RECYCLING OF VULCANIZED EPDM-RUBBER

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Recycling of Vulcanized EPDM-Rubber
Mechanistic studies into the development of a continuous process using amines as devulcanization aids

By Kuno Dijkhuis

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With references – With summary in English and Dutch

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The picture illustrates the Melting Clock by Salvador Dali. The clock is a metaphor for vulcanized rubber transformed into plasticized material.

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RECYCLING OF VULCANIZED EPDM-RUBBER

MECHANISTIC STUDIES INTO THE DEVELOPMENT OF A CONTINUOUS PROCESS USING AMINES AS DEVULCANIZATION AIDS

PROEFSCHRIFT

Ter verkrijging van
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Chapter 1

General Introduction

This chapter gives an introduction into the research topic of the thesis by discussing the problem of rubber waste in general and EPDM production-scrap in particular. A description of EPDM-rubber and its qualities and applications is given. The aim of this study is explained and the structure of the thesis is given.

1.1 THE PROBLEM OF RUBBER WASTE

The extensive utilization of rubber in various applications, e.g. the automotive sector, causes a problem in terms of rubber waste. Finding a solution for this problem is a challenge for the rubber industry nowadays, especially regarding the upcoming European legislation concerning automotive vehicles recycling. Because of this new legislation[1], the rubber-producing and –consuming society is more and more urged to consider the possibilities of recycling. This legislation obliges the automotive industry to recycle 95% of the weight of used cars from January 2015 onwards. Therefore, the rubber industry cannot avoid to consider recycling of used rubber products.

The tire industry is the largest producer of vulcanized rubber. In 2000, about 2.5 million tons of post-consumer tires were wasted in Europe[2]. In the USA, a similar quantity was removed. About one billion post consumer tires were removed from all types of vehicles worldwide. Amongst all possible ways of handling post-consumer tires, one of the most commonly applied outlets is to dump them in a landfill, creating potential breeding places for disease-carrying insects and rodents. Furthermore, these piles can catch fire, which are practically impossible to extinguish and cause air, soil and surface-water pollutions. It is for these reasons that at the present moment landfill is still allowed only to a small extent in Western-Europe.

The problem of rubber recycling relates to the special structure of the material: elastomers are thermosetting. Polymers in general can be divided into two groups: thermoplastics and thermosetting materials. Thermoplastics soften when heated, making it possible to (re-)shape them at higher temperatures. Thermosetting materials, like rubbers, are crosslinked on heating and therefore cannot be softened or remodeled by temperature increase. This makes thermosets more difficult to recycle compared to thermoplastics: the three-dimensional network has to be broken in order to make the material re-processable, the so-called reclaiming process. In this process, either sulfur crosslinks connecting the polymer chains or carbon-carbon bonds within the polymer backbone are to be broken. The first process is the preferred one, as the backbone of the polymer remains intact.

Reclaiming of sulfur-cured Natural Rubber (NR), e.g. truck-tire treads, has been a common technology for many decades. Attempts to apply the same technology to recycling of rubber articles made from Ethylene-Propylene-Diene (EPDM)-rubber, e.g. car parts like window and door seals, radiator hoses and building and construction articles like roof coverings and window profiles, were made in the early nineties. These attempts were not successful, because the chemistry of the NR-devulcanization could not simply be transposed onto EPDM. Rubber manufacturers currently have to pay money for disposal of their production waste, while EPDM-reclaim as a replacement for virgin raw material can reduce the production costs, provided that the material properties do not deteriorate significantly.

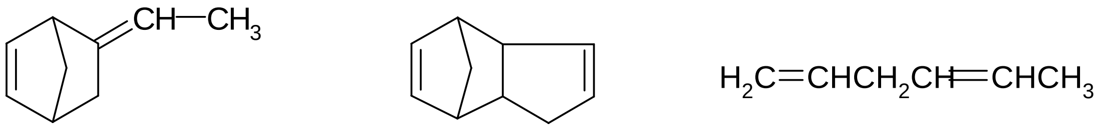
1.2 EPDM-RUBBER

EPDM-rubber is the abbreviation of ethylene-propylene-diene rubber. The letter “M” refers to polymers with a saturated backbone according to the nomenclature given by ISO 1629. The monomers are statistically distributed along the molecular chain and depending on the ethylene / propylene ratio, the material is mainly amorphous. EPDM is the mostly used non-tire elastomer among the synthetic rubbers[3]. Sales have grown to more than 1200 metric tons[4] (or 2.6 billion pounds) in 2005 since commercial introduction in the early 1960’s[5].

A great variety of dienes was studied for the unsaturated third monomer, of which only two (formerly three) are commercially used. A common characteristic of the structure of the commercially used third monomers is the presence of two non-conjugated double bonds in the molecule. They are either linear diolefins or cyclic dienes with a bridged-ring structure.

The most widely used third monomer is 5-ethylidene-2-norbornene, or ENB, see Figure 1.1a. With respect to polymerization, the double bond in the bridged, or strained ring is the more active one, and the five-membered ring with its double bond is left as a pendant substituent to the main polymer chain.

Another and less commonly used third monomer is dicyclopentadiene, or DCPD, see Figure 1.1b. The third one is 1,4-hexadiene, or HD, see Figure 1.1c, but this one became obsolete a few years ago.



(a) ENB (b) DCPD (c) HD

Figure 1.1: Monomers used commercially as dienes in EPDM

The commercially most widely used type of EPDM with ENB as diene-monomer is shown in Figure 1.2. Combinations of more than one third monomer are occasionally applied. In the main chain of the polymer, the weight ratio of ethylene to propylene varies between 45:55 and 75:25 in industrially produced EPDM rubbers, which leads to glass transition temperatures between -60ºC and -45ºC, with some crystallinity for the higher ethylene-containing grades.

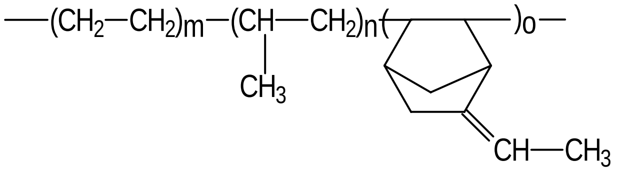


Figure 1.2: Molecular structure of EPDM with ENB

1.2.1 Properties

The properties of EPDM-rubber depend on additional features: the amount and type of unsaturation introduced by the third monomer, the way the third monomer is distributed (more or less randomly) along the chain, and long-chain branching. These structural parameters can be regulated via the operating conditions during polymerization and the chemical composition of the catalyst. General properties of EPDM rubber are[3, 6]:

- Excellent ozone resistance in comparison with NR and its synthetic counterpart poly-isoprene rubber (IR), styrene-butadiene rubber (SBR) and poly-butadiene rubber (BR);
- Ability to be extended with fillers and plasticizers to a high level in comparison with other elastomers, still giving good processability and properties of the final products;

- Very good heat-, oxygen- and ozone resistance;
- The carbon-carbon unsaturation in the side chains of the third monomer enables EPDM to be crosslinked by conventional sulfur vulcanization;
- Little moisture adsorption;
- Excellent resistance to weathering and polar chemicals, and
- Not classified as hazardous.

1.2.2 Applications

The main uses of EPDM are in automotive applications such as profiles, (radiator) hoses, and seals. It is used in building and construction as profiles, roof-sheeting and seals, as well as for electrical purposes like cable insulation and jacketing. Furthermore, EPDM is used in blends with general-purpose rubbers. With the host rubber comprising the principal portion of the blend, the ozone resistance is improved. This technique has been applied in enhancing the ozone and weathering resistance of tire sidewalls and cover strips. Considerable amounts of EPDM are also used in blends with thermoplastics, e.g., as impact modifier for polyamides, polystyrenes and particularly polypropylene. These products are used in many exterior automotive applications such as bumpers and body panels[3, 6].

1.3 AIM OF THIS THESIS

It was shown in an earlier study at the University of Twente[7-9], that sulfur-cured EPDM needs far more strenuous conditions to recycle compared to NR. Diaryldisulfides commonly used as devulcanization-aids for NR, are to some extent effective in promoting the reclaiming of EPDM. This results, however, in an EPDM-reclaim of which the chemical integrity is largely damaged and which is insufficiently active in renewed vulcanization. It was found, that α-H containing aliphatic amines are powerful devulcanization aids for EPDM, which were shown to restore the EPDM-molecules in their virgin, vulcanizable form.

The objective of the present project is to prove the feasibility of production scale recycling of EPDM-rubber, based on the outcome of the former project, by developing a continuous process for mechano-chemical reclaiming of EPDM-rubber waste – estimated at 60000 tons/year in Europe alone. Sources of this waste are in first instance production scrap of rubber articles, and in second instance end-of-life mechanical goods, e.g.:

- roof-sheeting;
- construction window profiles, and

- automotive door, hood and trunk seals.

In order to prove this feasibility, a great many variables needed to be screened from the perspective of the rubber compound composition as well as from the perspective of process development. This research was a joint project with the University of Groningen, Department of Chemical Engineering: their research was focused on the development of a continuous reclaiming process[10, 11]. The research described in this thesis is focused on the material: influence of the rubber compound composition on the process efficiency and product quality, optimization of the devulcanization aid and application studies.

Application development will focus on the use of such recycled EPDM as a raw material for roof-sheeting. This is a material which is commonly vulcanized to a low extent, in order to obtain optimal flexibility. It is the preferred application within this study, as a certain loss in vulcanization efficiency of the EPDM can be tolerated. The potential size of this market is very large, thereby providing an outlet for large amounts of recycled EPDM-rubber of various origins: automotive as well as building and construction profiles.

1.4 STRUCTURE OF THIS THESIS

A concise introduction into the different methods of rubber recycling throughout the years with special attention to EPDM recycling is presented in **Chapter 2**. One section is dedicated to the model description of main-chain and crosslink scission during reclaiming of a vulcanized rubber network. **Chapter 3** is focused on the relationship between crosslink system, network structure and material properties of a carbon black reinforced EPDM-rubber masterbatch used as base material for the work described in this thesis. In **Chapter 4**, a Design of Experiments study is performed on the reclaiming efficiency of hexadecylamine as devulcanization aid for two types of EPDM-rubber: a conventionally vulcanized one, with primarily polysulfidic crosslinks and an efficiently cured compound containing mainly monosulfidic bonds. The influence of the reclaiming parameters: time, temperature, rotor speed of the mixer and concentration of devulcanization aid is analyzed in detail. The quality of the reclaims is evaluated in an application study. A comparative evaluation of the reclaiming efficiency of hexadecylamine, diphenyldisulfide and o’o’-dibenzamidodiphenyldisulfide as devulcanization aids on conventionally and efficiently cured EPDM-rubber is done in **Chapter 5** and verified in an application study. **Chapter 6** reports an application study of reclaim, produced continuously on a twin-screw extruder using hexadecylamine as devulcanization aid and mixed into a virgin EPDM roof-sheeting masterbatch. An aging study is performed to determine the life-time expectancies of the blends containing varying proportions of reclaim. Upscaling of the continuous reclaiming process as developed at the University of Groningen[10, 11] to production scale is described in **Chapter 7,** and the quality of the reclaims is evaluated in an application study for EPDM roof-sheeting. Finally, the most important conclusions of this thesis as well as some suggestions for future work are given in **Chapter 8**.

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Chapter 2

Rubber Recycling throughout the Years: A Literature Overview

The different ways of rubber recycling, e.g. repeated use, material recycling, recovery of base chemicals and energy recycling, are briefly described in this chapter. The most effective recycling principle is the short loop of material recycling for re-use of upgraded rubber waste in new rubber articles. A high quality recyclate can be achieved by reclaiming, the breakdown of the polymer network. A comprehensive overview of all recycling methods in general, and reclaiming processes used for sulfur-cured rubber in particular is given, with special attention to reclaiming of EPDM-rubber. For a better understanding of the processes occurring during destruction of the rubber network, a model description of main-chain scission and crosslink breakage is given.

2.1 INTRODUCTION

Ever since tires and other rubber products have been produced and used, there has been the problem of scrap or used rubber parts. Rubber waste is a major problem due to its durability and the large quantities of post-consumer and production waste. Rubber products are designed in order to have long life-time expectancies, and as a consequence they degrade very slowly once they are disposed of. The problem of rubber waste can be illustrated by the estimation that approximately 21.4 million tons of virgin (green) rubber (natural and synthetic) were consumed world-wide in 2006[1]. This resulted in 43 million tons of rubber products. It is commonly assumed, that the average percentage of waste generated in a rubber production process is app. 10%[2]. This results in about 4 million tons of production waste generated annually during processing of rubber. After a few years of service life, the remaining 39 million tons of rubber products are classified as post-consumer waste. The production of EPDM – the rubber of interest in this thesis - amounted to over 1.2 million tons worldwide in 2005[3]; this is approximately 7% of the total rubber production.

Conspicuous examples of post-consumer waste are used tires. In the year 2005 approximately 1 million tons of tires were disposed of[4]. Improperly stored tires are potential breeding grounds for disease-carrying insects and rodents; the tires can catch fire, that is practically impossible to extinguish and can cause air, soil and surface-water pollutions. This is why rubber recycling is a large issue nowadays and many countries have become aware of the environmental impact and are installing legislative restrictions on disposal of rubber waste. Figure 2.1 shows the outlets for used tires.

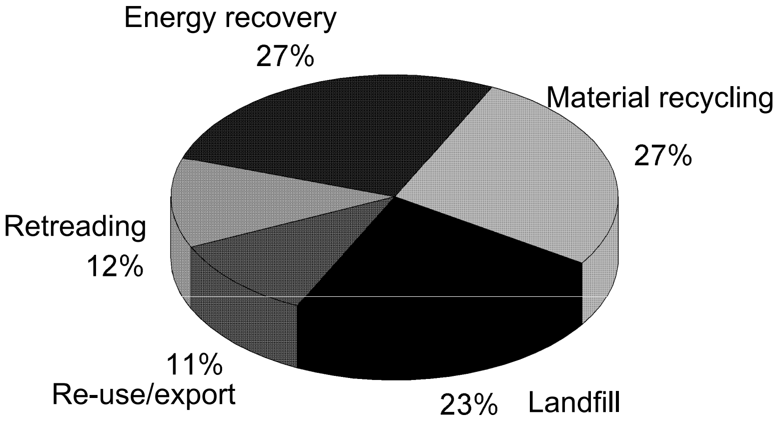

Figure 2.1: Outlets for waste tires in the EU in 2005[4]

Today, it is commonly understood that burning without energy recovery or landfilling needs to be avoided, because it is a waste of energy and material, as well as a burden on the environment. Other routes are preferred to recycle rubber waste and post-consumer products. Table 2.1 gives an overview of possible routes to recover material or energy stored in the rubbery materials.

Table 2.1 Different methods of rubber recycling

Repeated use	Re-use (e.g. of whole tires)
	Retreading
Material recycling	Grinding
	Surface activation of ground rubber
	Reclaiming
Recovery of base chemicals	Pyrolysis
	Gasification
	Hydrogenation
Energy recycling	Incineration

The most efficient way of recycling after repeated use is material recycling, as this route results in a new raw material with very low energy consumption.

2.2 REPEATED USE

Discarded tires or tire parts are directly used as playground equipment, for erosion control, highway crash barriers, agricultural purposes, flower planters, shoe soles, breakwaters and artificial reefs. However, the latter application lead to major problems: a project in Ft. Lauderdale, Florida, USA, used in 1972 3 million tires and annually added one million tires to create artificial reefs. In 1998, an estimated 120000-150000 tires were used annually in the construction of reefs[5, 6]. At the present moment those reefs are a major environmental problem, because these tires turn out to be natural reef killers, turning the ocean floor in a dead zone[7].

The most efficient way of tire recycling is retreading: when the tire tread is worn out, often the remaining tire material is still in a good shape. These tires can be equipped with a new tread; truck tires can be retreaded three till five times before finally being discarded. The main incentive to do so is that the price of new truck tires is very high and the use of retreated tires leads to a significant cost reduction. Passenger car tires are exported to 3rd world countries, and also retreading of used tires takes place on a small scale, limited by the poor integrity of many of the used passenger tires after first use.

2.3 MATERIAL RECYCLING

Material recycling of rubber is a short loop for vulcanized rubber, in which the material is ground to an appropriate particle size and re-used in rubber compounds. The ground rubber can be further upgraded by surface activation or reclaiming.

2.3.1 Grinding

Different processes are used for grinding of vulcanized rubber: cutting, shearing or impact grinding, depending on the equipment (e.g. knives, shredders, granulators, extruders, disc grinders, impact mills) and the grinding conditions (ambient, wet or cryogenic)[2, 8-12]. The choice of the process is based on the requirements of the final product, for example particle size and particle size distribution, morphology of the particles and purity of the rubber powder.

Cutting can reduce rubber products to a particular size of a few centimeters, and is therefore only a preliminary comminution step. The equipment used for further size reduction of these rubber parts by cutting are hydraulic or mechanical knives. Once the knives become blunt, the material is no longer purely cut, but also sheared. Smaller particles sizes can be achieved by shredding the material (app. 5x5 cm) with counter-rotating overlapping knives, followed by a further size reduction in granulators or hammer mills down to as small as 2 mm. To further reduce the size of rubber granulate, discs or corrugated mills are used. The final particle size, which can be achieved in this kind of equipment, is 500 μm to 1 mm. When water is used as cooling medium, the final particle size may be 250 μm or less. The disadvantage of this process is an extremely high energy consumption.

Solid-state shear extrusion (SSSE) is described as a mechano-chemical grinding process[13]. The twin screw extruder used in this technology exerts high shear forces and pressures on the material, which disintegrates under these conditions and at the same time is partly reclaimed by rupture of crosslinks.

Impact grinding is based on collisions between rubber particles or between rubber particles and parts of the grinding equipment. The particles need to have a high kinetic energy to disintegrate during the collision; this is achieved by acceleration to a very high speed inside the impact grinding unit.

A general problem of this grinding technology is heat build-up in the rubber. The particles tend to re-agglomerate and when the temperature increases, the rubber will degrade. This problem can be avoided by using an appropriate cooling medium, e.g. water (wet grinding) or liquid nitrogen (cryogenic grinding). Water can be the impact-exerting medium and at the same time remove the thermal energy from the rubber particles finally being reduced to a size of 200 μm. If the rubber is cooled down to a temperature in the glass transition area by liquid gasses, the material can efficiently be ground by impact. The advantage of the cryogenic technology is the possibility to produce a very fine powder, of the order of 200 μm, without any temperature stress. However, cryogenically ground powder has a smoother surface than ambiently ground material[10], and for this reason cryogenically ground rubber fails to physically bond to the polymer when blended into a new rubber compound.

2.3.2 Surface Activation

Rubber powder is used mainly in low quality rubber products and in blends with thermoplastic materials due to the low crosslinking activity of the surface. Different processes have been developed to increase the bonding strength with other rubber powder particles or to a surrounding matrix. The activation processes can be divided into 2 groups:

- Activation by addition of chemicals;
- Mechanical or physical activation.

2.3.2.1 Activation by Addition of Chemicals

The most common way of chemical activation is the treatment of the rubber powder with a crosslinkable polymer (latex or low molecular weight polymer) and a curing system[2, 8, 9]. When rubber powder is swollen in a low molecular weight liquid, other additives can be transported into the body of the rubber particle. These additives can carry functional groups, which connect to the polymer. These additives enhance the crosslinking reactivity of the rubber powder.

Another method is the halogenation of rubber crumb with for example chlorine, to increase the polarity of the surface of the rubber powder. This increases the compatibility, in particular with polar polymers such as polyurethane. A further effect is an increase of the concentration of double bonds on the surface of the powder, enhancing the curing efficiency.

The surface polarity of the rubber powders can also be changed with plasma treatments in oxygen, hydrogen or ammonia atmospheres[2]. Thus, adjustment of the surface polarity makes rubber crumb more compatible with thermoplastics and other polymeric materials.

2.3.2.2 Mechanical and Physical Activation

Mechanical surface activation of rubber powders can be achieved by high shearing forces, e.g. by milling the material on a two-roll mill with a small gap (down to 0.1 mm). Other possibilities for the mechanical treatment are milling, internal mixing or extrusion. The addition of reactive compounds can increase the efficiency of the mechanical surface activation. Accelerators can be added to react with the highly reactive sulfur groups generated during the activation process and peroxides can be added to activate double bonds at the surface of the rubber crumb[2, 8, 9].

2.4 RECLAIMING

Polymers can be divided into two groups: thermoplastics and thermosetting materials. Thermoplastics soften when heated, making it possible to (re-)shape them at higher temperatures. Thermosetting materials, like rubbers, are crosslinked on heating and therefore cannot be softened or remodeled by raising the temperature. Therefore, thermosets are more difficult to recycle compared to thermoplastics. The three-dimensional network has to be broken in order to make the material (re-)processable: the so-called reclaiming process. In this process, either sulfur crosslinks connecting the polymer chains or carbon-carbon bonds in the polymer backbone are broken. The first mechanism is preferred, as the backbone of the polymer remains intact. Scission can be obtained by heat, shear or chemical reactions. Basically, processes of rupturing the rubber network by crosslink or main-chain scission can be classified into five main groups[2, 8, 14-16]:

- Thermal reclaiming;
- Thermo-mechanical reclaiming;
- Mechano-chemical reclaiming;
- Reclaiming by radiation, and
- Microbial reclaiming.

In actual practice, combinations of thermal and mechanical reclaiming are mostly used, with in some cases the addition of a devulcanization aid for chemical reclaiming.

2.4.1 Thermal Reclaiming

For this kind of processes, heat (often combined with addition of chemicals) is used to break the sulfur bonds and thus to plasticize the rubber. Hall patented in 1858 one of the oldest and most simple processes in the rubber reclaiming industry, *the Heater* or *Pan process*. In this process, finely ground natural rubber powder is mixed with oils and reclaiming agents and treated with high or medium pressure steam at temperatures varying from 170°C to 200°C. The reclaiming time is long and the homogeneity of the reclaim is low, but this process is able to reclaim a large number of polymers: natural rubber (NR), styrene-butadiene rubber (SBR), chloroprene rubber (CR), acrylonitrile-butadiene rubber (NBR) and butyl rubber (IIR) and the equipment is rather inexpensive[2, 8].

The use of the heater or pan process became less popular after Marks patented the *Digester* or *Alkali process* in 1899. The fibers of the rubber scrap, remnants of the tire carcass, were first removed by mixing it with alkali, water, plasticizing oils and, if needed, chemical peptizers. The mixture was heated in a jacketed, agitator equipped autoclave to 180-210°C. The most important disadvantage of this process is the pollution generated by the chemicals. Modifications of this process minimized the pollution, but increased the reaction times[2, 8].

Processes with short reaction times are for example the *High Pressure Steam process*[17] or the *Engelke process*. In the first process, a fiber-free, coarse ground rubber is mixed with reclaiming agents, and reclaiming is done in a high-pressure autoclave at approximately 280°C. In the latter process, coarse ground rubber scrap is mixed with plasticizing oils and peptizers and is put into small autoclaves. The material is heated to very high temperatures for a short period of 15 minutes, after which it is lead through refiners (mills with very narrow gaps) and strainers[2, 8].

2.4.2 Thermo-Mechanical Reclaiming

The thermo-mechanical reclaiming processes make use of shearing forces to plasticize the rubber. Energy is introduced into the materials, resulting in a significant temperature increase, high enough to cause thermal degradation. The *Lancaster-Banbury process*[2, 18] is one of the oldest processes. Fiber-free coarse ground rubber scrap is mixed with reclaiming agents and sheared in a high speed, high-pressure internal mixer. When a continuously working, multiscrew devulcanizer is used instead of the internal mixer, the process is called the *Ficker reclaiming process*[2].

One of the first continuous reclaiming processes is the so-called *reclaimator process*. This is basically a single screw extruder that has been adapted to reclaim fibre-free rubber scrap in very short extrusion times[2, 6, 8]. The short extrusion times make this method suitable for SBR, that tends to harden when longer recycling times are applied.

Another mechanical reclaiming process is the *De-Link process*[2, 19-21]. In this process finely ground rubber powder is mixed with the De-Link masterbatch: a zinc salt of dimethyldithiocarbamate and mercaptobenzothiazole in a molar ratio of 1:1 to 1:12, dispersed in thiols and activated by stearic acid, zinc oxide and sulfur. Advantages of the process are its simplicity and the fact that standard rubber equipment is used.

The Toyota process[2, 22] is another development of mechanical reclaiming. In this process a mixture of ground rubber, virgin rubber, oils and a devulcanization aid is masticated on a two-roll mill or in an extruder. The result is a devulcanized rubber, ready for further processing[23].

Toyota developed another continuous process combining pulverization, reclaiming and deodorization[24, 25]. The rubber waste has to be ground to a particle size of less than 5 mm before it can be fed into an extruder with a pulverization zone and a reaction zone. The operating temperature is in the range of 100-300°C and 100-900 rpm screw speeds are applied.

2.4.3 Mechano-Chemical Reclaiming

Mixing of the rubber powder with a peptizer (chemicals used to reduce the viscosity of NR) and a reclaiming agent prior to the mechanical breakdown of the material improves the reclaiming process. The devulcanization aid is supposed to selectively break the sulfur crosslinks in the rubber network. This chemical breakdown is combined with input of thermal and/or mechanical energy, as the rate of this process is sufficiently high only at higher temperatures. The most common devulcanization aids are disulfides, e.g. aryl disulfides or diphenyl sulfides, thiophenols and their zinc salts and mercaptanes. These chemical compounds are radical scavengers: they react with the radicals generated by chain- or crosslink scission and prevent recombination of the molecules[8], see Figure 2.2. Typical concentrations for the reclaiming agents are 0.5 to 4 wt%. Suitable peptizers are aromatic and naphthenic oils with a high boiling point.

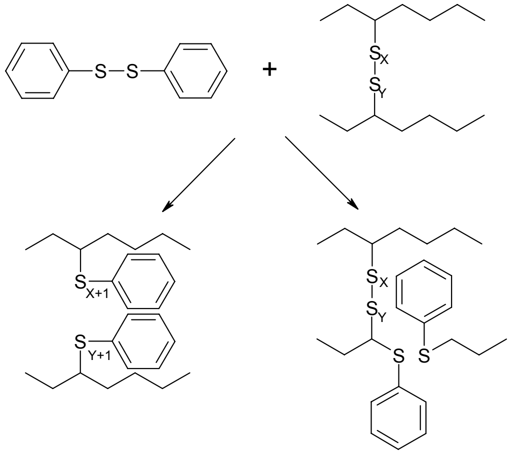

Figure 2.2: Proposed reaction mechanism of disulfides with a sulfur-vulcanized rubber network during mechano-chemical reclaiming

Other chemicals which are able to selectively break mono-, di- and polysulfidic crosslinks are chemical probes[26-29]. Compounds which can be used as chemical probes are: 2-propanethiol in combination with piperidine, and triphenylphosphine to break polysulfidic bonds; 1-hexanethiol and piperidine, lithium aluminumhydride, phenyl-lithium and sodium dibutylphosphite to break poly- and disulfidic bonds; and methyl iodide to break monosulfidic bonds. The disadvantages of chemical probes are the toxicity of the additives and the reaction conditions making it difficult to use them on an industrial scale[15].

2-Propanethiol selectively cleaves polysulfidic crosslinks in a nucleophilic displacement reaction with piperidine as base, see Figure 2.3. R represents a polymer chain.

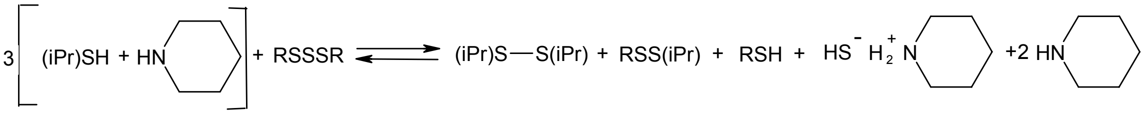

Figure 2.3: Reaction of the piperidinium-isopropanethiol ion pair with a trisulfidic crosslink

The thiol-amine combination gives a complex, possibly a piperidium propane-2-thiolate ion pair, in which the sulfur atom has enhanced nucleophilic properties, 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 2.4:

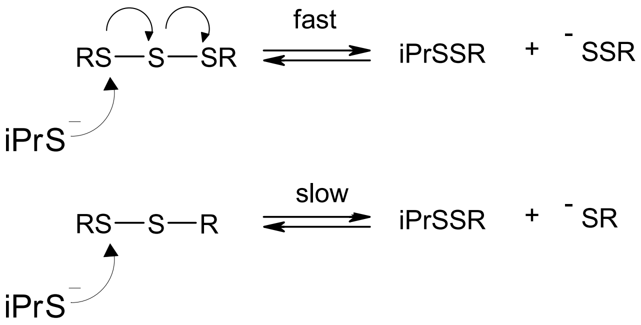

Figure 2.4: Cleavage of poly- and disulfidic crosslinks and p_{π} - d_{π} delocalization
($IPrS^{-}$ = nucleophilic thiol-amine associate)

Triphenylphosphine is also known to open polysulfidic crosslinks in a nucleophilic reaction, as shown in Figure 2.5. The broken end can recombine to crosslinks of lower sulfur rank. As the use of triphenylphosphine does not result in crosslink scission, it is used as an analytical reagent.

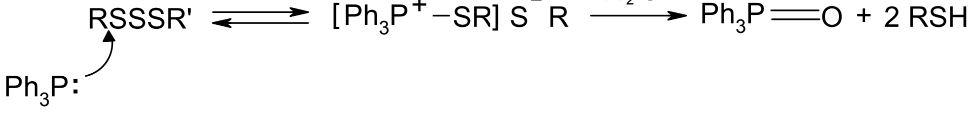

Figure 2.5: Reaction of triphenylphosphine with a polysulfidic crosslink

Lithium aluminum hydride converts poly- and disulfidic bonds into thiols, as shown in Figures 2.6 and 2.7.

$$RSS_xSR' \xrightarrow{LiAlH_4,\ H^+} RSH + xH_2S + HSR'$$

Figure 2.6: Reaction of lithium aluminium hydride with polysulfides

$$RSSR' \xrightarrow{LiAlH_4,\ H^+} RSH + HSR'$$

Figure 2.7: Reaction of lithium aluminium hydride with disulfidic bonds

Methyliodide can be used to estimate the amount of monosulfidic linkages in vulcanized rubber. The level of network-bound iodine after a reaction time of two to three days reflects the concentration of monosulfidic groups, since these groups react as shown in Figure 2.8.

$$RSR + CH_3I \longrightarrow R_2\overset{+}{S}CH_3I^-$$

Figure 2.8: Reaction of methyliodide with monosulfides

Other compounds used for sulfur crosslink scission are 1,8-diazabicyclo(5,4,0)undecane with p-toluene sulfonic acid, dipentene with cobalt or manganese compounds, redoxsystems, vulcanization accelerators and antioxidants[2, 8].

2.4.4 Reclaiming by Irradiation

The Goodyear Tire and Rubber Company patented[30] a microwave devulcanization process of sulfur-cured rubber, containing polar groups or components. The process consists of application of a controlled dose of microwave energy at a specified frequency and energy level to cleave carbon-sulfur and sulfur-sulfur bonds, but insufficient to cleave carbon-carbon bonds, as they have a higher bond energy, see table 2.2. According to the inventor, elastomer waste can be devulcanized without depolymerization and transformed into a material capable of being recompounded and revulcanized without a significant loss in properties.

Table 2.2 Typical bond energies

Bond type	Dissociation energy (kJ/mol)
Carbon-carbon bond	349
Carbon-sulfur bond	302
Sulfur-sulfur bond	273
Polysulfidic bond	256

In this process, coarse ground rubber with a particle size of 6 to 10 mm, preferably free of fibers, is transported in a transparent tube system through a microwave device. While passing the microwave source, the material rapidly heats up to 260-350°C and sulfur-links are broken. Fix[31] discussed the advantages of this method and he pointed out that the process is not energy intensive, can be highly automated, is quick and delivers a material which is uniform in properties and can easily be processed.

Isayev and coworkers[32-39] have developed a method for breaking down the three-dimensional network of vulcanized elastomers by application of ultrasonic shear at a conical extruder die. This treatment results in a softened material, able to be reprocessed and re-shaped in a manner similar to that of uncured elastomer. This process is suitable for the recycling of various rubbers including those from used tires.

Isayev[40, 41] has patented an apparatus for continuous recycling of vulcanized elastomers and thermosets. The reactor can be an extruder or any device that can transport vulcanized rubber, while simultaneously exerting pressure on it. The mechanism of rubber reclaiming under ultrasonic treatment is presently unclear; the mechanisms governing the conversion of mechanical ultrasonic energy to chemical energy are not understood[42].

2.4.5 Microbial Reclaiming

Thiobacillus-bacteria are able to oxidise the sulfur in polysulfonic bonds to sulphate. This reaction is limited to a surface layer of the rubber with a thickness of less than 1 μm and the oxidation takes several weeks. The thiophilic bacteria Sulfolobus Acidocaldarius is able to split carbon-sulfur bonds in a stepwise oxidation reaction of the carbon-bound sulfur into a sulfoxide, a sulfone and finally to a sulphate[8, 9]. The disadvantage of these processes is the low devulcanization rate.

2.5 RECOVERY OF BASE CHEMICALS

Several different processes have been developed to recover the base chemicals from disposed rubber. In these processes the polymer is cracked into chemical compounds with a low molecular weight. Although hardly used, the three most used back-to-feedstock processes are:

- Pyrolysis;
- Gasification;
- Hydrogenation.

Pyrolysis is the thermal degradation in an oxygen-free atmosphere at 400-800°C[43]. Higher temperatures yield lower molecular weight products. The thermal efficiency of this process is approximately 70%, but can be increased to 90% if the pyrolysis products are used as fuel. Variations of the process are reactions in water atmosphere, in supercritical steam or in a liquid salt bath[2, 8].

The development of a fluidized bed reactor made it possible to pyrolyse rubber waste within a few minutes. The solid residues containing carbon black, metal and fibers can be used in the steel industry or as additives for bitumen, whereas the gases and oils can be used as fuel.

Gasification takes place in a solid bed reactor at 1300°C with a batch time of 1 hour. The contaminant-free rubber crumb is partly oxidized by steam, air or oxygen and the preferred reaction products are low molecular weight hydrocarbons such as methanol and carbon monoxide[2, 8].

Hydrogenation takes place at 450°C and pressures up to 200 bar. The products are high-quality synthetic crude oils, which can be separated into fractions of gasoline, diesel fuel and gas oils. The rubber material must be free of contaminants[2, 8].

2.6 ENERGY RECYCLING

Only a fraction of the energy consumed during the production of a rubber article can be recovered. However, the energy content of post-consumer tires is comparable to the energy content of common sources of energy: the energy content of tires is 30 kJ/kg, whereas oil contains 44 kJ/kg and coal 28-32 kJ/kg[8, 44]. Therefore, tires can replace other fuels for energy generation, what finally is one environmentally sound way of reducing the amount of used tires.

Incineration of tires in order to generate energy is a well-known technique and is widely used in the cement, metal, paper and rubber processing industries. A power plant, utilizing worn-out tires as fuel, was opened in 1993 in Great Britain. The plant is designed to burn 90000 tons of waste tires per year, which generates 20 MW energy, which is enough for about 25000 homes. The main disadvantage of this process is the high costs of the energy produced compared to other types of power plants.

2.7 APPLICATIONS OF RECLAIMED RUBBER

Reclaim is used in a wide variety of products, ranging from floorings with a high percentage of reclaim to tires with a low percentage. Products in which reclaim is the sole source of polymer are mats, shoe soles and massive tires. In other cases, reclaim is blended with virgin synthetic or natural rubber. Examples are conveyor belts, protective sheets, seals and adhesives.

Reclaim is an interesting raw material as it reduces the production costs of new rubber articles, due to shorter mixing times and lower power consumption. The processing temperature is lower, and the material has a higher dimensional stability during calandering and extrusion due to the remaining three-dimensional network. The most important advantage of cured articles containing reclaim in terms of properties is an improvement of aging resistance[8].

2.8 EPDM RECYCLING

Most efforts to recycle EPDM-rubber were derived from tire recycling processes. Unfortunately, the recycling of tire rubber, which is a mixture of NR and SBR, cannot directly be applied to EPDM. Sutanto et al.[45] provided an overview of all investigations concerning EPDM recycling so far.

2.8.1 Ground EPDM rubber waste as filler

Ceni and coworkers[46, 47] looked at the effect of ground EPDM vulcanizate on the properties of EPDM rubber. The EPDM waste was ground at room temperature using a mechanical grinder with a silicone abrasive wheel rotating at 2950 rpm. Given that EPDM products contain high oil and filler loadings, EPDM powder may act as a low-modulus reinforcing filler. They found that ambiently ground EPDM vulcanizate (W-EPDM) acts as a filler in raw EPDM (R-EPDM) and its addition results in an increase in Mooney viscosity, but a decrease of scorch time, presumably as a result of accelerator migration from W-EPDM to the matrix R-EPDM. At higher loadings of vulcanizate powder, the maximum vulcanization decreases. This can be attributed to sulfur migration from the matrix to W-EPDM, causing a decrease of the crosslink density of the matrix. The tensile strength, tear strength, hysteresis and elongation at break improved, indicating the reinforcing nature of the carbon-black containing W-EPDM powder. In the case of low-strain modulus and hardness, the filler effect was counterbalanced by the crosslinking effect. A marginal increase in heat build-up and drop in resilience were attributed to the filler effect.

Replacing virgin EPDM by W-EPDM in blends with other polymers[48] was tested and it was found that, although addition of W-EPDM to R-EPDM/PP blends causes an initial drop in the mechanical properties, thermoplastic elastomers with enhanced properties could be obtained at higher loadings of W-EPDM. Up to 45% of R-EPDM can be replaced by W-EPDM without affecting the processability and the physical properties.

Solid EPDM rubber granulate is also used as the main component together with a binding system. The binder is blended with the rubber granulate and other additives such as curatives and chalk and cured into sheets, which are used as floorings[9].

2.8.2 Mechanistic Investigations

Verbruggen et al.[49, 50] investigated the effect of amines as devulcanization aids for EPDM-rubber. They found that EPDM could successfully be reclaimed with several types of amines. In the series of primary, secondary and tertiary aliphatic amines as well as benzylic amines, almost no difference in reactivity was found. The relative decrease in crosslink density obtained with amines was comparable with the results obtained with disulfides, where disulfides resulted in an uncrosslinkable material after reclaiming. 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-H atom was however suggested as the determining factor for the reactivity. The relative decrease in crosslink density was reported to be dependent on the concentration of the devulcanization aid. A higher concentration of amines led to a higher decrease in crosslink density.

2.8.3 Industrial Processes

Toyota developed a technology for continuously reclaiming rubber within a short time (10 minutes), using a twin-screw reactive extruder for vulcanized EPDM[13, 51, 52]. By optimizing the process conditions, which include the reaction temperature for the twin-screw extrusion processing, the shear distortion with special screw geometry and alignment, the screw rotational speed and the quantity of additives such as devulcanization aid and reclaiming oil, the continuous reclaiming process using an extruder was made possible.

The material is cut into pieces of 1 cm^2 and fed into the extruder. Processing oil and devulcanization aid are added to the rubber in a composition of 20:6:1 (weight rubber: weight processing oil: weight devulcanization aid), and the mixture is swollen for at least 24 hours at room temperature. The twin screw extruder is 1.2 meter long, with an output capacity of 5-20 kg/h. The screws have a diameter of 3 cm and rotated up to 500 rpm. The rubber temperature is increased quickly to the reclaiming temperature of 300°C. A temperature within the range of 280°C to 330°C is claimed to be most preferable for sulfur vulcanized EPDM, while the shear stress applied should preferably be between 1 and 15 MPa.

However, the application of this reclaimed EPDM-rubber is limited to parts, which do not require a high function or high quality appearance, such as trunk door weather strips, hose protectors, or headlamp cover seals. A maximum addition of 25% of the reclaimed EPDM is possible, from the process performance point of view, but it improves the compression set of the material.

2.8.4 Microwave Reclaiming of EPDM

The Goodyear Tire & Rubber Company tried to reclaim EPDM-rubber waste with microwave energy[30, 31]. A microwave frequency of either 915 or 2450 MHz and energy between 325 and 1404 kJ/kg was generated. The heating mechanism of EPDM-rubber by microwave is an indirect heating mechanism based on the absorption of the energy by polar groups. EPDM itself is a non-polar polymer, hence, it does not absorb the microwave energy. The latter is absorbed by the carbon black in the EPDM-rubber product, which in turn heats up the molecules in its surrounding by conduction. Since EPDM is usually highly loaded with carbon black, it can be rapidly heated in the microwave field. The mechanical properties after blending microwave reclaimed EPDM with virgin rubber did not deviate much from that of pure virgin rubber.

2.8.5 Ultrasonic Reclaiming of EPDM

Yun, Yashin and Isayev[32, 34, 36] performed research on the ultrasonic reclaiming of (carbon black filled) EPDM rubber. They used continuous extruders, which were preheated at 120°C. In the extruder, EPDM vulcanizate was compressed and conveyed by the screw to the reclaiming zone. The ultrasonic treatment of the rubber occurred in the gap between the horn and the die plate in the reactor. Gap size and ultrasonic amplitude could control the degree of reclaiming: an increase of the ultrasonic amplitude and a decrease of the gap size raised the degree of reclaiming for EPDM vulcanizate.

The reclaimed EPDM-rubbers were revulcanized by using the same recipe and cure conditions as the virgin EPDM. Concerning the dynamic visco-elastic properties, it was found that reclaimed EPDM was a more elastic material than uncured virgin EPDM, and revulcanized EPDM was less elastic than virgin EPDM vulcanizate at the same loss modulus level. It was also found that the tensile strength of revulcanized EPDM was significantly higher than that of the original vulcanizates with elongation at break being practically the same.

Crosslink density and gel fraction measurements indicated that more reclaiming was achieved at higher amplitude for all compositions of filler. However, less reclaiming of carbon black filled rubbers was obtained because a certain portion of ultrasonic energy was consumed to break the physical and chemical bonds between EPDM rubbers and carbon black, which possibly have a lower bond energy than the chemical bonds in polymer chains and crosslinks. Mechanical properties of the revulcanizates deteriorated with an increase in carbon black concentration since the fillers became deactivated under ultrasonic treatment.

Considerably better mechanical properties were obtained in blend vulcanizates containing various amounts of reclaimed rubber and virgin rubber. By addition of up to 25% of reclaimed EPDM rubber into virgin filled rubber, the material properties did not show a significant decrease.

In a comparative analysis of ultrasonically reclaimed unfilled SBR, NR and EPDM rubbers, it was found that it was more difficult to reclaim EPDM than NR and SBR[35]. Reclaiming of EPDM roof-sheeting[33] resulted in a good quality reclaim, which after revulcanization showed more or less equal mechanical properties compared to the virgin compound. The surface smoothness of the revulcanized compounds could be controlled by the process conditions.

2.9 MODEL DESCRIPTION AND ANALYSIS OF CROSSLINK SCISSION AND MAIN-CHAIN SCISSION OF A VULCANIZED RUBBER NETWORK

Most commercial rubber recycling processes involve shearing of the vulcanized rubber at elevated temperatures, causing main-chain scission and crosslink breakage of the cured rubber network to occur simultaneously. There are a few methods to determine whether main-chain scission or crosslink breakage is the dominant process during reclaiming. The sol-gel analysis, developed by Charlesby[53, 54] in his study on the relationship between crosslinking, main-chain scission and gelfraction in irradiated polymers, is based on the amount of soluble polymeric material. Horikx[55] assumed that that these relations were also applicable to determine the solfraction of a rubber sample undergoing network degradation by aging. Dobson and Gordon[56-58] developed another relation between the solfraction and the average fraction of monomers that are part of a crosslink, using Good's theory of stochastic processes.

2.9.1 Sol-Gel Analysis as a Means to Characterize the Creation or Destruction of Polymer Networks

Sulfur-cured rubbers are an example of a three-dimensional polymer network in which the branching units or crosslink sites are variable, but often taken as tetra-functional[59]. Methods based on sol-gel analysis in general neglect network imperfections like dangling chain-ends and trapped entanglements[60].

2.9.1.1 Network Formation by Crosslinking (Charlesby)

According to Charlesby[53, 54], polymers can be classified into two groups, according to their response when exposed to ionizing radiation:

1. Crosslinking of the polymer chains, leading first to an increase in molecular weight and, at sufficient doses, to the formation of an insoluble network;
2. Scission of the molecular chains, resulting in a decrease in average molecular weight.

Both processes occur simultaneously in many polymers, and the classification depends upon which of the two is predominant.

On the basis of a small probability p of breaking a bond, relative to the probability q of forming the bond, Charlesby derived a series of equations for the sol- and gel-fractions during crosslinking, which are generally applicable, irrespective of the molecular weight distribution of the original polymers. Most relevant in the present context are the following quantities and relations:

$$\gamma = \frac{q\overline{M}_n}{w} \qquad (2.1)$$

where γ is the crosslinking index, the average number of crosslinks per original polymer molecule, $\overline{M}_n$ is the number average molecular weight of the original polymer and w is the molecular weight of a monomer in the polymer chain, so that $\overline{M}_n/w$ is the number of monomers in a "number average" original polymer molecule, before crosslinking.

The crosslinking coefficient δ, equal to the average number of crosslinks per “weight average” polymer molecule, is related to $\overline{M}_w$ by:

$$\delta = \frac{q\overline{M}_w}{w} \tag{2.2}$$

where $\overline{M}_w$ is the weight average molecular size of the original polymer.

The gel- and sol-fractions during crosslinking are related to q:

$$g = 1 - s = 1 - \frac{\sum xN_x e^{(-qxg)}}{\sum xN_x} \tag{2.3}$$

where g is the gel-fraction, s is the sol-fraction, x is the number of monomers per primary polymer molecule, N_x is the number of polymer molecules with x monomer units and $\sum xN_x$ is the total number of monomers included in all polymers within the sample.

Equation (2.3) can be further detailed, if the molecular size (or weight) distribution for the primary polymer molecules is defined. For a mono-disperse distribution, all primary molecules are of the same size and the sol- and gel-fractions can be calculated as follows:

$$g = 1 - e^{(-qxg)} = 1 - e^{(-\gamma g)} \tag{2.4}$$

$$s = e^{(-\gamma g)} = e^{-\gamma(1 - s)} \tag{2.5}$$

This is in accordance with the fact that gel formation occurs only if $\gamma > 1$.

For a Poisson distribution, Charlesby defines the molecular weight distribution as:

$$N_x = Np(1 - p)^{(x-1)} \approx \frac{Npe^{-px}}{1-p} \approx Npe^{-px} \qquad \text{for } p<<1 \tag{2.6}$$

where N is the total number of polymer molecules in the distribution.

On basis of this distribution the following relationship for the sol-fraction s and gel-fraction g is derived:

$$s = 1 - g = \frac{1}{(1+\gamma-\gamma s)^2} \tag{2.7}$$

An implicit equation for s reads:

$$s = \frac{(2+\gamma)-\sqrt{\gamma^2+4\gamma}}{2\gamma} \tag{2.8}$$

There are also other relationships derived for this Poisson distribution, which are needed later in this chapter. The average initial molecular weight $\overline{M}_{gel}$ of the molecules incorporated in the gel, is given by:

$$\overline{M}_{gel} = \overline{M}_n \frac{(1+\gamma-\gamma s)}{\gamma} \tag{2.9}$$

The crosslinking index of the gelfraction, γ_{gel}, is equal to:

$$\gamma_{gel} = (1+s)(1+\gamma-\gamma s) \text{ for } \gamma>0.5 \tag{2.10}$$

2.9.1.2 Network Breakdown (Horikx)

Assuming that network breakdown leads to a Poisson distribution of molecular fragments, Horikx[55] used Charlesby's theory to develop a method in which a vulcanized rubber network is broken down again via two routes: main-chain scission and selective crosslink breakage.

As a measure of crosslink density, ν_0 is defined as the number of elastically effective polymer network chains per cm^3 including the sol-fraction before network breakdown. In this thesis, it is referred to as crosslink density. Inversely, $\frac{1}{2}\nu_0$ equals the number of crosslinks per cm^3 of a network for tetra-functional crosslinks. It can be deduced that:

$$\gamma = \frac{\nu_0}{N} \tag{2.11}$$

where N is the number of primary molecules per cm^3 of polymer.

It follows from equation (2.9), that the number of primary molecules per gram of network is given by:

$$N_{gel} = \frac{\gamma N}{(1+\gamma-\gamma s)} = \frac{\nu_0}{(1+\gamma-\gamma s)} \tag{2.12}$$

By combining equations (2.10), (2.11) and (2.12) it follows that the number of chains in the network, $\nu_{0,\,gel}$, is given by:

$$\nu_{0,\,gel} = \gamma_{gel} N_{gel} = \nu_0 (1+s) \tag{2.13}$$

Horikx assumed that the number of network chains, ν_0, is given by the chemically crosslinked chains only. Using equations (2.7) and (2.13), the following relation is obtained:

$$N_{gel} = \nu_0 \sqrt{s} \tag{2.14}$$

According to Flory[59], the number of elastically effective polymer chains in the network, ν_e, as determined by equilibrium swelling measurements, requires a correction for ν_0 to account for dangling chains ends:

$$\nu_e = \nu_0 - 2N \tag{2.15}$$

For tetra-functional crosslinks, it is this ν_e, which is determined via swelling using the well-known Flory-Rehner equation[61]:

$$\nu_e = \frac{v_r + \chi v_r^2 + \ln(1-v_r)}{V_s\left(0.5 v_r - v_r^{1/3}\right)} \tag{2.16}$$

$$v_r = \frac{m_r}{m_r + m_s \dfrac{\rho_r}{\rho_s}} \tag{2.17}$$

where v_r is the polymer volume fraction of the swollen sample, V_s is the solvent molar volume, m_r is the mass of the rubber network, m_s is the mass of solvent in the sample at equilibrium swelling, ρ_r is the density of the rubber, ρ_s is the density of the solvent and χ is the Flory-Huggins polymer-solvent interaction parameter.

