIR) and polybutadiene (BR) rubber. Table 2.1 summarizes the most important elastomers and blends used in different tire parts.

Tread.- The tread is probably the most critical component of the tire. It is responsible for the tire-road contact, which translates into safety and durability of the tire. Furthermore, it is the main contributor to the energy losses that in turn causes a rise in the tire's running temperature.

Belt.- The belt is made from rubber and brass coated steel cord. It provides a rigid support to the tread and offers a more controlled contact with the road. It therefore plays an important role in the wear of tires and the driving stability of vehicles[5].

Table 2.1 Polymers used in passenger car tires.

Component	Rubber
Tread	SBR, BR
Belt	NR
Sidewall	NR, BR
Carcass	SBR, NR, BR
Bead	NR
Apex	SBR, NR, BR
Cap-ply	NR, BR
Inner liner	SBR, NR, IIR

Sidewall.- The sidewall rubber provides protection for the body plies. It covers the thinnest part of the tire where most flexing occurs as the tire deflects. Therefore a sidewall needs to have a high flex resistance and good dynamic properties as well as excellent ageing resistance.

Carcass.- The carcass or body-ply of the tire is made from fabric yarns, nylon, rayon or polyester, twisted into parallel weftless cord layers known as plies. These plies are coated with a natural rubber based compound loaded with adhesion promoters to generate a bond between the cord surface and other tire components.

Bead.- The bead is monofilament steel wire coated with rubber, providing the tire with a secure fit to the wheel rim such that it does not move or dislodge as the vehicle undergoes severe manoeuvres.

Apex.- The apex or filler insert components provide the gradual shape and stiffness reduction from the rigid bead coil to the flexible mid-sidewall of the tire. This component needs to be very hard to provide good vehicle handling and to reduce the risk of flexural fatigue at the component endings.

Cap-ply.- Cap-plies are mostly used in high performance car tires. Having a circumferential cord direction, they provide an additional contractive force. Cap-plies require high moduli and good adhesion strength.

Inner liner.- The inner liner forms the vital internal membrane which holds the inflation medium at the elevated pressure within the structure of the tire. Generally, butyl or halobutyl rubber is used as inner liners[5].

END-OF-LIFE TIRES

Since polymeric materials do not decompose easily, disposal of waste polymers including rubbers is an urgent environmental problem. Strategies for dealing with scrap tires and the best way to recover, recycle and reuse them are global challenges. The term 'used tire' defines a tire at the end of its life cycle. Used tires are accumulated after replacement by a new one or when dismantling a vehicle. In some European countries, used tires are collected in tire service centres. Consumers pay a fee to the service centre for proper disposal of the used tire. For instance, consumers pay approximately €2 per tire for disposal in the Netherlands[3]. This amounts to €300 per metric ton of tires. Developed countries have been paying great attention to the comprehensive utilization of used tires in order to achieve the goals of protecting the environment and recycling the resources[6,7]. The recycling of used rubber has a significant impact in different fields[8] i.e., protection of the environment, conservation of energy and availability of a raw materials. Recycling of used rubber not only solves the waste disposal problem and reduces the environmental burden; it also saves the valuable and limited resource of fossil feedstock. The main outlets of post-consumer tire materials are shown in Table 2.2.

Landfill.- The European Commission passed a directive that banned the disposal of whole tires by 2003 and shredded tires by 2006[9]. Since the European ban on landfill is operational, monofills form a temporary solution in those European countries where capacities for processing of used tires are limited. A scrap tire monofill is a landfill that stores tires only. Monofills are more desirable than landfills as they facilitate material and energy recovery in the future. The problems related to landfilling of whole tires are: Tires occupy a large space and remain intact for decades and leaching of rubber additives and uncontrolled burning pose an environmental and public health risk. Besides, monofills still bear the risk of fire hazards; these fires may cause significant atmospheric and surface water pollution[10]. Since the prohibition of landfill of tires, the quantity of landfilled tires significantly decreased in the European countries. However, still 20% of the used tires were disposed of in landfills in the year of 2006[11].

Table 2.2 Outlets for used tire material

Outlet for used tire material	Processing	Application
1. Landfill	Landfill Monofill	
2. Reuse	Reuse as tire Reuse in other application	Re-treading Crash barrier Artificial reef Playground equipment
3. Energy recovery	Incineration	Deriving energy
4. Back-to-feedstock	Pyrolysis	Producing carbon black, oil and gas
5. Material recycling	Grinding Reclaiming Surface modification Other products	Powder or reclaim for new rubber products Construction Asphalt

Re-treading.- In the European countries, more than 10% of the used tires were re-treaded and returned to service in 2006[11]. Re-treading offers the most resource-efficient strategy for tire recovery, saving both material and energy[12]. It comprises removing the old tread from a worn-out tire and replacing it by a new one. The benefit of re-treading is that it extends the tire life span. It saves 80% of the raw materials and energy and reduces the quantity of waste to be disposed. The energy consumption for production of a new tire is 15 times higher than for re-treading[13], and the price of retreaded tires is 30 to 50% lower than the price of a new tire. Nevertheless, they deliver the same mileage as new tires[9,14]. Truck tires are often retreaded up to three times before finally being discarded, and this business is growing[15]. The percentage of retreaded passenger car tires is modest compared to truck tires due to cost reasons and the low acceptance of retreaded tires in the market. The most suitable passenger car tires are the high-quality tires for high-rank vehicles; however, these are also the ones with low market potential. They only present a small share of the tire market, and the retreaded tires are perceived to have a lower quality than new tires[16]. The main obstacles for a wider use of retreaded passenger car tires are difficulties in supply of retreadable casings, competition with cheap non-retreadable tires and the poor reputation of the retreaded tires quality. Nowadays, retreading in some European countries is still lacking[3].

Reuse in other applications.- Completely worn-out tires can be reused for civil engineering applications and agricultural uses. Whole tires are used for applications where their physical form, resilience to impact, and longevity are beneficial. Examples are breakwaters, erosion control, highway crash barriers, playground equipment, marine docks and reefs[12]. Used tires for breakwaters filled with foam displace 91 kg of water and can be used to float a number of devices such as marinas and docks[15]. They can be used in erosion control applications with other stabilization materials to reinforce unstable highway shoulders or to stabilize a channel slope. Construction costs were reduced from 50 to 75% compared to the lowest cost alternatives such as rock, gabion, or concrete protection. Used tires as crash barriers can reduce or absorb impact of automobiles travelling up to 144 km/h[17]. Three million used tires were used as reef in Ft. Lauderdale, Florida, USA in 1972 and for a period, one million tires per year were added to reefs[18]. This practice is now abandoned as those reefs create environmental problems by killing aquatic life.

Energy recovery: combustion for deriving fuel and energy.- Tires are made of elastomeric materials in the form of C_xH_y. It possesses a high carbon content making it a suitable material for energy recovery[19,20]. Direct burning of used tires is one method of recovering energy. Tires can be used as fuel either as a whole or in a shredded form, depending on the type of combustion furnace. Burning of tire material requires a sophisticated high-temperature combustion facility to keep emissions within environmental limits, and in the case of whole tire handling, special equipment for feeding them into the combustion chamber is necessary[15]. More than 30% of the used tires in the European Union (EU) are currently used as fuel[11]. Its relatively high heat content of app. 33MJ/kg is similar to the heat content of coal[11]. A considerable percentage of the used tires is used as a supplemental fuel in cement kilns. The very high temperatures and oxidizing atmosphere in the kiln provide complete combustion of the tires, including the volatile matter produced during combustion. Additionally, the volatilized iron oxide is contributing to the cement properties, reducing the costs of adding supplemental iron to the feed mix. A major advantage of using tires in cement kilns is that the process does not generate any solid waste, because the ash residues from the combustion are bound to the final product. Sulfur emissions are not a major concern as the sulfur is transformed and bound in gypsum, which remains in the final product[3]. Compared to coal, the tire fuel has less moisture, significantly more combustible matter, and less fixed carbon. However, Amari *et al.*[12] estimated that the tire combustion process recovers only 37% of the energy embedded in the tires. They conclude that it is more preferable to recycle rubber and re-use the material rather than to use it as a fuel.

Back-to-feedstock: pyrolysis for producing carbon black and oil.- Pyrolysis involves the thermal decomposition of a substance into low molecular weight products under an inert atmosphere. Used tire pyrolysis produces three principal products: gas, oil and char[20,21,22]. The gas and oil have energy contents similar to conventional products. The derived oils contain high concentrations of potentially valuable chemicals such as benzene, toluene and xylene. The solid char is a fine particulate composed of carbon black, ash, and other inorganic materials, such as zinc oxide, carbonates, and silicates. The carbon black has a significantly lower quality than the original carbon black used in the tire; it has to be upgraded before it can be used in low quality applications. According to Amari[12], the economic feasibility of tire pyrolysis is strongly affected by the value of the solid char residue[12]. Wojtowicz and Serio[23] propose of a scheme for processing scrap tires into higher value-added products. In their process, char upgrading is implemented in a closed-loop activation step that yields an activated carbon and eliminates undesirable by-products and emissions. The process yields substantial quantities of oils in addition to the char which undergoes processing for value-added products[12].

Material recycling: application in rubber products.- Tire shredding is primarily a physical process that breaks down the tire material. It can be followed by a grinding step to generate a powder. Basically, there are two grinding methods: an ambient temperature grinding process and a cryogenic crushing process. In the ambient mechanical grinding process, the tire is shredded, the steel is removed from the stream by magnetic separation and the textile is removed by wind sifting. The final powder is classified according to its dimensions. In the cryogenic crushing process, the tires are shredded into fine granules at extremely low temperatures: The temperature in the process is lower than the glass transition temperature, T_g, of the material. Cryogenic powders have better flow characteristics than mechanically shredded rubber[24]. The steel is removed by magnetic separation and the textile can be removed by aspiration.

The use of ground tire rubber as filler material in the tread and sidewall of new tires is generally limited to a few percent. However, tests performed jointly by Michelin and Ford, show that powder contents of up to 10% can be added to passenger tire compounds without compromising tire performance[25]. Ground rubber from used tires can be added to other polymers in order to modify the properties of the material. It acts as a modifying agent for thermoplastic resins, as an elastic component for improving the impact resistance of plastics and in elastic layers for elastic paving. It is used in functional composites which have the characteristics of safety, softness, flexibility, water permeability and water resistance[26]. Examples of applications are listed in Table 2.3.

The application of ground rubber from used tires is generally limited to low quality products and to low concentrations in higher quality rubber products.

In the reclaiming or devulcanization process, used tire rubber is initially ground, then reclaimed or devulcanized, and re-used in a virgin compound from which new rubber products are made. Reclaimed rubber can be used in high value applications such as tires, automotive moulded parts, soles and heels, etc. Using rubber reclaim can be even more profitable for the rubber industry, when production waste is recycled and reused within the factory where it is generated. This might result in additional revenues from eliminating waste disposal fees and transportation costs. However, reclaimed rubber has in general poorer mechanical properties than comparable virgin rubber due to the uncontrolled polymer scission which occurs during the reclaiming process. This limits the concentration of reclaimed rubber in high-quality applications such as tires. As more than half of the rubber products are tires, this means that reclaim has limited applicability for the major share of the rubber market. However, reclaimed rubber is a valuable raw material which can replace virgin rubber in many other rubber products. The main general advantage of using reclaim in virgin rubber compounds is an improvement of processing behaviour.

Table 2.3 Application of ground rubber from used tires.

Application in the products	Examples
1. Rubber mats and floorings	Mat, mat base for road, animal mat, mat block for roads, rubber plate, rubber floor materials, floor rising materials, sidewalk surface of golf-course exercise mat for golf-course, tennis court man-made, lawn materials, carpet materials, indoor decorative floor materials, pedal
2. Construction materials	Rubber bricks, paving materials, wall materials, half rubber wood product, insulative bakelite, protection block, elastic brick
3. Shoes	Interior shoes bottom, shoe heel, shoe core
4. Automotive	External parts of cars, splash board of car, dust proof of car, brake hand, detent of car, car tire, solid tire, foot mat block of car, bottom rubber

Surface modification methods aim at making ground rubber more reactive towards new polymers without breaking the bonds in the vulcanized material. Compound properties, which can be positively influenced by the addition of surface modified rubber crumb, are abrasion resistance and tear strength. Different processes have been developed to increase the bonding strength to the surrounding matrix or to neighbouring rubber powder particles. The activation processes can be divided into 3 groups[27]: chemical[28,29,30,31], mechanical[32,33], and microbial activation[34,35].

Material recycling: application in construction materials and asphalt.- Ground tire rubber is used as component in construction material. The most important applications in this field are in sport surfaces and floors, as a construction material and as an additive for bitumen in road surfaces. Particulate rubber makes surfaces more resilient and less rigid, while allowing the surface material to maintain traction and shape. Construction applications include amongst others flooring materials, patio decks, and railroad crossing blocks. Products molded from ground tire rubber include livestock mats and removable speed bumps. Ground rubber products are also used for athletic and recreational materials, such as running tracks and playground surfaces. One important application of ground rubber is rubberized asphalt, which reduces the noise of road traffic. A powdered rubber-asphalt combination has been used as coating for surface-treatment of badly cracked roads since the early 70ies[36]. A composite made of ground used tire material and asphalt is an effective seal coat for highways and airport runways. The product can contain up to 25% finely ground used tire material[37].

2.2 RECLAIMING AND DEVULCANIZATION

A variety of different recycling processes for rubber have been investigated and developed throughout the years. Several in-depth reviews discussing the state-of-the-art of rubber recycling were published in 1974[38], 2002[39] and 2012[27].

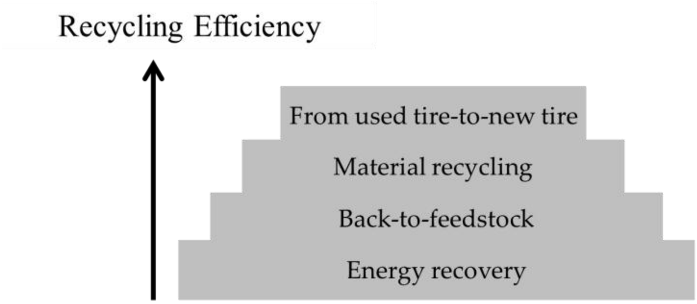


Figure 2.2 *Rubber recycling ladder.*

Figure 2.2 shows the main recycling methods hierarchically classified in the order of environmental and economic preference[40]. The lowest level is burning vulcanized rubber for energy recovery, and on the second level reside back-to-feedstock methods such as pyrolysis of used rubber to recover gas, oil and chemicals. The third method on the next level is material recycling by transforming used rubber into products with inferior quality compared to the original material or using recovered rubber for the production of new rubber products. Finally, the most efficient rubber recycling route or the highest level of the recycling ladder is transforming used rubber into products of characteristics equal to that of the original materials i.e., used tire rubber back into tires. This can be achieved by using a de-vulcanization process.

Reclaiming is a process in which vulcanized rubber is converted into a state that it can be mixed, processed, and vulcanized again by using conventional processes. Transforming the cured rubber into a re-processable material is done by breaking the links between and partly within the polymer chains. The general problem of the current reclaiming processes of rubber is the fact that apart from sulfur-crosslinks, the main polymer chains are also broken, and this influences the properties and reduces the quality of the recycled material. This technology is sometimes coincidently referred to as de-vulcanization.

De-vulcanization, the most ideal way of rubber recycling, is the process that aims to reverse vulcanization as far as possible without damaging the polymer. In sulfur vulcanization, formation of a rubber network by both carbon-sulfur bonds (C–S) and sulfur-sulfur bonds (S–S) takes place, therefore only these bonds should be broken during de-vulcanization. Devulcanization is the process of cleaving the monosulfidic (C-S-C), disulfidic (C-S-S-C) and polysulfidic (C-S_x-C) crosslinks of vulcanized rubber. An efficient devulcanization is needed in order to achieve a high-quality recycled rubber.

Reclaiming and devulcanization were often referred to as similar processes. In spite of the fact that they are similar in the procedure, they are fundamentally different in the degree of rubber network breakdown and the molecular structure of the polymeric material. In other words, the difference between “reclaimed” and “de-vulcanized” rubber lies in different ratios of crosslink and polymer chain scission. An illustration of “De-vulcanization versus Reclamation” is shown in Chapter 1. For reclaimed rubber, relatively poor mechanical properties are frequently reported, originating from structural changes of the molecular structure of the polymer that occur during the reclaiming process. Extensive polymer scission and a partly re-combination result in highly branched chain segments that differ greatly from the virgin rubber. The improvement of the properties of reclaimed rubber by developing efficient devulcanization processes is an important issue for the recycling technology. Table 2.4 gives an overview of the rubber reclaiming processes, which are divided into 2 groups: physical and chemical processes.

Table 2.4 Different rubber reclaiming processes

Physical Processes	Chemical Processes
Mechanical	Radical scavengers
Thermo-mechanical	Nucleophilic additives
Microwave	Catalyst systems
Ultrasonic	Chemical probes

RECLAIMING OF RUBBER BY PHYSICAL PROCESSES

Vulcanized rubber is reclaimed with the help of mechanical or thermal energy; the three-dimensional network of crosslinks breaks down in the presence of different energy sources. As these processes in general are non-selective in terms of sulfur-sulfur and carbon-carbon bonds, the latter type of bonds is broken and the polymer chains are transformed into smaller molecular weight fragments. Many attempts are made to use a specific amount of energy which is sufficient to cleave crosslinks but not the carbon-carbon bonds. This is expected to result in a high quality reclaimed rubber: viscoelastic in nature and with a property profile comparable to the virgin rubber. The different types of physical reclaiming processes described in literature are:

Mechanical processes.- In mechanical reclaiming processes, crumb rubber is placed on an open two-roll mill. In this process, a drastic molecular weight reduction takes place due to mechanical shearing. The shearing forces will affect the viscosity of the reclaimed rubber; i.e. Mooney viscosity decreases with decreasing the nip opening[41,42]. A substantial level of network breakdown of carbon black filled polyisoprene vulcanizates was reached during milling without addition of chemicals[43]. However, a reduction of the physical properties was caused by chain scission which occurred during the mechanical shearing process. Another shortcoming is the difficulty to achieve consistent properties for reclaimed rubber due to the inhomogeneous heating of the material during the reclaiming process.

In the work of Zhang[44] and Bilgili[45], different mechanochemical processes based on stress induced chemical reactions and structural changes of materials are described. A High Stress Mixer (HSM) as shown in Figure 2.3 was presented in 2009 as efficient mechanical reclaiming machine[46]. It is claimed that the HSM process employs mechanical strain and chemical reactions to cleave crosslink bonds while the polymer backbone remains unaffected.

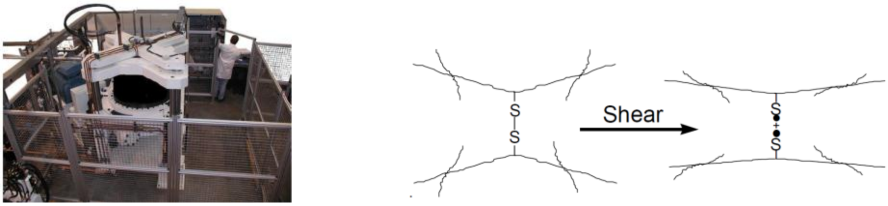


Figure 2.3 *HSM and preferential rapture of rubber network mechanism with high shearing forces.*[46]

Thermo-mechanical processes.- The thermo-mechanical reclaiming processes make use of shearing forces in order to plasticize the rubber and to heat the material. Shearing energy is introduced into the materials, resulting in a significant temperature increase, high enough to cause thermal degradation[47,48,49]. No chemical agents are added; it is a purely thermo-mechanical process. The disadvantage of this process is the extensive occurrence of main chain scission. Therefore, there is a considerable loss of physical properties when the recyclate is used by itself or when it is blended with a virgin compound, even if the two have the same formulation. A loss in properties of 1% per 1% recyclate added to the virgin material was reported[50].

A co-rotating twin screw extruder has been introduced for thermo-mechanical reclaiming processes based on the principle of synergetic action between thermal energy and high shearing forces and elongational strain on the material[51,52,53,54]. At high temperatures, the energy is mainly effective in crosslink bonds because of their lower elastic constant as shown in Figure 2.4. Crosslinks are therefore, in principle, selectively broken by the thermal energy, but due to the thermal inhomogeneity within the material and the rather small differences in bond energies, the process is in actual practice not selective. Furthermore, in order to obtain a stretching of the polymer chains, high strain levels are required; at lower strains, elasticity is dominated by entropic effects only.

EPDM, which was treated by a thermo-mechanical process under specific process conditions, i.e., screw configuration, reaction temperature, screw rotation speed, etc., exhibits excellent mechanical properties, which come close to the properties of the virgin material as shown in Figure 2.5.

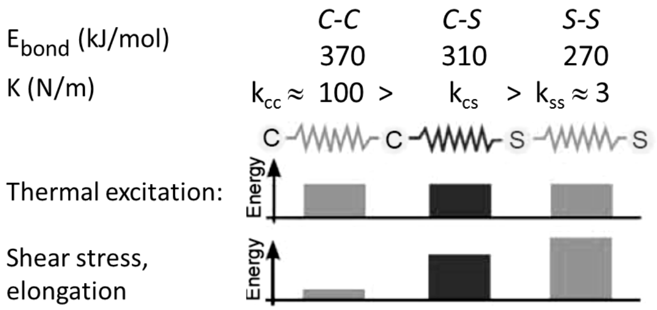


Figure 2.4 *Repartition of energy between polymer chain bond and crosslink bonds during thermal and mechanical excitation.*[51]

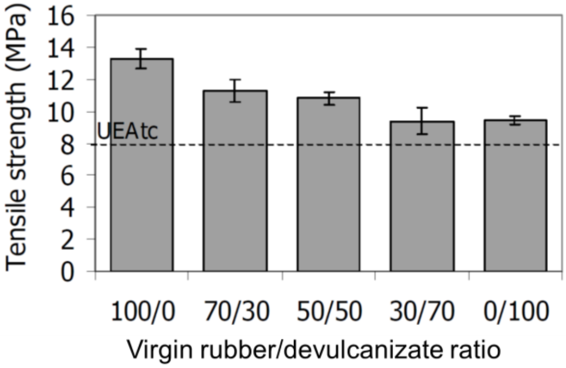


Figure 2.5 *Tensile strength of EPDM devulcanizate (0/100) compared to a virgin EPDM vulcanizate (100/0) and their blends. UEAtc: standard for EPDM roof sheeting.*[55]

Microwave processes: In the microwave technique, a controlled amount of microwave energy is used to cleave the bonds in a rubber vulcanizate network[56,57]. The rubber to be used in this process must be polar enough to absorb energy at a rate sufficient to generate the heat necessary to cut down the network structure. Microwave energy causes molecular motion in rubber molecules creating heat and thus raising the temperature of the material resulting in bond scission on the basis of the relative bond energies of C-C, C-S, and S-S bonds, as given in Figure 2.4. In theory, scission of the S-S and C-S crosslinks should occur first before C-C scission, according to their bond energies. However, the process is difficult to control due to the fast temperature increase in the microwave unit. Therefore, a cooling unit following the reclaiming step is essential. Figure 2.6 shows the process diagram of a microwave process.

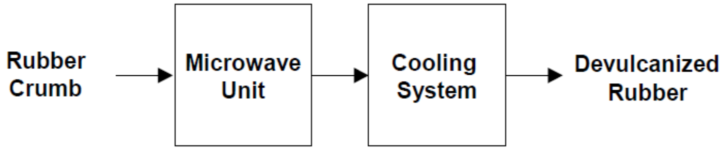


***Figure 2.6** Schematic diagram of a microwave devulcanization system*[58]

Ultrasonic processes.- Ultrasonic reclaiming processes were first studied in 1973 in a batch process by immersing bulky rubber articles in a liquid and then applying ultrasonic radiation in the range of 20 kHz[59]. The similar method was patented in 1987[60]. A small piece of vulcanized rubber was devulcanized using 50 kHz ultrasonic waves. It was claimed that that breakdown of C-S and S-S bonds occurred in this process, but that C-C bonds remained intact. The properties of the revulcanized rubber were reported to be very similar to those of the original vulcanizates.

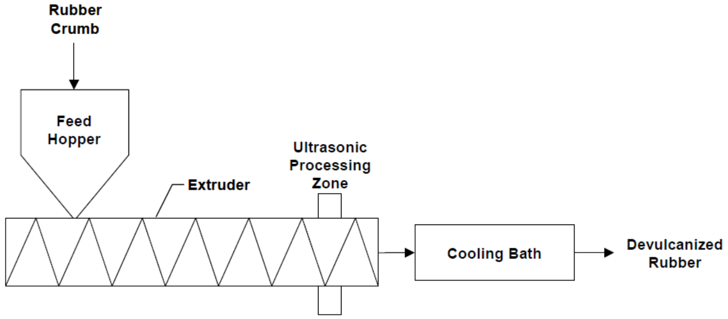


***Figure 2.7** Schematic diagram of an ultrasonic devulcanization system.*[58]

A continuous ultrasonic reclaiming technology was developed by Isayev and coworkers over the past 15 years. The experimental and theoretical studies have been published in more than 50 articles[61,62,63,64,65]. Figure 2.7 shows such a process based on the use of high-power ultrasound electromagnetic radiation in a rubber extruder. This process was described as very fast, simple, and efficient, and it was free of solvents and other chemicals. In the ultrasonic process, rubber network breakdown is caused by cavitations, which are created by high-intensity ultrasonic waves in the presence of pressure and heat. The ultrasonic energy should selectively cleave the C-S and S-S bonds since they are weaker than C-C bonds. However, a structure study of the ultrasonic treated rubbers showed that the breaking of chemical crosslinks was accompanied by partial degradation of the rubber chains.

RECLAIMING OF RUBBER BY CHEMICAL PROCESSES

The poor properties of reclaimed rubber, a consequence of the structural changes of the polymer molecules, is mainly caused by the intensive physical forces, i.e., shearing action and temperature. Under severe shear and high temperatures, various reactions occur during the reclaiming process causing main chain and crosslink scission. However, the utilization of reclaiming agents, which are effective in low concentrations, introduces new pathways for more effective and faster devulcanization. Chemical reclaiming processes are in general selective for cleaving crosslinks only.

Some of the industrial reclaiming processes make use of chemical reclaiming agents. A large number of chemical reclaiming agents for natural and synthetic rubbers have been developed. The function of these chemical agents is to initiate cleavage of sulfur crosslinks or to react with the free radical chains formed as a result of C-S, S–S and C–C bond cleavage. Various types of chemicals are used in reclaiming processes: organic compounds, e.g. mercaptanes, disulfides, phenols or amines, and inorganic additives such as metal chlorides, as well as chemical probes. Organic chemicals which are used as reclaiming agents react according to two different mechanisms: a radical or a nucleophilic mechanism. Almost the entire range of inorganic chemicals used as reclaiming aids reacts according to a catalytic reaction mechanism.

Reclaiming by a radical mechanism.-Various chemicals that were used in rubber recycling acted as radical stabilizing agents. Disulfides, thiols, phenols and phenolic compounds were added in order to scavenge radicals formed during the reclaiming process. A mechanism that is frequently proposed for the reaction of radical scavenger reclaiming agents with sulfur vulcanizates is the opening of crosslinks or the scission of polymer chains by heat and shearing forces, and the reaction of fragments with disulfide based radicals, which prevent recombination. Okamato[66] in 1980 used readily available chemicals, thiols and disulfides, on a two roll-mill to breakdown the vulcanized rubber network. They suggested that when a vulcanized rubber compound is plasticized by using mechanical shear forces, i.e.

milling, free radicals are produced that can cause the formation of main chain radicals. Chemicals like thiols and disulfides react with these radicals, thus preventing their recombination. Main chain scission occurs and crosslinks are opened, leading to a reduction in viscosity.

Disulfides are well-known reclaiming agents especially for natural rubber. As discussed in the rubber recycling review from 2002[67], De and co-workers[68,69] prepared reclaimed rubber using a two roll mill and two different reclaiming agents. One agent was a diallyl disulfide (DADS), and the other one was a renewable resource material (RRM), a vegetable product which is eco-friendly, and it contained a disulfide as the major component. They suggest that these reclaiming agents form radicals with increasing temperature by the action of shear. These radicals then combine with the polymer main chain radicals preventing their recombination. Studies of mechanochemical recycling processes of natural rubber and scrap rubber from tires indicated that DADS played an important role in the processes[70,71]. As a result, the mechanical properties, i.e., tensile strength, modulus and tear strength, of revulcanized DADS-containing rubber were higher than those of revulcanized rubber which was obtained without DADS.

Recently, the efficiency of various disulfides as recycling agents for natural rubber (NR) and ethylene propylene rubber[72,73] (EPDM) vulcanizates were reported. While devulcanization was observed on sulfur-cured NR at 200°C, a decrease in crosslink density of 90% was found when EPDM sulfur vulcanizates were heated to 275°C with diphenyldisulfide (DPDS) in a closed mold for 2 hours[74]. At the same time, EPDM cured with peroxide showed a decrease in crosslink density of about 40% under the same conditions. The effect of DPDS content on a continuous devulcanization of EPDM using a co-rotating twin screw extruder were studied[73]. The re-vulcanized EPDM showed an increase of elongation at break values with increase of DPDS concentration in the reclaiming process. Diphenyldisulfide was found to be an effective reclaiming agent for natural rubber[75]. Rajan *et al*. observed that the reclaiming agent helped in preventing the broken rubber chains to recombine. The ratio of main-chain scission to crosslink scission of natural rubber depends on both, the concentration of the reclaiming agent and the temperature of the process. The radical moieties of the chains can quickly recombine, unless a diphenyldisulfide molecule is present to act as a radical scavenger. In addition to this, the diffusion speed of the disulfide 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 diphenyldisulfide is shown in Figure 2.8. The radicals formed by scission of the disulfide are capable of hydrogen abstraction or addition to the double bonds in natural rubber[76]. Hydrogen abstraction is relatively easy because the allylic hydrogens are activated by the double bonds. The benzene-sulfide radical, therefore, abstracts the allylic hydrogen from the natural rubber vulcanizate to form benzenethiol and a natural rubber vulcanizate radical. The polymer radical can now undergo main-chain scission and/or crosslink scission.

However, one of the most important shortcomings of reclaiming with disulfide chemicals is the unpleasant odor during the reclaiming process and of the final reclaim. Tetramethyl thiuramdisulfide (TMTD) was introduced as an alternative by De *et al.*[77,78,79] TMTD is multi-functional and acts as a reclaiming agent during the reclaiming process and as a curing agent during revulcanization of the reclaimed rubber.

Another advantage of this reclaiming agent is the reduced smell during the reclamation process and of the final reclaims. Utilization of a suitable amount of TMTD caused a decrease in the gel fraction and crosslink density. A reaction scheme proposed for the reclamation of natural rubber with TMTD is shown in Figure 2.9: mechanical shearing forces break both, polymer chains and crosslinks, simultaneously with breaking of TMTD to form thiocarbamate radicals as shown in Scheme 1. Generally, the aliphatic disulfides have bond strengths of the order of 293 kJ/mol in the central S–S bond as well as in the C–S bond, which is too high to create radicals at moderate temperatures. In thiuram disulfides, potential resonance stabilization of the radicals should appreciably weaken the central bond and facilitate the formation of the thiocarbamate radical[77]. This radical may combine with a broken polymer radical as shown in Figure 2.9. When the reclaimed rubber prepared using TMTD as reclaiming agent is mixed with virgin SBR, the tensile strength increases by about 19% and 115% for 20% and 60% of reclaim respectively. Moreover, aging characteristics of the reclaimed rubber containing vulcanizates are superior compared to that of the control formulation, which does not contain any reclaim rubber. The thermal stability of the vulcanizate increases with increasing reclaimed rubber loading. However, due to high crosslink densities, vulcanizates containing rubber reclaim are vulnerable under mechanical stress[78].

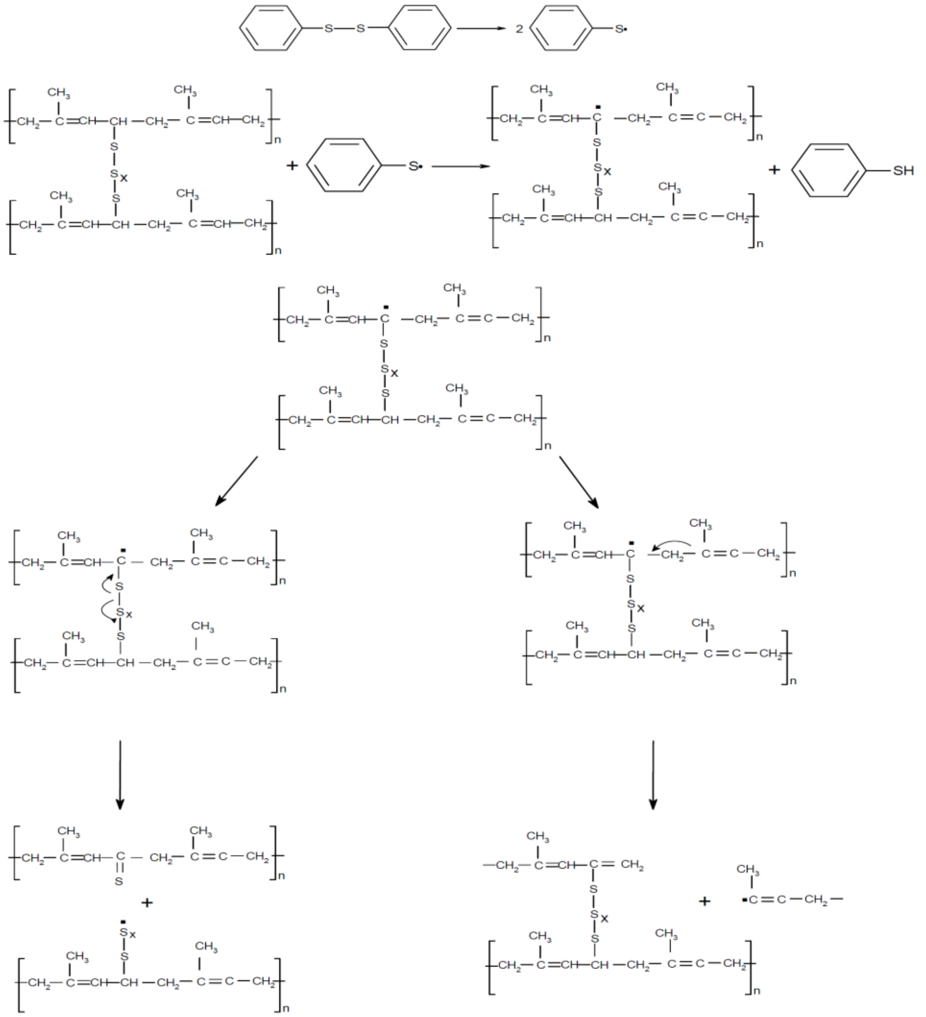
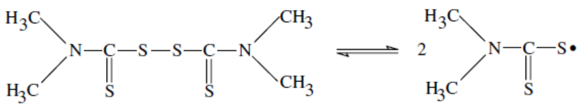
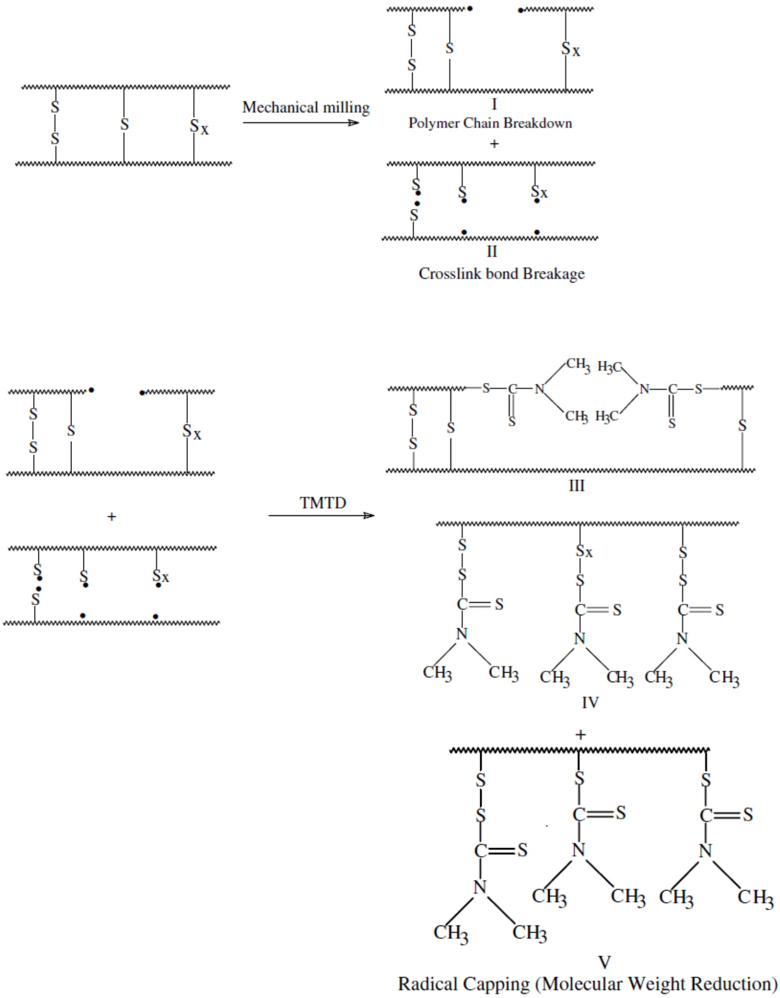


__Figure 2.8__ Simplified reaction scheme proposed for the reclamation of natural rubber by diphenyldisulfide.[75]



Scheme 1.



Scheme 2.

Figure 2.9 *Mechanical shearing forces breaking TMTD to form thiocarbamate (Scheme 1). Reaction scheme proposed for the rubber reclamation by TMTD (Scheme 2).*[77]

Reclaiming by a nucleophilic mechanism.- Suitable reclaiming agents often have a lone pair of electrons[80]; thiols and amines are examples of these types of compounds. Thiols are nucleophilic compounds and can act as hydrogen transfer agents. However, they can also react according to a radical mechanism[81]. Amines are the strongest nucleophiles; they are well known reclaiming agents making use of the fact that primary and secondary amines can cleave cyclic octasulfur (S_8).

The use of various amines and their derivatives in reclaiming of rubber was reported earlier: amines were used as reclaiming agents in the pan and digester process under both, neutral and alkaline conditions. Yamashita in 1981 stated that the scission of the rubber network occurred because amines were able to cleave the crosslinks in vulcanized rubber by a nucleophilic mechanism[82]. A reaction scheme proposed for the reclamation with amines is shown in Figure 2.10.

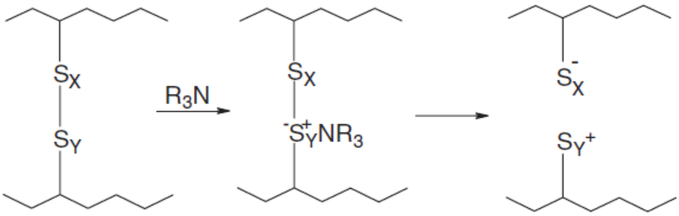


Figure 2.10 *Reaction scheme proposed for the reclamation with amines.*

Stronger amine nucleophiles were expected to be better reclaiming agents. Differences in amines that may influence the reclamation reaction are:

- type of amines (primary, secondary or tertiary),
- steric hindrance,
- basicity, and
- presence of α- hydrogen.

Verbruggen *et al.*[81] used various types of amines as reclaiming agents for EPDM rubber and found that there is almost no difference in reactivity of the different types of amines: primary, secondary and tertiary aliphatic amines as well as benzylic amines. The reactivity of the amines was neither influenced by the basicity nor by the number of protons attached to the nitrogen atom. The presence of an α-hydrogen atom was reported as the most important parameter for the reactivity. A general structure of an amine having an α-H is shown in Figure 2.11.

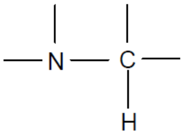


Figure 2.11 General structure of an amine having α-H.

The influence of various types and amounts of amines on the reclamation efficiency was studied[72,81,83,84]. For EPDM rubber, α- hydrogen-containing aliphatic amines, i.e. hexadecylamine (HDA), are found to be very effective[85]. The relative decrease in crosslink density was reported to be dependent on the concentration of the amines: a higher concentration of amines leads to a stronger decrease in crosslink density. The use of hexadecylamine in a comparative study of two different vulcanization systems for carbon black filled EPDM-rubber was investigated, and hexadecylamine was found to be suitable as reclaiming agent for EPDM rubber. Dijkhuis *et al.* stated that reclaimed rubber from conventionally vulcanized EPDM, mainly polysulfidic in nature, shows a decrease in crosslink density with increasing hexadecylamine concentration and at low reclaiming temperatures. After reclaiming at the lower limit of the experimental temperature window (i.e. 225°C), the concentration of remaining di- and polysulfidic crosslinks is higher than the concentration of monosulfidic bonds, while at the upper temperature level (i.e. 275°C), the concentration of monosulfidic bonds is highest, as shown in Figure 2.12. For efficiently vulcanized EPDM with primarily monosulfidic crosslinks, hexadecylamine again has a positive effect on the reclaiming efficiency at low reclaiming temperatures of max. 225°C. At higher temperatures, the crosslink density increases with increasing concentrations of hexadecylamine. A comparative study between two different vulcanization systems was done, and it was found that conventionally vulcanized EPDM devulcanizes to a larger extent by crosslink scission compared to the efficiently vulcanized material, which primarily shows main-chain scission. Both reclaimed materials can be added to a virgin masterbatch in concentrations up to 50 wt% with a limited influence on the properties. This is a rather high concentration of reclaimed rubber compared to the maximum loading of 15 wt%, commonly known to be the practical limit.

Aliphatic amines are also known to act as reclaiming agents for natural rubber. However, hexadecylamine is not working as a reclaiming agent for natural rubber based latex products. Instead of decreasing the viscosity and crosslink density of the rubber, it increases both properties relative to the thermal treatment, where no reclaiming agent is used. Figure 2.13 shows the increase in crosslink density with increasing hexadecylamine concentration for natural rubber reclamation. Rajan *et al.* found that using hexadecylamine as a reclaiming agent resulted in the formation of additional crosslinks compared to the rubber reclamation without reclaiming agent. This is explained by the presence of sulfur in the reclaimed rubber. During formation of crosslinks, polysulphide ions which were formed by cleavage of cyclic octasulfur are a crucial intermediate. Thus, this type of ions negatively influences the reclaiming process when an amine is used as reclaiming agent. Rubber reclaimed with hexadecylamine still has most of the polysulphidic crosslinks. This is explained by a complex formed by zinc-ions, which can be stabilized by amines as shown in Figure 2.14, thereby reducing the rate of crosslink scission

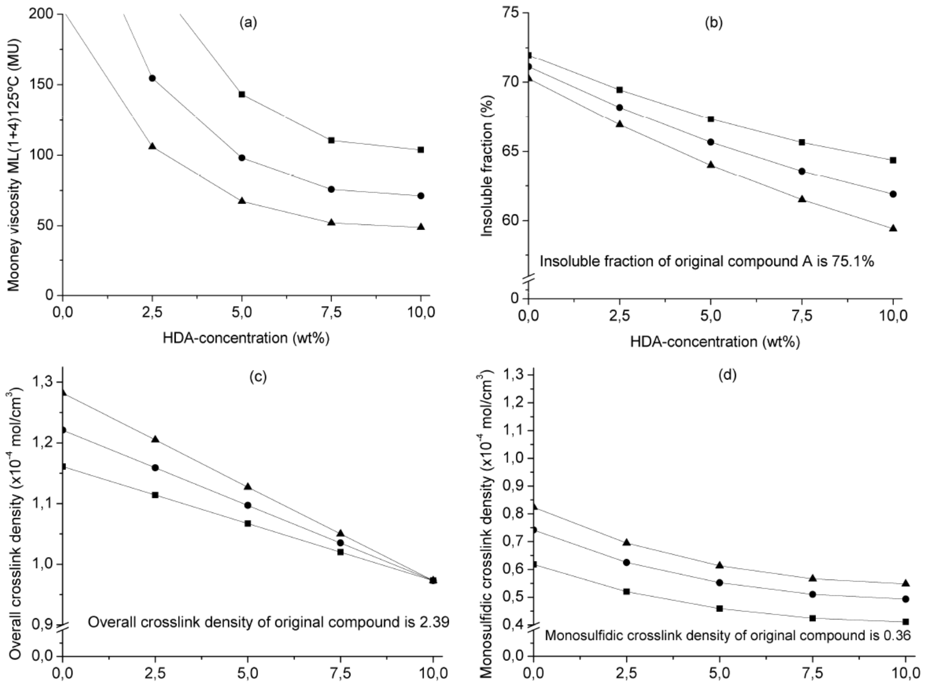


Figure 2.12 *Influence of HDA-concentration on (a): Mooney viscosity; (b): insoluble fraction; (c): overall crosslink density and (d): monosulfidic crosslink density of reclaimed EPDM; (■): 225°C; (●): 250°C; (▲): 275°C.*[86]

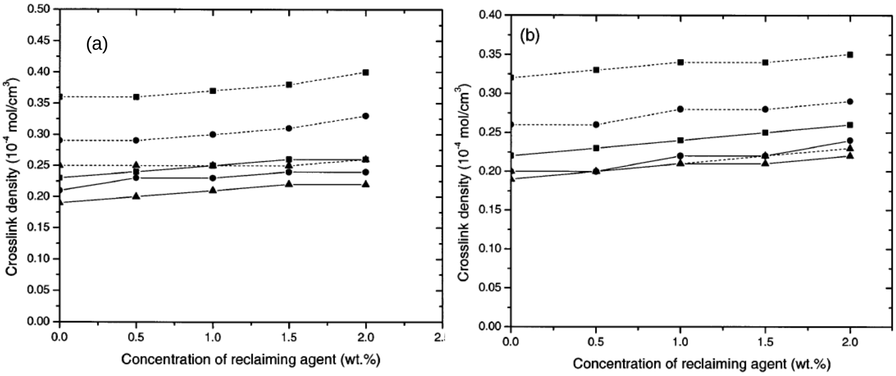


Figure 2.13 *Crosslink density of natural rubber reclaim as a function of hexadecylamine concentration at reclaiming temperatures of (a) 170 ℃ and (b) 180 ℃ and at various reclaiming times; (■): 5 min; (▲): 7 min; (●): 10 min.*[75]

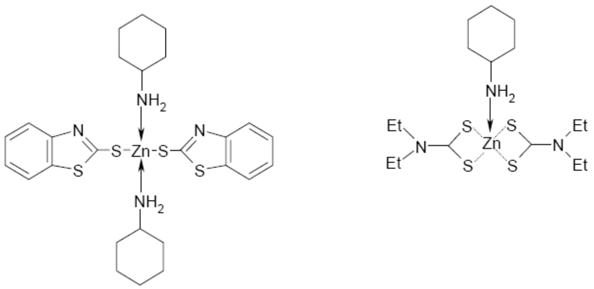


Figure 2.14 *Hypothetical complex stabilization by amines.*[87]

Reclaiming by an inorganic catalyst system.- Metal halides act as catalysts for the oxidative degradation of rubber hydrocarbons. With hydroperoxide as redox initiator, allylic radicals are easily produced in diene based rubbers and this can lead to breakdown of a bond in polymer molecules. The phenylhydrazine–ferrous chloride system was used for reclamation of various types of synthetic rubber vulcanizates[88]. Rubber vulcanizates were treated with phenylhydrazine and ferrous chloride for several hours at room temperature and atmospheric pressure. The formation of phenyl radicals by the oxidation of phenylhydrazine is accelerated by iron(II) chloride. The phenyl radical and related species might attack rubber molecules, causing network breakdown. Since the process was done in contact with air, hydroperoxides formed by the reaction of oxygen with the phenylhydrazine–ferrous chloride system could cause main chain scission. The network of the vulcanized rubber undergoes scission reactions in the following order:

polysulfide links > monosulfide links > carbon-carbon links[89]

Yehia *et al.*[90] studied the effect of metal chlorides in reclamation by the phenylhydrazine–ferrous chloride system. Reclamation was carried out in a Brabender premixer at 30 rpm rotor speed using phenyl hydrazine and 3 different types of metal chlorides, namely, $FeCl_2$, $FeCl_3$, and $ZnCl_2$. It was found that the most efficient reclaiming system is the combination of phenyl hydrazine with $ZnCl_2$ in a ratio of 1.5:1.0 phr.

