

University of Groningen

**Recycling of Passenger Car Tyre Rubber – Devulcanization of
Carbon Black Filled Styrene Butadiene Rubber**

Master Thesis

Chemical Engineering

By:

**Frank van Mastrigt
1732021**

Supervisors:

**Prof. dr. F. Picchioni
Prof. dr. A.A. Broekhuis
Ir. C. Herder**

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Abstract

The concept of sustainability is receiving a lot of attention lately. An important part of sustainability is the recycling or reuse of products at the end of their useful life. Due to their three-dimensional structure, recycling of rubber is very difficult, and recycled rubber tends to end up in low-value products. In this research the aim is to recycle rubber 'cradle-to-cradle'.

A chemical devulcanization method for devulcanization of carbon black (CB) filled styrene butadiene rubber (SBR) is described. Based on devulcanization results, an empirical model investigating the effect of process parameters during devulcanization with diphenyl disulphide (DPDS) in a batch reactor was realized. Devulcanization temperature, time, and concentration devulcanization agent were varied and the sol fraction and crosslink density of the devulcanized rubber were studied. A concentration of 15 mmol/100g compound DA was found to be effective in combination with a temperature up to 270°C, in terms of sol fraction and crosslink density of the devulcanizates. CB was found to make the devulcanization of filled SBR more challenging than gum SBR, as this filler is expected to act as radical acceptor and supplier.

The devulcanized rubber was subsequently subjected to a revulcanization process. In this process, devulcanized rubber was blended with virgin rubber and curatives and subjected to heat and pressure in order to set. Revulcanizates containing 40 – 60% devulcanized filled SBR were prepared. The devulcanization temperature in the range of 220 – 300°C was not found to have a significant effect on the tensile strength and shore A hardness of revulcanizates. Elongation at break of revulcanizates was found to be higher compared to vulcanized fresh SBR, however, samples containing rubber devulcanized at 300°C displayed a lower increase in elongation at break than samples devulcanized at 220 – 270°C. With the method described in this work, revulcanizates containing 40% devulcanized rubber were produced, which retained 94% of tensile strength and 132% of elongation at break compared to a reference SBR sample.

Chapter 1. General introduction

In this chapter, a general introduction on tyres and rubber is given. Furthermore, the issue with discarded tyres that needs to be addressed is described. Hereafter, the current status of rubber devulcanization and to some degree energy recovery is described, based on available scientific literature.

1. World energy consumption

From 1965 to 2011, world energy consumption has increased by more than threefold [1]. On top of that, world energy consumption is expected to rise by 39% from 2010 to 2030 [2]. Resulting from environmental concerns and depletion of fossil fuel reserves, the topic of sustainability has become increasingly important [3].

2. Tyres

Worldwide, 1.4 billion passenger car tyres are produced annually [4]. Approximately 70% of the world rubber production is used for the production of tyres [5]. Passenger car tyres make up a relatively large share of the total tyre production, namely 60% of total tyres produced [6].

According to the Rubber Manufacturers Association (RMA), Rubber tyres consist mainly of natural rubber, synthetic rubber, carbon black, steel, fabric, fillers, accelerators and anti-ozonants [7]. A regular passenger car tyre (e.g. Goodyear) weights approximately 10 kg and consists of 30 kinds of synthetic rubber; 8 kinds of natural rubber; 8 kinds of carbon black; steel cord; polyester and nylon fibers; steel bead wire, 40 different chemicals, waxes, oils, pigments, silica's and clays [8]. The most commonly used rubber in passenger car tyres is styrene butadiene rubber (SBR) [9]. This rubber typically consist of a monomer ratio of styrene:butadiene of 25:75 [10].

Carbon black is incorporated into the rubber as reinforcing filler. It can increase the strength of vulcanized rubber by more than tenfold [11]. This increase in strength is attributed to both chemical and physical interaction between the rubber particles and carbon black particles [12] [13] [14]. Incorporation of carbon black furthermore leads to the typical black colour of tyres.

3. Rubber

Elastomers can undergo elastic deformation under force, while returning to their original shape after removal of the force. Elastomers are built from long chains, with a flexible backbone. Elastomers are built from long chains, with a flexible backbone. The degree of flexibility is highly influenced by the attraction between multiple chains. In order to improve long-term stability of the elastomer matrix, crosslinks are applied between distinct chains. After crosslinking, elastomers are generally referred to as rubbers [15]. The mouldable elastomers display thermosetting behaviour after crosslinking. Due to the connections between the chains the molecular weight of the molecules increases, leading to an increase in boiling point and insolubility of the molecules. When heating the rubber, decomposition occurs before the melting point is reached, making it impossible to re-melt the polymer without additional steps [16].

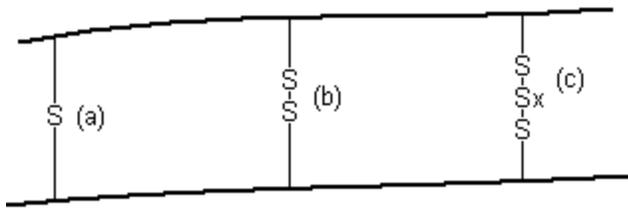


Figure 1. Three-dimensional crosslinked rubber structure. (a): Monosulphidic bond, (b): Disulphidic bond, (c): Polysulphidic bond.

A schematic overview of a rubber structure is displayed in Figure 1. Bond energy increases from sulphur – sulphur bonds (270 kJ/mol), followed by carbon – sulphur bonds (310 kJ/mol), up to 370 kJ/mol for carbon – carbon bonds [17]. Based on these values, unselective breakage of the bonds is expected when applying energy to the material, leading to main chain scission and degradation of material properties. The elasticity of the bonds, however, has a pronounced effect on the selectivity of breakage. The elasticity constant for sulphur – sulphur bonds is approximately 30 times smaller compared to carbon – carbon bonds [17], indicating significantly higher elasticity for the former. Application of shear results in the majority of the bonds in the rubber chains to become fully elongated. As a result of their lower elastic constant, the sulphur – sulphur bonds become more extended compared to carbon – carbon bonds, rendering them more prone to scission.