The number of elastically effective chains per unit volume of network is then given by combining equations (2.12), (2.13) and (2.14):

$$\nu_{gel} = \nu_{0,gel} - 2N_{gel} = \nu_0(1+s) - 2\nu_0\sqrt{s} \tag{2.18}$$

$$\nu_{gel} = \nu_0\left(1-\sqrt{s}\right)^2 \tag{2.19}$$

During main-chain scission, the number of crosslinks, ν_0, remains constant and soluble matter is created by randomly detaching small molecular fragments from the network. By virtue of equation (2.11), γ decreases as much as N increases. If equation (2.19) is formulated before (i) and after (f) the network scission and the ratio of both is taken as the relative decrease in network chain density, it can be expressed as a function of the soluble fractions before and after scission of the sample:

$$1-\frac{\nu_f}{\nu_i} = 1-\left[\frac{\left(1-s_f^{1/2}\right)^2}{\left(1-s_i^{1/2}\right)^2}\right] \tag{2.20}$$

where s_i is the soluble fraction of the untreated vulcanizate, s_f is the soluble fraction of the fractured network, ν_i is the crosslink density of the untreated vulcanizate and ν_f is the crosslink density of the fractured network.

To determine the soluble fraction in case of crosslink scission, N is taken constant and γ decreases. In this case, ν_0 remains in the equation. The relative decrease in crosslink density is now dependent on the crosslink index γ:

$$\nu_e = \nu_{0,gel} - 2N_{gel} = \nu_0\left(1-\sqrt{s}\right)^2 = \gamma N\left(1-\sqrt{s}\right)^2 \tag{2.21}$$

The relation between the effective number of network chains before and after the treatment is now given by:

$$1-\frac{\nu_f}{\nu_i} = 1-\left[\frac{\gamma_f}{\gamma_i}\frac{\left(1-s_f^{1/2}\right)^2}{\left(1-s_i^{1/2}\right)^2}\right] \tag{2.22}$$

where the parameters γ_f and γ_i are the average number of crosslinks per chain in the remaining insoluble network after and before crosslink scission, respectively.

Horikx used the measurement of the network chain density in the gel-fraction by equilibrium swelling together with the value measured of $\overline{M}_n$ measured by GPC to calculate γ_i:

$$\gamma_i = \frac{\nu_i \overline{M}_n}{\rho} \tag{2.23}$$

Another way to determine γ_i is by measuring the residual sol content immediately after vulcanization and then making use of equation (2.8). The experimental data are in better agreement with values calculated with equation (2.22) if γ_i is calculated according to equation (2.7), than according to equation (2.23)[62].

2.9.1.3 Intermediate Stages between Crosslink Breakage and Main-Chain Scission (Yashin and Isayev)

The disadvantage of the Horikx treatment is that it describes only the two extremes: pure crosslink breakage or pure main-chain scission. For intermediate cases, Yashin and Isayev[63] used the model of Dobson and Gordon to describe the sol-gel formation of devulcanized rubbers.

On basis of simulations of branched polymers, Dobson and Gordon[56-58] developed a model for a rubber network. This network is represented by a tree, starting from a primary chain or first generation, called the stem, to which chains of the second generation are attached, called the branches, and further branches of the third generation etc. Crosslinks connect pairs of chains of succeeding generations. Dobson and Gordon also developed a relation between the solfraction and the average fraction of monomers forming crosslinks similar to that of Charlesby. For randomly crosslinked mono-disperse primary chains they arrived at exactly the same equation (2.5). For polymer chains with a Flory or Poisson molecular weight distribution, they arrived at sol-fractions as given in the following equation:

$$s = \frac{2p + (1+p)\left[q(1-p) - \left(q^2\{1-p\}^2 - 4q\{1-p\}^2 + 4q\{1-p\}\right)^{1/2}\right]}{2q(1-p)^2} \tag{2.24}$$

This equation deviates from the original equation of Gordon in the sense that the Charlesby formalism for p is used, contrary to the commonly employed p for the extent of polymerization reaction as employed by Gordon[62].

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

$$1 - p(t) = (1 - p_0)^{e^{-k_p t}} \tag{2.25}$$

$$q(t) = q_0 e^{-k_q t} \tag{2.26}$$

where k_p and k_q are the scission rate constants for main-chain scission and crosslink breakage, respectively. In the same way as Horikx did, Yashin and Isayev normalized ν_e to the network chain density for the still fully vulcanized sample and did the same for the solfraction. By simulating network degradation in time and adjusting the ratio of the scission constants, the same type of curves can be constructed as those of Horikx. When k_p/k_q approaches infinity, practically only polymer chains are broken and when k_p/k_q approaches 0, only crosslinks are broken. By taking various ratios between k_p and k_q, intermediate curves can be constructed.

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Chapter 3

The Relationship between Crosslink System, Network Structure and Material Properties of Carbon Black Reinforced EPDM

The crosslink density and sulfur-ranks of crosslinks formed during vulcanization of a carbon black reinforced ENB-EPDM compound are analyzed as function of the selected curing system: conventional, semi-efficient, efficient and nitrosamine-safe. Each vulcanization system results in a specific crosslink concentration and sulfur-rank distribution: mono-, di- and polysulfidic of nature. Tensile properties, tear strength and compression set of the vulcanized materials, turn out to practically only depend on overall crosslink density, as resulting from the particular curing systems and vulcanization times. All trends in properties coincide when plotted as a function of the overall crosslink density. Surprisingly, the crosslink distribution: the ratios of mono- to di- and polysulfidic crosslinks, has only a minor effect on these properties. The differences in sulfur-rank as a function of the chosen vulcanization system turn out to be too small for EPDM to have a significant effect.

The trends found for all mechanical properties fit to the generally reported mastercurves of the properties versus crosslink density, except for elongation at break, which shows a very sharp initial increase before decreasing with increasing crosslink density.

The work described in this chapter has been submitted for publication to European Polymer Journal.

3.1 INTRODUCTION

EPDM is currently the largest non-tire elastomer and the market is still growing[1]. As a consequence, the amount of EPDM waste will keep on growing, making recycling and devulcanization a more and more important issue from a technological, economical and ecological point of view.

Rubber recycling has been common practice for a long period of time already and production waste and/or end-of-life products are currently recycled by several methods including repeated use[2], material recycling[3-5] (reclaiming, devulcanization, grinding and surface activation), recovery of base chemicals[3] (pyrolysis, gasification and hydrogenation) and energy recycling[3] (incineration), as mentioned more explicitly in Chapter 2.

Every rubber product is crosslinked with its own specific vulcanization system, resulting in variable properties. Basically, there are three types of sulfur crosslinks present in rubbers, namely C–S–C (monosulfidic), $C–S_2–C$ (disulfidic), and $C–S_x–C$ (polysulfidic). The crosslink length distribution and the sulfur-rank x in ENB-EPDM vulcanizates depend on:

(a) accelerator and crosslinker types and concentrations;
(b) curing time and temperature.

(a) Vulcanization systems are classified as CONventional Vulcanizing (CONV), Semi-Efficient Vulcanizing (SEV) and Efficient Vulcanizing (EV), based on the level of sulfur and the ratio of accelerator to sulfur employed, as shown in Table 3.1. A CONV vulcanization system is characterized by a low ratio of accelerators to sulfur, which results in the formation of a high percentage of polysulfidic crosslinks and cyclic structures[6]. A vulcanization system with a low ratio of sulfur or even sulfur-free, but containing a sulfur donor instead, is called an EV vulcanization system. A SEV vulcanization system has an accelerator-to-sulfur ratio in between those of the CONV and EV vulcanization systems. With increasing accelerator to sulfur ratio, the proportion of the shorter mono- and disulfidic crosslinks increases.

Table 3.1 Compositions of CONV, SEV and EV vulcanization systems in phr (parts per hundred rubber)

Type	Sulfur (phr)	Accelerator (phr)	Accelerator/Sulfur ratio
CONV	2.0-3.5	1.2-0.4	0.1-0.6
SEV	1.0-1.7	2.5-1.2	0.7-2.5
EV	0.8	5.0-2.0	>2.5

(b) In the initial stages of vulcanization, more C–S_x-C (x = 4 or 5) bonds are found than in a later stage: during the curing process, longer crosslinks are desulfurized[7] and converted into shorter crosslinks, all the way down to monosulfidic ones. The latter are mainly formed when the amount of accelerators is much larger than the amount of sulfur (elemental sulfur or released from sulfur donors). Curing at high temperatures results in a lower level of polysulfidic crosslinks than low temperature curing, even if the crosslink densities are identical. High accelerator-to-sulfur ratios, prolonged curing times and higher curing temperatures result in vulcanizates containing relatively low percentages of polysulfidic crosslinks. Side reactions as frequently observed for polydiene elastomers, such as cis-trans isomerization, allylic rearrangement and/or the formation of conjugated dienes and trienes, do not occur during vulcanization of ENB-containing EPDM: the tris-alkyl substituted unsaturation in ENB has a high stability and is isolated from other ENB units[7, 8].

As mentioned before in Chapter 2, nitrosamine-safe (NS) curing packages were developed to replace curing systems which develop nitrosamines during the vulcanization process. Gasses generated during curing consist for the major part of volatile components of extender oils and degradation products of the accelerators. Secondary N-nitrosamines, which are formed during vulcanization as condensation products from secondary amines released by certain accelerators and nitrous gasses, are known to belong to the most carcinogenic species to mankind. They are generated especially during vulcanization with most ultra-accelerators, like thiurams and dithiocarbamates. EPDM requires ultra-accelerators as its intrinsic curing activity is low. The traditionally used ultra-accelerators can be replaced by nitrosamine-safe systems, but the costs of these systems are much higher: due to the higher molecular weight but with the same reactivity on a molar basis of these nitrosamine-safe accelerators, larger amounts on a weight-basis have to be used[9-11].

The most ideal way of recycling is devulcanization, in which all sulfur crosslinks are broken, while the polymer chains remain intact and can be reprocessed again. Devulcanization can be done thermally[3], mechanically, chemically[4] and with micro- or ultrasound waves[12-15]. In all methods, except for chemical devulcanization, a combination of crosslink scission and main-chain scission of the polymer chains occurs[16]. Only by chemical devulcanization it is in principle possible to exclusively break sulfur crosslinks. However, sulfur cured vulcanizates have a certain crosslink length distribution, and the chemicals described so far in literature[4] are only able to break di- and polysulfidic crosslinks. Scission of monosulfidic bonds is possible only by using toxic or even carcinogenic chemicals.

The main goal of the present project is to analyze EPDM vulcanizates with different crosslink-characteristics and to devulcanize these materials. In this chapter a carbon black reinforced EPDM masterbatch is vulcanized in four different ways with a CONV, SEV, EV and NS curing system. The process of crosslink formation during curing of these compounds is investigated and the optimum curing time is determined. Each vulcanizate is characterized with respect to crosslink concentration and differences in percentages of mono-, di- and polysulfidic crosslinks. In order to being able to evaluate the quality of the devulcanizates later in this thesis, it is necessary to know the characteristics and mechanical properties of the virgin rubber compounds.

3.2 EXPERIMENTAL

Compound recipes and materials – The EPDM-rubber masterbatch was premixed on large scale by DSM Elastomers B.V., the Netherlands. This masterbatch had a typical composition for an automotive door seal profile and was vulcanized according to the recipes shown in Table 3.2.

Table 3.2 Composition of the masterbatch and curing recipes

Material	Compound			
Masterbatch	CONV (phr)	SEV (phr)	EV (phr)	NS (phr)
EPDM	100			
ZnO	5			
Stearic acid	1			
Carbon black N550	70			
Carbon black N772	40			
Paraffinic oil	70			
Curing system				
TMTD	1.0		1.0	
MBT	0.5			
MBTS-80				1.3
ZBEC-70				0.7
ZDBP-50				3.5
DPTH		0.8		
ZDMC		1.5		
CBS		1.5	1.5	
DPTT			0.8	
Sulfur	1.5	0.5		1.0

The EPDM used in this investigation: Keltan 2340A, consists of 53 wt% ethylene, 41 wt% propylene and 6 wt% 5-ethylidene-2-norbornene (ENB), not oil-extended. The Mooney viscosity ML(1+4)125°C is 25 MU. The plasticizing paraffinic oil used in the masterbatch is Sunpar 2280 (Sunoco, Inc.). Carbon black N550 gives the final vulcanizate medium abrasion resistance, high strength and a high resilience. Furthermore, it gives the compound low shrinkage and die swell as well as fast and smooth extrusion behavior. It is in general used in tire carcasses, tubing, cable jacketing, and in extruded goods requiring excellent dimensional stability. Carbon black N772 is characterized as a moderate reinforcer, which gives high resilience and excellent dynamic properties and is generally used in tire carcasses and mechanical goods. The masterbatch had a density of 1.108 kg/m^3.

The curing additives used for the vulcanization are shown in Table 3.3. The number included in the accelerator names in Table 3.2 represents the percentages of accelerator in a preblended form with an inert binder, in order to reduce dust.

Table 3.3 Materials used for vulcanization

Material	Abbr.	Supplier
Sulfur	S	Merck
2-Mercaptobenzothiazole	MBT	Merck
Tetramethylthiuram-disulfide	TMTD	Flexsys
N-cyclohexyl-2-benzothiazole-sulfenamide	CBS	Flexsys
Dipentamethylene-thiuramtetrasulfide	DPTT	Flexsys
Zinc-dimethyldithiocarbamate	ZDMC	Rhein Chemie Rheinau GmbH
Dimercaptobenzothiazole-disulfide	MBTS	Rhein Chemie Rheinau GmbH
Zinc-dibutyldithiophosphate	ZDBP	Rhein Chemie Rheinau GmbH
Zinc-dibenzyldithiocarbamate	ZBEC	Rhein Chemie Rheinau GmbH
Dipentamethylene-thiuramhexasulfide	DPTH	Rhein Chemie Rheinau GmbH

Decahydronaphtalene, a mixture of the cis- and trans-isomer with a purity of 98%, was used for swelling measurements. The solvents acetone and tetrahydrofuran (THF) (Biosolve) were used for extractions. 2-Propanethiol ≥98% pure (Merck), 1-hexanethiol 95% pure, piperidine 99% pure, n-heptane 99% pure (all from Sigma Aldrich) and a petroleum-ether fraction between 40°C and 60°C (Across) were used for the thiol/amine reactions.

Mixing and vulcanization – The curing additives shown in Table 3.2 were mixed into the EPDM-rubber masterbatch at room temperature on a laboratory size Schwabenthan two-roll mill (15 x 33 cm Polymix 80) with a friction ratio of 1:1.25. The compounds were sheeted off at a thickness of approximately 2 mm. The cure characteristics were determined using a Rubber Process Analyzer RPA 2000 from Alpha Technologies with a frequency of 0.833 Hz and a strain of 0.2 degrees at 170°C. The compounds were vulcanized in a Wickert laboratory press 1600/5×4/3 at 170°C and 100 bar for different periods of time to see the effect of time on the curing process and the resulting properties. The cured sheets had a thickness of 2 mm for tensile- and tear test samples, and a circular shape of 13x6 mm for compression set samples.

Tensile and tear tests – 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 tensile tests require a preload of 1N. Tear tests were carried out on nicked angle test pieces according to ISO 34. The tests were performed in both cases at a constant crosshead speed of 500 mm/min, using a load cell of 500N. The tear strength was calculated as:

$$\text{Tear strength} = \frac{F_{max}}{d} \tag{3.1}$$

where:
F_{max} = maximum force at which the test specimen breaks;
d = thickness of the test specimen.

Compression set – Compression set tests were performed on cylindrical shaped specimens with a diameter of 13 mm and a thickness of 6 mm at 23°C and 70°C for 24 hrs according to ISO 815. The samples were compressed between two steel plates using space bars with a thickness of 75% of the original sample thickness. The allowed recovery time after 24 hrs compression was 30 minutes. The compression set was calculated as:

$$\text{Compression set} = \frac{h_0 - h_2}{h_0 - h_1} \times 100\% \tag{3.2}$$

where:
h_0 = initial height of the sample;
h_1 = height of the sample during compression at a set temperature and time;
h_2 = height of the sample after recovery for the specified time.

Hardness – The hardness of the samples was measured using a Zwick Hardness-tester Shore A type according to DIN 53503.

Extractions – The soluble and insoluble fractions of the vulcanized compounds were determined by extraction in a soxhlet apparatus: initially for 24 hrs in acetone in order to remove polar substances like remains of activators and accelerators, followed by an extraction for 48 hrs in THF to remove the apolar components: oil and non-crosslinked polymer residues. The extraction was followed by drying the samples in a vacuum oven at 40°C and determining the weight loss until no further significant amount of solvent could be evaporated. The sol fraction was defined as the sum of the soluble fraction in acetone and THF.

Equilibrium swelling – The degree of swelling was measured on extracted samples in order to determine the crosslink density of the vulcanized compounds. The extracted EPDM samples were swollen in decahydronaphtalene 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[17], equations 3.3 and 3.4:

$$\nu_e = \frac{v_r + \chi v_r^2 + \ln(1 - v_r)}{V_s\left(0.5v_r - v_r^{1/3}\right)} \tag{3.3}$$

$$v_r = \frac{m_r}{m_r + m_s \frac{\rho_r}{\rho_s}} \tag{3.4}$$

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.

The Flory-Huggins parameter for the EPDM-decahydronaphtalene interaction was calculated using the relationship $\chi = 0.121 + 0.278v_r$, as reported by Dikland[18]. The Flory-Rehner equation is strictly spoken only valid for non-filled systems. For filled compounds the Kraus[19] correction should be applied, especially in cases when compounds with different filler compositions have to be compared. As in this case the compounds have the same filler composition, the relative crosslink densities of the four EPDM compounds can well be compared, without the Kraus correction.

Crosslink distributions – The specific sulfur rank distributions of the crosslinks in the vulcanizates were studied using thiol/amine chemical probes[20-23]. The thiol/amine probes were directly applied to the swollen samples used for the overall crosslink density determinations to ensure a good diffusion of the thiol/amine chemical probes. A solution of 0.4M 2-propanethiol and 0.4M piperidine in n-heptane was applied for 2 hrs at room temperature to selectively cleave polysulfidic crosslinks. 1M 1-hexanethiol in piperidine was used for 48 hrs at room temperature to break the poly- plus disulfidic crosslinks. The combination of the two treatments now allows for discrimination between the mono-, di- and polysulfidic crosslinks. The reactions were terminated by putting the samples in excess petroleum ether for 24 hrs, followed by soxhlet extraction in petroleum ether for another 24 hrs and in THF again for 24 hrs. The mono- and the sum of mono- and disulfidic crosslink densities of the samples after treatment were determined with equilibrium swelling for 72 hrs in decahydronaphtalene according to equation 3.3. A simple subtraction from the overall crosslink density before treatment results in the mono-, di-, and polysulfidic crosslink densities, separately.

3.3 RESULTS

3.3.1 Influence of Vulcanization Time on Physical and Mechanical Properties

Table 3.4 and Figure 3.1 show the cure characteristics of the EPDM compounds vulcanized with four different curing systems at 170°C. At lower curing temperatures all compounds show a marching modulus within the testing time of 30 minutes, while at curing temperatures higher than 170°C reversion occurs. The optimum curing times, t_{90}, differ significantly for the four systems. The maximum torque decreases in the order of the compound with the CONV curing system, over the SEV- and NS-cured compounds, to the EV-cured compound, indicating a decrease in crosslink density. The SEV-cured compound vulcanizes much faster than the NS-cured compound, but finally reaches approximately the same torque level.

Table 3.4 Cure characteristics

Compound	Vulcanization time at 170°C (s)							Maximum torque (dN·m)
	t_{02}	t_{50}	t_{60}	t_{70}	t_{80}	t_{90}	$2xt_{90}$	
CONV	48	174	213	262	334	481	961	8.7
SEV	26	105	116	134	160	221	442	6.6
EV	26	207	222	242	269	347	694	3.9
NS	45	211	265	335	437	628	1256	6.9

The various characteristic times (t_{xx}) mentioned in Table 3.4 correspond to the percentages (xx) of the actual torque increase, the maximum minus minimum torque in the rheograms. t_{02} is more commonly designated as “scorch time”, and t_{90} often as “optimum cure time”.

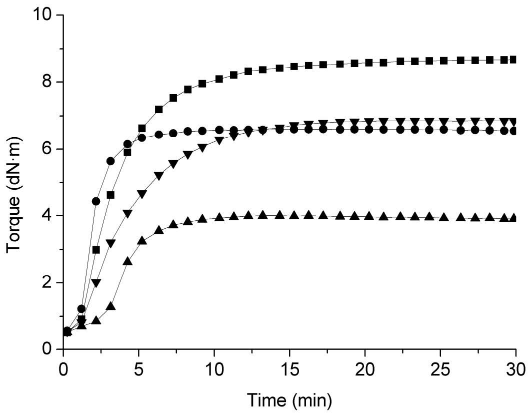

Figure 3.1: Rheograms of the differently vulcanized EPDM compounds at 170°C; (■): CONV; (•): SEV; (▲): EV and (▼): NS

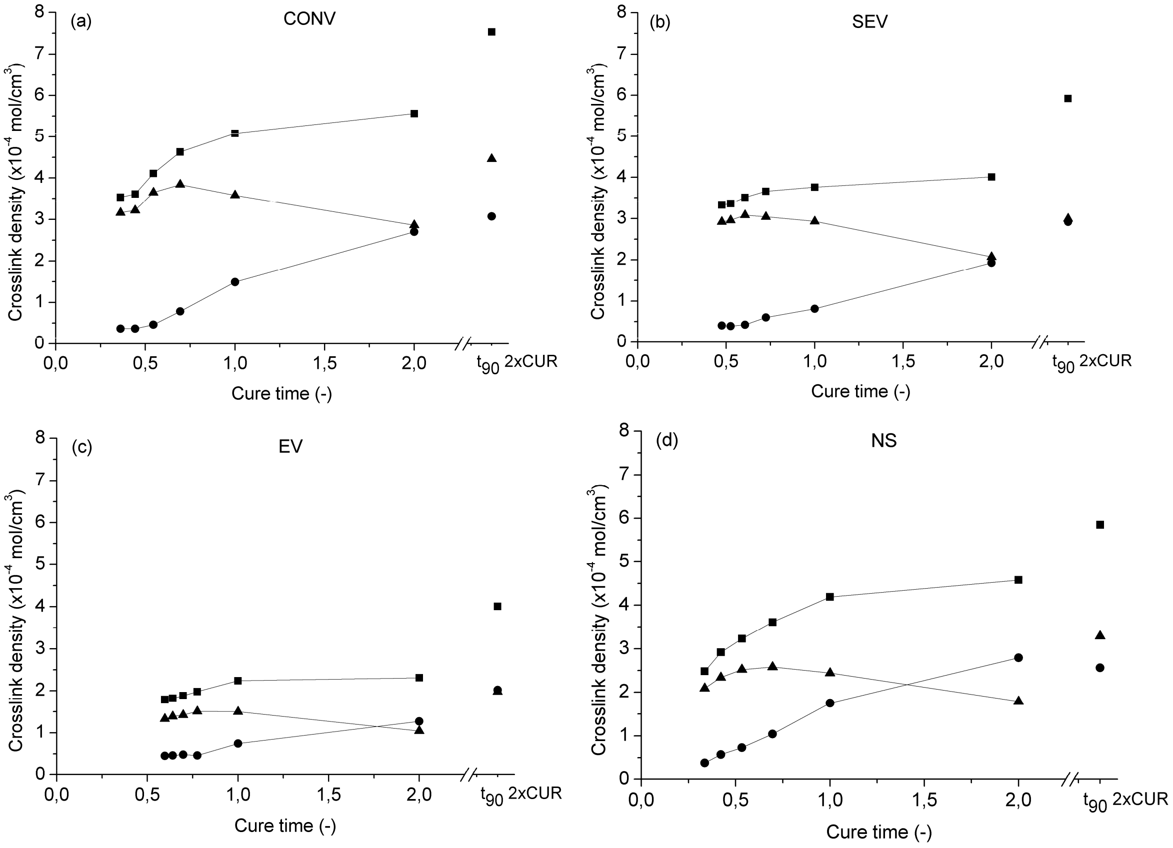

Figure 3.2: Specific crosslink densities versus normalized cure time (t_{90} = 1) of compounds (a) CONV; (b) SEV; (c) EV and (d) NS; (■): Overall; (●): Mono- plus disulfidic and (▲): Polysulfidic crosslink density

The trends of crosslink formation in time and network sulfur rank composition during vulcanization, given in actual concentrations and in percentages of the overall crosslink densities, are illustrated in Figure 3.2; the values are given in Table 3.5.

t_{90} 2xCUR means that the sample contains the double amount of curatives and is vulcanized till t_{90} belonging to this compound. In cases where the sum of the concentrations of mono- and disulfidic crosslinks is given, the concentrations could not be separated as the concentration of the monosulfidic bonds was below the detection limit.

Table 3.5 Specific crosslink densities of the different compounds as functions of curing time

	Sulfidic crosslink density (x10^{-4} mol/cm^3)					Sulfidic crosslink density (%)			
	Overall	Mono	Mono and Di	Di	Poly	Mono	Mono and Di	Di	Poly
CONV									
t_{50}	3.53	-	0.37	-	3.16	-	10	-	90
t_{60}	3.61	-	0.37	-	3.24	-	10	-	90
t_{70}	4.11	-	0.46	-	3.65	-	11	-	89
t_{80}	4.63	-	0.78	-	3.83	-	17	-	83
t_{90}	5.08	0.90	-	0.59	3.59	18	-	12	70
2xt_{90}	5.56	0.63	-	2.07	2.86	11	-	37	52
t_{90} 2xCUR	7.53	0.93	-	2.14	4.46	12	-	28	60
SEV									
t_{50}	3.33	-	0.40	-	2.93	-	12	-	88
t_{60}	3.36	-	0.39	-	2.97	-	12	-	88
t_{70}	3.51	-	0.43	-	3.08	-	12	-	88
t_{80}	3.66	-	0.60	-	3.06	-	16	-	84
t_{90}	3.76	-	0.83	-	2.93	-	22	-	78
2xt_{90}	4.01	0.98	-	0.96	2.07	24	-	24	52
t_{90} 2xCUR	5.92	0.44	-	2.48	3.00	7	-	42	51
EV									
t_{50}	1.79	-	0.46	-	1.33	-	25	-	75
t_{60}	1.82	-	0.45	-	1.37	-	25	-	75
t_{70}	1.88	-	0.47	-	1.41	-	26	-	74
t_{80}	1.98	-	0.46	-	1.50	-	23	-	77
t_{90}	2.24	-	0.74	-	1.50	-	33	-	67
2xt_{90}	2.31	0.96	-	0.31	1.04	42	-	13	45
t_{90} 2xCUR	4.01	0.94	-	1.09	1.98	23	-	27	50
NS									
t_{50}	2.48	-	0.39	-	2.09	-	15	-	85
t_{60}	2.92	-	0.58	-	2.34	-	20	-	80
t_{70}	3.23	-	0.72	-	2.51	-	23	-	77
t_{80}	3.61	-	1.03	-	2.58	-	29	-	71
t_{90}	4.19	0.46	-	1.29	2.44	11	-	31	58
2xt_{90}	4.58	0.73	-	2.06	1.79	16	-	45	39
t_{90} 2xCUR	5.85	0.48	-	2.08	3.29	8	-	36	56

For all compounds, the overall crosslink density increases with increasing curing times. The concentration of polysulfidic bonds increases in the beginning and then decreases. However, the percentage of these bonds in relation to the overall crosslink density steadily decreases from the very beginning: polysulfidic bonds are chemically less stable and are transformed into di- and monosulfidic crosslinks. The actual concentrations and percentages of mono- and disulfidic crosslinks both increase in time for all compounds.

Figure 3.3 shows a slight increase in insoluble fraction with increasing overall crosslink density, which levels off at a certain crosslink concentration. A substantial part of the soluble fraction is the 70 phr oil, corresponding to 24.5 wt%. The carbon black and ZnO-loadings add up to a total of 40.2 wt%, and are included in the insoluble fraction. It demonstrates that at overall crosslink densities of approximately 3×10^{-4} mol/cm^3 and higher, practically no soluble uncrosslinked rubber polymer remains. However, this increase in insoluble fraction is less than expected: apparently at a crosslink density of 1.5×10^{-4} mol/cm^3 a good network is already achieved.

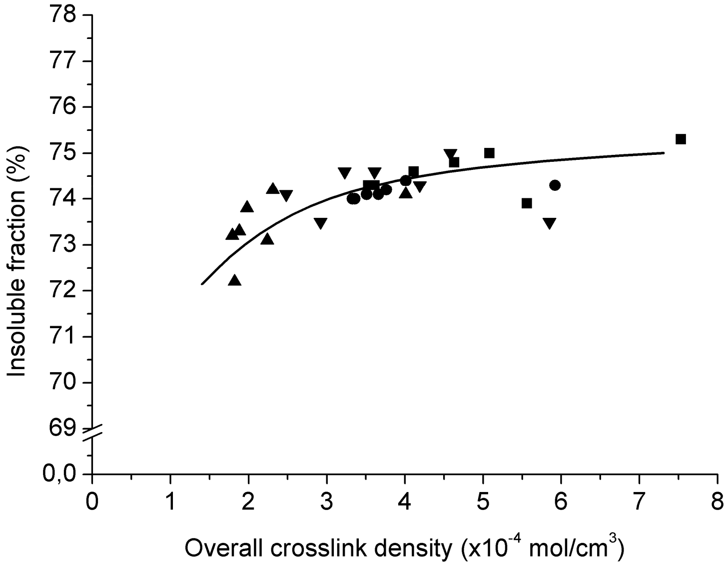

Figure 3.3: Insoluble fractions of the four differently vulcanized EPDM compounds versus overall crosslink density; (■): CONV; (•): SEV; (▲): EV and (▼): NS

The mechanical properties of the separate compounds after curing for different times are shown in Table 3.6. The CONV-, SEV- and NS-cured compounds show a decrease of elongation at break and tear strength with increasing curing time, thus with increasing crosslink density. The EV-cured compound shows a maximum in elongation at break and tear strength with increasing crosslink density. All compounds show an increase in tensile strength with increasing curing time. Only the EV-cured compound shows an increase in tensile strength when using double the amount of curatives, relative to single loading.

Table 3.6 Mechanical properties of the differently vulcanized compounds at different curing times

	M_{100} (MPa)	M_{300} (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)	Hardness (Shore A)
CONV						
t_{50}	2.0	6.0	10.5	595	35.0	50.6
t_{60}	1.9	6.1	10.5	584	34.2	51.9
t_{70}	2.4	7.1	11.2	508	31.9	54.6
t_{80}	2.9	8.2	11.8	447	30.4	56.9
t_{90}	3.4	10.0	11.7	363	24.0	59.1
$2xt_{90}$	3.7	11.3	11.9	317	17.6	62.0
t_{90} 2xCUR	5.1	-	10.9	228	13.4	68.4
SEV						
t_{50}	1.5	5.2	10.1	680	34.1	47.3
t_{60}	1.6	5.2	10.6	669	32.7	48.9
t_{70}	1.5	5.2	10.6	658	31.8	49.4
t_{80}	1.8	5.8	11.2	619	31.5	50.2
t_{90}	2.0	6.2	11.6	584	28.8	51.7
$2xt_{90}$	2.3	6.8	11.7	521	20.4	53.5
t_{90} 2xCUR	3.3	8.8	10.5	366	14.2	63.2
EV						
t_{50}	0.6	1.3	1.6	426	22.2	41.8
t_{60}	0.7	1.6	2.3	482	30.8	42.9
t_{70}	0.7	1.7	2.9	574	32.9	43.5
t_{80}	0.9	2.3	4.8	791	35.6	43.8
t_{90}	1.2	3.6	7.9	836	39.3	45.4
$2xt_{90}$	1.2	3.9	8.2	760	40.4	46.9
t_{90} 2xCUR	2.0	5.9	11.0	598	28.0	57.9
NS						
t_{50}	1.2	3.7	7.6	779	37.7	45.9
t_{60}	1.4	4.4	9.0	719	35.0	47.7
t_{70}	1.5	4.9	9.8	674	33.0	51.2
t_{80}	1.9	5.6	10.9	627	29.8	55.6
t_{90}	2.3	6.8	11.6	526	27.2	56.2
$2xt_{90}$	2.6	8.4	11.4	433	22.1	58.2
t_{90} 2xCUR	3.2	8.8	10.3	354	16.1	62.9

Figure 3.4 shows the mechanical properties of all compounds as a function of the crosslink density: surprisingly, all properties fit to the same mastercurves, independent of the curing system, but dependent on the crosslink density. The different curing systems determine the concentration and length distribution of the crosslinks, but the crosslinks distribution apparently does not play an appreciable role for the mechanical properties of these compounds. The trends in properties of the EV-cured compounds are continued by the properties of the SEV- and NS-cured compounds and, finally by the properties of the CONV-vulcanized compounds for the highest crosslink densities.

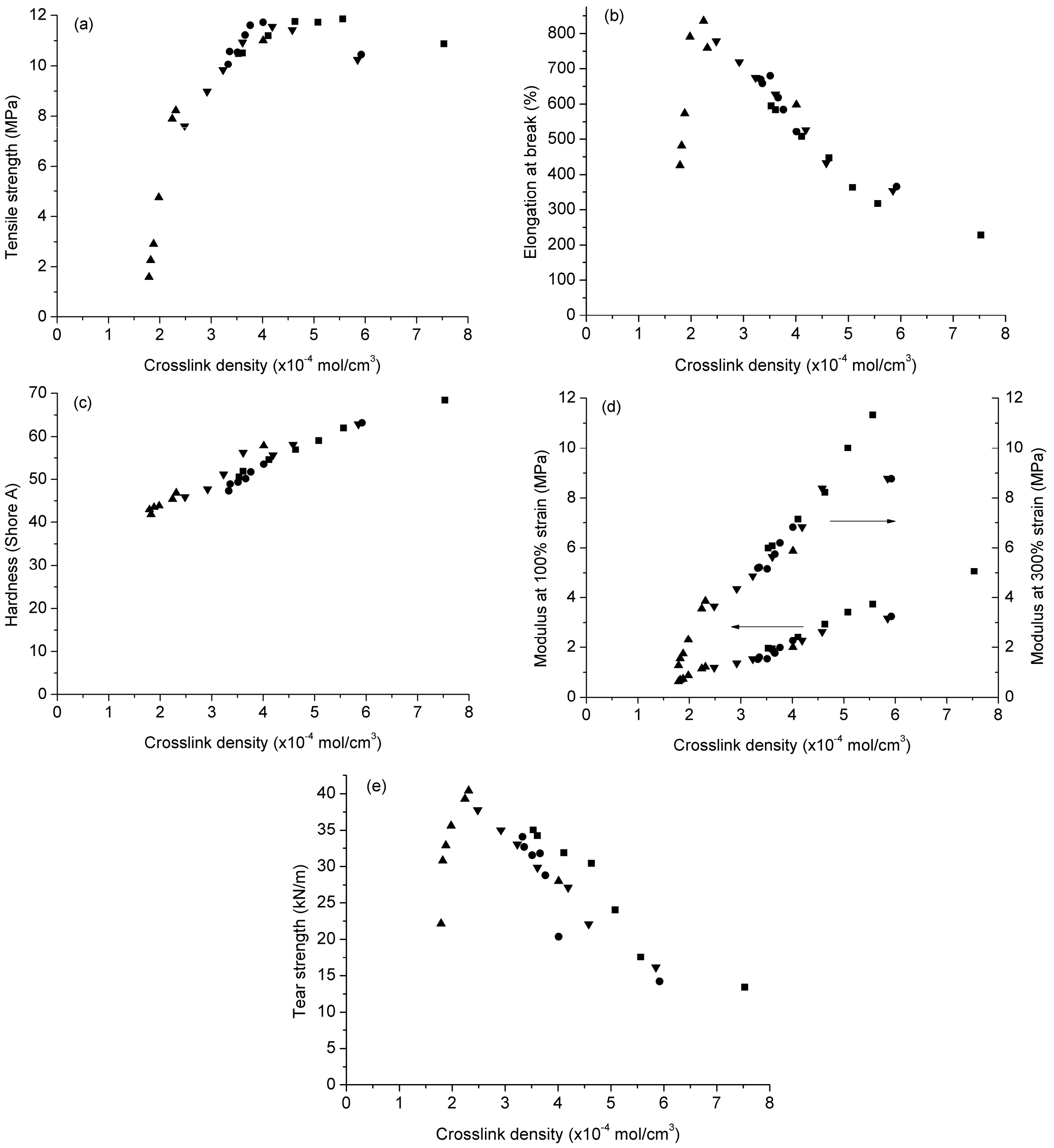

Figure 3.4: (a) Tensile strength; (b) elongation at break; (c) hardness; (d) modulus at 100% and 300% strain and (e) tear strength of differently vulcanized EPDM compounds versus the overall crosslink density; (■): CONV; (•): SEV; (▲): EV and (▼): NS

From these mastercurves it is obvious that the tensile strength initially steeply increases with increasing crosslink density but this increase finally levels off to a certain extent at a crosslink density of approximately 4×10^{-4} mol/cm^3. Elongation at break decreases steadily with increasing crosslink density, after a very sharp initial increase. The tear strength values show the same trend: a maximum at a crosslink density of approximately 2.5×10^{-4} mol/cm^3. The hardness and moduli at 100% (M_{100}) and 300% (M_{300}) strain increase with increasing crosslink density, although at high crosslink densities the moduli of the SEV- and NS-cured compounds tend to level off.

3.3.2 Characterization of the Thoroughly Vulcanized Compounds

The four different compounds were cured for t_{90} + 130 seconds: 130 seconds additional were taken to make up for the slower heating of thicker specimens in the press compared to the cure-rheometer. The crosslink densities, crosslink distributions and the percentages of insoluble fraction of the four compounds are given in Table 3.7.

When the insoluble fraction is determined based on the polymer content only, it is called the gel fraction. For the calculation of the gelfraction the assumption is made that ZnO, sulfur and carbon black are fixed within the network and contribute to the insoluble fraction. The other chemicals, in particular the oil and accelerator residues, may be extracted out of the samples.

Table 3.7 Crosslink densities and insoluble fractions of the thoroughly cured EPDM compounds at 170°C

Compound	Crosslink density ($\times 10^{-4}$ mol/cm^3)				Insoluble fraction (%)	Gel fraction (%)
	Overall	Monosulfidic	Disulfidic	Polysulfidic		
CONV	5.32	0.81 (15%)	1.60 (30%)	2.90 (55%)	75.1	>100
SEV	4.04	1.00 (25%)	1.02 (25%)	2.02 (50%)	74.1	>100
EV	2.23	1.17 (52%)	1.08 (48%)		71.9	93
NS	4.22	0.45 (11%)	2.30 (55%)	1.47 (35%)	74.3	>100

The insoluble fractions differ only slightly: the soluble fractions consist almost completely of oil, which represents 24.5 wt% of the recipe. However, the crosslink densities of the compounds show significant differences in the amounts of crosslinks as well as in the distribution of the lengths of the crosslinks. The CONV-cured compound contains the highest amount of crosslinks, of which only 15% is monosulfidic. The EV-cured compound has the lowest crosslink density, of which more than 50% is monosulfidic. The SEV- and NS-cured compounds have equal overall crosslink densities, but with a totally different sulfur rank distribution.

The stress-strain curves of the four differently vulcanized EPDM compounds, as shown in Figure 3.5, show that the elongation at break value increases, while the M_{100} and M_{300} decrease with decreasing crosslink density. The tensile strength of the EV-cured compound is significantly lower than the other compounds, which have comparable tensile strength values.

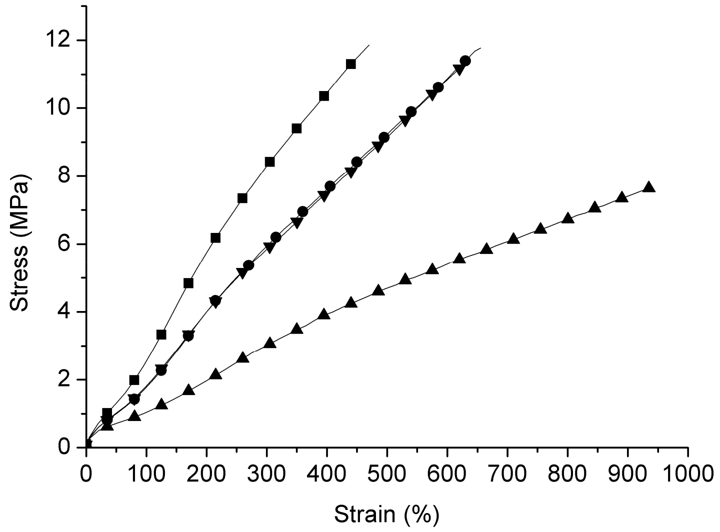

Figure 3.5: Stress-strain curves of the four differently vulcanized EPDM compounds; (■): CONV, crosslink density 5.32×10^{-4} mol/cm^3; (•): SEV, crosslink density 4.04×10^{-4} mol/cm^3; (▲): EV, crosslink density 2.23×10^{-4} mol/cm^3 and (▼): NS, crosslink density 4.20×10^{-4} mol/cm^3

The compression sets, both at 23°C and 70°C after 24 hours, and the tear strength values are given in Figures 3.6 and 3.7.

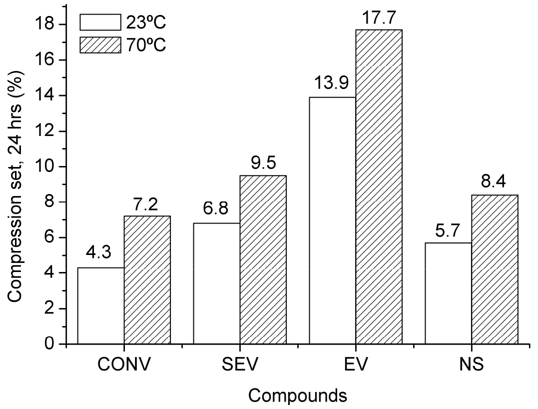

Figure 3.6: Compression set at 23°C and 70°C of the differently vulcanized EPDM compounds

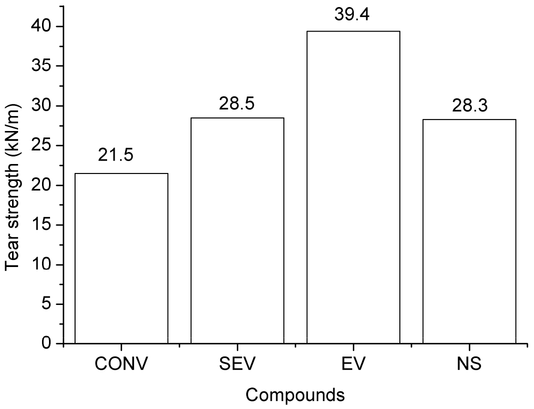

Figure 3.7: Tear strength of the differently vulcanized EPDM compounds

Compression set and tear strength show opposite behavior. Compression set, both at 23°C and 70°C, deteriorates with decreasing crosslink density, while tear strength improves with decreasing amounts of crosslinks. Again, the SEV- and NS-cured compounds show similar properties, in between those of the CONV- and EV-cured compounds.

As the basic composition of the masterbatch is the same for all four compounds, it is possible to compare the properties versus the overall crosslink densities irrespective of the cure system, as shown in Figure 3.8.

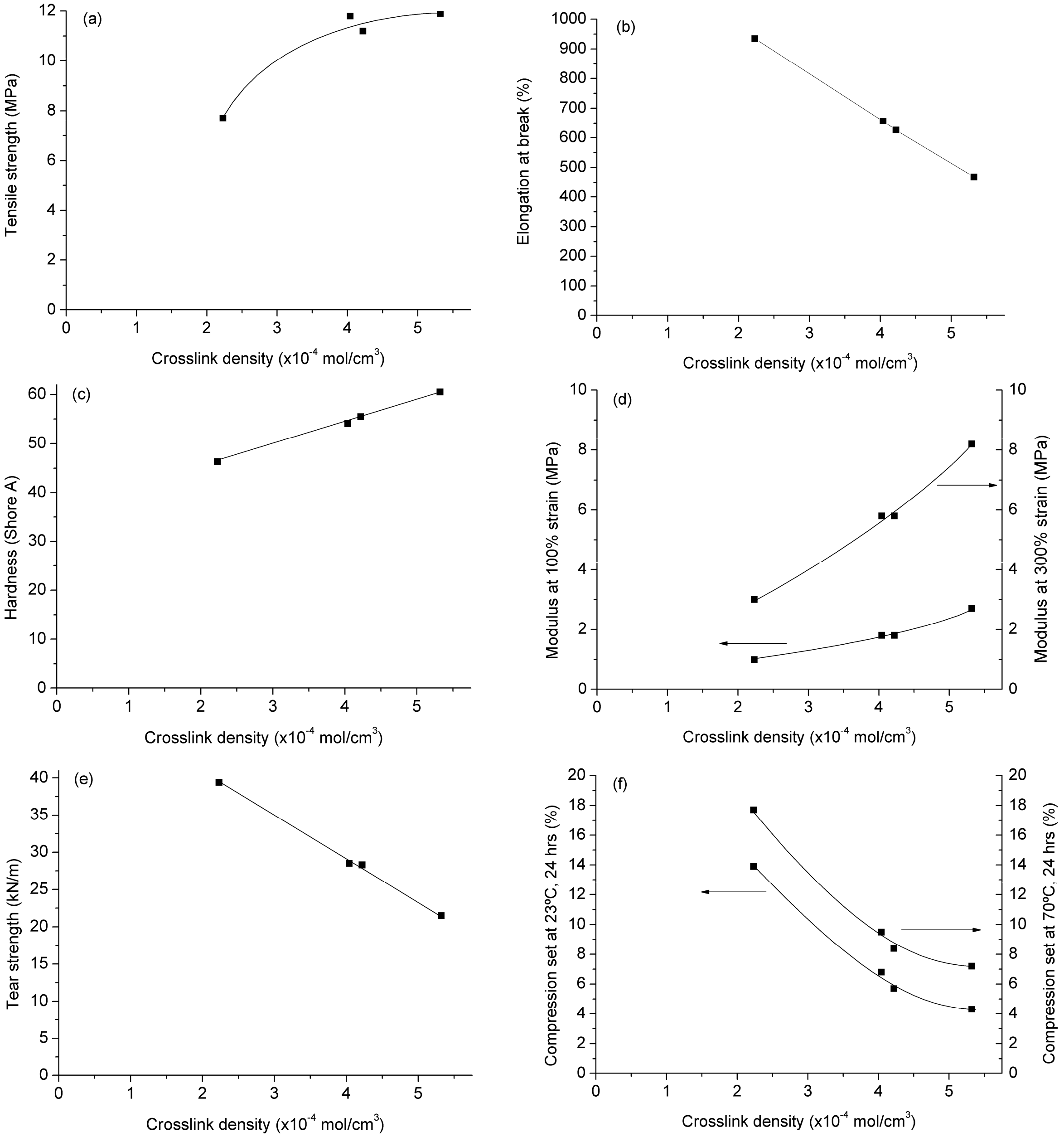

Figure 3.8: (a) Tensile strength; (b) elongation at break; (c) hardness; (d) modulus at 100% and 300% strain; (e) tear strength and (f) compression set at 23°C and 70°C versus the overall crosslink density

Elongation at break and tear strength decrease, whereas hardness and moduli at 100% and 300% strain increase with increasing crosslink density. Tensile strength and compression set values improve with increasing crosslink density, while these properties level off at the highest crosslink densities obtained.

A summarizing overview of all mechanical properties of the four EPDM compounds is given in Table 3.8.

Table 3.8 Mechanical properties of differently vulcanized EPDM compounds

Property	Compound			
	CONV	SEV	EV	NF
Hardness (Shore A)	60.5	54.1	46.3	55.5
M_{100} (MPa)	2.7	1.8	1.0	1.8
M_{300} (MPa)	8.2	5.8	3.0	5.8
Tensile strength (MPa)	11.9	11.8	7.6	11.2
Elongation at break (%)	468	656	935	628
Tear strength (kN/m)	21.5	28.5	39.4	28.3
Compression set at 23°C (%)	4.3	6.8	13.9	5.7
Compression set at 70°C (%)	7.2	9.5	17.7	8.4

3.4 DISCUSSION

The cure characteristics as given in Table 3.4 in comparison with the overall crosslink densities in Table 3.5 show, that the maximum torque values of the four different compounds correspond to the crosslink densities: almost equal results for the SEV- and NS-cured compounds, a significantly higher torque and crosslink density for the CONV-cured compound, and the lowest values for the EV-cured compound. The differences in scorch time (t_{02}), optimum vulcanization time (t_{90}) and specific crosslink distribution are well known to be caused by the compositions of the curing systems[24].

In the CONV-cured compound TMTD is used as accelerator, which is a very fast reacting ultra-accelerator and at the same time a sulfur-donor. It releases elemental sulfur to the compound during vulcanization. The reaction-rate is slowed down by the presence of MBT, which results in a moderate cure rate. In combination with the high amount of sulfur, it results in a high crosslink density with a high concentration of poly- and disulfidic bonds.

The EV-cured compound also contains TMTD. The optimum cure time of this compound is reached earlier compared to the CONV-cured compound, because TMTD is used in combination with CBS, which gives a medium to fast cure with a delayed scorch. The third accelerator is DPTT, which can incorporate 2 of its 4 sulfur atoms in mono- or disulfidic crosslinks. No free sulfur is added, resulting in a low crosslink density with a high percentage of mono- and disulfidic bonds.