The utilization of alkaline metals to break the crosslinks in rubber was patented in 1997[91]. In this process, worn-out tires and tire factory waste were devulcanized by desulfurization of rubber crumb having a particle size between 0.6 and 2.0 mm in a solvent such as toluene, naphtha, benzene or cyclohexane in the presence of sodium. The alkali metal cleaves mono-, di-, and polysulfidic crosslinks of the suspended swollen crumb at around 300°C in absence of oxygen. However, this process is very questionable in terms of environmental impact, toxicity of the chemicals and costs.

In the phase transfer catalysis reclaiming process, the transport of hydroxide ions from water into the rubber particle is described to be a crucial part in the cleavage of the crosslinks, with little main chain scission. It was firstly reported by Nicholas[92,93], who found an decreasing crosslink density with increasing amounts of catalyst.

Nicholas also investigated the reaction mechanism of reclaiming by phase transfer catalysis. Figure 2.15 illustrates the transport of an anion X^- from water into an organic phase by a quaternary ammonium chloride catalyst (Q^+Cl^-). The anion X^- is made soluble in the organic phase by its association with Q^+, which is usually substituted with large hydrocarbon radicals.

$$(Q^+Cl^-)_{org} \quad + \quad X^-_{aq} \quad \longleftrightarrow \quad (Q^+X^-)_{org} \quad + \quad Cl^-_{aq}$$

Figure 2.15 *The transportation of an anion from water into an organic phase by a catalyst.*

A process based on phase transfer catalysis was discussed in a former review[67]. It makes use of the fact that the hydroxyl anion (OH^-) is the entity that actually attacks and breaks the crosslinks. Using such an anion that abstracts a proton and forms water makes the process safe, since the disposal of dangerous by-products is not required. Two reactions could take place for the OH^- anion to react with a S-S bond without breaking the main chain, as shown in Figure 2.16 and Figure 2.17. In the first step, the disulfides could be converted to thiolates and sulfinates. The second step is the formation of methylated monosulfide: first the methylation to methyl sulfonium chloride, followed by a β-elimination to an olefin and methyl sulfide.

$$\begin{array}{llllllll}
 & 2RS\text{-}SR & + & 2OH^- & \rightleftharpoons & 2RSOH & + & 2SR^- \\
 & 2RSOH & & & \rightleftharpoons & RSOSR & + & H_2O \\
 & RSOSR & + & 2OH^- & \rightleftharpoons & RSO_2^- & + & SR^- + H_2O \\
\hline
\text{Overall} & 2RS\text{-}SR & + & 4OH^- & \rightleftharpoons & RSO_2^- & + & 3SR^- + H_2O
\end{array}$$

Figure 2.16 *Hydroxylation cleaves the crosslink in rubber molecules.*

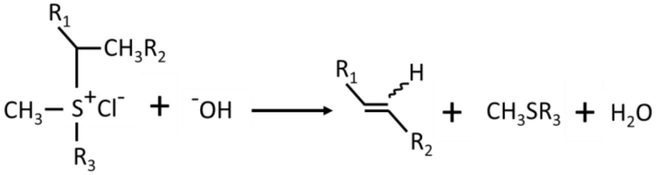


Figure 2.17 *β-elimination to methyl sulfonium chloride.*

Zeolites are molecular sieves composed of aluminosilicates. Their molecular structure is shown in Figure 2.18.

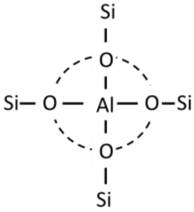


Figure 2.18 *Simplified schematic model for zeolites (aluminosilicates).*[94]

Hydrogenolysis or hydrodesulfuration use zeolites as a catalyst, and the former results in the cleavage of a chemical bond of type C-X, where C is a carbon atom and X is sulfur, nitrogen or oxygen. The net result of a hydrogenolysis reaction is the formation of C-H and H-X chemical bonds. As an example, the hydrodesulfurization reaction can simply be expressed as shown in Figure 2.19.

$$C_2H_5SH + H_2 \xrightarrow[\Delta]{\text{Zeolite}} C_2H_6 + H_2S$$

Figure 2.19 *Hydrodesulfuration of a sulfur compound.*

The hydrogen ions formed by the zeolite are able to attack sulfur resulting in the formation of hydrogen sulfide (H_2S). However, the hydrogen ions are powerful and can facilitate cracking of hydrocarbons, an unwanted reaction for devulcanization.

Reclaiming of rubber by chemical probes.- Reclaimed rubbers mostly exhibit poor mechanical properties because of main chain scission of the polymer. Schnecko[95] reviewed elastomer recycling and reported the development of chemical probes for devulcanization of crosslinked rubber. These chemical probes selectively cleave carbon–sulfur and sulfur–sulfur bonds, but they do not cleave carbon–carbon bonds. The agents for selective scission of sulfur crosslinks are thiol-amine reagents, methyliodide, triphenylphosphine, lithium aluminium hydride, hydroxyl ions, Raney nickel and sodium dibutyl phosphate. Most agents for selective scission of sulfur crosslinks act through nucleophilic displacement reactions. Different chemical probes used in chemical reclaiming processes are presented in Table 2.5. The reaction of thiol-amine reagents with sulfur crosslinks is schematically depicted in Figure 2.20. The major disadvantages of chemical probes are the toxicity of the additives and the reaction conditions that make them difficult to be applied on industrial scale.

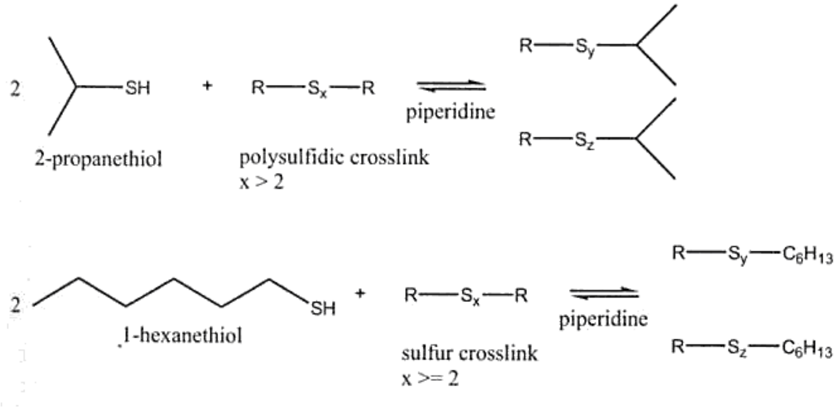


Figure 2.20 *Schematic representation of the reaction of thiol-amine reagents with sulfur crosslinks.*[81]

Table 2.5 Properties of different chemical probes[96]

Name of the chemical probes	Mechanism
Triphenylphosphine	Polysulfides transformed into monosulfides and to a lesser extent to disulfidic links
Sodium di-n-butyl phosphite	Di- and polysulfide crosslinks are broken
Propane-thiol/piperidine	Polysulfidic links are broken
Hexane-1-thiol	Poly- and disulfidic links are broken
Dithiothreitol	Disulfide bonds split into two thiol groups
Lithium aluminium hydride	Disulfide and polysulfide bonds are broken
Phenyl lithium in benzene	Polysulfide and disulfide bonds are broken
Methyl iodide	Monosulfidic links are broken

The thiol-amine combination forms a complex, possibly a piperidium propane-2-thiolate ion pair, in which the sulfur atom has an enhanced nucleophilic character and is capable of cleaving organic trisulfides and higher polysulfides. Disulfides react at a rate which is slower by a factor of one thousand. The polysulfide cleavage is faster due to p_π-d_π delocalization of the displaced σ-electron pair of RSS^- as outlined in Figure 2.21.

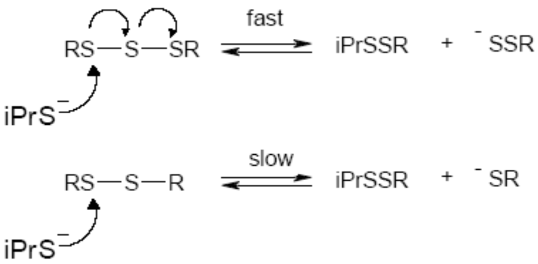


Figure 2.21 *Cleavage of poly- and disulfidic crosslinks and p_π-d_π delocalization (IPrS⁻ = nucleophilic thiol-amine associate).*

Other reaction mechanisms of chemical probes for sulfur crosslink scission, triphenylphosphine, lithium aluminum hydride, and methyliodide, are shown in Figure 2.22 to Figure 2.25.

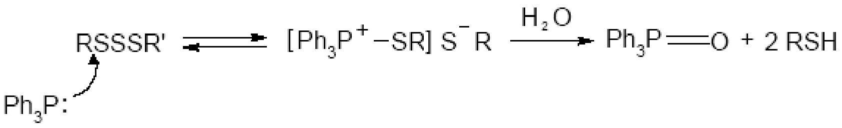


Figure 2.22 *Reaction of triphenylphosphine with a polysulfidic crosslink.*

$$RSS_xSR' \xrightarrow[H^+]{LAH} RSH + xH_2S + HSR'$$

Figure 2.23 *Reaction of lithium aluminum hydride with polysulfides.*

$$RSSR' \xrightarrow[H^+]{LAH} RSH + HSR'$$

Figure 2.24 *Reaction of lithium aluminum hydride with disulfidic bonds.*

$$R_2S + CH_3I \longrightarrow R_2\overset{+}{S}\,CH_3\,I^-$$

Figure 2.25 *Reaction of methyliodide with monosulfides.*

Reclaiming in swollen state.- The effect of adding reclaiming agents together with a swelling medium is discussed. The rubber is swollen by various types of liquids which are often descried as reclaiming oils. The reclaiming oil has several roles apart from raising the plasticity of the reclaimed rubber, such as an accelerating action on the oxidation of the rubber[97] and a gel preventing action by acting as a radical acceptor. It also facilitates the dispersion of the reclaiming agent in 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 molecules. It is assumed that these activated molecules formed by the auto-oxidation reaction accelerate the oxidation of the rubber[97,98].

NR vulcanizates are attacked by swelling in benzene with a sulfoxide compound like dimethyl sulfoxide (DMSO), di-n-propyl sulfoxide (DPSO) or a mixture of these with thiophenol, methyl iodide or n-butyl amine in a mechanochemical process on a mill[98]. A thiol and DMSO react to form a disulfide and a nucleophilic agent with the chemical composition $S(CH_3)_2$. It is reported that these reagents cause selective scission of sulfur 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. A disadvantage of this process is that solvents like DMSO and methyl iodides are highly toxic.

Swelling of ground tire rubber (GTR) in an industrial processing oil, a mixture of naphthenic hydrocarbons, is found to enhance thermochemically reclaiming of GTR[99]. In the study, the GTR was swollen in the industrial processing oil at 25 °C for 72 hours prior to the reclaiming process. The swollen GTR was then mixed with a reclaiming agent on a mill followed by thermal heating at 130 °C for 0-6 hours. Mixtures of rosin, indene-coumarone, mineral rubber, and phthalic anhydride have been used in this process as a reclaiming agent. In case of 4 hours heating, the degree of devulcanization increases from 1.4% to 6.0% in this process.

A new reclaiming process was developed in which supercritical carbon dioxide ($scCO_2$) was used along with devulcanizing agents[100]. It was expected that $scCO_2$ can be used for swelling the rubber vulcanizate similar to hydrocarbon solvents such as toluene. An advantage of using $scCO_2$ as a solvent is the easy removal as CO_2 is gaseous at ambient temperature. Unfilled polyisoprene rubber was subjected to different types of reclaiming agents using $scCO_2$: mercaptobenzothiazole (MBT), triphenyl phosphine (TP), diphenyl disulfide (DPDS) and a thiol-amine reagent from mixture of thiophenol (PhSH) and n-butylamine ($n\text{-}BuNH_2$) were used.

The thiol-amine reagent was found to be the most effective one among several devulcanizing 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 increases with increase in CO_2 pressure. In the supercritical fluid state of CO_2, the vulcanizate is more efficiently devulcanized than in an ordinary gaseous state of CO_2. The sol fraction strongly depends on the crosslink distribution in the vulcanizate. These results suggest that the devulcanizing agents penetrate and diffuse better into the vulcanizate in the presence of $scCO_2$.

2.3 MOTIVATION AND FOCUS OF THE PROJECT

Re-utilization of post-consumer tire material in new tire compounds is a necessity, but this implies that the properties of the material should not suffer by blending it with recycled rubber. The most promising way to achieve this is *de-vulcanization*, the most ideal way of rubber recycling: the process that aims to reverse vulcanization as far as possible without damaging the polymer.

The focus of the project of this thesis will be to provide further understanding regarding the themo-chemical de-vulcanization of whole passenger car tire rubbers with the main constituent SBR. In the first part subject of this thesis, the influence of material composition on the de-vulcanization efficiency[101] and material properties, on choosing an appropriate de-vulcanization aid, on optimizing the de-vulcanization process conditions, and on an application study, are investigated. In the second part, the follow-up study is to develop a continuous de-vulcanization process for passenger car tire rubber, as sensitive to tire compound compositions.

2.4 REFERENCES

[1] J.L. Zelibor, M.H. Blumenthal and F.E. Timmons, “Recycling scrap tires into new tires”, Scrap Tire Management Council, Washington D.C. (1991).

[2] A.H. Purcell, Resources, Conservation and Recycling., **2(2)**, 137 (1978).

[3] P.J.H. van Beukering and M. A. Janssen, Resources, Conservation and Recycling, **33**, 235 (2001).

[4] www.apollovredestein.com

[5] R. Datta, " Rubber curing systems " in Current Topics in Elastomer Research, ed. Bhowmick, A.K., CRC Press, USA (2008).

[6] J.R. Serumgard, presented at the meeting of Rubber Division, ACS, September 1995, Florida (USA).

[7] M. Akiba, Recycling of Rubber and Elastomers., **48(2)**, 79 (1996).

[8] Y. Fang, M. Zhang and Y. Wang, Materials and Design, **22**, 123 (2001).

[9] European Commission (EC). Directive: IP/06/1764, Brussels (2006).

[10] P.M. Lemieux and J.V. Ryan, Journal of the Air and Waste Management Association, **43**, 1106 (1993).

[11] European Tyre Recycling Association (ETRA), Introduction to Tyre Recycling, (2008).

[12] T. Amari, N.J. Themelis and I.K. Wernick, Resources Policy, **25**, 179 (1999).

[13] M. Rosendorfova´, I. Vy´bochova´ and P.J.H. van Beukering, “Waste management and recycling of tyres in Europe” Amsterdam: Institute for Environmental Studies. IVM Report Number R98/13, (1998).

[14] G. Ferrer, Resources, Conservation and Recycling, **19**, 221 (1997).

[15] J.W. Jang, T.S. Yoo, J.H. Oh and I. Iwasaki, Resources, Conservation and Recycling, **22**, 1 (1998).

[16] Used Tyre Working Group. Fourth annual report of the Used Tyre Working Group (UTWG). NTDA – National Tyre Distributors Association, UK. (2000).

[17] R.L. Hershey, “Waste Tire Utilization” US Department of Energy, (1987).

[18] F.G. Smith and W.B. Klingensmith, presented at the meeting of Rubber Division, ACS, October 1990, Washington, D.C. (USA).

[19] D.Y.C. Leung and C.L. Wang, Fuel Processing Technology, **84**, 175 (2003).

[20] W. Kaminsky, M. Predel, A. Sadiki, Polymer Degradation and Stability, **85**, 1045 (2004).

[21] J. Shah, M.R. Jan, F. Mabood and M. Shahid, Journal of the Chinese Chemical Society, **53**, 1085 (2006).

[22] S. Galvagno, S. Casu, T. Casabianca, A. Calabrese and G. Cornacchia, Waste Management, **22**, 917 (2002).

[23] M.A. Wojtowicz and M.A. Serio, Chem. Tech., **26 (10)**, 48 (1996).

[24] B. Adhikari, D. De and S. Maiti, Prog. Polym. Sci., **25**, 909 (2000).

[25] M. Phillips, Recycling Today, **35**, 42 (1997).

[26] E. Staff, Rubber Industry, Taiwan ed., **20(4)**, 28-37 (1998).

[27] M. Myhre, S.Saiwari, W.K. Dierkes and J.W.M. Noordermeer, Rubber Chem. Technol., **85**, 408 (2012).

[28] ADVAC Elastomers of Wisconsin, technical information on Tirecycle™, October (2002).

[29] F. J. Stark, presented at Australian Plastics & Rubber Institute’s 10th National Conference, October 1997, Leura (Australia).

[30] O. Grigoryeva, A. Fainleib, J. Grenet and J.M. Saiter, Rubber Chem. Technol., **81**, 739 (2008).

[31] F. G. Smith and E. J. Daniels, Resources, Conserv. Recycling, **15**, 133 (1995).

[32] A. Kolinski and T. Barnes, presented at a meeting of the Rubber Division, ACS, September 1998, Nashville (USA).

[33] V. van Binh, P. Hagemann, W. Eckart, U. Morgenstern, H. Straube and F. Francuskiewicz, WO 9602372 (1996).

[34] K. Bredberg, J. Persson, M. Christiansson, B. Stenberg and O. Holst, Appl. Microbiol. Biotechnol., **55**, 43 (2001).

[35] Tire-eating bacteria under study, Rubber Plast. News II, 10.07.(1995).

[36] J.A. Stokeley and C.H. McDonald, Public Works, **103(7)**, 46 (1972).

[37] G. Crane, R.A. Elefritz, E.L. Kay and J.R. Laman, Rubber Chem. Technol., **51**, 577 (1978).

[38] J.A. Beckman, G. Crane, E.I. Kay and J.R. Laman, Rubber Chem. Technol., **47**, 597 (1974).

[39] M. Myhre and D.A. MacKillop, Rubber Chem. Technol., **75**, 429 (2002).

[40] V.G. Gomes, presented at India Rubber Expo, IRE09, January 2009, Kolkata (India).

[41] R. Kohler and J. O'Neill, presented at a meeting of the Rubber Division, ACS, October 1995, Louisville (USA).

[42] K. Baranwal, J. W. Rogers, P. M. Standley, presented at a meeting of the Rubber Division, ACS, September 1998, Nashville (USA).

[43] G.P. Goncharuk, S.K. Flolova, B.D. Sokolov and V.F. Dorzdovskii, Int. Polym. Sci. Technol., **19**, T/3 (1992).

[44] X.X. Zhang, C.H. , Lu and M. Liang, Plast. Rubber Compos., **7(8)**, 370 (2007).

[45] E. Bilgili, A. Dybek, H. Arastoopour and B. Bernstein, J.Elastomers Plast., **35(3)**, 235 (2003).

[46] D. Brown, M. Burgoyne, and W. Maddever, presented at a meeting of the Rubber Division, ACS, October 2009, Pittsburgh (USA).

[47] M. Mouri, N. Sato, H. Okamoto, M. Matsuhita, K. Fukumori, H. Honda and K. Nakashima, Rubber Chem. Technol., **72**, 805 (1999).

[48] L.K. Kostanski, J. F. Macgregor, M.D. Burgoyue, T.W. Pattenden, A. Kolinski and M. Schnekenburger, Rubber Chem. Technol., **72**, 242 (1999).

[49] A. Kolinski, T. Banes, G. Paszkoneski and A. Haber, Rubber Chem. Technol., **73**, 169 (2000).

[50] W. Klingensmith, K. Kelly, I. Morris and V. Nilolski, Rubber Chem. Technol., **72**, 241 (1999).

[51] E. Finazzi, A. Gallo and P. Lucci, Rubber World, **243(8)**, 21 (2011).

[52] K. Fukumori, M. Matsushita, M. Mouri, H. Okamoto, N. Sato, K. Takeuchi and Y. Suzuki, Kautsch. Gummi Kunstst., **59**, 405 (2006).

[53] A. Macsiniuc, A. Rochette and D. Rodrigue, Progr. Rubber Plast. Techn., **26/2**, 51 (2010).

[54] K. Fukumori, M. Matsushita, M. Mouri, H. Okamoto, N. Sato, K. Takeuchi and Y. Suzuki, Kautsch. Gummi Kunstst., **59**, 405 (2006).

[55] P. Sutanto, Ph.D.Thesis, University of Groningen, Groningen, The Netherlands (2006).

[56] Goodyear Tire & Rubber Co. Ltd., Plast. News., Sept, 9 (1979).

[57] J.R. Hunt and J.D. Hall, US 5362759 (1994).

[58] CalRecovery, Inc., Evaluation of Waste Tire "Devulcanization Technologies" (2004).

[59] A. H. Pelofsky, US 3725314 (1973).

[60] M. Okuda, Y. Hatano, JP 62121741 (1987).

[61] C.K. Hong and A.I. Isayev, Rubber Chem. Technol., **75**, 1 (2002).

[62] J.S. Oh, A.I. Isayev and E. Von Meerwall, Rubber Chem. Technol., **77**,745 (2004).

[63] A.I. Isayev, S.H. Kim and W. Feng, Rubber Chem. Technol., **78**, 606 (2005).

[64] X. Sun, A.I. Isayev, T.R. Joshi and E. Von Meerwall, Rubber Chem. Technol., **80**,854 (2006).

[65] X. Sun and A.I. Isayev, Rubber Chem. Technol., **81**,19 (2007).

[66] H. Okamoto, Int. Polym. Sci. Technol., **7**, T/59 (1980).

[67] M. Myhre and D.A. Mackillop, Rubber Chem. Technol., **75**, 429-474 (2002).

[68] D. De, S. Maiti and B. Adhikari, J. Appl. Polym. Sci., **73**, 2951 (1999).

[69] D. De, B. Adhikari and S. Maiti, Polym. Mater., **14**, 333 (1997).

[70] G.K. Jana and C.K. Das, Polym. Plast. Techn. Eng. , **44**, 1399 (2005).

[71] G.K. Jana, C.K. Das, Progr. Rubber Plast. Recycling Techn. , **21 (4)**, 319 (2005).

[72] K.A.J. Dijkhuis, J.W.M. Noordermeer and W.K. Dierkes, presented at a meeting of the Rubber Division, ACS, October 2008, Louisville (USA).

[73] A.R. Jalilvand, I. Ghasemi, M. Karrabi and H. Azizi, Progr. Rubber. Plast. Recycling Techn., **24**, 33 (2008).

[74] M.A.L. Verbruggen, L. van der Does, J.W.M., Noordermeer, M. van Duin and H.J. Manuel, Rubber Chem. Technol., **72**, 731 (1999).

[75] V.V. Rajan, W. K. Dierkes, J.W.M. Noordermeer and R. Joseph, Rubber Chem. Technol., **78**, 572 (2005).

[76] A. Z. Kuzmiski, Developments in polymer stabilization, G. Scott, Ed., Applied Science Publishers, London (1981).

[77] D. De, A. Das, D. De, B. Dey, S.C. Debnath and B.C. Roy, European Polym. J., **42**, 917 (2006).

[78] D. De, and D. De, Mat. Sci. App., **2**, 486 (2011).

[79] D. De, D. De and G. M. Singharoy, Polym. Eng. Sci., **47(7)**, 1091 (2007).

[80] H-J. Buschleb, Plast. Kautsch., **37**, 205 (1990).

[81] M.A.L. Verbruggen, Ph.D.Thesis, University of Twente, Enschede, The Netherlands (2007).

[82] S. Yamashita, Int. Polym. Sci. Techn., **8(12)**, T/77 (1981).

[83] P. Sutanto, F. Picchioni, P.B.M. Janssen, K. A. J. Dijkhuis, W. K. Dierkes and J. W. M. Noordermeer, Journal App. Polym. Sci., **102**, 5948 (2006).

[84] K.A.J. Dijkhuis, I. Babu, J. Lopulissa, J.W.N. , Noordermeer and W.K. Dierkes, Rubber Chem. Technol., **81**, 865 (2008).

[85] M. van Duin, J. W. M. Noordermeer, M. A. L. Verbruggen and L. van der Does

(to DSM) U.S. 6,956, 065 (2005).

[86] K.A.J. Dijkhuis, I. Babu, J. Lopulissa, J.W.N. , Noordermeer and W.K. Dierkes, Rubber Chem. Technol., **81**, 190 (2008).

[87] G. Heideman, Ph.D.Thesis, University of Twente, Enschede, The Netherlands (2004).

[88] S. Yamashita, N. Kawabata and K. Hatashi, Nippon Gomu Kyokai, **49**, 420 (1976).

[89] S. Yamashita, N. Kawabata, S. Sagan and K. Hatashi, J. Appl. Polym. Sci., **21**, 2201 (1977).

[90] A.A. Yehia, M.N. Ismail, Y.A. Hefny, E.M. Abdelbary and M.A. Mull, J. Elast. Plast., **33**, 109 (2004).

[91] R.D. Myers, P. Nicholson, J.B. MacLeod and M.E. Moir, US 5,602,186. (1997).

[92] P. P. Nicholas, Rubber Chem. Technol., **55**, 1499 (1982).

[93] P.P. Nicholas, US 4,161,464. (1979).

[94] P. B. Venuto, Microporous Mat., **2**, 297 (1994).

[95] H. Schnecko, Kautsch. Gummi Kunstst., **47**, 885 (1994).

[96] B. Adhikari, D. De and S. Maiti, Progr. Polym. Sci., **25**, 909–948 (2000).

[97] Kawasaki et al., Ordinary Overall Research Publication Meeting of the Jap. Rubber Soc., Lecture Reprints, **36**, 37 (1979).

[98] Y. Onouchi, S. Inagaki, H. Okamoto and J. Furukawa, Int. Polym. Sci. Techn., **55**, T/58 (1982).

[99] O. Grigoryeva, A. Fainleib, O. Starostenko, I. Danilenko, N. Kozak and G. Dudarenko, Rubber Chem. Technol., **76**,131 (2003).

[100] M. Kojima, K. Ogawa, H. Mizoshima, M. Tosaka, S. Kohjiya and Y. Ikeda, Rubber Chem. Technol., **76**, 957, (2003).

[101] M. M. Horikx, J. Polym. Sci., **19**, 445 (1956).

CHAPTER 3

THERMAL DE-VULCANIZATION OF SULFUR-VULCANIZED SBR

The general problem of reclaiming of rubber is the fact that besides crosslinks also polymer chains are broken in this process, and this influences the properties and reduces the quality of the recycled material. An efficient de-vulcanization is needed in order to achieve a high-quality recycled rubber.

Within this study, recycling of sulfur-cured SBR in a thermal de-vulcanization process is investigated in order to elaborate the correlation between the process conditions and the ratio of polymer chain to crosslink scission. The temperature range for the de-vulcanization is varied from 180 ℃ to 300 ℃, and the treatments are done in air and in a nitrogen atmosphere. Depending on the parameters used, the sol fraction increases as expected, and crosslink density first decreases, but increases again above a temperature threshold of 220 ℃. The reason for this increase in crosslink density is a complicated intra-molecular rearrangement of chain fragments due to uncontrolled degradation and oxidation effects. Preventing oxidation during thermal treatment reduces the degree of rearrangement and results in significantly improved SBR de-vulcanizate properties.

3.1 INTRODUCTION

Synthetic Styrene-Butadiene Rubber (SBR) is widely used in the rubber industry, especially in passenger car tire treads in which it provides a good balance of abrasion resistance, aging stability and dynamic properties. Solution-SBR (S-SBR) is used especially for silica-reinforced treads, as this combination reduces rolling resistance for about 30% compared to carbon black filled treads.

There have been many attempts to recycle SBR rubber. However, de-vulcanization of SBR is difficult due to the specific structure of the elastomer. In SBR de-vulcanization, network breakdown occurs, but at the same time network recombination takes place. The reaction mechanisms of SBR de-vulcanization are not very well documented. Although the molecular structures of SBR as well as of Natural Rubber (NR) have C=C double bonds in the main chain, they do not react in the same way under identical de-vulcanization conditions. A first comparative study of SBR and NR recycling or de-vulcanization was reported by Hader and le Beau[1] in 1951. They stated that molecular breakdown of SBR is complicated and difficult to explain, unlike the breakdown of natural rubber. In the NR de-vulcanization process, the predominant reaction is scission of the hydrocarbon molecule; recombination of chain fragments occurs only to a small extent. The complicated structure of SBR is related to the various possible molecular configurations inherent to the polymerization mechanism of the monomers, as well as to the specific behavior of the copolymer. In the SBR de-vulcanization process a considerable amount of main chain scission takes place, which is outbalanced by an extensive recombination of molecular fragments as the de-vulcanization process proceeds, resulting in progressive hardening of the elastomer. Consequently, plasticity decreases again after an initial increase. These unique characteristics of SBR were confirmed by studying ultrasonic de-vulcanization of SBR[2-8]. During ultrasonic treatment of SBR, network formation and chain branching occur simultaneously due to the formation of macroradicals. The generation of these macroradicals is induced by high energy density areas caused by the ultrasonic treatment.

In the present chapter, special attention will be devoted to the network breakdown and re-formation of sulfur-cured SBR in a thermal de-vulcanization process. To get a better understanding of the mechanisms that govern the changes of the molecular structure of SBR, the investigations were done under various conditions: The temperature range for the experiments was from 180°C to 300°C, and the treatments were done in air and under nitrogen. The mechanical properties of various de-vulcanized SBR vulcanizates are compared. Finally, an application study for re-utilization of the de-vulcanizate in a blend with a virgin compound is performed.

3.2 EXPERIMENTAL

MATERIALS

The SBR type used in this investigation was SBR 1723, an oil extended SBR containing 37.5 phr of treated distillate aromatic extracts (TDAE) oil, obtained from Dow Chemical, Germany. The polymer contained 23.5 wt% styrene, and its Mooney viscosity ML(1+4) measured at 100 °C was 40 MU. Zinc oxide, ZnO, and stearic acid were obtained from Flexsys, The Netherlands. The curatives: sulfur and N-tert-butyl-2-benzothiazolesulfenamide (TBBS) were both obtained from Merck. The solvents, acetone and tetrahydrofuran (THF), which were used for extractions, and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve.

PREPARATION OF DE-VULCANIZED SBR

Mixing and vulcanization.- The SBR was first compounded using a Brabender Plasticorder 350S mixer with a mixing chamber volume of 350 cm^3. The compounding formulation was according to ASTM D3185-99 as shown in Table 3.1, but excluding the carbon black for the material that is to be de-vulcanized. The mixer was operated at a rotor speed of 60 rpm; a fill factor of 0.75 and an initial temperature of 50°C were used. The final compound temperature before dumping was in the range of 70-90°C. The compounds was tested for its cure characteristics using a RPA 2000 dynamic mechanical curemeter from Alpha Technologies at 160 and 170°C, 0.833 Hz and 0.2 degree strain, according to ISO 6502. The SBR compounds were then vulcanized for $t_{c,90}$ + 5 minutes in a Wickert WLP1600 laboratory compression molding press at 170°C and 100 bar, into 2 mm thick sheets.

Grinding.- The vulcanized SBR sheets were subsequently ground in a Fritsch Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen. The particle size of the ground rubber was in the range of 0.85-2.00 mm.

Table 3.1 Formulation of the SBR compound according to ASTM D3185-99

Ingredient	phr
SBR 1723	100
Zinc oxide	3
Stearic acid	1
Sulfur	1.75
Accelerator (TBBS)	1.38
Carbon black (N375)	68.5

De-vulcanization.- The thermal de-vulcanization was performed in a batch process in an internal mixer Brabender Plasticorder PL-2000, having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.7 and a constant rotor speed of 50 rpm were used. The de-vulcanization temperature was varied from 180 to 300°C and the de-vulcanization time was 5 minutes. After de-vulcanization, the material was taken out of the internal mixer under 2 different conditions, into atmospheric air and into liquid nitrogen.

The following variations of the experimental conditions are compared in this study:

TT: thermal treatment without exclusion of oxygen;

TL: thermal treatment and quenching in liquid nitrogen after de-vulcanization;

TN: thermal treatment under nitrogen atmosphere and quenching in liquid nitrogen after de-vulcanization.

CHARACTERIZATION OF THE DE-VULCANIZATES.

Rubber soluble fraction.- The soluble (Sol) and insoluble (Gel) fractions of the reclaimed materials were determined by extraction in a Soxhlet apparatus. The vulcanized and de-vulcanized SBR samples were extracted initially for 48 hrs in acetone in order to remove low molecular polar substances like remains of accelerators and curatives, followed by an extraction for 72 hrs in THF to remove the apolar components: oil and non-crosslinked polymer residues or soluble polymer released from the network by the de-vulcanization process. The extraction was followed by drying the samples in a vacuum oven at 40°C and determining the weight loss until constant weight. The sol fraction was defined as the sum of the soluble fractions in acetone and THF. The correction for the oil contained in the original SBR has been made. The gel fraction was calculated by the following equation:

$$Gel\ fraction = 1 - \frac{wieght\ of\ rubber\ dissolved\ in\ solvents}{weight\ of\ pure\ rubber\ in\ compound} \qquad (1)$$

Crosslink density.- The extracted SBR samples were swollen in toluene for 72 hrs at room temperature. The weight of the swollen vulcanizates was measured after removal of surface liquid with absorption paper. The crosslink density was calculated according to the Flory-Rehner equation[9], equations 2 and 3:

$$\upsilon_e = \frac{V_r + \chi V_r^2 + \ln(1 - V_r)}{V_s\left(0.5V_r - V_r^{\frac{1}{3}}\right)} \qquad (2)$$

with

$$V_r = \frac{m_r}{m_r + m_r({}^{\rho_r}/_{\rho_s})} \qquad (3)$$

where:

ν_e = crosslink density per unit volume;

V_r = polymer volume fraction of the swollen sample;

V_s = solvent molar volume;

m_r = mass of the rubber network;

m_s = weight of solvent in the sample at equilibrium swelling;

ρ_r = density of the rubber;

ρ_s = density of the solvent;

χ = Flory-Huggins polymer-solvent interaction parameter (0.37 for the system SBR/toluene[10,11])

This calculated crosslink density is based on the volume of gel rubber in the rubber network after extraction. However, in order to compare these data with the Horikx theory, it has to be realized that the latter defines the crosslink density after de-vulcanization with the sol fraction still present. During the swelling test this sol fraction is also extracted, therefore needs to be included again in the calculation of the real crosslink density ν_{real}, remaining after the de-vulcanization but before the extraction. Consequently, to obtain the actual remaining crosslink density of the de-vulcanizate, the volume of total rubber is needed to be taken into account. Correction for this real crosslink density was made according to equation 4:

$$\nu_{real} = \frac{\text{Number of crosslinks}}{\text{Volume of } \underline{\text{total rubber}}} = \nu_e \text{ x } (1\text{-sol fraction}) \qquad (4)$$

where

ν_{real} = the final corrected crosslink density for the de-vulcanizate.

Viscosity.- Complex viscosity values were analyzed via dynamic viscoelastic measurements performed with the RPA 2000. The oscillation frequency was set in the range of 0.01-33 Hz at a constant strain of 0.56%. This strain was chosen in order to assure linear viscoelastic behavior during the test. The frequency-sweeps of cured specimens were performed after vulcanization for t_{90} at the appropriate temperature, followed by a cooling step to reach 100°C in the RPA. The storage (G') and loss shear (G'') modulus were measured. The complex viscosities, η^*, were then calculated by the following equations when ω is the frequency in radians per second:

$$(\eta *)^2 = (\eta')^2 + (\eta'')^2 \qquad (5)$$

where

$$\eta' = {G''}/{\omega} \qquad (6)$$

$$\eta'' = {G'}/{\omega} \qquad (7)$$

Thermogravimetric analysis (TGA).- The thermal decomposition behavior of vulcanized and de-vulcanized SBR was analyzed by thermogravimetric analysis (TGA) using a TGA7 from Perkin Elmer. Approximately 5-10 mg of the sample were heated with a heating rate of 10°C/min. in a nitrogen atmosphere.

FT-IR spectroscopy.- Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer 100 Series system using an Attenuated Total Reflectance (ATR) attachment, which enables samples to be examined in the solid or liquid state without further preparation. The spectra were recorded with a resolution of 4.0 cm^{-1}; the number of scans was 16 and the scan range 4000-650 cm^{-1}.

RE-VULCANIZATION AND MECHANICAL PROPERTIES.

After the de-vulcanization, selected de-vulcanized material (de-vulcanized rubber at de-vulcanization temperature of 220°C) was blended with the original virgin SBR at a blending ratio of 50/50 and compounded with the formulation according to ASTM D3185-99 shown in Table 3.1 In this case carbon black was included. The following notations were used:

SBR/D-TT: blend of virgin SBR with de-vulcanizate from thermal treatment without exclusion of oxygen;

SBR/D-TL: blend of virgin SBR with de-vulcanizate from thermal treatment with quenching in liquid nitrogen after de-vulcanization;

SBR/D-TN: blend of virgin SBR with de-vulcanizate from thermal treatment under nitrogen atmosphere and quenching in liquid nitrogen after de-vulcanization.

The de-vulcanized rubber, virgin SBR and the blends as well as the curing additives were mixed on a laboratory scale Schwabenthan two-roll mill (15 x 33 cm Polymix 80). The amounts of curatives were based on the total SBR polymer content, including the polymer content of the de-vulcanized rubber. The compounds were sheeted off at a thickness of approximately 2 mm and vulcanized again as described above. The cured sheets had a thickness of 2 mm for tensile test samples.

Tensile tests were carried out on dumb-bell shaped specimens (type 2) according to ISO 37, using a Zwick Z1.0 tensile testing machine. The tests were performed at a constant crosshead speed of 500 mm/min, using a load cell of 500N.

The hardness of the samples was measured with a Zwick hardness tester, Shore A type, according to ASTM D2240-02.

3.3 RESULTS AND DISCUSSION

RUBBER SOL FRACTIONS AFTER DE-VULCANIZATION.

The sol fractions of the TT, TL and TN de-vulcanizates are depicted in Figure 3.1 as a function of the de-vulcanization temperature.

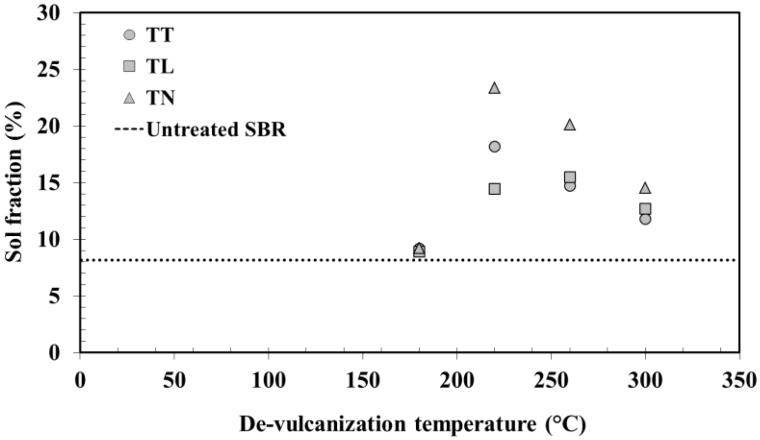


Figure 3.1 *Sol fraction as a function of the de-vulcanization temperature for de-vulcanized SBR compared to untreated vulcanized SBR (dotted line).*

Thermal treatment of sulfur-cured SBR at 180°C exhibits a sol fraction similar to the sol fraction of untreated SBR. This is an indication that at this temperature the rubber network is still fully intact. The soluble fraction then increases with increasing de-vulcanization temperature up to 220°C: The increase of the rubber sol fraction indicates the extent to which the rubber network is broken. Above this temperature, the sol fractions decrease again. This may be attributed to a more extensive generation of reactive radicals and to the complex chemical transformations taking place at higher de-vulcanization temperatures. These chemical transformations are main chain scission, breakup of poly-, di- and monosulfidic crosslinks, transformation of sulfidic crosslinks into cyclic sulfidic structures on the elastomer backbone, and transformation of polysulfidic crosslinks into di- and monosulfidic crosslinks[6]. Prominence of these phenomena with increasing de-vulcanization temperature lead to formation of new inter- and intramolecular bonds[12] resulting in a decrease of the rubber sol fraction above a certain temperature threshold. Additionally, it can be seen that the sol fraction increases with exclusion of oxygen in de-vulcanization process. The TN sample, treatment under nitrogen atmosphere, shows the highest rubber sol fractions for all temperatures. Exclusion of oxygen, or in other words, an inert de-vulcanization condition leads to suppression of the generation of reactive radicals followed by reduction of the complex chemical transformations. With increasing temperature, the difference in sol fraction between the samples is reduced: breakdown of the polymer chains and reformation of bonds is mainly governed by temperature and less by the presence of oxygen. At temperatures from 250°C onwards, the sol fractions of the two samples without nitrogen atmosphere, TL and TT, are almost equal and significantly lower than the sol fraction of the TN sample. This emphasizes the importance of an oxygen-free atmosphere during de-vulcanization.

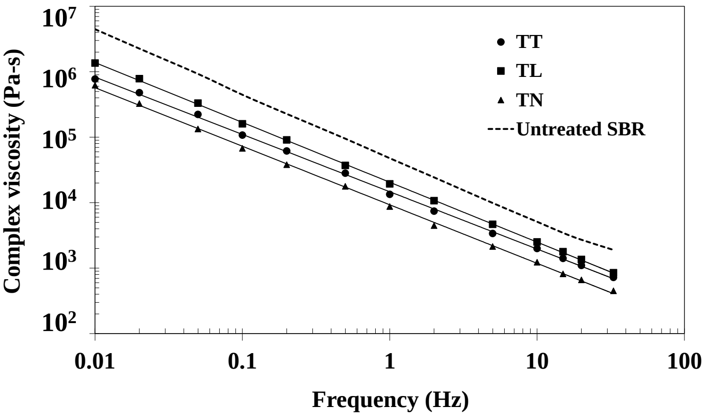


Figure 3.2 *Complex viscosity as a function of frequency of de-vulcanized SBR compared to untreated vulcanized SBR; de-vulcanization temperature: 220 °C.*

VISCOSITY

Plots of complex viscosity versus oscillating frequency of the 220°C de-vulcanized SBR materials are shown in Figure 3.2. The viscosity levels of the de-vulcanized SBR samples are significantly lower than that of untreated SBR, due to the cleavage of the three dimensional rubber networks during de-vulcanization by both main-chain and crosslink scission. The viscosity curve of the de-vulcanized materials treated under nitrogen atmosphere and quenched in liquid nitrogen is the lowest. The trend of the viscosity curves corresponds well with the trend of the extracted rubber sol fraction (Figure 3.1). This indicates that the generation of small molecular chains during de-vulcanization which are extracted in the rubber sol fraction measurement, is also explicitly demonstrated in the low viscosity of the material.

CROSSLINK DENSITY

The crosslink densities of the three de-vulcanized SBR samples, TT, TL and TN, are shown in Figure 3 as a function of de-vulcanization temperature. Increase of the de-vulcanization temperature up to 220°C results in a decrease of the crosslink density. There is a slight difference between the 3 samples to the benefit of TN. At temperatures above 220°C, a significant influence of the de-vulcanization condition on the crosslink density is observed. Within this temperature range, the crosslink density first decreases, but increases again at higher temperature. This effect occurs under all de-vulcanization conditions and is most pronounced for the thermal treatment without exclusion of oxygen: TT. This is in accordance with the trend found for the sol fraction. Therefore, the nitrogen blanket prevents to a large extent the increase in crosslink density due to air or oxygen.