Worldwide rubber production was 24 million tonnes in 2010, consisting of 10 million tonnes natural rubber and 14 million tonnes synthetic rubber [18]. The largest share of synthetic rubber consists of SBR. The chemical structure of SBR is shown in Figure 2. The ratio between styrene and butadiene is typically 1:3 [10]. Applications for SBR range from tyres to shoe heels, chewing gum, gaskets, and even coated paper [19] [20] [21] [22] [23]. Annual production of SBR equals 6 million tonnes, corresponding with circa 40% of the synthetic rubber production [24].

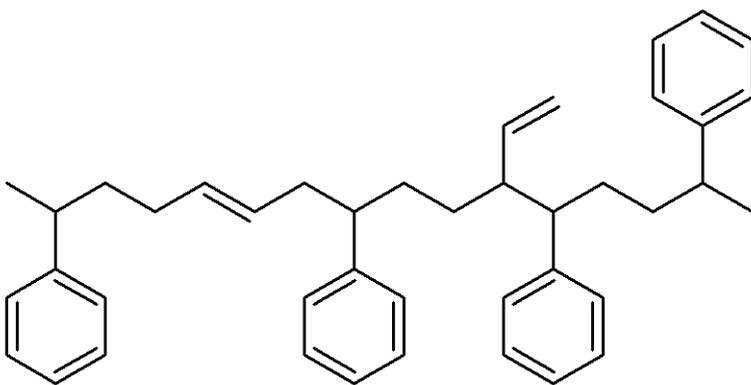


Figure 2. Chemical structure of Styrene butadiene rubber (SBR) (fragment)

4. Problem statement

After a relatively short life, tyres are discarded and are subjected to retreading, energy recovery, material recycling, back-to-feedstock processes, or end up in landfills. The importance of recycling of tyres has become apparent in the last years [25]. Contrarily to thermoplastic materials, which can be re-melted and remoulded into new products, the three-dimensional crosslinked network of vulcanized rubbers requires a different approach. Recycling, however, is difficult as a result of the structure of the material. Due to their critical application, tyres require certain properties. In particular photochemical resistance, non-biodegradability, chemical resistance, and thermal resistance are important factors. These properties make recycling of tyres more challenging.

Annually, more than 100 million tonnes of polymeric materials are discarded. Rubber is one of the three main contributors to this polymeric waste, whereby the largest share of rubber waste consists of rubber tyres, namely 290 million in 2003 in the U.S. only [26]. Currently, approximately 40% of waste tyres in the European Union are incinerated, 17% exported or reused, 9% recycled, and circa 20% finds a different application [27]. Discarded rubber products tend to accumulate at disposal sites, leading to two problems, environmental pollution and conservation of energy [28].

First, discarded tyres may leak additives of low molecular weight from the surface of the tyre to the environment. These additives might influence the local ecosystem as they are not eco-friendly [29]. On top of that, piles of tyres facilitate the breeding of for instance mosquitos, due to their water retaining properties. Furthermore piles of tyres catching fire are difficult to extinguish and can burn for extended periods of time. These fires lead to the release of hazardous thick black smoke and an oily residue [30].

Second, the feedstock for the rubber industry consists for a large share of petroleum originated resources. In countries where natural rubber resources are scarce, more than 70 wt% of the feedstock for rubbers originates from the petroleum industry [28]. Due to increasing concerns regarding petroleum based feedstocks, recycling of rubber has gaining attention. Moreover, the waste rubber contains a significant amount of energy, namely 3.3×10^4 kJ/kg, which is comparable to the heat of combustion of coal [28].

In order to prevent tyres from being discarded and dumped in outdoor areas, recycling of the tyres is required. Since rubber is crosslinked into a three dimensional network, the material cannot be remoulded and reused readily, or be dissolved in organic solvents [16]. In order to recycle the rubber, the polymer network has to be broken down into pieces of lower molecular weight, which can be obtained by cleavage of carbon – carbon, carbon – sulphur or sulphur – sulphur bonds. The products of this cleavage, however, can be different from the starting elastomer, especially when carbon – carbon bonds are broken. It is therefore desirable to selectively break sulphur – sulphur and carbon – sulphur bonds, making recycling of rubbers a difficult process.

Recycling of rubber obtained from tyres is especially challenging, due to the complication of the presence of several types of rubbers originating from different types of tyres. On top of that the rubber composition differs among the several parts of the tyre. Recycling of this blend of rubbers is considered therefore more difficult than single rubbers [31].

Several techniques can already be applied in recycling of tyres, however, the degree to which the rubber can be recycled and the economic viability highly differs. Grinding of the rubber at elevated temperatures for instance leads to some devulcanization of the rubber. However, the majority of bonds broken are expected to be from the carbon – carbon type [31]. Incorporation of this ground rubber tyre into certain parts of newly produced tyres is possible up to a certain extent, typically 5 – 10 wt%, since physical properties of the rubber deteriorate at higher recycled rubber content [29]. The recycled rubber functions as a non-reinforcing filler in the rubber matrix [29]. In this research a model compound is required to study the effects of a devulcanization process on the rubber. SBR is used as this is a more strenuous component of the rubber blend and relatively limited research is available on this topic [32].

5. Devulcanization

In order to recycle the rubber and process it into new products, devulcanization of the rubber network is required. This process, in which it is desirable to obtain a material with the mechanical properties of the unvulcanized virgin rubber, is named devulcanization. The purpose of devulcaning rubber is obtaining a rubber material with properties that make it suitable for revulcanization (with virgin material). Several opportunities are present for devulcanization, however, they can be divided into three categories: physical devulcanization methods, chemical devulcanization methods, and biological devulcanization methods.