The SEV- and NS-cured compounds have comparable overall crosslink densities, as their sulfur to accelerator ratios are comparable. There is a higher amount of free sulfur in the NS-cured compound, but in the SEV-cured compound DPTH is used as accelerator, which donates its build-in sulfur to the compound during vulcanization. The SEV-cured compound vulcanizes much faster, because it contains the fast accelerator CBS and the ultra-accelerator ZDMC, while the NS-cured compound contains the slower dithiophosphate-accelerator ZDBP and MBTS, which first has to decompose into MBT components before vulcanization starts.

When doubling the optimal cure time (2xt_{90}), the crosslink densities are still slightly increased. None of the compounds show reversion at 170°C. Doubling the amount of curatives results in significantly higher crosslink densities for all compounds at the optimum cure time, but with more or less the same crosslink sulfur rank distribution as found for single dosage.

Figure 3.3 and Table 3.7 show that the insoluble fractions of the CONV-, SEV- and NS-cured compounds cured at 170°C are approximately the same, while that of the EV-cured is slightly lower. The gel fractions, the insoluble fraction calculated on the basis of the polymer only, of the CONV-, SEV- and NS-cured compounds are sligthly higher than 100%, while that of the EV-cured compound is 93%. Values higher than 100% can be explained by the fact that a carbon black-filled rubber is a two phase system. One phase is the free polymer, where no carbon black is present. The second phase is the carbon black with tightly attached polymer: the carbon black particles are surrounded by a small layer of polymer, the so called “bound rubber”. It has been shown[25] that the carbon black-polymer aggregate phase has less tendency to be crosslinked by the sulfur curing additives. These polymer chains should end up in the sol fraction, but as they are tightly bound to the carbon black particles they can not be extracted out of the sample. As a result, the experimentally determined gel fraction may be slightly higher than the value which would correlate with the really vulcanized fraction. The experimentally determined gel fraction of the EV-cured compound is 93%, meaning that not all EPDM-rubber chains are bound to the polymer network and that some polymer chains still can be extracted.

Figures 3.4 and 3.8 clearly show the influence of the overall crosslink density on the mechanical properties of the EPDM compounds. The moduli at 100% and 300% strain as well as the hardness show the same pattern: they increase with increasing crosslink density. In general it is assumed that the hardness of an EPDM formulation is mainly determined by type and amount of filler and oil. An approximate formula to calculate the hardness for well-cured press plates, applicable over the range 35 to 85 Shore A, is as follows[26]:

$$\text{Hardness (Shore A)} = C + (A \times \text{phr filler}) - (B \times \text{phr oil}) \qquad (3.5)$$

Where:
C is 60 for amorphous grades of EPDM, 62-64 for semi-crystalline grades; it is a gumstock hardness, without filler and oil added.

A is a hardness factor for different filler types:

A = 0.35 for High Abrasion Furnace (HAF) (e.g. N330) high reinforcing blacks
A = 0.30 for silica
A = 0.25 for Fast Extrusion Furnace (FEF) blacks (e.g. N550)
A = 0.20 for Semi Reinforcing Furnace (SRF) blacks (e.g. N772)
A = 0.10 for Medium Thermal (MT) blacks (e.g. N990)
A = 0.10 for clays
A = 0.05 for calcium carbonate

B is 0.33 for paraffinic type of oils

Furthermore, it is advised that 1-5 hardness points have to be subtracted for vulcanizates of a lower state of cure e.g. continuous profiles or some peroxide cured articles.

The masterbatch shown in Table 3.2 should have a calculated hardness of 62 Shore A, according to equation 3.5. However, Figures 3.4 and 3.8 show that the hardness significantly depends on the crosslink density and ranges from 42 to 68 Shore A. Equation 3.5 and the correction given above for undercured articles apparently do not sufficiently take into account the influence of crosslink density on hardness.

Tensile strength increases with increasing crosslink density, but tends to level off at a certain crosslink concentration. Besides the influence of crosslink density there is also an influence of crosslink length on the strength of a cured rubber material. The material with the highest amount of polysulfidic bridges commonly shows the highest tensile strength values, whereas the material with the highest amount of monosulfidic bonds shows the lowest strength. This is the inverse order of the bond energies of the crosslinks: networks with stronger crosslinks yield a lower tensile strength. Various mechanisms have been suggested to explain this effect, as discussed in an overview by Engelbert van Bevervoorde-Meilof[27]. However, all these mechanisms show contradictions and there is not a generally accepted mechanism for this phenomenon. The most widely accepted mechanism is the increase of tensile strength by the higher mobility of polysulfidic crosslinks[28].

Elongation at break increases with decreasing crosslink density, because a lower number of crosslinks makes the material more flexible. The sharp initial increase in elongation at break with increasing crosslink density as shown in Figure 3.4(b) has never been shown before. Van Gunst et al.[29] have shown that the elongation at break of unvulcanized amorphous EPDM-rubber lies in the range of 200% and 400%. The vulcanized EPDM-rubbers examined in this chapter show that elongation at break values of more than 800% are obtained at low crosslink densities. So at some point there should be a steep increase in elongation at break. Figure 3.4(b) shows that this occurs at appr. 1.8×10^{-4} mol/cm^3 by means of a very sharp increase within a very small crosslink density range of less than 0.2×10^{-4} mol/cm^3.

Tear strength decreases with increasing crosslink density due to embrittlement of the material. The length of the sulfur bonds is of minor influence on tear resistance in this case. Generally, maximum stiffening from crosslinking combined with high tear resistance is attributed to flexible polysulfidic crosslinks. Non-flexible monosulfidic linkages result in earlier embrittlement, whereas with polysulfidic bonds a higher crosslink density can be tolerated before the vulcanizate becomes brittle[30]. In the present investigation the differences in polysulfidic crosslink concentration are too small to show an effect on tear strength.

Compression set improves with increasing crosslink density at both temperatures, 23°C and 70°C, because more crosslinks are present to pull the material back into its original shape after deformation. The length of the crosslinks in general also plays a role, because polysulfidic bonds tend to rearrange at high temperature forming new, short crosslinks, which eventually prevent the full recovery of the deformed material.

The results of this investigation coincide with the generally accepted trends of the properties with changing crosslink density as commonly quoted in literature, see Figure 3.9[6, 31]. Even the experimentally determined maximum in tear strength at a somewhat lower degree of crosslinking of 2.5×10^{-4} mol/cm^3 relative to the maximum in tensile strength at a crosslink density of 4×10^{-4} mol/cm^3, coincides with common practice. The initial upturn of elongation at break at very low crosslink densities is a feature not commonly observed.

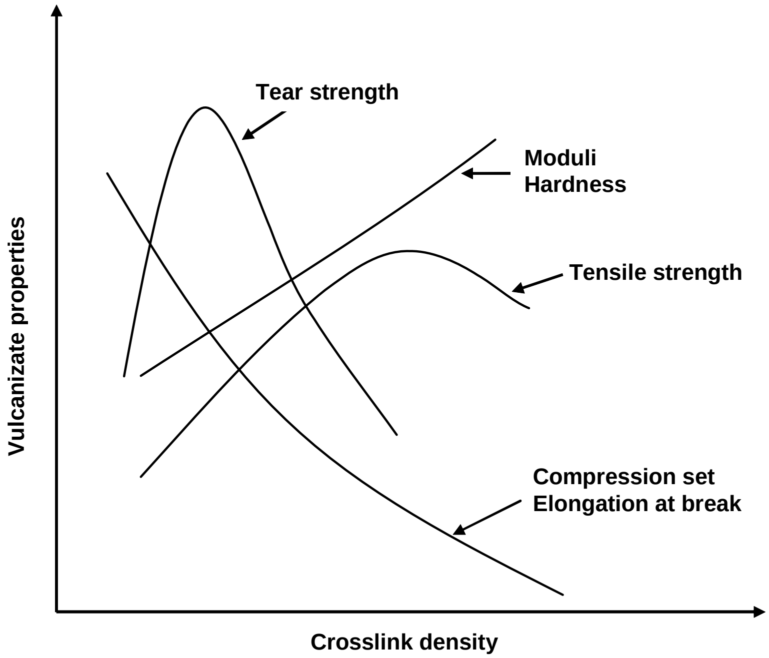

Figure 3.9: Vulcanizate properties versus crosslink density

3.5 CONCLUSIONS

The vulcanization of an ENB-EPDM masterbatch with four different curing systems results in cured materials with different crosslink densities, crosslink length distributions and mechanical properties. The conventionally cured compound shows the highest crosslink density and concentration of polysulfidic bonds, resulting in relatively high values for hardness and moduli and low values for elongation at break, tear strength, and compression set. The efficiently cured compound shows a relatively low crosslink density and a high amount of monosulfidic bridges, resulting in high tear strength, elongation at break and compression set and low tensile strength, hardness and moduli. The semi-efficient and nitrosamine-free cured vulcanizates have similar characteristics and properties with values in between those of the conventionally and efficiently cured compounds.

The influence of vulcanization time on the physical and mechanical properties of EPDM-rubber vulcanizates is significant. The changes in material properties are mainly determined by the differences in crosslink density depending on the curing system and time. The crosslink distribution, mainly the ratio of mono- plus disulfidic to polysulfidic crosslinks, is of minor influence in this case as the differences are too small to have a significant effect.

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Chapter 4

Reclaiming of Carbon Black Reinforced EPDM-Rubber Vulcanizates with Hexadecylamine as Devulcanization Aid in an Internal Mixer

This chapter gives an overview of the influence of temperature, time, shear and concentration of hexadecylamine (HDA) as devulcanization aid on the reclaiming efficiency of different EPDM-based sulfur-vulcanized rubbers: conventionally cured, grossly polysulfidic of nature; and efficiently vulcanized, mainly monosulfidic. It turns out that of the four variable factors examined, temperature clearly has the largest influence on the reclaiming efficiency within the experimental ranges. HDA is suitable as devulcanization aid for different EPDM compounds, taking into account the parameter settings for each single compound.

Reclaim from conventionally vulcanized EPDM, mainly polysulfidic of nature, shows the largest decrease in remaining crosslink density with increasing HDA concentration and at lower reclaim temperatures. After reclaiming at the lower limit of the experimental temperature window applied: 225°C, the concentration of remaining di- and polysulfidic crosslinks is higher than the concentration of monosulfidic bonds, while at the upper temperature level: 275°C, the concentration of monosulfidic bonds is highest. For efficiently vulcanized EPDM with primarily monosulfidic crosslinks, HDA again has a positive effect on the reclaim efficiency at low applied reclaiming temperatures of max. 225°C. At higher temperatures, the crosslink density increases with increasing concentrations of HDA. Application of the treatment proposed by Horikx shows, 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 up to 50 wt% to a virgin masterbatch, with a limited decrease in properties. This is a high amount compared to max. 15 wt% addition of ground powder rubber, commonly known to be the practical limit.

Parts of the work described in this chapter have been presented at the Fall 170th Technical Meeting of the Rubber Division, ACS, October 10-12 2006, in Cincinnati (USA) (Paper no. 24), at the PPS-23, the Polymer Processing Society, May 27-31 2007, in Salvador (Brazil) (Paper no. P18-004) and at the Fall 172nd Technical Meeting of the Rubber Division, ACS, October 16-18 2007, in Cleveland (USA) (Paper no. 73), and has been accepted for publication in the May/June 2008 edition of Rubber Chemistry and Technology. It has also been submitted for publication to Gummi Fasern Kunststoffe and will be submitted to Polymer Degradation and Stability.

4.1 INTRODUCTION

Rubber can be recycled in different ways, of which the most common variant is the reuse of ground cured rubber. However, upgrading the quality of the ground material by devulcanization is of interest as it broadens the possibilities for the utilization of the recycled material. In these processes, the vulcanizate network is broken down and converted into a material which ideally can be processed like the original unvulcanized compound. The processes used in the reclaiming industry commonly result in a combination of crosslink-scission and main-chain scission of the constitutive polymer chains in the rubber networks, caused by heat, shear and chemical reactions. Therefore, a clear distinction must be made between devulcanization and reclaiming[1]:

- Devulcanization: only crosslinks are broken, the hydrocarbon backbone remains intact;
- Reclaiming: crosslink scission as well as main-chain scission occurs.

Reclaiming of sulfur-cured natural rubber (NR) is a common technology for many decades already. Earlier attempts to apply the same technology to rubber articles made out of EPDM-rubber – automotive parts like window- and door-seals, radiator hoses, and building and construction articles like roof-sheeting and window profiles – were not successful, because the chemistry of the NR-reclaiming could not simply be transposed onto EPDM. Former work at the University of Twente[2-4] has shown that sulfur-cured EPDM needs far more strenuous conditions to reclaim than NR. Diaryldisulfides, commonly used as devulcanization-aids for NR, are to some extent effective in promoting the devulcanization of EPDM. They result however in EPDM-reclaims, of which the chemical integrity is largely damaged and which are insufficiently active in revulcanization. α-H-containing aliphatic amines are found to be more effective as devulcanization aids for EPDM-rubber[2].

In the present chapter, special attention will be given to the efficiency and mechanistical aspects of the reclaiming of two different EPDM-rubber compounds: CONventionally Vulcanized (CONV) and Efficiently Vulcanized (EV) EPDM-rubbers are reclaimed in a Brabender Plasticorder with hexadecylamine (HDA) as devulcanization aid. The influence of temperature, time, shear and amount of devulcanization aid on the reclaiming of the two EPDM-rubber types is thoroughly investigated. An application study for re-utilization of the reclaim in the same type of EPDM-rubber compound is performed.

4.2 EXPERIMENTAL

Compound recipes and materials – Reclaiming was performed on ground conventionally and efficiently vulcanized EPDM-rubber. The EPDM-rubber masterbatch used in this investigation, see Table 4.1, is the same as described in detail in Chapter 3.

Table 4.1 Masterbatch and curing recipes

Material	Compound A CONV system (phr)	Compound B EV system (phr)
Masterbatch		
EPDM	100	
ZnO	5	
Stearic acid	1	
Carbon black N550	70	
Carbon black N772	40	
Paraffinic oil	70	
Curing recipes		
TMTD	1.0	1.0
MBT	0.5	
CBS		1.5
DPTT		0.8
Sulfur	1.5	

The curing additives used for the vulcanization are shown in Table 4.2.

Table 4.2 Materials used for vulcanization

Material	Abbr.	Supplier
Sulfur	S	Merck
2-Mercaptobenzothiazole	MBT	Merck
Tetramethylthiuram disulfide	TMTD	Flexsys
N-Cyclohexyl-2-benzothiazole sulfenamide	CBS	Flexsys
Dipentamethylene thiuramtetrasulfide	DPTT	Flexsys

Hexadecylamine (HDA) 92% pure (Merck) was used as devulcanization aid. Paraffinic oil was used as reclaiming oil, the same Sunpar 2280 as used for the original compound.

Decahydronaphtalene, a mixture of the cis- and trans-isomer with a purity of 98%, was used for swelling measurements. The solvents acetone and tetrahydrofuran (THF) (Biosolve) were used for extractions. 2-Propanethiol ≥98% pure (Merck), 1-hexanethiol 95% pure, piperidine 99% pure, n-heptane 99% pure, (all from Sigma Aldrich) and a petroleum-ether fraction between 40 and 60°C (Across) were used for the crosslink distribution determinations.

Mixing and vulcanization – Mixing and vulcanization was performed as described in detail in Chapter 3. The curing time was taken as $1.5 \times t_{90}+130$

seconds: 130 seconds were added to compensate for the longer heating time of thicker specimens in the press compared to the cure-rheometer. The factor 1.5 was necessary in order to correct for the larger thickness of the sheets: 6 mm instead of 2 mm for the standard samples.

Grinding – The vulcanized EPDM-rubber sheets were cryogenically ground in a Bauknecht grinder. The rubber samples were immersed in liquid nitrogen before grinding, the material was then ground until it passed a 8 mm screen.

Reclaiming – The ground EPDM-rubber particles were reclaimed in a Brabender Plasticorder PL 2000. Its mixing chamber had a volume of 35 ml and a cam-type rotor. The fill factor was 0.7. The devulcanization aid was HDA and the parameters: temperature, time, rotor speed and amount of devulcanization aid were varied as shown in Table 4.3. 5 wt% of reclaiming oil relative to the vulcanizate was added to each batch. The reclaims based on compounds A (conventionally cured EPDM-rubber) and B (efficiently cured) are further referenced as reclaims A and B, respectively.

Design of Experiments – A statistical approach was taken to evaluate the most important influential factors for the reclaiming of EPDM-vulcanizates. Changing every separate factor of a process, one at a time, until no further improvement is accomplished, makes the effort and cost required for such a study prohibitive and unrealistic. The solution is to design a statistically selected set of experiments, in which all relevant factors are varied simultaneously.

Because the relative importance of all factors was not known in advance, a Design of Experiments (DOE) approach was adopted[5]. Prior to doing any experiments, the input conditions such as the number of variable factors: reclaiming temperature and time, rotor speed and amount of devulcanization aid, and their ranges, respectively the number of responses: Mooney viscosity, crosslink densities and insoluble fraction, and the experimental objective need to be specified. Then the experimental design is created and the experiments can be carried out. Each experiments results into values for the responses, which can be analyzed using regression analysis . This gives a model equation relating the changes in the responses to the changes in the factors. The model equation indicates which factors are important, and how they combine in influencing the responses.

To optimize the parameter settings for the most complete reclaiming, Response Surface Modeling was used. The objective of this optimization is:

1. to predict the response values for all possible combinations of factors within the experimental regime;
2. to identify an optimal experimental point.

MODDE 6.0, the software from Umetrics, was used to model the response properties. For the research presented in this chapter, a central composite face-centered (CCF) design, a quadratic model, is the most appropriate.

Figure 4.1 shows possible outcomes of response distributions. When the experimental response results are positively skewed, it is necessary to perform a logarithmic transformation to obtain a workable model. When the responses are negatively skewed, it is necessary to perform a negative logarithmic transformation on the responses.

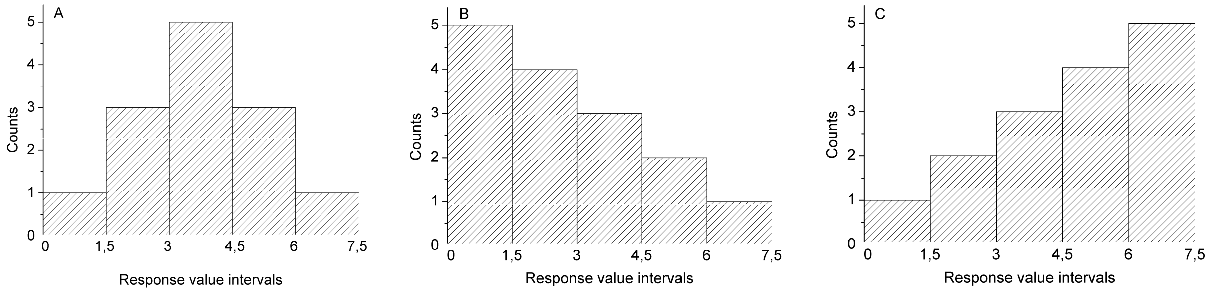

Figure 4.1: Histograms of responses which are (A): normally distributed; (B): positively skewed and (C): negatively skewed

Least squares analysis is applicable to many factors. When this is applied to the modeling of several factors, it is commonly known as Multiple Linear Regression (MLR), the numerical algorithm used to compute regression results. The most important tools to quantify the performance of the resulting model are the two parameters R^2 and Q^2. The former is known as *goodness of fit* and is a measure of how well the regression model fits the raw data. R^2 varies between 0 and 1, where 1 indicates a perfect fit and 0 no fit at all. R^2_{adj} is corrected for the amount of variables used to obtain the model: it reflects the balance between a good fit and the simplicity of the model. The value of R^2_{adj} is always lower than R^2, but in the ideal case very close to R^2. A more suitable guidance for validity of a regression model is given by the Q^2-parameter. It is called *goodness of prediction*, because it estimates the predictive power of the model. This is a more realistic and useful performance indicator, as it reflects the final goal of modeling. For a MLR-model to pass the diagnostic test, both R^2 and Q^2 should be high and preferably not separated by more than 0.2-0.3. Generally, a Q^2>0.5 implies a good model and a Q^2>0.9 implies an excellent model.

The ranges of the variable factors used in this investigation are shown in Table 4.3. This results in an experimental design as shown in Table 4.4.

Table 4.3 Reclaiming conditions used in DOE

Parameter	
Temperature	225, 250 and 275ºC
Time	5, 7.5 and 10 min
Rotor speed	50, 75 and 100 rpm
Amount of devulcanization aid	0, 5 and 10 wt%

Table 4.4 Experimental design for EPDM-rubber reclaiming

Exp. No.	Temperature (°C)	Time (min)	Rotor speed (rpm)	Amount of devulcanization aid (wt%)
1	225	5	50	0
2	275	5	50	0
3	225	5	100	0
4	275	5	100	0
5	225	10	50	0
6	275	10	50	0
7	225	10	100	0
8	275	10	100	0
9	225	5	50	10
10	275	5	50	10
11	225	5	100	10
12	275	5	100	10
13	225	10	50	10
14	275	10	50	10
15	225	10	100	10
16	275	10	100	10
17	225	7.5	75	5
18	275	7.5	75	5
19	250	7.5	50	5
20	250	7.5	100	5
21	250	5	75	5
22	250	10	75	5
23	250	7.5	75	0
24	250	7.5	75	10
25	250	7.5	75	5
26	250	7.5	75	5
27	250	7.5	75	5

Mooney Viscosity – Mooney viscosities ML(1+4)125ºC were determined using a Mooney viscometer MV2000 VS from Alpha Technologies according to ISO R289.

Extractions – The extractions were carried out as described in detail in Chapter 3.

Equilibrium swelling – The degree of swelling was measured on extracted samples; this allows to determine the crosslink density of the vulcanized compounds and of the reclaims after removal of the sol fraction, as described in detail in Chapter 3. The crosslink density was calculated according to the Flory-

Rehner equation[6]. This equation is strictly spoken valid only for non-filled systems. Therefore the Kraus[7] 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[8]:

$$\nu_{\text{actual}} = \frac{\nu_{\text{apparent}}}{1 + K \times \Phi} \tag{4.1}$$

$$\Phi = \frac{\text{Weight fraction of carbon black} \times \text{Density of compound} \times W_b}{\text{Density of carbon black} \times W_a} \tag{4.2}$$

$$K = 0.0179 \times \text{DBP value (ml/100 g)} + 2.29 \tag{4.3}$$

where ν_{apparent} is the measured chemical crosslink density, ν_{actual} is the actual chemical crosslink density, K is a constant for a given filler, Φ is the volume fraction of filler in the specimen, W_b is the weight of specimen before extraction and W_a is the weight of specimen after extraction of all soluble material: polymer sol fraction, oil and soluble chemical residues.

Thiol-amine reactions – The specific crosslink distributions of the vulcanizates were studied using thiol/amine chemical probes[9-12], as described in Chapter 3.

Light Microscopy: 0.5 grams of reclaim A or B, reclaimed at 250ºC at a rotor speed of 75 rpm for 7.5 min with the addition of 5 wt% of HDA, was mixed into virgin EPDM-stock on a two-roll mill. The material was put under a light microscope under a magnification of 5-20x.

Mixing and vulcanization of the revulcanizates – After reclaiming, the reclaimed material was blended in varying proportions with the original virgin EPDM-rubber masterbatch. The blends were either conventionally or efficiently cured again, with the same curing recipe as was applied for the original vulcanizates: Table 4.1. The reclaim and curing additives were blended into the virgin EPDM masterbatch at room temperature on a laboratory scale Schwabenthan two-roll mill. The amounts of curatives were based on the total EPDM polymer content, including the polymer content of the reclaim. No correction was made for residues of curatives in the reclaim. Mixing and curing was done as described in detail in Chapter 3, with the modification that for the present purpose the curing time was chosen as t_{90} + 130 seconds.

Mechanical properties – Tensile and tear tests were carried out according to ISO 37 and ISO 34, respectively. Compression set tests were performed according to ISO 815. The hardness of the samples was measured with a Zwick hardness-meter Shore A type according to DIN 53503. See Chapter 3 for the detailed descriptions.

4.3 RESULTS

4.3.1 Reclaiming of Compounds A and B

The crosslink densities, specific crosslink distributions and insoluble fractions of the vulcanized compounds A and B used in this study, thus before reclaiming, are given in Table 4.5. Compound A, the conventionally cured one, is characterized by a relatively high overall crosslink density with a high percentage of poly- plus disulfidic crosslinks and only 15% of monosulfidic bonds. Compound B on basis of the efficient-curing system has 48% poly- plus disulfidic crosslinks, and a surplus of 52% monosulfidic, at an overall crosslink density less than half of compound A. The insoluble fraction of compound A is higher than that of compound B, corresponding to the higher overall crosslink density.

Table 4.5 Crosslink densities and insoluble fractions of the original compounds

Feed stock	Crosslink density (×10^{-4} mol/cm^3)			Insoluble fraction (%)
	Overall	Monosulfidic	Di- plus polysulfidic	
Compound A	2.39	0.36 (15%)	2.03 (85%)	75.1
Compound B	0.97	0.51 (52%)	0.46 (48%)	71.9

After grinding, both vulcanized compounds A and B, as described in the experimental paragraph, were reclaimed under various conditions as input variables defined in the DOE: Table 4.4. All results were used for the Response Surface Modeling with Modde 6.0 software. To obtain good representative models, it was necessary to perform an additional logarithmic transformation of the monosulfidic crosslink density results for reclaims A and B, and on the Mooney viscosity for reclaim A. This was necessary, as these responses were too skewed for modeling, see Figure 4.1. The validity of the mathematical models was controlled in a set of extra experiments, which were executed with parameter settings different from those given in Table 4.4.

Figures 4.2 - 4.5 show the predicted versus the experimentally determined results for Mooney viscosity, insoluble fraction, overall crosslink density and monosulfidic crosslink density of the reclaims A and B at the parameter settings selected according to the design and at additional parameter settings, which were arbitrarily chosen within the experimental ranges chosen for the DOE.

These graphs show a good correlation between experimental and predicted results; the experimental results are within the 95% probability range from the theoretically predicted lines. All mathematical response models show good or excellent Q^2-values. It can be concluded that the mathematical models are able to represent the results of experiments within the chosen experimental window with good accuracy.

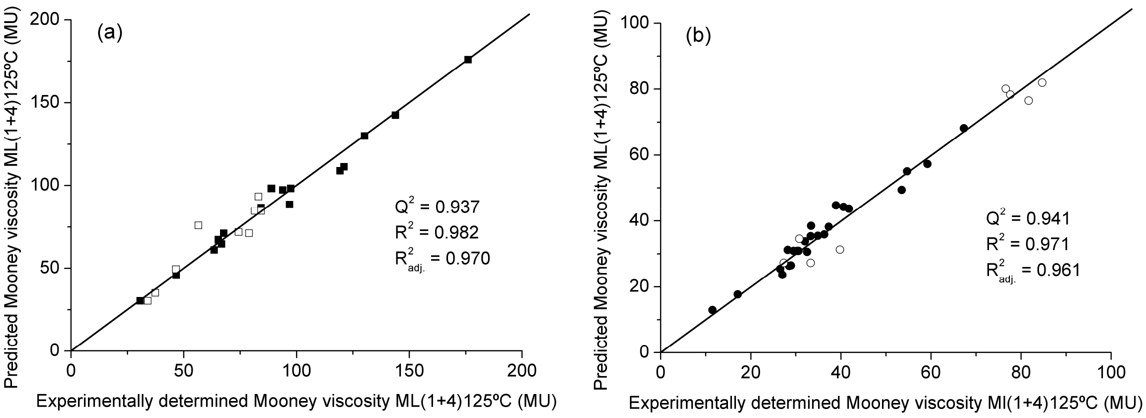

Figure 4.2: Predicted Mooney viscosity versus experimentally determined Mooney viscosity of (a): reclaim A; (■): model experiments; (□): extra experiments; and (b): reclaim B; (●): model experiments; (○): extra experiments

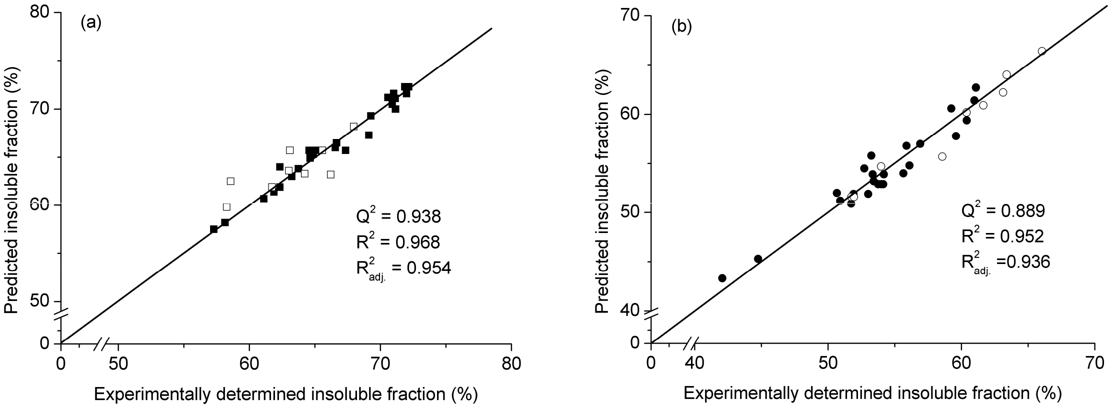

Figure 4.3: Predicted insoluble fraction versus experimentally determined insoluble fraction of (a): reclaim A; (■): model experiments; (□): extra experiments; and (b): reclaim B; (●): model experiments; (○): extra experiments

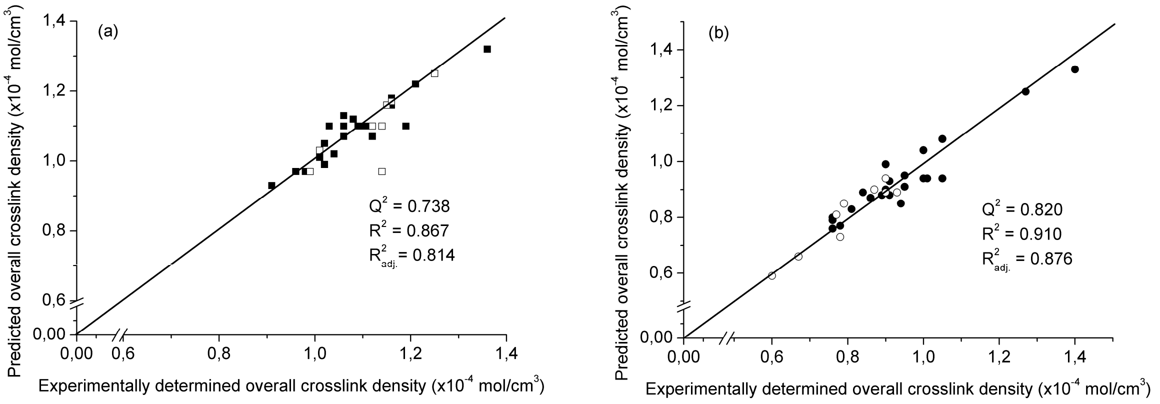

Figure 4.4: Predicted overall crosslink density versus experimentally determined overall crosslink density of (a): reclaim A; (■): model experiments; (□): extra experiments; and (b): reclaim B; (●): model experiments; (○): extra experiments

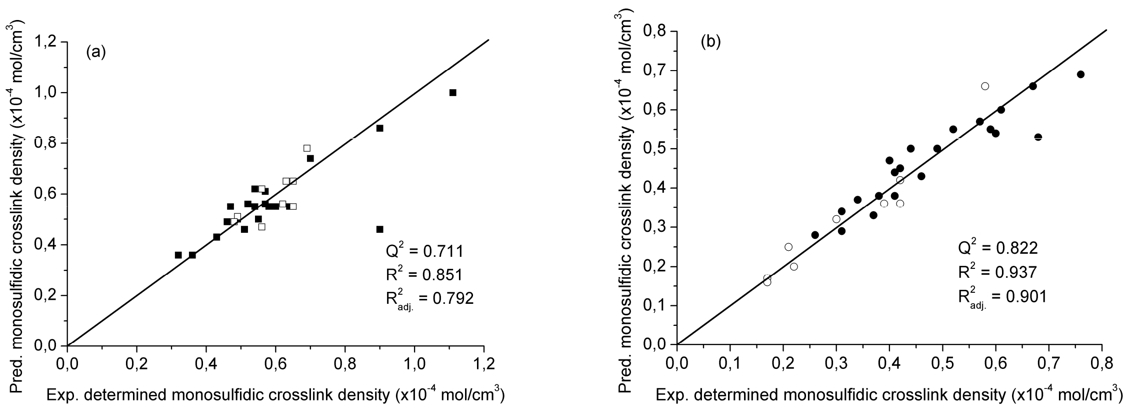

Figure 4.5: Predicted monosulfidic crosslink density versus experimentally determined monosulfidic crosslink density of (a): reclaim A; (■): model experiments; (□): extra experiments; and (b): reclaim B; (●): model experiments; (○): extra experiments

4.3.1.1 Reclaiming of Compound A

The influence of the variable factors: reclaiming temperature and time, rotor speed and HDA-concentration on the responses Mooney viscosity, insoluble fraction and overall, resp. monosulfidic crosslink densities of reclaim A are shown in Figures 4.6 - 4.9. When parameters needed to be set constant for creating the figures, they were fixed at: reclaiming temperature: 250°C; reclaiming time: 7.5 minutes; rotor speed: 75 rpm, and amount of devulcanization aid: 5 wt%.

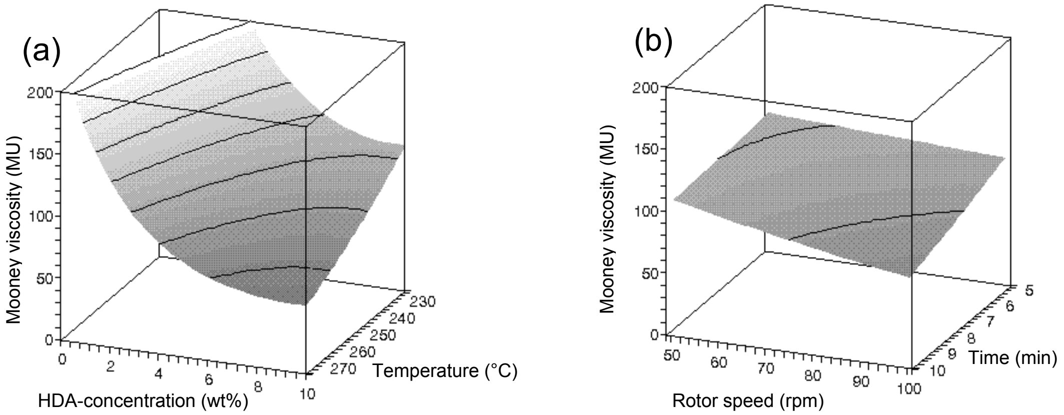

Figure 4.6: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the Mooney viscosity of reclaim A

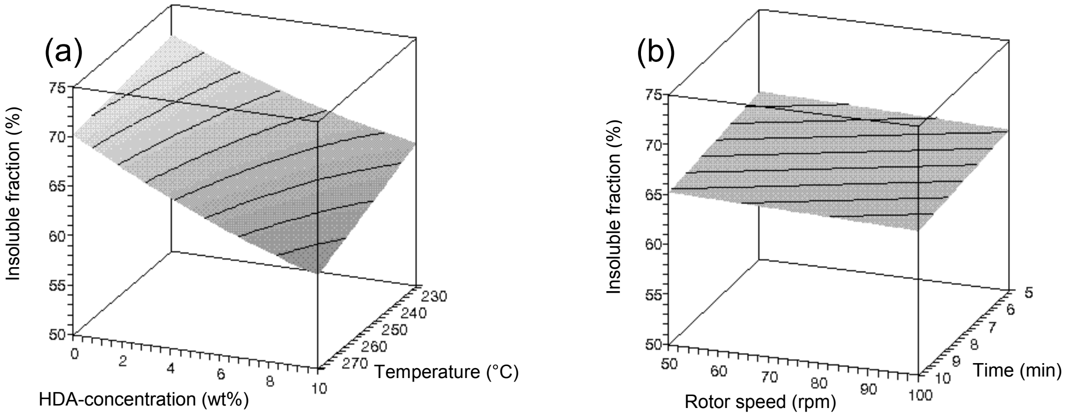

Figure 4.7: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the insoluble fraction of reclaim A

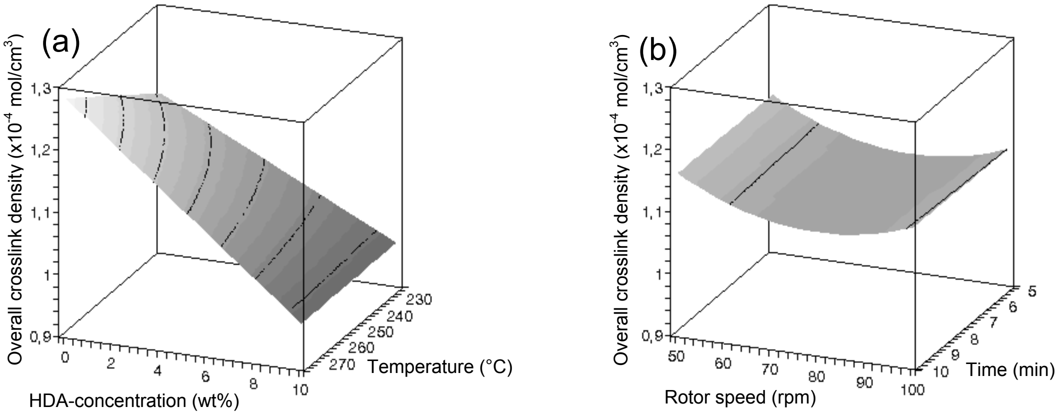

Figure 4.8: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the overall crosslink density of reclaim A

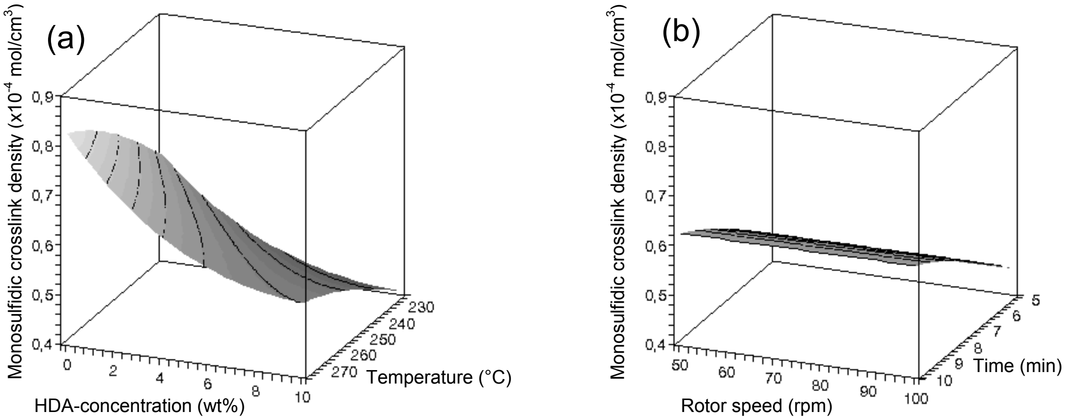

Figure 4.9: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the monosulfidic crosslink density of reclaim A

Figures 4.6 – 4.9 show that there is only a minor influence of the factors rotor speed and reclaiming time on the responses within the experimental window, compared to the influence of the factors reclaiming temperature and HDA-concentration. Therefore, a detailed analysis will be made of the influence of the factors reclaiming temperature and HDA-concentration only on the responses of reclaim A.

Figure 4.10 illustrates the influence of reclaiming temperature and HDA-concentration on Mooney viscosity, insoluble fraction and the overall, as well as the monosulfidic crosslink densities. Figure 4.10(a) shows that the influence of the amount of HDA on the Mooney viscosity is quite strong up to a concentration of approximately 5 wt%, to level off at higher concentrations for all temperatures. Without the addition of HDA, the predicted Mooney viscosity values of reclaim A are above 200 MU, outside the measuring range of the Mooney viscometer. The Mooney viscosity decreases significantly with increasing temperature. In Figure 4.10(b), the insoluble fraction decreases with increasing concentration of HDA and higher reclaiming temperature. At high concentrations of HDA, the influence of temperature is most pronounced. With increasing HDA-concentration, a linear decrease in overall crosslink density is obtained for reclaim A in Figure 4.10(c). For reclaiming with and without the addition of HDA, the final crosslink density is lower when reclaiming is done at a lower temperature. Without the addition of HDA, just by a thermo-mechanical treatment, the crosslink density already decreases from the original value of 2.39×10^{-4} to approximately $1.16 – 1.28 \times 10^{-4}$ mol/cm^3, dependent on the temperature applied. The main decrease in crosslink density for reclaim A is therefore caused by the mere thermal process. Addition of HDA has only little additional effect. Figure 4.10(d) shows that HDA is able to break monosulfidic crosslinks at all temperatures, although the influence of HDA is not strong enough to compensate for the extra formed monosulfidic bonds by mere thermal reclaiming.

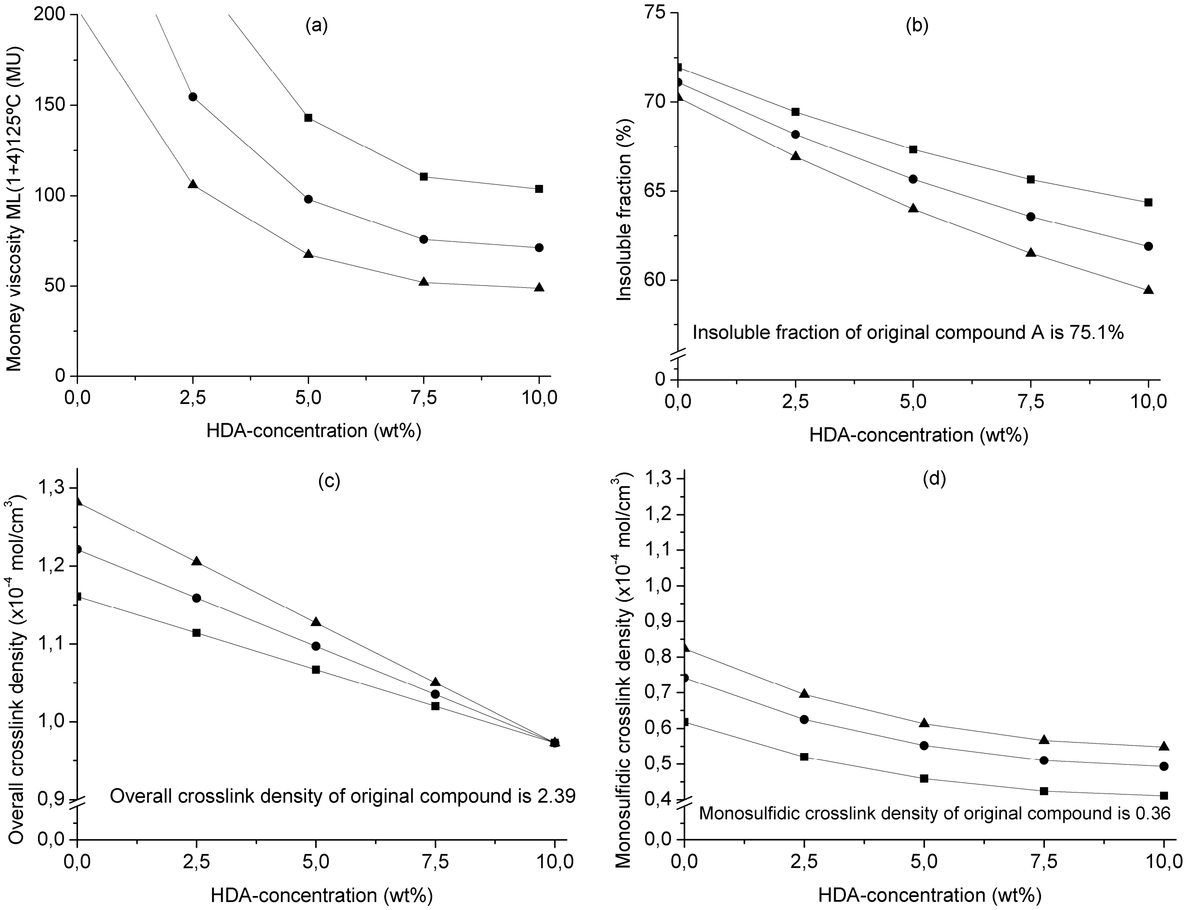

Figure 4.10: Influence of the HDA-concentration on (a): Mooney viscosity; (b): insoluble fraction; (c): overall crosslink density and (d): monosulfidic crosslink density of reclaim A; (■): 225°C; (●): 250°C; (▲): 275°C

Figure 4.11 shows that the concentration of di- and polysulfidic crosslinks decreases significantly for all temperatures compared to the corresponding value for the original compound A, as given in Table 4.5. There is little influence of reclaiming temperature on the overall crosslink density. Therefore, the decrease in di- plus polysulfidic crosslink density with higher reclaiming temperature, is compensated by a rise in monosulfidic crosslinks. All monosulfidic crosslink densities are higher than 0.36×10^{-4} mol/cm^3 for the original compound A. Consequently, additional monosulfidic bonds are generated during reclaiming, and higher temperatures enhance this effect.

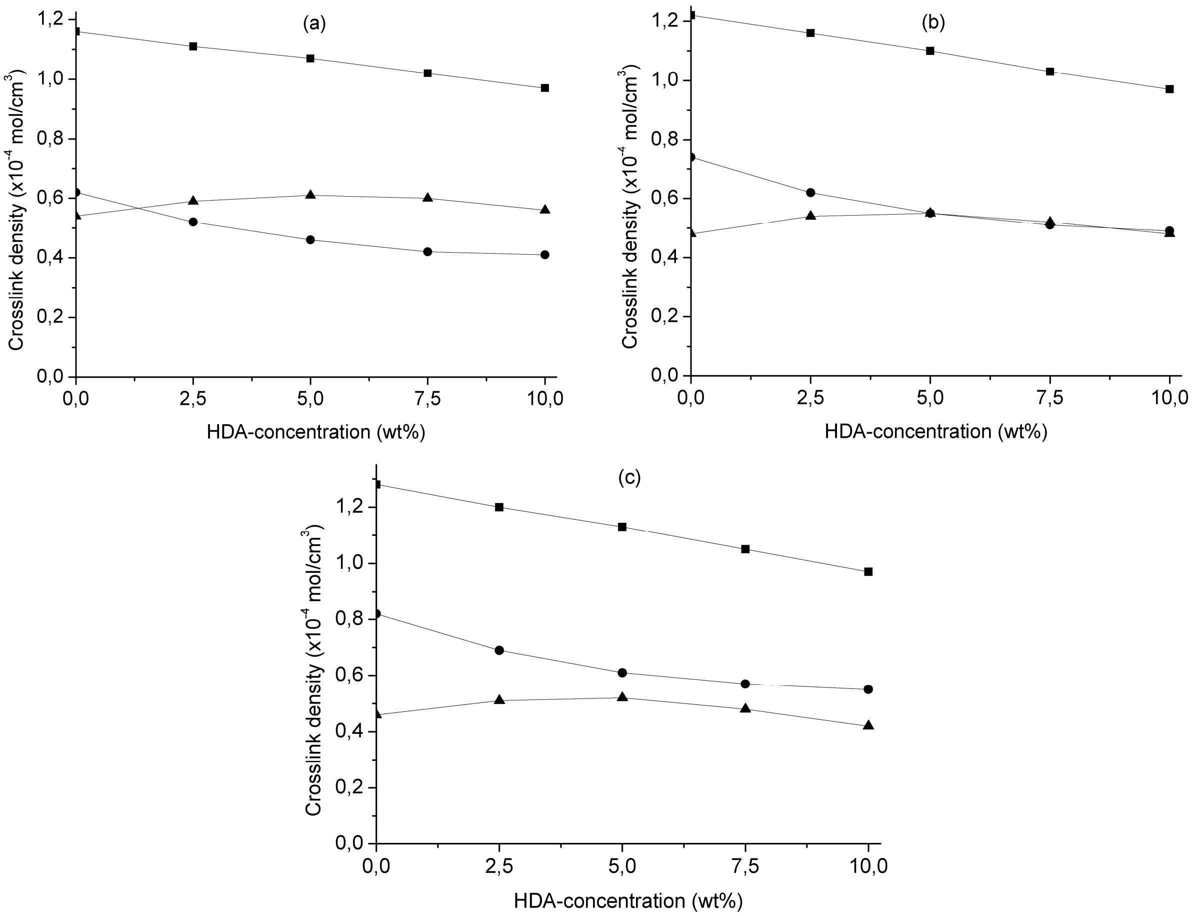

Figure 4.11: Influence of HDA-concentration on the specific crosslink densities of reclaim A at (a): 225°C; (b): 250°C and (c): 275°C; (■): Overall; (●): monosulfidic and (▲): di- plus polysulfidic crosslink densities

Figure 4.12 shows light microscope homogeneity pictures of reclaim A in the EPDM gumstock.