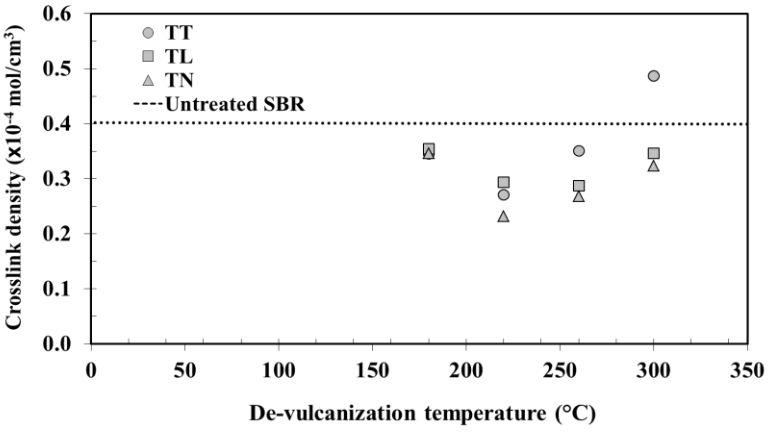


Figure 3.3 *Crosslink density as a function of de-vulcanization temperature for de-vulcanized SBR, compared to untreated vulcanized SBR (dotted line).*

MECHANISTIC CONSIDERATIONS.

A useful tool to further understand the de-vulcanization mechanism is the method developed by Horikx[13]: the rubber sol fraction of the de-vulcanizates and the crosslink density of the rubber gel fractions are correlated. Horikx derived a theoretical relationship between the soluble fraction generated after degradation of a polymer network and the relative decrease in crosslink density, as a result of either main-chain scission or crosslink breakage. This treatment of polymer degradation can equally well be applied to rubber reclaiming, where also a mix of main-chain scission and crosslink breakage takes place. When main-chain scission takes place, the relative decrease in crosslink density is given by:

$$1-\frac{\nu_f}{\nu_i}=1-\left[\frac{\left(1-s_f^{1/2}\right)^2}{\left(1-s_i^{1/2}\right)^2}\right] \qquad (8)$$

where s_i is the soluble fraction of the rubber network before degradation or reclaiming, s_f is the soluble fraction of the reclaimed vulcanizate, ν_i is the crosslink density of the network prior to treatment and ν_f is the crosslink density of the reclaimed vulcanizate. For pure crosslink scission, the soluble fraction is related to the relative decrease in crosslink density by:

$$1-\frac{\nu_f}{\nu_i}=1-\left[\frac{\gamma_f\left(1-s_f^{1/2}\right)^2}{\gamma_i\left(1-s_i^{1/2}\right)^2}\right] \qquad (9)$$

where the parameters γ_f and γ_i are the average number of crosslinks per chain in the insoluble network after and before reclamation, respectively. The values for γ_f and γ_i are determined as described by Verbruggen[14]. Figure 3.4 gives a graphical representation of equations 8 and 9. The curves in the figures correspond to the situation where only main chains are broken (solid curve) and where only crosslinks are broken (dashed curve). In the case of crosslink scission only, almost no sol is generated until most of the crosslinks are broken; only then the long chains can be removed from the network. In the case of main-chain scission, sol is produced at a much earlier stage, because random scission of the polymers in the network results in small loose chains, which can easily be removed.

Figure 3.5 shows the experimentally determined sol fractions of de-vulcanized SBR at various de-vulcanization temperatures as a function of the relative decrease in crosslink density. For the thermally treated material, TT in Figure 3.5(a), an increase of the de-vulcanization temperature to 220°C results in a shift of the data point to the upper right hand side of the graph, which indicates an increase of sol fraction and decrease of crosslink density. Nevertheless, a further increase of de-vulcanization temperature to 260°C results in a back turn of the experimental data point to the left, which is the reverse of the expected decrease of crosslink density. This reversion phenomenon is even more pronounced for de-vulcanization up to 300°C; for this temperature the data point is even found at the left hand side of the value for untreated SBR. The detrimental effect of the presence of oxygen in the de-vulcanization process causes inefficient de-vulcanization, in which the crosslink density of the de-vulcanized rubber is even higher than that of the untreated vulcanized one.

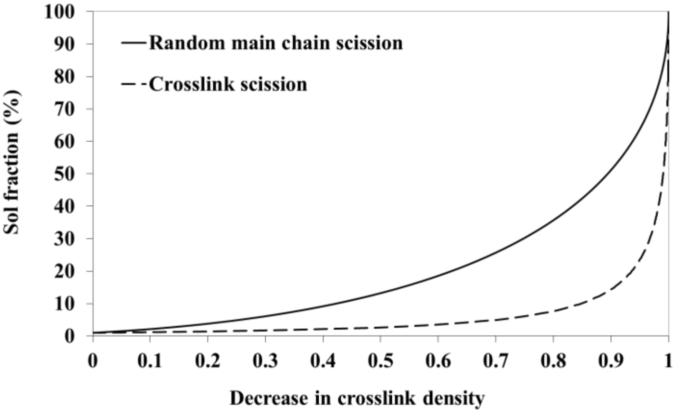


Figure 3.4 *Random main chain scission and crosslink scission curves in a Horikx plot.*

A suppression of the inefficient de-vulcanization is observed when oxygen is excluded; the results of the TL and TN sample are shown in Figure 3.5 (b) and (c), respectively. These figures illustrate that the experimental data for treatment at 180°C are situated at more or less the same position as the data for TT. An increase of the de-vulcanization temperature to 220°C exhibits the same trend as found for TT: the percentage of soluble polymer is increased and the crosslink density is decreased. For TL, the values after treatment at 260°C are more or less at the same position as the values for the materials de-vulcanized at 220°C; however, the reversion phenomenon still occurs when the de-vulcanization temperature is further raised above 260°C. For TN, the data points first move to the right hand side for a treatment temperature of 220°C, but then turn back to the left hand side for de-vulcanization temperatures of 260°C and 300°C.

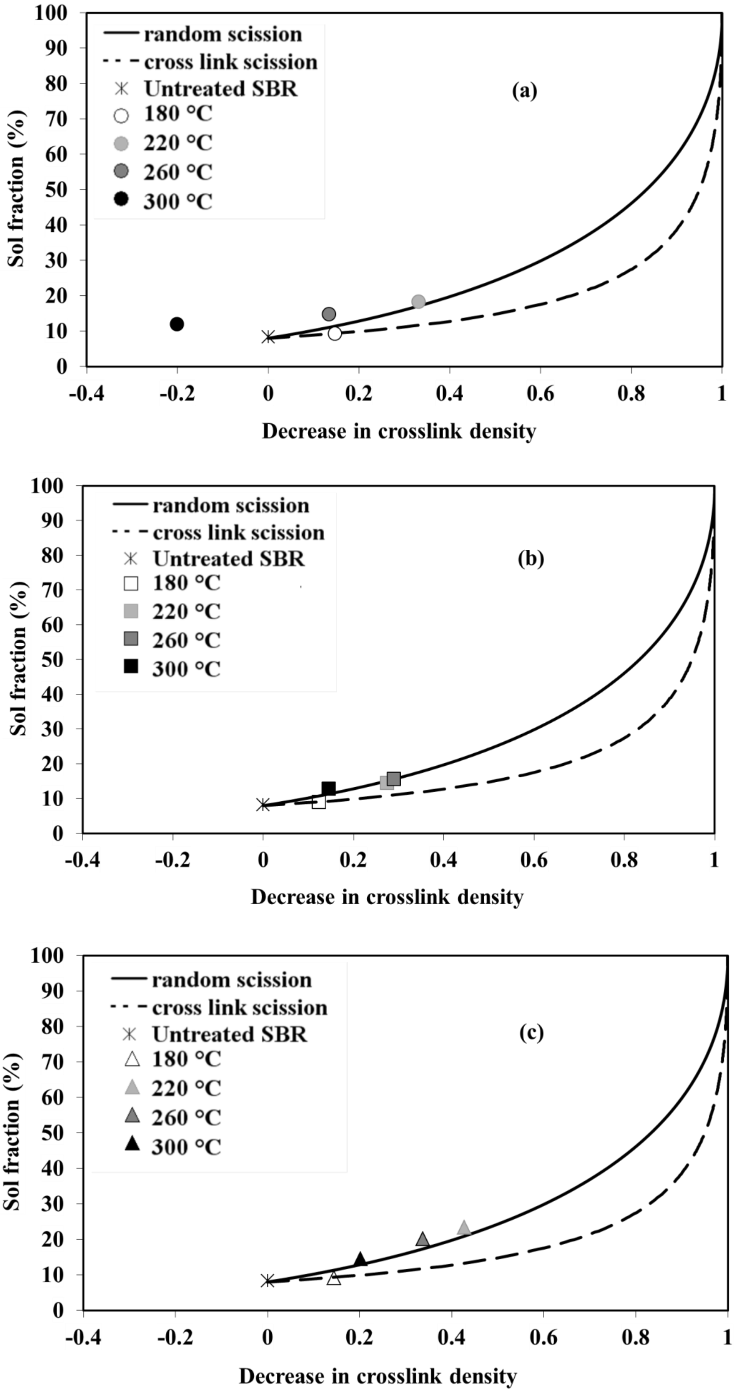


Figure 3.5 *Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of de-vulcanized SBR. a: TT; b: TL; c: TN.*

However, the detrimental effect of the presence of oxygen in the de-vulcanization is smallest with nitrogen present during de-vulcanization and quenching in liquid nitrogen.

The reversion phenomenon is less progressive in this case as the crosslink densities observed are still lower than the crosslink densities of de-vulcanized rubber treated at 180°C and untreated rubber. Thus, it must be concluded that working under exclusion of oxygen during and after de-vulcanization is a requirement for an efficient de-vulcanization process of SBR, and the temperature of 220°C is the optimum for de-vulcanization. Above 220°C reversion phenomena appear, whatever conditions are used. Based on the results, it is to be concluded that the de-vulcanization as obtained under the present conditions is primarily via the mechanism of main-chain scission. Theoretically, the scission of C-S bonds and S-S bonds which have lower bond strength than C-C bonds should be the priority mechanism in network scission. However, practically, the data showed that main-chain scission mainly occurs. This is due to uncontrolled scission of the rubber network in a thermal process. As there is a majority of C-C bonds compared to C-S and S-S bonds, the probability of cleavage of the polymer backbone is higher.

FTIR CHARACTERIZATION

Infrared absorption spectra of the de-vulcanized SBR: TT, TL and TN, are shown in Figures 3.6(a), (b) and (c), respectively. The intensity of the infrared absorption peaks at 966 and 699 cm^{-1}, which are assigned to aromatic C-C stretching modes of SBR[14,15], are independent of the de-vulcanization conditions. Other SBR peaks at 912 and 757 cm^{-1} are attributed to the trans 1,4 structure and the γ_{CH} of the single substituted benzene ring and the CH out of plane deformation[15,16], are also observed. The intensity of the infrared absorption peak at 1640 cm^{-1}, which is assigned to the stretching vibration of carbonyl groups[15,16], increased with increasing de-vulcanization temperature in Figure 3.6(a) and 3.6(b), however it shows no changes in Figure 3.6(c) for TN . This indicates oxidative degradation of SBR molecules during de-vulcanization without full exclusion of oxygen. In addition, the carbon disulfide peaks[17] of the absorption band at 1540 cm^{-1} is not changing with the de-vulcanization temperature for the TL and TN materials. However, for the TT material, the peak increases with increasing de-vulcanization temperature. The results are in agreement with the previous ones indicating that TN de-vulcanized rubber has the lowest chemical structural damage due to oxygen.

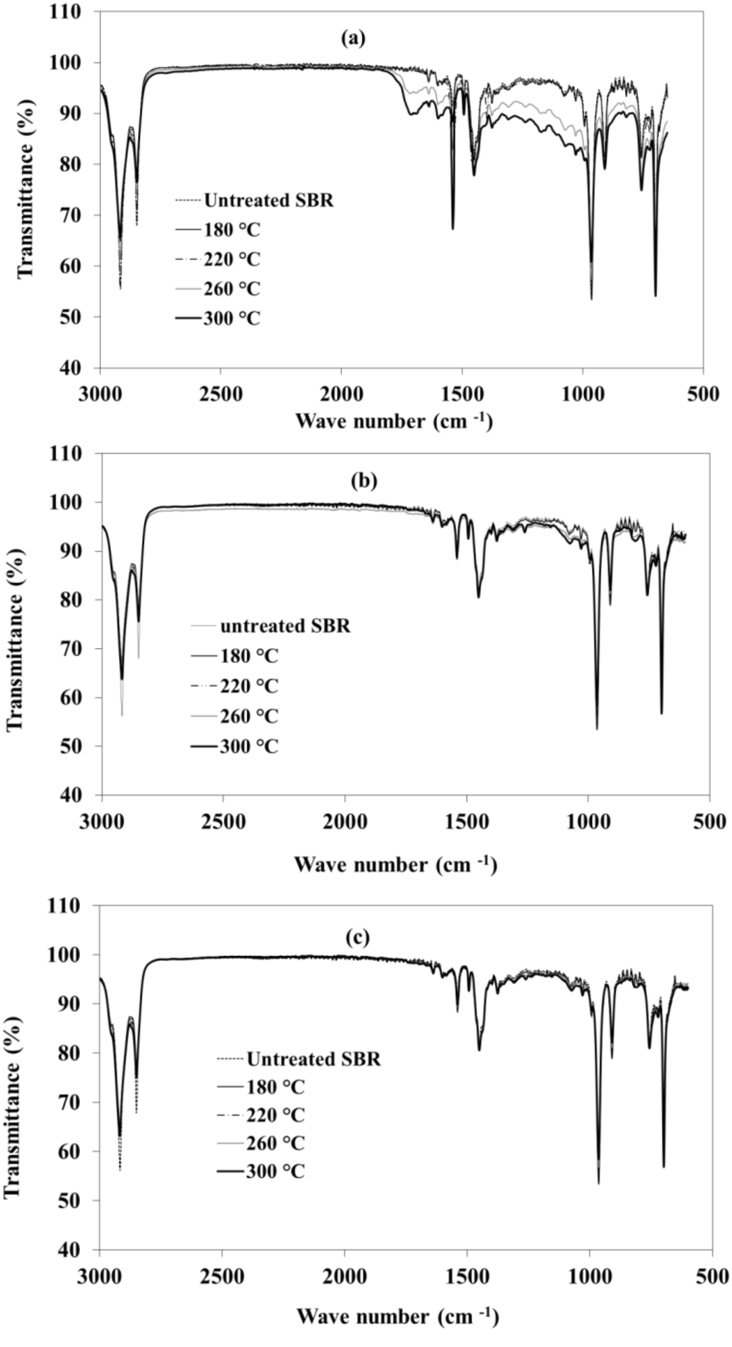


Figure 3.6 *Infrared spectra of de-vulcanized SBR compared to vulcanized SBR a: TT; b: TL; c: TN.*

THERMAL STABILITY

The thermogravimetric plots of vulcanized and de-vulcanized SBR for various de-vulcanization conditions and a de-vulcanization temperature of 220°C are given in Figure 3.7. Two regions of degradation are observed: The first degradation step starts at 231°C and is completed at 430°C. The second stage of degradation occurs in the region between 430°C and 510°C. The first stage is due to evaporation of the oil present in material; the second stage is caused by degradation of the SBR. The decomposition temperatures of all samples are found to be in the range between 470 and 480°C, which corresponds to the degradation of saturated and unsaturated carbon chains in SBR[18]. The TGA curves of the untreated vulcanized SBR and the various de-vulcanized SBR samples are very similar. A small shift of the TGA traces to a lower decomposition temperature is observed for the de-vulcanized SBR samples. The thermal stability can be ranked according to the presence of oxygen during the de-vulcanization process: TN>TL>TT. This may be attributed to an increasing trend towards rearrangement of intermolecular chain connections in the presence of oxygen during de-vulcanization.

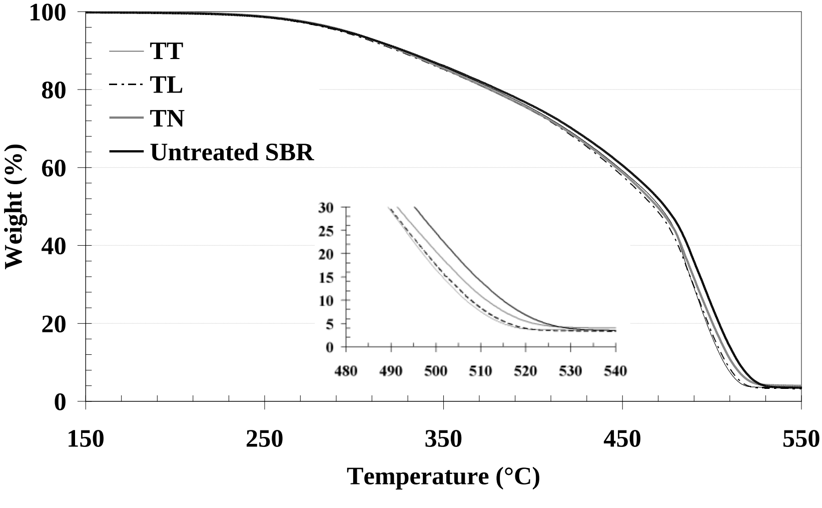


Figure 3.7 *Thermogravimetric analysis of de-vulcanized SBR compared to untreated SBR.*

MECHANICAL PROPERTIES

Stress-strain curves of vulcanized compounds of the original SBR and of 50/50 blends of SBR de-vulcanizates with the original SBR according to the ASTM formulation in Table 1. are shown in Figure 3.8.

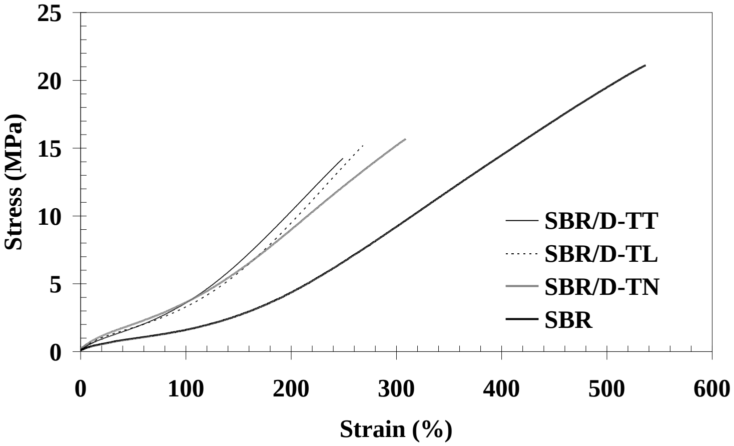


Figure 3.8 *Stress-strain curves of vulcanized SBR and SBR/de-vulcanized rubber blends (50/50 wt%).*

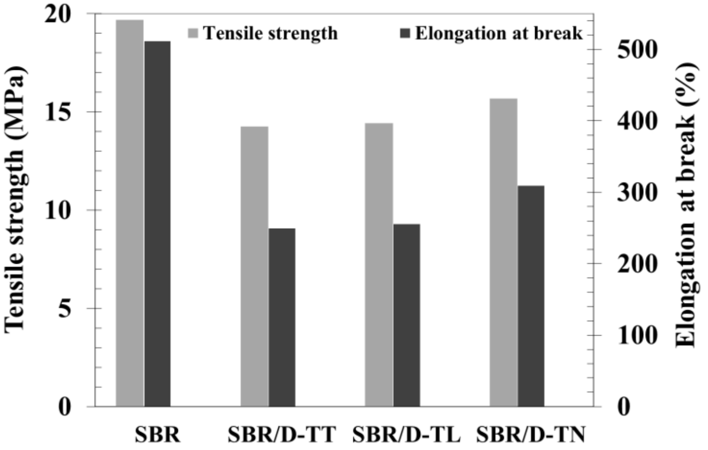


Figure 3.9 *Tensile strength and elongation at break of vulcanized SBR and SBR/de-vulcanized rubber blends (50/50 wt%).*

The tensile strength and elongation at break values of the different materials are depicted in Figure 3.9. It is clearly seen that the tensile strength of the blends is lower than the strength of the original vulcanized SBR. Such a decrease in tensile strength with addition of de-vulcanized SBR is reported by many researchers[19-23], and explanations given for the decrease in strength are:

- Flaws in the structure of the blend interface between original and reclaimed material, as co-vulcanization between the two phases in general is poor;

- An abrupt modulus change from the original compound, the continuous phase, to the reclaim particles, the discontinuous phase, resulting in inhomogeneities in stress distribution.

Figure 3.10 illustrates this effect: the modulus is approximately doubled and the hardness significantly increased for the 50/50 blend of de-vulcanized material with virgin SBR, compared to the original SBR rubber. This mismatch in properties can significantly reduce the strength of the material. The stress accumulates on the interface between the de-vulcanized particles and the matrix and fracture starts from this point[23]. Elongation at break values of the blends are also lower than the values of the original rubber, and they follow the same trend as the tensile strength values. Finally, conclusions as well as suggestions for a further study are given in Chapter 9.

Typically, the mechanical properties of a blend of virgin and de-vulcanized rubber are affected by many factors[23] such as:

- presence of gel in the reclaim;
- bonding between reclaim and matrix;
- particle size of the reclaim;
- sulfur distribution between the matrix and reclaim;
- crosslink density and distribution.

As can be seen from Figure 3.9, the re-vulcanized SBR/D-TT blend suffers 28% decrease in tensile strength and 51% decrease in elongation at break in comparison with the virgin vulcanized SBR. However, the influence on tensile strength and elongation at break is less when the de-vulcanization process is performed in a nitrogen atmosphere. The best tensile properties are obtained for the SBR/D-TN blend, which exhibits a 20% decrease in tensile strength and 40% decrease in elongation at break in comparison with the virgin vulcanized SBR for 50% of de-vulcanized rubber added. This improvement of tensile strength and elongation at break is clearly due to the suppressed damage of the polymer during de-vulcanization under exclusion of oxygen.

Under normal industrial compounding operations, the increase in hardness and modulus at 100% strain values of the materials as shown in Figure 3.10, would have been corrected by adjustment of the compound recipe. The most probable cause is a higher crosslink density in the blends, as the de-vulcanized rubber is only partially de-vulcanized and still contains reactive curatives. The use of less vulcanization ingredients would most probably have compensated for the hardness increase and brought the tensile properties more close to those for the virgin SBR vulcanizates.

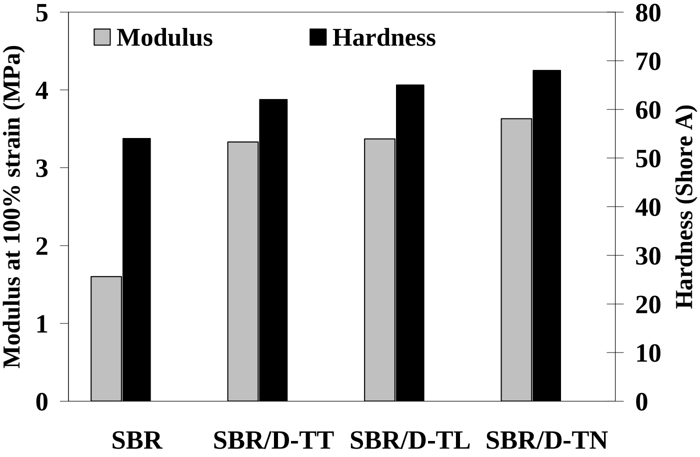


Figure 3.10 *Modulus at 100% strain and hardness of vulcanized SBR and SBR/de-vulcanized rubber blends (50/50 wt%)*

3.4 CONCLUSIONS

In thermal de-vulcanization of sulfur-cured SBR, intra-molecular rearrangements of chain fragments due to uncontrolled degradation and oxidation affect the properties of the material. Interestingly, an increase of the de-vulcanization temperature results in a decrease of the crosslink density in first instance, but it increases again above a temperature threshold of 220°C. This effect occurs independently of the presence of oxygen during the de-vulcanization process, but it is most pronounced for a thermal treatment without exclusion of oxygen. Optimal properties of de-vulcanized SBR are achieved by working at an optimized temperature of 220 °C and in a nitrogen oxygen-free atmosphere. FT-IR spectra showed that the presence of oxygen during de-vulcanization causes molecular rearrangements during breakdown of the polymer network.

The 50/50 wt% blend compounds of virgin SBR with material de-vulcanized at low temperature and under nitrogen, showed better mechanical properties than the blend with mere thermally treated material in present of oxygen. It exhibited a 20% decrease in tensile strength in comparison with virgin vulcanized

SBR, while the addition of de-vulcanizate in presence of oxygen resulted in a reduction of almost 30%.

3.5 REFERENCES

1 R. N. Hader and D. S. le Beau, *Industrial and Engineering Chemistry*, **43(2)**, 250 (1951).

2 V. Yu Levin and S. H. Kim, A. I. Isayev, *Rubber Chem. Technol*., **70**, 120 (1997).

3 S. T. Johnston, J. Massey, E. von Meerwall, S. H. Kim, V. Yu Levin and A. I. Isayev, *Rubber Chem. Technol*., **70**, 120 (1997).

4 J. Choi and A. I. Isayev, *Rubber Chem. Technol*., **84**, 55 (2011).

5 A. I. Isayev, S.H. Kim and W. Feng, *Rubber Chem. Technol*., **78**, 606 (2005).

6 V. Yu Levin, S.H. Kim and A. I. Isayev, *Rubber Chem. Technol*., **70**, 641 (1997).

7 V. Yu Levin, S.H. Kim, A.I. Isayev, J. Massey and E. von Meerwall, *Rubber Chem. Technol*., **69**, 104 (1996).

8 J. S. Oh, A. I. Isayev, and E. von Meerwall, *Rubber Chem. Technol*., **77**, 745 (2004).

9 P.J. Flory and J.Rehner, J. Chem. Phys., **11**(11), 521-526 (1943).

10 "Thermal Degradation of Organic Polymers," S.L. Madorsky, Ed.,Washington DC, 1964.

11 S.C. George, K.N. Ninan and S. Thomas, *Polym. Compos*., **7**, 343 (1999).

12 S.L. Abd-El-Messieh and K.N. Abd-El-Nour, *J. Appl. Polym. Sci*., **88**, 1613 (2003).

13 M. M. Horikx, *J. Polym. Sci*. **19**, 445 (1956).

14 M. A. L. Verbruggen, L. van der Does, J. W. M. Noordermeer, M. van Duin and H. J. Manuel, *Rubber Chem. Technol*., **72**, 731 (1999).

15 D. A. Baeta, J. A. Zattera, M. G. Oliveira and P. J. Oliveira, *Brazilian J. Chem. Eng.*, **26**, 1, 23 (2009).

16 J-F. Masson, L. Pelletier and P. Collins**,** *J. Appl. Polym. Sci.,* **79**, 1034 (2001)

17 "Infrared Characteristic Group Frequencies," G. Socrates, Ed., John Wiley&Sons, Bath, 1980.

18 C. K. Radhakrishnan, A. Sujith and G. Unnikrishnan, *J. Therm. Anal. Cal*., **90**, 191 (2007).

19 K. Fujumoto, T. Nishi and T. Okamoto, *Int. Polym. Sci. Technol*. **8** (8), T/30 (1981).

20 M. Burgoyne, G. Leaker and Z. Krekic, *Rubber Chem. Technol*., **49**, 375 (1976).

21 E. M. Fesus and R. W. Eggleton, *Rubber World*, **203** (6), 23 (1991).

22 K. Knorr, *Kautsch. Gummi Kunstst*. **47**, 54 (1994).

23 V. V. Rajan, W. K. Dierkes, R. Joseph, J. W. M. Noordermeer, *J. Appl. Polym. Sci.,* **102**, 4194 (2006).

CHAPTER 4

THERMO-CHEMICAL DE-VULCANIZATION OF SULFUR-VULCANIZED SBR

From a mechanistic point of view, the de-vulcanization process of polybutadiene and butadiene based elastomers shows a unique characteristic: network breakdown occurs parallel with recombination. In thermal treatment of vulcanized SBR, a threshold temperature was found above which the degree of chain recombination increases with increasing treatment temperature, which is resulting in inefficient de-vulcanization.

Using small amounts of de-vulcanization aid is one of alternatives to reach a more efficient de-vulcanization. Thermo-chemical de-vulcanization of sulfur-cured SBR (Styrene Butadiene Rubber) using disulfides, diphenyldisulfide (DPDS), dibutyldisulfide (DBDS) and di(2-aminophenyl)disulfide (APDS), as de-vulcanization aids is investigated. The addition of small concentrations of disulfides results in a significant increase in the rubber soluble fraction and a decrease in crosslink density compared to untreated and thermally treated SBR. The performance of the three different types of disulfides is compared, and the compatibility of the de-vulcanization aids with SBR turns out to play a major role for the properties of the de-vulcanizates. DPDS is found to be the most effective de-vulcanization aid, while APDS is least effective, a conclusion that is supported by the difference in solubility parameters: it is the highest for the APDS/SBR combination. Even though DBDS has a solubility parameter close to SBR, the de-vulcanizate shows good properties only after de-vulcanization at low temperatures. The best de-vulcanization conditions for SBR are elaborated, and the mechanisms behind the different breakdown processes are discussed.

4.1 INTRODUCTION

Degradation of polybutadiene and butadiene based polymers follows a unique pathway due to the specific chemical structure of the polymer[1]. In degradation, polymer breakdown occurs, but at the same time recombination of chain segments takes place. In a thermal de-vulcanization process of sulfur-cured SBR, the occurrence of these two reactions, chain scission and formation of active chain segments, depends on the de-vulcanization conditions[2]. When working under non-optimized de-vulcanization conditions, the active radicals are more likely to recombine to a new network, thereby reducing the sol fraction and increasing the crosslink density. This finally leads to inefficient de-vulcanization.

The combination of a chemical with a thermal de-vulcanization step is one of the alternatives to reach an efficient de-vulcanization. Using small amounts of a "de-vulcanization aid" during thermal treatment was reported to be a superior option[3-7]. It selectively breaks down the rubber network at crosslinking positions and creates sulfur-bridges during vulcanization thanks to the disulfide moiety in the molecule.

Disulfides are well-known de-vulcanization aids and used in rubber recycling as radical stabilizing agents. The efficiency of various disulfides as recycling agents for natural rubber[3-5] (NR) and ethylene propylene diene rubber[6-7] (EPDM) vulcanizates were reported. Diphenyldisulfide was found to be an effective reclaiming agent for natural rubber. Rajan *et al*. observed that the reclaiming agent helped in preventing the broken rubber chains to recombine. A mechanism that is frequently proposed for the reaction of radical scavenger de-vulcanization agents like DPDS with sulfur vulcanizates is the opening of crosslinks or the scission of polymer chains by heat and shearing forces, and the reaction of fragments with disulfide based radicals, which prevent recombination. A simplified reaction scheme proposed for the rubber de-vulcanization with DPDS is given in Figure 2.8[3] in Chapter 2.

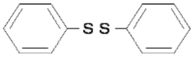
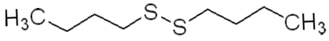
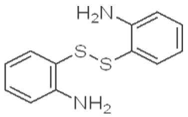
In this chapter, special attention is devoted to the choice of the best de-vulcanization aid for SBR vulcanizates. Three different types of disulfides are investigated on their performance as de-vulcanization aid: diphenyldisulfide (DPDS), dibutyldisulfide (DBDS) and di(2-aminophenyl)disulfide (APDS). Both DPDS and APDS are aromatic disulfides, and DBDS was chosen as a representative of aliphatic disulfides. DPDS is commonly used for natural rubber reclaiming. APDS was chosen to study the effect of a combination of a disulfide and an amine group. The efficiency of the de-vulcanization aids is discussed considering the melting point, thermal stability at the de-vulcanization temperature and chemical structure. Further, de-vulcanization parameters and the properties of the de-vulcanizate are optimized, and the SBR de-vulcanization mechanism is discussed.

4.2 EXPERIMENTAL

MATERIALS

The SBR type used in this investigation was SBR 1723, an oil extended emulsion-polymerized SBR containing 37.5 phr of treated distillate aromatic extract (TDAE) oil, obtained from Dow Chemical, Germany. The polymer contained 23.5 wt% styrene and 76.5 wt% butadiene, and its Mooney viscosity ML(1+4) measured at 100°C was 40 MU. Zinc oxide (ZnO) and stearic acid were obtained from Flexsys, the Netherlands. The curatives, sulfur and N-tert-butyl-2-benzothiazylsulfenamide (TBBS), were obtained from Merck. The solvents, acetone and tetrahydrofuran (THF), which were used for extractions, and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve. TDAE oil used as processing oil for the de-vulcanization was supplied by Hansen&Rosenthal, Germany. The three types of disulfides used as de-vulcanization aid were obtained from Sigma-Aldrich, Germany. Chemical names and structures of the de-vulcanization aids are given in Table 4.1.

Table 4.1 Chemical names and structures of the different disulfides

Chemical name	Chemical structure
Diphenyldisulfide, DPDS	
Dibutyldisulfide, DBDS	
Di(2-aminophenyl)disulfide, APDS	

PREPARATION OF DE-VULCANIZED SBR

Mixing and vulcanization.- The SBR was first compounded using a Brabender Plasticorder 350S mixer with a mixing chamber volume of 350 cm^3. The compound formulation is shown in Table 4.2. The mixer was operated at a rotor speed of 60 rpm; a fill factor of 0.75 and an initial temperature of 50°C were used. The mixing time was 5 minutes. The final compound temperature before dumping was in the range of 70-90°C. The compound was tested for its cure characteristics using a RPA 2000 dynamic mechanical curemeter from Alpha Technologies at 170°C, 0.833 Hz and 0.2 degree strain, according to ISO 6502. The compounds were then vulcanized for $t_{c,90}$ + 5 minutes in a Wickert WLP1600 laboratory compression molding press at 170°C and 100 bar, into 2 mm thick sheets.

Grinding.- The vulcanized SBR sheets were subsequently ground in a Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen. The particle size of the ground rubber was in the range of 0.85-2.00 mm.

Table 4.2 Formulation of the SBR compound

Ingredient	phr
SBR 1723	100
ZnO	4.13
Stearic acid	2.06
Sulfur	2.75
Accelerator (TBBS)	1.38

De-vulcanization.- The thermo-chemical de-vulcanization was performed batchwise in an internal mixer (Brabender Plasticorder PL-2000), having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.7 and a constant rotor speed of 50 rpm were used. The de-vulcanization temperature was varied from 180 to 300°C and the de-vulcanization time was 5 minutes. After adding ground rubber and TDAE oil (5% w/w) into the mixer, the disulfide was added. The practical amount of disulfide was 30 mmol/100 g compound, which is the optimum concentration based on a previous screening study. The variations of the experimental conditions in this study are given in Table 4.3.

Table 4.3 De-vulcanization conditions

Factors	Variation conditions
De-vulcanization aids	DPDS, APDS, DBDS
De-vulcanization temperatures (°C)	180, 220, 260, 300
De-vulcanization aid concentration	30 mmol/100 g compound

CHARACTERIZATION OF THE DE-VULCANIZATES

Rubber soluble fraction.- The soluble (Sol) fraction of the de-vulcanizates were determined by extraction in a Soxhlet apparatus, as described in Chapter 3.

Crosslink density.- The extracted samples were subsequently swollen in toluene for 72 hours at room temperature. The crosslink density was calculated according to the Flory-Rehner[8,9,10], as described in Chapter 3.

Viscosity.- Complex viscosity values were analyzed via dynamic viscoelastic measurements performed with the RPA 2000, as described in Chapter 3.

Thermogravimetric analysis (TGA).- The thermal decomposition behavior of vulcanized and de-vulcanized SBR was analyzed by thermogravimetric analysis (TGA) using a TGA7 from Perkin Elmer. Approximately 5-10 mg of the sample were heated with a heating rate of 10°C/minute in a nitrogen atmosphere.

Solubility parameter.- The solubility parameters of SBR and the de-vulcanization aids can be calculated by the method developed by Hoftijzer and van Krevelen[11], which is based on the addition of the contributions from all functional groups in a molecule. The solubility parameters, δ ($J^{1/2}/cm^{3/2}$), were calculated by the following equation:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (1)$$

Where δ_d = Component from dispersive forces

δ_p = Component from polar forces

δ_h = Component from hydrogen bonding

4.3 RESULTS AND DISCUSSION

INFLUENCE OF DE-VULCANIZATION AID TYPE

Rubber sol fraction and crosslink density.- The sol fractions as a function of the de-vulcanization temperature of SBR de-vulcanizates in presence of the three different types of de-vulcanization aids, DPDS, DBDS and APDS, are depicted in Figure 4.1. The rubber sol fractions initially increase with increasing de-vulcanization temperature. However, they decrease again above a threshold temperature of 220°C for DPDS and DBDS, and 260°C for APDS. The increase of the rubber sol fraction indicates breakdown of the rubber network which occurs during de-vulcanization. Figure 4.2 shows the crosslink densities of the three de-vulcanized SBR samples as a function of de-vulcanization temperature. Within this temperature range, the crosslink density first decreases, but increases again with higher temperatures. There is a slight difference between the 3 samples: The turning point from decrease to increase is at 220°C in the case of DPDS and DBDS. However for APDS, the lowest crosslink density is found at a temperature of 180°C.

Basically, the de-vulcanization agents were added in order to scavenge radicals formed during the de-vulcanization process. However, at high de-vulcanization temperatures, i.e. above 220°C, a more intensive generation of reactive radicals occurs. The threshold temperature indicates the optimum de-vulcanization temperature at which the rubber network can be broken in a controlled manner. Above this temperature, a high amount of reactive radicals leads to an uncontrolled molecular polymer breakdown. It induces the formation of inter- and intramolecular bonds resulting in a decrease of rubber sol fraction and renewed increase in crosslink density.

Consideration of de-vulcanization efficiency.- A useful tool to understand the de-vulcanization mechanism is the method developed by Horikx[12]: the rubber sol fraction of the de-vulcanizates and the crosslink density of the rubber gel fractions can be correlated, as described in Chapter 3. The experimentally determined sol fractions of SBR de-vulcanized with DPSD at various temperatures as a function of the relative decrease in crosslink density are shown in Figure 4.3(a): An increase of the de-vulcanization temperature up to 220°C results in a shift of the data points to the right hand side of the graph, which indicates an increase in sol fraction and a decrease of crosslink density. Nevertheless, a further increase of the de-vulcanization temperature above 220°C results in a back turn of the experimental data points to the left, which is the reverse of the expected decrease of crosslink density. This indicates inefficient de-vulcanization, in which the crosslink density of the de-vulcanized rubber is increased rather than decreased with increasing treatment temperature.

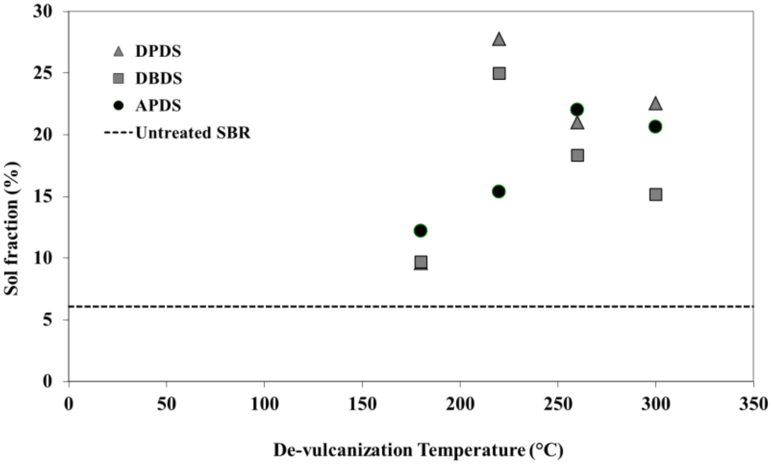


Figure 4.1 *Sol fraction as a function of the de-vulcanization temperature for de-vulcanized SBR compared to untreated vulcanized SBR (dotted line).*

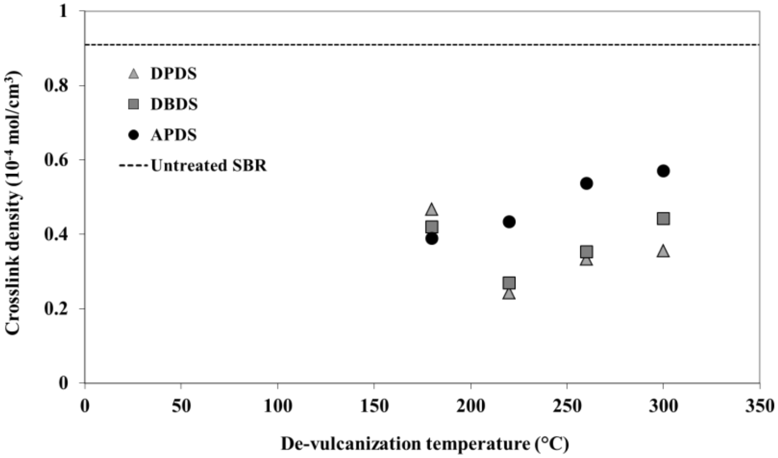


Figure 4.2 *Crosslink density as a function of de-vulcanization temperature for de-vulcanized SBR, compared to untreated vulcanized SBR (dotted line).*

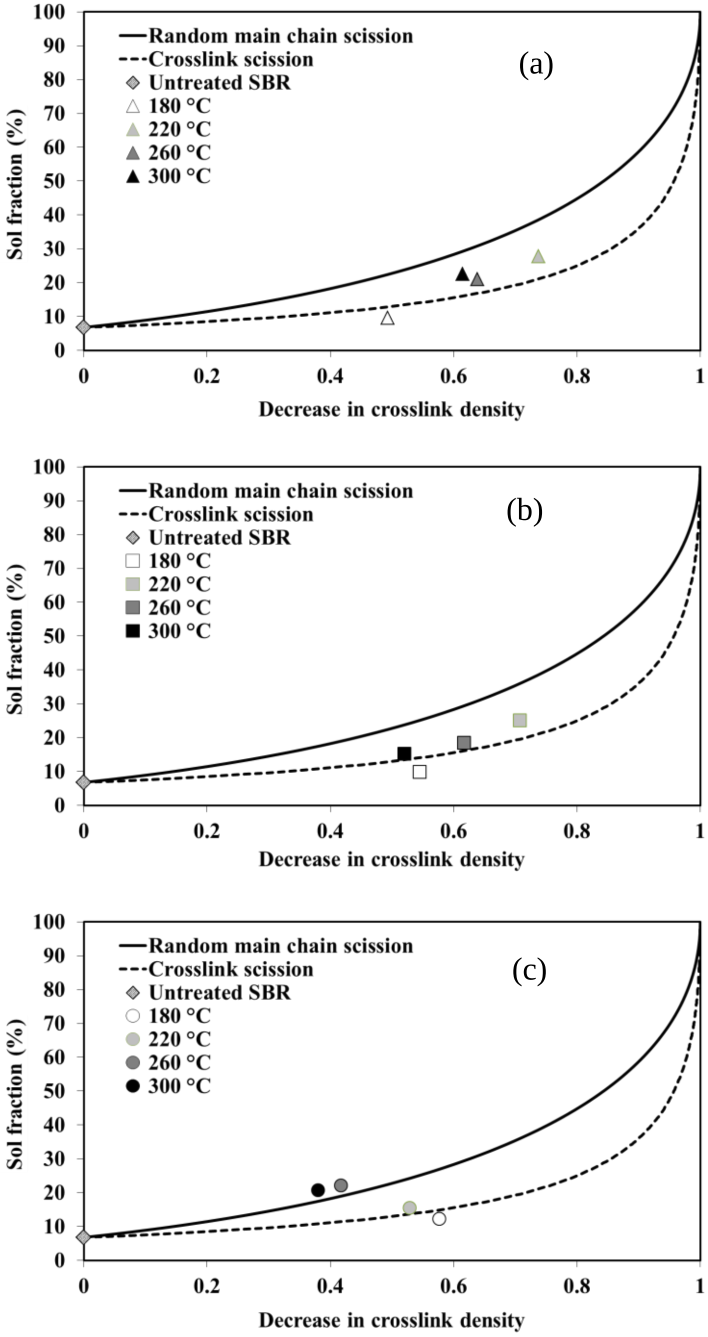


Figure 4.3 *Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of de-vulcanized SBR using a:DPDS, b:DBDS and c:APDS, as de-vulcanization aids.*

Figures 4.3(b) and 4.3(c) show the experimentally determined sol fractions as a function of the relative decrease in crosslink density at various de-vulcanization temperatures in presence of DBDS and APDS, respectively. In case of DBDS, an increase of the de-vulcanization temperature up to 220°C shows the same trend as found for DPDS as de-vulcanization aid: a shift of the data points to the upper right hand side of the graph while a further increase of de-vulcanization temperature to 260°C results in a back turn of the experimental data points to the left. However, in case of APDS de-vulcanized SBR, the back turn shifting occurs already at lower temperature of 180°C. The reversion phenomenon is most pronounced for de-vulcanization up to 300°C; for this temperature the data point is even moved to left hand side.

The sol fractions as a function of the relative decreases in crosslink density of SBR de-vulcanizates using all three types of de-vulcanization aids are gathered in Figure 4.4. It can clearly be seen that the reversion phenomenon occurs in all cases, but is more or less pronounced depending on the type of de-vulcanization aid. Each disulfide is effective till a different particular threshold temperature. Above this threshold temperature, de-vulcanization becomes inefficient. Degradation is more likely to occur at higher de-vulcanization temperatures, which is attributed to an excessive and uncontrolled generation of reactive radicals as mentioned before.

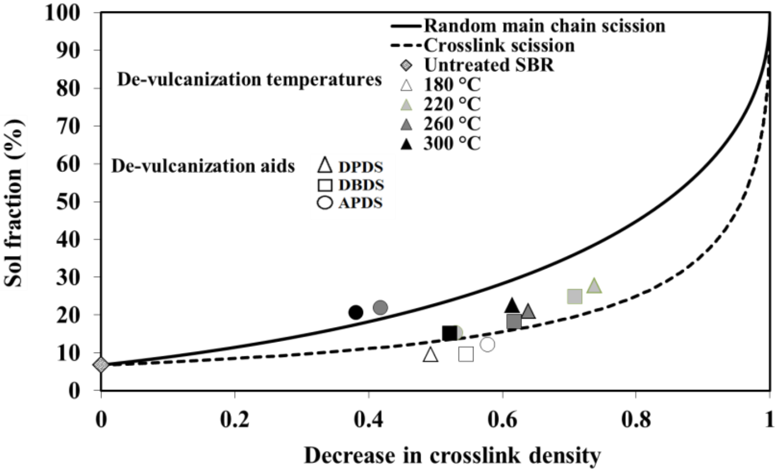


__Figure 4.4__ Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of de-vulcanized SBR using 3 different types of de-vulcanization aid: DPDS, DBDS and APDS.