5.1 Physical devulcanization

In physical devulcanization external energy is applied to the rubber network in order to break certain bonds in the three dimensional structure. Due to the breakage of bonds, the molecular weight of the material decreases, leading to the formation of material with properties better comparable to the virgin rubber. By controlling process parameters, sulphur-sulphur bonds can be broken with certain selectivity. Breakage of the latter has the advantage the material can be incorporated into new rubber products while acting as reinforcing filler. Contrarily, incorporation of non-treated ground rubber particles is possible up to a limited extend, since the particles act only as non-reinforcing filler material [29].

5.1.1 (Thermo-)mechanical

In mechanical processes the energy required to break bonds is obtained by mechanical shear and high temperature. This shear is obtained by rotating mixer equipment inside a (heated) static shell. Due to the mixing equipment the majority of the bonds in the rubber chains become fully elongated. As a result of their lower elastic constant the sulphur – sulphur bonds become more extended compared to carbon – carbon bonds, rendering the former more prone for scission.

E. Bilgili et al. [33] investigated the mechanical devulcanization of filled natural rubber. The rubber was devulcanized in a single screw extruder. Samples extruded at 135°C were subsequently mixed with sulphur in a Brabender mixer and thereafter compression molded for 15 min. The mechanical properties of the resulting slabs were compared to the original slabs. The revulcanized material maintained circa 90% of the crosslink density of the virgin material, 81% of the elongation at break and 35% of the tensile strength. This significant decrease in tensile strength makes the material not suitable for high-end applications, however, the material could be applied for non-demanding products as tiles, pads and flooring underlay.

Fukumori et al. [34] researched continuous devulcanization of NR, SBR and IIR in an extruder. Actual process conditions for the devulcanization process are not mentioned, however, the results of the process are available. Up to 30 wt% of devulcanized rubber was incorporated into virgin rubber and subsequently revulcanized. Incorporation of 30 wt% devulcanized NR generated in the manufacturing process into virgin NR resulted in retention of more than 90% of the tensile strength and elongation at break. Comparable results were obtained by incorporating devulcanized SBR generated in the manufacturing process into virgin SBR. Isobutylene Isoprene Rubber obtained from the manufacturing process was devulcanized and subsequently revulcanized without incorporation of virgin rubber. Retention of mechanical properties was at least 85% for tensile strength and break at elongation. Furthermore experiments were conducted with NR based tread rubber obtained from truck tyres and SBR based rubber obtained from passenger car tyres. Incorporating 30 wt% NR (truck tyre) into virgin NR led to retention of at least 80% of the mechanical properties. Comparable results were identified with incorporating SBR obtained from scrap tyres in virgin SBR. Finally, NR based tread rubber obtained from truck tyres was devulcanized and incorporated into new truck tyres. Truck tyres were produced with incorporation of 10 wt% of the devulcanized rubber in the tread and subsequently subjected to a road test for 200.000 km. Tread wear behaviour was found to be almost equal to the regular tyre without incorporated devulcanized rubber.

Jana et al. [35] investigated the devulcanization of unfilled natural rubber in presence of thiol acid, however, also experiments were conducted without presence of a chemical agent. Revulcanization of the devulcanized NR resulted in retention of 15% of the tensile strength, 45% of the elongation at break, 98% of the hardness and 43% of the crosslink density. Incorporation of the chemical agent, however, led to retention of more than 85% of the mechanical properties.

5.1.2 Cryomechanical

In cryomechanical treatment, rubber is cooled to below its glass point and subsequently pulverized, typically with a hammer mill [36]. The rubber mixture is generally cooled with liquid nitrogen and therefore nitrogen gas is a byproduct of the treatment. Due to the low temperature, the rubber compound shatters into small particles. Particle sizes obtained are typically 0.15 mm, compared to >0.40 mm for samples obtained from grinding at ambient temperature. Cryogenic grinding offers some additional advantages over ambient grinding; separation of non-rubbery (e.g. metal) parts from the rubber is obtained easily by screening and higher conversion is obtained compared to ambient grinding using the same size equipment [36]. However, the process is not applied extensively, mainly caused by two disadvantages; on the one hand the process is relatively expensive due to the consumption of liquid nitrogen. On the other hand the obtained rubber powder does not have a form suitable for reuse in rubber products and ends up mainly in asphalt [36].

Another route for obtaining small ground rubber particles is applying the 'Gould method' [37]. While this method is actually no cryomechanical process, it is focused on producing particles with a very small size and therefore described in this section. The process is suitable for obtaining particles with a size that is generally less than 0.02 mm. The method consists of milling the rubber with a fatty acid (oleic acid) for ten minutes. Subsequently, solid alkali (sodium hydroxide) is added and the mixture is milled for an additional ten minutes at 60°C. The compound along with water is placed in a hopper and

subsequently milled with a disc mill. The obtained rubber crumb is washed with water, separated from the water by a centrifugal dryer and finally dried in a vacuum oven. Ground passenger car tyre rubber treated by the described process was incorporated into virgin SBR and revulcanized. In total 33.4 wt% recycled rubber was incorporated into the samples. An overview of the results, in comparison with other available processes is shown in Table 1. Tensile strength of the blend decreased with incorporation of the recycled rubber, however, this effect was less pronounced for the ‘Gould method’. Nearly 79% of the tensile strength was retained (sample 4), compared to 65% for the non-treated sample (sample 2). Furthermore, 84% of the elongation at break, compared to 69% for the non-treated sample was maintained. The devulcanized sample (sample 3) did perform inferior compared to the sample treated with the ‘Gould method’. However, the devulcanization procedure was not described, rendering the comparison meaningless.