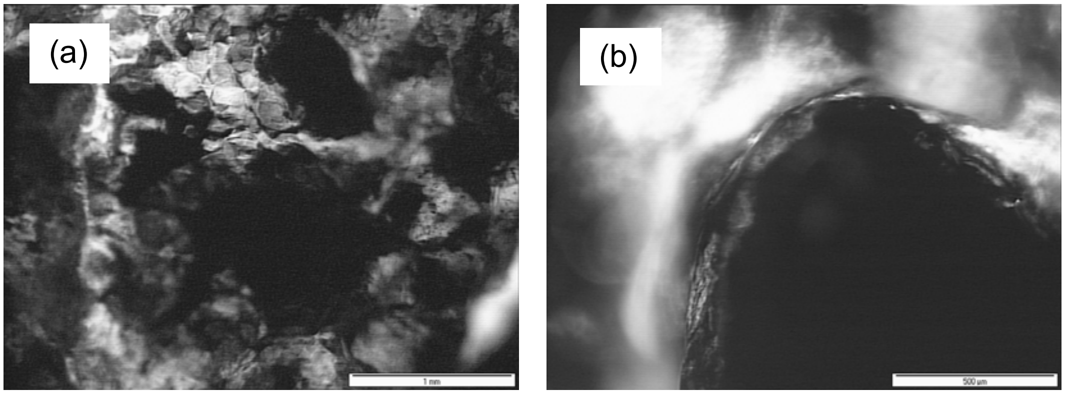

Figure 4.12: Microscope picture of reclaim A in EPDM gumstock with (a): 5x magnification and (b): 10x magnification

Figure 4.12(a) shows the occurrence of reclaim particles with a diameter larger than 1 mm. Figure 4.12(b) illustrates sharp edges of a reclaim particle in the matrix of virgin EPDM gumstock. A clear distinction between the white area of the virgin rubber gumstock and the black regions of the reclaim particles is visible.

4.3.1.2 Reclaiming of Compound B

For compound B, the efficiently vulcanized material, the experimental range was widened to a lower temperature. At 275°C, the reclaim had a very low viscosity and showed tacky behavior. Therefore, experiments at 200°C were performed in order to obtain a material with a higher viscous and less tacky behavior.

Figures 4.13 – 4.16 show the influence of the four variable factors on Mooney viscosity, insoluble fraction and the overall, resp. the monosulfidic crosslink densities of reclaim B. When parameters needed to be set constant for creating the figures, they were fixed at: reclaiming temperature: 250°C; reclaiming time: 7.5 minutes; rotor speed: 75 rpm, and amount of devulcanization aid: 5 wt%.

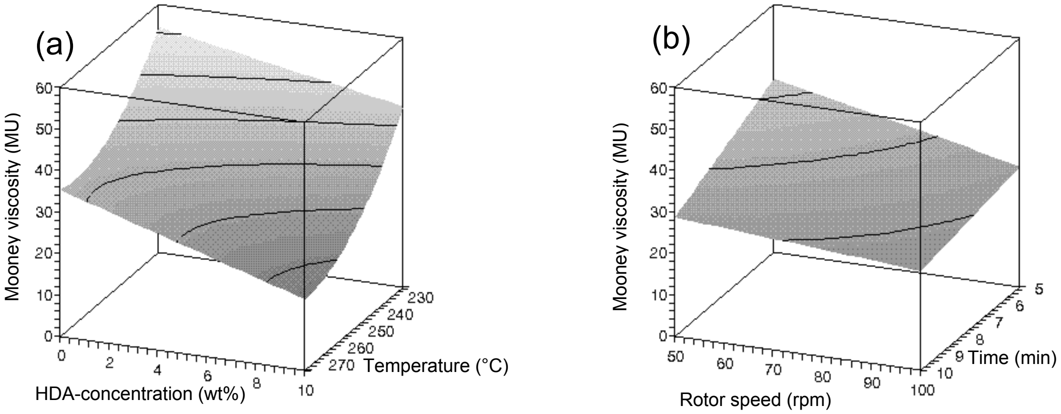

Figure 4.13: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the Mooney viscosity of reclaim B

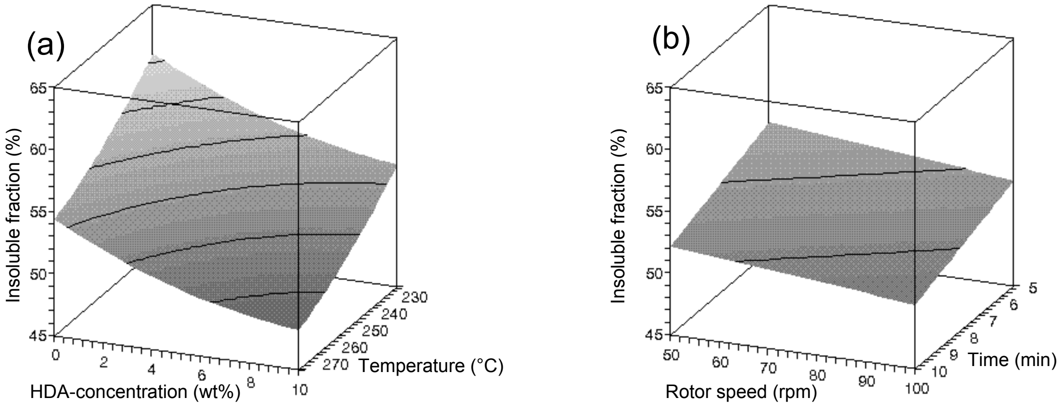

Figure 4.14: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the insoluble fraction of reclaim B

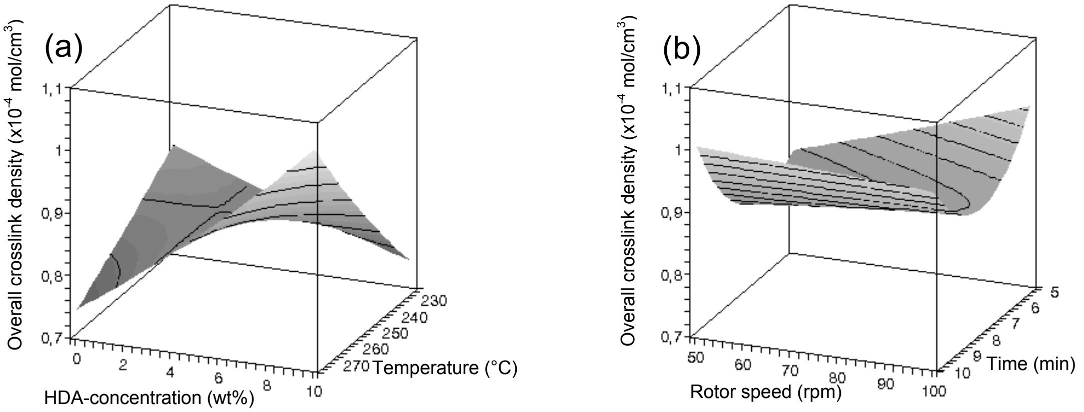

Figure 4.15: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the overall crosslink density of reclaim B

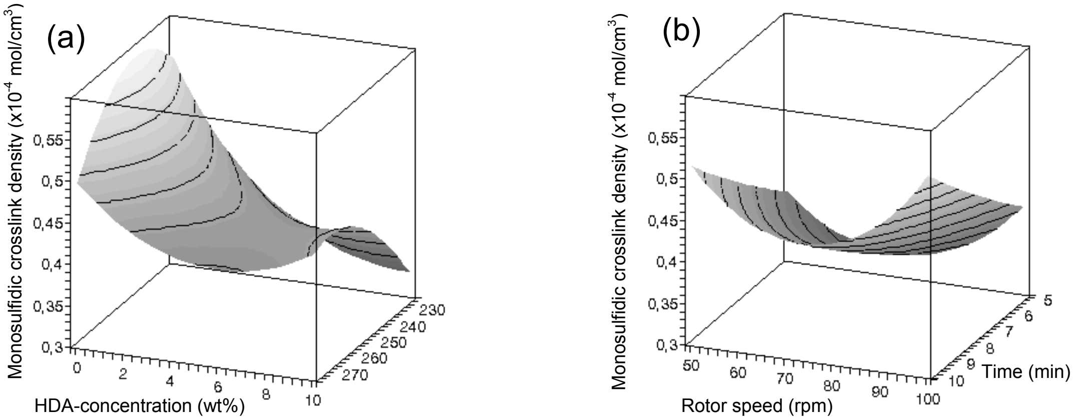

Figure 4.16: Influence of (a): HDA-concentration and temperature and (b): rotor speed and reclaiming time on the monosulfidic crosslink density of reclaim B

Figures 4.13 – 4.16 show again only a minor influence of the factors rotor speed and reclaiming time on the responses of reclaim B, as already seen for compound A. Reclaiming temperature and HDA-concentration have a strong effect on the responses of reclaim B.

Contrary to the results obtained for reclaim A, Figure 4.17(a) shows a linear decrease in Mooney viscosity with increasing HDA-concentration. The influence of temperature on the Mooney viscosity levels off with increasing temperature. The insoluble fraction decreases with rising temperature and higher HDA-concentrations.

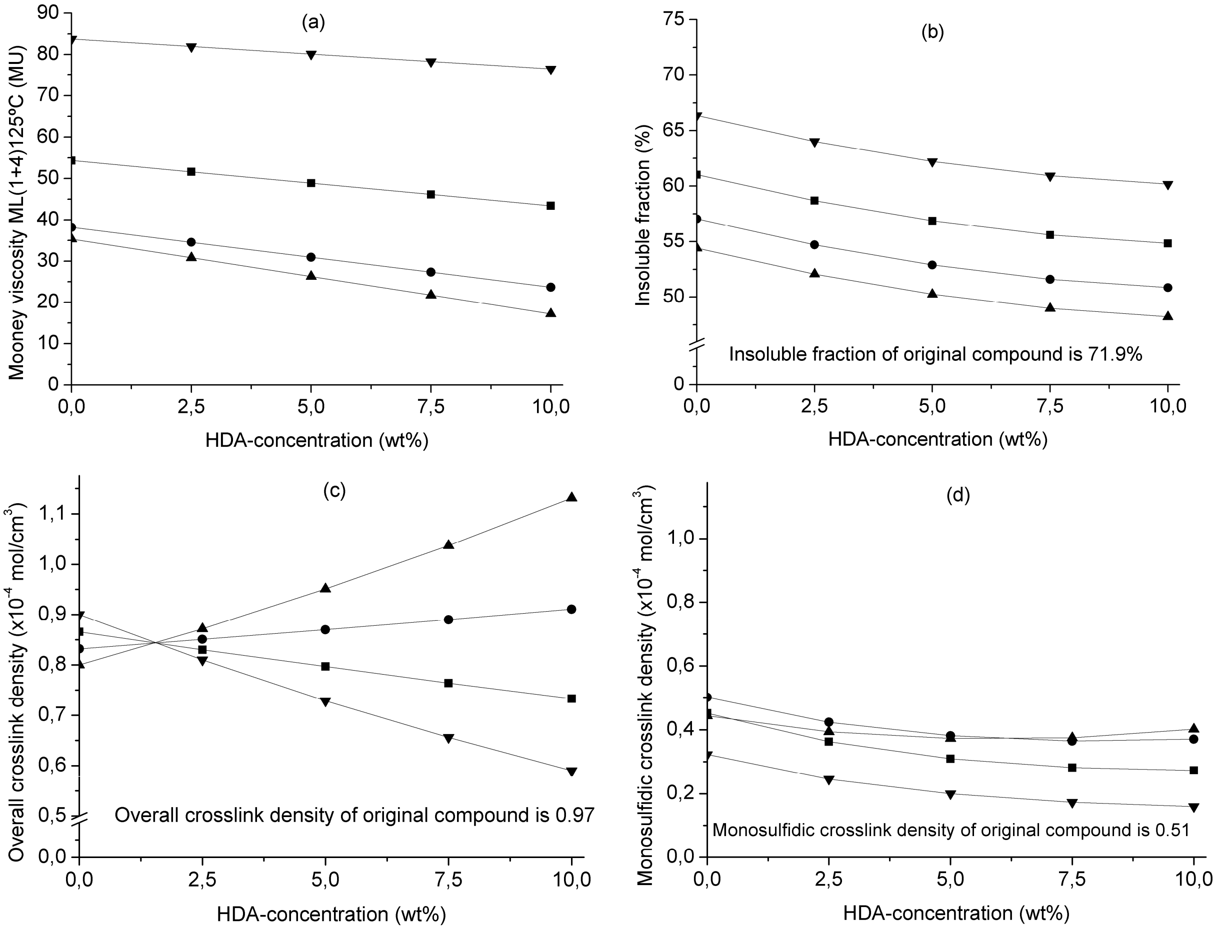

Figure 4.17: Influence of the HDA-concentration on (a): Mooney viscosity; (b): insoluble fraction; (c): overall crosslink density and (d): monosulfidic crosslink density of reclaim B; (▼): 200°C; (■): 225°C; (●): 250°C; (▲): 275°C

Figure 4.17(c) shows that reclaim of compound B behaves quite differently from the reclaim from conventionally cured rubber: without the use of HDA, the crosslink density of the insoluble fraction remains more or less equal to the crosslink density of the original vulcanized compound B (Table 4.5) for all reclaiming temperatures employed: thermal treatment alone does not lead to a decrease of the crosslink density. When HDA is applied, a decrease in overall crosslink density of the insoluble fraction with increasing concentration of HDA is observed for reclaiming temperatures of 200°C and 225°C, while the crosslink density at 250°C and 275°C rises with addition of HDA: a moderate reclaiming temperature and the addition of HDA as devulcanization aid is required for a significant decrease in crosslink density, otherwise the opposite effect is obtained. After reclaiming at 275°C, reclaim B has a much lower Mooney viscosity compared to reclaim A and demonstrates tacky behavior, even though the crosslink density of the remaining insoluble fraction after extraction of this reclaim increases with increasing HDA-concentration. Figure 4.17(d) demonstrates that the addition of HDA enhances monosulfidic bond scission at all temperatures except at 275°C. For the other reclaiming temperatures, the monosulfidic crosslink density of the reclaim is always lower than that of the original compound B.

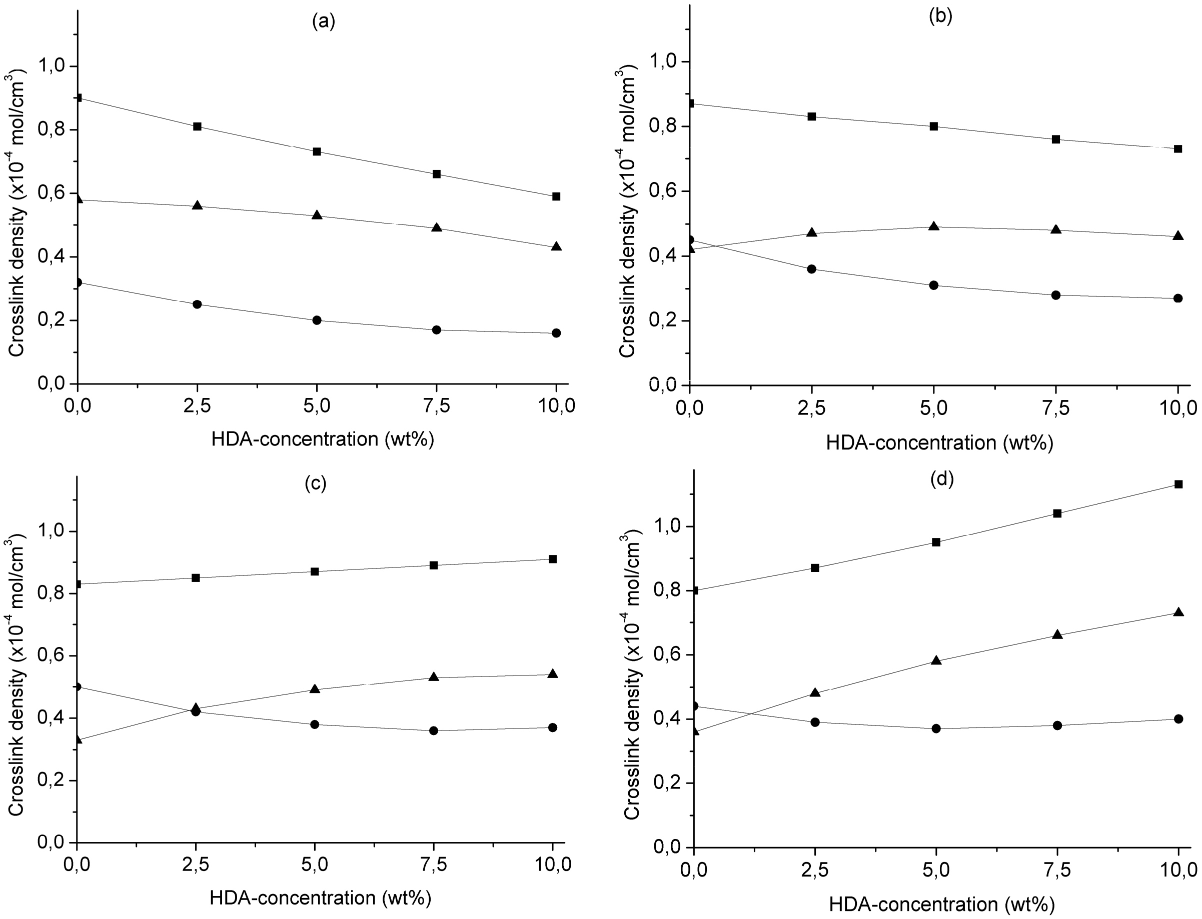

Figure 4.18: Influence of HDA-concentration on the specific crosslink densities of reclaim B at (a): 200°C; (b): 225°C; (c): 250°C and (d): 275°C; (■): Overall; (●): monosulfidic and (▲): di- plus polysulfidic crosslink densities

Figure 4.18 shows that the decrease in overall crosslink density with increasing HDA-concentration at 200°C is caused by a reduction of the monosulfidic, as well as of the di- plus polysulfidic crosslink densities. The less pronounced decrease in crosslink density at 225°C compared to the reduction at 200°C is due to a slight increase in di- and polysulfidic crosslink density with increasing HDA-concentration. The rise in crosslink densities at 250°C and 275°C is caused by growing di- plus polysulfidic crosslink densities and a more or less constant or even increasing monosulfidic crosslink concentration, respectively, with larger amounts of HDA used.

Figure 4.19(a) shows light microscopy homogeneity pictures of reclaim B embedded in virgin rubber gumstock. Particles with a diameter of less than 500μm are shown, and Figure 4.19(b) illustrates that these reclaim particles do not demonstrate the clear contours as seen for reclaim A in Figure 4.13. They are more apt to be smeared out in the rubber matrix during mixing.

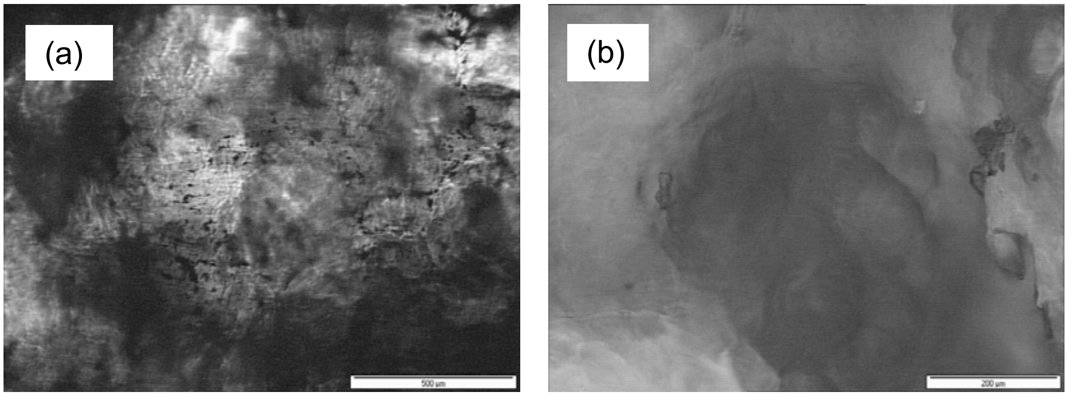

Figure 4.19: Microscope picture of reclaim B in EPDM gumstock with (a): 10x magnification and (b): 20x magnification

4.3.2 Application Study of Reclaims A and B

Based on the reclaiming experiments described above, the following optimized conditions were chosen to produce larger quantities of reclaims of compounds A and B:

- reclaiming time: 7.5 minutes;
- rotor speed: 75 rpm;
- amount of HDA as devulcanization aid: 5 wt%, and
- reclaiming temperature: 250°C for reclaim A and 225°C for reclaim B.

These reclaims were blended with the original virgin EPDM masterbatch in varying proportions to investigate their influence on properties.

The maximum torque values of the blends of reclaim A and B with the virgin EPDM masterbatch cured at 170°C are shown in Figure 4.20.

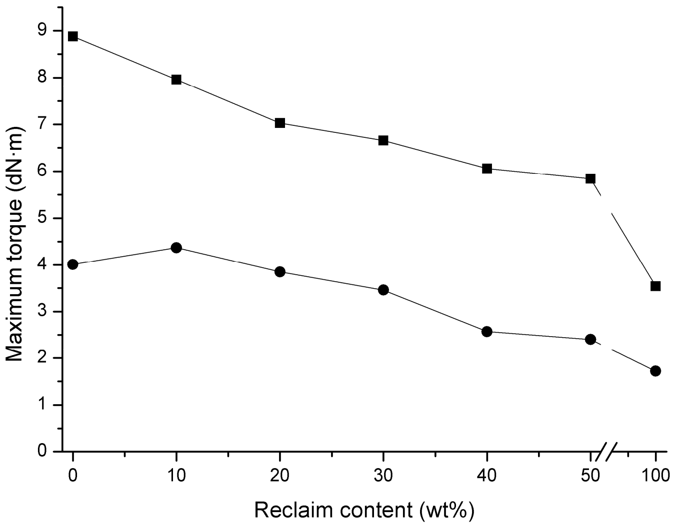

Figure 4.20: Influence of reclaim content on the maximum torque of reclaim (■): A, and (●): B

A decreasing maximum torque with increasing reclaim content for the compounds containing reclaim A, is indicative of a decrease in crosslink density with increasing amount of reclaim A. For reclaim B an increasing maximum torque is shown when 10 wt% of reclaim is added, but again a decrease in the maximum torque for higher concentrations is observed.

Figure 4.21 shows compression molded sheets of 50/50 reclaim/virgin blends. The blends containing reclaim A made from a granulate with an initial particle size of less than 8 mm show a rough surface, while in Figure 4.22 no surface irregularities are present when granulate of less than 3.35 mm is used. Reclaim B with an initial particle size smaller than 8 mm gave a perfectly smooth surface when blended with virgin masterbatch.

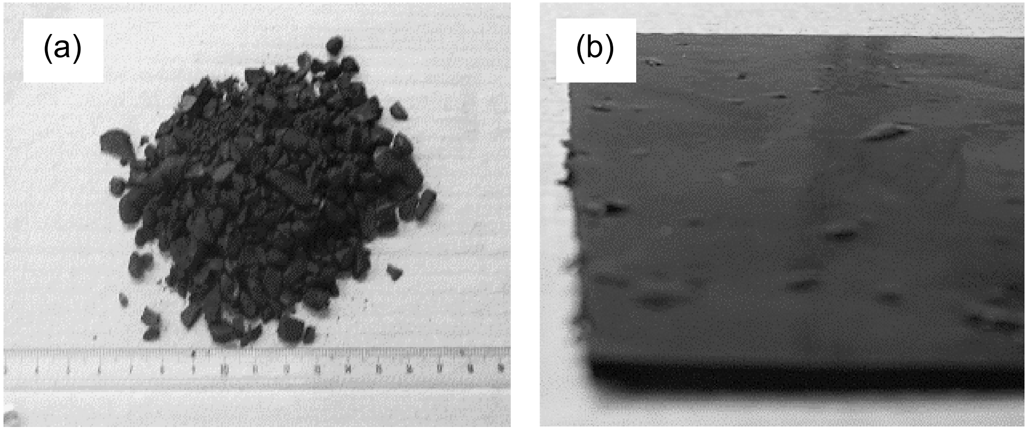

Figure 4.21: (a): Granulate screened over a 8 mm screen and (b): cured sheet with reclaim A of this initial particle size

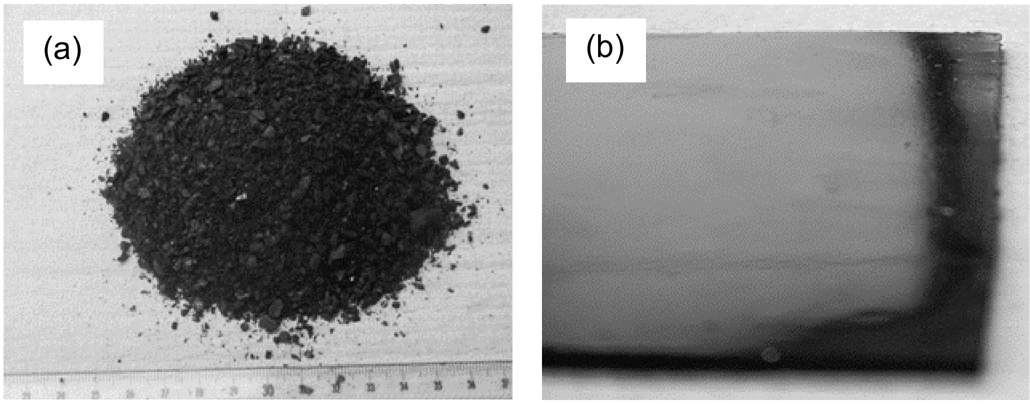

Figure 4.22: (a): Granulate screened over a 3.35 mm screen and (b): cured sheet with reclaim A of this particle size and reclaim B of the initial particle size

Figure 4.23(a) shows a constant decrease in insoluble fraction with increasing content of reclaim A, while a slight increase in insoluble fraction is seen for 10 wt% of reclaim B added, followed by a decrease with larger additions of reclaim B. The influence of the reclaim based on the smaller granulate is perfectly in line with the influence of the coarser particles A.

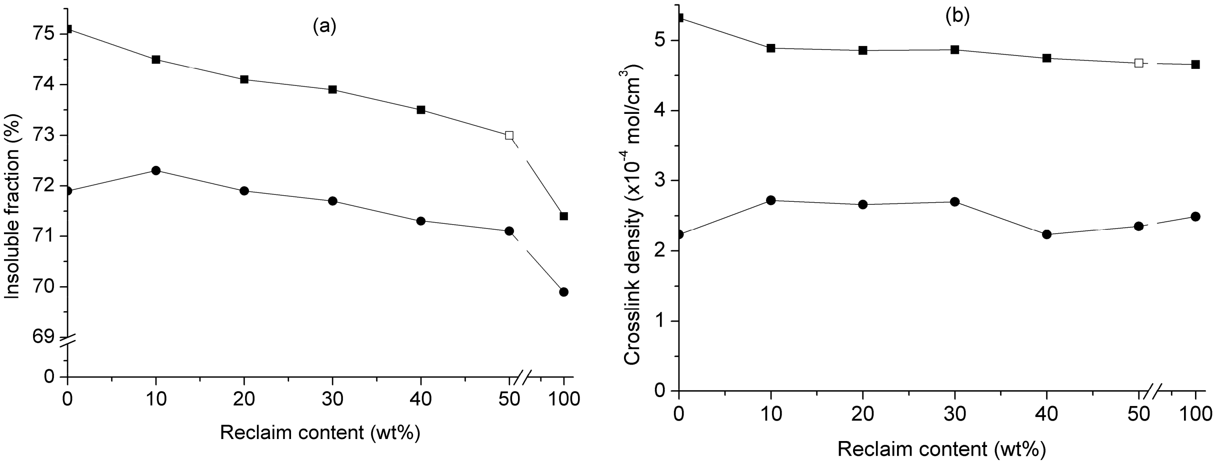

Figure 4.23: (a): Insoluble fraction and (b): crosslink density as a function of the reclaim content; (■): reclaim A; (□): reclaim A, 3.35 mm powder and (●): reclaim B

The crosslink density changes only slightly with addition of reclaims A and B. Reclaim A shows a slight decrease with increasing contents of reclaim A, as shown in Figure 4.23(b), while reclaim B again shows an initial increase. The value for the smaller granulate A is again in line.

The mechanical properties of the revulcanized blends containing reclaim A and B in quantities up to 50 wt%, resp. of the pure revulcanized reclaim are shown in Figure 4.24. Tensile strength, elongation at break and hardness decrease with increasing contents of reclaim A, while the compression set at 70°C shows a strong rise. Compression set at 23°C and modulus at 300% strain remain constant and tear strength shows a maximum with increasing amounts of reclaim A. The 50/50 blend with reclaim A of initial particle size smaller than 3.35 mm shows somewhat better properties compared to the same compound with reclaim of the initial particle size smaller than 8 mm, with hardness being independent of initial particle size.

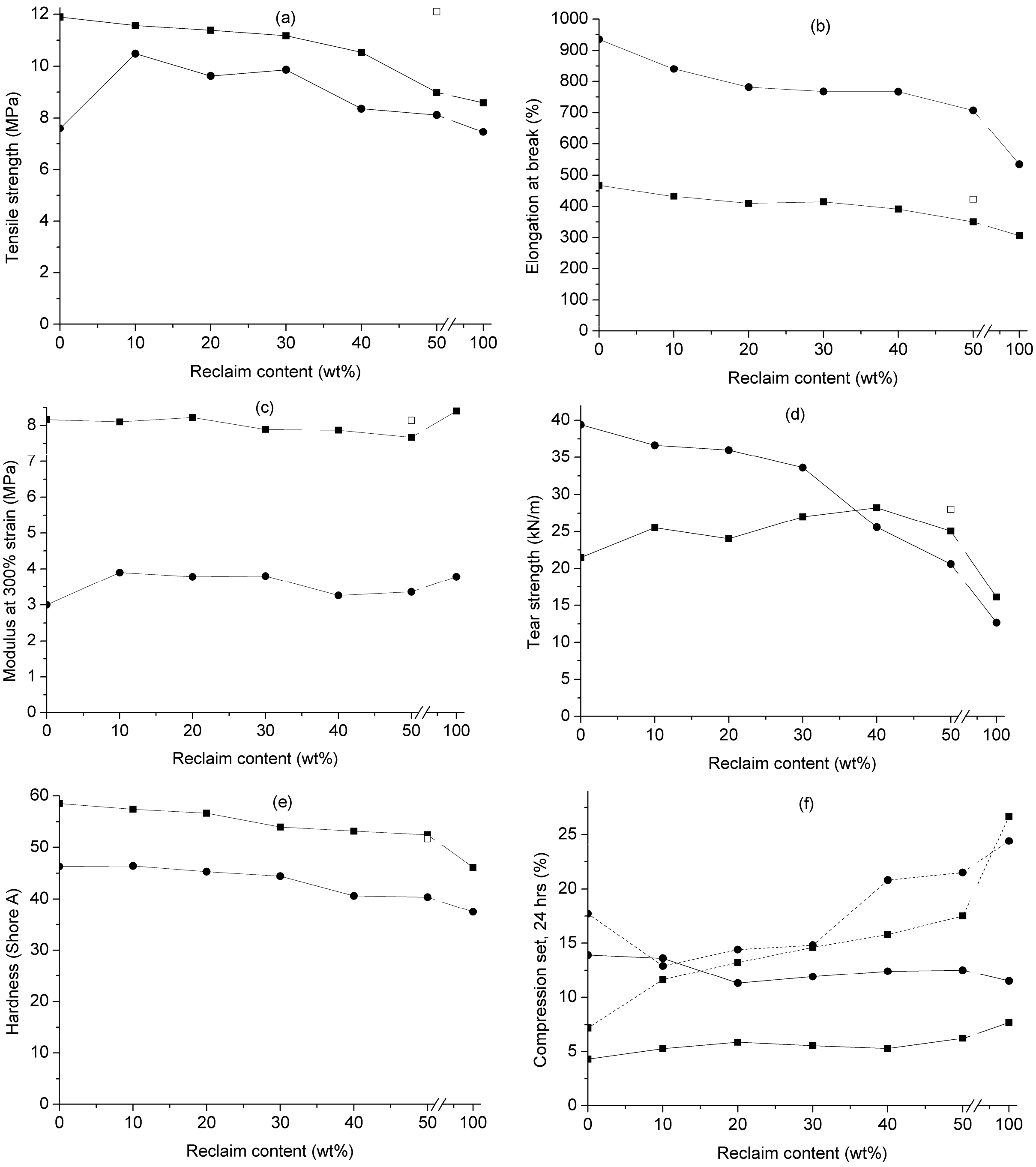

Figure 4.24: (a): Tensile strength; (b): elongation at break; (c): modulus at 300% strain; (d): tear strength; (e): hardness and (f): compression set, (——): 23°C and (– –): 70°C as a function of the reclaim content; (■): reclaim A; (□): reclaim A, fine powder and (●): reclaim B

The revulcanizates containing reclaim B show a maximum in tensile strength and a decrease in tear strength with increasing concentration of reclaim. For all other properties, the same trends as for the blends with reclaim A are found.

4.4 DISCUSSION

4.4.1 Devulcanization of Compounds A and B with Hexadecylamine

It is well known that monosulfidic crosslinks have a higher dissociation energy than di- or polysulfidic bonds. Consequently, it was anticipated that vulcanizates with a high percentage of poly- and/or disulfidic crosslinks would be more prone to devulcanize than those with mainly monosulfidic bonds. This would favor compound A for easier devulcanization than compound B. However, the outcome of this study shows a different picture.

A conspicuous difference is observed in the reclaiming behavior of compounds A and B in Figures 4.10 and 4.17. For compound B, even by simple thermal treatment without use of HDA, low Mooney values are obtained; whereas for compound A, thermal treatment alone is insufficient and addition of HDA is required. Where the most obvious difference between compound A and B was the more than double crosslink density of compound A before reclaiming, a noticeable breakdown of the network and detachment of polymer chains is achieved only by a combined action of heat and reclaiming agent.

Another difference is that the addition of increasing amounts of HDA enhances the temperature effect for compound A, whereas for material B the temperature-sensitivity is not dependent on the HDA-concentration. This again is an indication that HDA plays a more important role in reclaiming of compound A compared to material B, and that the reaction initiated by HDA is temperature-dependent. Furthermore, compound B in general shows higher temperature-sensitivity than material A.

For compound A, thermal treatment alone results only in a little decrease of the insoluble fraction, slightly dependent on the temperature applied. Or conversely, only 3-5% soluble reclaimed matter is generated in addition to the original vulcanized compound A, resulting in still unmeasurable high Mooney viscosity values. However, Figure 4.10(c) shows that throughout the insoluble fraction, a significant decrease in crosslink density is achieved relative to the initial value. The additional shift from poly- and disulfidic crosslinks to an increased amount of monosulfidic crosslinks, as shown in Figure 4.11, is a well known phenomenon in rubber vulcanization. During prolonged vulcanization, desulfurization of polysulfidic crosslinks takes place and the liberated sulfur reacts to form new, short sulfur bridges. This reduces the average crosslink length.

For compound B the opposite effect is seen: significant amounts of soluble material are generated, simply when the material is thermally treated. Dependent on the temperature applied, 6-18% sol fraction is generated in addition to the original vulcanized compound B, while the crosslink density within the non-soluble matter after reclaiming is essentially still equal to that of the material before reclaiming. Dependent on the reclaiming temperature, the crosslink density de- or increases when HDA is added. Above a temperature of appr. 240°C, HDA reacts as crosslinking promoter rather than as devulcanization aid.

This difference in regeneration mechanisms between compound A and compound B can further be detailed, making use of method developed by Horikx. 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[13]. When main-chain scission takes place, the relative decrease in crosslink density is given by equation 4.4:

$$1-\frac{\nu_f}{\nu_i}=1-\left[\frac{\left(1-s_f^{1/2}\right)^2}{\left(1-s_i^{1/2}\right)^2}\right] \tag{4.4}$$

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 equation 4.5:

$$1-\frac{\nu_f}{\nu_i}=1-\left[\frac{\gamma_f}{\gamma_i}\frac{\left(1-s_f^{1/2}\right)^2}{\left(1-s_i^{1/2}\right)^2}\right] \tag{4.5}$$

where the parameters γ_f and γ_i are the average number of crosslinks per chain in the remaining insoluble network after and before reclamation, respectively. The γ's are determined as described by Verbruggen[3]. Figure 4.25 gives a graphical representation of equations 4.4 and 4.5. 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.

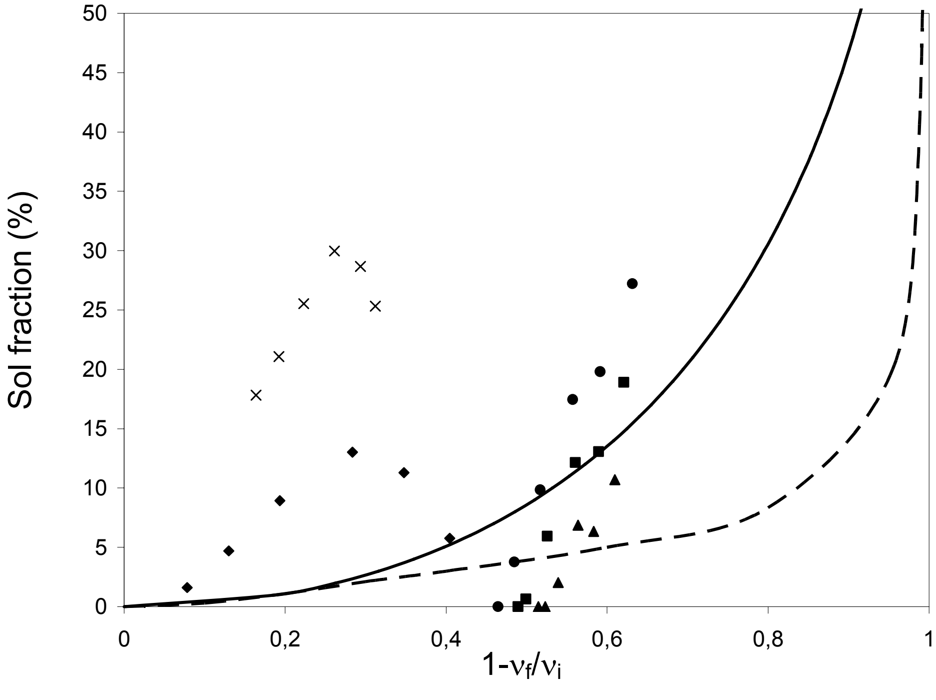

Figure 4.25: Fraction of sol generated during reclaiming versus the relative decrease in crosslink density. (—): only main-chain scission; (– –): only crosslink scission; (▲): reclaim A at 225°C; (■): reclaim A at 250°C; (●): reclaim A at 275°C; (♦): reclaim B at 200°C and (×): reclaim B at 225°C

Figure 4.25 also shows the experimentally determined sol fractions of reclaim A and reclaim B, as a function of the relative decrease in crosslink density. A correction was made for the presence of HDA and reclaiming oil in the soluble fraction, when calculating the sol fractions. For reclaim A, some experimental data points cluster around the line describing crosslink scission: this is the prevalent breakdown mechanism. Other points are in between the two lines and some are even above the main-chain scission only line. The data points for reclaim B are all above the line for main-chain scission, but at a much lower relative decrease in crosslink density.

A limitation of the Horikx representation is, that it assumes homogeneous breakdown of the vulcanized network throughout the particles. However, the results for reclaim B, and less so for A, indicate a different mechanism: peeling of the outer layers of the particles, while the inner cores of the particles stay more or less untreated at constant crosslink density. 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. Consequently, the data points in Figure 4.25 are shifted to the left vs. where they would have been situated for the same amount of network degradation all through the particles. Still it is seen that the data points for reclaim B are all situated more to the left side of the plot than those for reclaim A. Even though these points cannot directly be related with the theoretical lines, it clearly indicates that reclaim B is qualitatively more due to main-chain scission in comparison with reclaim A. This must be the result of the higher ratio of the lower bond energy di- and polysulfidic crosslinks vs. the monosulfidic ones in the original compound A, in comparison with compound B. The fact that some new monosulfidic crosslinks are formed during reclaiming, is then of minor importance.

In case of the efficiently vulcanized compound B, a proper choice of the process temperature together with HDA as devulcanization aid is important in order to prevent an increase in crosslink density in the insoluble fraction: Figure 4.17. Earlier investigations have shown that HDA can also act as a crosslink promoter for EPDM[14, 15]. It is well known that amines in general have an enhancing effect on sulfur crosslinking. Thus, a proper combination of relatively low temperature and addition of HDA as devulcanization aid is crucial for obtaining a good quality recyclate. Figures 4.10(d) and 4.17(d) clearly indicate that HDA is even able to chemically break the thermally stable monosulfidic crosslinks.

It can be concluded that both vulcanizates, the conventional polysulfidic one and the efficiently vulcanized primarily monosulfidic one, can be reclaimed. Temperature is the main governing factor and addition of HDA can significantly enhance the effects. Rotor speed and treatment time have a minor effect. Breakdown of the material is under the chosen circumstances a fast process, and after a few minutes of treatment no significant changes are observed anymore. However, the difference in crosslink density and distribution leads to different breakdown mechanisms as is schematically depicted in Figure 4.26.

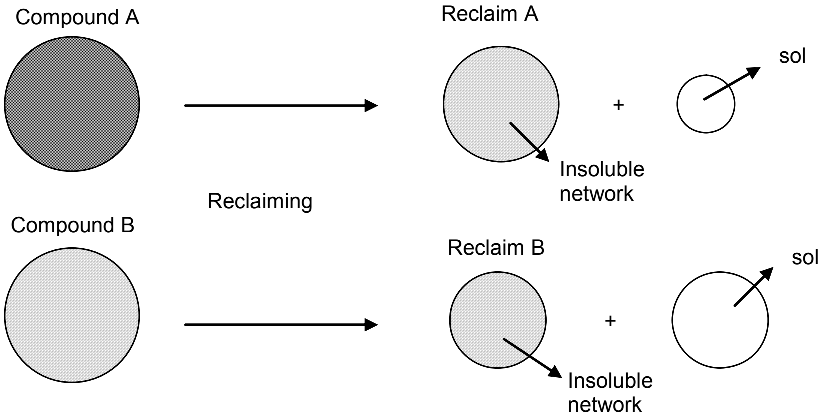

Figure 4.26: Schematic representation of the reclamation of compounds A and B

4.4.2 Application Study of Reclaims A and B

In spite of the different reclaiming mechanisms, both reclaims perform very well in the application study. The mechanical properties of compounds containing increasing amounts of reclaim are only mildly influenced up to 50 wt% of reclaim added. These are very high amounts compared to e.g. the use of ground non-reclaimed rubber powder, which already leads to a significant property decrease when more than 10-15 wt% in virgin compounds is applied[16].

It is of no use to try to interpret all separate properties of the re-vulcanizates on basis of crosslink densities, because of the different nature of both reclaims and the degenerate nature of the polymer molecules contained therein. Most conspicuous is that the differences in re-vulcanizate properties of the reclaim-containing compounds are largely retained up till 50 wt% reclaim: the compounds with the conventional curing package still give overall the best properties in comparison with the efficient system. The tear strength deteriorates substantially for reclaim B, while for reclaim A no tear strength decrease is seen up till 50% reclaim in Figure 4.24. Reclaim B was shown to still consist of practically untreated particles embedded in reclaimed plasticized material. Even though Figure 4.19 seems to indicate a better homogeneity for reclaim B than for reclaim A, the data in Figure 4.24 seem to indicate the opposite.

The effect of initial particle size: 3.35 mm vs. 8 mm leading to slightly better mechanical properties, may be due to a more homogeneous reclaiming, resp. a relatively higher efficiency of the peeling off the particles. The smaller the particles to begin with, the better the reclaiming, leading to some improvement in properties: in particular tensile strength and elongation at break, two properties well known to be most sensitive to inhomogeneities in vulcanized compounds.

4.5 CONCLUSIONS

The mechanism and efficiency of reclaiming of sulfur vulcanized EPDM compounds with hexadecylamine as devulcanization aid strongly depends on their crosslink density and crosslink distribution. During thermal reclaiming of a conventionally cured, primarily poly- and disulfidic EPDM-vulcanizate, a significant reduction in crosslink density of more than 50%, is obtained for a temperature in the range of 225ºC till 275ºC. The application of hexadecylamine as devulcanization aid results in a further decrease in crosslink density. Primarily poly- and disulfidic crosslinks are broken and some are transformed into monosulfidic bonds, even though HDA is able to break a sizeable portion of the monosulfidic bonds as well.

The reclaiming process of an efficiently vulcanized, primarily monosulfidic EPDM-vulcanizate shows different characteristics. Thermal treatment without the aid of HDA causes mainly random main-chain scission of the rubber network, resulting in small oligomeric fragments released from the network. The crosslink density of the remaining non-soluble material responds to the addition of HDA with a decrease in crosslink density at low treatment temperatures of 200ºC and 225ºC, but with an increase at higher temperatures of 250°C and 275ºC.

Reclaiming of the conventionally vulcanized compound therefore takes place primarily by sulfur crosslink scission or devulcanization, while that of the efficiently vulcanized compound happens mainly by main-chain scission. HDA is a valuable devulcanization aid for both types of EPDM compounds. It is even able to break monosulfidic crosslinks, taking into account the different reclaiming parameter settings for each single compound. The temperature clearly has the largest influence on the amount of reclaiming within the experimental ranges investigated.

All compounds with up till 50 wt% of reclaims A or B added to a virgin EPDM masterbatch show good mechanical properties compared to the values of the original compounds A and B.

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Chapter 5

Reclaiming of EPDM-Rubber: A Comparative Evaluation of Hexadecylamine, Diphenyldisulfide and o’o’-Dibenzamidodiphenyldisulfide as Devulcanization Aids

The influences of hexadecylamine (HDA), diphenyldisulfide (DPDS) and o’o’-dibenzamidodiphenyldisulfide (BAFD) as devulcanization aids on the reclaiming efficiency of two types of carbon black filled EPDM-rubber: a conventionally cured primarily polysulfidic, and an efficiently vulcanized mainly monosulfidic compound differ significantly.

DPDS and BAFD are not effective in helping the break-down of the conventionally cured rubber network, whereas HDA has a strong positive effect. DPDS and BAFD do not lead to reclaims plasticized to such an extent that acceptable Mooney viscosities are obtained, unless for the highest reclaiming temperatures and additions of these devulcanization aids. HDA does for all temperatures, even at low dosages. In all cases the reclaims can be added up to 50 wt% to a virgin EPDM masterbatch without significantly influencing the properties of the revulcanized compounds.

The devulcanization aids act differently when used for reclaiming a largely monosulfidic compound. Because of the low crosslink density of the compound to start with, it can easily be plasticized even without addition of devulcanization aids at the lowest temperature of 200°C employed. DPDS and BAFD plasticize the compound to a higher extent compared with HDA. The reclaims obtained with HDA as well as with BAFD provide good mechanical properties when added to a virgin masterbatch: some properties are even improved by addition of these reclaims. In contrast to this, the DPDS treated material is difficult to revulcanize, resulting in a significant reduction of the material properties.

The observations confirm the different reclaiming mechanisms for the two types of EPDM: mainly homogeneous reclaiming/devulcanization of the conventionally cured compound, vs. peeling-off plasticized shells of the efficiently vulcanized compound. However, these two differences do not necessarily reflect in poor properties of the revulcanized blends of these reclaims with virgin compound.

It can be concluded that HDA is the most universally applicable devulcanization aid, because it gives for both types of EPDM well plasticized materials and good mechanical properties of revulcanized blends with up to 50 wt% of these reclaims. BAFD can be a good alternative, but results in less processable reclaims in the case of the conventionally cured compound. DPDS is no option as devulcanization aid, as the reclaim based on the efficiently cured material is not suitable for revulcanization.

The work described in this chapter will be submitted for publication to Rubber Chemistry and Technology.

5.1 INTRODUCTION

A comparative study is done on the performance of three different chemicals as devulcanization aids for carbon black filled EPDM-rubber: diphenyldisulfide (DPDS), hexadecylamine (HDA) and o'o'-dibenzamidodiphenyldisulfide (BAFD). DPDS was chosen, because it is the most widely used devulcanization aid for natural rubber (NR): sulfur-vulcanized NR can be reclaimed at 200-225°C by using this disulfide[1]. The obtained product improves processing of a compound, as it reduces the mixing-energy[2]. As already mentioned in Chapter 4, previous research at the University of Twente[3-5] has shown that synthetic rubbers, and especially sulfur-cured EPDM, need far more strenuous conditions for reclaiming than NR. Diaryldisulfides, are to some extent also promoting the devulcanization of EPDM. However, they result in EPDM-reclaims, of which the chemical integrity is largely damaged and which are insufficiently active in revulcanization.

Various aliphatic amines and their derivatives were applied in reclaiming synthetic rubbers basically since the time of the Second World War, making use of the fact that primary and secondary amines can cleave cyclic octa-sulfur. In previous research, α-H-containing aliphatic amines were found to be effective as devulcanization aids for EPDM-rubber[3]. Therefore, HDA was selected as a second devulcanization aid in this study.

BAFD is used in the rubber industry as peptizing agent for NR and synthetic butadiene-styrene rubber (SBR)[6]. This chemical compound is a combination of a disulfide and an amide. DPDS reacts via a radical mechanism, while HDA reacts in a nucleophilic way. Although it is not an α-H-containing aliphatic amine, it is interesting to investigate whether a combination of these two reaction mechanisms in one molecule can enhance the efficiency of EPDM-rubber reclaiming.

In the present chapter, a correlation will be made between the reclaiming efficiency and the suitability of the resulting reclaim for revulcanization. Increasing amounts of the differently reclaimed materials are blended with a virgin EPDM masterbatch and cured with a conventional or efficient curing package. The influence of the different reclaims on the physical and mechanical properties is investigated in an application study.

5.2 EXPERIMENTAL

Compound recipes and materials – Reclaiming was performed on ground material of two types: conventionally and efficiently vulcanized EPDM-rubber.

The EPDM masterbatch used for this investigation was the same as described in Chapter 3.