The efficiency for de-vulcanization of these three disulfides is related to their thermal reactivity. DBDS, a representative of aliphatic disulfides, was found to be an effective de-vulcanization aid only at low de-vulcanization temperatures up to 220°C. This is attributed to its thermal stability and a boiling temperature of 188°C. One of the aromatic disulfides, DPDS, with a higher boiling point than the previous one, was more effective in de-vulcanization at higher temperatures. APDS is an aromatic disulfide which was chosen to study the effect of a combination of a disulfide and an amine group. However, it turned out to be the least effective de-vulcanization aid, even though it has the highest boiling point of the three de-vulcanization aids. This is attributed to the presence of the amine group which reacts according to a nucleophilic mechanism[13] and has a positive effect on the de-vulcanization efficiency only at low treatment temperature[6].

Another factor that can play a role in the efficiency of the de-vulcanization aids is the compatibility between rubber and the de-vulcanization aids, which can be estimated by their respective solubility parameters. The calculated values of the solubility parameters of SBR and the three disulfides are shown in Table 4.4. A larger difference in the solubility parameter results in a higher incompatibility of SBR with the de-vulcanization aids, which may affect the efficiency of de-vulcanization. The largest difference is found for the system APDS/SBR, which corresponds with the observation that APDS is the least effective de-vulcanization aid. DBDS and SBR have the closest solubility parameters, but here the low boiling point of DBDS prevails. DPDS is found to be the most effective de-vulcanization aid due to the high boiling point in spite of the differences in solubility parameter compared to SBR.

Table 4.4 Solubility parameter

Chemical	Solubility parameter $(J/cm^3)^{1/2}$
SBR 1723	17.3
Diphenyldisulfide	22.5
Dibutyldisulfide	17.9
Di (2-aminophenyl) disulfide	26.0

Viscosity of SBR de-vulcanizates.- Figure 4.5 shows the complex viscosity versus oscillating frequency for the 220°C de-vulcanized SBR materials, in comparison with untreated vulcanized SBR. The viscosity levels of the de-vulcanized SBR samples are much decreased relative to the untreated SBR, due to the cleavage of the three dimensional network during de-vulcanization, and the addition of the de-vulcanization aid. The viscosity values of SBR de-vulcanized with APDS are higher than the ones of the DPDS and DBDS based materials, indicating again that APDS is a less effective de-vulcanization aid. The generation of small molecular chains during the process which are extracted in the rubber sol fraction measurement, is also explicitly demonstrated in the low viscosity of the material. The trend of the viscosity curves corresponds well with the trend of the extracted rubber sol fraction.

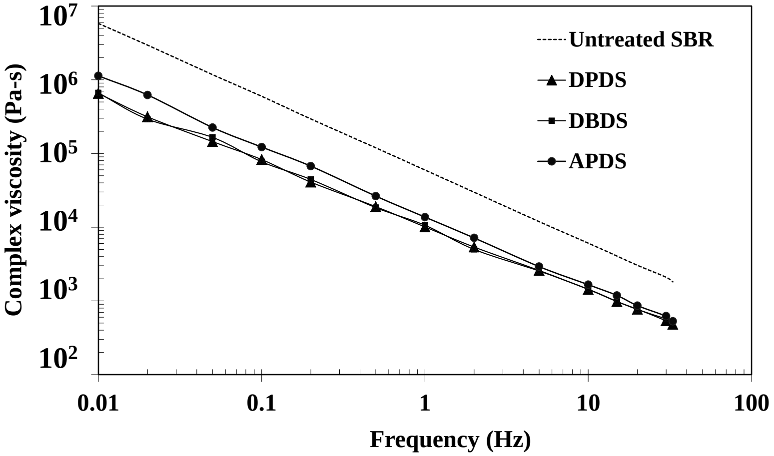


Figure 4.5 *Complex viscosity as a function of frequency of de-vulcanized SBR compared to untreated vulcanized SBR; de-vulcanization temperature: 220 ℃.*

Thermal analysis by of SBR de-vulcanizates.- The thermogravimetric plots of the vulcanized and 220°C de-vulcanized SBR materials are given in Figure 4.6. The TGA curves of the untreated vulcanized SBR and the various de-vulcanized SBR samples are very similar. Two regions of degradation are observed: The first degradation step starts at 231°C and is completed at 430°C. The second stage of degradation occurs in the region between 430°C and 510°C. The first stage is due to evaporation of the oil present in material; the second stage is caused by degradation of the SBR. The decomposition temperatures of all samples are found to be in the range between 470°C and 480°C, which corresponds to the degradation of saturated and unsaturated carbon chains in SBR[14]. A small shift of the TGA traces to a higher decomposition temperature is observed for the APDS de-vulcanized SBR sample. This may be caused by rearrangement of intermolecular chain connections in the presence of the more temperature-stable amine in APDS.

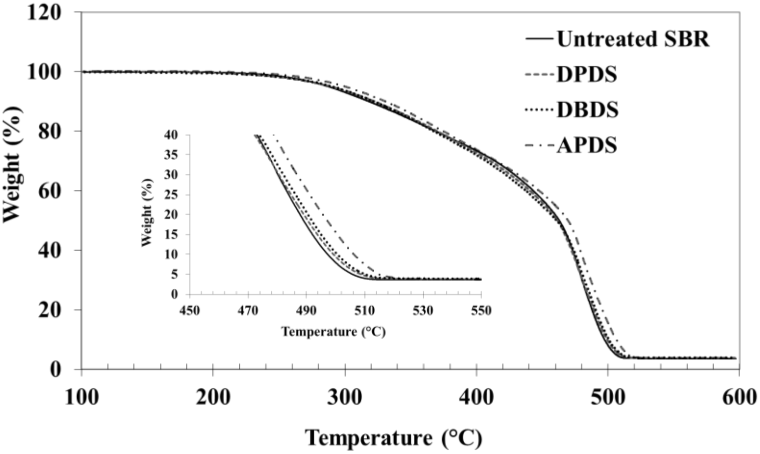


Figure 4.6 *Thermogravimetric analysis of de-vulcanized SBR.*

SBR DE-VULCANIZATION MECHANISM

Figure 4.7 is a schematic depiction of the degradation of polybutadiene and butadiene based polymers. Basically, two reactions can occur during degradation of polybutadiene: chain scission and formation of active chain segments. Chain scission occurs when breaking of the C-C bonds (carbon-carbon bonds) in the polymer chains is accompanied by hydrogen transfer[15], and results in polymers with a lower molecular weight. Another reaction, the formation of radically active chain fragments, apparently takes place from 3 possible reactions as shown in Figures 4.8 and 4.9. Reaction (A) in Figure 4.8 is known as a hydrogen transfer reaction. It is initiated by breaking of the C-C bonds in the polymer chains due to physical forces: heat, light, and mechanical forces. It is accompanied by hydrogen transfer which results in polymer chain scission. However, re-formation of unstable radicals to polymers could possibly take place when scission of C-C bonds in the chain is not accompanied by a hydrogen transfer[15]. It is reported that for a degradation in air atmosphere, with the main active component oxygen, hydrogen transfer is less. Therefore, the active radicals tend to recombine to a new polymer.

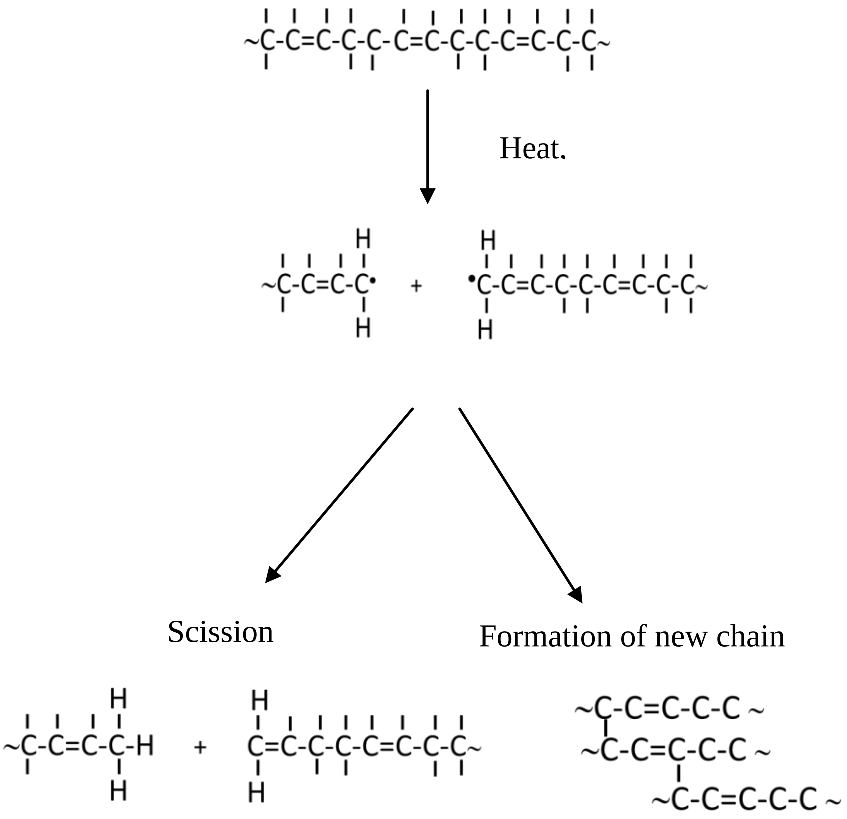


Figure 4.7 *Simplified reaction scheme proposed for the degradation of polybutadiene and butadiene based polymers.*

Reaction (B) in Figure 4.8 is the chemical structure transformation reaction. It is associated with thermal isomerization: cis-trans isomerization, cyclization and volatilization of small fregments[16-18]. These chain rearrangements are undeniably enhanced with increasing temperature and occur at the initial decomposition step of SBR.

Reaction (C) in Figure 4.9 involves generation of active groups derived from the presence of oxygen. The initial predominant attack of aerial oxygen (O_2) takes place on the double bonds. It continues with the generation of hydroperoxide radicals which then decompose to give carbonyl (>C=O) funtionalities[19]. These reactions typically take place at high temperature. Accordingly, when carbonyl functionalities are generated, the possibility of creating a rubber soluble fraction is less: the bond energy of C=O (724 kJ/mol) is considerably higher than that of C-C (410 kJ/mol) or carbon hydrogen bonds, C-H (335 kJ/mol).

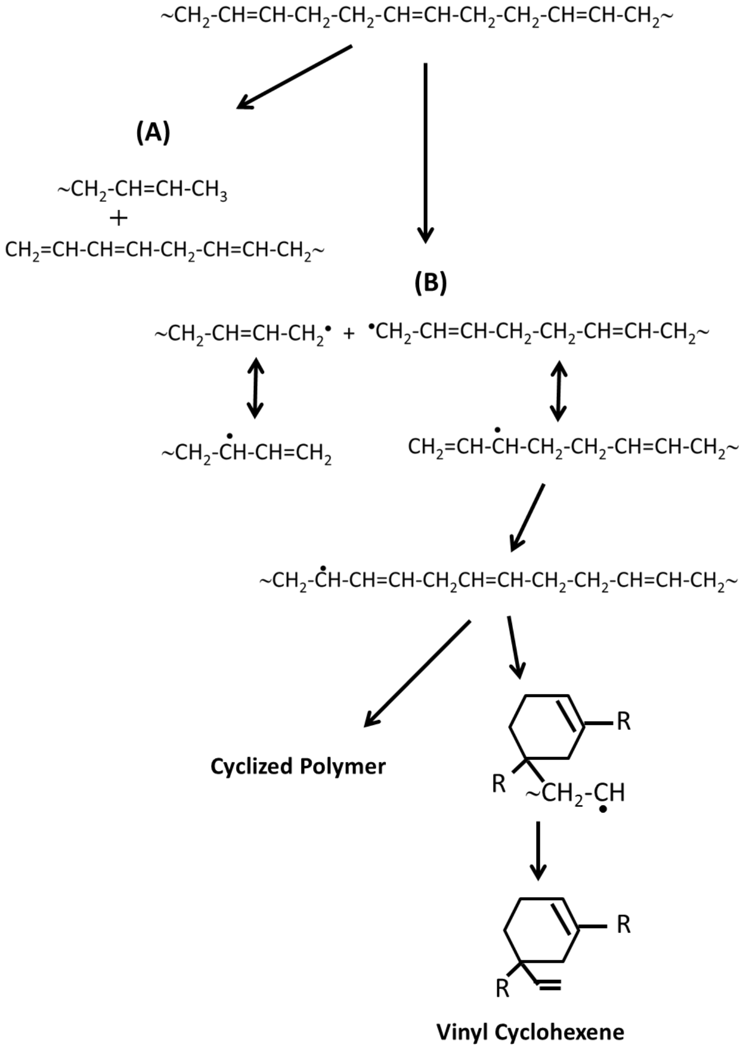


Figure 4.8 Re-formation of active bond fragments in the specific degradation mechanism of polybutadiene and butadiene based polymers.

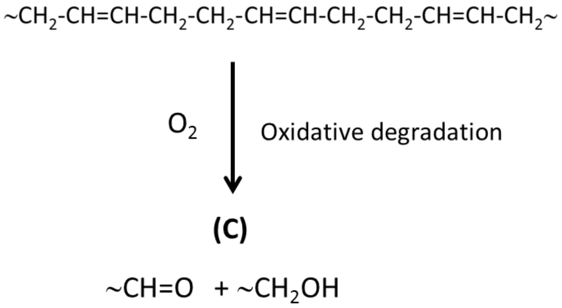


Figure 4.9 *Simplified oxidative degradation mechanism of butadiene based polymers (See Chapter 5).*

All these three reactions, (A), (B) and (C), can conjointly occur in the SBR de-vulcanization process particularly at high treatment temperatures. These result in reduction of the sol fraction and increase of the crosslink density above the threshold temperatures stated above. In order to achieve a higher de-vulcanization efficiency, further studies are worked out in more detail in Chapter 5.

4.4 CONCLUSIONS

In thermo-chemical de-vulcanization of SBR using disulfides as de-vulcanization aids, an increase of the de-vulcanization temperature results in a reduction of the crosslink density in first instance, but it increases again above a certain temperature threshold. Although the network breakdown is enhanced by increasing the temperature, it is necessary to keep the de-vulcanization temperature as low as possible to prevent uncontrollable reactions. Particularly at high de-vulcanization temperatures, i.e. the above the threshold temperature, three possible reactions can jointly occur. These lead to re-formation of partially crosslinked or branched polymers from unstable chain segments, which results in a reduction of the sol fraction and increase of the crosslink density above stated threshold temperature. The optimal de-vulcanization temperature for SBR is 220 °C, and DPDS is found to be the most effective de-vulcanization aid. These de-vulcanization conditions result in a maximum increase in the soluble fraction from 6.8 % to 27.8 %, and a decrease in crosslink density from 0.92 to 0.24 x 10^{-4} mol/cm^3.

4.5 REFERENCES

[1] R.N. Hader and D.S. le Beau, *Ind. Eng. Chem.*, **43(2)**, 250 (1951).

[2] S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, presented at the meeting of the Rubber Division, ACS, Oct. 11-13, 2011, Cleveland (OH, USA).

[3] V.V. Rajan, W.K. Dierkes, J.W.M. Noordermeer and R. Joseph, *Rubber Chem. Technol*., **78**, 855 (2005).

[4] V.V. Rajan, W.K. Dierkes, R. Joseph and J.W.M. Noordermeer, *J. Appl. Polym. Sci.,* **102**, 4194 (2006).

[5] A.R. Jalilvand, I. Ghasemi, M. Karrabi and H. Azizi, *Progr. Rubber. Plast. Recycling Techn*., **24(1)**, 33 (2008).

[6] K.A.J. Dijkhuis, I. Babu, J.S. Lopullissa, J.W.M. Noordermeer and W.K. Dierkes, *Rubber Chem. Technol*., **81**, 190 (2008).

[7] M.A.L. Verbruggen, L. van der Does, J.W.M. Noordermeer, M. van Duin and H.J. Manuel, *Rubber Chem. Technol*., **72**, 731 (1999).

[8] P.J. Flory, *J. Am. Chem. Soc*., **63**, 3096 (1941).

[9] S.C. George, K.N. Ninan and S. Thomas, *Polym. Compos*., **7**, 343 (1999).

[10] S.L. Abd-El-Messieh and K.N. Abd-El-Nour, *J. Appl. Polym. Sci*., **88**, 1613 (2003).

[11] D.W. van Krevelen and P.J. Hoftijzer, “Properties of Polymers”, 3rd edition, Elsevier, Amsterdam, 1990. p.189.

[12] M.M. Horikx, *J. Polym. Sci*. **19**, 445 (1956).

[13] S. Yamashita, *Int. Polym. Sci. Technol.* **8**, T/77 (1981).

[14] C.K. Radhakrishnan, A. Sujith and G. Unnikrishnan, *J. Therm. Anal. Cal.*, **90**, 191 (2007).

[15] S.L. Madorsky “Thermal Degradation of Organic Polymers”, Polymer Reviews, H.F. Mark and E.H. Immergut eds., Interscience Publishers, New York, U.S., 1964.

[16] M.D. Sarkar, P.G. Mukunda, P.P. De and A.K. Bhowmick, *Rubber Chem. Technol*., **70**, 855 (1997).

[17] M.A. Golub, *Rubber Chem. Technol*., **51**, 677 (1978).

[18] M.A. Golub, *J. Polym. Sci., Polym. Lett. Ed.* **16**, 253 (1978).

[19] J.R. Shelton, *Rubber Chem. Technol*., **45**, 359 (1972).

CHAPTER 5

THERMO-CHEMICAL DE-VULCANIZATION OF SULFUR-VULCANIZED SBR ASSISTED BY DE-VULCANIZATION AIDS AND OXIDATION STABILIZERS

Thermo-chemical de-vulcanization of sulphur-cured SBR using diphenyldisulfide (DPDS) as de-vulcanization aid is investigated. A reduction of the crosslink density of the de-vulcanizate is observed with increasing de-vulcanization temperature from 180 ℃ to 220 ℃. However, above a temperature threshold of 220 ℃, the crosslink density rises again. This is due to complicated intra-molecular rearrangements of chain fragments of butadiene moieties from uncontrolled degradation and oxidation effects. Oxidation stabilizers are added to the DPDS de-vulcanization to reduce the degradation and interrupt the oxidation cycles. Above a temperature threshold of 220 ℃, a further decrease in crosslink density without creating more sol fraction is observed in this way. Combination of DPDS and oxidation stabilizers significantly enhances the de-vulcanization efficiency of SBR versus the one obtained when DPDS is used alone. The results are interpreted in terms of mechanisms of main chain and sulfur bridge scissions and the degradative cycles triggered by the presence of oxygen.

5.1 INTRODUCTION

The poor properties of de-vulcanized rubber, caused by the structural changes of the polymer molecules is mainly due to intensive physical forces, i.e., shearing and high temperature. Under severe shear and high temperature, various reactions occur during the de-vulcanization process causing main chain breakage next to crosslink scission. However, the utilization of de-vulcanization aids, which are effective in low concentrations, introduces new pathways for a more effective and faster de-vulcanization. Themo-chemical de-vulcanizations are in general more selective for cleaving crosslinks only.

Diphenyldisulfide was found to be an effective de-vulcanization, also called reclaiming agent for natural rubber by Rajan *et al.*[1] They observed that the reclaiming agent helped in preventing broken rubber chains to recombine. The ratio of main-chain scission to crosslink scission of natural rubber depended on both the concentration of the reclaiming agent and the temperature of the process. The radical moieties of the chains can quickly recombine, unless a diphenyldisulfide molecule is present to act as a radical scavenger.

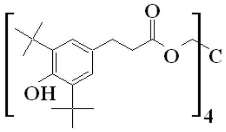
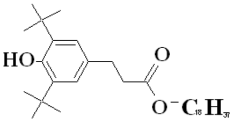
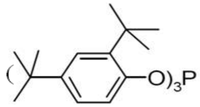
In the present paper, special attention will be devoted to thermo-chemical de-vulcanization of sulfur-cured SBR using diphenyldisulfide as de-vulcanization aid. Oxidation stabilizers are further investigated in order to suppress the reaction of radicals or other reactive species and interrupt the oxidation cycle due to the presence of oxygen-species during de-vulcanization. Two groups of stabilizers, hindered phenolic- and phosphite-type stabilizers are compared.

5.2 EXPERIMENTAL

MATERIALS

The SBR type used in this investigation was SBR 1723, an oil extended emulsion-polymerized SBR containing 37.5 phr of Treated Distillate Aromatic Extract (TDAE) oil, obtained from Dow Chemical, Germany. The polymer contained 23.5 wt% styrene and 76.5 wt% butadiene, and its Mooney viscosity ML(1+4) measured at 100°C was 40 MU. Zinc oxide (ZnO) and stearic acid were obtained from Flexsys, the Netherlands. The curatives: sulfur and N-tert-butyl-2-benzothiazylsulfenamide (TBBS) were obtained from Merck. The solvents, acetone and tetrahydrofuran (THF), which were used for extractions, and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve. TDAE oil used as de-vulcanizing processing oil was supplied by Hansen&Rosenthal, Germany. Diphenyldisulfide (DPDS) used as de-vulcanization aid was obtained from Sigma-Aldrich, Germany. The three types of oxidation stabilizers used were obtained from Ciba Specialty Chemicals Inc., Switzerland. Chemical names and structures of the stabilizers are given in Table 5.1.

Table 5.1 Chemical names and structures of thermal stabilizer investigated.

Chemical name	Commercial name	type	Chemical structure
Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	Irganox 1010	Hindered Phenolic	
Octadecyl-3-(3,5-di-tert-butyl-4- hydroxyphenyl) propionate	Irganox 1076	Hindered Phenolic	
Tris(2,4-ditert-butylphenyl)phosphite	Irgafos 168	Phosphite	

PREPARATION OF DE-VULCANIZED SBR

Mixing and vulcanization.- The SBR was first compounded using a Brabender Plasticorder 350S mixer with a mixing chamber volume of 350 cm^3. The compounding formulation is shown in Table 5.2. The mixer was operated at a rotor speed of 60 rpm; a fill factor of 0.75 and an initial temperature of 50°C were used. The final compound temperature before dumping was in the range of 70-90°C. The compound was tested for its cure characteristics using a RPA 2000 dynamic mechanical curemeter from Alpha Technologies at 170°C, 0.833 Hz and 0.2 degree strain, according to ISO 6502. The compounds were then vulcanized for $t_{c,90}$ + 5 minutes in a Wickert WLP1600 laboratory compression molding press at 170°C and 100 bar, into 2 mm thick sheets.

Table 5.2 Formulation of the SBR compound

Ingredient	phr
SBR 1723	137.5
ZnO	4.13
Stearic acid	2.06
Sulfur	2.75
Accelerator (TBBS)	1.38

Grinding.- The vulcanized SBR sheets were subsequently ground in a Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen. The particle size of the ground rubber was in the range of 0.85-2.00 mm.

De-vulcanization.- The thermo-chemical de-vulcanization was performed in a batch process in an internal mixer Brabender Plasticorder PL-2000, having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.7 and a constant rotor speed of 50 rpm were used. The de-vulcanization temperature was varied from 180 to 300°C and the de-vulcanization time was 5 minutes. The variations of the experimental conditions in this study are given Table 5.3.

Table 5.3 De-vulcanization conditions

Factors	Varied conditions
De-vulcanization aid	DPDS (30 mmol/100 g compound = 3.27 g/100 g compound)
De-vulcanization temperatures	160, 180, 200, 220, 260, 300 (°C)
Oxidation stabilizers	Irganox 1010, Irganox 1076 and Irgafos 168 (1 g/100 g compound)

CHARACTERIZATION OF THE DE-VULCANIZATES

Rubber soluble fraction.- The soluble (Sol) fraction of the de-vulcanizates were determined by extraction in a Soxhlet apparatus, as described in Chapter 3.

Crosslink density.- The extracted samples were subsequently swollen in toluene for 72 hours at room temperature. The crosslink density was calculated according to the Flory-Rehner[2], as described in Chapter 3.

5.3 RESULTS AND DISCUSSION

INFLUENCE OF OXYGEN STABILIZER ON DE-VULCANIZATION EFFICIENCY

The sol fractions and crosslink densities of the remaining gel as a function of the de-vulcanization temperature of SBR de-vulcanizates in presence of DPDS are depicted in Figures 5.1 and 5.2, respectively. Basically, the increase of the rubber sol fraction and decrease of crosslink density indicate the extent to which the rubber network is broken. Thermo-chemical de-vulcanization of sulfur-cured SBR using DPDS as de-vulcanization aid shows an increase of rubber soluble fraction with increasing de-vulcanization temperature up to 220°C; above this temperature, the sol fractions decrease again. Furthermore, it can be seen in Figure 5.2 that above this temperature of 220°C also a significant increase in crosslink density is observed again. Basically, DPDS as de-vulcanization agent was added in order to scavenge radicals formed during the reclaiming process. However, at high de-vulcanization temperature, i.e. above 220°C, a more extensive generation of reactive radicals occurs. These lead to formation of new inter- and intramolecular bonds resulting in a decrease of the rubber sol fraction and renewed increase in crosslink density.

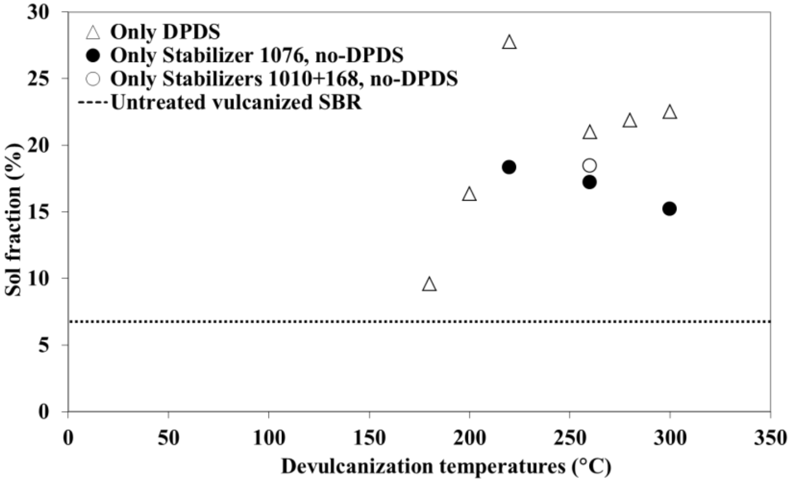


Figure 5.1 *Sol fraction as a function of the de-vulcanization temperature for de-vulcanized SBR compared to untreated vulcanized SBR (dotted line).*

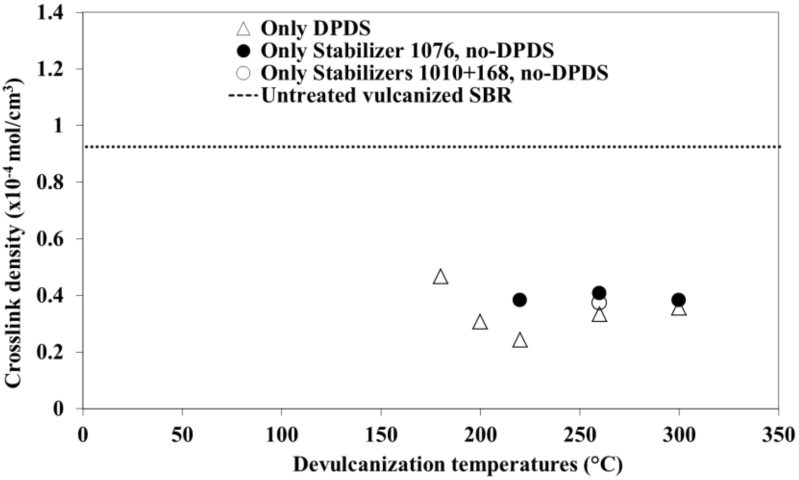


Figure 5.2 *Crosslink density as a function of de-vulcanization temperature for de-vulcanized SBR, compared to untreated vulcanized SBR (dotted line).*

Characterization of de-vulcanization level by Horikx plot[3,4].- The experimentally determined sol fractions of DPDS de-vulcanized SBR at various de-vulcanization temperatures as a function of the relative decrease in crosslink density are shown in Figure 5.3. An increase of the de-vulcanization temperature to 220°C results in a shift of the data point to the right hand side of the graph, which indicates a small increase in sol fraction and large decrease of crosslink density. Nevertheless, a further increase of de-vulcanization temperature to 260°C results in a back turn of the experimental data points to the left, which is the reverse of the expected decrease of crosslink density. This reversion phenomenon is even more pronounced for de-vulcanization up to 300°C; for this temperature the data point is even found at the utmost left hand side. This indicates inefficient de-vulcanization, in which the crosslink density of the de-vulcanized rubber is increased rather than decreased with increasing treatment temperature.

A first attempt to improve the de-vulcanization efficiency at high de-vulcanization temperature: above 220°C, was made by replacing DPDS with the oxidation stabilizers. However, it can be seen from Figures 5.1 and 5.2 that there is no significant improvement with switching to the stabilizers. Replacement of DPDS by the oxidation stabilizers, shows lower soluble fractions and higher crosslink densities than obtained by using only DPDS. This indicates a more inefficient de-vulcanization, as can be seen in Figure 5.3 where the data points are shifted to the left hand side of the graph.

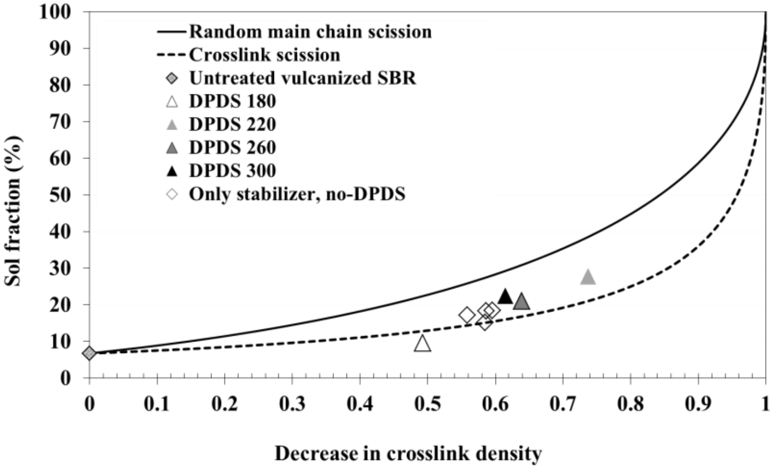


Figure 5.3 *Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of de-vulcanized SBR.*

A more efficient de-vulcanization is observed for de-vulcanization using combinations of DPDS and the oxidation stabilizers, as de-vulcanization aids. It can be seen in Figure 5.4 that addition of these stabilizers results in a smaller decrease of rubber sol fraction with increasing the de-vulcanization temperature above 220°C compared to the de-vulcanizates in which only DPDS is used. Furthermore, the increase of crosslink density with increasing de-vulcanization temperature above 220°C is absent with addition of oxidation stabilizers, as can be seen in Figure 5.5. The positive effect of using the combination of these two chemical species as de-vulcanization aid is clearly seen in Figure 5.6. The experimental data for treatment above 220°C are situated at even slightly higher position than the data for the de-vulcanizate treated at 220°C with only DPDS. The reversion phenomenon is noticeably absent in this case as there is no move of the data points to the left hand side with increase of de-vulcanization temperature up to 300°C. Therefore, the utilization of the developed synergism of de-vulcanization aid with oxidation stabilizers results in a more efficient and controlled de-vulcanization.

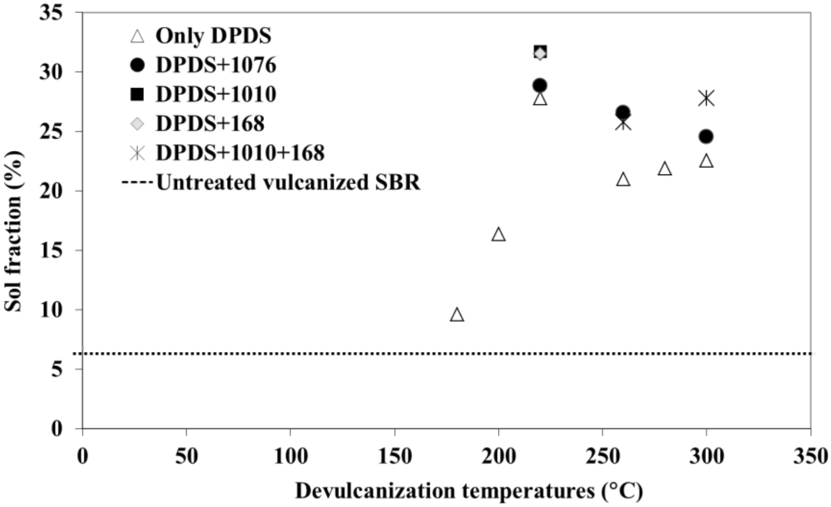


Figure 5.4 *Sol fraction as a function of the de-vulcanization temperature for de-vulcanized SBR using combinations of DPDS and stabilizers as de-vulcanization aids compared to untreated vulcanized SBR (dotted line).*

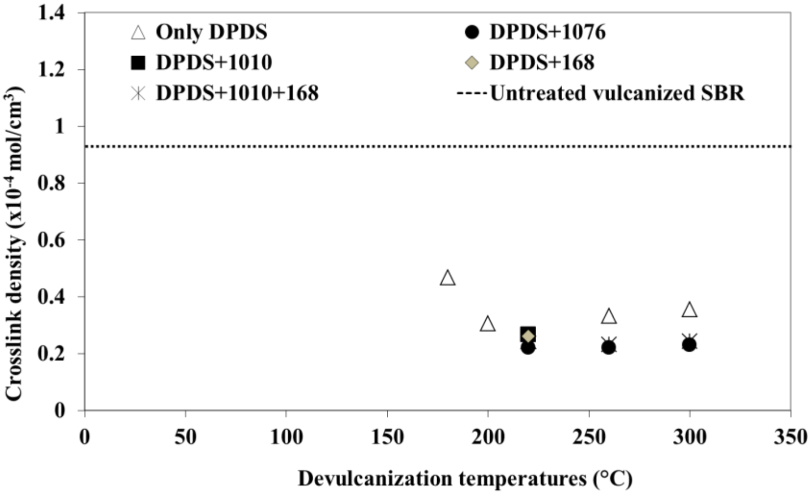


Figure 5.5 *Crosslink density as a function of de-vulcanization temperature for de-vulcanized SBR using combinations of DPDS and stabilizers as de-vulcanization aids, compared to untreated vulcanized SBR (dotted line).*

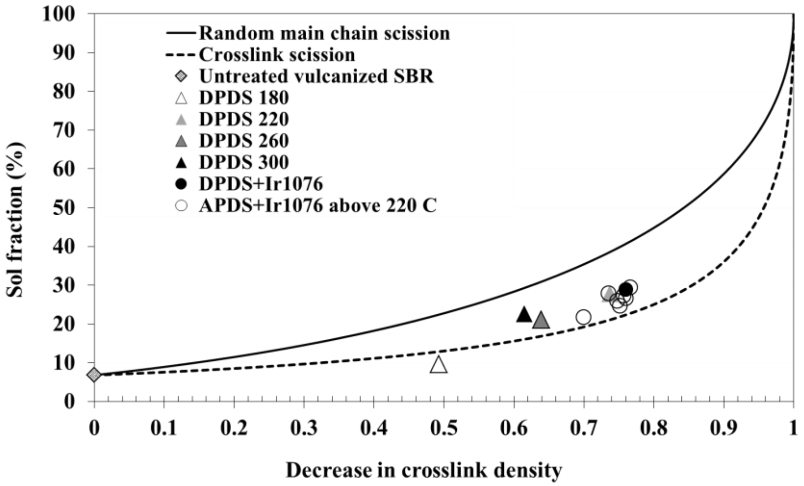


Figure 5.6 *Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of de-vulcanized SBR using combination of DPDS and stabilizer as de-vulcanization aid.*

MECHANISTIC CONSIDERATIONS

DPDS is reported to be an effective de-vulcanization aid. A mechanism that is frequently proposed for the reaction of radical scavenger de-vulcanization agents like DPDS with sulfur vulcanizates is the opening of crosslinks or the scission of polymer chains by heat and shearing forces, and the reaction of fragments with disulfide based radicals, which prevent recombination. A simplified reaction scheme proposed for the rubber de-vulcanization with DPDS is given in Figure 5.7. Based on the results, it is to be concluded that DPDS is an effective de-vulcanization aid till a temperature up to 220°C. Above this threshold temperature inefficient de-vulcanization happens. This may be attributed to an excessive and uncontrolled generation of reactive radicals so that degradation is more likely to occur at the higher de-vulcanization temperature.

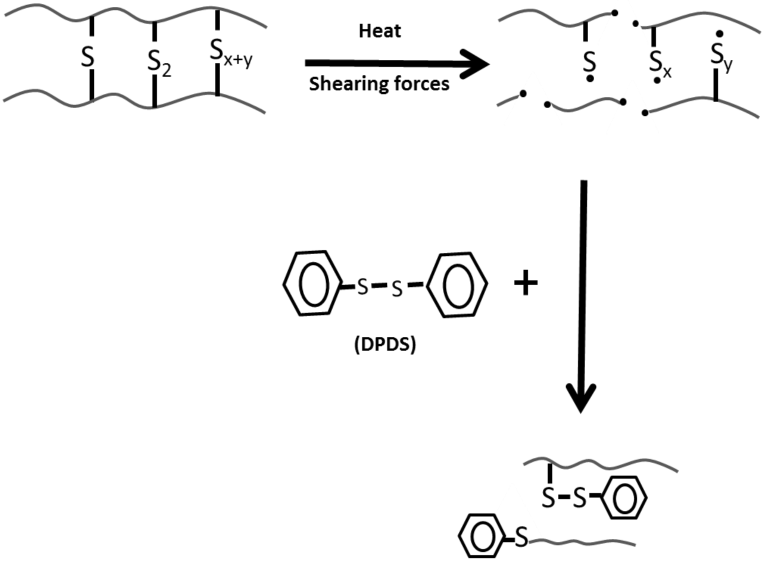
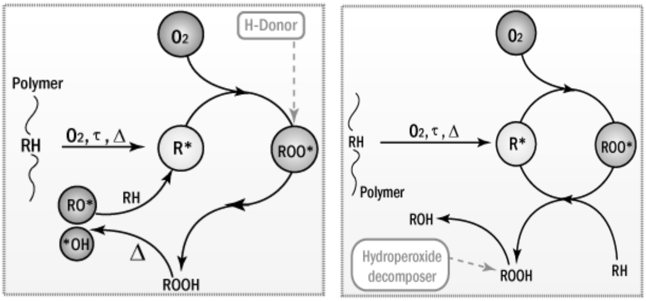


Figure 5.7 *Simplified reaction scheme proposed for rubber de-vulcanization using diphenyldisulfide as de-vulcanization aid.*



(a) **(b)**

Figure 5.8 *Preventing degradation by an oxidation stabilizer*[5]*:*
a) Hindered phenolic stabilizer; b) phosphite compound.

Generally, polymer degradation initiates by breaking C-H and C-C bonds along the polymer chains. Consequently, unstable carbon radicals ($R^\bullet$) are formed. These radicals readily react with oxygen (if present) to form peroxy radicals ($ROO^\bullet$) which subsequently abstract a hydrogen atom from other polymer molecules to form hydroperoxides (ROOH) and propagate in an oxidative degradation cycle[6]. Once oxidation starts, it sets off a chain reaction which accelerates degradation unless an oxidation stabilizer is present to interrupt the cycle. The principle mechanism of degradation and the effect of an oxidation stabilizer is shown in Figure 5.8[7]. Oxidation stabilizers are capable of scavenging or destroying these chain propagation species: alkoxy radicals ($RO^{\bullet}$), hydroxy radicals ($HO^{\bullet}$) and peroxy radicals ($ROO^{\bullet}$). Therefore, the oxidative degradation cycle can be prevented either by using an oxidation stabilizer or by totally eliminating oxygen in the de-vulcanization process. Two types of oxidation stabilizers were used in this present work: hindered phenolic and phosphite compounds. Hindered phenolic stabilizers act as hydrogen donor. The stabilizer reacts with peroxy radicals to form hydroperoxides and prevents the abstraction of the hydrogen from polymer molecules. Phosphite compounds function as hydroperoxide decomposers, the stabilizer prevents the split of hydroperoxide into extremely active radicals: alkoxy and hydroxyl[8-10].

Degradation of polybutadiene and butadiene based polymers follows a unique pathway due to the specific chemical structure of the polymer[11]. In degradation network breakdown occurs, but at the same time network recombination takes place. The degradation mechanisms are schematically depicted in Figure 4.7 in Chapter 4. Basically, two reactions can occur during degradation of polybutadiene:

- Chain scission and formation of inactive molecules;
- Formation of active chain segments.

Chain scission occurs when breaking of the C-C bonds (carbon-carbon bonds) in the polymer chains is accompanied by hydrogen transfer[12], and results in polymers with a lower molecular weight. The formation of active bond fragments presumably takes place when hydrogen transfer is not possible. In presence of oxygen, the hydrogen transfer reaction is less likely[11] . Therefore, the active radicals are more likely to recombine to a new network, thereby reducing the sol fraction and increasing the gel-level.

Based on the results, efficient de-vulcanization is observed with using a combination of DPDS and oxidation stabilizers as de-vulcanization aids. Combination of two different functional chemicals frequently gives better protection against polymer degradation than would be expected from each compound alone, commonly called synergism. A decrease in crosslink density without creating more sol fraction is found for the combination of an oxidation stabilizer and DPDS. Figure 5.9 emphasizes the importance of the developed “synergistic de-vulcanization aid”.

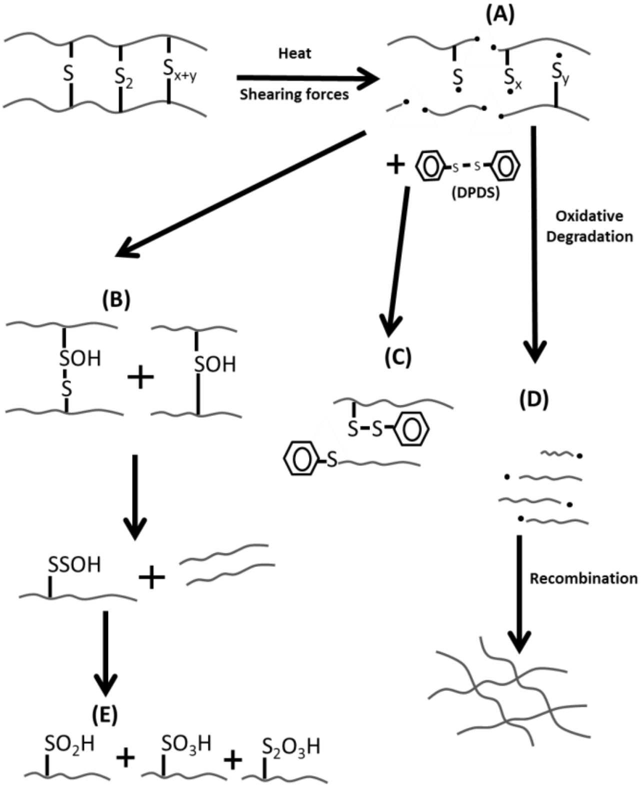


Figure 5.9 *Simplified reaction scheme proposed for thermo-chemical de-vulcanization*

Reaction (A): The initial step is opening of crosslinks or the scission of polymer chains by heat and shearing forces. Unstable radicals are formed. Generally, it happened somewhat at low temperature, but is of greater importance with increasing temperature[13]. Subsequently, these unstable radicals further react in secondary reaction steps in the presence of oxygen: (B), (C) and (D). These 3 reactions can jointly occur depending on the de-vulcanization conditions[11-14].

Reaction (B): As hydroperoxide is formed in subsequent oxidative aging of the vulcanizate, a variety of oxidized organic sulfur groups will result from reaction of the various mono-, di-, polysulfide groups with hydroperoxides. The sulfenic acids (RSOH) and thiosulfoxylic acids (RSSOH) formed from the oxidized sulfur vulcanized network, would be expected to react with hydroperoxides to form sulfinic (RSO_2H), sulfonic (RSO_3H) and thiosulfuric (RS_2O_3H) acids. All of these acids can contribute to the destruction of hydroperoxides to non-radical products and thus function as preventive antioxidants[14].

Reaction (C): The reaction of active radical fragments with disulfide based radicals, which prevent recombination of rubber molecules. In addition to this, the diffusion speed of the disulfide into the polymer matrix increases at high temperatures, enhancing the chance of combination of one radical with another rubber radical[15].

Reaction (D): Main-chain scission is caused by degradation. At higher treatment temperature, further activating the developing reactions, the probability of the generated reactive groups to undergo oxidative degradation increases. The radical products formed during the high treatment temperature that may participate in chain transfer are increased. This results in severe main chain scission of the rubber network and leads to a high network recombination as previously shown in Figure 5.9. This reaction needs an oxidation stabilizer to prevent the uncontrolled breakage of the rubber network.

At low temperature, the occurrence of reactions (B) and (C) is predominant, therefore DPDS functions satisfactorily under these circumstances. However uncontrolled generation of reactive groups occurs at higher temperatures, which leads to the predominant occurrence of reaction (D). The stabilizers prevent this to a large extent.

5.4 CONCLUSIONS

The de-vulcanization efficiency of SBR is affected by uncontrolled degradation and oxidation during thermo-chemical de-vulcanization. Using only DPDS as de-vulcanization aid, an increase of the de-vulcanization temperature results in a decrease of the crosslink density in first instance, but an increase again above a temperature threshold of 220°C.