Table 1. Comparison between ‘Gould method’ and other processes (adapted from [37])

Sample	1 (reference)	2	3	4
Type of additive	-	Tyre crumb (250 μm)	Tyre crumb devulcanizate ¹	Micronized crumb
Tensile strength (MN/m²)	23.7	15.5	15.9	18.7
Elongation at break (%)	580	400	520	490
Modulus at 100% extension	1.5	1.7	1.6	1.6
Modulus at 300% extension	8.9	9.7	7.2	8.6
Hardness (IRHD)	63	63	62	61
Taber abrasion loss (g/1000 cycles)	0.1345	0.2202	0.2459	0.1454

Furthermore, ground tyre rubber was treated according to the ‘Gould method’, however, in this case tyre crumb with a size of 0.595 mm was milled and subsequently swollen in THF. The compound was hereafter milled at a disc mill, followed by the addition of water. The product was filtered and subsequently dried in a vacuum oven. The recycled rubber was subsequently revulcanized and compared with the virgin material. An overview of the results in displayed in Table 2. Mechanical properties deteriorated, however, the material displayed sufficient retention of properties to be used for the production of non-critical products [36]. However, due to the high liquid nitrogen consumption, the process is not economically viable for tyre rubber [38].

¹ Devulcanization method not described in the patent

Table 2. Comparison between revulcanized rubber obtained from 'Gould method' versus virgin rubber (adapted from [37])

Sample	1 (reference)	2
Type of additive	-	Micronized crumb
Tensile strength (MN/m ²)	23.7	13.2
Elongation at break (%)	580	300
Modulus at 100% extension	1.5	2.3
Modulus at 300% extension	8.9	12.4
Hardness (IRHD)	63	64
Taber abrasion loss (g/1000 cycles)	0.1345	0.45

5.1.3 Microwave

In microwave devulcanization the heat required to break crosslinks in the rubber is obtained from microwaves. By controlling the intensity and frequency of the waves, selective breakage of the crosslinks is attempted to be obtained, while leaving the main chain unaffected. In microwave devulcanization, polar components are required to absorb the microwave radiation. Therefore the rubber along with incorporated chemicals should be sufficiently polar to generate the required amount of heat necessary for the devulcanization [38]. While the rubber components in passenger car tyres are of the non-polar type, carbon black is present in the blend in high amounts. This carbon black is capable of absorbing the microwave energy and subsequently heating up the adjacent rubber molecules [39]. Advantages of microwave devulcanization are the possibility for treating a high amount of rubber at the same time, easy adaptations of process parameters in order to process a different type of rubber, short treatment times (typically up to five minutes), and the possibility for continuous operation [29] [40].

Zanchet et al. [40] conducted research on microwave devulcanization of filled SBR extruded profile scraps. The scraps were grinded and thereafter devulcanized for 2 – 4 minutes in a microwave at 900W while stirring at 40 rpm. Samples treated for 3 and 4 minutes were revulcanized and their mechanical properties were compared with a control sample. The results are displayed in Table 3. Samples devulcanized for three minutes retained 25% of the tensile strength and 47% of the elongation at break. This deterioration of the mechanical properties is mainly attributed to degradation of the main chain [40]. Even though properties of the revulcanized material improved significantly after postcurement at 70°C for 170h, the rubber obtained in this research is only suitable to be applied in non-critical products. Incorporation of devulcanized rubber into new rubber, however, was not researched.

Table 3. Comparison between revulcanized SBR obtained by microwave devulcanization versus virgin rubber (adapted from [40])

Sample	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)	Tear strength (kN/m)	Compression set (%)	Crosslink density (mol/cm ³)
Control	82±2	10.0±2.2	184.0±24.3	24.0±2.75	7.3±1.3	(1.05±0.01) ×10 ⁻⁴
dSBR-r (3 min)	62±4	2.5±0.5	85.8±9.7	9.8±0.91	7.9±0.7	(9.10±0.01) ×10 ⁻⁵
dSBR-r (4 min)	61±3	1.5±0.2	74.8±6.0	5.9±0.55	8.9±0.5	(2.43±0.01) ×10 ⁻⁵

Wicks et al. [41] described a method for microwave devulcanization of truck tyre treads. Rubber particles (40 mesh) were devulcanized for 4 or 8 minutes at temperatures ranging from 360 – 380 °C. The obtained devulcanized rubber was subsequently incorporated into new tyre rubber (addition of 20 wt% recycled rubber). An overview of the results is displayed in Table 4. As shown, the mechanical properties of the microwave devulcanized rubber are slightly better than the untreated crumb. Up to 80% of the tensile strength was retained by incorporating 20 wt% microwave devulcanized rubber, versus 76% for untreated crumb. Elongation at break was not altered significantly by incorporation of either untreated crumb or microwave devulcanized crumb. According to the authors, it is possible to use 100% of the microwave devulcanized rubber for the production of non-critical products such as belts, hoses or shoe treads. Furthermore, the treated rubber can be incorporated in moderate amounts into tyre sidewall formulations.

Table 4. Comparison of incorporation of microwave treated rubber crumb versus untreated rubber crumb (adapted from [41])

Properties	Fresh tyre rubber	20% untreated crumb	20% microwave treated crumb			
Treatment properties						
T	-	-	360	380	360	380
t	-	-	4	4	8	8
Cured properties						
Shore Hardness	67.7	66.1	68.2	70.4	67.0	67.9
Modulus at 100% (MPa)	2.43	2.02	2.17	2.51	2.12	2.20
Modulus at 300% (MPa)	3.44	2.66	2.53	2.91	2.72	2.71
Tensile strength (MPa)	21.51	16.38	16.74	17.16	17.28	17.27
Elongation at break (%)	421	414	431	404	425	425

5.1.4 Ultrasound

In ultrasonic devulcanization, crosslinks are broken by applying ultrasonic waves to the rubber in presence of heat and pressure. Rubber is extruded and subsequently fed along an ultrasonic transducer, applying energy required to break sulphur – sulphur bonds and carbon – sulphur bonds selectively.