Table 5.1 Masterbatch and curing recipes

Material	Compound A CONV system (phr)	Compound B EV system (phr)
Masterbatch		
EPDM	100	
ZnO	5	
Stearic acid	1	
Carbon black N550	70	
Carbon black N772	40	
Paraffinic oil	70	
Curing recipes		
TMTD	1.0	1.0
MBT	0.5	
CBS		1.5
DPTT		0.8
Sulfur	1.5	

The curing additives used for the vulcanization are further detailed in Table 5.2.

Table 5.2 Materials used for vulcanization

Material	Abbr.	Supplier
Sulfur	S	Merck
2-Mercaptobenzothiazole	MBT	Merck
Tetramethylthiuramdisulfide	TMTD	Flexsys
N-Cyclohexyl-2-benzothiazole sulfenamide	CBS	Flexsys
Dipentamethylene thiuramtetrasulfide	DPTT	Flexsys

Hexadecylamine (HDA) 92% pure (Merck), diphenyldisulfide (DPDS) and o’o’-dibenzamidodiphenyldisulfide (BAFD) were used as devulcanization aids, of which the chemical structures are shown in Table 5.3. Paraffinic oil was used as reclaiming oil, the same Sunpar 2280 as used for the original compound. The solvents and chemical probes for the crosslink distribution determinations were the same as used in Chapter 4.

Mixing and vulcanization as well as *grinding* were performed as described in Chapter 4.

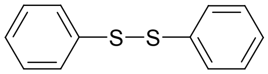
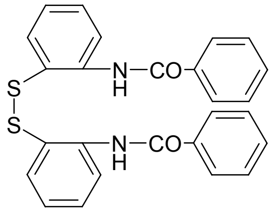
Reclaiming – EPDM-rubber particles were reclaimed in a Brabender Plasticorder PL 2000. Its mixing chamber had a volume of 35 ml, fitted with a cam-type rotor. A fill factor of 70% was applied. The reclaiming conditions are summarized in Table 5.4. In Chapter 4 it was already demonstrated that rotor speed and reclaiming time only had a minor influence on the reclaiming efficiency compared to reclaiming temperature and concentration of devulcanization aid.

Therefore, time and rotor speed were fixed at 7.5 minutes and 75 rpm respectively, while the reclaiming temperature and the concentrations of devulcanization aids were varied.

5 wt% of reclaiming oil relative to the vulcanizate was added to each batch. The assumption was made that DPDS and BAFD split in two reactive groups during reclaiming, and therefore half the concentration in mmol of molecules, or equal concentration in mmol of active groups was taken for these two reclaiming agents compared to HDA. The concentrations of devulcanization aids are expressed in amounts of active groups, as shown in Table 5.5, in mmol of active groups per 100 g compound to be reclaimed.

The reclaims based on compounds A, the conventionally cured EPDM-rubber, and B, the efficiently cured material, are further referenced as reclaims HDA, DPDS and BAFD A and B, respectively.

Table 5.3 Molecular structures of the devulcanization aids

Chemical name	Chemical structure
Hexadecylamine (HDA) (MW = 241 g/mol)	$CH_3 — (CH_2)_{15} —NH_2$
Diphenyldisulfide (DPDS) (MW = 218 g/mol)	
o'o'-Dibenzamidodiphenyldisulfide (BAFD) (MW = 457 g/mol)	

The results obtained with HDA as devulcanization aid were taken from the DOE model as described previously in Chapter 4, while the data for DPDS and BAFD were experimentally determined in the present context.

Table 5.4 Reclaiming conditions

Parameter	Range
Temperature	200; 225; 250 and 275ºC
Time	7.5 min
Rotor speed	75 rpm

Table 5.5 Concentrations of devulcanization aids

Concentration of active groups (mmol/100 g compound)	Concentration of devulcanization aid (wt%)		
	HDA	DPDS	BAFD
0	0	0	0
4.14	1	0.45	0.95
10.35	2.5	1.13	2.37
20.71	5	2.26	4.73
31.06	7.5	3.39	7.09
41.41	10	4.52	9.47

Mooney Viscosity – The Mooney viscosity ML(1+4)125ºC of the reclaims was determined using a Mooney viscometer MV2000 VS from Alpha Technologies according to ISO R289.

Extractions – Extractions were carried out as described in Chapter 3.

Swelling measurements – The degree of swelling was measured on extracted samples; this allows to determine the crosslink density of the vulcanized compounds and of the remains of reclaim after removal of the solfraction, as described in Chapter 3. The crosslink density was calculated according to the Flory-Rehner equation[7]. This equation is only valid for non-filled systems. Therefore, the Kraus correction[8] for filled compounds had to be used in order to obtain the correct values of the different crosslink densities. The Kraus correction was used in its simplified form[9], as described in Chapter 4.

Crosslink distributions – The specific sulfur-rank distributions of the crosslinks in the vulcanizates and in the reclaims were determined using thiol/amine chemical probes[10-13], as described in Chapter 3.

Mechanical properties – Tensile and tear tests were carried out according to ISO 37 and ISO 34, respectively. Hardness of the samples was measured with a Zwick Hardness-meter Shore A type according to DIN 53503. Chapter 3 provides details of the measurements.

5.3 RESULTS

5.3.1 Reclaiming of Compounds A and B

The crosslink densities, specific crosslink distributions and insoluble fractions of the original vulcanized compounds A and B used in this study, before reclaiming, are given in Table 5.6. Conventionally cured compound A is characterized by a relatively high overall crosslink density with a high percentage of poly- plus disulfidic crosslinks and only 15% of monosulfidic bonds. Compound

B on basis of the efficient-curing system has 48% poly- plus disulfidic crosslinks, and a surplus of 52% monosulfidic, at an overall crosslink density less than half that of compound A. The insoluble fraction of compound A is higher compared to compound B, corresponding to the higher overall crosslink density.

Table 5.6 Crosslink densities and insoluble fractions of the original compounds

Feed stock	Crosslink density ($\times 10^{-4}$ mol/cm^3)			Insoluble fraction (%)
	Overall	Monosulfidic	Di- plus polysulfidic	
Compound A	2.39	0.36 (15%)	2.03 (85%)	75.1
Compound B	0.97	0.51 (52%)	0.46 (48%)	71.9

After grinding, both vulcanized compounds A and B were reclaimed under conditions as mentioned in Tables 5.4 and 5.5, using DPDS and BAFD as devulcanization aids. The results with HDA as devulcanization aid were taken from the DOE described in Chapter 4.

5.3.1.1 Reclaiming of Compound A

The influences of reclaiming temperature and concentration of devulcanization aid on the Mooney viscosity, the insoluble fraction and the overall, as well as monosulfidic crosslink density of reclaim A are shown in Figures 5.1 – 5.4. Compound A reclaimed with HDA resulted in plasticized batches at all temperatures and for all concentration levels of the devulcanization aid, although the viscosity of the reclaim for low concentrations is rather high. For DPDS and BAFD, a reasonable reclaiming effect was only achieved for the highest concentration of the devulcanization aid at 225°C. At 250°C, the amount of devulcanization aid needed was 20.71 mmol of active groups per 100 grams of compound for a good reclaim. Reclaiming without devulcanization aid resulted for all temperatures investigated in reclaims with too high Mooney viscosities, outside the measuring range of the Mooney viscometer.

HDA clearly has the most significant influence on Mooney viscosity in the case of reclaim A, within the whole temperature range, compared to the other two devulcanization aids. In the whole temperature and concentration window of this investigation, the Mooney viscosity is lowest for HDA as devulcanization aid, as shown in Figure 5.1. The Mooney viscosity decreases significantly with increasing temperature and concentration of all devulcanization aids, but levels off at concentrations above app. 20 mmol of active groups.

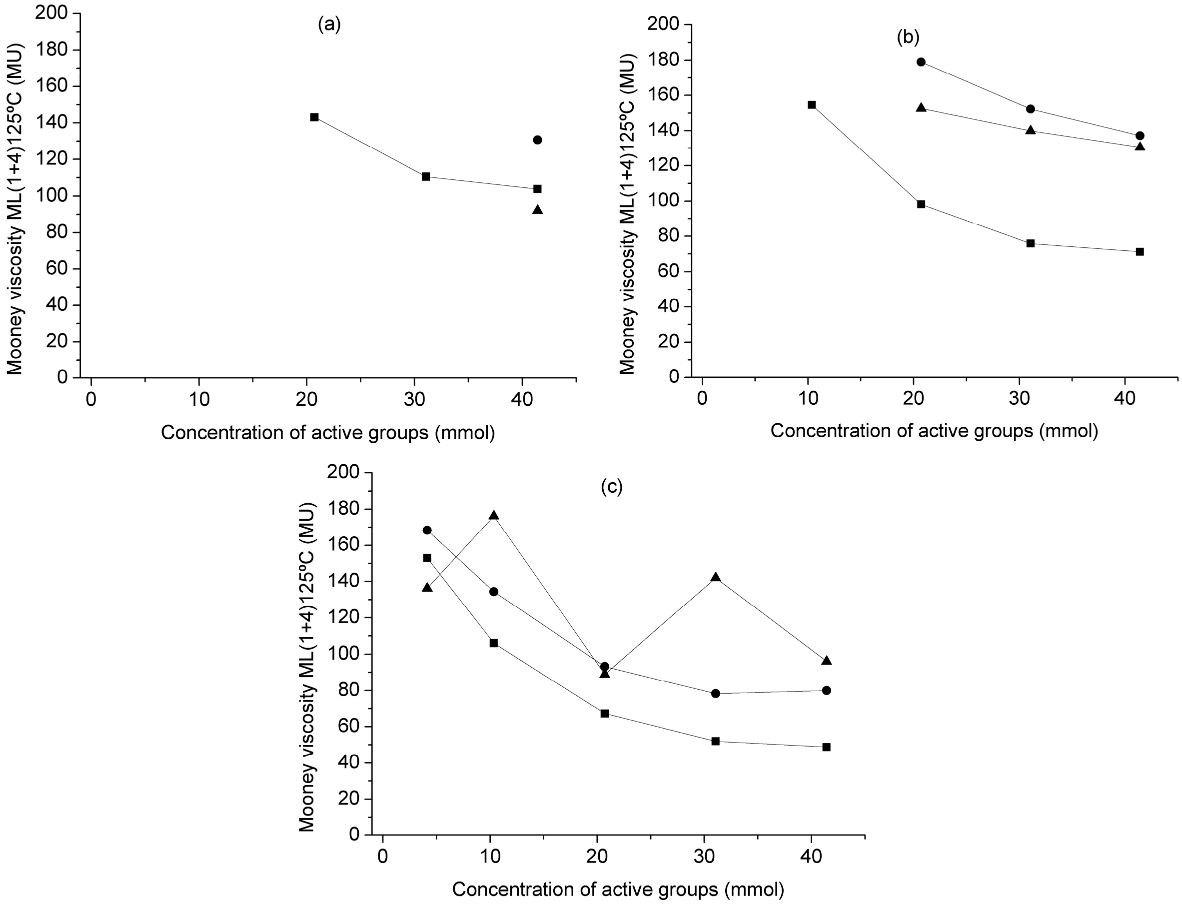


Figure 5.1: Influence of concentration of devulcanization aid on Mooney viscosity of reclaim A at (a): 225°C; (b): 250°C and (c) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

The influence of the devulcanization aids on the insoluble fractions of reclaim A, as shown in Figure 5.2, demonstrates the same pattern as seen above for the Mooney viscosity values. The insoluble fractions decrease in all cases with increasing temperature and concentration of devulcanization aids. The lowest insoluble fractions – so highest soluble fractions – are obtained with HDA as devulcanization aid for all concentrations and temperatures, while DPDS and BAFD give more or less similar results.

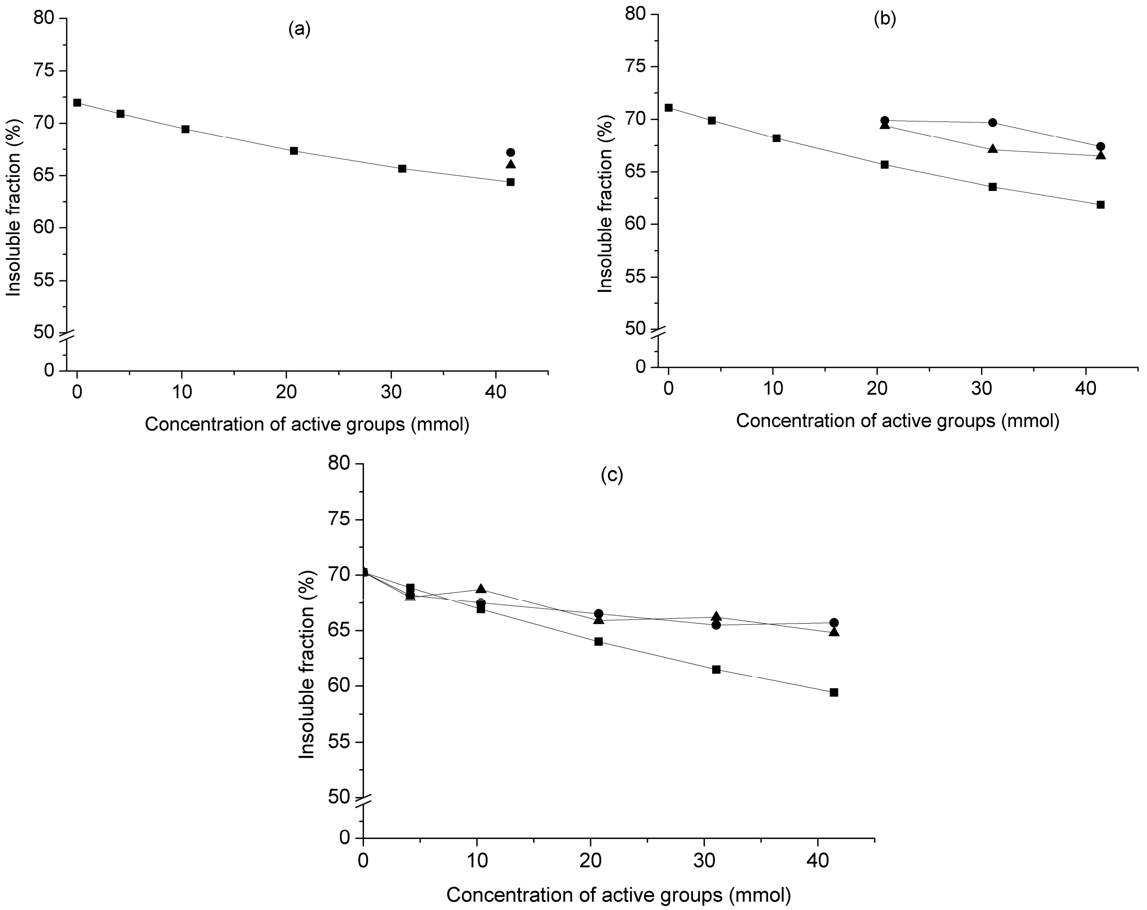


Figure 5.2: Influence of concentration of devulcanization aid on insoluble fraction of reclaim A at (a): 225°C; (b): 250°C and (c) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

Without the addition of a devulcanization aid, by only thermo-mechanical treatment, the crosslink density decreases from the original value of 2.39 to 1.16 – 1.28×10^{-4} mol/cm^3, dependent on the temperature applied, as shown in Figure 5.3. The major part of the network breakdown for reclaim A is therefore caused by the mere thermal process. Addition of a devulcanization aid has some additional effect. The addition of devulcanization aids on both the overall and monosulfidic crosslink densities of reclaim A: Figure 5.4, shows different trends depending on the type used: for HDA, the concentration of the crosslinks is monotonously reduced with increasing amount of devulcanization aid. In the case of DPDS and BAFD, both the overall and monosulfidic crosslink density show an increase with higher amounts of devulcanization aid, relative to reclaims without the addition of a devulcanization aid. These increases level off at higher concentrations of devulcanization aid. For all devulcanization aids, the reduction in overall crosslink density relative to the original compound A becomes larger with decreasing temperature. An exception to the latter are the reclaims at 250°C with BAFD as devulcanization aid, which show the most pronounced reduction in crosslink density. At all conditions applied, both the overall and monosulfidic crosslink densities are lowest for the reclaims with HDA as devulcanization aid and the highest for DPDS.

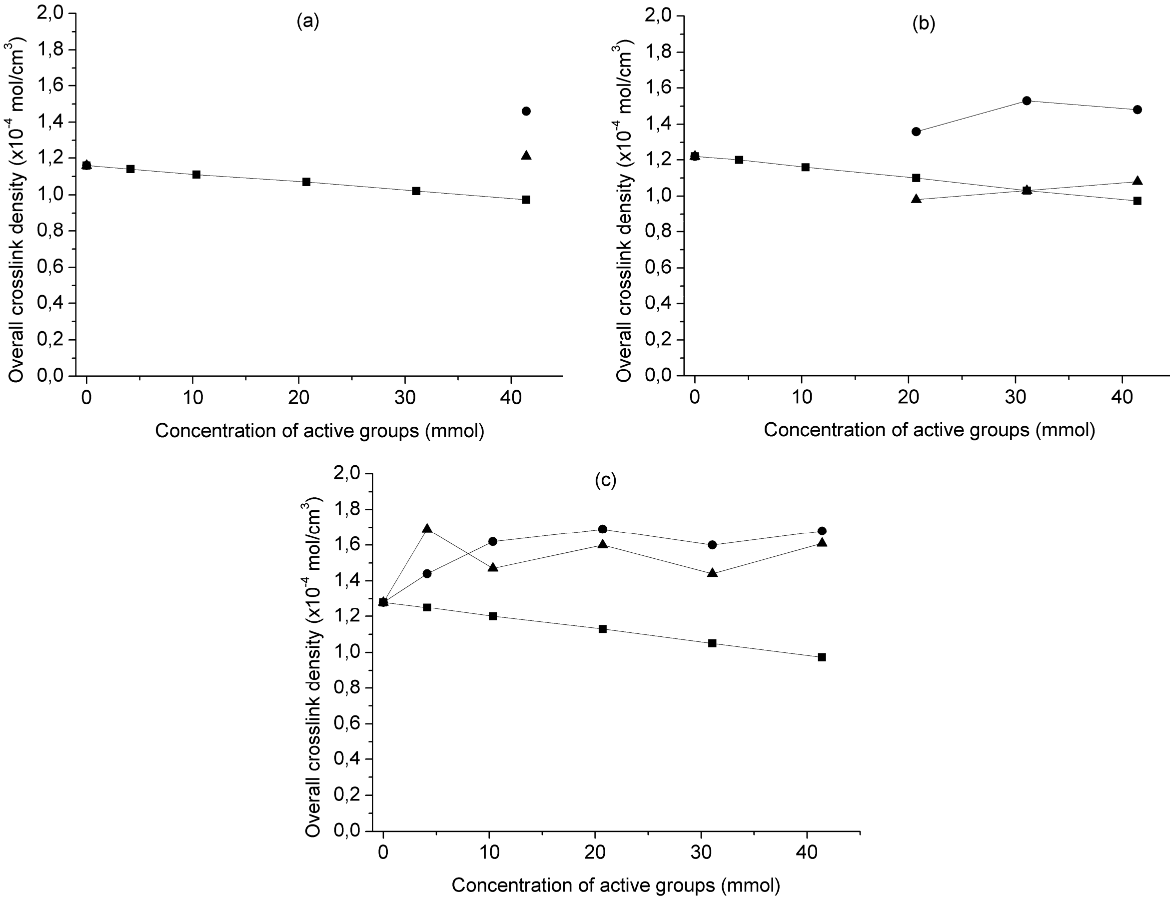


Figure 5.3: Influence of concentration of devulcanization aid on overall crosslink density of reclaim A at (a): 225°C; (b): 250°C and (c) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

Figure 5.4 also shows that HDA is able to break monosulfidic crosslinks at all temperatures, although the influence of HDA is not strong enough to compensate for the extra formed monosulfidic bonds by mere thermal reclaiming. The addition of DPDS or BAFD actually enhances monosulfidic crosslink formation in the reclaims.

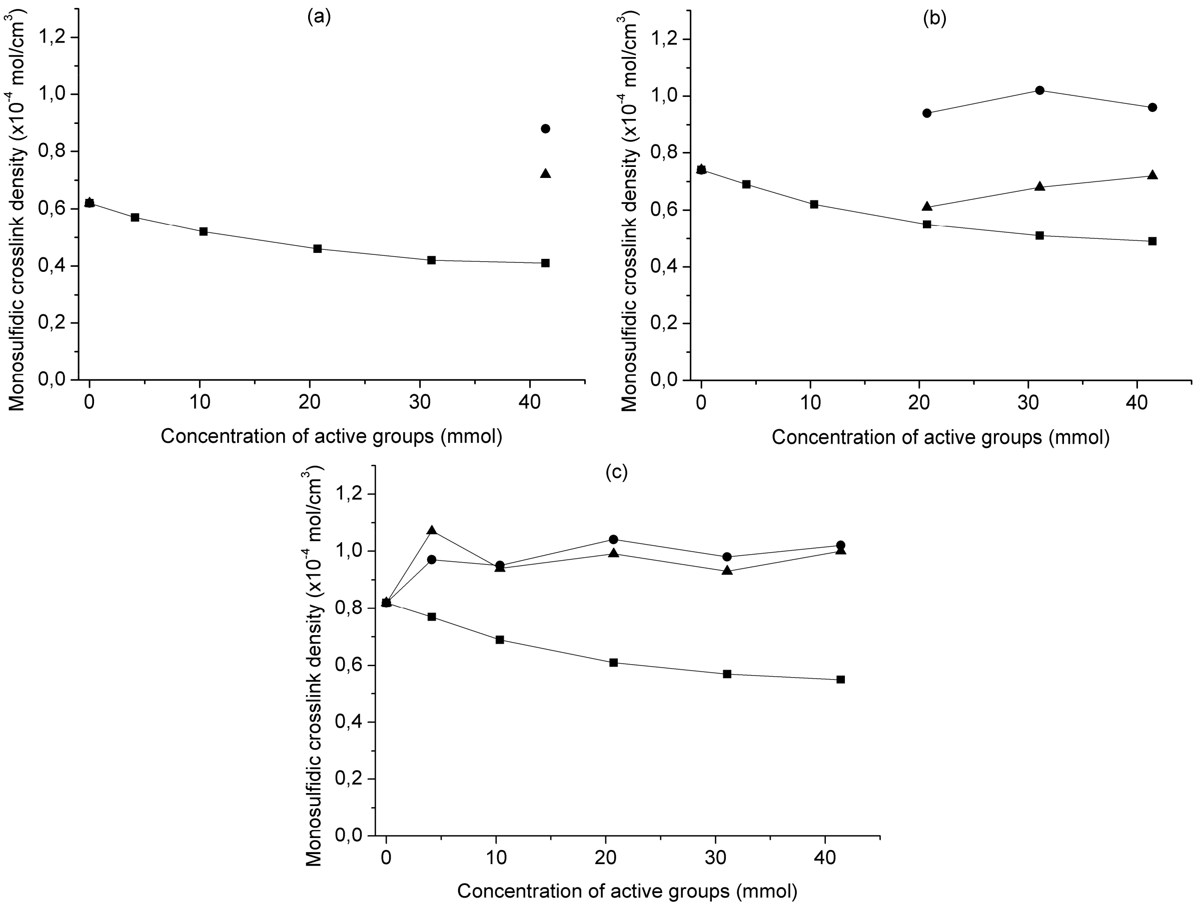


Figure 5.4: Influence of concentration of devulcanization aid on monosulfidic crosslink density of reclaim A at (a): 225°C; (b): 250°C and (c) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

Figure 5.5 shows the Horikx-plots: fraction of sol generated during reclaiming, versus the relative decrease in crosslink density of reclaim A for all temperatures and devulcanization aids applied. As shown, addition of HDA results in reclaims with the highest sol fractions and the largest relative decreases in crosslink density, as compared to DPDS and BAFD as devulcanization aids.

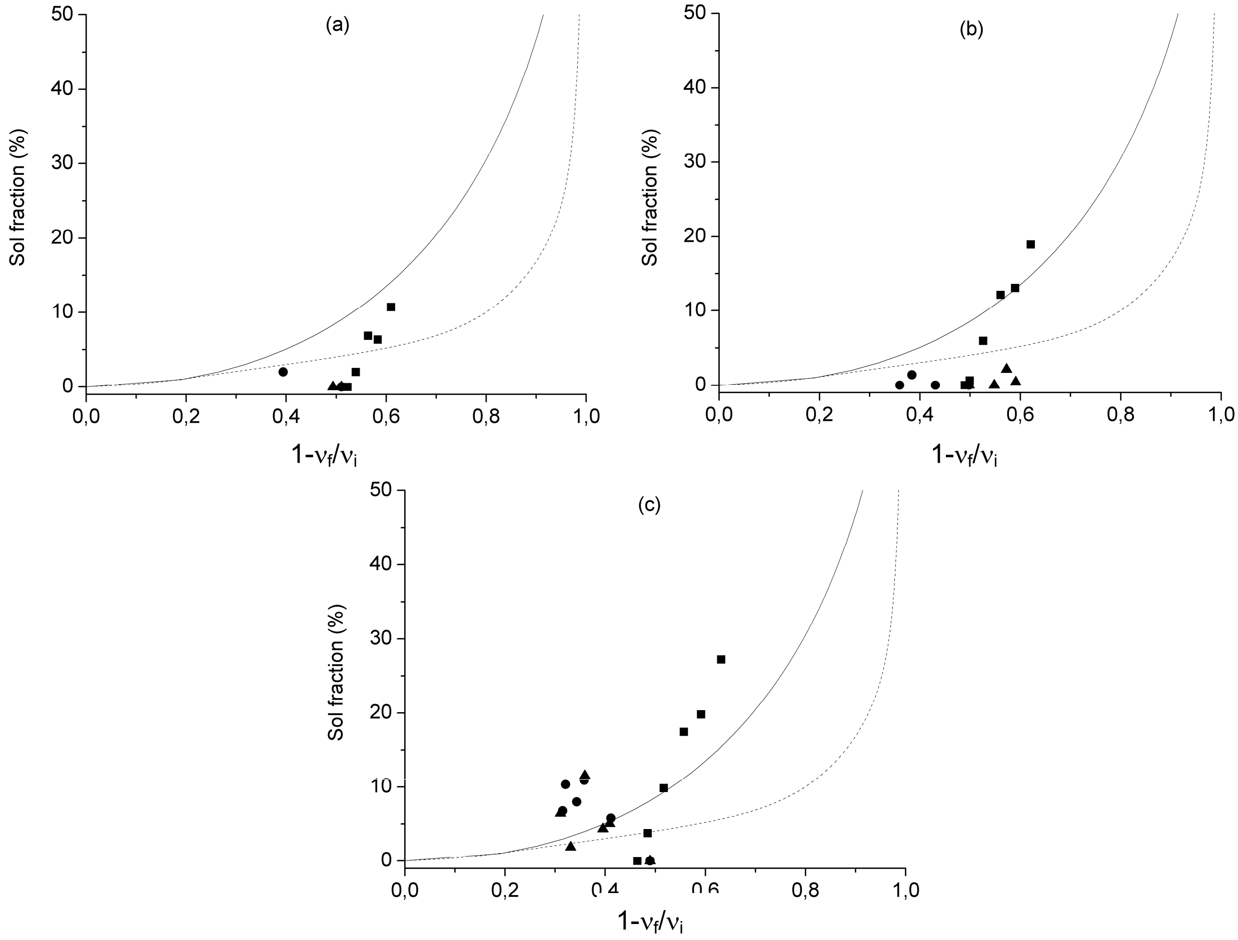


Figure 5.5: Fraction of sol generated during reclaiming versus the relative decrease in crosslink density for reclaim A. (—): only main-chain scission; (– –): only crosslink scission; (a): 225°C; (b): 250°C and (c) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

5.3.1.2 Reclaiming of Compound B

For compound B, the efficiently vulcanized material, the experimental range was widened to a lower temperature. At 275°C the reclaim had a very low viscosity and showed tacky behavior. Therefore, additional experiments at 200°C were performed in order to obtain a material with a higher viscous and less tacky behavior. Compound B behaves significantly different during reclaiming with addition of devulcanization aids, compared to compound A. Where for reclaim A HDA had the most pronounced influence as devulcanization aid on the reduction in Mooney viscosity, insoluble fraction and overall as well as monosulfidic crosslink densities, the opposite is the case for reclaim B. Figure 5.6 demonstrates that reclaiming with HDA results in materials with the highest Mooney viscosities compared to both other devulcanization aids. Addition of a small amount of DPDS or BAFD results in a significant decrease in Mooney viscosity, while further addition of these chemicals hardly has any influence on the viscosity anymore. The effect of reclaiming temperature is small in the higher range: increasing the temperature from 200°C to 225°C results in a significant reduction of the viscosity in all cases, while the change from 250°C to 275°C hardly influences the Mooney of reclaim B.

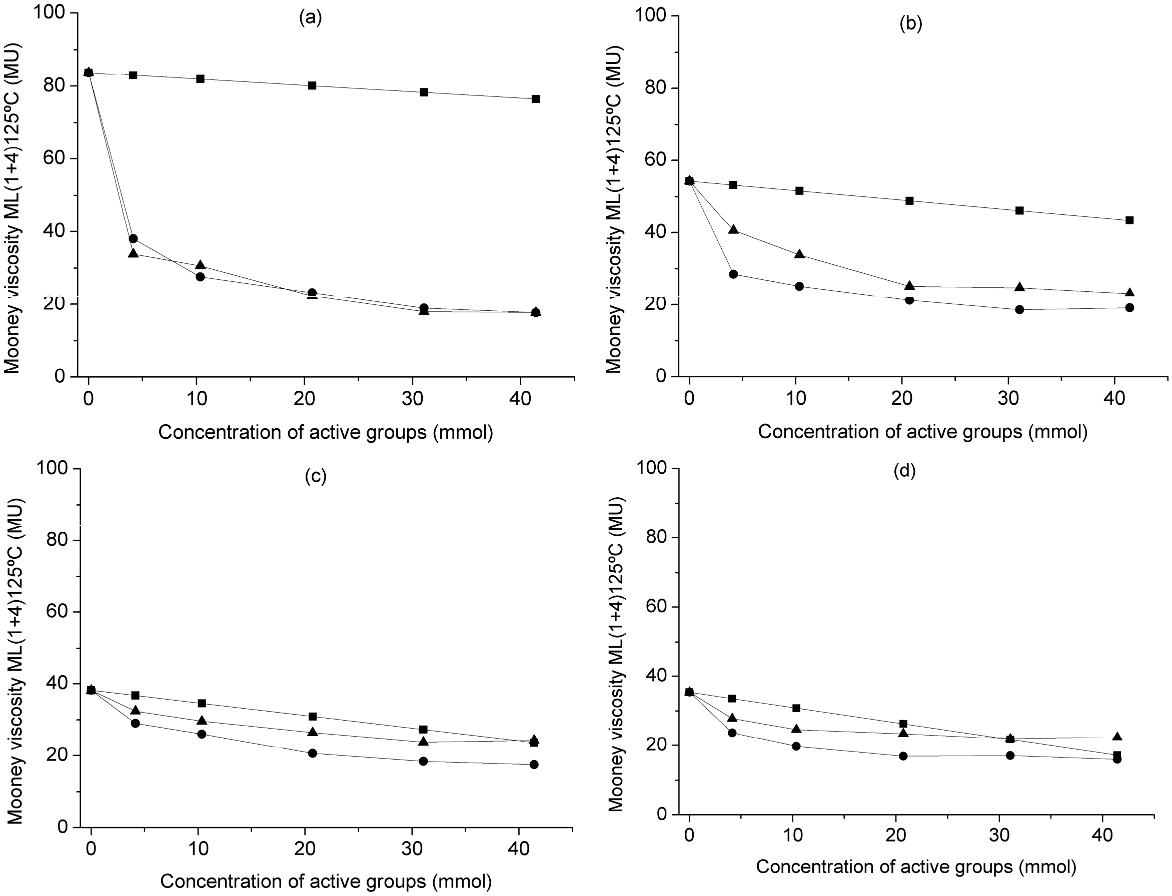


Figure 5.6: Influence of concentration of devulcanization aid on Mooney viscosity of reclaim B at (a): 200°C; (b): 225°C; (c) 250°C and (d) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

Figure 5.7 demonstrates that after reclaiming at 200°C, the values of the insoluble fractions are highest for HDA and lowest for BAFD. At higher temperatures, the opposite is observed: HDA results in the lowest insoluble, so highest soluble fractions. BAFD generally shows the largest insoluble amounts, although the difference with DPDS is almost negligible. Reclaiming with DPDS at 225°C in concentrations larger than 20 mmol results in reclaims containing no insoluble material, apart from the carbon black contained in the compound.

Increasing temperature and concentration of devulcanization aid results in materials with progressively reduced insoluble fractions, when HDA is used. The concentration effect is also clearly observed for DPDS and BAFD at 200°C. At higher temperatures, DPDS and BAFD treated reclaims show a decrease in insoluble fractions with increasing temperature, while the influence of the amount of devulcanization aid is small.

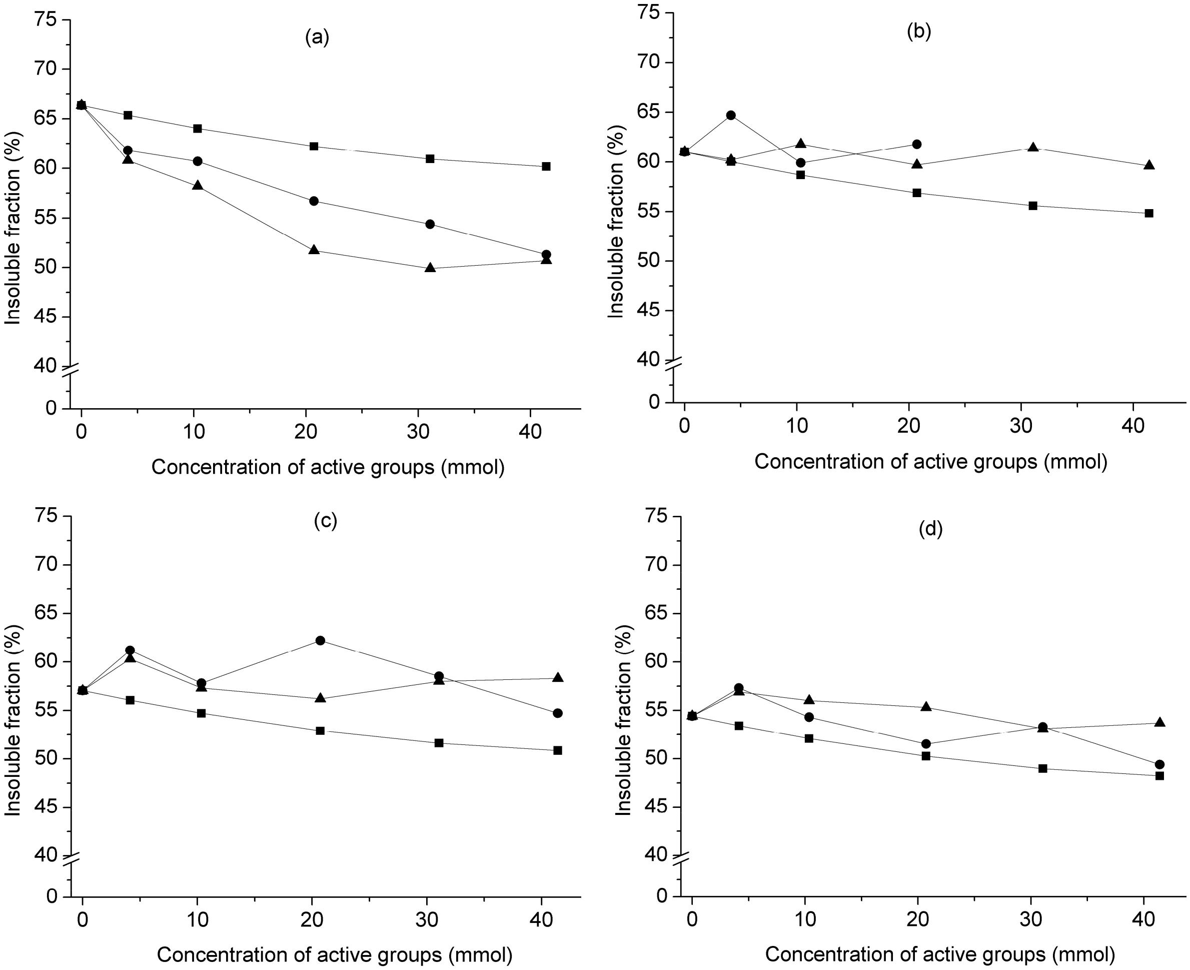


Figure 5.7: Influence of concentration of devulcanization aid on insoluble fraction of reclaim B at (a): 200°C; (b): 225°C; (c) 250°C and (d) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

As shown in Figure 5.8, the reclaim from compound B again behaves quite differently from the reclaim based on conventionally cured rubber, compound A: without the use of a devulcanization aid, the crosslink density of the insoluble fraction remains more or less equal to the crosslink density of the original vulcanized compound B (Table 5.6) for all reclaiming temperatures employed. Thermal treatment alone does not lead to a decrease of crosslink density. Furthermore, significant differences in the overall crosslink densities of the reclaims are observed, when reclaimed with HDA on one hand, and DPDS and BAFD on the other. When HDA is applied, a decrease in overall crosslink density with increasing HDA concentration occurs for reclaiming temperatures of 200°C and 225°C, while the crosslink density at 250°C and 275°C rises with addition of HDA: a moderate reclaiming temperature and addition of HDA as devulcanization aid is required for a significant decrease in crosslink density, otherwise the opposite effect is obtained. DPDS and BAFD as devulcanization aids result at all temperatures in an initial decrease in crosslink density with addition of a small amount of devulcanization aid, followed by a grossly constant value with higher additions of the devulcanization aids. The experimental results for the overall crosslink density of the reclaims treated with DPDS and BAFD show a lot of scatter: this is because the remaining crosslink density was so low, that a gelly material was obtained, of which the amount of crosslinks could not be determined with great accuracy. The differences in crosslink density of the reclaims with DPDS and BAFD as devulcanization aids are therefore not really significant.

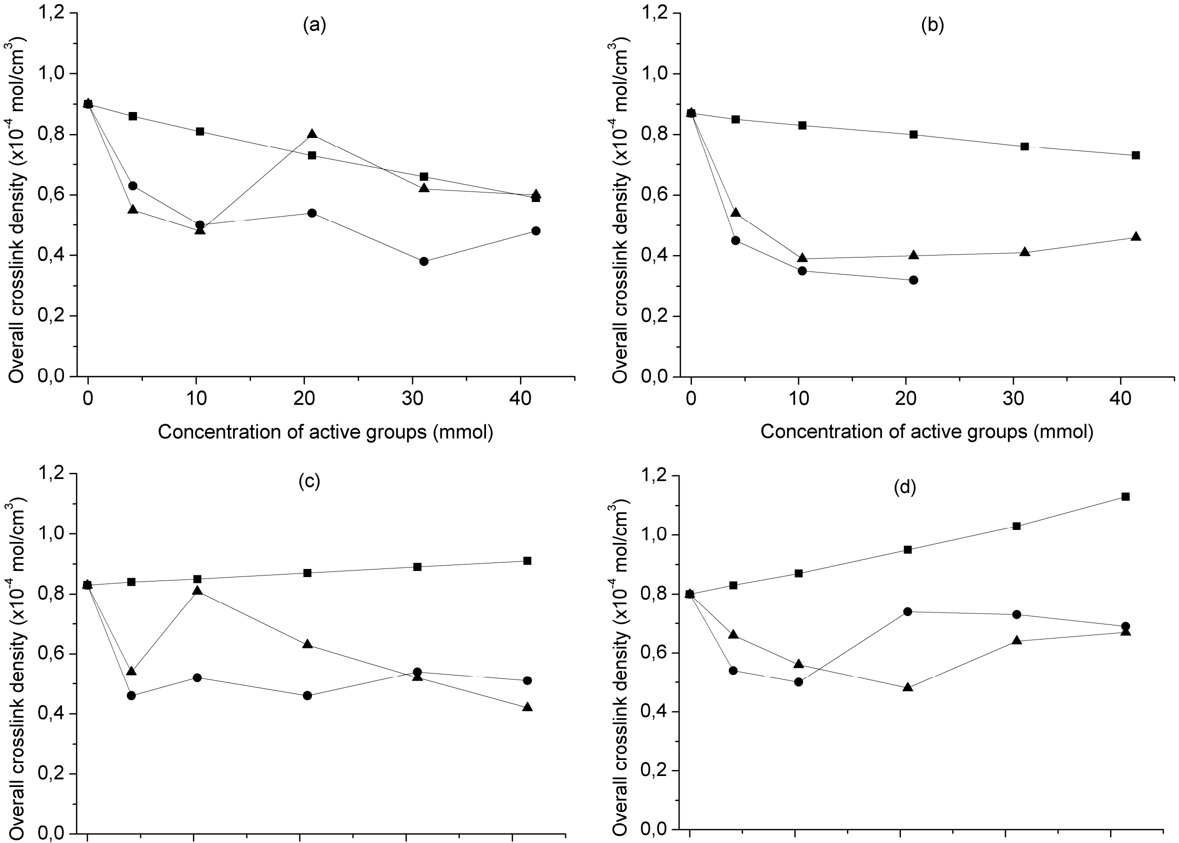


Figure 5.8: Influence of concentration of devulcanization aid on overall crosslink density of reclaim B at (a): 200°C; (b): 225°C; (c) 250°C and (d) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

The fractions of sol generated during reclaiming versus the relative decreases in crosslink density of reclaim B, for all temperatures and devulcanization aids applied, are shown in Figure 5.9.

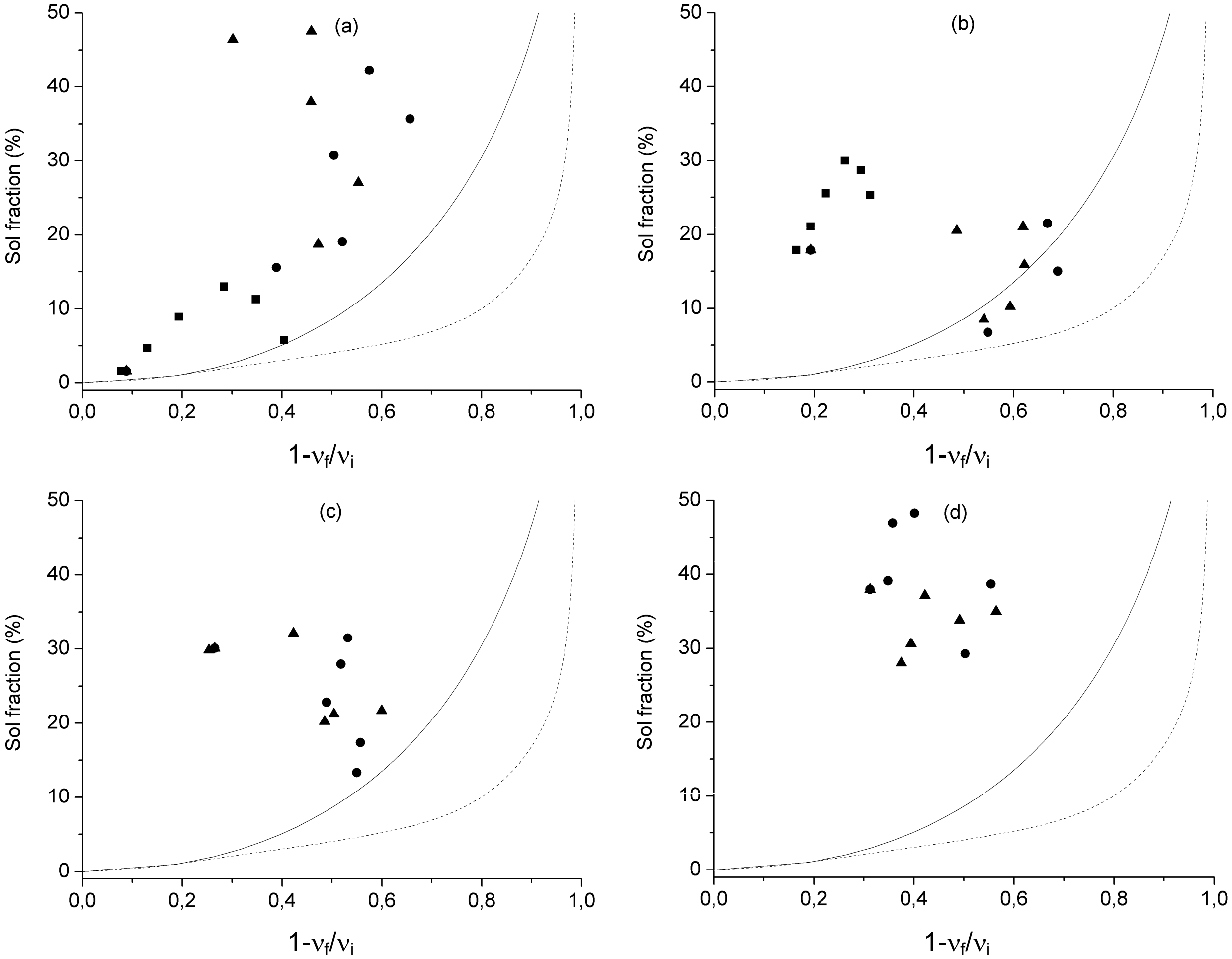


Figure 5.9: Fraction of sol generated during reclaiming versus the relative decrease in crosslink density for reclaim B. (—): only main-chain scission; (– –): only crosslink scission; (a): 200°C; (b): 225°C; (c) 250°C and (d) 275°C; (■): HDA; (●): DPDS; (▲): BAFD

It is clear from Figure 5.9, that HDA produces reclaims with the lowest relative decrease in crosslink density – so with the highest concentration of crosslinks in the insoluble fraction of the reclaims – at 200°C and 225°C. At 200°C this is accompanied by the lowest sol fractions, while at 225°C the largest amounts of soluble polymer fraction are generated compared to DPDS and BAFD as devulcanization aid. At temperatures above 225°C, HDA acts as crosslink promoter of the insoluble fraction and the crosslink density after reclaiming is even higher than before. Therefore, the Horikx-plots at 250°C and 275°C only contain values for DPDS- and BAFD-treated reclaims. At all reclaiming temperatures applied, there is no significant difference between the reclaiming behavior of DPDS or BAFD as devulcanization aids.

It was not possible to separately determine the mono-, di- and polysulfidic crosslink densities of the materials reclaimed with DPDS and BAFD, because the reclaims were degraded to such an extent that a gelly material was obtained that could not further be treated with swelling. In Chapter 4, the monosulfidic crosslink densities were given for HDA applied as devulcanization aid: a decrease in monosulfidic crosslink density with addition of HDA at all temperatures, with the exception of a temperature of 275°C, for which a small minimum was found.

5.3.2 Application Study of Reclaims A and B

Even though it was already concluded from the Mooney viscosity results for reclaim A, shown in Figure 5.1, that addition of the devulcanization aids DSPD and BAFD did not result in plasticized and re-processable materials, an application study was still performed with the conditions mentioned below. The compounds used in this application study were blends of a virgin EPDM masterbatch with reclaims A and B, respectively. The reclaiming conditions chosen on basis of the results obtained, were:

- reclaiming time: 7.5 minutes;
- rotor speed: 75 rpm;
- amount of devulcanization aid: 5 wt%, and
- reclaiming temperature: 250°C for reclaim A and 225°C for reclaim B.

Increasing amounts of reclaim A and B were mixed into the masterbatch and cured according to the curing recipes for compound A and B, as shown in Table 5.1. The amounts of curatives were based on the total polymer content, including the polymer content of the reclaim. No correction was made for residues of curatives in the reclaim. Mixing and curing was done as described in Chapter 3, with the adjustment of the curing time to t_{90} + 130 seconds.

The addition of 50 wt% of compound A treated with DPDS resulted in sheets with the best surface finishing: the lowest number and the smallest size of reclaim particles. BAFD reclaimed material showed revulcanized sheets with the roughest surfaces. Revulcanized blends containing 50 wt% of reclaim B treated with HDA, DPDS or BAFD all resulted in sheets with perfectly smooth surfaces, as already seen for HDA in Chapter 4, Figure 4.22(b).

The maximum torque values of the blends of reclaims A and B with the virgin EPDM masterbatch, cured at 170°C, are shown in Figure 5.10. For reclaim A, increasing amounts of material reclaimed with HDA and DPDS result in a reduction of the maximum torque values, while BAFD reclaimed material first shows a slight maximum for low concentrations of reclaim. HDA results in blends with the lowest maximum torques and BAFD in revulcanized compounds with the highest values.

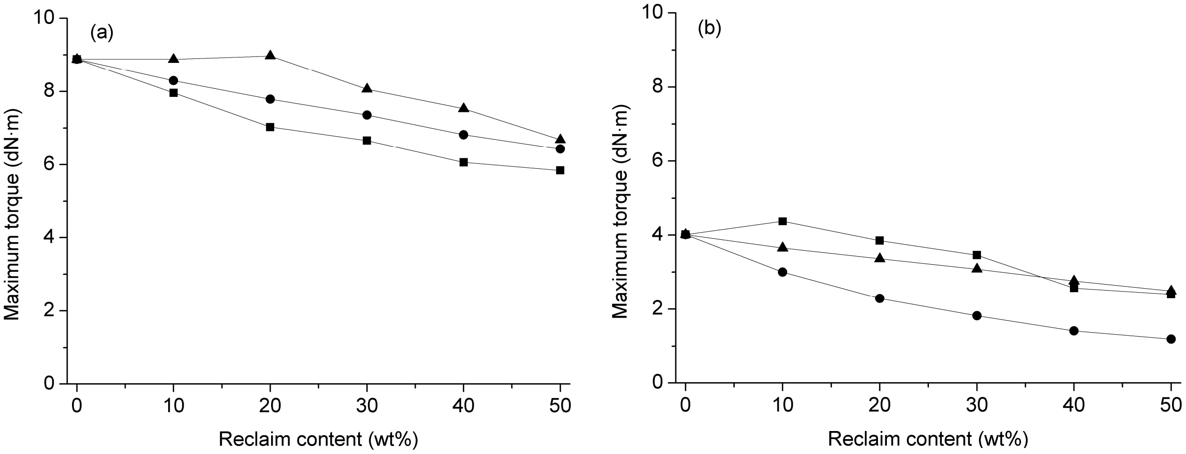


Figure 5.10: Influence of reclaim content on maximum torque of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

Revulcanizates with reclaim B show a different picture. With increasing amounts of material reclaimed with DPDS and BAFD, the blends show constantly decreasing maximum torque values, while HDA reclaim shows an initial increase with further decrease. In general, blends with DPDS reclaimed material result in compounds with the lowest maximum torques, while those with reclaim treated with HDA and BAFD show more or less comparable values.