Using a combination of DPDS and one or more oxidation stabilizers results in a more efficient de-vulcanization, especially at high de-vulcanization temperatures. A decrease in crosslink density without creating more sol fraction is found for a combination of an oxidation stabilizer and DPDS. DPDS scavenges formed reactive radicals, preventing recombination of the rubber network. The stabilizers suppress the reaction of oxygen, which accelerates the degradation of the polymers and recombination into new crosslinks. The synergistic function of these two chemicals results in the most efficient de-vulcanization for SBR.

5.5 REFFERENCES

[1] V.V. Rajan, W.K. Dierkes, J.W.M. Noordermeer and R. Joseph, *Rubber Chem. Technol.*, **78**, 855 (2005)

[2] P.J. Flory, *J.Am.Chem.Soc.*, **63**, 1941, 3096

[3] M.M. Horikx, *J.Polym.Sci.*, **19**, 1956, 335

[4] M.A.L. Verbruggen, L. van der Does, J.W.M., Noordermeer, M. van Duin and H.J. Manuel, *Rubber Chem. Technol.*, **72**, 1999, 731

[5] www.specialchem4adhesives.com (April, 2013)

[6] A.G. Ferradino, *Rubber Chem. Technol.*, **76**, 2003, 694

[7] N.M. Huntink, Ph.D. Thesis, University of Twente, Enschede, the Netherlands, 2003.

[8] H. Zweifel, "Stabilization of Polymeric Materials", Springer-Verlag, Berlin, Germany, 1998.

[9] W.L. Hawkins, "Polymer degradation and stabilization", Springer-Verlag, Berlin, Germany,1984.

[10] H.H.G. Jellinek, "Degradation and stabilization of polymers", Elsevier, Amsterdam, the Netherlands, 1983.

[11] M.D.Sarkar, P.G. Mukunda, P.P.De, and A.K. Bhowmick, *Rubber Chem. Technol.*, **70**,1997, 855.

[12] S.L. Madorsky, "Thermal degradation of organic polymers", Interscience Publishers, New York, U.S., 1964, p.203.

[13] W. Hofmann, "Rubber Technology Handbook", Hanser/Garder Publications, Cincinnati, U.S., 1994.

[14] G. Scott, "Development in Polymer stabiliation-4", Applied Science Publishers, London, U.K., 1981, p.65.

[15] V.V. Rajan, Ph.D.Thesis, University of Twente, Enschede, The Netherlands (2005).

CHAPTER 6

COMPARATIVE INVESTIGATION OF THE DE-VULCANIZATION PARAMETERS OF TIRE RUBBERS

The optimal process conditions for a high ratio of de-vulcanization to polymer degradation have been investigated for tire rubbers: SBR, BR, NR and CIIR. These polymers all show their own particular breakdown characteristics. The temperature dependence of the breakdown mechanism was investigated by measuring sol fractions and crosslink densities. For SBR and BR, the highest reduction in crosslink density was found at a temperature of 220°C, together with a moderate increase in sol content. According to the Horikx theory, which correlates sol fraction and decrease in crosslink density, this is the result of a high degree of crosslink scission. Higher process temperatures result in a lower decrease in crosslink density due to recombination of active chain fragments. NR and CIIR show different behaviour. Breakdown of NR in this temperature range results in an almost complete destruction of the polymer network; crosslink density is reduced to almost zero and the sol fraction is close to 100%. The same result is found for CIIR at higher temperatures. Although different rubbers react via other de-vulcanization mechanisms, the best de-vulcanization compromise for whole passenger car tire material is elaborated.

6.1 INTRODUCTION

Rubber is a very durable material, in particular tire rubber, and this poses a major challenge for recycling. For end-of-life tires, incineration is currently the most important outlet, impeding the re-use of this valuable raw material in new rubber products. A considerable share of material recycling can only be achieved if tire material can be used in real recycling loops: tires back into tires.

Passenger car tire material is a blend of different polymers: styrene butadiene rubber (SBR), butadiene rubber (BR), natural rubber (NR) and isobutylene isoprene rubber or its halogenated counterpart (IIR, CIIR or BIIR), with the main component being SBR. Each polymer has its own specific function in tires and all show their own particular degradation and de-vulcanization characteristics. Therefore, the optimal process conditions for a high ratio of de-vulcanization to polymer degradation have to be balanced not only for the main component: SBR, but also for BR, NR and IIR.

One possibility to shift the balance towards de-vulcanization is the use of an de-vulcanization aid. The substantial function of a de-vulcanization aid is to initiate cleavage of sulfur crosslinks or to terminate the free radical chains formed as a result of C-S, S–S and C–C bond cleavage. A large number of de-vulcanization aids such as disulfides, phenols, phenolic compounds, amines, and metal chlorides for natural and synthetic rubbers de-vulcanization which react according to different mechanisms: a radical[1-4] or nucleophilic[5,6] mechanism, or a catalytic[7-9].

Within this study, the above mentioned polymers were de-vulcanized and investigated concerning their tendency for crosslink versus main chain scission, with the lead polymer being SBR. The present work applies thermo-chemical de-vulcanization which is very likely to occur via a radical mechanism[2]. Consequently, diphenyldisulfide (DPDS), which was reported to be an effective de-vulcanization chemical[1-3] and which was applied in rubber recycling as radical stabilizing agent[10], was used as de-vulcanization aid in this investigation. Furthermore, de-vulcanization was done under nitrogen atmosphere and the de-vulcanized material was quenched in liquid nitrogen immediately after the process in order to suppress the reaction of radicals or other reactive species in the de-vulcanizate with oxygen or with other reactive species[4]. In this paper, the mechanisms behind the breakdown processes of the different elastomers are discussed, and the best de-vulcanization conditions for whole passenger car tire material are elaborated.

6.2 EXPERIMENTAL

MATERIALS

The SBR type used in this investigation was SBR 1723, an oil extended emulsion-polymerized SBR containing 37.5 phr of treated distillate aromatic extract (TDAE) oil, obtained from Dow Chemical, Germany. The polymer contained 23.5 wt% styrene and 76.5 wt% butadiene, and its Mooney viscosity ML(1+4) measured at 100°C was 40 MU. The BR (cis-1,4 polybutadiene) grade Buna CIS 132 was produced by nickel catalysis; it is a stereospecific polybutadiene with high cis-1,4 content, obtained from Dow Chemical, Germany. Its Mooney viscosity ML(1+4) measured at 100°C was 45 MU. The butyl rubber was a halogenated grade, CIIR (chlorinated butyl rubber), obtained from Lanxess, Germany. The Mooney viscosity ML(1+4) measured at 100°C was 38 MU. Natural rubber was TSR20 (Technically Specified Rubber) with a Mooney viscosity ML(1+4) measured at 100°C of 80 MU. Zinc oxide (ZnO) and stearic acid were obtained from Flexsys, the Netherlands. The curatives, sulfur and N-tert-butyl-2-benzothiazylsulfenamide (TBBS), were obtained from Merck. The solvents, acetone and tetrahydrofuran (THF), which were used for extractions, and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve. TDAE oil used as processing oil for the de-vulcanization was supplied by Hansen&Rosenthal, Germany. Diphenyldisulfide (DPDS) used as de-vulcanization aid was obtained from Sigma-Aldrich, Germany.

PREPARATION OF DE-VULCANIZATES

Mixing and vulcanization.- Gum rubbers were first compounded using Laboratory Branbury mixer with a mixing chamber volume of 1.4 liters. The compounding formulations are shown in Table 6.1. The recipes are simplified from tire parts formulations[12] however, no fillers were added in order to facilitate the analysis of the material. The cure characteristics were measured using a RPA 2000 dynamic mechanical curemeter from Alpha Technologies at 170°C, 0.833 Hz and 0.2 degree strain, according to ISO 6502. The compounds were then vulcanized for $t_{c,90}$ + 5 minutes in a Wickert WLP1600 laboratory compression molding press at

170°C and 100 bar, into 2 mm thick sheets.

Table 6.1 Formulations of the rubber compounds

Ingredient	phr			
SBR	100	-	-	-
BR	-	100	-	-
NR	-	-	100	-
CIIR	-	-	-	100
ZnO	4.13	3.00	3.00	3.00
Stearic acid	2.06	2.00	1.00	2.00
Sulfur	2.75	2.00	2.00	0.50
TBBS*	1.38	1.00	1.00	-
MBTS**	-	-	-	1.00

* TBBS: N-tert-butyl-2-benzothiazyl sulfenamide

** MBTS: Merceptobenzothiazyl disulfide

Grinding.- The vulcanized rubber sheets were subsequently ground in a Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen. The particle size of the ground rubber was in the range of 0.85-2.00 mm.

De-vulcanization.- Thermo-chemical de-vulcanization was performed batchwise in an internal mixer (Brabender Plasticorder PL-2000), having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.7 and a constant rotor speed of 50 rpm were used, and the chamber temperature was 220°C. After adding ground rubber and TDAE oil (5% w/w) into the mixer, the DPDS (30 mmol/100 g compound) was added. The de-vulcanization was carried out under nitrogen atmosphere at 2 different temperatures: 220°C and 260°C. The de-vulcanization time was 5 minutes. After de-vulcanization, the material was taken out of the internal mixer and directly quenched into liquid nitrogen.

CHARACTERIZATION OF THE DE-VULCANIZATES

Rubber soluble fraction.- The soluble (Sol) fraction of the de-vulcanizates were determined by extraction in a Soxhlet apparatus, as described in Chapter 3.

Crosslink density.- The extracted samples were subsequently swollen in toluene for 72 hrs at room temperature. The weight of the swollen vulcanizates was measured after removal of surface liquid with absorption paper. The crosslink density was calculated according to the Flory-Rehner [13], as described in Chapter 3. In this chapter, the Flory-Huggins polymer-solvent interaction parameter used in the calculation are: 0.37 for the system SBR/toluene[14,15], 0.34 for the system BR/toluene[16,17], 0.39 for the system NR/toluene[18] and 0.56 for the system CIIR/toluene[19].

6.3 RESULTS AND DISCUSSION

DE-VULCANIZATION OF SBR

The sol fractions and crosslink densities of the remaining gel as a function of the de-vulcanization temperature of the SBR de-vulcanizates (D-SBR) are depicted in Figure 6.1. Principally, the increase of the rubber sol fraction and decrease of crosslink density indicate the extent to which the rubber network is broken. Thermo-chemical de-vulcanization of sulfur-cured SBR using DPDS as de-vulcanization aid shows initially an increase of the rubber soluble fraction with increasing de-vulcanization temperature, but for very high temperatures in the range of 260°C the sol fraction decreases again. Furthermore, at a temperature of 260°C, a significant increase in crosslink density is observed as well. Basically, DPDS as de-vulcanization agent was added in order to scavenge radicals formed during the reclaiming process and thus avoid secondary reactions of the polymer parts; however, this works only at lower de-vulcanization temperatures. At high de-vulcanization temperatures, i.e. 260°C, an extensive generation of reactive radicals occurs. These lead to formation of new inter- and intramolecular bonds[20] resulting in a decrease of the rubber sol fraction and renewed increase in crosslink density.

The sol fraction of SBR de-vulcanizates as a function of the relative decrease in crosslink density according to Horikx[21] is shown in Figure 6.2. A de-vulcanization temperature of 220°C results in a shift of the data point to the right hand side of the graph, which indicates an increase in sol fraction and large decrease of crosslink density compared to the untreated SBR. However, a further increase of the de-vulcanization temperature to 260°C results in a back turn of the experimental data points to the left, which is the reverse of the expected decrease of crosslink density. This indicates inefficient de-vulcanization, in which the crosslink density of the de-vulcanized rubber is increased rather than decreased with increasing treatment temperature. All data points are rather close to the line of crosslink scission: This is the dominant breakdown process under these conditions for this polymer.

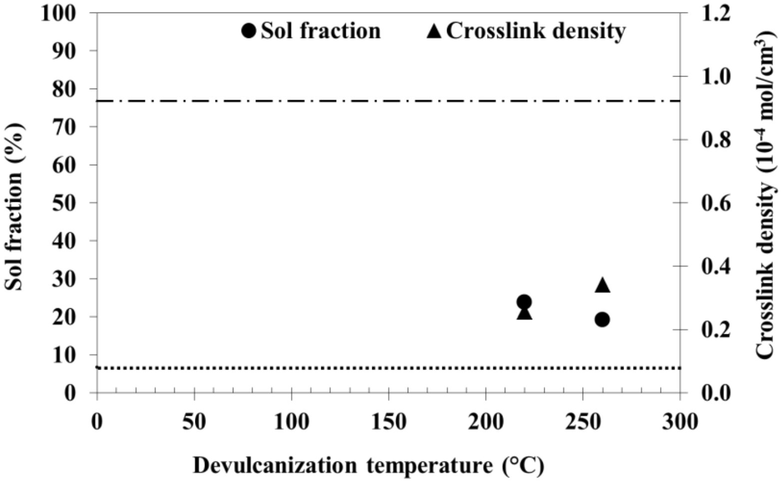


Figure 6.1 *Sol fraction and crosslink density of SBR de-vulcanizates versus de-vulcanization temperature; (▪▪▪▪▪▪): Sol fraction of untreated rubber vulcanizate; (▬ ▪ ▬): Crosslink density of untreated rubber vulcanizate.*

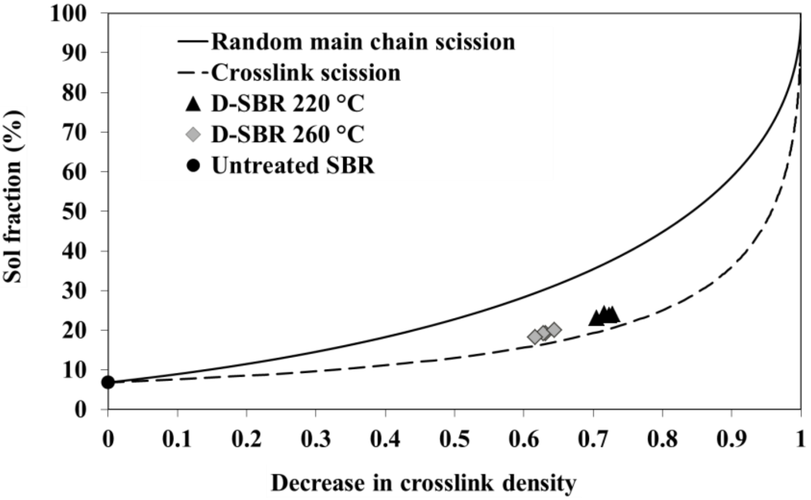


Figure 6.2 *Relative decrease in crosslink density versus sol fraction of SBR de-vulcanizates (Results of single measurements).*

A simplified reaction scheme proposed for the de-vulcanization of SBR with DPDS is given in Figure 5.7 in Chapter 5. The initial step is opening of crosslinks or scission of polymer chains by heat and shearing forces. In this process, unstable radicals are formed. Generally, this happens only to a limited extent at low temperatures, but is of growing importance with increasing temperature[23]. Subsequently, these unstable radicals further react in secondary reaction steps with disulfide-based radical species, which prevent recombination of rubber molecules.

DE-VULCANIZATION OF BR

The sol fraction and crosslink density of BR de-vulcanizates (D-BR) as a function of de-vulcanization temperature are shown in Figure 6.3. A de-vulcanization temperature of 220°C results in a significant increase in sol fraction and a decrease in crosslink density; the values of the material de-vulcanized at 260°C show values in-between. The sol fraction of BR de-vulcanizates as a function of the relative decrease in crosslink density according to Horikx[21] is shown in Figure 6.4. At a de-vulcanization temperature of 220°C, all experimental data are situated above the line of main-chain scission with about 60% decrease in crosslink density compared to untreated BR; the data points of BR de-vulcanizates at a de-vulcanization temperature of 260°C are closer to the line of main-chain scission but at a much lower relative decrease in crosslink density. This means that a de-vulcanization temperature of 220°C is more effective than a temperature of 260°C, as the percentage of soluble polymer is higher and the final crosslink density is lower. However, a considerable amount of main chain scission occurs in both cases, as the sol content is rather high.

The differences in the de-vulcanization behavior at the two different de-vulcanization temperatures may be attributed to the complexity of the degradation mechanism of the polybutadiene based polymer[24-28]. Degradation of polybutadiene and other butadiene based polymers follows a unique pathway due to the specific chemical structure of the polymer[29]. In a degradation process network breakdown occurs, but at the same time network recombination takes place. The degradation mechanisms are schematically depicted in Figure 4.7 in Chapter 4. Basically, two reactions can occur during degradation of polybutadiene:

- Chain scission and formation of inactive molecules;
- Formation of active chain segments.

Chain scission occurs when breaking of the C-C bonds (carbon-carbon bonds) in the polymer chains is accompanied by hydrogen transfer[2], and results in chemically inactive polymer segments with a lower molecular weight. The formation of active bond fragments presumably takes place when hydrogen transfer is not possible. Both, hydrogen transfer as well as radical scavenging by the de-vulcanization aid of the active chain fragments are apparently more effective at a de-vulcanization temperature of 220°C, leading to a higher sol fraction and a lower crosslink density compared to a temperature of 260°C. For this polymer, the de-vulcanization temperature should be as low as possible.

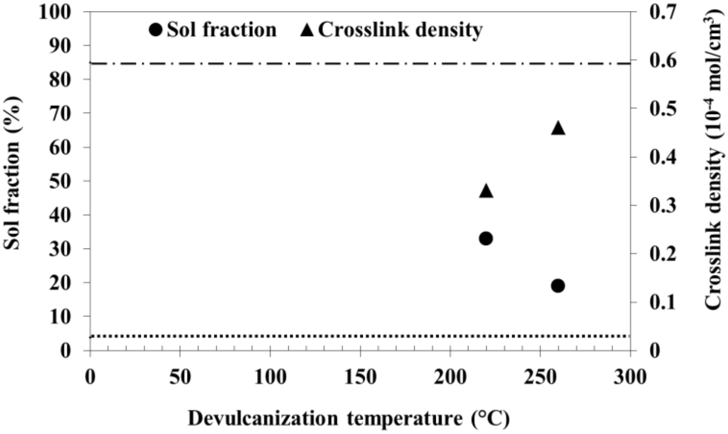


Figure 6.3 *Sol fraction and crosslink density of BR de-vulcanizates versus de-vulcanization temperature; (......): Sol fraction of untreated rubber vulcanizate; (▬ · ▬): Crosslink density of untreated rubber vulcanizate.*

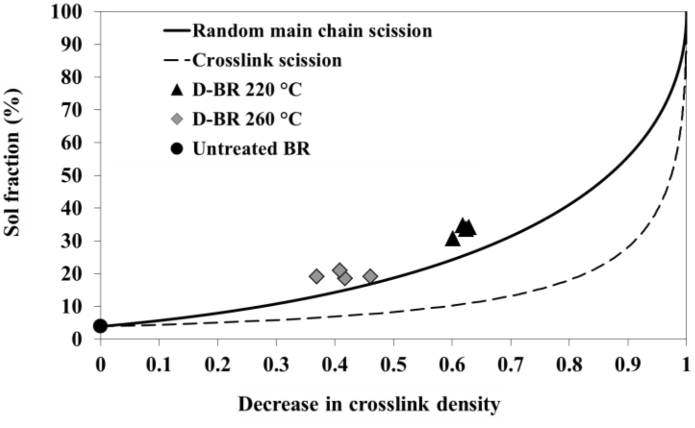


Figure 6.4 *Relative decrease in crosslink density versus sol fraction of BR de-vulcanizates.*

DE-VULCANIZATION OF NR

The sol fraction and crosslink density of NR de-vulcanizates as a function of the de-vulcanization temperature are shown in Figure 6.5. Almost 100% sol fraction of NR de-vulcanizates (D-NR) is observed at both de-vulcanization temperatures, 220°C and 260°C. Moreover, the crosslink densities of the de-vulcanizates treated at these temperatures are reduced to almost zero. This indicates that breakdown of NR in this temperature range results in an almost complete destruction of the NR network.

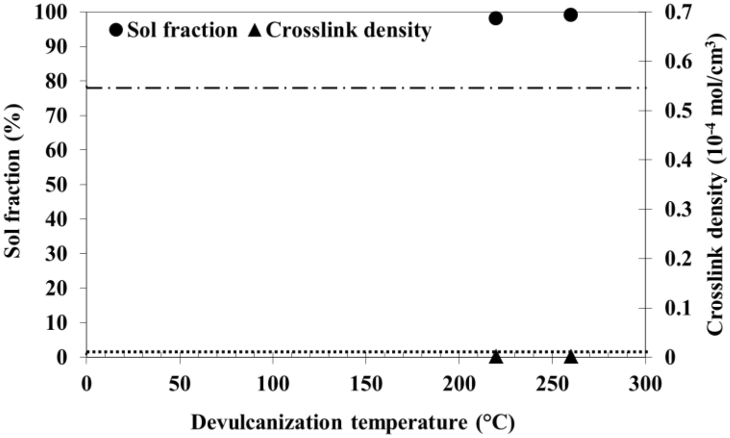


Figure 6.5 *Sol fraction and crosslink density of NR de-vulcanizates versus de-vulcanization temperature; (▪▪▪▪▪▪): Sol fraction of untreated rubber vulcanizate; (▬ ▪ ▬): Crosslink density of untreated rubber vulcanizate.*

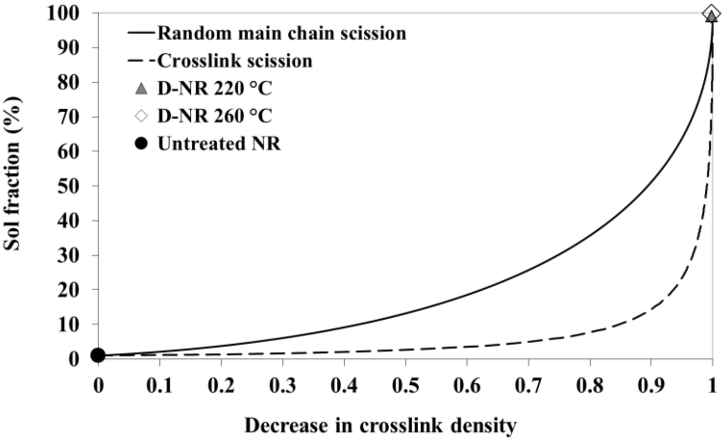


Figure 6.6 *Relative decrease in crosslink density versus sol fraction of NR de-vulcanizates.*

It was reported[2] before that the NR vulcanizate network can strongly be decreased in crosslink density at temperatures above 170 °C. Moreover, DPDS was reported[1-3] to be an effective de-vulcanization aid for NR. Temperature is the main governing factor and addition of DPDS can significantly enhance the effects. The sol fraction of NR de-vulcanizates as a function of the relative decrease in crosslink density according to Horikx[21] is shown in Figure 6.6. As can be seen, the data points for NR de-vulcanizates reach the joint top point of both lines, main-chain and crosslink scission: This material is completely soluble; no network connections are remaining between the polymer molecules. Both NR de-vulcanizates had a very low viscosity and showed tacky behavior, another indication of a complete breakdown of the network. For this polymer, the de-vulcanization temperature is not critical within this temperature range, as long as the polymer chains stay intact. The simplified reaction scheme proposed for breaking an NR network by using DPDS is shown in Figure 2.8 in Chapter2.

DE-VULCANIZATION OF CIIR

Figure 6.7 shows the changes in sol fraction and crosslink density of CIIR de-vulcanizates as a function of de-vulcanization temperature. The relative decrease in crosslink density is shown in Figure 6.8. An increase in sol fraction with increasing de-vulcanization temperature was observed: the sol fractions were about 36% and more than 95% after de-vulcanization of CIIR at 220°C and 260°C, respectively. Consequently, the de-vulcanized CIIR at 260°C had a very low viscosity and showed tacky behavior. However, in terms of crosslink density it was found that there was no significant decrease at a de-vulcanization temperature of 220°C. It can clearly be noticed from Figure 6.8 that all experimental data are situated above the line of main-chain scission and at less than 40% decrease in crosslink density compared to untreated CIIR. They are clustered at the left hand side which indicates that the crosslink density of the treated rubber is more or less the same as the crosslink density of the untreated one. This may be attributed to a de-vulcanization mechanism which is not uniform and homogeneously distributed throughout the rubber particles, and for which the validity of the Horikx plot is limited. The two different de-vulcanization mechanisms, uniform and non-uniform, are schematically depicted in Figure 6.9[30].

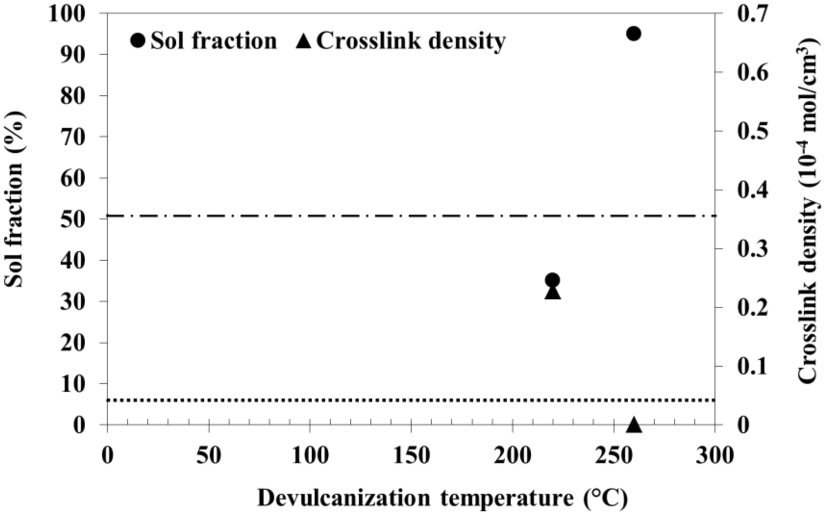


Figure 6.7 *Sol fraction and crosslink density of CIIR de-vulcanizates versus de-vulcanization temperature; (......): Sol fraction of untreated rubber vulcanizate; (– · –): Crosslink density of untreated rubber vulcanizate.*

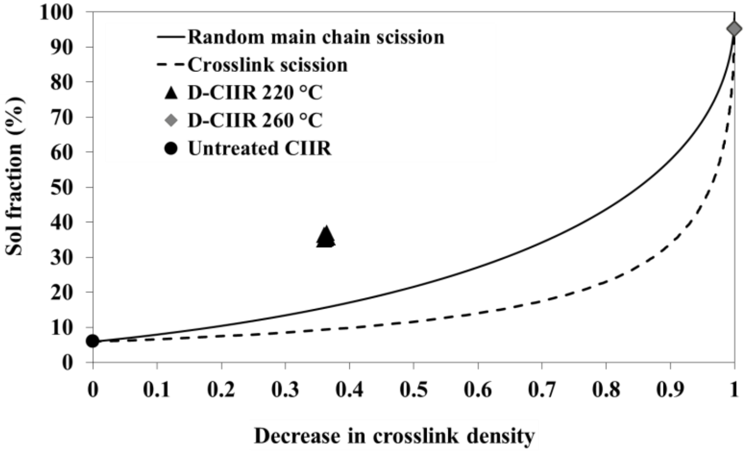


Figure 6.8 *Relative decrease in crosslink density versus sol fraction of CIIR de-vulcanizates.*

A limitation of the Horikx representation is, that it assumes homogeneous breakdown of the vulcanized network throughout the particles (A). However, the results for de-vulcanized CIIR at 220°C indicate a different mechanism: peeling off of the outer layers of the particles, while the inner cores of the particles stay more or less untreated at constant crosslink density (B). This inhomogeneity causes in actual practice a lower decrease in crosslink density at a particular sol fraction, than would have been obtained for homogeneous breakdown.

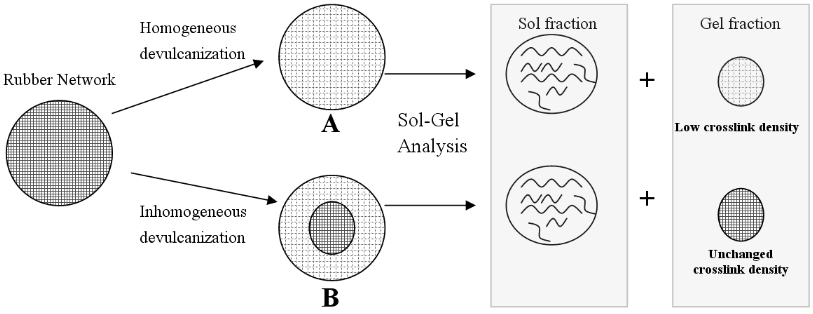


Figure 6.9 *Schematic representation of two different de-vulcanization mechanisms, A: Homogeneous de-vulcanization and B: Inhomogeneous de-vulcanization*[30]*.*

The difficulties of whole tire de-vulcanization are caused by the fact that this material consists of several types of elastomers, fillers and other additives. In this study, the de-vulcanization conditions are optimized for SBR, and as BR chemically resembles SBR they are also applicable for this polymer. NR turned out to be rather forgiving in terms of de-vulcanization conditions and could be treated in the same manner as SBR and BR. However, the de-vulcanization of CIIR are not optimal, but as the percentage of CIIR in a tire is rather small its effect is expected to be small. Taking all de-vulcanization parameters and trends of the different types of elastomers into account, a compromise for the whole passenger car tire de-vulcanization conditions was found. Temperature is the most important parameter, and homogenous breakdown of the vulcanized network is required. Based on these results, it is necessary to keep the de-vulcanization temperature as low as possible. It should be mentioned that in this part of the study, the effect of fillers was not included.

6.4 CONCLUSIONS

SBR, BR, NR and CIIR react according to different de-vulcanization mechanisms. BR behaves more or less the same as SBR: it shows chain recombination with increasing de-vulcanization temperatures. Using a de-vulcanization temperature of 220°C leads to a decrease in crosslink density for at least 60% in case of BR and 70% in case of SBR compared to original vulcanizates. For NR, the network is easily broken down with a treatment temperature higher than 170°C, but it is a combination of polymer and crosslink scission. Therefore, it is necessary to keep the de-vulcanization temperature as low as possible to prevent the destruction of the NR molecular chain and to shift the balance to crosslink scission. CIIR acts differently from the other types of rubber: The network breakdown is enhanced by increasing the de-vulcanization temperature within the temperature window used in this study. However, at lower temperatures, the breakdown is not uniformly distributed throughout the particles; for a uniform breakdown a higher temperature has to be used. Taking all these factors into consideration, a good compromise for the de-vulcanization conditions for all types of rubber can be proposed. For the best de-vulcanization of tire rubbers, it is necessary to keep the de-vulcanization temperature as low as possible for an efficient de-vulcanization, a high ratio of crosslink to main chain scission, and a homogenous breakdown of the vulcanized network. The main processing parameter is temperature, however it has an adverse effect on these three characteristics.

6.5 REFERENCES

[1] V.V. Rajan, W.K. Dierkes, R. Joseph and J.W.M. Noordermeer, *J. Appl. Polym. Sci.,* **102**, 4194 (2006).

[2] V.V. Rajan, W.K. Dierkes, J.W.M. Noordermeer and R. Joseph, *Rubber Chem. Technol.*, **78**, 855 (2005).

[3] A.R. Jalilvand, I. Ghasemi, M. Karrabi and H. Azizi, *Progr. Rubber. Plast. Recycling Techn.*, **24**(1), 33 (2008).

[4] G.K. Jana and C.K. Das, *Polym. Plast. Techn. Eng.* , **44**, 1399 (2005).

[5] K.A.J. Dijkhuis, I. Babu, J. Lopulissa, J.W.N. Noordermeer and W.K. Dierkes, *Rubber Chem. Technol.*, **81**, 865 (2008).

[6] M. van Duin, J. W. M. Noordermeer, M. A. L. Verbruggen and L. van der Does (to DSM) U.S. 6,956, 065 (2005).

[7] S. Yamashita, N. Kawabata, S. Sagan and K. Hatashi, *J. Appl. Polym. Sci.,* **21**, 2201 (1977)

[8] A.A. Yehia, M.N. Ismail, Y.A. Hefny, E.M. Abdelbary and M.A. Mull, *J. Elast. Plast.,* **33**, 109 (2004)

[9] R.D. Myers, P. Nicholson, J.B. MacLeod and M.E. Moir, US 5,602,186. (1997).

[10] M. Myhre, S. Saiwari, W.K. Dierkes and J.W.N. Noordermeer, *Rubber Chem. Technol.,* **85**, 408 (2012).

[11] S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, presented at a meeting of the Rubber Division, ACS, October 2011, Cleveland (USA).

[12] R.N. Datta, "Rubber curing systems" In: Current Topics in Elastomers Research, A.K. Bhowmick, ed., Taylor & Francis Group, LLC, New York, U.S., 2008.

[13] P.J. Flory, *J. Am. Chem. Soc*., **63**, 3096 (1941).

[14] S.C. George, K.N. Ninan and S. Thomas, *Polym. Compos*., **7**, 343 (1999).

[15] S.L. Abd-El-Messieh and K.N. Abd-El-Nour, *J. Appl. Polym. Sci*., **88**, 1613 (2003).

[16] W.L. Hergenrother, *J. Appl. Polym. Sci*., **16**, 2611 (1972).

[17] W.O.Parker, A. Ferrendo, D. Ferri and V. Canepari, *Macromolecules*, **40**, 5787 (2007).

[18] M. Kojima, A. Tosaka and Y. Ikeda, *Green Chem*., **6**, 84 (2004).

[19] J.T. Sunil and R. Joseph, *Int. J. Polym. Mat*., **56**, 743 (2007).

[20] " Thermal Degradation of Organic Polymers", S.L. Madorsky, ed., Interscience Publishers, New York, U.S., 1964.

[21] M.M. Horikx, *J. Polym. Sci*. **19**, 445 (1956).

[22] M.A.L. Verbruggen, L. van der Does, J.W.M. Noordermeer, M. van Duin and H.J. Manuel, *Rubber Chem. Technol*., **72**, 731 (1999).

[23] W. Hofmann, "Rubber Technology Handbook", Hanser/Garder Publications, Cincinnati, U.S., 1994.

[24] R.N. Hader and D.S. le Beau, *Industrial and Engineering Chemistry*, **43(2)**, 250 (1951).

[25] V. Yu Levin, S.H. Kim and A.I. Isayev, *Rubber Chem. Technol*., **70**, 120 (1997).

[26] J. Choi and A.I. Isayev, *Rubber Chem. Technol*., **84**, 55 (2011).

[27] A.I. Isayev, S.H. Kim and W. Feng, *Rubber Chem. Technol*., **78**, 606 (2005).

[28] J.S. Oh, A.I. Isayev and E. von Meerwall, *Rubber Chem. Technol*., **77**, 745 (2004).

[29] M.D. Sarkar, P.G. Mukunda, P.P. De and A.K. Bhowmick, *Rubber Chem. Technol*., **70**, 855 (1997).

[30] K.A.J. Dijkhuis, I. Babu, J.S. Lopullissa, J.W.M. Noordermeer and W.K. Dierkes, *Rubber Chem. Technol*., **81**, 190 (2008).

CHAPTER 7

DE-VULCANIZATION OF WHOLE PASSENGER CAR TIRE MATERIAL

Ground tire rubber (GTR) from whole passenger car tires is composed of several types of rubbers and fillers, making de-vulcanization of this material a challenge. Each elastomer has its own specific de-vulcanization conditions, as our previous studies have shown. The elaboration of the optimal de-vulcanization process for GTR is more complex than just finding the best compromise of the de-vulcanization parameters for the single types of elastomers used in a passenger car tire. Whatever de-vulcanization conditions are chosen, the optimal parameters for an individual elastomer type or a compromise based on all different elastomer types, inhomogeneous de-vulcanization will occur. In actual practice, this inhomogeneity in de-vulcanization causes a reduced decrease in crosslink density at a particular sol fraction than would have been obtained from a homogeneous breakdown.

Swelling of GTR in a mixture of an oil (Treated Distillate Aromatic Extract, TDAE) and an appropriate de-vulcanization aid (diphenyldisulfide, DPDS) before de-vulcanization was studied as a way to improve the dispersion of DPDS in the crosslinked rubber matrix and to achieve a more homogenous breakdown of the crosslink network. This process step results in a slight increase of the soluble polymer content, but it significantly reduces the crosslink density during the de-vulcanization process. The process is optimized in terms of TDAE concentration and de-vulcanization time for efficient de-vulcanization. By using these optimized de-vulcanization conditions, a high degree of crosslink density reduction can be achieved for GTR.

7.1 INTRODUCTION

Tires consist of several types of vulcanized rubber and various reinforcing materials. When a complete passenger car tire at the end of its life cycle is ground, the resulting rubber powder on average has a composition as given in Table 7.1[1]. This blend of several types of rubbers makes de-vulcanization rather complicated. Many attempts to recycle GTR via mechanical[2,3], mechanochemical[4-6], thermomechanical[7-9] and thermochemical processes[1,10] have been reported. However, the resulting de-vulcanizates have poor properties. They can be used only in low quality rubber products or in very small quantities in high performance rubber products. Amongst all processes, the thermo-chemical processes is the preferred one in order to produce high quality de-vulcanizates due to the selective breakdown of the crosslink network.

Table 7.1 Ground tire rubber composition[1]

Composition	Content, phr
Polymer Base:	100
Natural rubber	30
SBR (styrene-butadiene rubber)	40
BR (butadiene rubber)	20
Butyl- and halogenated butyl rubber	10
Carbon black	32-36
Free textile <1,0 mm	0.8
Free textile > 1,0 mm	1.2

In thermo-chemical de-vulcanization, several factors affect the properties of the de-vulcanized GTR (D-GTR). One of predominant problems is inhomogeneous de-vulcanization which is caused by pour diffusion of the de-vulcanization aid into the rubber particles. Swelling of GTR before de-vulcanization in an oil containing the chemicals was reported as a way to improve the diffusion and consequent dispersion: Plasticizers such as terpenes and pine oil were added to ground rubber together with de-vulcanization aids. The softeners swell and soften the surface, and facilitate penetration of the reactive chemicals into the particle[1].

Within this present study, the GTR was de-vulcanized using the optimal conditions which are a compromise for all single types of elastomers used in a passenger car tire. A study was performed concerning the de-vulcanization efficiency, measured as the tendency for crosslink versus main chain scission. Furthermore, the dispersion of DPDS in the rubber matrix and its significance for a homogenous breakdown of the crosslink network was monitored. Finally, the de-vulcanization conditions for GTR are optimized. Furthermore, the mechanisms of the breakdown processes of GTR are discussed.

7.2 EXPERIMENTAL

MATERIALS

The ground rubber from whole passenger car tires used in this investigation was obtained from Rubber Resources BV, the Netherlands. It was mainly based on synthetic rubber and had a particle size of typically 0.35 mm. TDAE oil used as processing oil for the de-vulcanization was supplied by Hansen&Rosenthal, Germany. Diphenyldisulfide (DPDS) used as de-vulcanization aid was obtained from Sigma-Aldrich, Germany. The solvents, acetone and tetrahydrofuran (THF), which were used for extractions, and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve.

PREPARATION OF DE-VULCANIZATES

De-vulcanization.- Thermo-chemical de-vulcanization was performed batchwise in an internal mixer (Brabender Plasticorder PL-2000), having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.5 and a constant rotor speed of 50 rpm were used, and the chamber temperature was 220°C. Initially, the de-vulcanization of GTR was carried out using the optimized process conditions as elaborated for the tire rubbers in Chapter 6 and given in Table 7.2. After adding ground rubber and TDAE oil (5 phr) into the mixer, the DPDS (30 mmol/100 g compound) was added. The de-vulcanization was carried out under nitrogen atmosphere at 220°C, and the de-vulcanization time was 6 minutes. After de-vulcanization, the material was taken out of the internal mixer and directly quenched in liquid nitrogen.

Further studies with the purpose to optimize the de-vulcanization process conditions for GTR were performed. The optimization of the de-vulcanization process parameters for GTR was done with respect to three factors, and for the successive steps the earlier optimized conditions were applied.

1. Effect of swelling before de-vulcanization.- This experiment was performed batchwise in an internal mixer. Before putting the rubber into the mixer, GTR was swollen in a mixture of TDAE and DPDS for 30 and 60 minutes at 65°C, as the temperature where DPDS is dissolved in TDAE. The de-vulcanization was carried out under nitrogen atmosphere at 220°C. The de-vulcanization time was 6 minutes. After de-vulcanization, the material was taken out of the internal mixer and directly quenched in liquid nitrogen.
2. Effect of amount of de-vulcanization oil.- In this study, various amounts of TDAE oil were applied: 5%, 15%, 30% and 50% relative to the GTR content. The GTR was then swollen in the mixture of TDAE and DPDS for 30 minutes. The de-vulcanization was carried as described above.
3. Effect of de-vulcanization time.- In this series of experiments, the de-vulcanization time was varied: 6 and 10 minutes. The GTR was pre-swollen in a mixture of TDAE and DPDS for 30 minutes, using 30% TDAE oil. The de-vulcanization was carried out under nitrogen atmosphere at 220°C. After de-vulcanization, the material was taken out of the internal mixer and directly quenched in liquid nitrogen.

Table 7.2 Initial de-vulcanization conditions.

Factors	Conditions
De-vulcanization aid	DPDS 30 mmol/100 g compound
De-vulcanization oil	TDAE 5% w/w
De-vulcanization temperature	220°C
De-vulcanization atmosphere	With nitrogen gas purging
Dumping condition	In liquid nitrogen

Table 7.3 Various experimental de-vulcanization conditions.

Factors	Conditions
Swelling time	0, 30 60 minutes
De-vulcanization oil	5, 15, 30 and 50 % w/w
De-vulcanization time	6 and 10 minutes

CHARACTERIZATION OF THE DE-VULCANIZATES

Rubber soluble fraction.- The soluble (Sol) fraction of the de-vulcanizates were determined by extraction in a Soxhlet apparatus, as described in Chapter 3.

Crosslink density.- The extracted samples were subsequently swollen in toluene for 72 hours at room temperature. The crosslink density was calculated according to the Flory-Rehner[11], as described in Chapter 3. For Flory-Huggins polymer-solvent interaction parameter, in this case is taken 0.40 as an average value between SBR, BR and NR in toluene.

The Flory-Rehner equation is strictly spoken only valid for non-filled systems. Therefore the Kraus[12] correction for filled compounds was used to give the correct values of the different crosslinks densities. In its simplified form, the Kraus correction is given by[13]:

$$\nu_{actual} = \frac{\nu_{apparent}}{1 + K + \Phi}$$

with

$$\Phi = \frac{\text{Weight fraction of fillers x Density of compound x } W_b}{\text{Density of fillers x } W_a}$$

where:

$\nu_{apparent}$ = the measured chemical crosslink density;

ν_{actual} = the actual chemical crosslink density;

K = a constant for a given filler;

Φ = the volume fraction of filler in the specimen which is calculated;

W_b = the weight of the specimen before extraction;

W_a = the weight of the specimen after extraction.

7.3 RESULTS AND DISCUSSION

DE-VULCANIZATION USING CONDITIONS ELEBORATED IN CHAPTER 6

The sol fractions and crosslink densities of untreated GTR and GTR de-vulcanizates (D-GTR) are shown in Figure 7.1. When using the initial conditions as elaborated for the model materials in Chapter 6, the de-vulcanization process results in a significant increase in sol fraction and decrease in crosslink density.

The sol fraction of GTR de-vulcanizates as a function of the relative decrease in crosslink density is shown in Figure 7.2. It can clearly be noticed that the

D-GTR experimental data are clustered on the right hand side of the graph, which indicates that the crosslink density of the treated rubber is reduced. However, they are located above the line of main-chain scission. This may be attributed to an inhomogeneous process: the de-vulcanization is not uniform throughout the rubber particle, but outer layers of the particles are de-vulcanized and peeled off, while the inner cores of the particles stay more or less unchanged at the initial crosslink density. This inhomogeneity in de-vulcanization causes in actual practice a smaller decrease in crosslink density at a particular sol fraction than would have been obtained for homogeneous breakdown.

The optimal de-vulcanization conditions used in this study are a good compromise for the single elastomers used in a passenger car tire, and it is expected to work also for real ground tire rubber. However, in actual practice not only the various types of rubber have to be taken into account, but also the ratio of the different rubber types in conjunction with the filler and oil contained in the material. Therefore, the de-vulcanization conditions need to be optimized again taking these factors into consideration. The peeling-off mechanism as concluded from the first experiment gives an indication how to improve the process: the de-vulcanization aid has to be more homogenously distributed within the rubber particles. The method of choice to achieve this is swelling of the rubber powder in a blend of oil and de-vulcanization aid prior to the de-vulcanization process.