Hong and Isayev investigated ultrasonic devulcanization of unfilled NR/SBR blends [42]. Blends of NR and SBR were formulated in 0/100 up to 100/0 ratios. In a continuous process with an extruder heated to 120°C, blends were devulcanized at a frequency of 20 kHz and amplitudes ranging from 5 – 10 μm . Devulcanizates were subsequently revulcanized and mechanical properties were investigated. An overview of the results is displayed in Figure 3. As can be seen, tensile strength and elongation at break decrease with increasing the SBR content of the unfilled rubber. The obtained results for the samples containing 50% or more SBR display very low mechanical properties. Tensile strength of the revulcanized samples is lower than that of the virgin samples, however, this effect becomes less pronounced at higher SBR content. The revulcanization recipe was tailored to the 50/50 blend and the authors claim better properties are to be expected when tailoring the recipe to specific samples. Unfortunately the authors do not provide a table with the results.

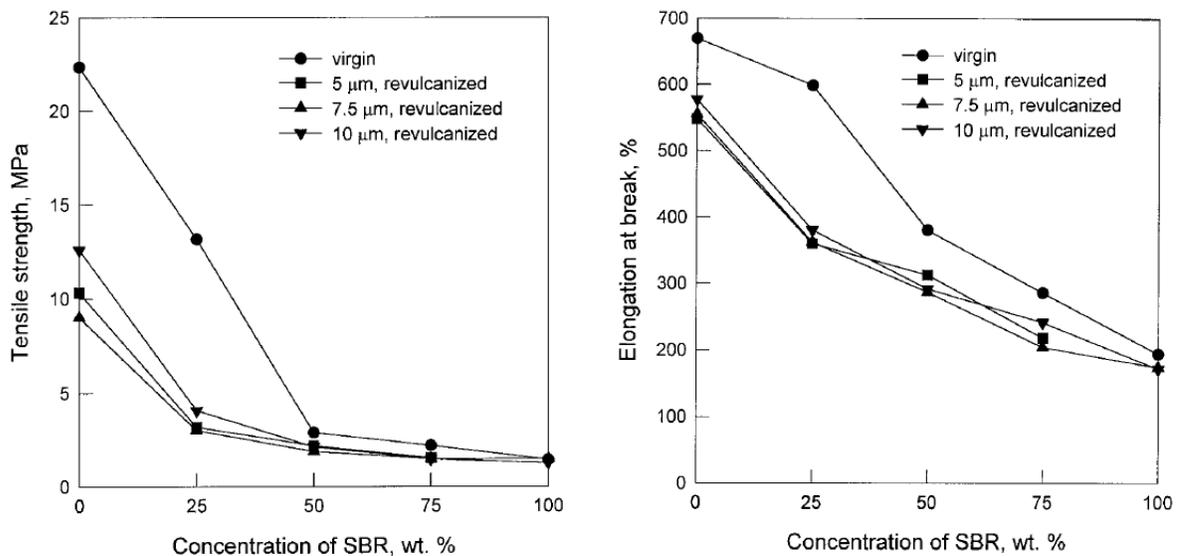


Figure 3. Mechanical properties of virgin and revulcanized blends of NR and SBR (adapted from [42])

Sun conducted research on ultrasonic devulcanization of isoprene rubber (IR) [43]. Rubber devulcanized under optimal conditions (120°C, at an amplitude of 10 μm with a gap size of 2.54 mm) was blended in several ratios with virgin IR and subsequently revulcanized. Also grounded IR (not treated with ultrasound) was incorporated into virgin IR. An overview of the tensile strength of the blends is displayed in Figure 4. As shown, ultrasonically devulcanized IR (dIR) displayed superior behavior compared to grounded IR (gIR). Furthermore, a significant decrease in tensile strength is observed when incorporating devulcanized IR into the blend. Using 100% devulcanized IR leads to retention of approximately 28% of the tensile strength. Using 50% devulcanized IR mixed revulcanized with 50% virgin IR leads to retention of circa 61% of the tensile strength. Mixtures with ground rubber, however,

displayed significantly worse mechanical properties. A similar trend was observed for the elongation of break of the compounds, however, the decreasing trend when incorporating devulcanized IR into the blend was less pronounced.

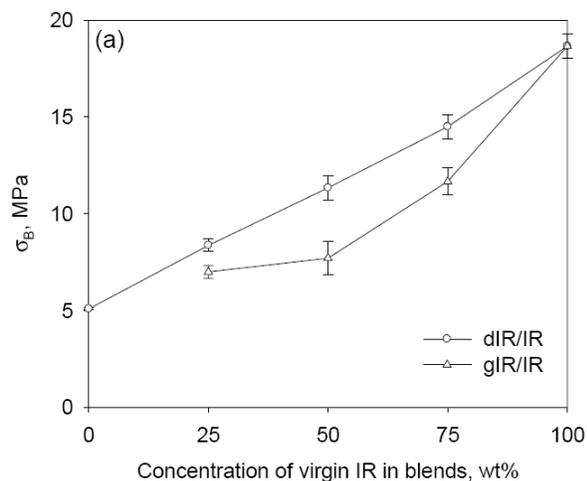


Figure 4. Tensile strength of blends of virgin IR and devulcanized IR obtained by ultrasonic treatment (adapted from [43])

5.1.5 Other physical methods

A recent patent describes rubber devulcanization by applying an alternating radio frequency dielectric field [44]. The method is very similar to the microwave method, however, waves of longer frequency are used to devulcanize the rubber. Experiments were conducted in a batch setup, however, also continuous operation is claimed to be possible. Ground passenger tyre rubber of two mesh sizes was devulcanized at a voltage between 4000 and 6000 V at a frequency of 27.12 MHz for a period between 30 – 50 seconds. Subsequently the devulcanized rubber (DGCTR) was blended with 30 wt% fresh rubber (FR). This rubber has different specifications than the passenger car tyre rubber. The results are displayed in Table 5. As shown, devulcanized blends display relatively good mechanical properties. No reference values for the mechanical properties of the tyre rubber are, however, supplied by the author. Since the tensile strength of the blend with 70% DGCTR of mesh 105 is superior compared to the tensile strength of the FR, the FR is expected to have worse mechanical properties compared to the tyre rubber. Elongation at break of this blend is comparable to the FR and hardness is slightly higher. In order to make statements the mechanical properties of the passenger car tyre rubber are required. Wicks et al. [41] identified a tensile strength for passenger car tyre rubber of 21.51 MPa (219.3 kg/cm²), which is indeed a factor 2 higher than the FR blend.