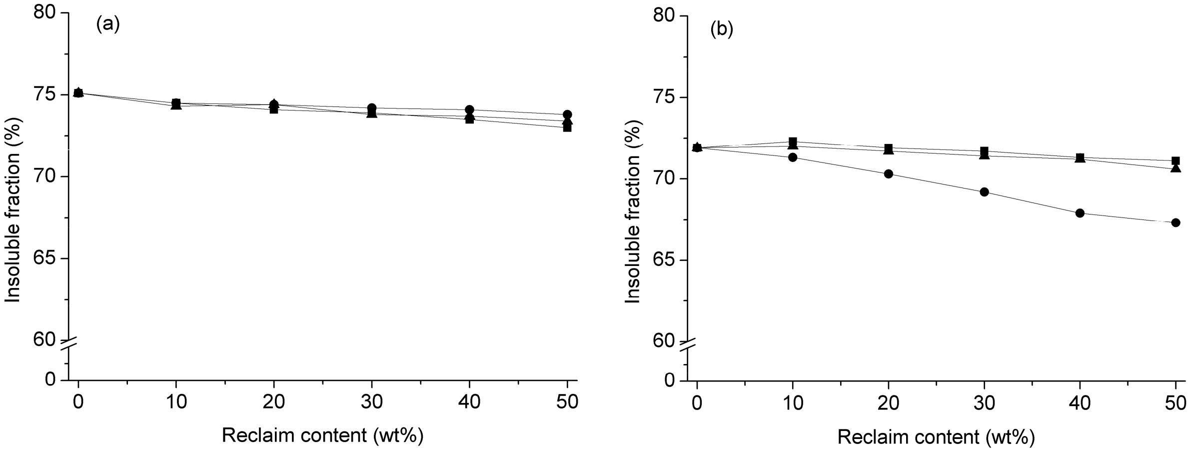


Figure 5.11: Influence of reclaim content on insoluble fraction of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

There is hardly any difference in the insoluble fraction values obtained between the revulcanizates containing reclaim A treated with one of the three devulcanization aids, as seen in Figure 5.11(a). The insoluble fractions of revulcanizates containing reclaim B treated with the different devulcanization aids show more or less the same trends as observed for the maximum torque.

The crosslink densities of the revulcanizates change only slightly with addition of reclaims based on compound A. The addition of reclaim A treated with any of the three devulcanization aids, results in a slight initial decrease, after which the overall crosslink density remains constant, as shown in Figure 5.12(a). The blends with reclaim B show an initial increase for the addition of HDA-treated reclaim, a slightly increasing crosslink density for growing amounts of BAFD-reclaimed material, while a significant decrease is observed with DPDS-treated material.

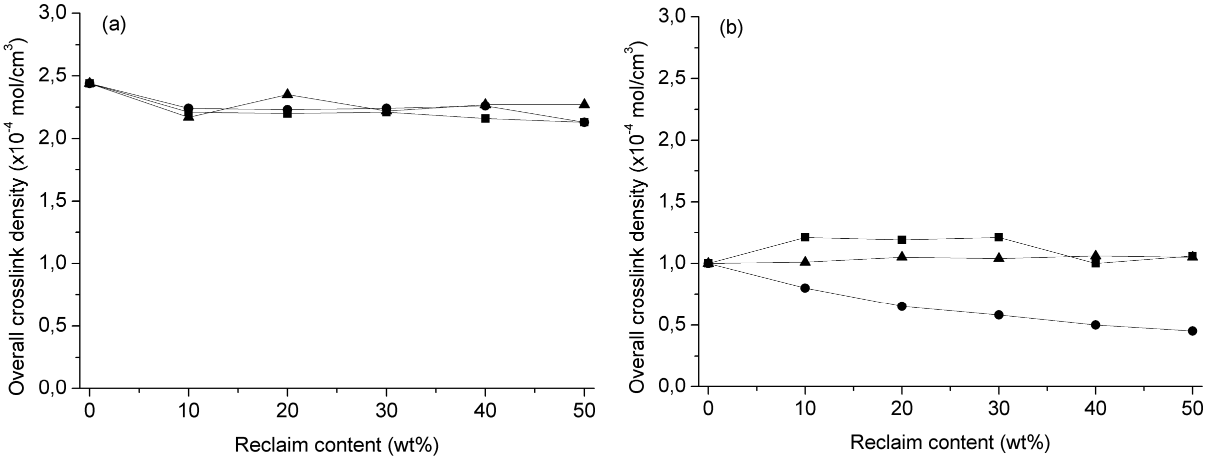


Figure 5.12: Influence of reclaim content on overall crosslink density of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

The mechanical properties of the revulcanized blends containing reclaims A and B in quantities up to 50 wt% are shown in Figures 5.13 - 5.17. Revulcanizates with increasing amounts of HDA-treated reclaim A show some reduction in tensile strength, elongation at break and hardness, while the modulus at 300% strain stays more or less constant and tear strength shows a slight increase. Increasing amounts of BAFD-treated reclaim A also result in decreasing tensile strength and elongation at break, but show an increase in modulus at 300% strain, a maximum in hardness and a more or less constant value for tear strength. Higher concentrations of material A reclaimed with DPDS show a decrease in elongation at break and a maximum in the other mechanical properties.

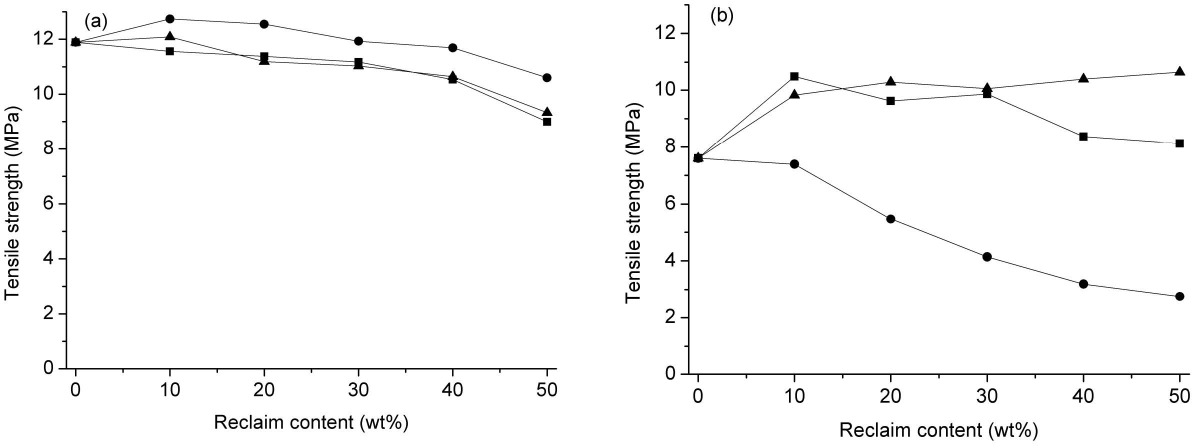


Figure 5.13: Influence of reclaim content on tensile strength of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

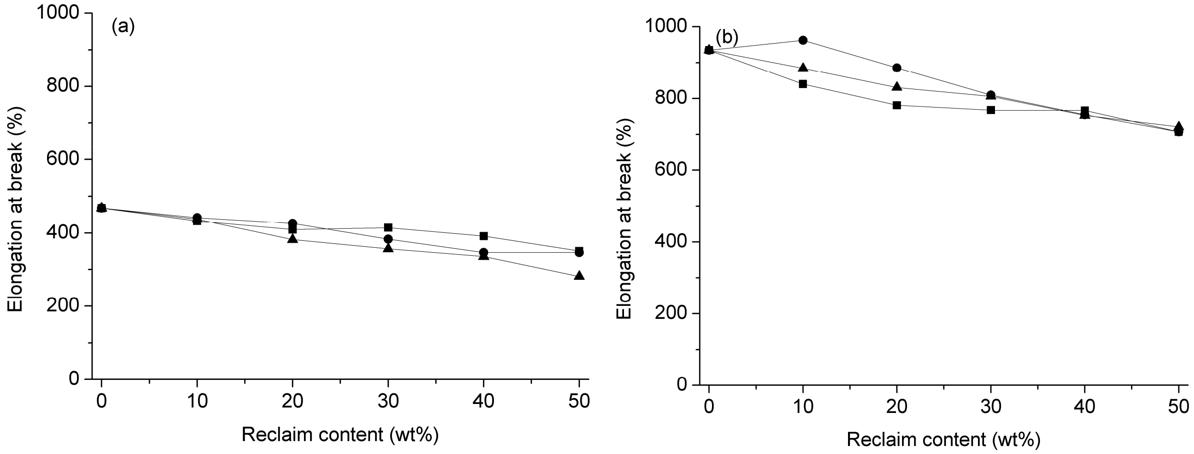


Figure 5.14: Influence of reclaim content on elongation at break of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

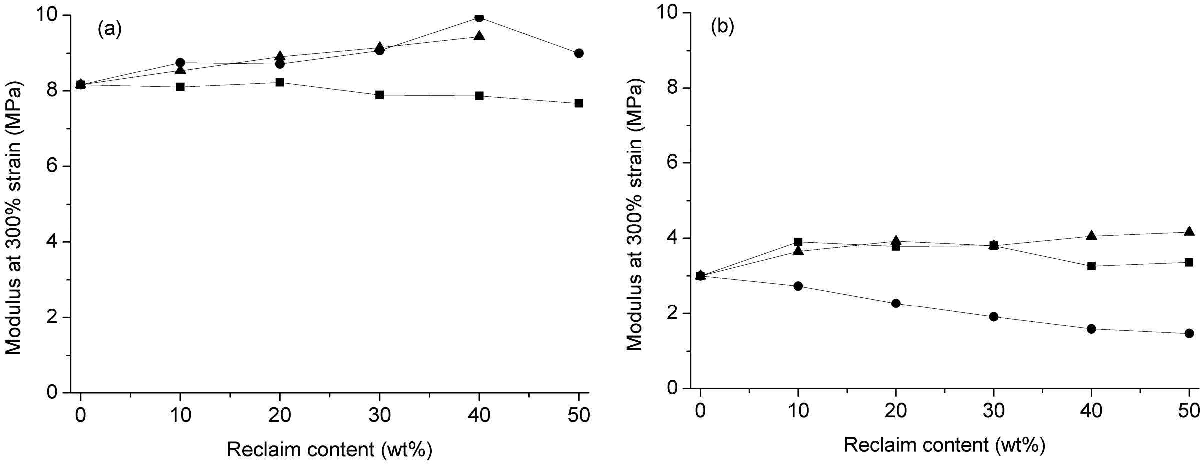


Figure 5.15: Influence of reclaim content on modulus at 300% strain of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

For material B increasing amounts of DPDS-treated reclaim result in strong reductions of tensile- and tear strength, elongation at break, modulus at 300% strain and hardness, while higher amounts of reclaim with HDA and BAFD only show a slight reduction in elongation at break, hardness and tear strength. Blends with HDA-reclaim result in an initial increase in tensile strength followed by a slight reduction with further addition of this reclaim, while BAFD-reclaim results in an increase over the whole concentration range, which is very strong for low concentrations. The modulus at 300% strain increases steadily for BAFD-treated reclaim, while a sort of maximum is observed for blends with increasing amounts of HDA-reclaimed material.

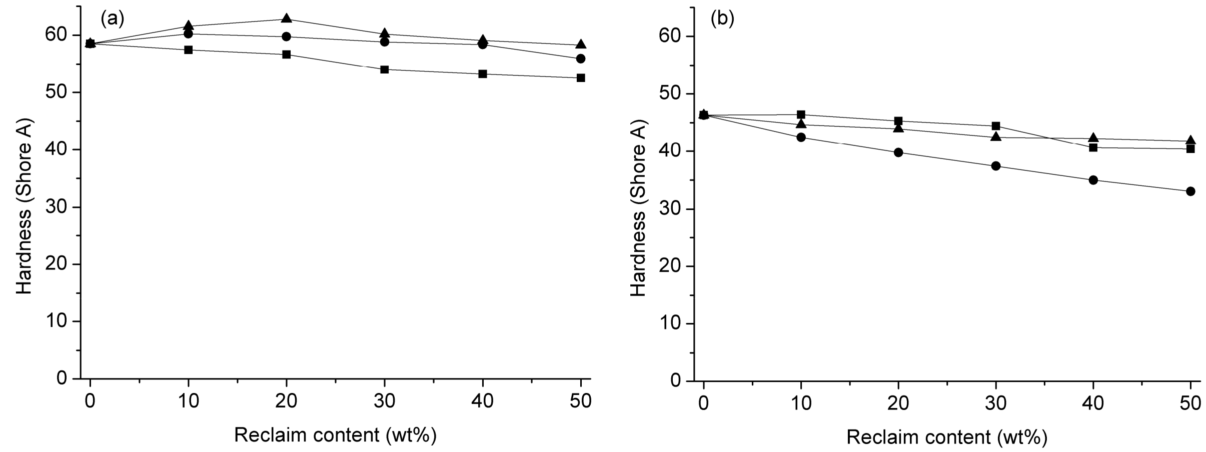


Figure 5.16: Influence of reclaim content on hardness of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

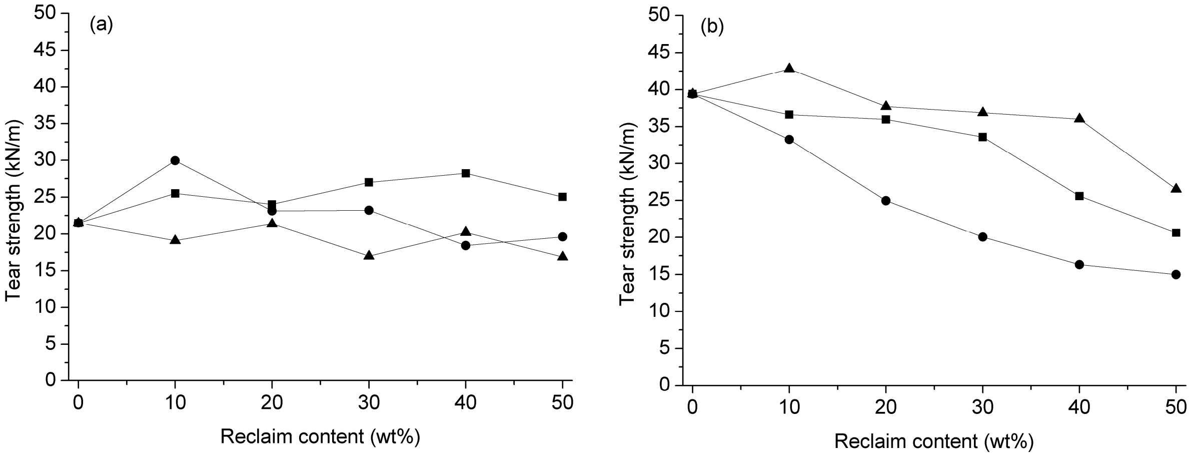


Figure 5.17: Influence of reclaim content on tear strength of revulcanizates with (a): reclaim A and (b): reclaim B; (■): HDA; (●): DPDS; (▲): BAFD

Overall, DPDS-treated reclaim B results in the most pronounced reduction in mechanical properties. The materials reclaimed with HDA and BAFD demonstrate more or less comparable positive results, although BAFD seems to perform just a little better for high concentrations of reclaim up till 50 wt%.

5.4 DISCUSSION

The most important factor in recycling of EPDM-rubber is the balance between breakdown of the vulcanized network and the ability to be revulcanized afterwards. When a devulcanization aid breaks all sulfur crosslinks, but does it in such a way, that the crosslink sites are damaged, the recycled rubber cannot replace virgin rubber. This recyclate can then only be used in small amounts as processing aid.

For reclaim A, the devulcanization aids DPDS and BAFD require higher temperatures compared to HDA in order to generate plasticized and re-processable materials, and these are still difficult to reprocess due to their high Mooney viscosity. This appears to be due to a crosslinking effect of these first two devulcanization aids. Addition of DPDS and BAFD increases the overall, as well as the monosulfidic crosslink densities in the insoluble fraction of the reclaims relative to pure thermal treatment, while HDA lowers the overall and monosulfidic concentrations of crosslinks. This is proven by the Horikx-plots, Figure 5.5, which show for DPDS and BAFD a low relative decrease in crosslink density with hardly no generation of sol. These plots also seem to indicate some increased tendency to main-chain scission for reclaim A with HDA at higher temperatures, while the overall crosslink densities do not change. On the other hand, it may be questioned if these experimental data are accurate enough to fit them to Horikx theory, given the complicated composition of the compounds and the assumptions made for these plots.

Consequently, for material A reclaiming in the presence of at least 20 mmol/100 g HDA and at temperatures of 250°C and 275°C is practically the only feasible combination which results in re-processable Mooney viscosities lower than 100 units. Therefore, the application study with reclaim A obtained with DPDS and BAFD as devulcanization aid is further of limited practical value. Although DPDS and BAFD are not effective as devulcanization aids and even increase the overall and especially the monosulfidic crosslink densities of the insoluble fractions during reclaiming of compound A, the properties of the resulting revulcanized material do not differ much. The crosslink densities are more or less equal for comparable blends independent of the type and concentration of devulcanization aids, as shown in figure 5.12(a). Similarly, there are only marginal differences in mechanical properties found. Taking the conclusion of Chapter 4 into account, that HDA breaks the sulfur crosslinks in compound A and restores the vulcanization ability of EPDM, the present results confirm this conclusion. HDA-reclaim A had the lowest crosslink density before revulcanization, to match these of DPDS- and BAFD-based reclaims after revulcanization.

Reclaim B shows a significantly different behavior. Where for reclaim A HDA was the only feasible devulcanization aid to reduce Mooney viscosity and crosslink density of the polymer network, reclaim B shows somewhat opposite results. HDA needs a minimal temperature of 225°C and preferably 250°C to become practically effective as devulcanization aid for compound B, while DPDS and BAFD show a Mooney-reducing effect at 200°C. Also, the overall crosslink densities of the remaining insoluble fractions of reclaim B are lower for DPDS and BAFD than for HDA. Taking into account the observations in Chapter 4, that HDA achieves peeling of the outer skin of particles of vulcanizate B rather than devulcanization throughout the particles, it seems that DPDS and BAFD are more prone to penetrate in the particles in order to achieve some degree of devulcanization or chain-scission there as well. The Horikx-plots for reclaim B, figure 5.9, are more difficult to understand, mainly because of this peeling effect, which is not taken into consideration in the theory. These plots, in combination with Figure 5.7 for the insoluble fractions, show that the use of HDA raises the amount of sol generated with higher reclaiming temperature; more so than DPDS and BAFD do. However, the increase in overall crosslink density of the insoluble fraction for HDA-reclaim with higher temperatures over-compensates the amount of sol formed, which makes the points move off the scale at the left hand side in Figure 5.9 for 250 and 275°C. Again, it is no use to try to rigorously interpret these results in terms of the Horikx theory. However, if the revulcanizability of the sol fractions is sufficiently guaranteed and the peeled-off particles end-up small and soft enough, still a valuable reclaim is the result In this context an additional advantage of compound B was the much lower crosslink density to start with, relative to compound A.

The application study made clear that reclaim B treated with DPDS resulted in blends which were unable to revulcanize again and demonstrated dramatic losses in mechanical properties. The crosslink sites must have degenerated, as was already found by Verbruggen[4].

Even though HDA was less able to plasticize compound B, the application study shows that the revulcanizates containing HDA-treated reclaim demonstrates practically equal properties – taking the measurement errors into account – compared to the blends containing reclaim based on BAFD as devulcanization aid. Although, the latter shows somewhat superior properties at the highest reclaim ratios.

The results with HDA as well as BAFD demonstrated that compound B was not fully crosslinked to begin with, because addition of these reclaims raised the crosslink density of the resulting revulcanized blends. Reclaim B treated with whichever devulcanization aid did not show any reclaim particles left in the revulcanized sheets, making the crosslink density the determining factor for the properties. This differs from the results obtained for reclaim A.

From a practical point of view, the overall crosslink density and specific sulfur-rank distribution of a vulcanized EPDM-compound are not known in general, unless at the cost of unpractically much analytical work. For a reclaim operation to be technically and commercially feasible, reclaims of different types of compounds need to be produced in one production line. In this context, HDA has proven itself as the most versatile devulcanization aid, because for both types of EPDM it results in well plasticized materials, which show good properties when blended with virgin compound in concentrations up to 50 wt%. DPDS and BAFD did not result in acceptable Mooney viscosities for compound A, the conventionally cured EPDM: representative for the majority of EPDM applications. The results in this chapter have again proven the suitability and wide applicability of HDA as devulcanization aid for various sorts of sulfur-cured EPDM.

5.5 CONCLUSIONS

Reclaiming of two compounds of EPDM, a conventionally cured: mainly polysulfidic one, and an efficiently vulcanized material containing a high percentage of monosulfidic crosslinks, with HDA, DPDS and BAFD as devulcanization aids results in significantly different phenomena. The observations confirm the different reclaiming mechanisms for the two types of EPDM: mainly homogeneous reclaiming/devulcanization of the conventionally cured compound, vs. peeling-off plasticized shells of the efficiently vulcanized compound. However, these two differences do not necessarily reflect in poor properties of the revulcanized blends of these reclaims with virgin compound.

Reclaiming of the conventionally cured EPDM compound in the presence of DPDS and BAFD results in plasticized and re-processable reclaims only at the highest reclaiming temperatures in combination with high devulcanization aid concentrations. Even then, these reclaims have a high Mooney viscosity compared to reclaims obtained with HDA as devulcanization aid. Therefore, the application study with reclaim A obtained with DPDS and BAFD as devulcanization aids is further of little practical value, in spite of the fact that blends of virgin masterbatch with increasing amounts of these reclaims show good mechanical properties. Addition of HDA-treated reclaim A still results in somewhat worse but yet acceptable mechanical properties of the revulcanized blends.

DPDS cannot be used as devulcanization aid for reclaiming of the mainly monosulfidic EPDM compound, because the obtained reclaims cannot be revulcanized again to result in good material properties. Addition of HDA- and BAFD-treated reclaims to virgin masterbatch results in both cases in revulcanizates with fully acceptable mechanical properties.

Where the conventionally and efficiently cured compound cover the whole range of conventionally, semi-efficiently, nitrosamine-safe and efficiently EPDM compounds, HDA has proven to be the most versatile devulcanization aid, which can be used with only minor changes for all types of EPDM compounds.

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Chapter 6

Application of Amine-Reclaimed EPDM-Rubber, Carbon Black Reinforced, for Roof-Sheeting Purposes

Sulfur-cured EPDM building-profile material was reclaimed in a co-rotating twin-screw extruder using hexadecylamine as devulcanization aid. This reclaim is blended with increasing amounts of a virgin EPDM roof-sheeting masterbatch and cured at temperatures allowing for a reversion-free vulcanization. Roof-sheeting was chosen for this application, because this material can tolerate some loss in curing efficiency due to its low degree of vulcanization.

The trends in cure characteristics show that increasing amounts of reclaim employed in the blends lower the reversion-free cure temperature and the maximum torque values, while the vulcanization speed is increased. The insoluble fraction and crosslink density both decrease, while the ratio of mono- to di- plus polysulfidic crosslinks increases with growing reclaim contents. It is found that reclaim enhances the elasticity of uncured compounds, while it reduces the elasticity of the cured materials. A SEM-EDX morphology study of the blends, done in order to evaluate the dispersion of the reclaim into the virgin rubber matrix shows, that even large amounts of reclaimed material result in homogeneous and smooth compounds.

In terms of mechanical properties, tensile strength, modulus at 300% strain and hardness decrease, while elongation at break, tear strength and compression set at 70°C increase with higher reclaim ratios. Irrespective of the blend ratios, the mechanical properties all fulfill the most stringent UEAtc specifications for EPDM roof-sheeting.

An aging study is performed in order to investigate the influence of reclaim on the long-term performance of the material and to judge the suitability of the compounds for roof-sheeting. Increasing reclaim contents improve the aging resistance and prolong the time before a practical threshold value for elongation at break of 250% for EPDM roof-sheeting purposes is reached.

Parts of the work described in this chapter have been presented at the Fall 172nd Technical Meeting of the Rubber Division, ACS, October 16-18 2007, in Cleveland (USA) (Paper no. 137) and as poster presentations at the International Rubber Conference, IRC, June 7-9 2005, Maastricht (the Netherlands) and the Deutsche Kautschuk-Tagung, DKT, July 3-6 2006, Nuremberg (Germany) and have been submitted for publication to Rubber Chemistry and Technology and Gummi Fasern Kunststoffe.

6.1 INTRODUCTION

The preferred solution for the problem of rubber production waste or end-of-life products is recycling and reuse in new rubber products. However, the difficulty of rubber recycling is that the crosslink network prevents the material from being reprocessed. The most commonly used technology is grinding of the vulcanized material and adding the resulting powder as filler to virgin compounds. Most studies in this area were done for natural rubber compounds[1-3], while Seo at al.[4] examined the addition of ground rubber particles to EPDM-rubber. Different kinds of processes have been developed to make rubber reprocessable in the sense, that it is plasticized by devulcanization or network scission: commonly summarized by the term “Reclaiming”, see Chapter 2. Addition of reclaimed rubber into virgin rubber compounds is already common practice for many years for natural rubber. Maridass et al.[5], Fukimori et al.[6], Yehia et al.[7] and Sreeja and Kutty[8] added reclaimed tire rubber to natural rubber compounds. For sulfur-cured EPDM it was discovered earlier[9, 10], that the use of an α-hydrogen containing amine as devulcanization aid allows for the production of well plasticized reclaims. They are characterized by a good revulcanization behavior, as the carbon-carbon unsaturation contained in the EPDM is restored rather than denaturated by the reclaiming process using such amines. Addition of such reclaimed EPDM rubber to replace virgin EPDM is a relatively new concept. Sutanto et al.[11] have shown some pilot-scale results of a reclaiming study with an amine as devulcanization aid: this chapter is a follow up to this work.

In this chapter, the reclaiming of carbon black reinforced EPDM building-profile scrap material in a co-rotating twin-screw extruder is investigated using hexadecylamine as devulcanization aid. This reclaim is blended with increasing amounts of a virgin EPDM roof-sheeting masterbatch. EPDM roof-sheeting is commonly characterized by a low degree of vulcanization to ensure optimal elasticity. This is therefore a preferred application for this study, because a slight loss in curing efficiency as a consequence of reclaiming can be tolerated. The reclaim can perform as a high quality and cost-efficient raw material for this application, to be used in high concentrations.

6.2 EXPERIMENTAL

Compound recipes and materials – Vulcanized EPDM building profile scrap was used as starting material for reclaiming. The basic recipe of this material is given in Table 6.1. The EPDM used in this building-profile: Keltan 4703 (DSM Elastomers, the Netherlands), consists of 48 wt% ethylene, 43 wt%

propylene and 9 wt% 5-ethylidene-2-norbornene (ENB). The Mooney viscosity ML(1+4)125°C is 65 MU. The plasticizing oil used in this compound is Texpar 100 (Texaco, the Netherlands B.V.) and the whiting used is chalk Microsohl 40 (Damman, Germany).

Table 6.1 Recipe for EPDM building-profile

Material	phr
EPDM	100
ZnO	5
Stearic acid	1
Carbon black N550	110
Whiting	25
CaO	7
Paraffinic oil	60
Accelerators	6
Sulfur	0.7
Total phr	314.7

After reclaiming, this material was blended with a virgin EPDM-rubber masterbatch for roof-sheeting applications, of proprietary composition from Hertalan B.V., the Netherlands. This masterbatch contained 298 phr in total, including the rubber.

Hexadecylamine (HDA) (Acros) was used as devulcanization aid and Sunpar 150 (Sunoco, Inc.) as reclaiming aid. Decahydronaphtalene, a mixture of cis- and trans-isomer with a purity of 98%, was used for equilibrium swelling measurements. The solvents acetone and tetrahydrofuran (THF) (Biosolve) were used for extractions. 2-Propanethiol ≥98% pure (Merck), 1-hexanethiol 95% pure, piperidine 99% pure, n-heptane 99% pure (all from Sigma Aldrich) and a petroleum-ether fraction between 40°C and 60°C (Across) were used for the specific crosslink distribution determinations.

Reclaiming – Reclaiming of the EPDM building-profile scrap was performed at the University of Groningen[12] in a co-rotating twin-screw extruder from APV Baker with a length of 1.25 m and a screw diameter of 50 mm, under the conditions given in Table 6.2. Figure 6.1 depicts the quality of the reclaim used in this study after leaving the extruder.

Table 6.2 Reclaiming conditions of the EPDM building-profile scrap in a co-rotating twin-screw extruder

Parameter	Conditions
Temperature	250°C
Screw speed	25 rpm
Rubber feed rate	10 kg/hr
HDA feed rate	12.5 wt%
Oil feed rate	0.5 kg/hr

The HDA feed rate was not optimized at this stage. The investigation discussed in Chapter 4 has already shown that the concentration of HDA can be reduced to 5 wt% to still obtain a good reclaiming efficiency.

Figure 6.1: Picture of reclaimed EPDM building-profile material after extrusion[12]

Mixing and vulcanization – Various amounts of the EPDM building-profile reclaim were blended with the virgin EPDM roof-sheeting masterbatch and cured after addition of the curing package as shown in Table 6.3.

Table 6.3 Curing recipe for EPDM roof-sheeting

Material		phr	Supplier
EPDM	-	100	DSM Elastomers
Zinc oxide	ZnO	5	Merck
Stearic acid	-	1	Sigma Aldrich
Mercaptobenzothiazole-disulfide	MBTS	0.5	Rhein Chemie Rheinau GmbH
Tetrabenzylthiuram-disulfide	TBzTD	2.0	Rhein Chemie Rheinau GmbH
Sulfur	S	1.5	Merck

While the virgin masterbatch was a typical EPDM roof-sheeting recipe, the curing-recipe had to be adjusted: for this investigation, compression molding was used to vulcanize the compounds rather than autoclave curing, as commonly employed for EPDM roof-sheeting. The reclaim and the curing additives were blended with the virgin EPDM roof-sheeting masterbatch at room temperature on a laboratory size Schwabenthan two-roll mill (15 x 33 cm Polymix 80) with a friction ratio of 1:1.25. The amounts of curatives were based on the total EPDM polymer content, including the polymer content contained in the reclaim. No correction was made for residues of curing additives in the reclaim. The cure characteristics of the blends were determined with a Rubber Process Analyzer RPA 2000 from Alpha Technologies with a frequency of 0.833 Hz and a strain of 0.2 degrees at different temperatures, in order to find a cure temperature without marching modulus and reversion for each blend. The compounds were subsequently vulcanized in a Wickert laboratory press 1600/5×4/3 at the appropriate temperature and 100 bar for t_{90} + 130 seconds: 130 seconds were added to compensate for the longer heating times of thicker specimen in the press compared to the cure-rheometer. Compression set samples, cylindrical shapes of 6×13 mm, were cured for 1.5×t_{90}+130 seconds. The factor 1.5 was necessary in order to correct for the larger thickness of the samples: 6 mm instead of 2 mm for the standard sheets.

Mooney viscosity – Mooney viscosity ML(1+4)125°C was determined using a Mooney viscometer MV200 VS from Alpha Technologies according to ISO R289.

Dynamic viscoelastic measurements – Dynamic viscoelastic measurements of the uncured and cured compounds were performed with the RPA 2000. Frequency-sweeps of uncured compounds were done at 100°C and 14% strain and of cured compounds at 60°C and 3.49% strain. Frequency-sweeps of the cured specimens required vulcanization at t_{90}, at the appropriate temperature, followed by a cooling step to reach 60°C. The frequency, in both cases, varied from 0.1 to 209 rad/s. Temperature sweeps were executed on uncured samples at 49.94% strain and 0.5 Hz.

Extractions – The extractions were carried out as described in detail in Chapter 3.

Equilibrium swelling – The degree of swelling was measured on extracted samples; this allows determining the crosslink density of the vulcanized compounds and of the remains of reclaim after removal of the solfraction, as described in detail in Chapter 3. The crosslink density was calculated according to the Flory-Rehner equation[13]. This equation is strictly spoken only valid for non-filled systems. Therefore, the Kraus[14] correction for filled compounds had to be applied in order to obtain the correct values of the different crosslink densities. The Kraus correction was used in its simplified form[15], as described in detail in Chapter 4.

Crosslink distributions – The specific sulfur-rank distributions of the crosslinks in the vulcanizates were studied using thiol/amine chemical probes[16-19], as described in detail in Chapter 3.

Mechanical properties – Tensile and tear tests were carried out according to ISO 37 and ISO 34, respectively. Compression set tests were carried out according to ISO 815. The hardness of the samples was measured using a Zwick Hardness-tester Shore A type according to DIN 53503. Chapter 3 gives a detailed description.

SEM-EDX measurements – A Scanning Electron Microscope coupled to an Energy Dispersive X-ray spectrometer (SEM-EDX) was used to obtain insight into the dispersion of reclaim in the matrix of virgin EPDM-rubber masterbatch. The surface of the samples was smoothened by shaving with a glass knife using a microtome (Leica EM FCS) at a temperature of -130°C. Prior to analysis, the samples were coated with carbon to improve the electrical conductivity. The SEM-EDX equipment used was a LEO 1550 FEG/Thermo Noran Instruments, model Vantage. The accelerating voltage was 15 kV and the sample distance 9 mm.

Accelerated heat-aging experiments – Accelerated heat-aging tests were carried out according to ISO 188 method B on dumb-bell shaped specimens. The specimens were exposed to different temperatures in the range of 70-130°C during time periods ranging from 1 day till 24 weeks.

6.3 RESULTS

6.3.1 Mooney viscosity

The influence of reclaim on the Mooney viscosity of uncured blends, already containing the curatives, is shown in Figure 6.2. The viscosity values show an interesting feature: at reclaim contents of 40 wt% or higher, the viscosities measured after 5 minutes are higher than the viscosities after only 1 minute of preheating

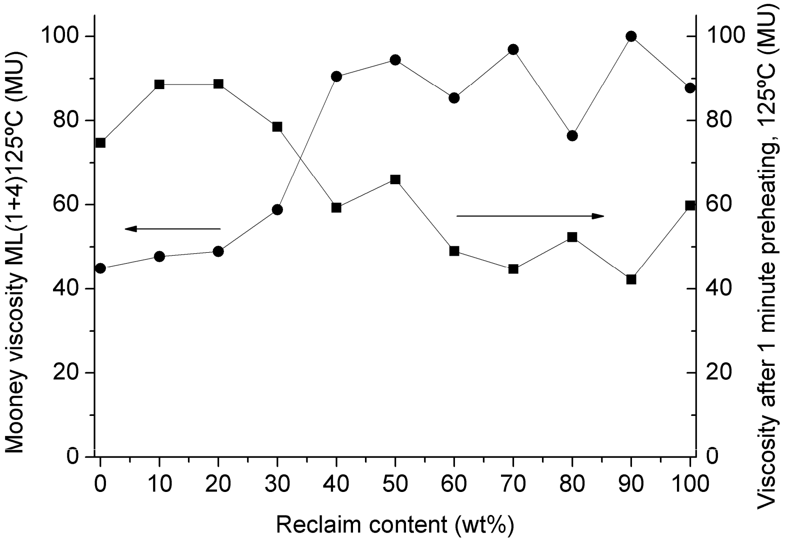

Figure 6.2: Influence of reclaim content on Mooney viscosity of uncured blends

6.3.2 Cure Behavior

Increasing amounts of reclaim required a decrease in cure temperature to obtain reversion-free cure-behavior. As shown in Figure 6.3(a), the maximum torque linearly decreases with increasing reclaim content; only the sample of pure reclaim does not follow this trend and shows a somewhat increased torque. Figure 6.3(b) shows that the optimum cure time, t_{90}, at a fixed temperature decreases with increasing reclaim content. It is also seen that lower cure temperatures increase the optimum cure time, as had been expected beforehand.

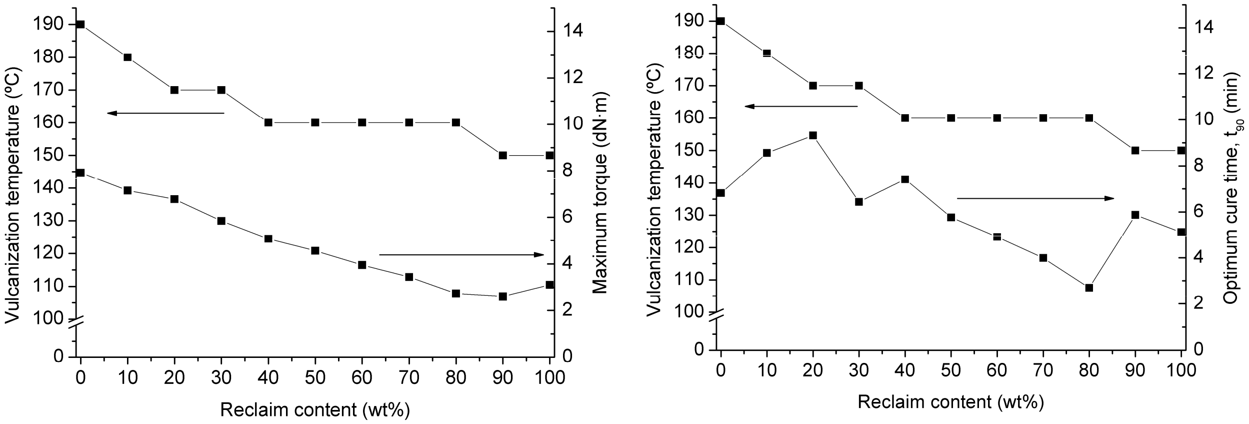

Figure 6.3: Influence of reclaim content on the reversion-free cure temperature and on (a): maximum torque, and (b): optimum cure time, t_{90}, of the revulcanizates

6.3.3 Physical Properties

The influence of reclaim on the crosslink density and sulfur-rank distribution, as well as on the insoluble fraction of the cured blends is depicted in Figure 6.4.

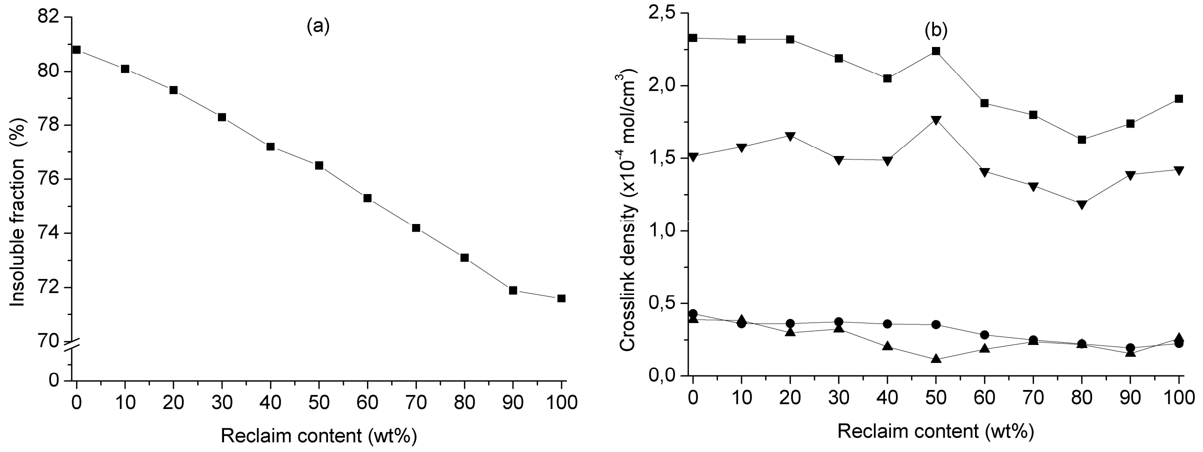

Figure 6.4: Influence of reclaim content on (a): insoluble fraction, and (b): crosslink densities of the revulcanizates; (■): Overall; (●): monosulfidic; (▲): disulfidic and (▼): polysulfidic crosslink densities

The insoluble fraction decreases with increasing reclaim content, due to the higher amount of low molecular weight extractable material in the reclaim; these polymer fragments are not re-connected to the rubber network after revulcanization. As a reference, the insoluble fraction of the pure reclaim before revulcanization was 62% and the crosslink density 0.50×10^{-4} mol/cm^3.

In general, the overall crosslink density after revulcanization decreases with increasing reclaim content. The slight increase in maximum torque, as already seen in Figure 6.3(a) for pure revulcanized reclaim, is also found for the crosslink densities for 90 wt% and 100% pure reclaim. Furthermore, the crosslink density shows an irregularity with the addition of 50 wt% reclaim. The monosulfidic crosslink density decreases over the whole range of reclaim contents, while the polysulfidic crosslink density follows the trend of the overall crosslink density. The disulfidic crosslink density shows in general a slight decrease and a more significant decrease at the addition of 50 wt% reclaim, corresponding to an increase in the amount of polysulfidic bonds at this concentration. The increase in crosslink density with the addition of 50 wt% of reclaim may indicate a phase shift from virgin EPDM-rubber to reclaim as the continuous phase, with virgin EPDM-rubber particles dispersed therein.

6.3.4 Dynamic Viscoelastic Measurements

Elastomers are viscoelastic, which means that they can reversibly store energy (elasticity), but they can also dissipate energy through viscous behavior: molecules undergo some form of flow or rearrangement. A good measure for the viscoelastic behavior of rubber is given by the loss angle tan δ:

$$\tan\delta = \frac{G''}{G'} \tag{6.4}$$

Where G'' is the loss modulus and corresponds to the viscous behavior, and G' is the storage modulus, corresponding to the elastic behavior of the rubbers.

The results of temperature-sweeps performed on the uncured blends of virgin EPDM roof-sheeting with EPDM building-profile reclaim are shown in Figure 6.5. Increasing reclaim contents lower the temperature at which the storage modulus starts to increase; the onset is between 160°C for the virgin compound and 110°C for pure reclaim. In this temperature range, the storage moduli basically increase with higher reclaim contents. At 200°C, the order is reversed and the storage moduli decrease with increasing reclaim content. The tan δ values of the blends with reclaim contents of 40 wt% and higher start to decrease already at a temperature around or lower than 110°C, while lower reclaim contents result in higher temperatures for the onset of decreasing tan δ values. Both, storage moduli and tan δ values, indicate that crosslink formation starts at lower temperatures with increasing reclaim content, coinciding with the observations on the cure characteristics.

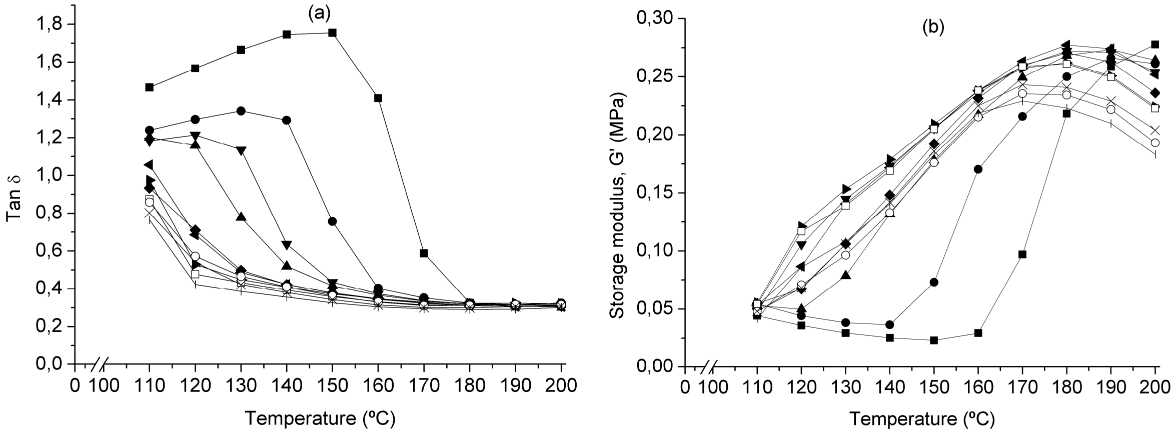

Figure 6.5: (a): Tan δ, and (b): storage modulus of the blends as a function of temperature; (■): 0 wt%; (●): 10 wt%; (▲): 20 wt%; (▼): 30 wt%; (◄): 40 wt%; (►): 50 wt%; (♦): 60 wt%; (□): 70 wt%; (○): 80 wt%; (×): 90 wt% and (ı): 100 wt% EPDM building-profile reclaim

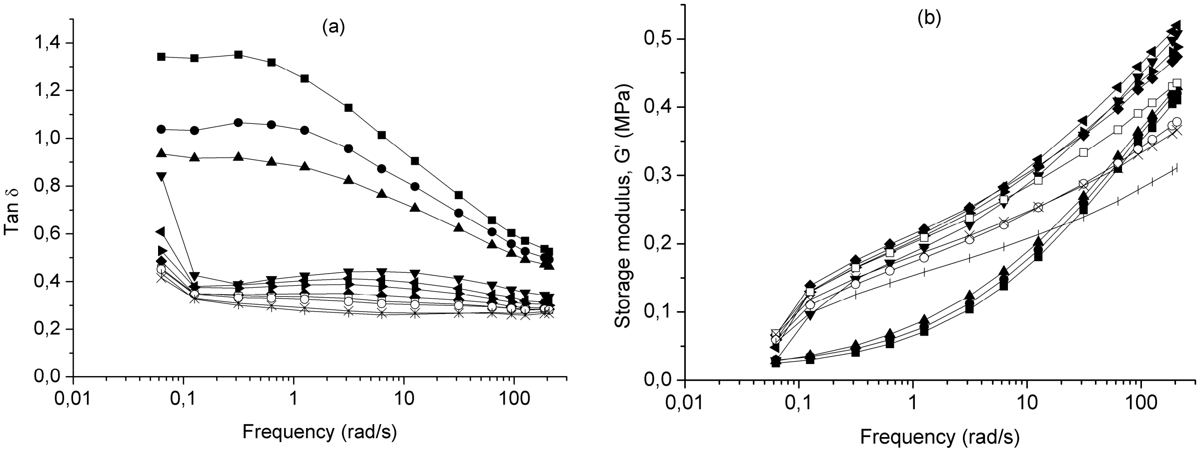

Figure 6.6: (a): Tan δ, and (b): storage modulus of the uncured blends as a function of frequency; (■): 0 wt%; (●): 10 wt%; (▲): 20 wt%; (▼): 30 wt%; (◄): 40 wt%; (►): 50 wt%; (♦): 60 wt%; (□): 70 wt%; (○): 80 wt%; (×): 90 wt% and (ı): 100 wt% EPDM building-profile reclaim

The results of frequency-sweep measurements performed on the uncured blends are shown in Figure 6.6. The storage modulus of the compounds containing 0, 10 or 20 wt% of reclaim is considerably less at lower frequencies, compared to the compounds containing higher concentrations of reclaim. Furthermore, at reclaim concentrations of 30 wt% or more, the storage modulus decreases with increasing reclaim content and this difference becomes more significant at higher frequencies. The tan δ values at all frequencies decrease with increasing reclaim content, although the differences are less pronounced in the high frequency range.

The results of frequency-sweep measurements performed on cured blends are shown in Figure 6.7. The storage modulus decreases with increasing amounts of reclaim. This is in accordance with the decreasing maximum torque with increasing reclaim content, when the temperature-effect is neglected. The tan δ values show the same pattern.

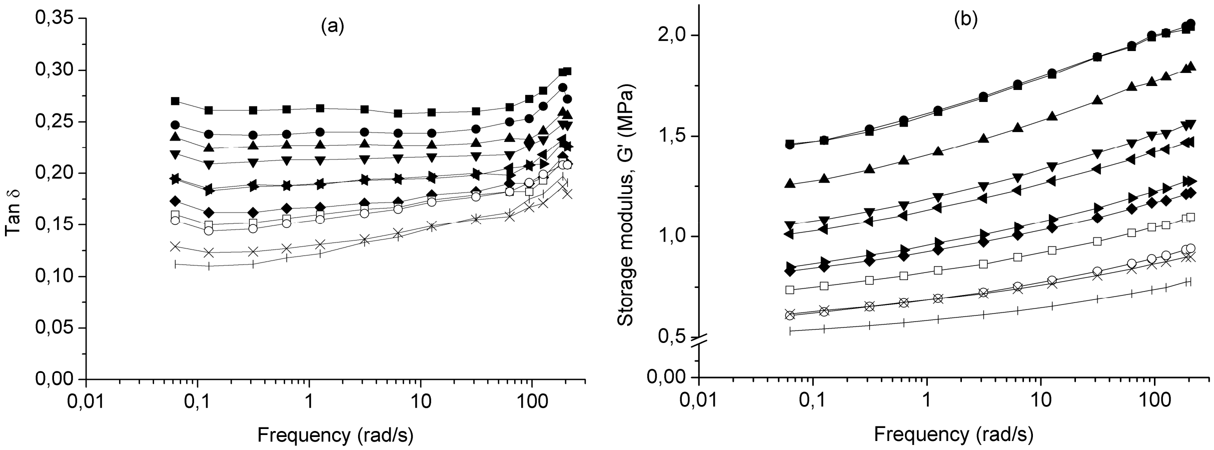

Figure 6.7: (a): Tan δ, and (b): storage modulus of the cured revulcanizates as a function of frequency; (■): 0 wt%; (●): 10 wt%; (▲): 20 wt%; (▼): 30 wt%; (◄): 40 wt%; (►): 50 wt%; (♦): 60 wt%; (□): 70 wt%; (○): 80 wt%; (×): 90 wt% and (ı): 100 wt% EPDM building-profile reclaim

6.3.5 Mechanical Properties

There are different specifications for EPDM roof-sheeting in use: EN 13956 (Norme Européenne), ASTM D 4637-04 and UEAtc[20] (Union Européenne pour l'Agrément technique dans la construction), of which the UEAtc standard is the most stringent one. For this reason, the revulcanizates were evaluated according to the UEAtc standard, see Table 6.4.