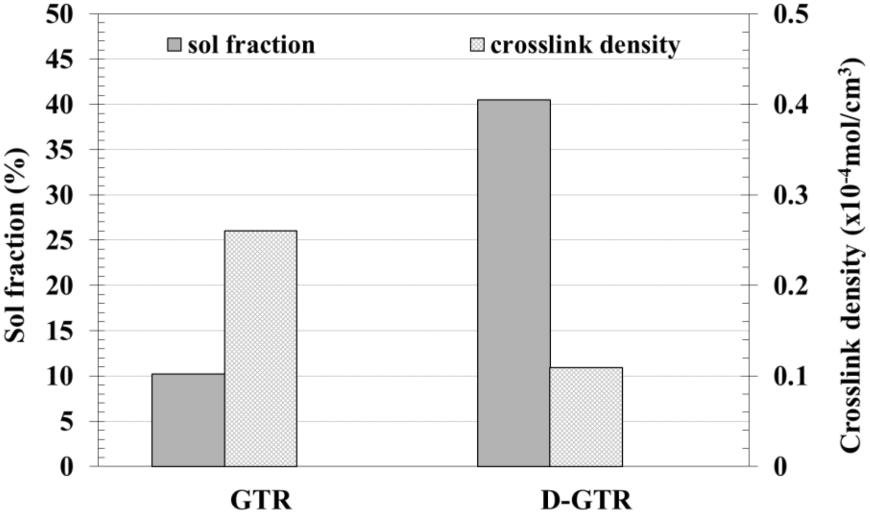


Figure 7.1 *Sol fraction and crosslink density of GTR and D-GTR.*

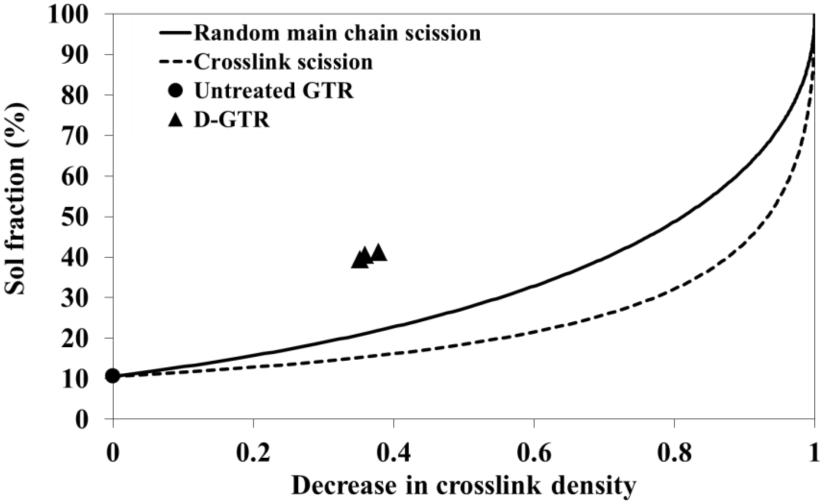


Figure 7.2 *Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of de-vulcanized GTR using initial conditions (de-vulcanization time: 6 minutes, oil: 5% TDAE, without swelling).*

EFFECT OF THE SWELLING PERIOD BEFORE DE-VULCANIZATION

Homogeneous de-vulcanization is one of the main factors affecting the de-vulcanization efficiency. Basically, a de-vulcanization oil, TDAE, is used with the aim of improving the dispersion of the de-vulcanization aid DPDS into the elastomer. Once DPDS is homogeneously dispersed within the rubber particles, a more homogeneous de-vulcanization will be achieved. Swelling of GTR in a mixture of TDAE and DPDS before de-vulcanization was studied as a way to improve the dispersion of DPDS in the rubber matrix. The sol fractions of the GTR de-vulcanizates after various swelling times as a function of the relative decrease in crosslink density are shown in Figure 7.3.

A significant improvement of the de-vulcanization efficiency is observed after the swelling process. For D-GTR swollen for 30 minutes, the experimental data move to right hand side with about a 30% further decrease in crosslink density compared to the un-swollen D-GTR. They are located close to the crosslink scission line. This means that swelling is a necessary process step for GTR de-vulcanization, as it increases the percentage of soluble polymer only slightly, but it significantly reduces the crosslink density. The improvement of the de-vulcanization efficiency may be attributed to the good dispersion of DPDS throughout the polymer particles which occurred during the swelling step. Moreover, some other chemicals involved in de-vulcanization might be activated during the swelling period. The differences observed between 30 and 60 swelling time are small. Why the points for 60 minutes swelling time are positioned left of the 30 minutes swelling time has most probably to do with experimental scatter, given the spread in the data. It proves anyway, that 30 minutes swelling time is sufficient to reach an acceptable dispersion of the DPDS in the 0.35 mm size ground rubber particles.

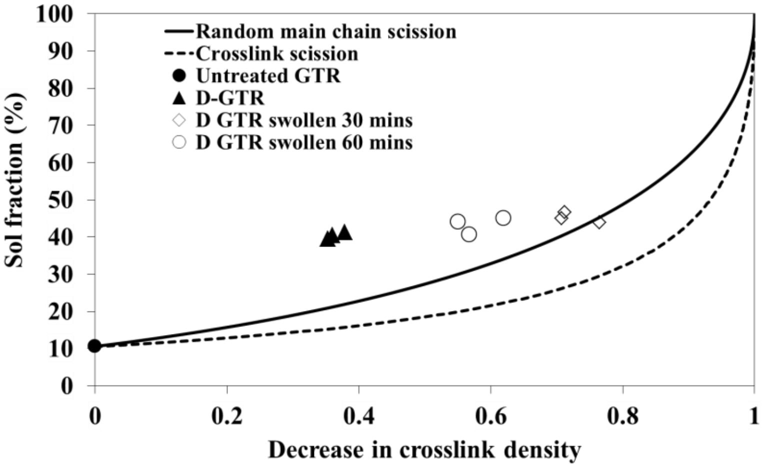


***Figure 7.3**. Sol fraction versus relative decrease in crosslink density of de-vulcanized GTR at various swelling periods (de-vulcanization time: 6 minutes, oil: 5% TDAE).*

EFFECT OF THE AMOUNT OF DE-VULCANIZATION OIL

Further experiments with the purpose to optimize the de-vulcanization process in terms of concentration of the de-vulcanization oil were performed. Various amounts of TDAE oil were applied in the swelling step with the aim of improving the DPDS dispersion in the elastomer. The sol fractions of the GTR de-vulcanizates as a function of the relative decrease in crosslink density are shown in Figure 7.4. An increasing TDAE oil amount from 5% to 15% by weight causes the experimental data points in the Horikx plot to move to the right hand side, to a further reduction of the crosslink density. However, when using a very high amount of TDAE oil, 30% and 50% by weight, the data points turn back to the left hand side, to higher final crosslink densities: The exceeding oil results in an inefficient de-vulcanization. An explanation for this effect might be that shearing forces are less effective when the materials has a lower viscosity and is lubricated by the excess oil.

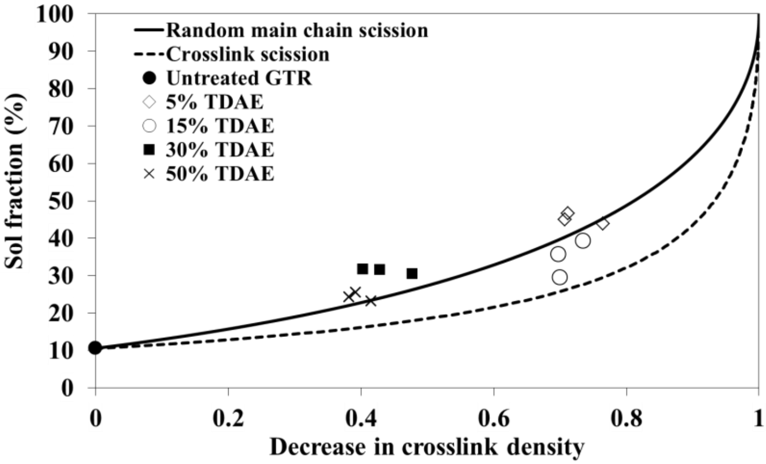


Figure 7.4 *Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density at various amounts of de-vulcanization oil (de-vulcanization time: 6 minutes, swelling period: 30 minutes).*

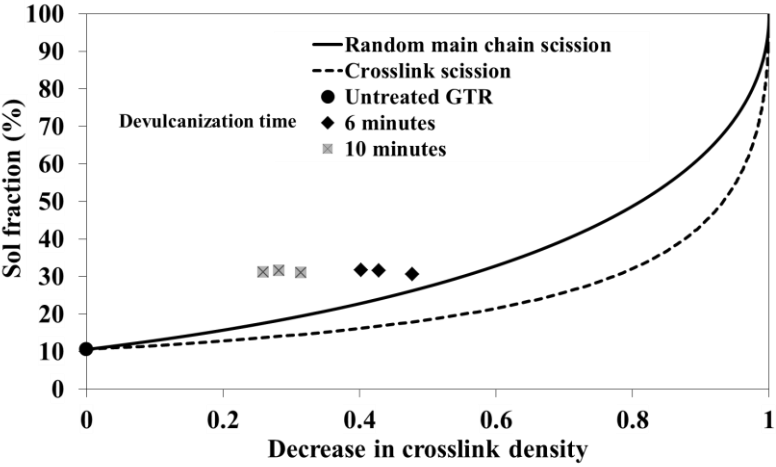


Figure 7.5 *Sol fraction versus the relative decrease in crosslink density at various de-vulcanization times (TDAE oil: 30%, swelling period: 30 minutes).*

EFFECT OF DE-VULCANIZATION TIME

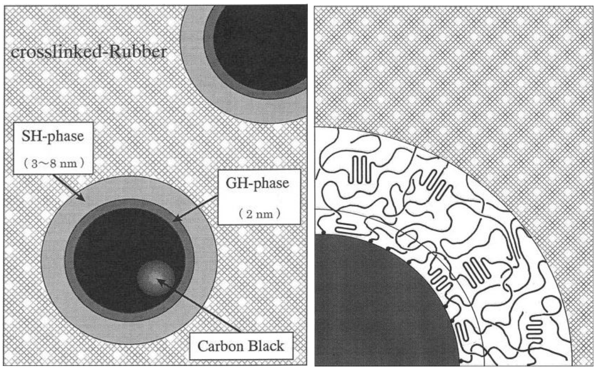
Figure 7.5 shows the sol fractions of GTR de-vulcanizates at 2 different de-vulcanization times as a function of the relative decrease in crosslink density: An increasing de-vulcanization time results in an increase in crosslink density. As discussed in Chapters 4 and 5, two reactions can occur during de-vulcanization: chain scission and recombination of active chain segments. It is crucial to achieve a breakdown of the polymer network as far as possible before the re-formation of polymer-polymer bonds from active chain fragments becomes the prevailing reaction. To avoid this, the de-vulcanization time should be as short as possible.

MECHANISTIC CONSIDERATIONS

The de-vulcanization of GTR is rather complicated since there are various aspects to be considered. The main factors involved are the presence of several types of elastomers in the different tire parts, various types of fillers and, as a consequence, different interactions between elastomers and fillers. When applying the de-vulcanization parameters as elaborated for the model materials, that is the best compromise of the de-vulcanization parameters for the single types of elastomers used in a passenger car tire, inhomogeneous de-vulcanization occurs: outer layers of the particles are de-vulcanized and peeled off, while the inner cores of the particles stay more or less unchanged at the initial crosslink density. Basically, in thermo-chemical de-vulcanization, there are three main factors contributing to the efficiency of the process: temperature, the chemical reaction and shear forces. However, the present experimental work is carried out using a lab scale internal mixer that allows variation of only the temperature and de-vulcanization aid, with little shear. Therefore, the dispersion of the de-vulcanization aid plays a major role for the efficiency of the process and the prevention of inhomogeneous de-vulcanization.

Based on the results, the optimized de-vulcanization conditions for GTR are given in Table 7.4. By using the optimum de-vulcanization conditions, D-GTR reaches a 70% decrease in crosslink density compared to the virgin GTR. This seems to be a limit for GTR de-vulcanization. The remaining 30% of crosslink density are partly due to remaining network and filler-polymer interactions commonly known as “bound rubber”. Bound rubber being rubber physically bound to carbon black before vulcanization, which cannot be released or dissolved in a solvent. 30% Bound rubber is quite normal for carbon black filled rubber. This puts a limit to the analysis of the de-vulcanization with swelling tests.

Figure 7.6 shows the rubber-filler interface model of a carbon black filled rubber: A double-layer model consisting of an inner polymer layer in a glassy state, a glassy hard or GH layer, and the outer polymer layer which is characterised as sticky hard or SH layer[14]. The molecular motion in both layers is considerably constrained[14,15] due to a strong molecular packing. The molecular structure of the GH layer is rather fixed and more immobile than that of the SH layer as shown in Figure 7.6 (b). The de-vulcanization process is focused on breaking of sulfur crosslinks, therefore strong filler-polymer bonds will not be affected. This polymer-filler network will not be broken during the de-vulcanization process, and will therefore remain as gel fraction within the rubber. Therefore, 100% sol will be never reached even if all crosslinks are broken because of the bound rubber remaining bound to the carbon black.



(a) (b)

Figure 7.6 *a: Double-layer interface model consisting of a glassy hard (GH) layer and a sticky hard (SH) layer.*

b: Detailed molecular structures in both layers according to their molecular mobility[14].

Table 7.4 Final optimal de-vulcanization conditions for the GTR.

Factors	Conditions
De-vulcanization aids	DPDS 30 mmol/100 g compound
De-vulcanization oil	TDAE 5% w/w
Swelling time	30 minutes
Swelling temperature	65 °C
De-vulcanization time	6 minutes
De-vulcanization temperature	220 °C
De-vulcanization atmosphere	With nitrogen gas purging
Dumping condition	Exclusion from air/oxygen

7.4 CONCLUSIONS

The de-vulcanization of GTR is more complex than just finding the best compromise of the de-vulcanization parameters for the single polymers; a further optimization for this blend of polymers and compounds was required. The most efficient method for increasing the de-vulcanization efficiency is an improvement of the dispersion of the de-vulcanization aid (DPDS) in the rubber matrix by pre-swelling of the rubber powder in a blend of the de-vulcanization aid and oil. This results in a more homogeneous breakdown of the crosslink network throughout the rubber particles. After further optimizing the de-vulcanization parameters in terms of de-vulcanization oil loading and process time, D-GTR reaches a 70% decrease in crosslink density compared to the untreated GTR.

7.5 REFERENCES

[1] O. Grigoryeva, A. Fainleib, I. Starostenko, O. Danilenko, N. Kozak and G. Dudarenko, *Rubber Chem. Technol.*, **76**, 131 (2004).

[2] K. Fukumori, M. Matsushita, H. Okamoto, N. Sato, Y. Suzuki and K. Takeuchi, *JSAE Review*, **23**, 259 (2002).

[3] R. Kohler and J. O'Neill, *Rubber Chem. Technol.*, **70**, 162 (1997).

[4] D. De, A. Das, D. De, B. Dey, S.C. Debnath and B.C. Roy, *Europ. Polym. J.*, **42**, 917-927 (2006).

[5] G.K. Jana and C.K. Das, *Polym. Plast. Techn. Eng.* , **44**, 1399 (2005).

[6] G.K. Jana and C.K. Das, *Progr. Rubber Plast. Recycling Techn.*, **21 (4)**, 319 (2005).

[7] E. Finazzi, A. Gallo and P. Lucci, *Rubber World*, **243(8)**, 21 (2011).

[8] K. Fukumori, M. Matsushita, M. Mouri, H. Okamoto, N. Sato, K. Takeuchi and Y. Suzuki, *Kautsch. Gummi Kunstst.*, **59**, 405 (2006).

[9] A. Macsiniuc, A. Rochette and D. Rodrigue, Progr. *Rubber Plast. Techn.*, **26/2**, 51 (2010).

[10] M. Myhre, S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, *Rubber Chem. Technol.*, **85**, 408 (2012).

[11] P.J. Flory, *J. Am. Chem. Soc.*, **63**, 3096 (1941).

[12] G. Kraus, *J. Appl. Polym. Sci.*, **7**, 861 (1963).

[13] M. Porter, *Rubber Chem. Technol.*, **40**, 866 (1967).

[14] Y. Fukahori, *J. App. Polym. Sci.*, **95**, 60–67 (2005).

[15] V.M. Litvinov, R.A. Orza, M. Kluppel, M. van Duin and P.C.M.M. Magusin, *Macromolecules*, **44**, 4887 (2011).

CHAPTER 8

APPLICATION STUDY: RE-UTILIZATION OF THE DE-VULCANIZATE IN A TIRE TREAD

An application study is performed using de-vulcanized ground tire rubber (D-GTR) which is prepared by continuous de-vulcanization. In first instance, the fundamental properties of D-GTR: viscosity, cure behavior, and mechanical properties, are analyzed. Generally, the viscosity levels of D-GTR are lower than the levels of the virgin SBR compound, as results show from both Mooney viscosity as well as complex viscosity. Furthermore, tensile strength and elongation at break values of D-GTR are rather low. These properties are most likely a consequence of too excessive shearing exerted during the de-vulcanization process, which can be improved by further development of the de-vulcanization process conditions. Next, the D-GTR is blended with virgin tire tread compound at a ratio of 50/50. The cure behavior and mechanical properties of the blend are compared to the original tire tread properties. As expected, a decrease in mechanical properties with addition of D-GTR compared to the original tire tread vulcanizate is found, which however can be overcome by adjustments of the compounding recipe.

8.1 INTRODUCTION

Recycled ground tire rubber (GTR) is a valuable raw material which can replace virgin rubber in many rubber products[1]; application examples are listed in Chapter 2. However, recycled rubber after curing has in general poorer mechanical properties than the comparable virgin rubber. When adding recycled rubber to a virgin rubber compound, even if it is the same type of compound, the properties will change. This is due to the fact that the recycled rubber has already undergone a whole life cycle, which influences the properties of the material due to aging. Furthermore, the polymer-filler interaction is different, as this is mainly formed during the mixing process, which the recycled material has to undergo twice. Therefore, the application of the currently available reclaimed rubber is generally limited to low quality products and to low concentrations in higher quality rubber articles. The application of used tire material[2,3] in new tire compounds is a necessity, but this implies that the properties of the materials may not suffer significantly by blending it with recycled rubber. The most promising way to achieve this is de-vulcanization.

In this chapter, the application of a tire rubber de-vulcanizate (D-GTR) is studied. At first, continuous de-vulcanization of GTR from whole passenger car tires is performed in an extruder on pilot scale. The optimized de-vulcanization conditions elaborated in a Brabender internal mixer on laboratory scale in Chapter 7 are used as starting conditions in the extruder process. The properties and applications of this first-shot extruded de-vulcanizate material are studied in this chapter as preliminary investigation. In the first part of the study attention is paid to the analysis of the properties of the D-GTR, i.e., cure behavior, viscosity and mechanical properties. In the second part, D-GTR is blended with virgin rubber at a blending ratio of 50/50 using a typical tire tread formulation. Cure behavior and mechanical properties of the blend are measured and compared to the original tire tread properties. A problem to decide upon in the application of D-GTR is the presence of curing additives in the recycling material, which are still partly active. Therefore, the curing system and conditions for a blend of virgin and de-vulcanized rubber have to be adjusted in order to build a vulcanized rubber network with properties as close to the properties of the original material as possible. Therefore, adjustments of the curatives and compounding recipe to improve the properties of the blend are performed.

8.2 EXPERIMENTAL

The study described in this chapter was done in a joint activity between the Department of Chemical Engineering/Product Technology, University of Groningen (RUG) and the Department of Elastomer Technology and Engineering, University of Twente (UT), The Netherlands.

MATERIALS

The ground tire rubber used in this investigation was obtained from Rubber Resources BV, the Netherlands. It was mainly based on synthetic rubber with a particle size of typically 0.35 mm. The SBR type for the tire tread compound used in this investigation was SBR 1723, an oil extended emulsion-polymerized SBR containing 37.5 phr of treated distillate aromatic extract (TDAE) oil, obtained from Dow Styron GmbH, Germany. The polymer contained 23.5 wt% styrene and 76.5 wt% butadiene, and its Mooney viscosity ML(1+4) measured at 100°C was 40 MU. The BR (cis-1,4 polybutadiene) grade Buna CIS 132 was produced by nickel catalysis; it is a stereospecific polybutadiene with high cis-1,4 content, obtained from Dow Styron GmbH, Germany. Its Mooney viscosity ML(1+4) measured at 100°C was 45 MU. Zinc oxide and stearic acid were obtained from Flexsys, The Netherlands. The curatives: sulfur; N-tert-butyl-2-benzothiazolesulfenamide (TBBS) and Diphenylguanidine (DPG) were obtained from Merck. TDAE oil used as processing oil for the de-vulcanization was supplied by Hansen&Rosenthal, Germany. The silane coupling agent used was bis-triethoxysilylpropyltetrasulfide (TESPT) which was obtained from Evonik GmbH, Germany. Diphenyldisulfide (DPDS) used as de-vulcanization aid was obtained from Sigma-Aldrich, Germany.

PREPARATION OF DE-VULCANIZATES

The de-vulcanization was performed at the University of Groningen in a co-rotating twin screw extruder from APV Baker with a length of 1.25 meter and screw diameters of 50 mm. The screw design was taken as the optimized configuration developed for EPDM de-vulcanization as shown in Figure 8.1[4], which was the most severe configuration out-of six.

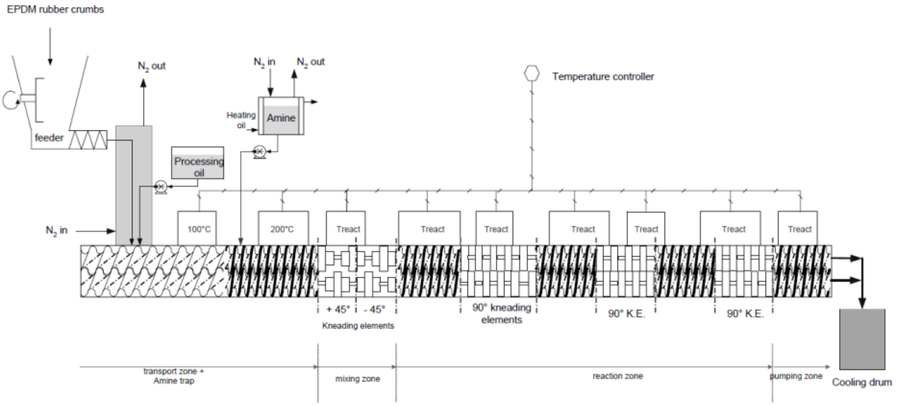


Figure 8.1 *Extruder screw configuration used in the de-vulcanization, as originally developed for EPDM.*[4]

Table 8.1 Compared de-vulcanization conditions: Brabender vs. twin-screw Extruder.

Factors	Brabender conditions optimized at UT (Recommended conditions)	First series at RUG Extruder conditions
De-vulcanization aid	DPDS 30 mmol/100 g compound	DPDS 30 mmol/100 g compound
De-vulcanization oil	TDAE 5% w/w	TDAE 5% w/w
Swelling time	30 minutes	30 minutes
Swelling temperature	65 °C	65 °C
De-vulcanization time	6 minutes	6 minutes
De-vulcanization temperature	±220 °C	±220 °C
De-vulcanization atmosphere	With nitrogen gas purging	With nitrogen gas purging
Dumping condition	In liquid nitrogen	In water
Drying	no	In air at room temperature: 48-72 hrs. and in 40 °C hot air oven: 24-48 hrs.

The de-vulcanizate was prepared using the optimized conditions as given in the previous chapter. However, due to limitations of the equipment in this initial work, some parameters had to be adjusted. The main change was the final quenching of the de-vulcanizate, which was planned to be done in liquid nitrogen, but here the de-vulcanizate was quenched into a water bath. Consequently, an extra drying step for the extruded de-vulcanizate was needed. Table 8.1 gives the optimized de-vulcanization conditions for the Brabender process, and the conditions used in actual practice for the extruder de-vulcanization. Before adding all recipes into the extruder, GTR was pre-swollen in a mixture of TDAE and DPDS for 30 minutes at 65°C. The de-vulcanization was carried out under nitrogen atmosphere at 220°C and the extruder feeding rate was 8.5 kg/hrs.

RE-VULCANIZATION OF THE D-GTR

Mixing of the de-vulcanizate (D-GTR) compounds.-

Compound formulation.- The de-vulcanized GTR was mixed with the curatives as given in Table 8.2. The amount of curatives was based on the total polymer content of the de-vulcanized rubber. As the starting material for the de-vulcanizate was based on whole passenger car tires, the composition was different compared to the tire tread compound in which it was tested. Therefore, the carbon black content of the virgin SBR compound was set to 65 phr, as measured by TGA on the D-GTR.

Mixing procedure.- Mixing of rubbers and compounding ingredients was done in an internal mixer (Brabender Plasticorder PL-2000), having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.65 and a constant rotor speed of 50 rpm were used. The compounds were mixed for 8 minutes and then sheeted off on a laboratory size (15 × 33 cm) two roll mill at a friction ratio of 1:1.25 at 50 °C at a thickness of approximately 2 mm.

Table 8.2 Formulation of the D-GTR compound.

Ingredient	D-GTR Compound (phr)	Virgin rubber compound (phr)
D-GTR*	100	-
SBR	-	137.5
ZnO	3.0	3.0
Stearic acid	2.0	2.0
Sulfur	2.5	2.5
Accelerator (TBBS)	1.5	1.5
Carbon black	65**	65

* Calculated on basis of the polymer content of the D-GTR

** The remaining carbon black in D-GTR.

Silanization.- A silanization step was studied in order to investigate the optimal reinforcement by some silica contained in D-GTR. Mixing as well as silanization were performed in the internal mixer and under the circumstances mentioned above. The initial temperature setting of the mixer was 100 °C. D-GTR, ZnO, stearic acid and silane were added and mixed for 2 minutes. Mixing was continued for another 5 minutes at a temperature of 150 °C. The compounds were then discharged, sheeted out and cooled at room temperature for 12 hours. In the second mixing step, the temperature setting of the mixer was 150 °C and the mixing time was 3 minutes. The compound was then discharged, sheeted out on a two-roll mill and kept overnight prior to the incorporation of TBBS and sulfur on the two-roll mill. To investigate the influence of variable contents of silane coupling agents and DPG, a series of tests was done. Table 8.3 shows the variable amounts of silane and DPG applied in this part of the work.

Table 8.3 Variable quantities of silane (TESPT) and DPG in the rubber formulations for the silanization study.

Set I	varying silane content				
Silane	wt% relative to silica	0	5.0	10.0	15.0
	phr	0	1.3	2.6	3.9
Set II	varying DPG content; TESPT was fixed at 10 wt% relative to silica				
DPG	wt% relative to silica	0	3.8	7.7	
	phr	0	1.0	2.0	

Table 8.4 Tire tread formulation.

Ingredients	Phr
SBR	89.4
BR	35.0
Carbon black N375	80.0
Zinc Oxide	3.0
Stearic acid	2.0
Sulfur	1.5
TBBS	1.5
6PPD	1.0
TMQ	2.0
Microcrystalline wax	3.0
TDAE oil	10.6

Blending of D-GTR/Virgin rubber (50/50).-

The D-GTR was blended with the original virgin rubbers at a blending ratio of 50/50 using a typical tire tread formulation as shown in Table 8.4. The amount of curatives and filler were based on the total polymer content, including the polymer content of the de-vulcanized rubber.

In order to compensate for the low curing activity and strength properties of the blend, the amount of certain additives was adjusted. Variation of carbon black in the blend was investigated to see its reinforcement effect. Table 5 shows the variable amounts of curatives and the filler used in this work. The following parameters were investigated:

1. Sulfur content
2. Zinc oxide content
3. N-tert-butyl-2-benzothiazyl sulfenamide content
4. Carbon black content

Re-vulcanization.- All compounds were tested for their cure characteristics using a RPA 2000 dynamic mechanical curemeter from Alpha Technologies at 170°C, 0.833 Hz and 0.2 degree strain, according to ISO 6502. The compounds were then vulcanized for $t_{c,90}$ + 5 minutes in a Wickert WLP1600 laboratory compression molding press at 170°C and 100 bar, into 2 mm thick sheets.

Table 8.5 Varying curatives and carbon black for blended tire tread.

Ingredients	Tire tread		Variation of the ingredients								
	Virgin	Blend	Sulfur			TBBS	ZnO	Carbon black			
			1	2	3			1	2	3	4
D-GTR*	-	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
SBR	89.4	44.7	44.7	44.7	44.7	44.7	44.7	44.7	44.7	44.7	44.7
BR	35.0	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
CB-N375	80.0	80.0	80.0	80.0	80.0	80.0	80.0	**45.0**	**65.0**	**85.0**	**105.0**
Zinc Oxide	3.0	3.0	3.0	3.0	3.0	3.0	**6.0**	3.0	3.0	3.0	3.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulfur	1.5	1.5	**2.5**	**5.0**	**7.5**	2.5	2.5	1.5	1.5	1.5	1.5
TBBS	1.5	1.5	1.5	1.5	1.5	**3.0**	1.5	1.5	1.5	1.5	1.5
6PPD	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wax	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
TDAE oil	10.6	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8

* Calculated on basis of the polymer content of the D-GTR

CHARACTERIZATION OF THE DE-VULCANIZATES AND RE-VULCANIZED RUBBER

Viscosity.- The complex viscosity values were analyzed using the RPA 2000, as described in Chapter 3.

Thermal decomposition behavior.- The thermal behavior of the de-vulcanizates was analyzed by thermogravimetric analysis (TGA) using a TGA7 from Perkin Elmer. Approximately 5-10 mg of the sample were heated with a heating rate of 10°C/min. in a nitrogen atmosphere and secondly in an air atmosphere.

Composition of the material.- Ash composition was analyzed by a Scanning electron microscope (SEM), Jeol JSM-6400 which is configured with a Noran energy dispersive X-ray analyzer (EDS system). The SEM/EDS analysis system enables to perform compositional analysis on specimens.

Mechanical properties.- Tensile tests were carried out on dumb-bell shaped specimens (type 2) according to ISO 37, using a Zwick Z1.0 tensile testing machine. The tests were performed at a constant crosshead speed of 500 mm/min, using a load cell of 500N. The hardness of the samples was measured with a Zwick hardness tester, Shore A type, according to ASTM D2240-02.

8.3 RESULTS AND DISCUSSION

PROPERTIES OF D-GTR

Characterization of the pure GTR de-vulcanizate.-

D-GTR composition.- The thermogravimetric plot of D-GTR is given in Figure 8.2. Three regions are observed. The first step (A) starts at 230°C and is completed at 400°C: This is the evaporation of oil contained in D-GTR. The second region covers the temperature range from 400°C to 600°C, and is caused by decomposition of the rubber components in GTR[5,6]. Two decomposition temperatures are found in this region: First, a decomposition temperature range from 410 to 440°C (B), showing the decomposition of natural rubber (NR) with a typical decomposition temperature of 413°C, and butyl rubber (IIR) with a typical decomposition temperature of 438°C. Second, a decomposition temperature range of 450 to 600°C (C), for the decomposition of SBR at typically 475°C and BR at 512°C. The third region is in the temperature range above 550°C (D), in which the TGA is carried out under air. This indicates the amount of fillers contained in the sample; carbon black is decomposed in this temperature range only under air atmosphere.

The remaining ash was proven by SEM/EDS to be composed of mainly silica. The amount of polymer, oils and fillers were calculated as given in Table 8.6.

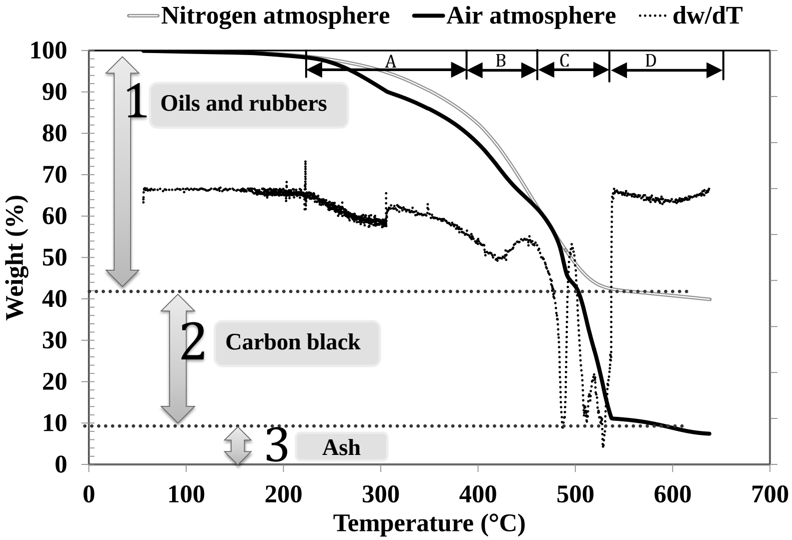


Figure 8.2 *Thermogravimetric analysis of GTR in air and nitrogen atmosphere (dw/dT is the derivative weight loss curve testing under air atmosphere).*

Table 8.6 Composition of the D-GTR compound.

Ingredient	%	phr
Polymers	46	100
Oils	12	26
Fillers		
- Carbon black	30	65
- Ash/mainly silica	12	26

Characterization of de-vulcanization level by Horikx plot.- The sol fraction as a function of the relative decrease in crosslink density of extruded de-vulcanizate (ED-GTR) and the de-vulcanizate prepared by Brabender (BD-GTR) in Chapter 7 is compared as shown in Figure 8.3. It can be seen that both BD-GTR and ED-GTR experimental data are clustered on the right hand side of the graph, which indicates that the crosslink density of the de-vulcanizates is reduced to more or less the same level. They are located above the line of main-chain scission. However, the ED-GTR data point is positioned at a higher sol fraction compared to BD-GTR, which indicates an excessive polymer network breakdown: mainly polymer main-chain scission. This may be attributed to too high shearing caused by the severe screw configuration, which was not optimized yet for SBR.

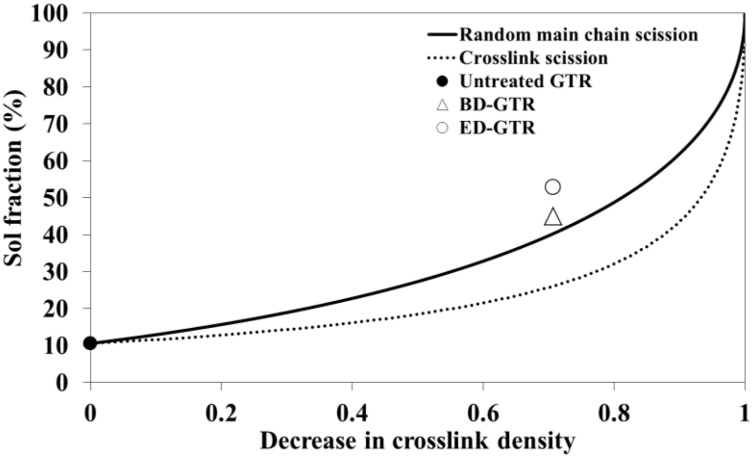


Figure 8.3 *Sol fraction generated during de-vulcanization versus the relative decrease in crosslink density of D-GTR de-vulcanized in Brabender (BD-GTR) and twin-screw extruder (ED-GTR).*

Cure behavior, viscosities and physical properties.- Figure 8.4 shows the cure properties of D-GTR compared to the carbon black filled virgin SBR compound. The D-GTR shows a pronounced scorch and cure time reduction. This is a normal characteristic of de-vulcanized rubber[7], which is attributed to the presence of active functional sites in the de-vulcanizate[8]. Moreover, both minimum and maximum torque of D-GTR are much lower than the delta torque values of the virgin SBR compound.

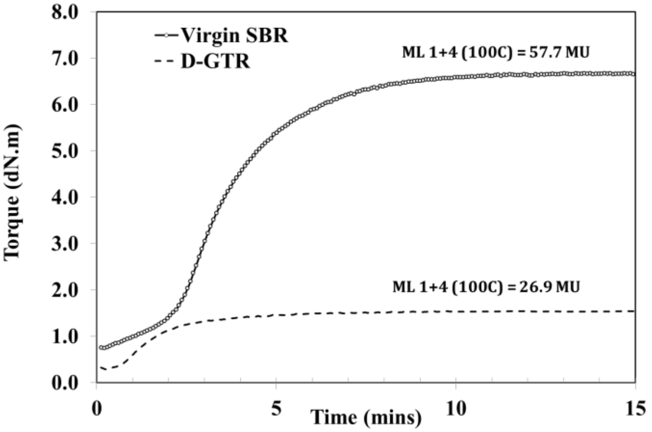


Figure 8.4 *Cure curves of pure D-GTR and carbon black filled virgin SBR.*

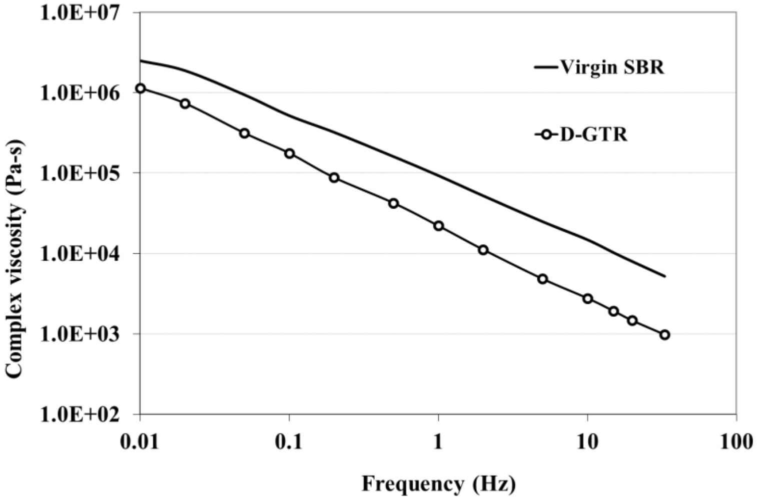


Figure 8.5 *Complex viscosity curves of D-GTR and carbon black filled virgin SBR vulcanizate.*

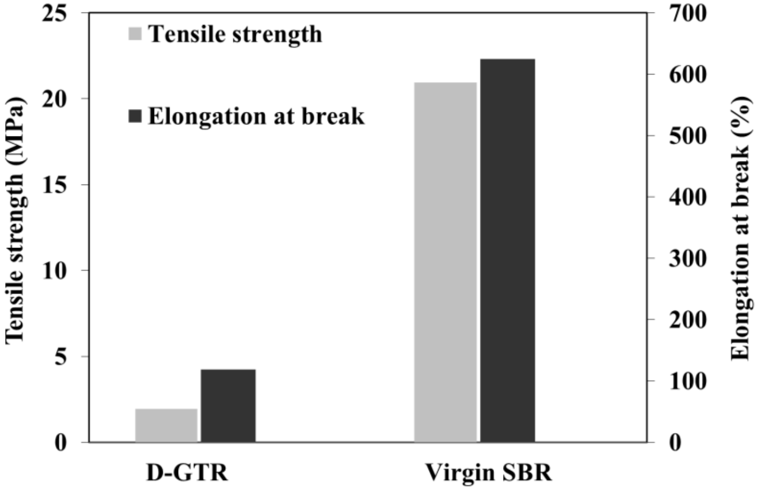


Figure 8.6 *Tensile strength and elongation at break of pure D-GTR and carbon black filled virgin SBR vulcanizates.*

The plot of complex viscosity versus oscillating frequency of virgin SBR and D-GTR after re-vulcanization are shown in Figure 8.5. The viscosity levels of the D-GTR are significantly lower than the levels of the virgin SBR compound, which is most likely due to excessive cleavage again of the rubber network during the de-vulcanization process which is mainly due to scission of polymers. The lower initial torque value and complex viscosity curve correspond well with the low

Mooney viscosity of the material: the de-vulcanizate has a Mooney viscosity of 26.9 MU, which is too low for practical applications, especially when it has to be blended with virgin rubber. As a consequence, the morphology will be inhomogeneous and thus tensile strength and elongation at break values will be negatively influenced, as depicted in Figure 8.6.

Silica effects.-

The material composition might also have an influence on the de-vulcanizate properties. Thermogravimetric analysis of the de-vulcanizate showed that D-GTR consists of several types of rubbers and fillers: there is 30% w/w of carbon black and 12% w/w of ash, mainly silica as determined by SEM/EDS, in D-GTR. In silica compounding a silanization step is needed in order to obtain optimal reinforcement of the rubber[9-11]. An additional mixing step for the silanization of silica in D-GTR was included in the mixing cycle to see the effect of presence and amount of silane as coupling agent and DPG as accelerator.

Effect of amount of silane.- Cure curves of D-GTR and silanized D-GTR with 5, 10 and 15 wt% of silane relative to the silica content are shown in Figure 8.7. The maximum torque is increased by the additional silanization step and a sufficiently high amount of silane. The normal percentage of silane in virgin tire compounding relative to the silica content is 10 wt%; here 10-15 wt% have to be added to see a significant effect. The silane seems to be less effective in the D-GTR than in a virgin compound, which can be explained by the earlier embedding of the silica in the polymer and as a consequence a lower reactivity. However, the improvement in properties observed may be related to increased interaction between rubber and filler enhanced by the silanization. Additionally, the increment of maximum torque with increasing silane content may also be caused by the increase of amount of total sulfur in the compound which is elaborated and discussed in more detail later in this chapter.

The viscosity curves of silanized D-GTR with 5, 10 and 15 wt% of silane compared to the virgin SBR compound are shown in Figure 8.8. The viscosity levels of all D-GTR are again located way below the curve of virgin SBR and all clustered together.

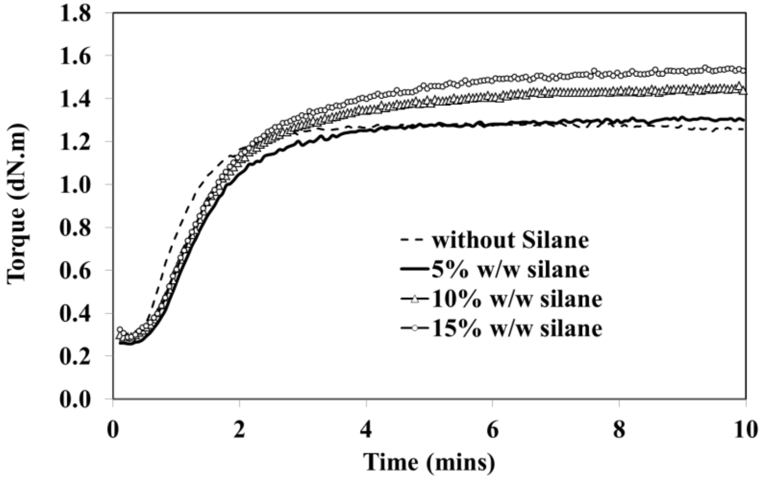


Figure 8.7 *Cure curves of pure D-GTR and D-GTR with various amounts of silane.*

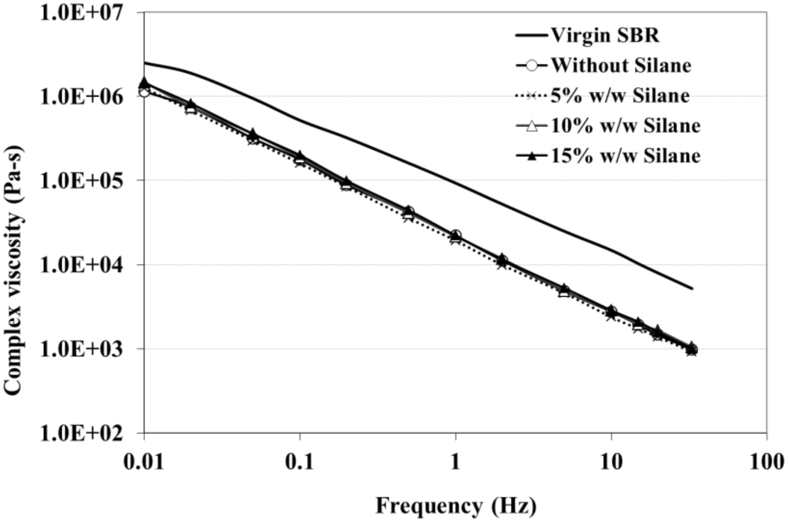


Figure 8.8 *Complex viscosity curves of D-GTR and D-GTR with various amounts of silane.*

The tensile strength and elongation at break values of silanized D-GTR are shown in Figure 8.9: The addition of 15 wt% of silane to D-GTR results in just a slight increase in tensile strength compared to the strength of D-GTR without silane. Overall the effect is small.

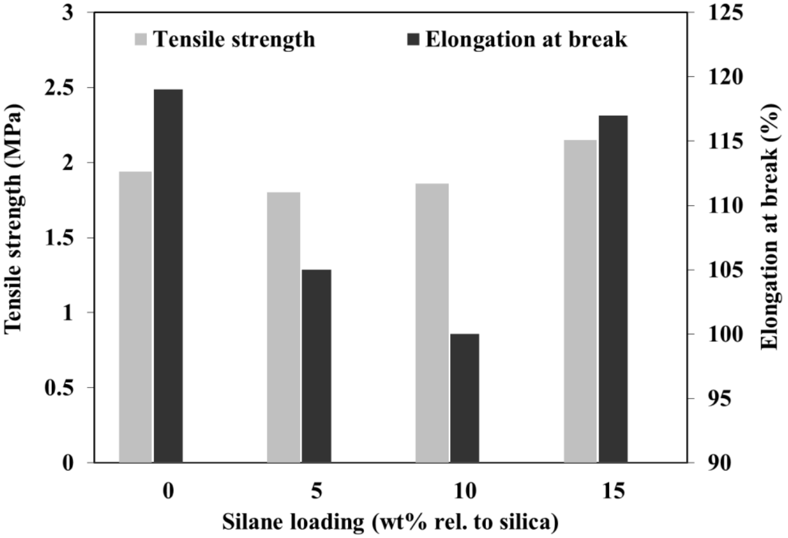


Figure 8.9 *Tensile strength and elongation at break of D-GTR with various amounts of silane.*

Effect of amount of DPG.- DPG is normally used as secondary accelerator in sulfenamide accelerated sulfur vulcanization systems. In silica filled rubber it is used to enhance the silanization reaction, to cover remaining silanol groups on the filler surface and to minimize the accelerator adsorption on the silica surface[12]. In addition, it improves the cure characteristics of silica compounds. Hence, apart from the amount of silane, the amount of DPG is one of the important factors in this reaction. The cure and viscosity curves of D-GTR and silanized D-GTR with various amounts of DPG are shown in Figures 8.10 and 8.11, respectively. It is clear again that there is no significant improvement with the additional loading of DPG. The same is valid for the stress strain properties as can be seen in Figure 8.12. Based on these results, it can be concluded that extra DPG is not necessary in this case.