Table 5. Incorporation of radio wave devulcanized rubber (adapted from [44])

Properties	100% FR	30% FR, 70% DGCTR (mesh 40)	30% FR, 70% DGCTR (mesh 105)
Tensile strength (kg/cm ²)	113	129.5	125
Elongation at break (%)	450	350	440
Hardness Shore A	69	73	72

5.2 Chemical devulcanization

Chemical devulcanization is a surface treatment method in which a chemical agent or a mixture of chemical agents is added to the rubber in order to facilitate or enhance the devulcanization process. The processes are generally executed at elevated pressure and temperature, comparable to the (thermo-)mechanical processes.

5.2.1 *Organic disulfides and mercaptans*

Already in 1947 a patent [45] describes the successful devulcanization of inner tube and tyre tread scrap by the chemical agents xylyl mercaptan, thiophenol, phenyl sulphide, diphenyl disulphide, benzyl disulphide, isoamyl mercaptan, butyl mercaptan, diamyl disulphide, isoamyl disulphide, n-amyl disulphide, n-butyl disulphide, terpinolene, C18 unsaturated ketones, phorone, and Antox. Mercaptans and sulphides were said to be identified as especially advantageous in the devulcanization process, however, no concrete data are available.

Albert [46] patented a chemical devulcanization process for natural and synthetic rubber by the devulcanization agent bis(trialkylphenol) sulphide. The method consists of heating up the rubber to at least 149°C, for typically 4 – 10 hours in presence of the softening and swelling agent bis(trialkylphenol) sulphide. Cook et al. [47] patented a method for devulcanization of SBR by tetraalkylphenol sulphides. Rubber blends were devulcanized for four hours using the pan process at 12 bar and 192°C. Analysis was based on thickness of the rubber after squeezing the rubber between two rolls, visual inspection, tackiness, and adherence of the rubber sheet to the mixing rolls.

Anderson patented [48] a process for devulcanization of rubber obtained from pneumatic rubber tyres by an aryl disulphide agent. The process consisted of heating the rubber (mesh 6 – 30) in a tank to 180°C in presence of reclaim oil, water and an aryl disulphide peptizer. The mixture was kept at a pressure of approximately 17 bar for three hours. A mixture of diphenyl disulphide, dicresyl disulphide and dixulyl disulphide was used, however, also a volatile mercaptan fraction was present (5 wt%). A comparison of revulcanizates of this mixture with that of a distilled mixture (mercaptan fraction removed) displayed no difference in physical properties. Actual data of the measured physical properties are not shown in the patent, making it difficult to compare this method to other methods.

De et al. [49] compared the devulcanization of filled NR by diallyl disulphide (DADS) with a renewable resource material (RRM), consisting of mainly diallyl disulphide with cyclic monosulfides, polysulfides, different disulfides, and sulfone compounds. NR was vulcanized and subsequently aged for 72 h at 70°C. Thereafter, the rubber was devulcanized at 60°C for 35 minutes on a two-roll mixing mill. An overview of the result is shown in Table 6. As shown the mechanical properties of the revulcanizates are deteriorated. Between 15 and 19% of tensile strength is retained, 57 – 60% of elongation at break and 50 – 52% of the hardness. Blending 40% devulcanized NR, however, with 60% fresh rubber and subsequently vulcanizing the mixture, results in a material with reasonable properties. Circa 84% of tensile strength of vulcanized virgin NR was obtained, along with 90% of elongation at break and 114% of hardness.

Table 6. Overview of results obtained by devulcanization of filled NR by RRM and DADS (adapted from [49])

Properties	Vulcanized NR	Re vulcanized NR by RRM	Re vulcanized NR by DADS	40% devulcanized NR & 60% fresh NR
Tensile strength (MPa)	22.88	4.34	3.52	19.13
Elongation at break (%)	500	283	300	450
Hardness Shore A	66	34	33	75

Knörr described [50] a method for devulcanization of several rubbers in an autoclave by Aktiplast 6 (containing sulphides such as diaryl disulphide). The diaryl disulphide is spread over the rubber and left to swell for 12 hours. Rubber is applied in thin layers onto talcum powder trays in order to facilitate penetration of oxygen. The trays are put in an autoclave and subsequently subjected to a pressure of 4 bar of oxygen and steam. While maintaining proper air circulation, the pressure is increased by forcing steam of 8 – 9 bar into the autoclave until a temperature of approximately 190°C is reached. Typical treatment times range from 3 – 5 hours, excluding preheating time. Passenger car tyres, containing 80 – 100% SBR (typical tread composition) treated according to this method and subsequently revulcanized displayed the following mechanical properties: Tensile strength: 7.4 MPa, elongation at break: 200%. This indicates mediocre mechanical properties, however, the curing recipe was not mentioned in the article.