Table 6.4 Specifications for EPDM roof-sheeting

Property	UEAtc	EN 13956	ASTM D 4637-04
Tensile strength	≥ 8 MPa	≥ 6 MPa	≥ 9 MPa
Elongation at break	≥ 400%	≥ 300%	≥ 300%
Tear strength ISO 34-B with nick	≥ 20 kN/m	-	-

The influence of reclaim content on the mechanical properties after press vulcanization is depicted in Figure 6.8.

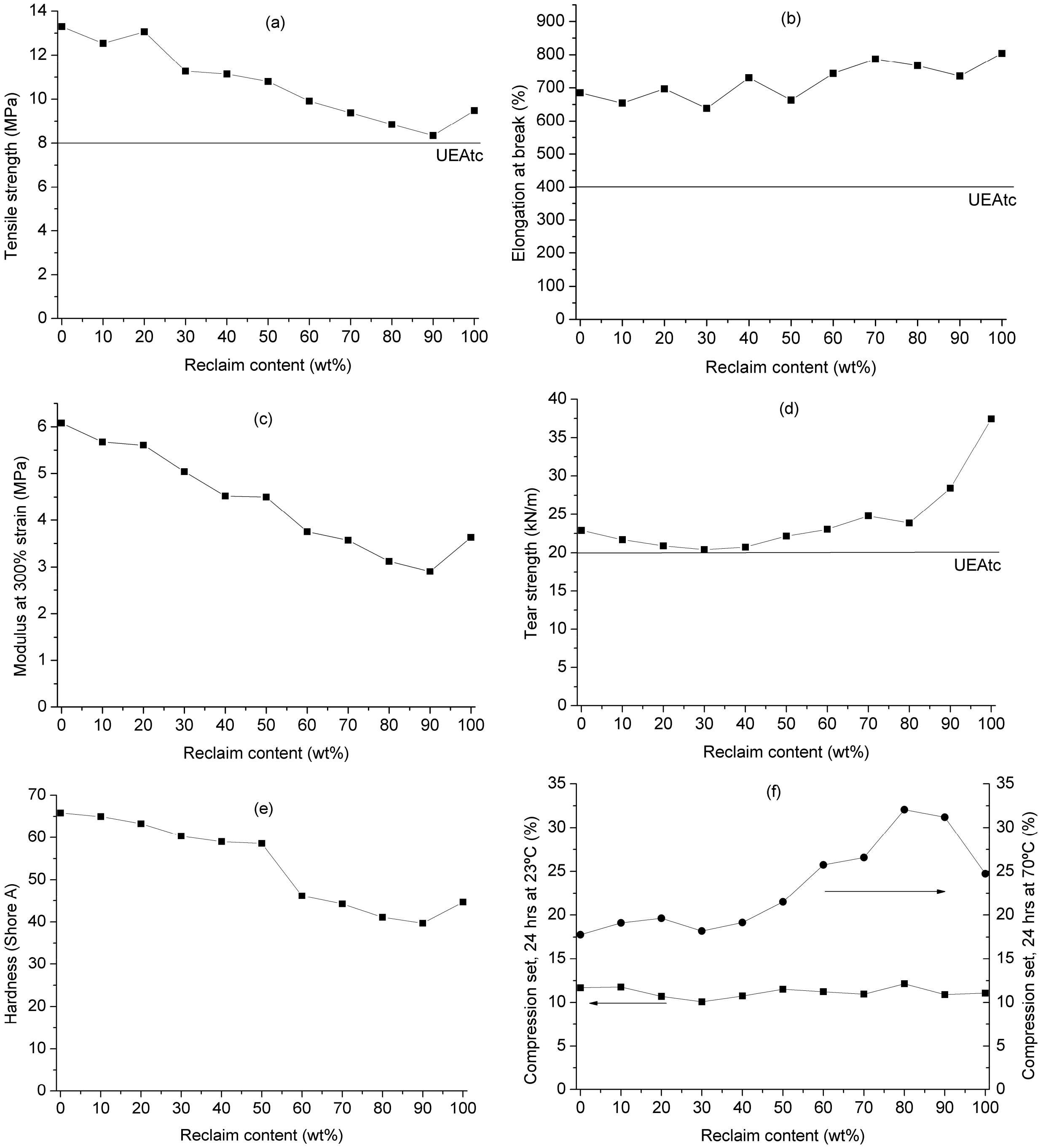

Figure 6.8: Influence of reclaim content on (a): tensile strength; (b): elongation at break; (c): modulus at 300% strain; (d): tear strength; (e): hardness, and (f): compression set of the revulcanizates

Tensile strength, modulus at 300% strain and hardness decrease, while elongation at break shows a slight increase with the addition of reclaim. Compression set at 23°C stays constant over the whole reclaim content range, while at 70°C an initial period of constant values is followed by an increase starting at reclaim contents of 50 wt%, and finally another reduction of compression set is found for the revulcanizate containing 100% reclaim. Tear strength decreases slightly with addition of reclaim up to 40 wt%, and significantly increases afterwards for higher reclaim contents.

6.3.6 SEM-EDX

A morphology study was conducted with SEM-EDX in order to obtain insight in the dispersion of the reclaim particles within the rubber matrix and to detect a possible phase shift from the virgin EPDM masterbatch as continuous phase to the reclaim. Figures 6.9 – 6.11 show SEM-pictures of samples containing 10 wt%, 40 wt% and 90 wt% of reclaim. These pictures were taken at a magnification of 2000x. When 10 wt% of reclaim is added, distinct reclaim particles are still visible, while no reclaim particles are visible anymore for addition of 40 wt% or 90 wt% of reclaim. Figures 6.10 and 6.11 show a smoother surface with increasing reclaim content, most probably due to the additional sol fraction in the reclaim, which may act as a plasticizer.

An additional EDX study was performed to determine the sulfur distribution in the reclaim-containing EPDM-rubber compounds. A concentration difference between these two phases: virgin vs. reclaim, may create a cure mismatch, resulting in early failure of the compounds. The EDX spectral images corresponding to the SEM-pictures are also shown in Figures 6.9 - 11. They show a clear concentration difference between the reclaim particles and the virgin masterbatch for the sample with 10 wt% reclaim, where the reclaim particles contain higher concentrations of sulfur. At higher reclaim concentrations, the blends are homogeneous. Figures 6.10 and 6.11 show that no reclaim particles and no clear sulfur concentration differences are detected, so the possible phase shift is not observed. It is visible though, that the sulfur concentration in the compounds increases with increasing reclaim content, because no correction was made for the sulfur residues already present in the reclaim.

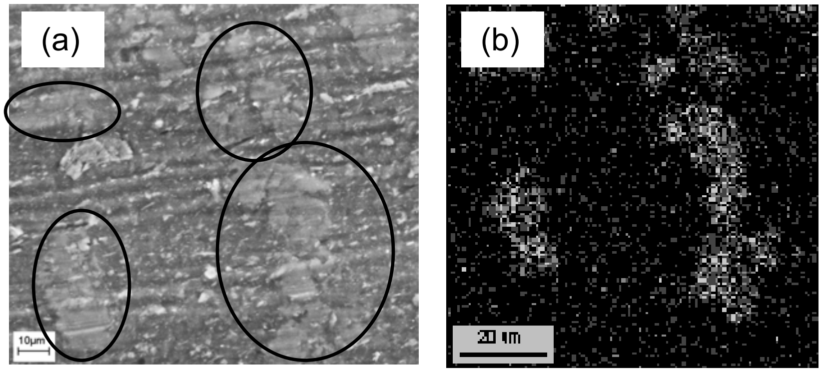

Figure 6.9: (a): SEM picture of virgin EPDM roof-sheeting with 10 wt% EPDM building-profile reclaim, and (b): EDX spectral image of sulfur for this sample

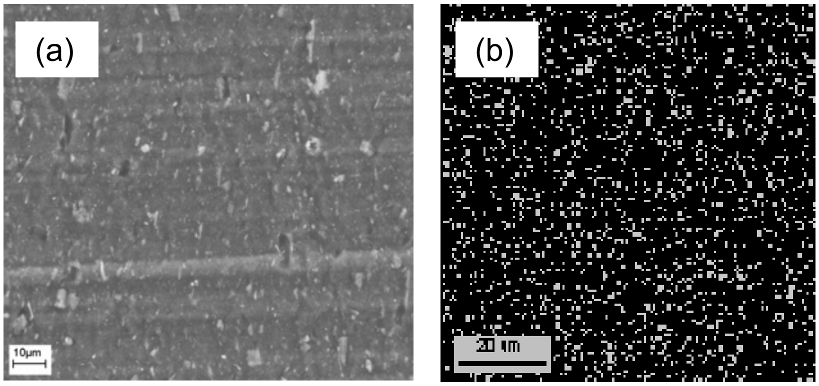

Figure 6.10: (a): SEM picture of virgin EPDM roof-sheeting with 40 wt% EPDM building-profile reclaim, and (b): EDX spectral image of sulfur for this sample

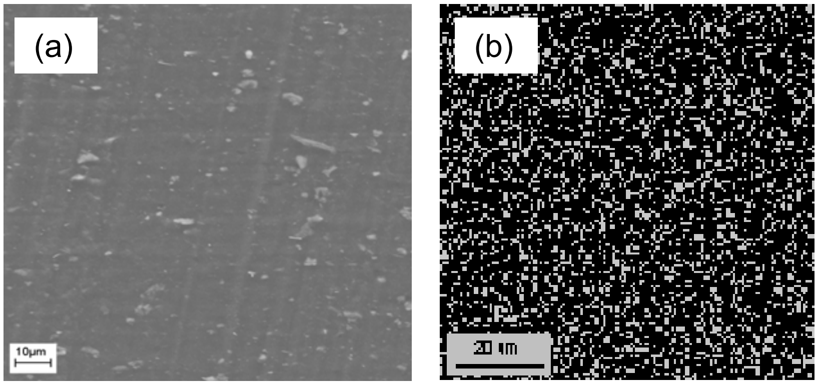

Figure 6.11: (a): SEM picture of virgin EPDM roof-sheeting with 90 wt% EPDM building-profile reclaim, and (b): EDX spectral image of sulfur for this sample

6.3.7 Accelerated Heat-Aging

Accelerated-heat aging experiments were done at different temperatures for various time-periods in order to estimate the life-time expectancy of the roof-sheeting compounds, according to ISO 11346. The most important functional factor for roof-sheeting is the elongation at break. There is no clear standard for this property in relation to practical performance. Elongation values as low as 150% or even 100% are sometimes chosen as still practically acceptable. For practical reasons, threshold values of 300% and 250% were chosen in the present study, otherwise the aging experiments would have taken a very long period of time, or they would have to be done at very high, practically irrelevant temperatures. The time period after which the elongation at break reached the threshold values of 300% and 250% was determined as a function of aging temperature, by interpolating the values using the Arrhenius relation:

$$\ln K(T) = B - \frac{E}{RT} \qquad (6.5)$$

Where K(T) is the temperature dependent reaction rate, B is a constant, E is the activation energy, R is the gas constant and T is the absolute temperature. The degree of aging is given by the relation:

$$F_x(t) = K(T) \times t \qquad (6.6)$$

Where $F_x(t)$ is a function which describes the stage the reaction has reached, and t is the reaction time.

For every exposure temperature, elongation at break values are plotted against time, and for each plot, the time to reach the threshold value is determined. In the next step, the logarithm of the time to reach the threshold value is correlated with the reciprocal value of the absolute temperature and a best-fit straight line through these points is calculated by least square methods. The time to reach the threshold value can then be calculated for every single temperature by interpolation.

Figure 6.12 shows two typical examples of the influence of aging time on elongation at break: for the virgin compound and for the one containing 40 wt% reclaim. Generally, the aging resistance improves with increasing addition of reclaim. The differences would probably be even more pronounced for further aging, but lower elongation at break threshold values could not be applied for reasons of practical feasibility of the required aging periods. The pure reclaim did never reach the threshold value of 300% within the time and temperature windows applied.

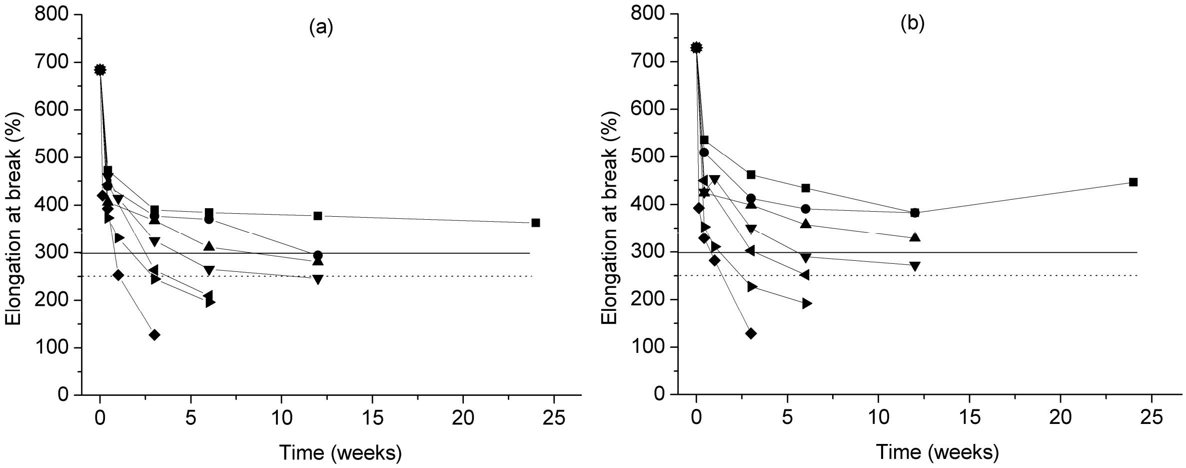

Figure 6.12: Influence of aging time on elongation at break of compounds containing (a): 0 wt%, and (b): 40 wt% reclaim at (■): 70°C; (●): 80°C; (▲): 90°C; (▼): 100°C; (◀): 110°C; (▶): 120°C and (♦): 130°C

Figure 6.13(a) shows slightly increasing insoluble fractions for the samples during aging at 70°C. The initial increase for the samples containing 80 wt% of reclaim is somewhat higher compared to the other blends. Aging at 130°C has a more significant effect on the insoluble fractions of the different revulcanizates, as shown in Figure 6.13(b).

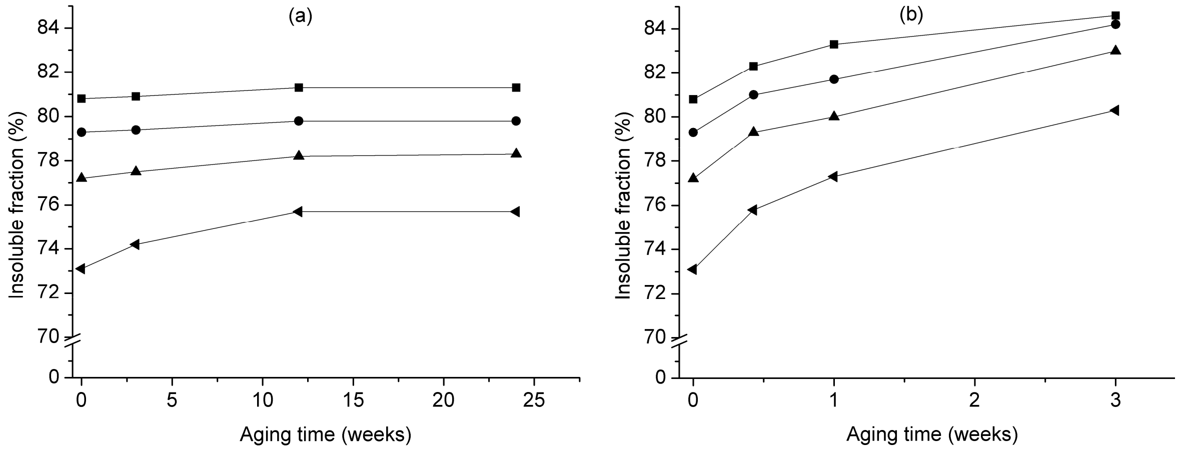

Figure 6.13: Influence of aging time on insoluble fraction at (a): 70°C, and (b): 130°C of compounds containing (■): 0 wt%; (●): 20 wt%; (▲): 40 wt%, and (◀): 80 wt%

Figure 6.14(a) shows a slight increase in crosslink density during aging at 70°C for all blends. The compounds containing 0 wt% and 20 wt% show a little decrease at the beginning of aging, while the revulcanizate with 80 wt% demonstrates a significant initial increase, followed by a further slowly increasing crosslink density. Aging at 130°C results in a more significant increase in crosslink density for all compounds.

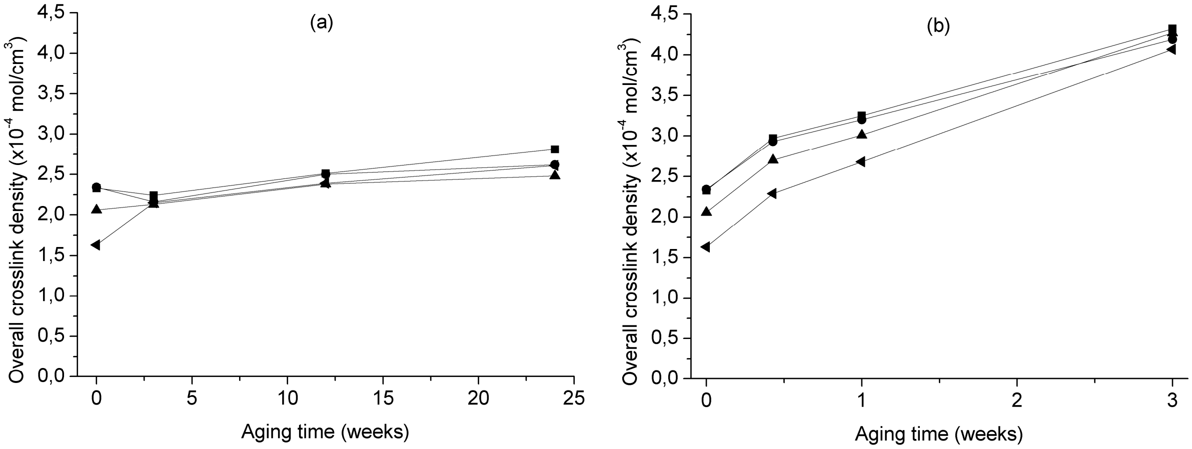

Figure 6.14: Influence of aging time on overall crosslink density at (a): 70°C, and (b): 130°C of compounds containing (■): 0 wt%; (●): 20 wt%; (▲): 40 wt%, and (◄): 80 wt%

Tables 6.5 en 6.6 show the life-time expectancy in years to reach the threshold values in relation to aging temperature and reclaim concentration.

Table 6.5 Life-time expectancy of compounds containing increasing amounts of reclaim, to reach 300% elongation at break

Reclaim content (wt%)	Goodness of fit, R^2	Life-time expectancy in years at different temperatures					
		30°C	40°C	50°C	60°C	70°C	80°C
0	0.980	9.9	4.3	2.0	1.0	0.5	0.3
10	0.946	29	11	4.4	1.9	0.8	0.4
20	0.939	28	11	4.5	2.0	0.9	0.4
30	0.993	17	7.3	3.3	1.6	0.8	0.4
40	0.975	>100	34	12	4.2	1.6	0.6
50	1	>100	44	16	5.8	2.3	1.0
60	0.977	>100	>100	>100	42	10	2.8
70	0.942	>100	37	12	4.4	1.7	0.7
80	0.922	>100	>100	41	12	3.9	1.3
90	0.949	2.2	1.2	0.7	0.4	0.2	0.1
100	◄ No failure ►						

Table 6.6 Life-time expectancy of compounds containing increasing amounts of reclaim, to reach 250% elongation at break

Reclaim content (wt%)	Goodness of fit, R^2	Life-time expectancy in years at different temperatures					
		30°C	40°C	50°C	60°C	70°C	80°C
0	0.943	>100	53	17	6.1	2.3	0.9
10	0.930	>100	>100	39	13	4.4	1.6
20	0.927	>100	45	17	6.6	2.7	1.2
30	0.994	86.8	32	12	5.0	2.1	1.0
40	0.984	>100	79	26	9.1	3.4	1.3
50	0.933	64.9	3.1	1.7	1.0	0.6	0.4
60	0.984	>100	>100	>100	40	11	3.4
70	0.983	>100	96	30	10	3.7	1.4
80	0.994	>100	>100	91	26	7.7	2.5
90	0.996	>100	>100	39	13	4.5	1.7
100	◄── No failure ──►						

Although there is some scatter in the observed trends – the compound containing 60 wt% of reclaim roughly performs best after aging compared to all other compounds - this investigation demonstrates that addition of reclaim at least extends the life-time expectancy for EPDM roof-sheeting, a material already known for its excellent aging resistance. The fact that the 50/50 virgin/reclaim blend has a lower life-time expectancy for a threshold value of 250% elongation at break compared to that of 300% is most probably an artifact in the results.

Figures 6.15 and 6.16 show the influence of aging time and temperature on tensile strength and hardness of the compounds containing increasing amounts of reclaim.

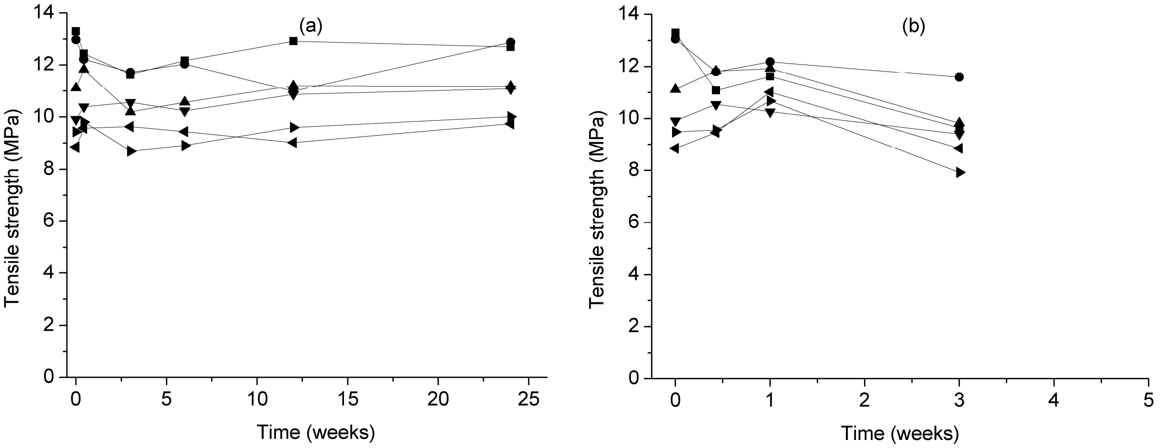

Figure 6.15: Influence of aging time on tensile strength at (a): 70°C, and (b): 130°C of compounds containing (■): 0 wt%; (●): 20 wt%; (▲): 40 wt%; (▼): 60 wt%; (◄): 80 wt% and (►): 100 wt% reclaim

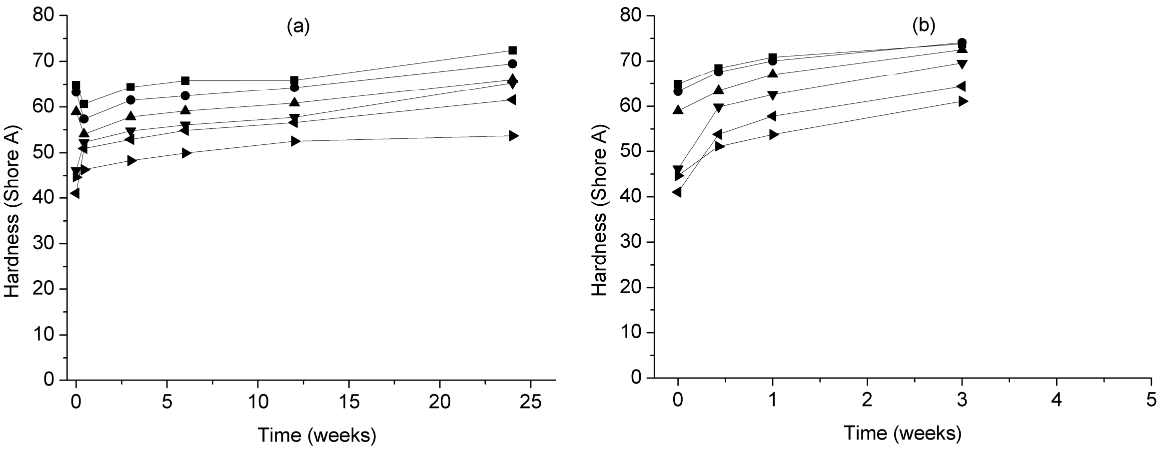

Figure 6.16: Influence of aging time on hardness at (a): 70°C, and (b): 130°C of compounds containing (■): 0 wt%; (●): 20 wt%; (▲): 40 wt%; (▼): 60 wt%; (◀): 80 wt% and (▶): 100 wt% reclaim

The influence of aging at 70°C on tensile strength is practically negligible, while aging at 130°C does give some decrease with time. Both temperatures, 70°C and 130°C, result in increasing hardness values, and this hardening effect is obviously stronger at 130°C. For compounds with a reclaim concentration higher than 50 wt%, the initial hardness increase is a lot stronger than for compounds with lower reclaim concentrations. In comparison with the mechanical properties of the unaged compounds, as shown in Figure 6.8, the properties after aging also show a decreasing trend with increasing reclaim content, although the slight improvement in properties for the pure reclaim, as visible in Figure 6.8, does not show anymore after aging.

6.4 DISCUSSION

6.4.1 Physical and Mechanical Properties

The decrease of the insoluble fraction, or otherwise increase of the amount of soluble, mostly polymer material with progressive addition of reclaim to the virgin roof-sheeting masterbatch, may be related to the decreasing crosslink density of the resulting revulcanizate. During reclaiming, active sites for crosslinking are damaged, resulting in reclaim particles with a somewhat lower crosslink ability during revulcanization. In addition, the average molecular weight of the EPDM in the reclaim is 1.5 times lower than the one used for the virgin masterbatch, as shown by Sutanto[12]. This results in more polymer chain fragments not being embedded in the rubber network. Both factors express themselves in reduced maximum torque values of the cured compounds.

It has been reported by others[7, 21, 22], that reclaim enhances the curing speed due to the presence of accelerator residues still present in the reclaimed rubber, even though the activity of these residues is quite low[12]. This corresponds to the results found in the present investigation: for a fixed curing temperature the optimum cure time generally reduces with increasing reclaim content.

The premature curing or scorch sensitivity at 125°C of the compounds with reclaim contents of 40 wt% or higher, is most probably caused by the fact that HDA can also act as a crosslink promoter[11, 23]. This was confirmed by adding the same amount of HDA to the pure virgin masterbatch as used in a blend containing 50 wt% reclaim, causing this compound to scorch at 125°C. Vulcanization is enhanced in an alkaline environment, and HDA indeed makes the material more alkaline.

The higher storage moduli of the uncured compounds having a reclaim content of 30 wt% or more, as shown in Figure 6.6, is most probably caused by the presence of gel particles in the reclaimed material, which impart a certain elastic contribution to the unvulcanized specimen. At higher reclaim concentrations, this effect is neutralized by the larger amounts of low molecular weight material, acting as plasticizer.

The effect of the gel particles present in the reclaimed material is totally different for the cured compounds. The gel particles are bound to the matrix and loose their flexibility. They have a higher network density, as the reclaim was still crosslinked to a certain degree before revulcanization. Therefore, these particles act as harder spheres with reduced elastic properties.

The decrease in tensile strength and increase in elongation at break with higher reclaim contents might be caused by a decrease in crosslink density, although different levels of filler reinforcement between the original building-profile compound and the roof-sheeting masterbatch may also play a role. In addition, an increasing ratio of mono- to di- and polysulfidic crosslinks with higher reclaim concentrations can also be held responsible for the reduction of tensile strength[24]. Similar arguments apply to the changes in hardness and modulus at 300% strain. Another frequently reported observation is, that reclaim particles act as fracture sites and thus lower the strength. Sample failure is initiated at the interfaces, simultaneously at multiple points[8]. Still another possible reason can be a plasticizing effect of the low molecular weight moiety contained in the reclaim. Under tear test conditions, the situation is different: propagation of cracks through the material is a critical step. The reclaim particles tend to stop or deflect the crack front, resulting in better tear strength values.

Various properties show a discontinuity around 50 wt% reclaim concentration, which possibly can be explained by a matrix shift: starting from a matrix of virgin polymer with reclaim particles embedded as the discontinuous phase, the reclaim islands grow with increasing reclaim contents. Finally the reclaim becomes the continuous phase with virgin compound embedded therein. The SEM pictures indeed show separate reclaim particles when 10 wt% reclaim is added, but once 40 wt% of reclaim is added, no inhomogeneities are visible anymore. In general, the best degree of mixing of two materials with a large plasticity difference can be achieved when equal or higher amounts of the high-viscosity component are blended with smaller amounts of a low-viscosity component.

Aging of rubber vulcanizates changes the network structure considerably. Yehia et al.[7] and Deuri et al.[25] have shown that during aging two factors play important roles: crosslink scission and desulfurization of polysulfidic bonds into mono- and/or disulfidic crosslinks. Additionally formed crosslinks are one cause for the increasing insoluble fractions during aging at both 70°C and 130°C. Another reason for the higher insoluble fractions is the evaporation of plasticizer during aging. Both factors also explain the more significant increase in insoluble fractions during aging at 130°C compared to 70°C.

Compression set in general deteriorates with decreasing degree of crosslinking. The increase in compression set with addition of reclaim at 70°C indicates desulfurization of polysulfidic crosslinks, eventually preventing a full recovery of the deformed material. At 23°C, the situation is different: the sulfur network is stable, resulting in almost constant compression set values.

The decrease in tensile strength with aging time is most probably caused by a combination of factors. First, evaporation of plasticizers makes a compound more brittle, resulting in lower tensile strength. Second, Figure 6.14(b) has shown a significant increase in crosslink density with aging at 130°C. Tensile strength is to a certain extent dependent on the crosslink density. Increasing crosslink density commonly manifests itself in a maximum in tensile strength. The crosslink densities after aging are relatively high, and therefore might already be on the downward trend of the tensile strength. Both factors also explain why the effect of aging at 70°C is less pronounced.

Hamza[26] linked the increasing hardness of the compounds during aging to increasing crosslink density. But for the same reasons as before, it can be due to evaporation of plasticizer and other low molecular weight polymer fragments of the sol fraction in the reclaim.

6.4.2 Application in Roof-Sheeting

All blends investigated in this study do fulfill the UEAtc specifications, with the proviso that the vulcanization in the present investigation was done by compression molding for practical purposes, which is not a common procedure for EPDM roof-sheeting curing.

Tables 6.5 and 6.6 show the life-time expectancy in years to reach the threshold values in relation to aging temperature and reclaim concentration. There is no general consensus about the temperature which should be taken to practically mimic the life-time of EPDM roof-sheeting, as the service temperatures reach from sub-zero temperatures during winter times to temperatures as high as 80°C in the summer. Even at fulltime exposure of the roof-sheeting to a temperature of 80°C, the material still shows acceptable life-times before reaching the threshold values of 300% and 250% elongation at break, taking into account that such high temperatures only occur on flat roofs during a limited period of time throughout the year. It has been stated though, that this aging method does not take into consideration the influence of exposure to all kinds of other weather conditions, like (acid) rain, dirt, hail and excessive ozone attack.

Figure 6.12 shows that the decrease in elongation at break is very strong in the beginning and levels off with aging time. Only for the higher temperatures employed in this study, the threshold value of 250% in elongation is reached within the period of this study. If lower threshold values would have been chosen as practically realistic values, the times to reach a threshold value of e.g. 150% elongation at break would have required very long periods of aging, resulting in even significantly increased life-time expectancies of the compounds in roof-sheeting.

6.5 CONCLUSIONS

Reclaiming of sulfur-cured EPDM building-profile scrap in a co-rotating twin-screw extruder with HDA as devulcanization aid results in a qualitatively excellent material. It can be blended in practically all proportions with a virgin EPDM roof-sheeting compound, where the resulting revulcanizates all fulfill the most stringent industrial UEAtc specifications. The life-time expectancy of virgin roof-sheeting compound with reclaim added is even extended relative to pure virgin compound. All blends perform well for very long periods of time before reaching a practical threshold value for elongation at break of 250%.

Increasing amounts of EPDM reclaim added to the virgin compound result in a decrease in vulcanization time and cure temperature for reversion-free vulcanization. The overall crosslink density shows a decrease with increasing reclaim content, while the ratio of mono- to di- and polysulfidic crosslinks increases. The insoluble fraction decreases with increasing reclaim content, still indicating some loss of revulcanization ability of the reclaim relative to the virgin compound. Above a critical HDA-concentration, the material starts vulcanizing at 125°C already: next to being a devulcanization aid, HDA also has an activating effect on crosslinking. Reclaim enhances the elasticity of uncured compounds, while it reduces the elasticity of the cured blends.

Tensile strength, modulus at 300% strain and hardness decrease with increasing reclaim content, while elongation at break, tear strength and compression set at 70°C show an increase.

The morphology study shows that low proportions of reclaim are dispersed as separate particles in a continuous matrix of virgin rubber, while at higher reclaim concentrations no phase separation could be detected anymore, favoring high amounts of reclaim to be employed.

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Chapter 7

Scale-up of a Continuous Reclaiming Process for Carbon Black Reinforced Sulfur-Cured EPDM-Rubber

A continuous reclaiming process for carbon black reinforced EPDM-rubber was scaled-up from laboratory to production scale. Hexadecylamine was used as devulcanization aid, and reclaiming done in a combination of a twin-screw kneading extruder with a single-screw transport extruder. This reclaiming process resulted in high quality reclaims, which can be added in concentrations up till 50 wt% to virgin EPDM roof-sheeting masterbatches with limited reduction in revulcanized material properties.

Coarsely ground EPDM-rubber production waste with a particle size between 20 and 40 mm results in a reclaim with no significant reduction or even an increase in crosslink density of the non-solubilized fraction relative to the feedstock, while a considerable amount of polymer sol fraction is generated. Reclaiming of EPDM-rubber with an initial particle size between 0.8 and 2.5 mm results in reclaim with a crosslink density reduction of 66% of the insoluble fraction relative to the feedstock, while little polymer sol fraction is generated.

The revulcanized pure reclaims show better properties when material with the smaller initial particle size is used for the reclaiming process. However, there is only little influence of initial particle size of the feedstock on the material properties of blends with up to 50 wt% of the virgin compound. All reclaims can be added to at least 40 wt% to a virgin EPDM roof-sheeting masterbatch with limited reduction in properties. These still fulfill the UEAtc specifications for EPDM roof-sheeting.

Further process optimization seems justified in order to reduce the temperature of 330°C measured after the reclaiming in the twin-screw extruder, to more feasible temperatures $<$275°C, held responsible for hard nibs in the reclaim: most probably degenerated material at this high temperature.

7.1 INTRODUCTION

This chapter describes the factory scale-up of the pilot-scale continuous reclaiming process as developed within the context of this total research project, at the University of Groningen[1, 2]: see Chapter 6. The plant experiments were performed at Rubber Resources BV (Maastricht, the Netherlands), which company commercially reclaims natural rubber truck tire treads and butyl-rubber inner-tubes.

The reclaiming process was performed on the production line, which generally is in use for reclaiming butyl-rubber inner-tubes. In the process, the inner-tubes are transported on a conveyor belt into a rotating drum, where the material is washed with water to remove dirt. The cleaned material is subsequently transported to a shredder, where it is ground to chips with a particle size of 20 – 40 mm. The wet rubber passes through a hot-air dryer, followed by cyclones in which the material is separated from stones and other contaminations. The ground and cleaned material is then reclaimed in a twin-screw extruder. It is passing a refiner on which hard particles are removed and the viscosity of the reclaim is further reduced. The reclaim is finally extruded, cooled, automatically cut into slabs and packed.

In the case of EPDM compounds used for these plant trials, the material had to be ground externally as the cutting, grinding, washing and drying steps in the existing line were not optimized for this material. It was processed in the truck tire grinding line at Re-Tyre (Lommel, Belgium). The sheets were shredded and ground, and steel and other magnetic contaminations were removed from the product stream using magnets. Screening was done by returning the top fraction to the grinding unit, and separating the bottom fraction with a particle size of 0.8 – 2.5 mm. This fraction was further cleaned from iron, stones and other contaminations. This material was then transported to Rubber Resources BV.

The quality of the various reclaims is evaluated in this chapter in an application study for EPDM roof-sheeting.

7.2 EXPERIMENTAL

Materials and compound recipes – A mixture of three vulcanized EPDM foils was used as feedstock for the reclaiming process: 70% roof-sheeting, 15% pond lining and 15% other foil, all from Hertalan B.V., the Netherlands. After reclaiming, this material was blended with a virgin EPDM-rubber masterbatch for roof-sheeting purposes of proprietary composition from Hertalan B.V.

Hexadecylamine (HDA) 95% pure (Alfa Aesar GmbH & Co KG, Karlsruhe, Germany) was used as devulcanization aid. Decahydronaphtalene, a mixture of the cis- and trans-isomer with a purity of 98%, was used for swelling measurements. The solvents acetone and tetrahydrofuran (THF) (Biosolve) were used for extractions.

Reclaiming – Reclaiming of the EPDM foils was performed at Rubber Resources (Maastricht, the Netherlands) in a co-rotating twin-screw extruder, Berstorff ZE 130AX18D, with a length of 2.6 m. The reclaiming conditions are shown in Table 7.1. A much lower HDA feed-rate was used in this study then was applied in the pilot-scale continuous reclaiming process as performed by Sutanto[1], because the present experiments did not show a need for such large quantities. The reclaim then passed a single-screw, Berstorff Extruder GE 200 KS×6D, with a screw diameter of 20 cm and a L/D ratio of 6:1.

Table 7.1 Reclaiming conditions of the EPDM foils at Rubber Resources BV

Parameter	Twin-screw extruder conditions
Set temperature	240°C
Screw speed	Particle size 20 – 40 mm: 2150 rpm Particle size 0.8 – 2.5 mm: 1500 rpm
Rubber feed rate	900 kg/hr
HDA feed rate	Particle size 20 – 40 mm: 0, 1 and 2.5 wt% Particle size 0.8 – 2.5 mm: 0, 1 wt%

Mooney viscosity – Mooney viscosity ML(1+4)100°C was determined using a Mooney viscometer MV200 VS from Alpha Technologies, according to ISO R289.

Mixing and vulcanization – Various amounts of the EPDM reclaim were blended up till 50 wt% with the virgin EPDM roof-sheeting masterbatch and cured after addition of the curing package as shown in Table 7.2, according to the detailed description given in Chapter 6. Because former chapters have shown that addition of reclaim in concentrations higher than 50 wt% to a virgin masterbatch resulted in a significant reduction in material properties, it was decided to limit the reclaim concentration till maximally 50 wt%. In addition, pure revulcanized reclaim was evaluated.

Table 7.2 Curing recipe for EPDM roof-sheeting

Material		phr	Supplier
EPDM	-	100	DSM Elastomers
Zinc oxide	ZnO	5	Merck
Stearic acid	-	1	Sigma Aldrich
Mercaptobenzothiazole-disulfide	MBTS	0.5	Rhein Chemie Rheinau GmbH
Tetrabenzylthiuram-disulfide	TBzTD	2.0	Rhein Chemie Rheinau GmbH
Sulfur	S	1.5	Merck

Extractions – The extractions were carried out as described in Chapter 3.

Equilibrium swelling – The degree of swelling was measured on extracted samples; this allows to determine the crosslink density of the vulcanized compounds and of the reclaims after removal of the sol fraction, as described in Chapter 3. The crosslink density was calculated according to the Flory-Rehner equation[3]. This equation is strictly spoken only valid for non-filled systems. The Kraus[4, 5] correction for filled compounds needs to be applied to get the correct values of the different crosslink densities. However, for secrecy reasons the compound composition was not disclosed to the author and it is for this reason that the Kraus correction could not be applied. Therefore, the results can only be interpreted in terms of differences of the overall crosslink density and not in terms of actual values.

Mechanical properties – Tensile and tear tests were carried out according to ISO 37 and ISO 34, respectively. Compression set tests were carried out according to ISO 815. The hardness of the samples was measured using a Zwick Hardness-tester Shore A type according to DIN 53503. Chapter 3 gives a description of these methods.

7.3 RESULTS

7.3.1 Characteristics of the Reclaims

The first series of experiments was performed with EPDM granulate with a particle size of 20 - 40 mm. The reclaims are referred to as reclaim 0 (LP), 1 (LP) and 2.5 (LP), according to the concentrations of HDA added during reclaiming in the twin-screw extruder: 0, 1 and 2.5 wt%. Reclaiming of the material with a particle size between 0.8 and 2.5 mm, without addition of HDA, resulted in a non-processable crumbly material, which could not be transported as a continuous stream through the production line. Therefore, this material was not further investigated and no data are reported. When 1 wt% of HDA was added as devulcanization aid, the reclaim was processable. It was encoded as reclaim 1 (SP). This reclaim 1 (SP) showed sticky behavior on the refiners, what again lead to processing problems.

The temperature of the reclaims measured immediately after the extruder was approximately 330°C; very high compared to the reclaiming temperatures employed in previous chapters and in the thesis of Sutanto[1].

The characteristics of the feed stock and the different reclaims are shown in Table 7.3. The insoluble fraction and overall crosslink density of the feedstock was determined in sixfold, to investigate the homogeneity of the blended mixture of three different EPDM foils. All six measurement showed comparable results.

Table 7.3 Characteristics of the original vulcanized feedstock and the different reclaims

Material	Mooney viscosity (MU)			Insoluble fraction (%)	Overall crosslink density ($x10^{-4}$ mol/cm^3)
	After extruder step	After refiner step	After storage of 2.5 weeks		
Feedstock	-	-	-	80.2	3.6
Reclaims					
0 (LP)	121	81	83	66.4	5.3
1 (LP)	110	70	67	65.1	3.2
2.5 (LP)	102	96	100	65.6	4.3
1 (SP)	92	77	80	73.9	1.2

The Mooney viscosity values immediately after the extruder of reclaims 0 (LP), 1 (LP) and 2.5 (LP) decrease with increasing HDA-concentration. However, the Mooney viscosity of reclaim 2.5 (LP) after the refiners is significantly higher than those of reclaims 0 (LP) and 1 (LP). The viscosity of the reclaims is not increasing during storage, what normally happens for other types of reclaim, e.g. based on Natural Rubber. Therefore, this high Mooney viscosity of sample 2.5 (LP) after the refining step remains an unsolved question. Reclaim 1 (SP) shows the lowest Mooney viscosity of all reclaims after the extrusion step, and the reduction in viscosity between extrusion and refining is less than with the corresponding reclaim made from coarse material.

There is no influence of HDA-concentration on the insoluble fraction of the reclaims made from an original particle size of 20 – 40 mm. All reclaims show significantly lower insoluble fraction values compared to the original feedstock. However, the insoluble fraction of the reclaim made from the original particle size between 0.8 and 2.5 mm, treated with 1 wt% HDA as devulcanization aid, is significantly higher than those of the reclaims from the larger initial particle size. Comparing the crosslink densities, it is obvious that reclaim 1 (SP) shows a significantly lower value than the original feedstock, while the crosslink densities of reclaims 0 (LP), 1 (LP) and 2.5 (LP) show values similar to the value of the feedstock, or even considerably higher crosslink concentrations. The higher crosslink density of 0 (LP) relative to the feedstock is most probably because the material crosslinks to a higher value at 330°C without the addition of a devulcanization aid. Addition of 1 wt% of reclaim starts breaking down the crosslinks. The high crosslink density value of reclaim 2.5 (LP) is, as was also seen for the Mooney viscosity, an unsolved question.

7.3.2 Application Study

Because reclaims 0 (LP) and 1 (LP) showed Mooney viscosities in the processable range, the application study was limited to these reclaims, together with reclaim 1 (SP). Table 7.4 shows the reversion-free cure temperatures needed for the blends, while Figure 7.1 demonstrates the maximum torque and optimum cure time to reach 90% cure: t_{90}. The reversion-free cure temperature is the temperature at which no marching modulus or reversion occurs.

Table 7.4 Reversion-free cure temperatures of the blends of virgin masterbatch with reclaim

Reclaim content (wt%)	Reversion-free cure temperature (°C) of reclaim		
	0 (LP)	1 (LP)	1 (SP)
0	190	190	190
10	190	180	180
20	190	180	180
30	190	180	180
40	190	180	180
50	180	180	170
100	150	150	160

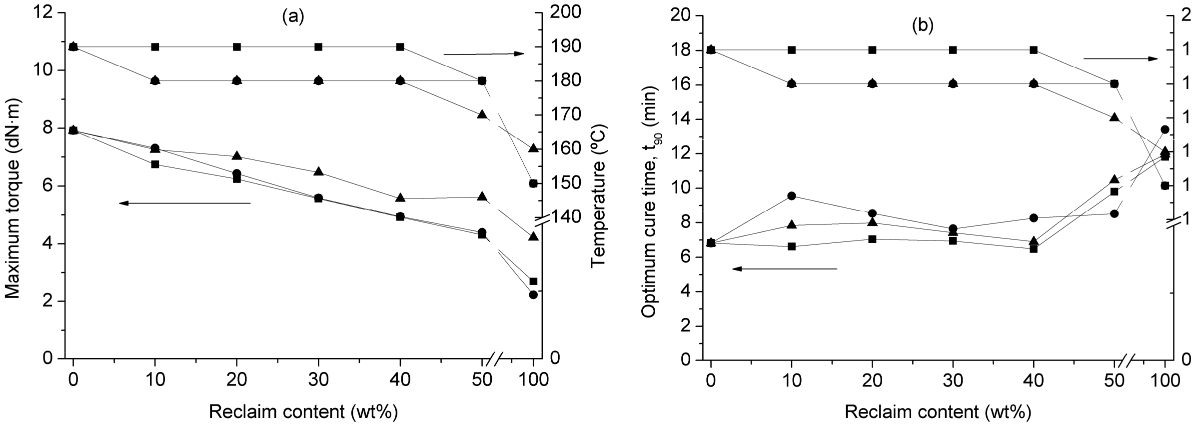

Figure 7.1: Influence of reclaim content on the reversion-free cure temperature and on (a): maximum torque, and (b): optimum cure time, t_{90}, of the revulcanizates; (■): Reclaim 0 (LP); (●): 1 (LP) and (▲): 1 (SP)

The maximum torque values of these blends decrease with increasing reclaim content, and show the highest values for blends with reclaim 1 (SP) added. The optimum cure time, t_{90}, does not change significantly up to 40 wt% of reclaim. For higher amounts of reclaim it increases considerably because of the lower vulcanization temperatures applied to obtain reversion-free curing. In general, blends with reclaim 0 (LP) can be cured at higher temperatures, resulting in shorter cure times. Figures 7.2 and 7.3 show the influence of reclaim on the insoluble fraction and the overall crosslink density of the revulcanized blends.

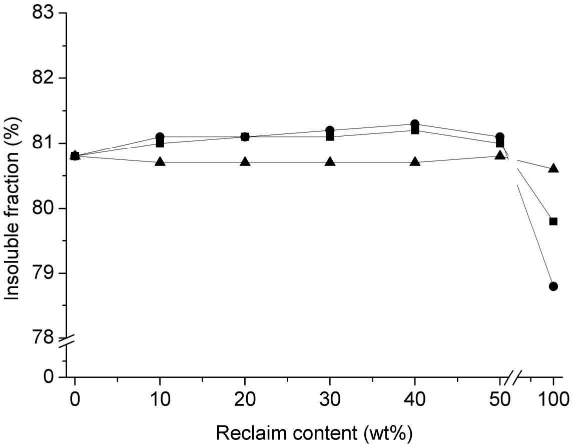

Figure 7.2: Influence of reclaim content on the insoluble fraction of revulcanized blends; (■): Reclaim 0 (LP); (●): 1 (LP) and (▲): 1 (SP)

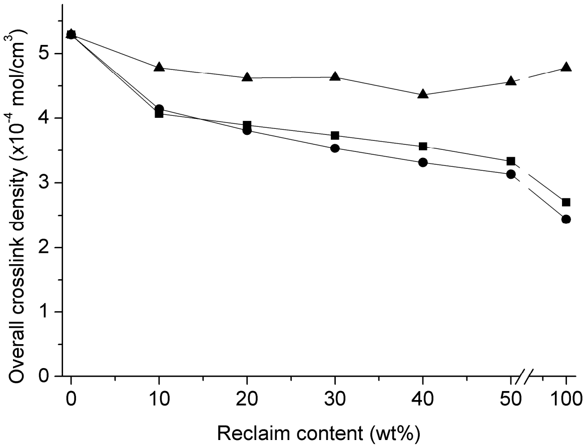

Figure 7.3: Influence of reclaim content on the overall crosslink density of revulcanized blends; (■): Reclaim 0 (LP); (●): 1 (LP) and (▲): 1 (SP)

The addition of reclaim does not have a significant influence on the insoluble fractions of the revulcanized blends up to 50 wt% of reclaimed material added. Addition of reclaim 1 (SP) results in blends with slightly lower insoluble, therefore higher soluble fractions compared to addition of reclaims 0 (LP) and 1 (LP). Interesting are the results in relation to the insoluble fractions of the vulcanizates of pure reclaim: for reclaim 0 (LP) and 1 (LP), the value for the pure reclaim revulcanizate is significantly lower than the values of the blends. In the case of reclaim 1 (SP), the values of the pure reclaim revulcanizate and of the blends are practically the same.