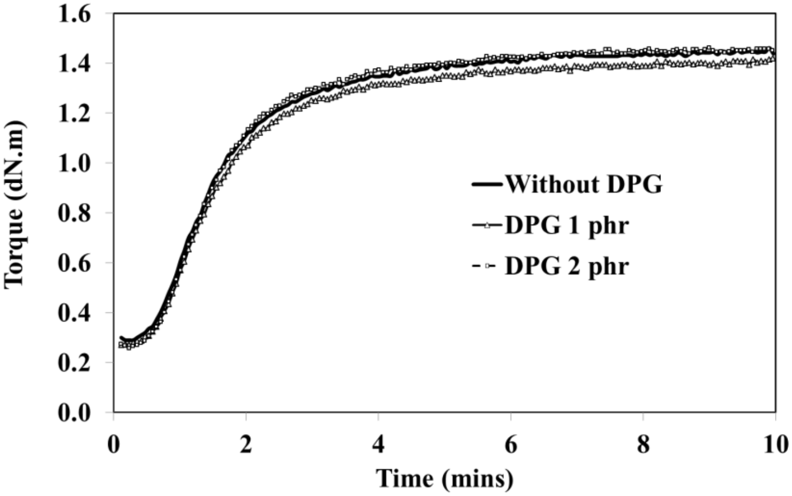


Figure 8.10 *Cure curves of D-GTR with various amounts of DPG.*

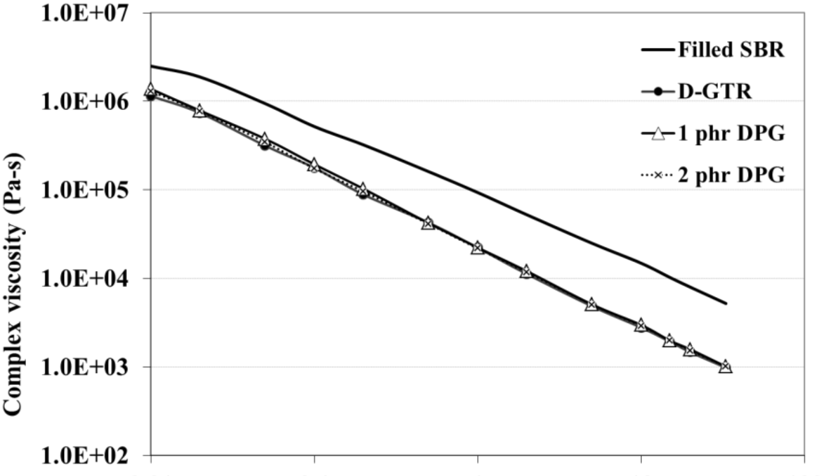


Figure 8.11 *Complex viscosity curves of D-GTR and D-GTR with various amounts of DPG.*

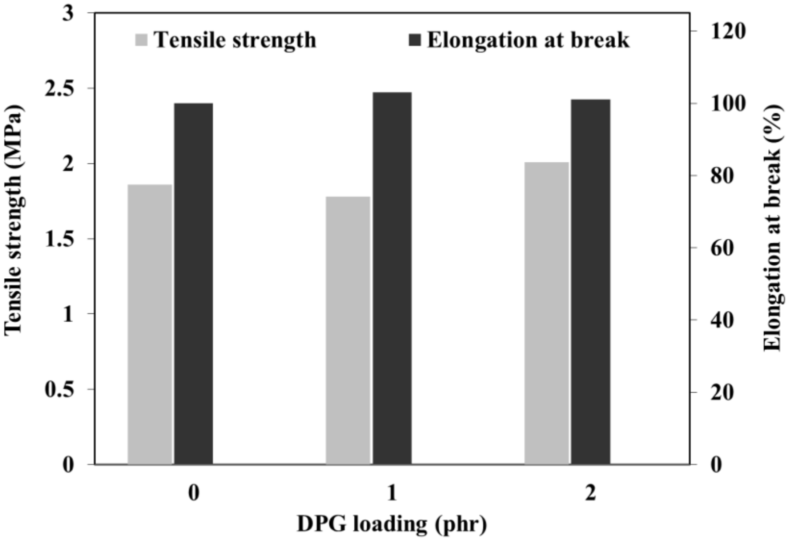


Figure 8.12 *Tensile strength and elongation at break D-GTR with various amounts of DPG.*

BLEND OF D-GTR/VIRGIN RUBBER

In this part of the study, the D-GTR was applied in a tire tread compound in a 50/50 ratio. The cure curves of the virgin tire tread compound and the blend are shown in Figure 8.13. A significant decrease in scorch and cure time was found for the blend compared to the virgin tire tread compound. The maximum torque as well as the difference between final and initial torque of the blend are also lower than that of the virgin tire tread compound. Generally, the increase in the torque difference reflects an increase in crosslink density. Thus, the lower maximum torque of the blend can be attributed to incomplete network formation originating from the de-vulcanizate. This is affecting the mechanical properties of the vulcanizate as shown in Figure 8.14. Tensile strength and elongation at break of the blend are lower compared to the level of the virgin tire tread material. This decrease in properties was expected, as several factors influence the property profile of the blend: incomplete re-vulcanization and a less developed network as the polymer of the de-vulcanizate was severely damaged during the de-vulcanization process. Other possible factors influencing the properties are the presence of gel in the de-vulcanizate, poor co-vulcanization between the two phases and inhomogeneities in the material structure leading to stress accumulation.

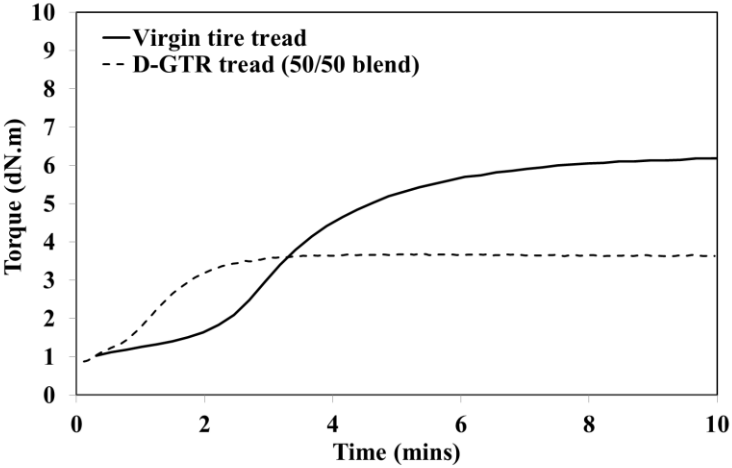


Figure 8.13 *Cure curves of the virgin tire tread compound and the 50/50 blend of D-GTR tire with the virgin rubber.*

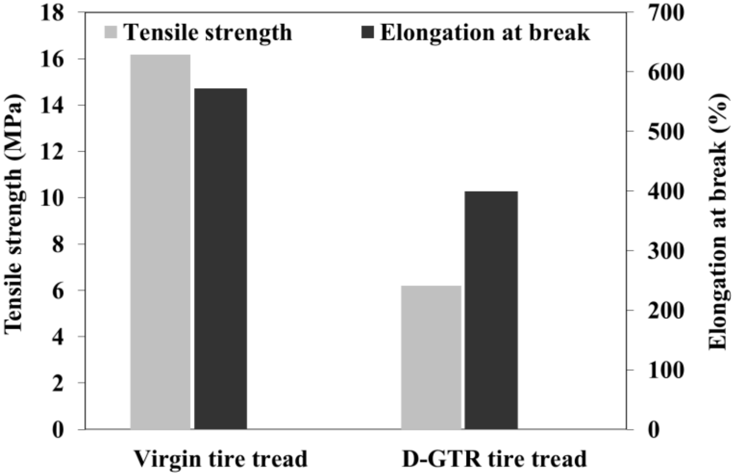


Figure 8.14 *Tensile strength and elongation at break of the virgin tire tread compound and the 50/50 blend of D-GTR tire with virgin rubber.*

Further attempts were subsequently made in order to improve the quality of the blend: The amount of cure additives and filler used in the compounding formulation were adjusted.

Effect of sulfur content.-

The effect of additional sulfur on the vulcanization and properties of the blend was studied. Cure curves and mechanical properties of the virgin compound and of the tread from the 50/50 blend of D-GTR with the virgin compound with various amounts of sulfur are shown in Figures 8.15 and 8.16, respectively. The maximum torque drastically increases with increase of the sulfur content in the compound. Theoretically, the maximum torque of a vulcanizate is proportional to the crosslink density. When the number of crosslinks increases, the elastomer chains are more restricted in their motion and the force required to produce a deformation becomes higher. Therefore, the low vulcanization activity of the de-vulcanizate can be enhanced by a higher amount of sulfur. However, tensile strength and elongation at break do not follow the same trend as the maximum torque: Tensile strength increases with an increase of sulfur content up to 2.5 phr, while an increase of the sulfur content up to 5 and 7.5 phr causes no further improvement in tensile strength. This can be due to two factors: once again the damaged polymer chains resulting in a less developed network, and the common tendency of a maximum in tensile strength with increasing crosslink density as shown in Figure 8.17[14]. Elongation at break generally decreases with increasing crosslink density which is a result of the progressively greater restriction in mobility of the polymer chains with increasing crosslinking[13,14].

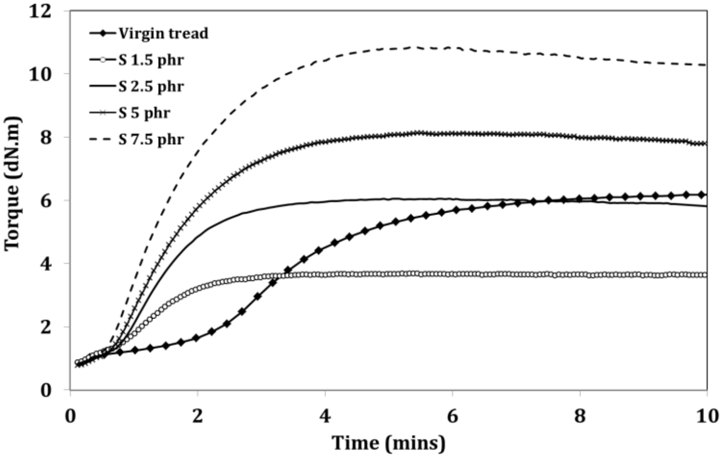


Figure 8.15 *Cure curves of the virgin tire tread compound and the 50/50 (D-GTR/virgin) blend tire tread with various amounts of sulfur.*

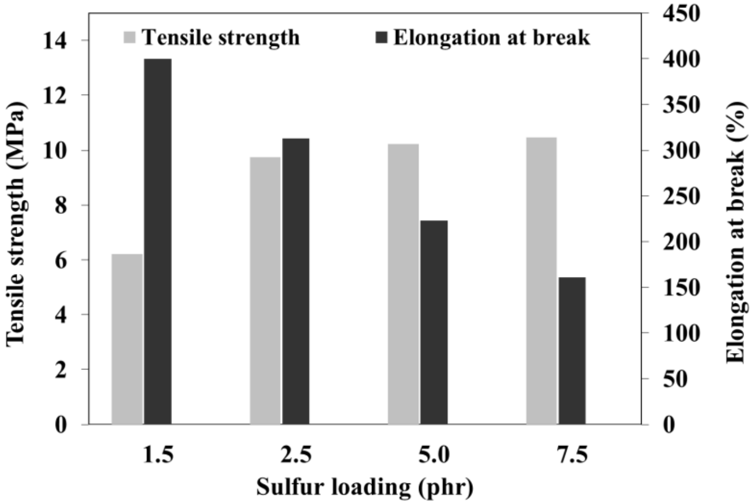


Figure 8.16 *Tensile strength and elongation at break of the 50/50 (D-GTR/virgin) blend tire tread with various amounts of sulfur.*

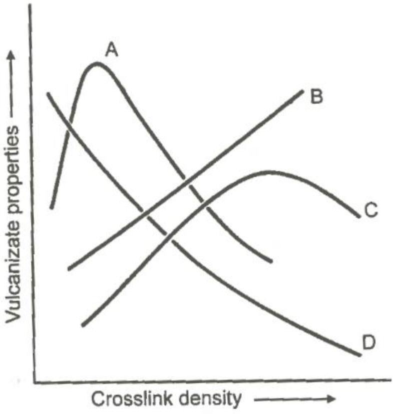


Figure 8.17 *Effect of crosslink density on properties, where A represents tear strength, fatigue life and toughness; B, elastic recovery and modulus; C, tensile strength and D, elongation at break, hysteresis, permanent set and friction coefficient.*[14]

Effect of TBBS and ZnO content.-

In order to improve the network structuring of the blend, the effect of additional TBBS as accelerator and ZnO as activator was studied. However, there was no significant improvement in mechanical properties of the blend with addition of TBBS and ZnO, as can be concluded from Figures 8.18 and 8.19. Therefore, the curing package with the initial amount of TBBS and ZnO is sufficient to reach the optimal cure stage.

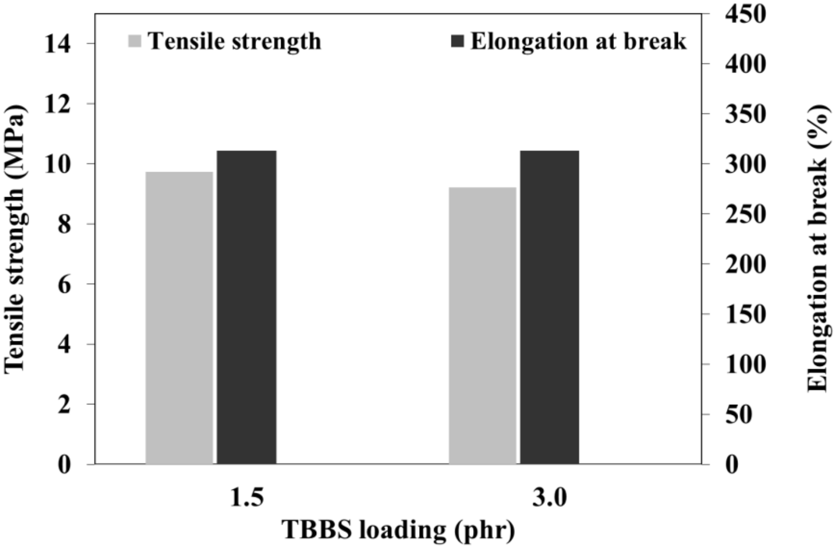


Figure 8.18 *Tensile strength and elongation at break of the 50/50 (D-GTR/virgin) blend tire tread with various amounts of TBBS (using 2.5 phr of sulfur).*

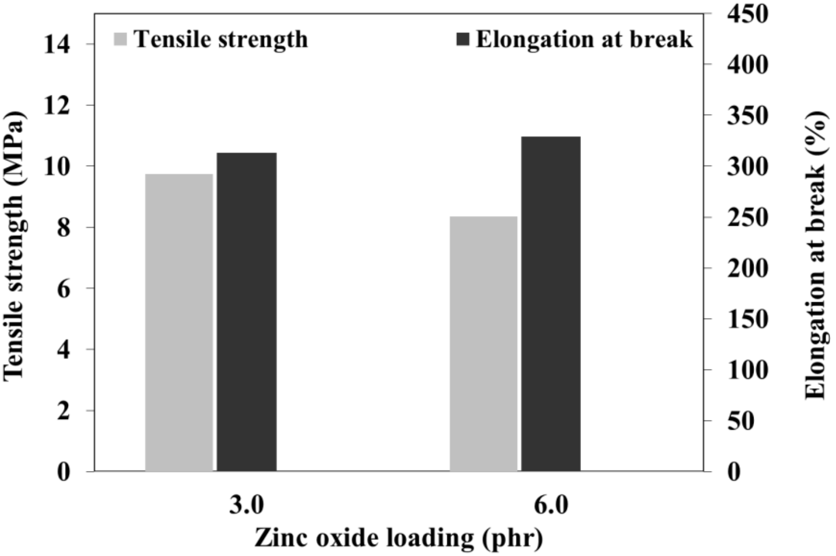


Figure 8.19 *Tensile strength and elongation at break of the 50/50 (D-GTR/virgin) blend tire tread with various amounts of zinc oxide (using 2.5 phr of sulfur).*

Effect of filler content.-

The effect of the amount of carbon black loading on the curing behavior and mechanical properties of the tire tread blend is also studied. Cure curves and mechanical properties of tire tread from virgin rubber and of the tread from the 50/50 blend with various amounts of carbon black are shown in Figures 8.20 and 8.21, respectively. In terms of curing behavior, an increasing amount of carbon black results in an increase of the maximum torque and the delta torque. This is mainly due to the higher content of the rigid reinforcing filler particles in the network and not to extra crosslinking. Moreover, the formation of a special interface between carbon black particles and the rubber matrix as described in Chapter 7 leads to a more interconnected network structure. The tensile strength at first instance improves with increase of carbon black content up to 85 phr, but it decreases again with further increase of carbon black loading up to 105 phr. This is expected as the tensile strength reaches a maximum value and then decreases again when the polymer chains cannot follow the deformation forces due to restricted chain movement. Elongation at break decreases with the addition of carbon black for the same reason.

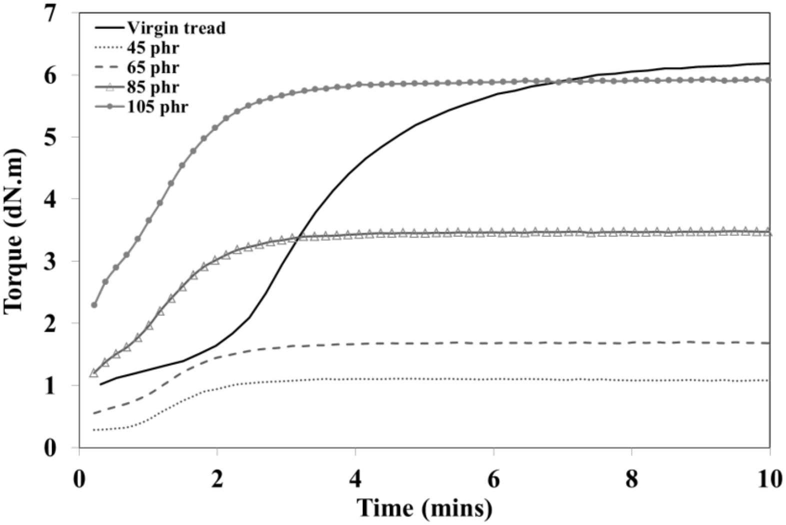


***Figure 8.20** Cure curves of the virgin tire tread compound and the 50/50 (D-GTR/virgin compound) blend with various amounts of carbon black (using 1.5 phr of sulfur).*

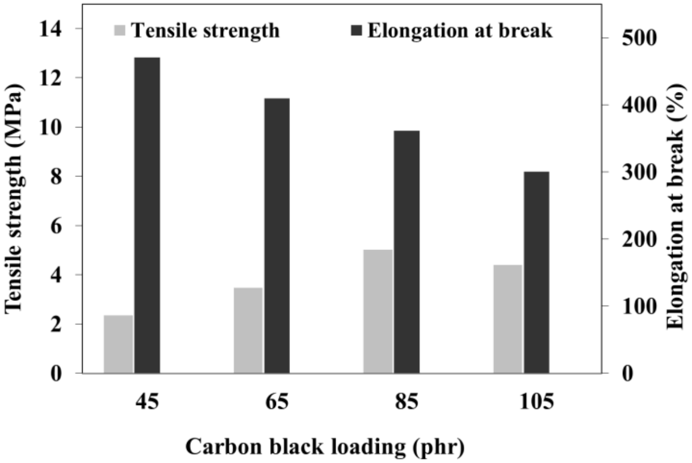


Figure 8.21 *Tensile strength and elongation at break of the 50/50 (D-GTR/virgin compound) blend with various amounts of carbon black (using 1.5 phr of sulfur).*

CONSIDERATIONS FOR FURTHUR UPSCALING

The results of this first shot of continuous extruder de-vulcanization of GTR are not satisfactory yet. The main reason for that is most probably the severity of the screw design, as explained before. The design was the most severe out-of a series of six screws, optimized for EPDM-de-vulcanization. In retrospect this may not have been the optimal choice for SBR and whole tire rubber. Tire rubber is very tough in comparison with the softness of EPDM. Therefore, a logical consequence would be to choose a less severe screw design for GTR, to achieve the same level of shearing. The screw design, therefore, needs to be optimized, which is the contents of follow-up of this preliminary study at the University of Groningen.

Considerations for receiving optimal properties.-

Based on the present first-shot experimental results, a first adjustment of the compound formulation for the D-GTR tire tread blend is recommended in Table 8.7. Figures 8.22 and 8.23 show the cure behaviour and mechanical properties of the improved D-GTR blend with using the suggested formulation. It can clearly be seen that the maximum torque of the improved D-GTR blend reaches the same value as the virgin tire tread: the network formation is comparable for both materials.

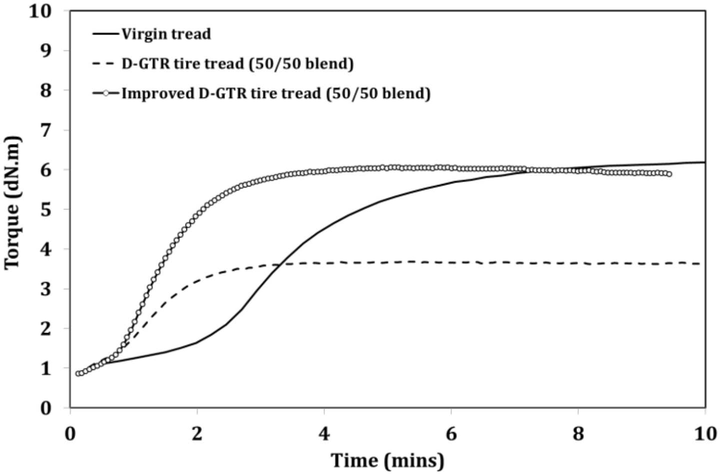


Figure 8.22 *Cure curve of the improved D-GTR tire tread blend compared to the virgin tire tread compound and the original.*

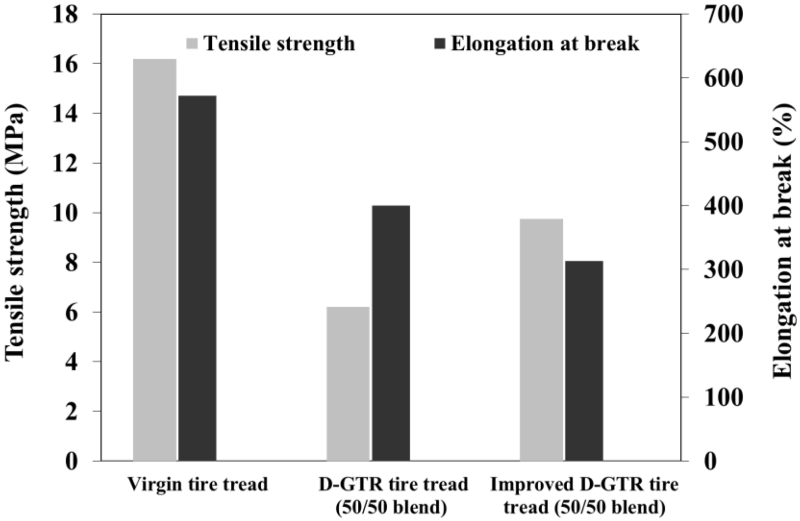
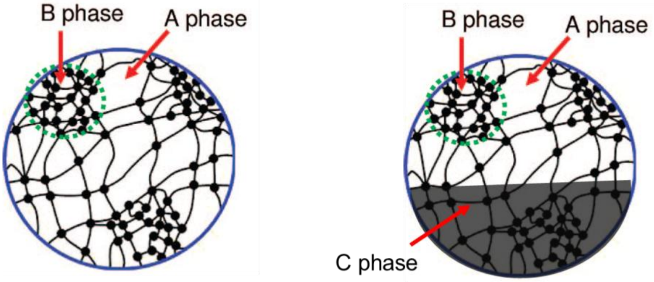


Figure 8.23 *Tensile strength and elongation at break of the improved D-GTR tire tread blend compared to the virgin tire tread compound and the original.*

However, the tensile properties for this blend are still lower than the tensile strength of the virgin material, which is at least partly due to the polymer breakdown. Additionally, network inhomogeneity may also play a role. Figure 8.24 (a)[15] illustrates a typical two-phase network structure of the virgin vulcanizate: phase A, the matrix with low network chain density; and phase B, network domains with high network chain density. The domains of high network-chain density are embedded in the rubber network matrix. The network inhomogeneity caused by these two phases was reported to be a main factor affecting the mechanical properties of rubber materials[15]. Consequently, in the D-GTR/virgin rubber blend the network structure can also be formed inhomogeneously, giving at least 3 phases as shown in Figure 8.24(b). These lead to a pronounced effect on the mechanical properties of the blend. It was stated that the proper curatives package can improve the network homogeneity[15].



(a) (b)

***Figure 8.24** The inhomogeneity of the network structure,*

(a): Two phase model network structure, phase A: matrix with low network density, phase B: network domain with high network density

(b): Three phases model network of virgin rubber/D-GTR blend.[15]

Table 8.7 Recommended formulation for

50/50: D-GTR/virgin rubber blend tire tread.

Ingredients	Phr
D-GTR*	50.0
SBR	44.7
BR	17.5
Carbon black N375	80.0
Zinc Oxide	3.0
Stearic acid	2.0
Sulfur	2.5
TBBS	1.5
6PPD	1.0
TMQ	2.0
Microcrystalline wax	3.0
TDAE oil	9.8

* Calculated on basis of the polymer contents of the D-GTR.

As present results show, the material properties can significantly be improved by adjustment of the curative as well as other compounding ingredients. However, in order to obtain the best mechanical properties of the blend, several factors need to be taken into consideration:

- Optimization of the extruder conditions
- Viscosity mismatch
- Limited compatibility within the immiscible blend
- Weak spots from remaining cross-links of the D-GTR
- Migration of curatives between the blend phases

These aspects are not covered in this thesis; therefore they should be the topic of further studies in order to further optimize the properties of the D-GTR/virgin rubber blend.

8.4 CONCLUSION

The continuous de-vulcanization process in the twin-screw extruder has to be optimized, as the currently used parameters cause too much damage of the polymer chains. This drastically affects the properties of the extruded D-GTR as can be seen from the tensile properties. The polymer degradation explicitly shows in a too large reduction of the Mooney viscosity of the D-GTR, which may be attributed to the excessive shearing during the de-vulcanization process. In order to reduce the degradation and to obtain a higher quality de-vulcanizate, the continuous de-vulcanization process has to be optimized for a better control of the shearing forces.

The property level of the 50/50 wt% blend is lower than the level of the cured virgin rubber; the main reason being the low curing activity and possibly network inhomogeneity. However, the material properties can significantly be improved by adjustment of the curative as well as the compounding recipe. This allows to increase the tensile strength up to about 2/3 of the level of virgin material. A further increase the quality of the material must be achieved from a further improvement of the de-vulcanization process conditions.

8.5 REFERENCES

[1] M. Myhre, S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, *Rubber Chem. Technol.*, **85**, 408 (2012).

[2] W. Feng and A.I. Isayev, *J. Mat. Sci*., **40** 2883 (2005)

[3] O. Grigoryeva, A. Fainleib, O. Starostenko, N. Nosak and G. Dudarenko, *Rubber Chem. Technol*., **76**, 131 (2003).

[4] P. Sutanto, Ph.D. Thesis, University of Groningen, the Netherlands (2006).

[5] A.K. Naskar, S.K. De, A.K. Bhowmick, P.K. Pramanik, R. Mukhopadyay, *Rubber Chem. Technol*., **73**, 902 (2000).

[6] P.T. Williams, S. Besler, *Fuel*, **74(9)**, 1277 (1995).

[7] V.M. Makarov, V.F. Drozdovski, “Reprocessing of tires and rubber wastes”, Ellis Howard, New York, U.S., 1991.

[8] D. De, A. Das, D. De, B. Dey, S.C. Debnath, B.C. Roy, *Europ. Polym. J*., **42**, 917 (2006).

[9] U. Görl, A. Hunsche, A. Müller, H.G. Koban, *Rubber Chem. Technol*., **70**, 608 (1997).

[10] W. Kaewsakul, K. Sahakaro, W. Dierkes, J.W.M. Noordermeer, *Rubber Chem. Technol.*, **85**, 277 (2012).

[11] A.I. Madalia, *Rubber Chem. Technol*., **47**, 411 (1974).

[12] S. Mihara, R.N. Datta, J.W.M. Noordermeer, *Rubber Chem. Technol*., **82**, 524 (2009).

[13] P. Ghosh, S. Katare, P. Patkar, J.M. Caruthers, V. Venkatasubramanian, K.A. Walker, *Rubber Chem. Technol*., **76**, 592 (2003).

[14] W. Klinggensmith, W. Klamp, M. Fath, K. Baranwal, R. Ohm, R.S. Fell, B. Roger, “Rubber Compounding”, Encyclopedia of Chemical Technology, 4th Edition, Vol. 21, John Wiley & Sons, New York, U.S., 1997.

[15] Y. Ikeda, N. Higashitani, K. Hijikata, Y. Kokubo, Y. Morita, M. Shibayama, N. Osaka, T. Suzuki, H. Endo, S. Kohjiya, *Macromolecules*, **42**, 2741 (2009).

SUMMARY

This chapter provides a summary of the work described in this thesis. A general evaluation of the results obtained is given, together with some remarks. Finally, some suggestions for further research are given.

SUMMARY

Enabling recycling loops for used passenger car tires is a challenge and an opportunity. The challenge lies in the presence of SBR as the main elastomer in this type of tires, which makes this material difficult to reclaim due to the tendency of the elastomer chain fragments to re-combine. The opportunity lies in the wide availability of the material and in the fact that passenger car tires form a huge potential market for recycled rubber. Various recycling routes of post-consumer tire materials were comprehensively reviewed in **Chapter 2.** As a conclusion, material recycling in the sense of using recuperated rubber in products equal in quality to that of the original material is the most efficient route of recycling. This can be achieved by de-vulcanization. To reach efficient de-vulcanization by increasing the ratio of crosslink to polymer chain scission is the focus of this thesis.

Polymer chain scission mainly occurs during physical treatment, as shown in a preliminary study of sulfur-cured SBR de-vulcanization by thermal treatment in **Chapter 3**. The de-vulcanization process was investigated under various conditions. Interestingly, an increase of the de-vulcanization temperature results in a decrease of the crosslink density in first instance, but it increases again above a temperature threshold of 220°C. The reason for this increase in crosslink density is a complicated intra-molecular rearrangement of chain fragments due to uncontrolled degradation and oxidation effects. Preventing oxidation during thermal treatment reduces the degree of rearrangement and results in significantly improved SBR de-vulcanizate properties.

To define the pathway for the most efficient de-vulcanization process of SBR, a further study is performed and discussed in terms of de-vulcanization chemistry in **Chapter 4**. In a thermo-chemical de-vulcanization process of SBR using disulfides as de-vulcanization aids, a shift of the balance between physical and chemical breakdown leads to a higher ratio of crosslink scission to polymer chain breakage. Although the network breakdown is enhanced by increased temperatures, it is necessary to keep the de-vulcanization temperature as low as possible to prevent uncontrollable reactions. Particularly at high de-vulcanization temperatures, i.e. above the threshold temperature of 220 °C, three possible reactions can jointly occur: hydrogen transfer and chemical structure transformation reactions as well as generation of active groups derived from the presence of oxygen. These lead to re-formation of partially crosslinked or branched polymers from unstable chain segments, which results in a reduction of the sol fraction and increase of the crosslink density above the threshold temperature. In Chapter 4, special attention is paid to the choice of the best de-vulcanization aid for SBR sulfur vulcanizates. Three different types of disulfides are investigated concerning their performance as de-vulcanization aid: diphenyldisulfide (DPDS), dibutyldisulfide (DBDS) and di(2-aminophenyl)disulfide (APDS). DPDS is found to be the most effective de-vulcanization aid and the optimal de-vulcanization temperature for SBR is 220°C.

A further study regarding the inter- and intra-molecular rearrangements of chain fragments of butadiene moieties in SBR from uncontrolled degradation and oxidation effects was performed in **Chapter 5**. Oxidation stabilizers were added to the DPDS de-vulcanizate in order to reduce degradation and interrupt oxidation cycles. Using a combination of DPDS and one or more oxidation stabilizers results in a more efficient de-vulcanization, especially at high de-vulcanization temperatures. DPDS scavenges highly reactive radicals, preventing recombination of the rubber network. The stabilizers suppress the reactions of oxygen, which accelerate the degradation of the polymers and recombination into new crosslinks. The synergistic function of these two chemicals results in the most efficient de-vulcanization for SBR. From **Chapter 3** to **Chapter 5**, it can be concluded that it is necessary to interrupt the oxidation cycle as much as possible in order to reach efficient de-vulcanization. The oxidation cycle can be prevented either by using a thermal stabilizer or by eliminating oxygen in the de-vulcanization processes, e.g. by de-vulcanization under nitrogen atmosphere.

A best compromise for the de-vulcanization process conditions for all tire rubbers was elaborated in **Chapter 6**. The difficulties of whole tire de-vulcanization are caused by the fact that this material consists of several types of elastomers, fillers and other additives. SBR, BR, NR and CIIR or BIIR react according to different de-vulcanization mechanisms. BR behaves more or less the same as SBR: it shows chain recombination with increasing de-vulcanization temperatures. The de-vulcanization conditions are optimized for SBR, and as BR chemically resembles SBR, they are also applicable for this polymer. For NR, the network is easily broken down with a treatment temperature higher than 170 °C, but it is a combination of polymer and crosslink scission. NR turned out to be rather forgiving in terms of de-vulcanization conditions and could be treated in the same manner as SBR and BR. CIIR acts differently from the other types of rubber: The network breakdown is enhanced by increasing the de-vulcanization temperature. However, at lower temperatures, the breakdown is not uniformly distributed throughout the particles; for a uniform breakdown a higher temperature has to be used. In this study, the de-vulcanization conditions are not optimal for CIIR, but as the percentage of this polymer in a tire is rather low its effect is expected to be small. For the best de-vulcanization of a blend of the tire rubbers, it is necessary to keep the de-vulcanization temperature as low as possible for a high ratio of crosslink to main chain scission, a homogenous breakdown of the vulcanized network, and an efficient de-vulcanization

In **Chapter 7,** the efficiency of the optimized de-vulcanization conditions as elaborated in Chapter 6 for whole passenger car tire material were investigated. The de-vulcanization of Ground whole Tire Rubber (GTR) is more complex than just finding the best compromise of the de-vulcanization parameters for the single polymers; a further optimization for this blend of polymers and compounds was required. An efficient method for increasing the de-vulcanization efficiency is an improvement of the dispersion of the de-vulcanization aid in the rubber matrix by pre-swelling of the rubber powder in a blend of the de-vulcanization aid and oil. This results in a more homogeneous breakdown of the crosslink network throughout the rubber particles. After further optimization of the parameters in terms of de-vulcanization oil loading and process time, de-vulcanized ground tire rubber (D-GTR) reached a 70% decrease in crosslink density compared to the untreated GTR.

Finally, an application study was performed and discussed in **Chapter 8**. Continuous de-vulcanization of GTR from whole passenger car tires was performed in an extruder on pilot scale. The properties and application of this un-optimized, first-shot extruded de-vulcanizate material were studied. It turned out that the process parameters cause too much damage of the polymer chains; therefore the continuous de-vulcanization process in the twin-screw extruder has to be further optimized. The polymer breakdown drastically affects the properties of the extruded D-GTR as can be seen from the decrease in Mooney viscosity and tensile properties. The results of this first continuous extruder de-vulcanization of GTR are not satisfactory yet. The main reason for that is most probably the severity of the screw design, which was originally optimized for EPDM-de-vulcanization. In retrospect this may not have been the optimal choice for SBR and whole tire rubber. Tire rubber is very tough in comparison with the softness of EPDM. The screw design, therefore, needs to be optimized, which is the topic of continued study at the University of Groningen.

This D-GTR is blended with a virgin tire tread compound at a ratio of 50/50. The property level of the 50/50 wt% blend is lower than the level of the cured virgin rubber; the main reason being the low curing activity and possibly network inhomogeneities. However, the material properties can significantly be improved by adjustment of the curative system as well as the compounding recipe. However, the main potential to improve the properties of the de-vulcanizate is a further optimization of the continuous de-vulcanization process conditions.

SUGGESTIONS FOR FURTHER RESEARCH

In this part, the two main challenges of recycling of post-consumer tires back into new tires will be addresses. These challenges are:

De-vulcanization, and
Re-utilization,

DE-VULCANIZATION

The most prominent shortcoming of the existing reclaiming/de-vulcanization processes is their influence on the polymer structure. These processes are mainly developed in view of producing a processable rubber material, and less on keeping the functionality of the material intact. The latter requirement is now coming to the fore and more in-depth studies on the effect of the reclaiming and de-vulcanization processes have to be performed.

The future technologies for recycling of rubber need to focus on de-crosslinking, with minimum possible influence on the polymer and thus on the functionality of the material. However, it will always be a balance between crosslink-scission and polymer breakdown; the challenge is to shift this balance to de-vulcanization as far as possible and avoid polymer degradation.

Parameters of the de-vulcanization process have to be well elaborated in order to limit thermal and mechanical breakdown of the polymer chains. This means that more fine-tuning of the conditions for the recycling processes has to be done in order to elaborate the best process for a certain material and application.

The de-vulcanization-technology within this thesis is developed for carbon black filled rubber. However, the influence of changes in tire composition need to be taken into consideration as well. The influence of the increasing amounts of silica related to modern low rolling resistance “Green Tires” was investigated within this project, but is not part of the thesis.

A mechanistic study of the polymer degradation and re-arrangements in the de-vulcanization process is necessary to understand the correlation between process parameters and material properties. This should be investigated in a related study.

RE-UTILIZATION

Compounding principles for blends of virgin with de-vulcanized rubber need to be developed. When adding recycled rubber to a virgin rubber compound, even if it is the same type of compound, the properties will change. This is due to the fact that the recycled rubber has already undergone a whole life cycle, which will influence the properties of the material due to aging. Furthermore, the polymer-filler interaction is different, as this is mainly formed during the mixing process, which the recycled material has undergone twice. In order to obtain the best property profile for this blend, several factors need to be studied:

- Viscosity mismatch between the virgin and the de-vulcanized material;
- Limited compatibility within the blend of thermodynamically immiscible polymers;
- Weak spots in the de-vulcanizate from remaining cross-links in the D-GTR;
- Migration of curatives between the blend phases.

These aspects are not covered in this thesis; therefore they should be the topic of further studies.

SAMENVATTING

Dit hoofdstuk bevat een samenvatting van de werkzaamheden zoals beschreven in dit proefschrift. Een algemene evaluatie wordt gegeven van de verkregen resultaten, samen met enkele opmerkingen achteraf. Tenslotte worden enkele suggesties voor vervolg-onderzoek voorgesteld.

SAMENVATTING

Het inrichten van recycling kringlopen voor gebruikte personenwagen banden is een uitdaging, maar biedt ook een groot voordeel. De uitdaging ligt in de aanwezigheid van SBR als belangrijkste elastomeer in dit type banden, hetgeen dit materiaal moeilijk maakt voor terugwinning vanwege de neiging van de rubber keten-fragmenten om te recombineren. Het voordeel ligt in de ruime beschikbaarheid van dit materiaal en in het feit dat personenwagen banden een geweldige potentiële markt vormen voor herverwerkte/gerecycelde rubber. Verschillende recycling routes voor materialen verkregen uit gebruikte banden worden samenvattend behandeld in **Hoofdstuk 2**. De conclusie is, dat materiaal recycling in de zin van hergebruik van teruggewonnen rubber in eindproducten van gelijke kwaliteit als op basis van het oorspronkelijke materiaal, de meest efficiënte recycling route vertegenwoordigt. Dit kan worden bereikt met de-vulcanisatie. Het verkrijgen van efficiënte de-vulcanisatie middels verhogen van de verhouding tussen crosslink- en polymeer keten-breuk is de doelstelling van dit proefschrift.

Keten-breuk van polymeren vindt voornamelijk plaats gedurende fysische behandeling, zoals aangetoond in een vóórstudie van de-vulcanisatie van zwavel-vernette SBR door thermische behandeling in **Hoofdstuk 3**. Het de-vulcanisatie proces is onderzocht onder verschillende condities. Verrassenderwijs resulteert een toename van de de-vulcanisatie temperatuur in eerste instantie in een afname van de crosslink-dichtheid, maar neemt weer toe boven een temperatuur-drempel van 220^{o}C. De reden voor deze toename in crosslink dichtheid is een gecompliceerde intra-moleculaire her-rangschikking van keten-fragmenten vanwege ongecontroleerde degradatie en oxidatie-effecten. Het voorkomen van oxidatie gedurende thermische behandeling vermindert de mate van her-rangschikking en resulteert in significant verbeterde SBR de-vulcanisaat eigenschappen.

Teneinde de weg te definiëren voor het meest efficiënte de-vulcanisatie-proces voor SBR, wordt een verdere studie verricht en besproken in de zin van de-vulcanisatie chemie in **Hoofdstuk 4**. In een thermo-chemisch de-vulcanisatie proces voor SBR met gebruikmaking van disulfiden als de-vulcanisatie hulpmiddelen leidt een verschuiving van het evenwicht tussen fysische en chemische afbraak tot een hogere verhouding tussen crosslink breuk en polymere keten-splijting. Ofschoon netwerk-afbraak wordt bevorderd door hogere temperaturen, blijft het nodig om de de-vulcanisatie temperatuur zo laag mogelijk te houden om ongecontroleerde reacties te voorkomen. In het bijzonder bij hoge de-vulcanisatie temperaturen, d.w.z. boven de drempelwaarde van 220 ^{o}C, kunnen er drie mogelijke reacties gelijktijdig optreden: waterstof overdracht en chemische structuur-veranderings reacties evenals vorming van actieve groepen tengevolge van de aanwezigheid van zuurstof. Deze leiden tot her-vorming van deels gecrosslinkte of vertakte polymeren uit onstabiele keten-segmenten, die resulteren in een afname van de sol (oplosbare) fractie en toename van de crosslink dichtheid boven de drempel-temperatuur. In Hoofdstuk 4 wordt speciale aandacht besteed aan de keuze van het beste de-vulcanisatie hulpmiddel: difenyldisulfide (DPDS), dibutyldisulfide (DBDS) en di(2-aminofenyl)disulfide (APDS). DPDS blijkt het meest effectieve de-vulcanisatie hulpmiddel bij een optimale de-vulcanisatie temperatuur voor SBR van 220 ^{o}C.

Een verder onderzoek wordt verricht in **Hoofdstuk 5** naar de inter- en intra-moleculaire herschikkingen van keten fragmenten van butadiëen-eenheden in SBR tengevolge van ongecontroleerde degradatie en oxidatie effecten. Oxidatie stabilisatoren worden toegevoegd aan het DPDS de-vulcanisaat teneinde degradatie te verminderen en oxidatie-cycli te onderbreken. Gebruikmaking van een combinatie van DPDS en één of meer oxidatie stabilisatoren resulteert in een efficiëntere de-vulcanisatie, vooral bij hoge de-vulcanisatie temperaturen. DPDS vangt hoog reactieve radicalen weg en voorkomt daarmee recombinatie van het rubber netwerk. De stabilisatoren onderdrukken de reacties van zuurstof, die de afbraak van de polymeren en hun recombinatie in nieuwe crosslinks versnellen. De synergistische werking van deze twee chemicaliën resulteert in de meest efficiënte de-vulcanisatie van SBR. Uit **Hoofdstukken 3** en **5** kan worden geconcludeerd, dat het noodzakelijk is om de oxidatie-cyclus zo veel mogelijk te onderbreken om efficiënte de-vulcanisatie te bereiken. De oxidatie-cyclus kan worden voorkomen, hetzij door gebruik te maken van een thermische stabilisator of door zuurstof te elimineren in het de-vulcanisatie proces, bijv. door de-vulcanisatie in stikstof atmosfeer uit te voeren.

Het beste compromis voor de devulcanisatie proces condities voor alle banden rubbers wordt uitgewerkt in **Hoofdstuk 6**. De moeilijkheden bij het de-vulcaniseren van hele banden worden veroorzaakt door het feit, dat het materiaal bestaat uit verschillende elastomeren, vulstoffen en andere additieven. SBR, BR, NR en CIIR of BIIR reageren elk volgens verschillende de-vulcanisatie mechanismen. BR gedraagt zich min of meer hetzelfde als SBR: het vertoont keten recombinatie met toenemende temperaturen. De de-vulcanisatie condities worden geoptimaliseerd voor SBR, en omdat BR chemisch lijkt op SBR, zijn die ook toepasbaar voor dit polymeer. Bij NR wordt het netwerk gemakkelijk afgebroken met een temperatuur behandeling hoger dan 170 °C, maar dit resulteert in een mengeling van polymeer en crosslink breuk. NR blijkt nogal ongevoelig voor de specifieke de-vulcanisatie condities en kan op dezelfde wijze worden behandeld als SBR en BR. CIIR reageert anders dan de andere typen rubber: de netwerk afbraak wordt bevorderd door verhoging van de de-vulcanisatie temperatuur. Echter, bij lagere temperaturen is de netwerk afbraak niet uniform verdeeld door de deeltjes heen; voor een uniforme afbraak moet een hogere temperatuur worden toegepast. In dit onderzoek zijn de condities voor CIIR niet optimaal, maar aangezien het percentage van dit polymeer in een band nogal laag is, wordt het effect daarvan laag ingeschat. Voor de beste de-vulcanisatie van een mengsel van banden rubbers is het nodig de de-vulcanisatie temperatuur zo laag mogelijk te houden ten behoeve van een hoge verhouding tussen crosslink en hoodketen breuk, een homogene afbouw van het gevulcaniseerde netwerk en een efficiënte de-vulcanisatie.

In **Hoofdstuk 7** wordt de efficiëntie van de geoptimaliseerd de-vulcanisatie condities, zoals uitgewerkt in Hoofdstuk 6 voor hele personenwagen banden materiaal nader onderzocht. De de-vulcanisatie van Gemalen Banden Rubber (GTR) is complexer dan alleen maar het vinden van het beste compromis voor de de-vulcanisatie parameters voor de enkelvoudige polymeren; een verdere optimalisatie voor dit mengsel van polymeren en compounds bleek vereist. Een goede methode om de de-vulcanisatie efficiëntie te verhogen is verbetering van de dispersie van het de-vulcanisatie hulpmiddel in de rubber matrix door vooraf zwellen van het rubber poeder in een mengsel van het de-vulcanisatie hulpmiddel en olie. Dit resulteert in een homogenere afbraak van het crosslink netwerk door de rubber deeltjes heen. Na verdere optimalisatie van de parameters t.a.v. dosering van de de-vulcanisatie olie en proces tijd werd 70% afname in crosslink dichtheid bereikt voor gede-vulcaniseerd Gemalen Banden Rubber (GTR) vergeleken met het onbehandelde GTR.