De et al. [51] investigated the devulcanization of ground tyre rubber obtained from passenger car and truck tyres by tetra methyl thiuram disulphide (TMTD). Ground rubber was blended with 10 phr spindle oil and 1.5 – 3.25 phr TMTD and subsequently devulcanized on an open two-roll mill around ambient temperature for 20 or 40 minutes. Samples were subsequently revulcanized with 0.5 or 1.75 phr sulphur. Samples obtained tensile strength of circa 3.6 – 5.8 MPa, where the higher tensile strength was obtained for the samples milled for 40 minutes. Furthermore, 0.5 phr sulphur was identified to be superior to 1.75 phr. Elongation at break varied from 83 – 197 % and the same pattern related to the amount of sulphur was obtained. Longer milling times resulted in better mechanical properties, while the elongation at break decreased with TMTD content.

5.2.2 Inorganic compounds

Nicholas [52] investigated the devulcanization of tyre rubber by Aliquat 336, a quaternary ammonium salt. Ground tyre rubber of 30 – 60 mesh was stirred in a 3-neck flask with benzene and Aliquat 336. Aqueous sodium hydroxide was added and the mixture was subsequently refluxed for two hours. After washing with water the rubber was dried in a vacuum oven overnight. The crosslink density of the rubber decreased with increasing the concentration of Aliquat 336 up to 7.5 phr. Incorporating 7.5 phr Aliquat 336 led to a decrease in crosslink density of 59%. Replacing 20% of benzene by benzyl chloride and refluxing for five hours reduced the crosslink density by 74%. Incorporating 20 wt% SBR/BR treated according to this invention into fresh rubber led to the following results according to the retention of mechanical properties. Tensile strength: 76%, elongation at break: 86%.

In the digester process, ground rubber along with water and a fibre destroying chemical (e.g. sodium hydroxide, calcium chloride or zinc chloride) is stirred in a closed container fed with steam. Glenn and

Markiewicz [53] patented a method for devulcanization of tyre rubber by the digester process. Rubber was blended with tall oil pitch, pine oil, mineral spirits, calcium chloride and water and subsequently digested for five hours at 197°C. The product was subsequently dried under several circumstances, and blended with fresh SBR. Revulcanizates containing 32 wt% devulcanized rubber were subjected to mechanical tests. The sample dried in a hot air dryer and vulcanized for 30 min at 144°C displayed a tensile strength of 14.5 MPa and an elongation at break of 580%.

Myers and MacLeod [54] patented a process for devulcanization of tyre rubber by sodium metal in an organic solvent. Rubber was added to an autoclave and toluene and sodium metal were added. The autoclave was put under a nitrogen atmosphere and subsequently under hydrogen at a pressure of 13.8 bar. The mixture was heated to 100°C while stirring and subsequently the temperature was left to increase to circa 250°C. After reaching 250°C the heating was put off and the pressure increased to 29.3 bar. After the mixture had cooled down to 225°C, water was added in order to quench the reaction. The product was described as a black slurry, which after a drying step became a strong rubbery material. Mechanical properties of the product are not displayed in the patent, however, the sulphur content was reduced with 80%.

Kawabata et al. [55] described a method for devulcanization of IR by Iron (II) chloride. Rubber was stirred in a flask with benzene and phenyl hydrazine. Subsequently Iron (II) chloride in methanol was added to the mixture and the flask was kept at 30°C. The crosslink density was reported to decrease in presence of oxygen, however, not in absence of oxygen. Iron (III) chloride was also subjected to the same experiments. Results indicated a comparable decrease in crosslink density, however, degradation became slower. This method was patented in 1981 by Marvik [56]. In this patent, also diphenyl guanidine was used as peptizing agent. An example stated in the patent: Rubber scrap obtained from passenger car tyres was added to a mixer, followed by diphenyl guanidine. Subsequently, a mixture of ferrous chloride dissolved in methanol was blended with tall oil pitch preheated to 30 – 40°C and added to the rubber. Addition time was five minutes, after which the mixer was operated for an additional 30 minutes. Subsequently, the devulcanizate was allowed to rest overnight followed by revulcanization. Sheets were vulcanized for 20 minutes at 160°C and a tensile strength of 11.8 MPa and an elongation at break of 260% was obtained.

5.2.3 Other chemicals

Sekhar [57] patented a method for devulcanization of rubber by a mixture of 2-mercaptobenzothiazole, zinc dimethyldithiocarbamate, stearic acid, zinc oxide, sulphur, and diethylene glycol (Delink mixture). Ground tyre was mixed on a two-roll mill for three minutes. Subsequently, 3 phr of the Delink mixture was added and milling was continued for two minutes. Afterwards an additional 3 phr of the Delink mixture was added and the mixing was continued for two minutes at a narrow nip. Milling is executed preferably at temperatures below 50°C. After mixing, the blend is ready to be revulcanized at approximately 150°C for 15 to 30 min. An overview of the mechanical properties of the revulcanizates is displayed in Table 7. As shown, reasonable mechanical properties are obtained for the revulcanizates. Tensile strength and elongation at break of the samples are roughly half of tensile strength of fresh, vulcanized NR. Ground tyre treads treated with this method displayed a tensile strength of 13 MPa,

compared to 18 – 21 MPa for fresh rubber tread. Elongation at break was 300%, compared to 350 – 500% for fresh rubber tread.

Table 7. Overview of mechanical properties of revulcanizates obtained by devulcanization of NR with Delink mixture (adapted from [57])

Country of origin	Malaysia		Europe	
Size (mm)	0.1 – 0.5	0.1 – 0.5	0.1 – 0.5	>1.0
Delink content (phr)	6	6	6	6
Vulcanization T (°C)	143	155	143	143
Tensile strength (MPa)	12.1	12.7	14.5	16
Elongation at break (%)	350	350	375	400

In a paper, Kohler and O’Neill did additional research on the Delink method [58]. NR and SBR was ground to 40 mesh and subsequently blended with fresh rubber and revulcanized. An overview of the mechanical properties of the (re-)vulcanizates is shown in Table 8. Incorporation of 30% devulcanized rubber did not alter the mechanical properties significantly. Circa 94% and 92% of tensile strength was retained for NR and SBR respectively, along with 92% and 96% for elongation at break.