The influence of reclaim on the crosslink density again shows a clear difference between the reclaims made from the original particle size of 20 – 40 mm and those of 0.8 – 2.5 mm. Addition of reclaim of a smaller particle size results in revulcanized blends with a slightly lower crosslink density compared to the pure masterbatch, while the values of the vulcanized pure masterbatch and the pure reclaim are comparable. However, all these samples show a significantly higher crosslink density than those with reclaims 0 (LP) and 1 (LP). Increasing amounts of reclaims 0 (LP) and 1 (LP) decrease the crosslink density of the revulcanized blends, while there was no significant influence of the concentration of reclaim 1 (SP) on the overall crosslink density of the revulcanized blends.

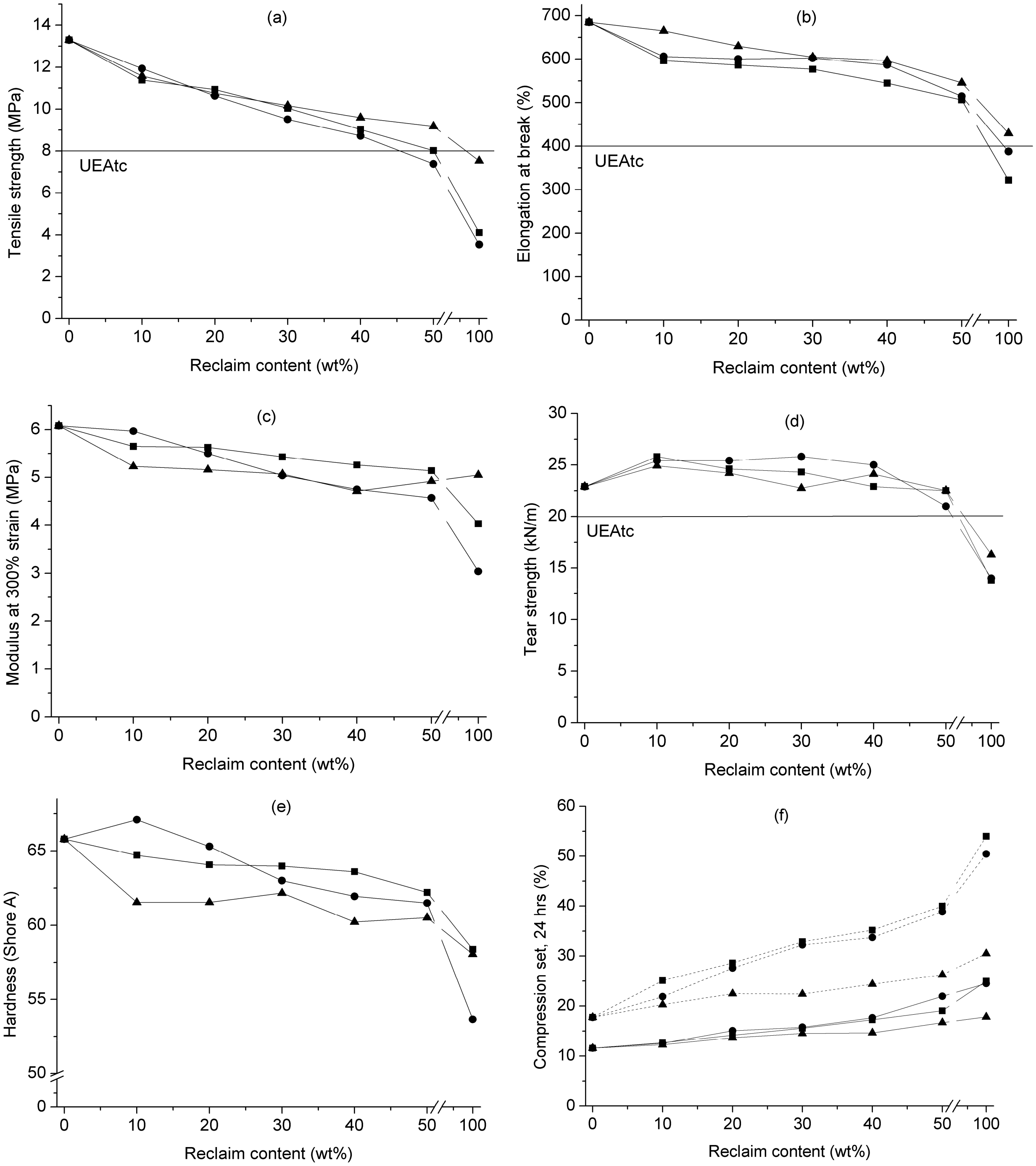

Figure 7.4: Influence of reclaim content on (a): tensile strength; (b): elongation at break; (c): modulus at 300% strain; (d): tear strength; (e): hardness, and (f): compression set at (—): 23°C and (- - -): 70°C of the revulcanized blends; (■): Reclaim 0 (LP); (●): 1 (LP) and (▲): 1 (SP)

Figure 7.4 shows the influence of reclaim on the mechanical properties of the revulcanized blends compared to the UEAtc[6] specifications for EPDM roof-sheeting as described in Chapter 6. Addition of increasing amounts of reclaims 0 (LP), 1 (LP) and 1 (SP) in general results in decreasing tensile strength, elongation at break, modulus at 300% strain and hardness values, while a maximum is observed for tear strength and an increasing trend for compression set, both at 23°C and 70°C. Reclaim 1 (SP) shows the best results in compression set, especially at 70°C, while the other mechanical properties do not show a significant difference between the three different reclaims up to 50 wt% of reclaim added to the virgin EPDM roof-sheeting masterbatch. Cured pure reclaim 1 (SP) shows the best results for all mechanical properties of all pure reclaims tested. All revulcanized blends fulfill the UEAtc specification up till addition of at least 40 wt% of reclaim.

7.4 DISCUSSION

Table 7.3 shows that addition of HDA during reclaiming reduces the Mooney viscosity of the materials compared to pure thermal reclaiming without devulcanization aid. This is important as viscosities below 120 MU are needed to ensure a continuous material stream within the processing line. It is also shown that the reclaims based on the larger feedstock with an original particle size of 20 – 40 mm show a significant reduction in insoluble fraction. In other words a considerable amount of soluble fraction, approximately 15%, is generated during reclaiming. The overall crosslink densities of the insoluble fractions of the reclaims after extraction of the sol, do not show a significant reduction, rather an increase compared to the value of the original material. This indicates a peeling-off mechanism as reported in Chapter 4 for the efficiently vulcanized compound: reclaimed material is peeled-off from the outer layer of the particles resulting in an increasing amount of soluble fraction, while no scission of crosslinks occurs in the core of the particles.

Reclaim 1 (SP) on the other hand, shows a clear reduction in crosslink density of approximately 2/3 compared to the value of the feedstock, in combination with a relatively small amount of sol fraction generated, approximately 6%. This indicates a devulcanization-dominated process: scission of crosslinks without an appreciable generation of a soluble low molecular weight polymer fraction.

This apparently contradictory effect for these two feedstocks is illustrative for a technical commercial plant, where the quality of the feedstocks, their degree and type of curing is not known beforehand. It could be, that the feedstock used for the larger particle size was more of the efficiently cured type and that used for the smaller size more of the conventionally cure type. However, this is not very likely. We rather assume that the difference in the breakdown mechanism is caused by the higher relative surface area and the smaller particle size. The devulcanization aid covers a larger surface and migrates relatively closer to the core of the smaller particles during the reclaiming cycle, whereas for the larger particles only the outer layer is affected. However, the positive effect of a smaller particle size is limited by the lower efficiency of shear on fine powders. In contrast to the situation as described in Chapter 4, where the difference in reclaiming mechanism is based on a difference in network structure of the feedstock, the cause for the different breakdown behavior in this case is the difference in particle size.

The slightly higher maximum torque values for blends containing reclaim 1 (SP) compared to compounds with reclaims 0 (LP) or 1(LP), correlates with the higher overall crosslink density of the blends of the former. The fact that reclaim 1 (SP) shows a much lower crosslink density than the original feedstock, but that the revulcanized blends contain a comparable amount of crosslinks relative to the pure masterbatch, indicates that this reclaim is very suitable for revulcanization: as already stated above, crosslinks are broken in a way that the active crosslink sites are not degenerated. Furthermore, the polymer chains also remain intact, and both factors guarantee good crosslinking reactivity. This is also proven by the high crosslink density obtained for the vulcanized pure reclaim 1 (SP), as shown in Figure 7.3.

All revulcanized blends fulfill the UEAtc specification for EPDM roof-sheeting up until addition of at least 40 wt% of reclaim. There are no significant differences in mechanical properties between the blends with the various reclaims up to 50 wt% of reclaimed material, except for compression set. The compression set at 70°C does not increase significantly with addition of reclaim 1 (SP), which again points at good revulcanizability and may be taken as indication that the crosslinks formed during revulcanization are rather short and stable. This prevents the well-known effect of desulfurization, that increases compression set values by formation of new crosslinks.

The industrial process used in this chapter requires a significantly lower amount of HDA compared to the concentration used in Chapter 6, because in this process HDA is assisted by a higher amount of shear obtained in the industrial twin-screw extruder resulting in a significantly higher material temperature and therefore a larger plasticizing effect. It is also shown in the previous chapters that the temperature is very important on lab scale, while in industrial processes it is mostly dependent on the power of the motor used and can therefore be less controlled.

Within this study, the revulcanized blends did not show any clearly visible reclaim particles at the surface or inside the test samples. Such inhomogeneities need to be avoided, as they form weak spots, where the sheets tend to tear.

However, the way of molding has to be taken into consideration when looking at the surface smoothness of the sheets. As already mentioned in Chapter 6, within this investigation the EPDM roof-sheeting compounds are cured by compression molding, while autoclave curing is commonly used in the roof-sheeting industry. Autoclave curing of the blends containing reclaim, done at Hertalan B.V. resulted in sheets with some surface irregularities. These spots are most probably burned rubber particles, because the temperature of the reclaim exiting the extruder reached approximately 330°C, which is in the temperature range for degradation of EPDM-rubber and far outside the proper temperature regime: 200 – 275°C, optimal for EPDM-reclaiming. Such high temperatures need to be avoided by optimizing the extruder settings in a way that the material is reclaimed at a lower temperature, rather by applying a less intensive screw configuration than by more intensive cooling, which may even have an opposite effect. This needs further optimization in the plant.

Overall, it can be stated that production size scale-up of the reclaiming process developed at the University of Groningen in the context of the present project results in high quality reclaims with HDA used as devulcanization aid, which can be added up till at least 40 wt% and still fulfill the UEAtc specifications. The process conditions still need optimization, to further improve the reclaim quality. The processing problems when larger particles are used may be solved by applying feedstock of smaller particle size. The sticky behavior problem at a stage after reclaiming of the material when smaller particles are used is more than counterbalanced by the good quality of the reclaim.

7.5 CONCLUSIONS

Ground EPDM sheet material can be reclaimed in a continuous process with addition of hexadecylamine as devulcanization aid. Scale-up to production-scale of the reclaiming process as developed in pilot-scale at the University of Groningen results in high quality reclaims. Reclaiming of EPDM-rubber scrap of an original particle size between 20 and 40 mm, without and with 1 wt% hexadecylamine as devulcanization aid, results in reclaims of which the insoluble fraction does not show a significant reduction or even an increase in crosslink density. However, a considerable amount of polymer sol, 15% is generated: polymer chains are peeled-off from the outer layer of the particles, while no scission of crosslinks occurs in the core of the particles. Reclaiming of EPDM-rubber scrap with an original particle size between 0.8 and 2.5 mm with 1 wt% of hexadecylamine results in reclaimed material with a 66% lower crosslink density of the insoluble remaining fraction relative to the feedstock, and with only 6% of polymer sol fraction generated. In this case, real devulcanization is the main process: scission of crosslinks with generation of only a very small amount of a soluble, low molecular weight polymer fraction.

All reclaims can be added to at least 40 wt% to a virgin EPDM roof-sheeting masterbatch with limited reduction in properties and still fulfilling the UEAtc specifications for EPDM roof-sheeting. When pure reclaim is vulcanized, the material based on the smaller particle size performs by far the best within this series of reclaims. However, for the reclaims blended with virgin masterbatch, only small differences between the different reclaims are seen in the mechanical properties of the revulcanized blends.

Even though the reclaiming process is not optimized yet, it results in high quality reclaims. However, some practical problems have to be solved before the process can be commercialized. Prior to reclaiming, the EPDM foils have to be ground to fine particles, but as a consequence the reclaim sticks to the refiners. Furthermore, the material temperature during the reclaiming process should also be reduced till the practical range below 275°C, in order to avoid thermal degradation of the material.

7.6 REFERENCES

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Chapter 8

Summary and Final Remarks

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.

8.1 THE RESEARCH

The objective of this project was to prove the feasibility of production scale recycling of EPDM-rubber, based on the outcome of a former project, by developing a continuous process for mechano-chemical reclaiming of EPDM-rubber waste, using amines as devulcanization aids. In order to prove this feasibility, a great many variables needed to be screened from the perspective of the rubber compound composition as well as from the perspective of process development. This research was a joint project with the University of Groningen, Department of Chemical Engineering, and their research was focused on the development of the continuous reclaiming process. The research described in the present thesis is focused on the material: influence of the rubber compound composition on the process efficiency and product quality, optimization of the devulcanization aid and application studies. Application development focused on the use of such reclaimed EPDM as a raw material for roof-sheeting. This is a material which is commonly vulcanized to a low extent, in order to obtain optimal flexibility of the material. It was the preferred application for this study, as a certain loss in vulcanization efficiency of the EPDM could be tolerated. The potential size of this market is very large, thereby providing an outlet for large amounts of recycled EPDM-rubber of various origins: automotive as well as building and construction profiles.

8.2 GENERAL SUMMARY

Chapter 1 gives an introduction into the research topic of the thesis by discussing the problem of rubber waste in general and EPDM production-scrap in particular. A description of EPDM-rubber and its qualities and applications is given. The aim of this study is explained and the structure of the thesis is given.

The different ways of rubber recycling, e.g. repeated use, material recycling, recovery of base chemicals and energy recycling, are briefly described in **Chapter 2**. The most effective recycling principle is the short-loop of material recycling for re-use of upgraded rubber waste in new rubber articles. The best quality recyclate can be achieved by reclaiming: the breakdown of the polymer network. A comprehensive overview of all recycling methods in general, and reclaiming processes used for sulfur-cured rubber in particular is given, with special attention to reclaiming of EPDM-rubber. For a better understanding of the processes occurring during destruction of the rubber network, a model description of main-chain scission and crosslink breakage is given.

Chapter 3 analyzes the crosslink density and sulfur-ranks of crosslinks formed during vulcanization of a carbon black reinforced ENB-EPDM compound as a function of the selected curing system: conventional, semi-efficient, efficient and nitrosamine-safe. Each vulcanization system results in a specific crosslink concentration and sulfur-rank distribution: mono-, di- and polysulfidic of nature. Tensile properties, tear strength and compression set of the vulcanized materials turn out to practically only depend on overall crosslink density, as resulting from the particular curing systems and vulcanization times. All trends in properties coincide when plotted as a function of the overall crosslink density. Surprisingly, the crosslink distribution: the ratios of mono- to di- and polysulfidic crosslinks, has only a minor effect on these properties. The differences in sulfur-rank as a function of the chosen vulcanization system turn out to be too small for EPDM to have a significant effect.

The trends found for all mechanical properties fit to the generally reported mastercurves of properties versus crosslink density, except for elongation at break, which shows a very sharp initial increase before decreasing with increasing crosslink density.

Chapter 4 gives an overview of the influence of temperature, time, shear and concentration of hexadecylamine (HDA) as devulcanization aid on the reclaiming efficiency of different EPDM-based sulfur-vulcanized rubbers: conventionally cured, grossly polysulfidic of nature; and efficiently vulcanized, mainly monosulfidic. It turns out that of the four variable factors examined, temperature clearly has the largest influence on the reclaiming efficiency within the experimental ranges. HDA is suitable as devulcanization aid for different EPDM compounds, taking into account the parameter settings for each single compound.

Reclaim from conventionally vulcanized EPDM, mainly polysulfidic of nature, shows the largest decrease in remaining crosslink density with increasing HDA concentration and at lower reclaim temperatures. After reclaiming at the lower limit of the experimentally applied temperature window: 225°C, the concentration of remaining di- and polysulfidic crosslinks is higher than the concentration of monosulfidic bonds, while at the upper temperature level: 275°C, the concentration of monosulfidic bonds is highest. For efficiently vulcanized EPDM with primarily monosulfidic crosslinks, HDA again has a positive effect on the reclaim efficiency at low applied reclaiming temperatures of max. 225°C. At higher temperatures, the crosslink density increases with increasing concentrations of HDA. Application of the treatment proposed by Horikx shows, 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 up to 50 wt% to a virgin masterbatch, with a limited decrease in properties after revulcanization. This is a high amount compared to max. 15 wt% addition of ground powder rubber, commonly known to be the practical limit for this type of recycled rubber.

Chapter 5 shows that the influence of hexadecylamine (HDA), diphenyldisulfide (DPDS) and o’o’-dibenzamidodiphenyldisulfide (BAFD) as devulcanization aids on the reclaiming efficiency of two types of carbon black filled EPDM-rubber: a conventionally cured primarily polysulfidic, and an efficiently vulcanized mainly monosulfidic compound, differ significantly.

DPDS and BAFD are not effective in helping the break-down of the conventionally cured rubber network, whereas HDA has a strong positive effect. DPDS and BAFD do not lead to reclaims plasticized to such an extent that acceptable Mooney viscosities are obtained, unless for the highest reclaiming temperatures and additions of these devulcanization aids. HDA does for all temperatures, even at low dosages. In all cases the reclaims can be added up to 50 wt% to a virgin EPDM masterbatch without significantly influencing the properties of the revulcanized compounds.

The devulcanization aids act differently when used for reclaiming a largely monosulfidic compound. Because of the low crosslink density of the compound to start with, it can easily be plasticized even without addition of devulcanization aids at the lowest temperature of 200°C employed. DPDS and BAFD plasticize the compound to a higher extent compared with HDA. The reclaims obtained with

HDA as well as with BAFD provide good mechanical properties when added to a virgin masterbatch: some properties are even improved by addition of these reclaims. In contrast to this, the DPDS-treated material is difficult to revulcanize, resulting in a significant reduction of the material properties.

The observations confirm the different reclaiming mechanisms for the two types of EPDM: mainly homogeneous reclaiming/devulcanization of the conventionally cured compound, vs. peeling-off plasticized shells of the efficiently vulcanized compound. However, these two differences do not necessarily reflect in poor properties of the revulcanized blends of these reclaims with virgin compound.

It can be concluded that HDA is the most universally applicable devulcanization aid, because it gives for both types of EPDM well plasticized materials and good mechanical properties of revulcanized blends with up to 50 wt% of these reclaims. BAFD can be a good alternative, but results in less processable reclaims in the case of the conventionally cured compound. DPDS is no option as devulcanization aid, as the reclaim based on the efficiently cured material is not suitable for revulcanization.

Chapter 6 reports the reclaiming of sulfur-cured EPDM building-profile material in a co-rotating twin-screw extruder using hexadecylamine as devulcanization aid. This reclaim is blended with increasing amounts of a virgin EPDM roof-sheeting masterbatch and cured at temperatures allowing for a reversion-free vulcanization. Roof-sheeting was chosen for this application, because this material can tolerate some loss in curing efficiency due to its low degree of vulcanization required.

The trends in cure characteristics show that increasing amounts of reclaim employed in the blends allow for a lower reversion-free cure temperature and the maximum torque values, while the vulcanization speed is increased. The insoluble fraction and crosslink density both decrease, while the ratio of mono- to di- plus polysulfidic crosslinks increases with growing reclaim contents. It is found that reclaim enhances the elasticity of uncured compounds, while it reduces the elasticity of the cured materials. A SEM-EDX morphology study of the blends, done in order to evaluate the dispersion of the reclaim into the virgin rubber matrix shows that even large amounts of reclaimed material result in homogeneous and smooth compounds.

In terms of mechanical properties, tensile strength, modulus at 300% strain and hardness decrease, while elongation at break, tear strength and compression set at 70°C increase with higher reclaim ratios. Irrespective of the blend ratios, the mechanical properties all fulfill the most stringent European UEAtc specifications for EPDM roof-sheeting.

An aging study is performed in order to investigate the influence of reclaim on the long-term performance of the material and to judge the suitability of the compounds for roof-sheeting. Increasing reclaim contents improve the aging resistance and prolong the time before a practical threshold value for elongation at break of 250% for EPDM roof-sheeting purposes is reached.

Chapter 7 reports the upscaling of the continuous reclaiming process for carbon black reinforced EPDM-rubber from laboratory to production scale. Hexadecylamine was used as devulcanization aid, and reclaiming was done in a combination of a twin-screw kneading extruder with a single-screw transport extruder. This reclaiming process resulted in high quality reclaims, which can be added in concentrations up till 50 wt% to virgin EPDM roof-sheeting masterbatches with limited reduction in revulcanized material properties.

Coarsely ground EPDM-rubber production waste with a particle size between 20 and 40 mm results in a reclaim with no significant reduction or even an increase in crosslink density of the non-solubilized fraction relative to the feedstock, while a considerable amount of polymer sol fraction is generated. Reclaiming of EPDM-rubber with an initial particle size between 0.8 and 2.5 mm results in reclaim with a crosslink density reduction of 66% of the insoluble fraction relative to the feedstock, while little polymer sol fraction is generated.

The revulcanized pure reclaims show better properties when material with the smaller initial particle size is used for the reclaiming process. However, there is only little influence of initial particle size of the feedstock on the material properties of blends with up to 50 wt% of the virgin compound. All reclaims can be added to at least 40 wt% to a virgin EPDM roof-sheeting masterbatch with limited reduction in properties. These still fulfill the UEAtc specifications for EPDM roof-sheeting.

Further process optimization seems justified in order to reduce the temperature of 330°C measured after the reclaiming in the twin-screw extruder, to more feasible temperatures $<$275°C, held responsible for hard nibs in the reclaim: most probably degenerated material at this high temperature.

8.3 SUGGESTIONS FOR FURTHER RESEARCH

The work described in this thesis has demonstrated that hexadecylamine is very suitable as devulcanization aid for reclaiming sulfur-cured EPDM-rubber. Depending on the sulfur-rank distribution of the crosslinks in the rubber networks, hexadecylamine has a different influence on the reclaiming efficiency, but in all cases reclaims are obtained, which are very suitable for revulcanization and can be added up to appr. 50 wt% as raw material to virgin compounds, without significantly reducing the material properties.

It was shown in Chapter 4 and 7 that the particle size of the vulcanized rubber scrap influences the efficiency of breaking down the polymer network and the material properties of the reclaim containing revulcanized blends. Thereby, the particle size also influences the processability of the original vulcanized material and the reclaim in the production process, when reclaiming is performed commercially. It is therefore recommended to optimize the particle size for material properties of the reclaim as well as for the processability of the reclaiming process.

The reclaims perform very well when revulcanized by compression molding. However, autoclave curing has shown that specks/nibs are visible in the compounds, which can cause leakage of the roof-sheeting. These specks are most probably caused by combustion of the rubber due to the high temperature of 330°C, which is generated during the reclaiming process. Optimization of the extruder settings is necessary to obtain less shear inside the extruder, but to still produce well processable reclaims.

Chapter 5 has shown that BAFD has a large plasticizing effect on efficiently vulcanized EPDM-rubber. It is therefore recommended to try a mixture of BAFD and HDA as devulcanization aids. BAFD for the plasticizing effect at relatively low temperatures and HDA for breaking the crosslinks in such a way that the recreated crosslink sites are effective for revulcanization.

Overall, it can be concluded that when the process conditions can be optimized, a suitable method for reclaiming of various types of EPDM-rubber is now available. When it is also certain that the total costs for producing a kilogram of EPDM-rubber reclaim are not exceeding that of a kilogram of virgin rubber, this not only solves part of the waste problem, but also lowers the costs for EPDM-rubber manufacturers: it can be used as raw material and reduces the power consumption necessary for producing new compounds.

Samenvatting en afsluitende opmerkingen

Dit hoofdstuk bevat een samenvatting van het werk beschreven in dit proefschrift. Een algemene evaluatie van de resultaten wordt gegeven samen met enkele opmerkingen. Tenslotte worden er enkele suggesties voor verder onderzoek aangedragen.

HET ONDERZOEK

Het doel van dit project was om aan te tonen dat het mogelijk is om EPDM-rubber op produktieschaal te recyclen, door een continu mechanisch-chemisch reclaimingsproces voor EPDM-rubber afval te ontwikkelen, dat gebruik maakt van amines als devulkanisatiehulpmiddelen, voortbouwend op de uitkomst van een eerder project. Om de haalbaarheid van dit proces aan te tonen, moest een grote hoeveelheid variabelen worden onderzocht, zowel vanuit het oogpunt van de samenstelling van het rubber compound als ook ten behoeve van de procesontwikkeling. Dit onderzoek was een samenwerkingsproject met de Rijksuniversiteit Groningen, afdeling Chemische Technologie. Het onderzoek aldaar was gericht op de ontwikkeling van het continue reclaimingsproces. Het onderzoek beschreven in dit proefschrift richt zich op het materiaal en met name op de invloed van de samenstelling van het rubber compound op de efficiëntie van het proces en de kwaliteit van het verkregen produkt, optimalisatie van het devulkanisatiehulpmiddel en op de toepassing ervan. De toepassing spitste zich toe op het gebruik van het op deze wijze geregenereerde EPDM als grondstof voor dakbedekking. Dit is een materiaal dat in het algemeen een lage vernettingsgraad heeft om een optimale flexibiliteit van het materiaal te verkrijgen. De voorkeur ging uit naar deze toepassing, omdat een zekere mate van verlies van de vulkanisatie-efficiëntie getolereerd kon worden. De potentiële omvang van de markt is erg groot, en het verschaft een afzetmogelijkheid voor grote hoeveelheden gerecyclede rubber van verschillende oorsprong, zowel automobiel- als bouw- en constructieprofielen.

Hoofdstuk 1 geeft een introductie in het onderzoeksonderwerp door het probleem van rubberafval in het algemeen en EPDM produktieafval in het bijzonder te bespreken. Een beschrijving van EPDM-rubber en zijn eigenschappen en toepassingen wordt gegeven. Het doel van het onderzoek wordt uiteengezet en de indeling van het proefschrift wordt beschreven.

De verschillende manieren van rubberrecycling, zoals bijvoorbeeld hergebruik, materiaalrecycling, terugwinning van de oorsponkelijke chemische grondstoffen en energierecycling worden kort beschreven in **Hoofdstuk 2**. Het meest effectieve recyclingsprincipe is materiaalrecycling voor hergebruik van het verbeterde rubberafval in nieuwe rubberen artikelen. Recyclaat met de beste kwaliteit kan worden verkregen door reclaiming, de afbraak van het polymeer netwerk. Een uitgebreid overzicht van alle recyclingsmethoden in het algemeen en reclaimingsprocessen in het bijzonder wordt gegeven, met bijzondere aandacht voor het reclaimen van EPDM rubber. Voor een beter begrip van de processen, die plaatsvinden tijdens afbraak van een rubbernetwerk, wordt er een modelbeschrijving gegeven van zowel hoofdketen- als crosslinkbreuk.

Hoofdstuk 3 analyseert de crosslinkdichtheid en de zwavelketenlengte van de crosslinks, die gevormd worden tijdens de vulkanisatie van een met roet versterkt ENB-EPDM compound als functie van het gekozen vulkanisatiesysteem: conventioneel, semi-efficiënt, efficiënt and nitrosamine-vrij. Elk vulkanisatiesysteem resulteert in een specifieke crosslinkdichtheid en zwavelketenlengteverdeling: mono-, di- and polysulfidisch van aard. De trek-rek eigenschappen, scheursterkte en compression set van de gevulkaniseerde materialen blijken praktisch alleen af te hangen van de totale crosslink dichtheden, die weer afhankelijk zijn van het gekozen vulkanisatiesysteem en vulkanisatietijden. Alle verbanden vallen samen als ze uitgezet worden tegen de totale crosslinkdichtheid. Verrassend is het feit, dat de crosslinkverdeling: de verhoudingen mono- tot di- en polysulfidische crosslinks, slechts een geringe invloed heeft op deze eigenschappen. De verschillen in zwavelketenlengte als gevolg van het gekozen vulkanisatiesysteem blijken te klein voor EPDM om een significant effect op de vulkanisaateigenschappen te hebben.

De trends die gevonden worden voor alle mechanische eigenschappen komen precies overeen met de algemeen aanvaarde mastercurves van eigenschappen uitgezet tegen crosslinkdichtheid, behalve voor de rek bij breuk, welke een scherpe initiële stijging vertoont alvorens af te nemen met toenemende crosslinkdichtheid.

Hoofdstuk 4 geeft een overzicht van de invloed van temperatuur, tijd, wrijving en hexadecylamine-(HDA)-concentratie als devulkanisatiehulpmiddel op de reclaimingefficiëntie van verschillende, op EPDM gebaseerde, met zwavel gevulkaniseerde rubbers: conventioneel gevulkaniseerd, voornamelijk polysulfidisch van aard; en efficiënt gevulkaniseerd, vooral monosulfidisch. Het blijkt dat van de vier onderzochte variabele factoren temperatuur duidelijk de meeste invloed heeft op de reclaimingefficiëntie binnen het experimentele kader van dit onderzoek. HDA is geschikt als devulkanisatiehulpmiddel voor verschillende EPDM-compounds, mits er wel rekening gehouden wordt met de specifieke proces parametersettings voor elk verschillend compound..

Reclaim van conventioneel gevulkaniseerd EPDM, voornamelijk polysulfidisch van aard, vertoont de grootste afname in crosslinkdichtheid bij lagere reclaimtemperaturen en met toenemende HDA-concentratie. Na reclaimen aan de ondergrens van het experimenteel toegepaste temperatuurgebied: 225°C, is de concentratie van overgebleven di- en polysulfidische crosslinks hoger dan de concentratie monosulfidische bindingen, terwijl bij de hoogste temperatuur: 275°C, de concentratie monosulfidische crosslinks het grootst is. Bij het efficiënt gevulkaniseerde EPDM, met voornamelijk monosulfidische crosslinks, heeft HDA bij de lagere toegepaste temperaturen tot max. 225°C wederom een positief effect op de reclaimingefficiëntie. Bij hogere temperaturen neemt de crosslinkdichtheid toe met toenemende HDA-concentratie. Toepassing van een door Horikx voorgestelde bewerking van de experimentele gegevens laat zien dat conventioneel gevulkaniseerd EPDM grotendeels devulkaniseert middels crosslinkbreuk, in tegenstelling tot het efficiënt gevulkaniseerde materiaal, dat vooral afbreekt door hoofdketenbreuk.

Beide gereclaimde materialen kunnen tot 50 gewichtsprocent worden toegevoegd aan een maagdelijke masterbatch, met slechts een beperkte afname in eigenschappen na hervulkanisatie. Dit is een veel grotere hoeveelheid dan de max. 15 gewichtsprocenten gemalen rubber poeder, wat algemeen wordt beschouwd als de praktische limiet voor gerecyclede rubber

Hoofdstuk 5 laat zien dat de invloed van hexadecylamine (HDA), difenyldisulfide (DPDS) en o'o'-dibenzamidodifenyldisulfide (BAFD) als devulkanisatiehulpmiddelen op de reclaimingefficiëntie van twee types met roet versterkte EPDM-rubber: een conventioneel gevulkaniseerd, voornamelijk polysulfidisch, en een efficiënt gevulkaniseerd compound met voornamelijk monosulfidische crosslinks, significant verschillend is.

DPDS en BAFD blijken niet effectief ten aanzien van het afbreken van het conventioneel gevulkaniseerde rubbernetwerk, terwijl HDA hier een sterk positief effect op heeft. Toevoeging van DPDS en BAFD leidt niet tot reclaims die dusdanig zijn geplastificeerd dat acceptabele Mooney-viscositeiten worden verkregen, behalve bij de toepassing van de hoogste reclaimtemperaturen en de hoogste concentraties van deze devulkanisatiehulpmiddelen. HDA werkt wel bij alle temperaturen en zelfs bij lage doseringen. In alle gevallen kan tot 50 gewichtsprocenten reclaim worden toegevoegd aan nieuw, maagdelijk EPDM-masterbatch, zonder dat de eigenschappen van de gehervulkaniseerde compounds significant worden beïnvloed.

De devulkanisatiehulpmiddelen werken verschillend wanneer ze worden gebruikt voor het reclaimen van een grotendeels monosulfidisch compound. Vanwege de initiële lage crosslinkdichtheid van het compound kan deze gemakkelijk geplastificeerd worden, zelfs zonder toevoeging van devulkanisatiehulpmiddelen en bij de laagst toegepaste temperatuur van 200°C. DPDS en BAFD resulteren in een grotere mate van plastificering van het compound dan HDA. De reclaims verkregen met zowel HDA als BAFD geven goede mechanische eigenschappen, wanneer ze worden toegevoegd aan een nieuwe masterbatch: sommige eigenschappen worden zelfs beter door toevoeging van deze reclaims. Daartegenover laat het met DPDS behandelde materiaal zich moeilijk hervulkaniseren en resulteert toevoeging van dit materiaal aan een nieuw, maagdelijk EPDM-masterbatch in een afname van de materiaal eigenschappen.

De waarnemingen bevestigen de verschillende reclaiming mechanismen van de twee types EPDM: het voornamelijk reclaimen/devulkaniseren van het conventioneel gevulkaniseerde compound, versus het afpellen van geplastificeerde lagen van het efficiënt gevulkaniseerde compound. Deze verschillen hoeven daarentegen niet te resulteren in slechte eigenschappen van de gehervulkaniseerde blends van deze reclaims met nieuw compound.

Geconcludeerd kan worden dat HDA het meest universeel toepasbaar is als devulkanisatiehulpmiddel, omdat het voor beide types EPDM resulteert in goed geplastificeerde materialen en goede mechanische eigenschappen van de gehervulkaniseerde blends met toevoeging tot 50 gewichtsprocent van deze reclaims. BAFD kan een goed alternatief zijn, hoewel het resulteert in minder verwerkbare reclaims in het geval van het conventioneel gevulkaniseerde compound. DPDS is geen optie, omdat het reclaim op basis van het efficiënt gevulkaniseerde materiaal niet geschikt is voor hervulkanisatie.

Hoofdstuk 6 rapporteert het reclaimen van met zwavel gevulkaniseerde bouwprofielen in een co-roterende dubbelschroefs-extruder met HDA als devulkanisatiehulpmiddel. Dit reclaim wordt gemengd met toenemende hoeveelheden van een nieuwe dakbedekkings-masterbatch en gevulkaniseerd bij temperaturen resulterend in reversievrije vulkanisatie. Dakbedekking is gekozen voor deze toepassing, omdat dit materiaal een beperkt verlies in vulkanisatie-efficiëntie kan verdragen vanwege de lage mate van vulkanisatie welke vereist wordt.

De trends in vulkanisatiekarakteristieken laten zien dat toevoeging van toenemende hoeveelheden reclaim aan de blends correspondeert met een lagere reversievrije vulkanisatietemperatuur en lagere maximale torquewaarden, terwijl de vulkanisatiesnelheid toeneemt. De onoplosbare fraktie en crosslinkdichtheid nemen beide af, terwijl de verhouding van mono- tot di- plus polysulfidische crosslinks toeneemt met hogere reclaimconcentraties. Het blijkt, dat reclaim de elasticiteit van de ongevulkaniseerde compounds vergroot, terwijl het de elasticiteit van de gevulkaniseerde materialen verlaagt. Een morfologiestudie van de blends met SEM-EDX, om de dispersie van de reclaim in de matrix van maagdelijk rubber te kunnen waarnemen, laat zien dat zelfs toevoeging van grote hoeveelheden gereclaimd materiaal resulteert in homogene en gladde compounds.

Betreffende de mechanische eigenschappen nemen treksterkte, modulus bij 300% rek en hardheid af, terwijl de rek bij breuk, scheursterkte en compression set bij 70°C stijgen bij toenemende hoeveelheid reclaim. Ongeacht de blend-verhouding voldoen alle mechanische eigenschappen aan de strengste Europese UEAtc specificaties voor EPDM-dakbedekking.

Een verouderingsonderzoek is uitgevoerd om de invloed van reclaim op de lange-termijn prestaties van het materiaal in kaart te brengen en om te beoordelen of de compounds geschikt zijn voor dakbedekking. Toenemende hoeveelheden reclaim verbeteren de verouderingsweerstand en verlengen de tijd voordat een kritische waarde van 250% rek bij breuk wordt bereikt, vereist voor een langdurig gebruik als EPDM-dakbedekking.

Hoofdstuk 7 gaat over het opschalen van het continue reclaimingsproces voor met roet versterkte EPDM-rubber, van laboratorium- tot produktieschaal. Hexadecylamine is gebruikt als devulkanisatiehulpmiddel en reclaiming uitgevoerd in een combinatie van een dubbelschroefs kneedextruder met een enkelschroefs transportextruder. Dit proces resulteerde in reclaims met een hoge kwaliteit, die tot 50 gewichtsprocenten kunnen worden toegevoegd aan een maagdelijke EPDM dakbedekkingsmasterbatch, met slechts een beperkte afname van de materiaaleigenschappen van de hervulkanisaten als gevolg.

Grof gemalen EPDM-rubber produktieafval met een deeltjesgrootte tussen 20 en 40 mm resulteert in een reclaim zonder significante afname of zelfs met een toename van de crosslinkdichtheid van de niet-oplosbare fraktie ten opzichte van de feedstock, terwijl er een aanzienlijke hoeveelheid oplosbaar polymeermateriaal wordt gegenereerd. Reclaiming van EPDM-rubber met een initiële deeltjesgrootte tussen de 0.8 en 2.5 mm resulteert in reclaims met een crosslinkdichtheid afname van 66% van het onoplosbare deel ten opzichte van de feedstock, terwijl er weinig oplosbaar polymeermateriaal wordt verkregen.

De gehervulkaniseerde pure reclaims hebben betere eigenschappen wanneer voor het reclaimingsproces gebruik wordt gemaakt van materiaal met de kleinere intiële deeltjesgrootte. In blends met tot 50 gewichtsprocenten maagdelijk compound heeft de intiële deeltjesgrootte slechts een beperkte invloed op de uiteindelijke materiaaleigenschappen. Alle reclaims kunnen tot tenminste 40 gewichtsprocenten worden toegevoegd aan een maagdelijke EPDM-dakbedekkingsmasterbatch met een slechts een geringe afname van de eigenschappen. Deze blends voldoen nog steeds aan de UEAtc-eisen voor EPDM-dakbedekking.

Verder optimalisen van het proces is noodzakelijk om de temperatuur van 330°C, die gemeten wordt na reclaimen in de dubbelschroefs extruder, terug te brengen tot meer aanvaardbare temperaturen >275°C. Deze hoge temperatuur wordt verantwoordelijk gehouden voor de harde deeltjes in de reclaim, hetgeen waarschijnlijk verbrand materiaal is bij deze hoge temperatuur.

AANBEVELINGEN VOOR VERDER ONDERZOEK

Het werk beschreven in dit proefschrift heeft aangetoond, dat hexadecylamine zeer geschikt is als devulkanisatiehulpmiddel voor het reclaimen van met zwavel gevulkaniseerde EPDM-rubber. Afhankelijk van de zwavelketenlengte van de crosslinks in de rubbernetwerken heeft hexadecylamine een verschillende invloed op de reclaimingefficiëntie, maar in alle gevallen worden er reclaims verkregen, die zeer geschikt zijn voor hervulkanisatie en die tot ongeveer 50 gewichtsprocenten als grondstof aan maagdelijke compounds kunnen worden toegevoegd, zonder dat de materiaaleigenschappen wezenlijk achteruitgaan.

Er is aangetoond in Hoofdstukken 4 en 7, dat de deeltjesgrootte van het gevulkaniseerde rubberafval de efficiëntie van de afbraak van het polymeernetwerk en de materiaaleigenschappen van de op reclaim gebaseerde blends beïnvloedt. Tevens beïnvloedt de deeltjesgrootte de verwerkbaarheid van het originele gevulkaniseerde materiaal en de reclaim in het produktieproces, wanneer reclaiming op commerciële basis wordt toegepast. Er wordt daarom aanbevolen om de deeltjesgrootte te optimaliseren ten opzichte van de materiaal eigenschappen van de reclaims en de verwerkbaarheid voor het reclaimingsproces.

De reclaims presteren erg goed wanneer ze worden gehervulkaniseerd door middel van compressiepersen. Autoklaafvulkanisatie resulteert daarentegen in de aanwezigheid van harde deeltjes in de compounds en die kunnen leiden tot lekkage in de dakbedekking. Deze harde deeltjes worden hoogst waarschijnlijk veroorzaakt door verbranding van het rubber vanwege de hoge temperatuur van 330°C, welke wordt gegenereerd tijdens het reclaimingsproces. Optimalisatie van de schroefopbouw is vereist om minder wrijving in de dubbelschroefsextruder te krijgen, maar wel nog steeds verwerkbare reclaims te produceren.

Hoofdstuk 5 heeft aangetoond dat BAFD een groot plasticerend effect op efficiënt gevulkaniseerd EPDM-rubber heeft. Het kan darrom interessant om een mengsel van BAFD en HDA te proberen als devulkanisatiehulpmiddelen. BAFD voor het plastificerende effect bij relatief lage temperaturen en HDA voor het afbreken van de crosslinks op zo’n manier dat de verkregen crosslinkpunten in staat zijn om opnieuw crosslinks te vormen tijdens hervulkanisatie.

Samenvattend kan geconcludeerd worden, dat wanneer de procescondities geoptimaliseerd kunnen worden, er een geschikte methode is gevonden voor het reclaimen van verschillende types EPDM-rubber. Wanneer het ook nog zeker is dat de totale kosten voor het produceren van een kilogram EPDM-rubber reclaim niet hoger zijn dan die van een kilogram nieuw rubber compound, dan lost dit niet alleen het probleem van het rubberafval op, maar verlaagt het ook de kosten voor de rubberverwerkers: reclaim kan gebruikt worden als grondstof en verlaagt het energieverbruik wat nodig is voor het produceren van nieuwe compounds.

Symbols and Abbreviations

ASTM	American society for testing and materials
B	Constant factor
BR	Butadiene rubber
°C	Degrees Celsius
CaO	Calcium-oxide
CBS	N-cyclohexyl-2-benzothiazole-sulfenamide
CCF	Central composite face-centered
CH_3I	Methyliodide
cm	Centimeter
cm^3	Cubic centimeter
CONV	Conventional vulcanizing
C–S–C	Monosulfidic crosslink
$C–S_2–C$	Disulfidic crosslink
$C–S_x–C$	Polysulfidic crosslink
CR	Chlorprene rubber
CUR	Amount of curatives
d	Thickness of the test specimen
DOE	Design of experiments
DIN	Deutsches Institut für Normung
DPDS	Diphenyldisulfide
DPTH	Dipentamethylene-thiuramhexasulfide
DPTT	Dipentamethylene-thiuramtetrasulfide
E	Activation energy
EN	Norme Européenne
ENB	5-ethylidene-2-norbornene
EPDM	Ethylene propylene diene rubber
EU	European Union
EV	Efficient vulcanizing
F_{max}	Maximum force at which the test specimen breaks
$F_x(t)$	A function which describes the stage the reaction has reached
FEF	Fast extrusion furnace
g	Gelfraction
g	Gram
G''	Viscous or loss modulus
G'	Elastic or storage modulus
GPC	Gas permeation chromatography
h_0	Initial thickness of the sample
h_1	Thickness of the sample during compression
h_2	Thickness of the sample after recovery for a specified time

HAF	High abrasion furnace
HDA	Hexadecylamine
hr	Hour
hrs	Hours
Hz	Hertz
IR	Isoprene rubber, synthetic
IIR	Halogenated butyl rubber
ISO	International Organization for Standardization
K	Constant for a given filler
kg	Kilogram
kg/hr	Kilogram per hour
kN	KiloNewton
kN/m	KiloNewton per meter
k_p	Scission rate constant for random scission
k_q	Scission rate constant for crosslink scission
K(T)	Temperature dependent reaction rate
l	Liter
$LiAlH_4$	Lithium aluminium hydride
m	Meter
m_r	mass of the rubber network
m_s	Weight of solvent in the sample at equilibrium swelling
M_{100}	Modulus at 100% elongation
M_{300}	Modulus at 300% elongation
M_C	Average molecular weight between crosslinks
$\overline{M}_{gel}$	Number average molecular weight of the primary molecule incorporated in the gel
MBT	2-Mercaptobenzothiazole
MBTS	Dimercaptobenzothiazole-disulfide
Min	Minute
ML(1+4)	Mooney viscosity after 1 minute of preheating and 4 minutes of measuring, measured with a large rotor
MLR	Multiple linear regression
mm	Millimeter
$\overline{M}_n$	Number average molecular weight of the original polymer
MPa	Megapascal
MT	Medium thermal
MU	Mooney unit
$\overline{M}_w$	Weight average molecular size of the original polymer
MW	Megawatt
MW	Molecular weight
N	Total number of primary molecules in the polymer
N_{gel}	Number of primary molecules in the network
NBR	Butadiene acrylonitrile rubber
NR	Natural rubber
NS	Nitrosamine-safe vulcanizing
N_x	Number of polymer molecules with x monomer units
OODBDPDS	o'o'-Dibenzamidodiphenyldisulfide
p	Probability of breaking a given bond linking two molecules in the infinite chain, constituting the crosslinked network
phr	Parts per hundred rubber

Ph_3P	Triphenylphosphine
q	Probability of creating a bond or crosslink between two polymers
Q^2	Goodness of prediction
R	Gas constant
R^2	Goodness of fit
$R^2_{adj.}$	R_2 adjusted for the amount of variables
RPA	Rubber Process Analyzer
RSR’	Monosulfidic crosslink
RSSR’	Disulfidic crosslink
RSSSR’	Trisulfidic crosslink
RSS_xSR'	Polysulfidic crosslink
rpm	Rounds per minute
s	Solfraction
S	Sulfur
s_i	Soluble fraction of the untreated vulcanizate
s_f	Soluble fraction of the reclaimed vulcanizate
SBR	Styrene-butadiene rubber
SEM-EDX	Scanning electron microscope coupled to an energy dispersive x-ray spectrometer
SEV	Semi-efficient vulcanizing
SRF	Semi-reinforcing furnace
SSSE	Solid-state shear extrusion
t	Reaction time
t_{02}	Scorch time
t_{90}	Optimum curing time
t_{xx}	Curing time at the percentages of maximum minus minimum torque
T	Absolute temperature
$\tan \delta$	Loss angle
TBzTD	Tetrabenzylthiuram-disulfide
THF	Tetrahydrofuran
TMTD	Tetramethylthiuram-disulfide
UEAtc	Union Européenne pour l’agrément technique dans la construction
USA	United States of America
vs.	Versus
w	Molecular weight of a monomer in the polymer chain
x	Number of monomers per primary polymer molecule
ZBEC	Zinc-dibenzyldithiocarbamate
ZDBP	Zinc-dibutyldithiophosphate
ZDMC	Zinc-dimethyldithiocarbamate
ZnO	Zinc-oxide
v_r	Polymer volume fraction of the swollen sample
V_s	Solvent molar volume
W_a	Weight of specimen after extraction
W_b	Weight of specimen before extraction
wt%	Weight percent
ν_0	Number of elastically effective polymer network chains including the sol fraction
$\nu_{0,\,gel}$	Number of primary molecules in the network
ν_e	Crosslink density
ν_i	Crosslink density of the untreated vulcanizate

ν_f	Crosslink density of the reclaimed 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
ρ_r	Density of rubber
ρ_s	Density of solvent
χ	Flory-Huggins interaction parameter
$\nu_{apparent}$	Measured chemical crosslink density
ν_{actual}	Actual chemical crosslink density
Φ	Volume fraction of filler in the vulcanizate
μm	Micrometer
$\sum xN_x$	Total number of monomers included in all polymers within the sample
δ	Crosslinking coefficient

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Curriculum Vitae

Kuno Alphonsus Johannes Dijkhuis was born in Hengelo, the Netherlands on November 7th, 1978. He studied Chemical Technology at the University of Twente and did his undergraduate research in 2003 in the Biomedical group of Prof. Dr. Feijen on the subject: "Gamma-Radiation Induced Crosslinking of PTMC". He received his degree in September 2003.

In September 2003 he started his Ph. D. in the Department of Elastomer Technology and Engineering (the former Rubber Technology group) under the supervision of Prof. Dr. Ir. J.W.M. Noordermeer at the University of Twente on the topic "Devulcanization of EPDM-Rubber Vulcanizates with Amine Devulcanization Agents".

The author is married to Chantal and has two kids: a son named Mika and a daughter called Jasmijn.

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Kuno