Tenslotte, wordt een toepassings onderzoek verricht en bediscussieerd in **Hoofdstuk 8**. Continue de-vulcanisatie van GTR uit hele personenwagen banden was vooraf verricht in een extruder op pilot schaal. De eigenschappen en toepassing van dit niet geoptimaliseerde, "eerste schot" geëxtrudeerde de-vulcanisatie materiaal zijn bestudeerd. Het blijkt, dat de gebruikte proces parameters teveel schade toebrengen aan de polymere ketens; daarom moet het continue de-vulcanisatie proces in de dubbelschroefs extruder verder worden geoptimaliseerd. De afbraak van het polymeer tast de eigenschappen van het geëxtrudeerde D-GTR drastisch aan, zoals waarneembaar aan de afname in Mooney viscositeit en trek-rek eigenschappen. De resultaten van deze eerste continue extruder de-vulcanisatie van GTR zijn nog niet voldoende. De hoofdreden is meest waarschijnlijk de zwaarte van het schroef-ontwerp, oorspronkelijk geoptimaliseerd voor EPDM de-vulcanisatie. Achteraf bezien is dit niet de meest optimale keuze geweest voor SBR en hele banden rubber. Banden rubber is erg taai in vergelijking met het weke EPDM. Het schroef ontwerp moet daarom worden geoptimaliseerd, hetgeen het onderwerp is van voortgezet onderzoek aan de Universiteit van Groningen.

Dit D-GTR is gemengd in een 50/50verhouding met een maagdelijk banden loopvlak compound. Het eigenschappen niveau van het 50/50 mengsel is lager dan het niveau van gevulcaniseerde maagdelijke rubber; de belangrijkste reden is de lage vulcanisatie activiteit en mogelijk netwerk inhomogeniteiten. Echter, de materiaal eigenschappen kunnen wezenlijk worden verbeterd door aanpassing van het vulcanisatie systeem, evenals het compound recept. Evenwel, de belangrijkste mogelijkheid om de eigenschappen van het de-vulcanisaat te verbeteren blijft een verdere optimalisatie van de continue de-vulcanisatie proces condities.

VOORSTELLEN VOOR VOORTGEZET ONDERZOEK

In dit deel worden de twee belangrijkste uitdagingen voor recycling van post-consumer banden in nieuwe banden geadresseerd. Deze uitdagingen zijn:

De-vulcanisatie, en
Hergebruik.

DE-VULCANISATIE

De belangrijkste tekortkoming van de huidige reclaiming/de-vulcanisatie processen is hun invloed op de polymere structuur. Deze processen zijn voornamelijk ontwikkeld met het oog op het produceren van verwerkbaar rubber materiaal, en in mindere mate op het intact houden van de functionaliteit van het materiaal. De laatste eis komt heden ten dage naar de voorgrond en derhalve moeten diepere studies naar het effect van de reclaiming en de-vulcanisatie processen worden verricht.

De toekomstige technologieën voor de recycling van rubber moeten zich toeleggen op de-crosslinking, met zo weinig mogelijk invloed op het polymeer en derhalve op de functionaliteit van het materiaal. Echter, er zal altijd een balans moeten worden gezocht tussen crosslink breuk en polymeer afbraak; de uitdaging is om dit evenwicht zoveel mogelijk te verschuiven naar de-vulcanisatie en polymere afbraak te vermijden.

Parameters voor het de-vulcanisatie proces dienen goed te worden uitgewerkt teneinde thermische en mechanische afbraak van de polymere ketens te beperken. Dit betekent dat meer fine-tuning moet worden verricht van de condities voor de recycling processen om het beste proces voor een bepaald materiaal en toepassing te kunnen uitwerken.

De de-vulcanisatie technologie in dit proefschrift is ontwikkeld voor roet-gevulde rubber. Echter, de invloed van veranderingen in de banden-samenstelling moet mede in beschouwing worden genomen. De invloed van toenemende hoeveelheden silica in relatie tot moderne lage rolweerstand “Green Tires” is onderzocht binnen dit project, maar niet meegenomen in dit proefschrift.

Een mechanistische studie van de polymere afbraak en her-rangschikkinging in het de-vulcanisatie proces is nodig om de samenhang tussen proces parameters en materiaal eigenschappen te begrijpen. Dit moet nader worden onderzocht in een gerelateerd onderzoek.

HERGEBRUIK

Compounding principes voor mengsels van maagdelijke met gede-vulcaniseerde rubber moeten worden ontwikkeld. Wanneer gerecycelde rubber aan een maagdelijk rubber compound wordt toegevoegd zullen de eigenschappen veranderen, zelfs als het hetzelfde type compound betreft. Dit is het gevolg van het feit dat gerecycelde rubber reeds een hele levenscyclus heeft doorgemaakt, wat de eigenschappen van het materiaal beïnvloedt tengevolge van veroudering. Bovendien is de polymeer-vulstof wisselwerking anders, zoals dit voornamelijk ontstaat gedurende het meng-proces, dat het gerecycelde materiaal tweemaal ondergaat. Teneinde het beste eigenschappen profiel voor zo'n mengsel te bereiken moeten verschillende factoren worden onderzocht:

- De Viscositeits ongelijkheid tussen het maagdelijke en het gede-vulcaniseerde materiaal;
- De beperkte verdraagzaamheid binnen het mengsel van thermodynamisch onmengbare polymeren;
- Zwakke plekken in het de-vulcanisaat veroorzaakt door overgebleven crosslinks in het D-GTR;
- Migratie van vulcanisatie middelen tussen de verschillende mengsel fases.

Deze aspecten zijn niet behandeld in dit proefschrift; daarom zouden ze onderwerp moeten zijn van toekomstige onderzoeken.

บทสรุป

งานวิจัยในวิทยานิพนธ์เล่มนี้เป็นการศึกษาเพื่อพัฒนากระบวนการรีไซเคิลยางล้อรถยนต์ที่หมดอายุการใช้งานแล้วเพื่อนำยางรีไซเคิลที่ผลิตได้ไปเป็นส่วนผสมในการผลิตยางรถยนต์ใหม่อีกครั้งหนึ่ง ซึ่งโดยทั่วไปแล้วกระบวนการรีไซเคิลเศษวัสดุยางนั้นทำได้โดยใช้ 2 รูปแบบที่แตกต่างกัน คือ การรีเคลม (Reclamation) และ การดีวัลคาไนซ์ (De-vulcanization) ความแตกต่างระหว่างการรีเคลมและการดีวัลคาไนซ์อยู่ที่ปฏิกิริยาการตัดโครงสร้างแบบร่างแหของโมเลกุลยางในกระบวนการรีไซเคิล ยางรีเคลมที่ได้จากกระบวนการรีเคลมจะมีสมบัติทางกายภาพต่ำเนื่องจากโครงสร้างแบบร่างแหของโมเลกุลยางถูกตัดแบบสุ่ม นั่นคืออาจเกิดการตัดได้ทั้งบริเวณพันธะเชื่อมขวาง (Crosslink) ที่เกิดขึ้นจากสารวัลคาไนซ์ เช่น กำมะถัน ในระหว่างขั้นตอนการวัลคาไนซ์ยาง หรือบริเวณสายโซ่โมเลกุลหลักของยาง (Main-chain) แต่ยางดีวัลคาไนซ์ที่ได้จากกระบวนการดีวัลคาไนซ์จะมีสมบัติของยางที่ดี เนื่องจากเป็นวิธีการรีไซเคิลที่เน้นการตัดเฉพาะบริเวณพันธะเชื่อมขวางเท่านั้น

เนื่องจากในกระบวนการรีไซเคิลยางย่อมมีปฏิกิริยาการรีเคลมและปฏิกิริยาการดีวัลคาไนซ์เกิดขึ้นไปพร้อมๆกันเสมอ งานวิจัยนี้ได้เน้นการพัฒนากระบวนการรีไซเคิลผ่านการดีวัลคาไนซ์เพื่อให้กระบวนการรีไซเคิลที่เกิดขึ้นนั้นผ่านปฏิกิริยาการดีวัลคาไนซ์ให้มากที่สุด เป็นการเพิ่มสัดส่วนระหว่างการตัดโครงสร้างแบบร่างแหของโมเลกุลยางที่บริเวณพันธะเชื่อมขวางต่อการตัดบริเวณสายโซ่โมเลกุลหลักเพื่อให้ได้การดีวัลคาไนซ์ที่มีประสิทธิภาพสูงสุด

ในบทที่ 2 ได้รวบรวมวิธีการที่ใช้ในการรีไซเคิลวัสดุยาง โดยเน้นการรีไซเคิลขยะยางล้อรถยนต์ ทั้งนี้การรีไซเคิลยางล้อรถยนต์สามารถทำได้หลายวิธี เช่น การนำไปเผาเพื่อเป็นพลังงานเชื้อเพลิง การเผายางในระบบที่ควบคุมปริมาตรและชนิดของอากาศขณะเผาจะทำให้ได้น้ำมันและสารเคมีบางชนิดกลับคืนมา แต่วิธีการดังกล่าวเป็นการรีไซเคิลที่มีประสิทธิภาพต่ำเนื่องจากเป็นการใช้วัสดุยางอย่างไม่เต็มศักยภาพ นอกจากนี้ยังมีการบดเศษยางเป็นผงขนาดเล็กแล้วนำกลับมาใส่ในสูตรยางใหม่ในลักษณะของสารตัวเติมลดต้นทุน แต่จะมีผลให้ยางที่ได้มีสมบัติด้อยลงและใส่ได้ในปริมาณเล็กน้อยเท่านั้น ดังนั้นการนำวัสดุยางกลับมาใช้ใหม่ในการผลิตผลิตภัณฑ์ยางเพื่อให้มีสมบัติเทียบเท่ากับผลิตภัณฑ์เดิมเป็นวิธีการที่มีประสิทธิภาพสูงสุด ซึ่งทำได้โดยการดีวัลคาไนซ์

ยางรถยนต์ผลิตขึ้นจากการประกอบชิ้นส่วนยางต่างๆเข้าด้วยกัน เช่นดอกยาง หน้ายาง แก้มยาง เป็นต้น ซึ่งในแต่ละชิ้นส่วนยางจะต้องใช้ยางชนิดต่างๆกันเพื่อให้เหมาะกับหน้าที่ในการใช้งานนั้นๆ งานวิจัยนี้ศึกษาการรีไซเคิลยางล้อรถยนต์โดยสารทั้งชิ้น (Whole passenger car tire) ซึ่งโดยทั่วไปแล้วจะมียางหลายชนิดเป็นองค์ประกอบ โดยทั่วไปคือ ยางธรรมชาติ (Natural Rubber, NR) ยางสไตรีนบิวทาไดอีนหรือยางเอสบีอาร์ (Styrene Butadiene Rubber, SBR) ยางบิวทาไดอีน (Butadiene Rubber, BR) และยางบิวไทล์ (Isobutylene Isoprene Rubber, IIR) การศึกษาเบื้องต้นในบทที่ 3-5 ได้ทำการศึกษาการรีไซเคิลยาง SBR ซึ่งเป็นวัสดุยางหลักในยางล้อดังกล่าวนี้ เนื่องจาก

ปัจจุบันยังไม่มีวิธีการที่เหมาะสมและมีประสิทธิภาพในการรีไซเคิลยาง SBR ทั้งนี้เพื่อให้ได้วิธีการรีไซเคิลที่ดีที่สุดสำหรับยาง SBR จากนั้นจึงนำระบบดังกล่าวไปใช้และศึกษาต่อกับยางชนิดอื่นๆ ซึ่งรายงานในบทที่ 6 ทำให้สามารถสรุปวิธีการรีไซเคิลที่เหมาะสมที่สุดสำหรับยางทุกชนิด เพื่อนำระบบรีไซเคิลที่ได้ไปใช้สำหรับการรีไซเคิลยางล้อจริงดังรายงานในบทที่ 7 และสุดท้ายในบทที่ 8 เป็นการประยุกต์ใช้ยางรีไซเคิลที่ผลิตได้จากกระบวนการรีไซเคิลที่พัฒนาขึ้นในสูตรดอกยางรถยนต์

ในบทที่ 3 เป็นการทดลองการดีวัลคาไนซ์โดยใช้วิธีทางกายภาพด้วยการให้เพียงความร้อนเท่านั้น ซึ่งได้ทำการศึกษาเกี่ยวกับการตัดโครงสร้างแบบร่างแหของโมเลกุลยาง SBR ภายใต้สภาวะต่าง ๆ โดยใช้ช่วงอุณหภูมิในการศึกษาระหว่าง 180 ถึง 300 องศาเซลเซียส และทำปฏิกิริยาในสภาวะอากาศปกติและสภาวะบรรยากาศไนโตรเจน พบว่า ส่วนที่ละลายได้ในตัวทำละลาย (Sol fraction) มีค่าเพิ่มขึ้นและความหนาแน่นของพันธะเชื่อมขวางมีค่าลดลงตามอุณหภูมิการดีวัลคาไนซ์ที่เพิ่มขึ้นในช่วงเริ่มต้น แต่พันธะเชื่อมขวางจะเพิ่มขึ้นอีกครั้งเมื่ออุณหภูมิสูงกว่า 220 องศาเซลเซียส ทั้งนี้การเพิ่มขึ้นของพันธะเชื่อมขวางใหม่นี้เป็นผลมาจากการจัดเรียงตัวใหม่แบบซับซ้อนภายในโมเลกุลของพอลิเมอร์ และผลจากพฤติกรรมการสลายตัวภายใต้ความร้อนและปฏิกิริยาออกซิเดชันที่ไม่สามารถควบคุมได้ การป้องกันการเกิดปฏิกิริยาออกซิเดชันในระหว่างกระบวนการดีวัลคาไนซ์ ทำให้สามารถลดการจัดเรียงตัวใหม่ของโมเลกุลพอลิเมอร์ ซึ่งทำให้ได้สมบัติของยาง SBR ที่ดีขึ้น

ในบทที่ 4 เป็นการศึกษาเพื่อหาแนวทางในการเพิ่มประสิทธิภาพของการดีวัลคาไนซ์ โดยใช้ความร้อนร่วมกับวิธีทางเคมี (Thermo-chemical de-vulcanization) ศึกษาอิทธิพลและชนิดของสารช่วยการดีวัลคาไนซ์กลุ่มไดซัลไฟด์ พบว่าการใช้สารดีวัลคาไนซ์ดังกล่าวทำให้เพิ่มการตัดสายโซ่ยางแบบเคมีมากขึ้นซึ่งนำไปสู่การเพิ่มการตัดโครงสร้างแบบร่างแหที่บริเวณพันธะเชื่อมขวางมากขึ้น ถึงแม้ว่าการตัดโครงสร้างแบบร่างแหของโมเลกุลยางจะเพิ่มขึ้นตามการเพิ่มอุณหภูมิแต่ในกรณีนี้ควรใช้อุณหภูมิต่ำที่สุดเท่าที่จะทำได้ เพื่อลดปฏิกิริยาเคมีแทรกซ้อนต่าง ๆที่มักจะเกิดขึ้นที่อุณหภูมิสูง ๆ เช่น ปฏิกิริยาการย้ายที่ของไฮโดรเจน ปฏิกิริยาการเปลี่ยนแปลงโครงสร้างทางเคมี และปฏิกิริยาการเกิดหมู่ว่องไวใหม่จากการออกซิเดชัน ซึ่งทั้งสามปฏิกิริยาดังกล่าวทำให้เกิดการรวมตัวกันใหม่ของสายโซ่โมเลกุลที่ยังว่องไวอยู่ เป็นผลให้ส่วนของยางที่ละลายได้ลดลง (Sol fraction) และปริมาณพันธะเชื่อมขวางในยางเพิ่มขึ้น จากผลการศึกษาประสิทธิภาพของสารช่วยการดีวัลคาไนซ์ 3 ชนิดในกลุ่มไดซัลไฟด์ ได้แก่ ไดฟีนิลไดซัลไฟด์ (Diphenyl disulphide, DPDS) ไดบิวทิลไดซัลไฟด์ (Dibutyl disulphide, DBDS) และได(2-อะมิโนฟีนิล)ไดซัลไฟด์ (Di(2-aminophenyl)disulphide, APDS) สามารถสรุปได้ว่าสาร DPDS เป็นสารช่วยการดีวัลคาไนซ์ที่ดีที่สุด และอุณหภูมิที่เหมาะสมในการดีวัลคาไนซ์ คือ 220 $^{\circ}$C

ในบทที่ 5 เป็นการหาวิธีการควบคุมการจัดเรียงตัวทั้งภายในและระหว่างโมเลกุลของส่วนโมเลกุลยางใหม่ที่เกิดขึ้นเมื่อเกิดการแตกออกของสายโซ่โมเลกุลจากการเสื่อมสภาพของยางที่ไม่สามารถควบคุมระดับได้และผลจากการเกิดปฏิกิริยาออกซิเดชัน โดยพบว่าการใช้สารช่วยการดีวัลคาไนซ์ชนิด DPDS ควบคู่กับสารเพิ่มความเสถียรต่อออกซิเดชัน (Oxidation stabilizer) ทำให้เพิ่มประสิทธิภาพในการดีวัลคาไนซ์ โดยเฉพาะหากทำการดีวัลคาไนซ์ที่อุณหภูมิสูง DPDS จะช่วยป้องกันการรวมตัวของสายโซ่ที่มีปลายสายโซ่เป็นอนุมูลอิสระที่ว่องไว ในขณะที่สารเพิ่มความเสถียรต่อออกซิเดชันช่วยลดการเกิดปฏิกิริยากับออกซิเจนทำให้เกิดการเสื่อมสภาพน้อยลง

จากผลการวิจัยในบทที่ 3 ถึงบทที่ 5 สามารถสรุปได้ว่าการดีวัลคาไนซ์ยาง SBR ให้มีประสิทธิภาพสูงสุดจะต้องมีการควบคุมสภาวะในการดีวัลคาไนซ์ให้เหมาะสมโดยมีปฏิกิริยาการออกซิเดชันเกิดขึ้นน้อยที่สุด โดยทำการดีวัลคาไนซ์ภายใต้สภาวะที่ปราศจากออกซิเจน เช่น ภายใต้บรรยากาศไนโตรเจน หรือการใช้สารเพิ่มความเสถียรต่อความร้อนและออกซิเจน

ในบทที่ 6 ศึกษาการดีวัลคาไนซ์ของยางชนิดอื่นๆที่เป็นองค์ประกอบในยางรถยนต์ ได้แก่ ยาง BR, NR และ CIIR โดยใช้สภาวะการดีวัลคาไนซ์ที่เหมาะสมที่สุดสำหรับยาง SBR ที่ได้จากการศึกษาในบทที่ 3-5 ซึ่งยางแต่ละชนิดจะมีพฤติกรรมการดีวัลคาไนซ์ที่แตกต่างกัน พบว่ายาง BR มีพฤติกรรมการดีวัลคาไนซ์ใกล้เคียงกับยาง SBR คือ การเพิ่มอุณหภูมิการดีวัลคาไนซ์ทำให้เกิดการรวมตัวกันใหม่ของสายโซ่ที่ยังว่องไวหลังการแตกออกของพันธะมากขึ้น สภาวะของการดีวัลคาไนซ์ที่เหมาะสมสำหรับยาง SBR สามารถใช้ได้ดีกับการดีวัลคาไนซ์ยาง BR แต่สำหรับยาง NR ที่มีความว่องไวต่อความร้อนสูงกว่ายางสังเคราะห์ โดยทั่วไปการใช้อุณหภูมิการดีวัลคาไนซ์สูงกว่า 170 °C ทำให้โครงสร้างแบบร่างแหถูกสลายได้ง่ายโดยเป็นการตัดแบบสุ่ม นั่นคือเกิดการตัดทั้งบริเวณพันธะเชื่อมขวางและสายโซ่โมเลกุลหลักของยางควบคู่กัน สำหรับยาง CIIR พบว่ามีพฤติกรรมการดีวัลคาไนซ์ที่แตกต่างจากยางชนิดอื่นๆคือ การตัดโครงสร้างแบบร่างแหของยางจะเพิ่มขึ้นตามอุณหภูมิการดีวัลคาไนซ์ โดยการใช้อุณหภูมิต่ำทำให้เกิดการตัดสายโซ่แบบไม่สม่ำเสมอทั่วทั้งอนุภาคยาง แต่สามารถปรับปรุงได้โดยการใช้อุณหภูมิที่สูงขึ้น อย่างไรก็ตามสภาวะการดีวัลคาไนซ์ที่ใช้สำหรับยาง CIIR นี้อาจจะยังไม่ใช่สภาวะการดีวัลคาไนซ์ที่เหมาะสมที่สุด แต่เนื่องจากสัดส่วนของยางดังกล่าวในผลิตภัณฑ์ล้อยางรถยนต์มีแค่ปริมาณน้อย จึงคาดว่าจะมีผลกระทบต่อยางหลังการดีวัลคาไนซ์เพียงเล็กน้อยเท่านั้น จากการประมวลผลทั้งหมดในบทนี้จึงเห็นว่าจำเป็นต้องใช้อุณหภูมิในการดีวัลคาไนซ์ที่ต่ำที่สุดเท่าที่จะทำได้ เพื่อให้ได้การดีวัลคาไนซ์เศษยางล้อรถยนต์ที่มีประสิทธิภาพสูงสุด กล่าวคือ มีสัดส่วนระหว่างการตัดพันธะเชื่อมขวางต่อการตัดสายโซ่โมเลกุลหลักสูงสุด และมีการแตกออกของโครงสร้างแบบร่างแหของยางแบบทั่วถึงสม่ำเสมอทั่วทั้งอนุภาคยาง

ในบทที่ 7 ได้ศึกษาการดีวัลคาไนซ์เศษยางรถยนต์จริง โดยการทดลองเบื้องต้นได้ใช้สภาวะการดีวัลคาไนซ์ที่สรุปได้จากผลการทดลองในบทที่ 6 อย่างไรก็ตามจากผลการทดสอบเบื้องต้นพบว่าสภาวะดังกล่าวยังไม่ใช่สภาวะการดีวัลคาไนซ์ที่ดีที่สุดสำหรับยางล้อรถยนต์ที่มียางหลายชนิดผสมกันอยู่ เนื่องจากการทดลองในบทที่ 6 นั้นเป็นการทดลองสภาวะการดีวัลคาไนซ์ของยางแต่ละชนิดแยกกันและเป็นยางวัลคาไนซ์ที่ไม่มีสารตัวเติมใดๆ ซึ่งต่างจากยางล้อรถยนต์จริงที่ประกอบด้วยยางหลายชนิดและมีการใช้สารตัวเติมเสริมแรง เช่น เขม่าดำ ซิลิกา เป็นต้น ดังนั้นจึงต้องมีการหาสภาวะที่เหมาะสมสำหรับวัสดุเศษยางล้อรถยนต์อีกครั้ง จากการทดลองพบว่าสามารถเพิ่มประสิทธิภาพในการดีวัลคาไนซ์ได้โดยการปรับปรุงความสามารถในการกระจายตัวของสารช่วยการดีวัลคาไนซ์ในอนุภาคยาง ซึ่งทำโดยการแช่ยางผงในน้ำมันผสมสารช่วยการดีวัลคาไนซ์เป็นระยะเวลาหนึ่งก่อนที่จะทำการดีวัลคาไนซ์ พบว่าจะทำให้เกิดการตัดโครงสร้างแบบร่างแหของโมเลกุลยางได้อย่างสม่ำเสมอทั่วทั้งอนุภาคยาง ภายหลังการหาสภาวะที่เหมาะสมในการดีวัลคาไนซ์ยางล้อรถยนต์โดยการปรับปริมาณน้ำมันที่ใช้และเวลาการดีวัลคาไนซ์ พบว่า ภายใต้สภาวะที่เหมาะสมที่สุดจะสามารถลดปริมาณพันธะเชื่อมขวางระหว่างโมเลกุลยางได้ถึง 70%

การทดลองในบทที่ 3-7 นั้นได้ทำการดีวัลคาไนซ์ในเครื่องผสมแบบปิดขนาดเล็กบราเบนเดอร์พลาสติคอร์เดอร์ (Brabender plasticorder) ซึ่งเป็นเครื่องผสมที่เหมาะสมสำหรับการ

ทดลองในระดับห้องปฏิบัติการเท่านั้น ในบทสุดท้ายนี้ได้ทำการดีวัลคาไนซ์เศษยางล้อรถยนต์แบบต่อเนื่องในเครื่องอัดรีดแบบสกรูคู่ (Twin screw extruder) เพื่อเป็นการขยายขนาดการผลิตสำหรับนำไปประยุกต์ใช้กับการผลิตในเชิงอุตสาหกรรมต่อไป ในบทที่ 8 นี้ได้ใช้ยางดีวัลคาไนซ์ที่เตรียมในระดับขยายสเกลด้วยเครื่องอัดรีดแบบสกรูคู่ซึ่งเป็นยางดีวัลคาไนซ์ชุดแรกที่เตรียมโดยใช้เครื่องมือขนาดใหญ่นี้ อย่างไรก็ตามพบว่าสมบัติของยางดีวัลคาไนซ์ที่ได้ยังมีประสิทธิภาพต่ำ ทั้งนี้อาจจะเนื่องจากสภาวะการแปรรูปและรูปแบบสกรูที่ใช้ในเครื่องอัดรีดแบบสกรูคู่ดังกล่าวทำให้เกิดแรงเฉือนที่มากเกินไปซึ่งมีผลโดยตรงต่อการทำลายสายโซ่โมเลกุลยาง เมื่อนำไปใช้มีผลให้ยางที่ได้มีความหนืดมูนนี่และสมบัติเทนไซล์ด้อยลง ทั้งนี้รูปแบบสกรูที่ใช้ในครั้งแรกนี้เป็นรูปแบบที่เหมาะสมสำหรับการดีวัลคาไนซ์ยางอีพีดีเอ็มซึ่งนิ่มกว่า ดังนั้นการออกแบบสกรูที่เหมาะสมสำหรับการดีวัลคาไนซ์เศษยางล้อรถยนต์จึงต้องมีการศึกษาต่อไปเพื่อปรับปรุงสมบัติของยางดีวัลคาไนซ์ที่ได้ ซึ่งจะเป็นงานวิจัยต่อเนื่องจากงานวิจัยในวิทยานิพนธ์เล่มนี้โดยนักศึกษาปริญญาเอก ณ University of Groningen จากผลการนำยางดีวัลคาไนซ์ที่ได้จากการเตรียมในระดับขยายสเกลครั้งแรกนี้มาศึกษาสมบัติทางกายภาพเบื้องต้น ศึกษาความสามารถในการแปรรูปและการวัลคาไนซ์ และนำมาเบลนด์กับยางใหม่ในอัตราส่วนการเบลนด์ระหว่าง ยางดีวัลคาไนซ์/ยางใหม่ เท่ากับ 50/50 สำหรับสูตรดอกยางรถยนต์พบว่ายางเบลนด์มีสมบัติทางกายภาพด้อยกว่าการใช้ยางใหม่ ซึ่งเป็นผลเนื่องจากยางเบลนด์ดังกล่าวมีความว่องไวในการวัลคาไนซ์ต่ำกว่า และมีความไม่สม่ำเสมอของโครงสร้างการเชื่อมขวางโมเลกุลที่เกิดขึ้น เมื่อได้ทำการปรับปรุงสมบัติของยางเบลนด์โดยการปรับสูตรยาง ด้วยการศึกษาผลของการเพิ่มปริมาณกำมะถัน สารกระตุ้น สารตัวเร่ง และสารตัวเติม พบว่าสามารถทำให้สมบัติของยางเบลนด์ที่ได้ดีขึ้น

การศึกษาการรีไซเคิลยางล้อรถยนต์ที่หมดอายุการใช้งานแล้วในวิทยานิพนธ์เล่มนี้เป็นส่วนหนึ่งของการพัฒนาระบบรีไซเคิลวัสดุยางที่เหมาะสม เพื่อให้สามารถใช้วัสดุยางเก่าได้อย่างเต็มศักยภาพ อย่างไรก็ตามสมบัติที่ดีที่สุดของผลิตภัณฑ์จากยางดีวัลคาไนซ์จะต้องมีการศึกษาเพิ่มเติมและปรับปรุงต่อไป

MAIN SYMBOLS AND ABBREVIATIONS

ASTM	American society for testing and materials
APDS	Di(2-aminophenyl)disulfide
BR	Butadiene rubber
BD-GTR	Devulcanized ground tire rubber prepared by Brabender
°C	Degrees Celsius
C-C	Carbon-Carbon bond
C-H	Carbon-Hydrogen bond
C-S	Carbon-Sulfur bond
C–S–C	Monosulfidic crosslink
$C–S_2–C$	Disulfidic crosslink
$C–S_x–C$	Polysulfidic crosslink
CB	Carbon black
CBS	N-cyclohexyl-2-benzothiazolesulfenamide
CIIR	Chlorinated isobutylene isoprene rubber or chlorinated butyl rubber
D-BR	Devulcanized butadiene rubber
D-CIIR	Devulcanized chlorinated isobutylene isoprene rubber
D-GTR	Devulcanized ground tire rubber
D-NR	Devulcanized natural rubber
D-SBR	Devulcanized styrene-butadiene rubber
DADS	Diallyldisulfide
DBDS	Dibutyldisulfide
DPDS	Diphenyldisulfide
DPG	Diphenylguanidine
ED-GTR	Devulcanized ground tire rubber prepared by Extruder
EPDM	Ethylene propylene diene rubber
EU	European Union
EV	Efficient vulcanizing
G'	Elastic or storage modulus
G''	Viscous or loss modulus
Gel	Insoluble fraction
GTR	Ground tire rubber
HO•	Hydroxy radical
HDA	Hexadecylamine
Hz	Hertz
IIR	Halogenated butyl rubber
ISO	International organization for standardization
K	Constant for a given filler
m_r	mass of the rubber network
m_s	Weight of solvent in the sample at equilibrium swelling
MBT	2-Mercaptobenzothiazole
MBTS	Mercaptobenzothiazyl disulfide
ML(1+4)	Mooney viscosity after 1 minute of preheating and 4 minutes of measuring, measured with a large rotor
Mn	Number average molecular weight of the original polymer
MPa	Megapascal
MU	Mooney unit
MW	Molecular weight
NR	Natural rubber
phr	Parts per hundred rubber
ρ_r	Density of rubber
ρ_s	Density of solvent
R•	Carbon radical
RO•	Alkoxy radical
ROO•	Peroxy radical
ROOH	Hydroperoxide

RPA	Rubber Process Analyzer
rpm	Rounds per minute
RSR’	Monosulfidic crosslink
RSSR’	Disulfidic crosslink
RSSSR’	Trisulfidic crosslink
RSS_xSR'	Polysulfidic crosslink
RSO_2H	Sulfinic acid
RSO_3H	Sulfonic acid
RS_2O_3H	Thiosulfuric acid
s	Sol fraction
s_f	Soluble fraction of the reclaimed vulcanizate
s_i	Soluble fraction of the untreated vulcanizate
S	Sulfur
S-S	Sulfur-Sulfur bond
SBR	Styrene butadiene rubber
$ScCO_2$	Super critical carbon dioxide
SEM-EDX	Scanning electron microscope coupled to an energy dispersive x-ray spectrometer
Sol	Soluble fraction
t_{90}	Optimum curing time
TBBS	N-tert-butyl-2-benzothiazolesulfenamide
TDAE	Treated distillate aromatic extracts oil
TESPT	bis-triethoxysilylpropyltetrasulfide
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMQ	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
UEAtc	Union Européenne pour l’agrément technique dans la construction
V_r	Polymer volume fraction of the swollen sample
V_s	Solvent molar volume
ν_0	Number of elastically effective polymer network chains including the sol fraction
ν_e	Crosslink density
ν_i	Crosslink density of the untreated vulcanizate
ν_f	Crosslink density of the reclaimed vulcanizate
$\nu_{apparent}$	Measured chemical crosslink density
ν_{actual}	Actual chemical crosslink density
ν_{real}	The final corrected crosslink density for the de-vulcanizate
W_a	Weight of specimen after extraction
W_b	Weight of specimen before extraction
χ	Flory-Huggins interaction parameter
δ	Solubility parameter
Φ	Volume fraction of filler in the vulcanizate
γ	Crosslinking index, the average number of crosslinks per original polymer molecule
γ_i	Average number of crosslinks per chain in the network of the untreated vulcanizate
γ_f	Average number of crosslinks per chain in the remaining network after reclamation
η^*	Complex viscosity
ω	Frequency in radian per second
ZnO	Zinc oxide

BIBLIOGRAPHY

PATENT APPLICATION

1. A method of devulcanizing a rubber vulcanizate.
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Filed in November 2012.

JOURNAL PAPERS

1. Rubber recycling: Chemistry, processing and applications.
   M. Myhre, S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Rubber Chem. Technol., 85,408, 2012.
2. Comparative investigation of the chemical de-vulcanization parameters of tire rubbers.
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Rubber Chem. and Technol., submitted.
3. Devulcanization of whole passenger car tire material.
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Kautsch. Gummi Kunstst., submitted.
4. Thermal de-vulcanization of sulfur-vulcanized SBR.
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   J. Appl. Polym. Sci., in preparation.
5. Thermo-chemical de-vulcanization of sulfur-vulcanized SBR.
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   J. Appl. Polym. Sci., in preparation.

CONFERENCES, PROCEEDINGS AND POSTERS

1. Recycling of whole passenger car tires: poster
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Dutch Polymer Days (DPD), Veldhoven, The Netherlands, February 2010.
2. Recycling of whole passenger car tires: poster
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Energy and Resources Symposium, Enschede, The Netherlands, April 2011.
3. Pathway for high quality reclaim by thermal treatment of sulfur-vulcanized SBR: proceeding
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Meeting of the Rubber Division (American Chemical Society), Cleveland, USA, October 2011.

4. Pathway for high quality reclaim by thermal treatment of sulfur-vulcanized SBR: proceeding
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Dutch Polymer Days (DPD), Lunteren, The Netherlands, March 2012.
5. Pathway for high quality reclaim by thermal treatment of sulfur-vulcanized SBR: proceeding
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Tire Road Consortium, Enschede, The Netherlands, March 2012.
6. Efficient devulcanization of sulfur-vulcanized SBR: proceeding
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   International Rubber Conference (IRC), Jeju, Korea, May 2012.
7. Pathway for high quality reclaim from sulfur-vulcanized SBR: poster
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   German Rubber Conference (DKT), Nürnberg, Germany, July 2012.
8. Comparative investigation of the de-vulcanization parameters of tire rubbers: proceeding
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   Meeting of the Rubber Division (American Chemical Society), Cincinnati, USA, October 2012.
9. Tires back into tires; Devulcanization of tire rubbers : proceeding
   S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
   10th Fall Rubber Colloquium (Deutsches Institut für Kautschuktechnologie), Hannover, Germany, November 2012.
10. Devulcanization of whole passenger car tire material: proceeding
    S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
    International Rubber Conference (IRC), Paris, France, March 2013.
11. Re-utilization of ground tire rubber devulcanizate in a new tire tread: poster
    S.Saiwari, W.K. Dierkes, J.W.M. Noordermeer
    Dutch Polymer Days (DPD), Lunteren, The Netherlands, March 2013 .

ACKNOWLEDGEMENTS

ALHAMDULILLAH! My infinite gratitude is to God Almighty! I am thankful for the life I have received from Him.

Many people have contributed to this thesis and many have contributed to make my life in Enschede during the four years stay to a really good time.
I want to express my gratitude to everyone. I look back at a joyful period in my life. I feel proud and honoured to have been amongst you all, a feeling which will last forever. You all are and will be in my prayers.

I want to express my gratitude to RecyBEM for the financial support of this research project. Moreover, by supporting this project dealing with recycling of used tires, RecyBEM contributes to the benefit of mankind and the environment. This is an attitude that does appeal to me very much.

5 years ago I was in search for a location and a professor who has an excellent reputation in Rubber Technology to pursue my academic education.
Assoc. Prof. Dr. Charoen Nakason, my former advisor from Prince of Songkla University (PSU), Thailand was the one who has pointed me the worldwide acknowledged reputation of the ETE, Department of Elastomer Technology and Engineering in Rubber Technology. Moreover he is the first one who has taught me how to be a researcher and he is the first one who has introduced me to the incredible life of rubber technologist. Aj.Charoen, I am very grateful to have been your student.

I would like to acknowledge the people who offered me the opportunity to do a PhD in the Netherlands . Dr. Wilma Dierkes, who introduced this project to me while being in Pattani, Thailand at June 2008 and Prof. Noordermeer who interviewed me at Kuala Lumpur, Malaysia at October 2008.

I am grateful to Prof. Noordermeer for the motivation, the teaching and for instilling in my mind on his research style, deeply scientific but always with an eye to applications. I also want to thank him for being the promoter of my thesis, for discussions and comments on my work, moreover, for the Dutch summary of this thesis. Dear Prof. Noordermeer, under your guidance I have learned a lot: not only the scientific aspects with respect to rubber technology but also how to work as an independent researcher. I will always remember your phrase “Life is so difficult” and then again I will also remember your big smile after solving a huge problem. This is why I am so fond of you and your style of working.

This work could not have moved on and done without the daily source of inspiration, Wilma. Thank you, Wilma, for all the discussions and for the stimulating ideas that have led to this thesis. Working with you, I have learned a lot, challenging and validating the existing ideas, always with determination and enthusiasm. In addition, I want to thank you for the kindness and friendship that made me always feel comfortable. Thank you for the numerous correction of my English language. Although you used to say that you could not speak Thai you are the one who has perfectly corrected my 'Th-english' in several papers and chapters. I am glad to have known and to have worked with you. I am very honoured to have you as my supervisor.

This thesis is largely due to the technical meetings that were held every 6 months. I would like to thank my committee members for these technical meetings. Thank you Jaap Adrian and Cees van Oostenrijk (RecyBEM), Prof. Picchioni and Prof. Janssen (RUG), Nico Gevers and Gerard Nijman (Apollo-Vredestein) for the very nice discussions and support during these meetings. Thanks to Cynthia for nice working together. Thanks to Frank and Stefan for your work done for our project. The technical support of Apollo-Vredestein is appreciated.

I would like to thank my teachers and colleagues from Prince of Songkla University in Thailand. Firstly, Aj.Kannika for all your helps. Thank you for the tips and tricks how to live in the Netherlands. The great encouragement from you, helps me to improve my English and my working skills. I love discussing with you and your comments about Rubber Technology. Travelling with you is an impressive experience. Moreover, thanks for correction of the Thai summary. Thanks to Aj.Kea for being my nice office-mate and for helping me with the interview for applying the PhD position. Thanks to Aj.Azizon, Aj.Adisai, Aj.Arm, Aj.Saovane, Aj.Mie, Aj.P-Ann, Aj.P-Jame, Aj.P-Yai, Aj.Nan, Ka-Moh, B-Ma, P-Hama, P-Hme, P-Ake and P-Absorn for your all helps and encouragements. I would like to thank also Faculty of Science and Technology, PSU for financial support of my last 2 months staying in the Netherlands to finalize and defend of my thesis. Aj.Sukree and P-Achareeda, thank you for your assistance, accelerating and taking care of the application process.

I told my (real)father in Thailand that I have one more (not real, no offense Pocjik-Jacob!) father in the Netherlands. Pocjik-Jacob, I really respect you as my father. I could not refuse his willingness and all honest and sincere advices in all aspects. He is a VIP for me not only scientifically but also socially and regarding every-day-life skills. Imagine the time of experimental problems, broken instruments, clogged pump, missing samples, thiol smelling, without your helps, P-Jacob, this research would have not been completed in time. I really appreciate your helps, support and fatherly, grand-fatherly advices. To extend to this I would like to thank Ans for all nice chats we have had. Both of you are extraordinary Dutch!

My life in Enschede has always been hectic, thanks to some memorable characters. I was introduced as a *real* friend. All the events together with Thai-Indonesian-Malay friends I will cherish. I am thankful to many friends: P-May&P-Tom, P-weaw, Wisut&N-Toei, Karnda, P-Took, Odd, N-Big, Knot, Anee&Christoph, N-Pipe, N-Gift, N-Rex, N-Neung, Dewi, Ina, Jenny, Linda, Cheryl, Salina&Fauzi, Lilian, Sakiah, Surainee. Not only for being my friends, but also for sharing discussions about singing contest (The star), shopping, travelling and eating.

This list cannot be closed without acknowledging the friendship of the ETE colleagues(+partners) and friends: Yvonne, Ceciel, Prof.Noordermeer&Betty, Wilma&Jan, P-Jacob&Ans, Morteza&Somayeh, Agata&Wilco, Hongmei, Rui, Satoshi, Kuno, Francesca, Srikumar, SSS, Ernest&Rima, Nadia&..?, Andre, Ezgi, Gerda, I have had very nice time with you during group trips, coffee time, group meetings, alumni gatherings, lunch break, sport time, cake- and diner time. ETE toppers!, Thanks for "Ernest' s readiness helps", "Nadia's lovely friendliness", "Andre's caring office-mate".

Special thanks to my best friends and paranimfen: Salina and P-May. With you around me, my life is so blooming and happy. Thank you very much for such an excellent friendship. Xoxo! Salina, thanks a lot for the exceptional companionship and several times “Galley proof” of this thesis. P-May, thanks for being delightful friend. Thanks to K-Dayang for being a friend, room-mate and project co-worker. I’ve enjoyed working with you during your 3 months stay in ETE-group.

When I left Thailand 4 years ago, almost all members of my extensive family came to accompany me to Hadyai airport and to say goodbye with good wishes and hopes. The words that are still in my ears up till today is “You have to go and learn and come back and tell us how to be a learned person in our way”. Some of them are waiting back in Thailand to celebrate my success, though sadly some have passed away. Thank you for all encouragements.

- Wamaedeeza family: my uncles and aunts, Pangoh-kamnan Zalee, Mangoh, Poklong, Moklong, Pador, Mador, Jijo, Jitana, Poksu, Moksu, Masturee, Raheema, B-Rozaq, Firdaws, Poktek Karim, Pokcik Ma, Marne.
- Saiwaree family: Babo (poksu sufian), Jinah, Jiyah, Pokjileh, Kacha, Patee, Ahmad, Montiara, Hasan, Yala, Seetee, Kanee, Tuan Risa.
- Home Yalutong Family: Jek, Ta, Yayee, Jujeng, Suda, Hafis, Sawiyah.

Last but certainly not least, I am indebted to my beloved husband, Be-Nur for his incredible support and consolation in difficult moments. Your decision to accompany me to the Netherlands leaving a secure life back in Thailand has moved me. You actually have contributed a lot to this thesis starting from beginning of my literature study and ending with cover design of this thesis. We had a great time in Enschede. I thank you for your comprehension and your patience. You have been and will always be the only love of my life.

Dear Arif, I was trying to do my best to be the best mom for you. We have had a perfect 3 years life in Enschede. You were multilingual, speaking Thai, Malayu, English and Dutch. At some point I had to leave you with your Dad in Thailand. (Skype is a helpful tool to us fortunately!). Now you are 7, you cannot understand what I have written in this thesis. I wish when you grow older and that one day you will take a look in this thesis, you will be happy to know that I have done my best to raise you to be a wise and good man.

Finally, I would like to pay my sincere gratitude to my parents, Ayah and Mek, who always have prayed for me. Their prayers have been answered as far as one of their daughter’s life is concerned. They have always said that I have been a gift from God to them. They have raised me, taught me and supported me in a way that have made me the “SitiSaiyidah” I am now.
Mom and Dad, I am very proud to be your daughter.

Sitisaiyidah
April, 2013
Enschede

ขอขอบคุณพระเจ้า ที่ทำให้ทุกๆวันของฉัน เต็มเปี่ยมไปด้วยความหวัง ที่พร้อมจะเติมเต็มด้วย
“ความสำเร็จและประสบการณ์”

ขอขอบคุณพระเจ้า ที่ประทานสิ่งมีค่าทั้งสองนี้
“ความสำเร็จ เพื่อเป็นรางวัลจากความพยายาม
และ
ประสบการณ์เพื่อเป็นบทเรียนจากความล้มเหลว”

ซีตีไซยีดะห์ สายวารี
เมษายน 2556
ประเทศเนเธอร์แลนด์

CURRICULUM VITAE

SITISAIYIDAH SAIWARI

CONTACT ADDRESS

Department of Rubber Technology and Polymer Science,
Faculty of Science and Technology,
Prince of Songkla University (PSU), Pattani Campus.
Muang Pattani 94000, Thailand.
Tel. Office: +66-73313-931 # 1862
E-mail address: ssitisai@bunga.pn.psu.ac.th

EDUCATION

April 2005 **M. Sc. (Polymer Technology)**
Prince of Songkla University, Thailand.
M.Sc.Thesis: Preparation of Thermoplastic Elastomer from Maleated Natural Rubber and Polypropylene Blends.

July 2000 **B. Sc. (Rubber Technology)**
Prince of Songkla University, Thailand
B.Sc.Dissertation: Preparation of Block copolymer Emulsion for Natural Rubber Gloves Coating.

PROFESSIONAL EXPERIENCES

June 2005 to present **Lecturer**
Department of Rubber Technology and Polymer Science
Faculty of Science and Technology,
Prince of Songkla University, Pattani Campus, Thailand.

June 2001 to May 2003 **Chemistry teacher**
Darunsart Wittaya School
Saiburi Pattani, Thailand.

RESEARCH EXPERIENCES

Year	Research project titles	Funding bodies
2007-2008	The study of composition in reclaim rubber from natural rubber gloves The project was divided into 2 sub-projects: 1. Reclaimed rubber from waste natural rubber gloves. 2. Preparation and properties of natural rubber and reclaim rubber blends.	The Thailand Research Fund (TRF)
2006	Preparation and properties of maleated natural rubber and chlorosulfonated polyethylene blends	The Thailand Research Fund (TRF)
2005	Thermoplastic vulcanizete based on NR/LDPE/EVA blends	Faculty of Science and Technology, PSU