Table 8. Overview of mechanical properties of vulcanized blends of Delink devulcanized rubber with fresh rubber (adapted from [58])

Properties	NR (fresh)	70% fresh NR, 30% devulcanized	SBR (fresh)	70% fresh SBR, 30% devulcanized
Tensile strength (MPa)	29.44	27.72	26.75	24.68
Elongation at break (%)	534	489	358	345

Watabe et al. [59] [60] patented a process for devulcanization of synthetic rubber by the chemical agents 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), phenol salts of DBU, carboxylic acid salts of DBU, thiuramsulfide compounds, aromatic disulfides, and benzene sulfinic acid compounds. Aromatic disulfides were found to have little devulcanizing effect, however, when combined with one of the other compounds in the research they behave as effective chemical agents. Furthermore, incorporation of an aliphatic or alicyclic amine was found to enhance the devulcanizing effect of the former compounds. The method is more time efficient than the pan process as described by Cook, since it requires typical processing times of 5 – 60 minutes compared to 4 – 10 hours. Several mixing apparatuses can be used (e.g. roll, kneader, brabender, banbury, and reclaimeter) and typical temperatures applied range from 20 – 200°C, depending on the chemical agent. The majority of the experiments, however, were conducted at temperatures ranging from 40 – 60°C.

Dijkhuis investigated the devulcanization of filled EPDM-rubber in a batch reactor and an extruder with hexadecylamine (HDA) as DA [61]. Both conventionally cured (mainly polysulfidic) and efficiently cured (mainly monosulfidic) EPDM-rubber were subjected to devulcanization experiments. Temperature was

found to have the most significant influence on the reclaiming efficiency. For efficiently cured EPDM-rubber, increasing the temperature up to 225°C was found to have a favorable effect on the devulcanization. However, applying higher temperatures led to an increase in crosslink density with increasing the concentration of HDA.

5.3 Biological devulcanization

In biological devulcanization, microorganisms are used to selectively break sulphur bonds in the rubber. The microorganisms attack sulphur bonds at the surface of the ground rubber particles, in order to create a material with a plastic surface that is suitable to be revulcanized.

Straube et al. [62] described a process for devulcanization of tyre rubber by chemolithotropic microorganisms. In this invention, sulphur present in the rubber is in presence of air transformed to elementary sulphur and sulphuric acid. The species *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, and *Thiobacillus thioparus* are identified as effective bacteria in this process. Zinc oxide and other metal oxides are also stated to be split off during the devulcanization process. Treatment times and mechanical properties of the obtained rubber are not mentioned in the patent.

Recently, Li et al. [63] conducted research on devulcanization of ground tyre rubber by *Thiobacillus ferrooxidans*. *Thiobacillus ferrooxidans* was cultured for 24 h in a flask on a rotary shaker at 30°C and pH 2.5. Ground rubber was disinfected by immersion in 75% ethanol for 24h. Subsequently the disinfected ground rubber was added to the medium (5% (w/v)), and led to desulphurize for 30 days. Thereafter the desulphurized rubber (DGTR) was molded and compared with molded untreated rubber (GTR) particles. The results are displayed in Table 9, however, it was not mentioned whether curatives were added before revulcanization. As can be seen revulcanizates display poor mechanical properties, however, the desulphurized rubber has significantly better properties. The authors mention desulphurization only occurred up to a depth of several micrometers. Ground rubber and desulphurized rubber were also blended with fresh NR in several ratios and subsequently subjected to mechanical tests. An overview of the results is displayed in Table 10. In agreement with expectations, incorporation of desulphurized rubber particles into the fresh NR leads to better mechanical properties than incorporating untreated particles. Incorporation of 40 phr DGTR leads to retention of 72% of tensile strength and 97% of elongation at break, compared to 61% and 84% respectively for GTR.

Table 9. Mechanical properties of revulcanizates of desulphurized rubber versus ground rubber (adapted from [63])

Properties	Ground tyre rubber	Desulphurized ground tyre rubber
Hardness Shore A	67	63
Tensile strength (MPa)	2.5	4.9
Elongation at break (%)	153	178

Table 10. Vulcanized blends of NR and GTR or DGTR (adapted from [63])

Sample	GTR/phr	Hardness Shore A	Tensile strength (MPa)	Elongation at break (%)
NR	0	36	25.3	542
NR/GTR	10	40	21.9	513
	20	46	19.4	480
	30	48	17.6	472
	40	52	15.4	454
	NR/DGTR	10	39	22.8
	20	44	20.8	587
	30	47	20.2	547
	40	50	18.3	527

Neumann described a method [64] for devulcanization of rubber by anaerobic bacteria. Process parameters include a temperature of 33 – 37°C, a pH of 6 – 8, a particle size of 0.2 – 0.4 mm and a treatment time of six days. Desulphurization occurred by a mixture of the species *Desulphuromonas thiophila*, *Desulphuromonas palmitatis*, *Sulphurospirillum deleyianum*, and *Desulphuromonas acetoxidans*. Furthermore desulphurization was enhanced by methanogenic bacteria. An example regarding EPDM rubber is incorporated in the patent. Cryogenically milled EPDM rubber with particle size <0.4 mm was desulphurized in an anaerobic bioreactor for 8 days. A 4% desulphurization level was obtained. The devulcanized rubber was subsequently revulcanized with 50% fresh EPDM rubber. An overview of the results is displayed in Table 11. As shown, incorporating of EPDM rubber treated according to the described method is superior compared to incorporating untreated EPDM rubber crumb. Incorporation of 50% devulcanized EPDM rubber led to 89% retention of tensile strength and 93% of elongation at break.

Table 11. Physical properties of revulcanizates of EPDM (adapted from [64])

Sample	Tensile strength (MPa)	Elongation at break (%)
Control EPDM	28	595
50% treated EPDM + 50% fresh EPDM	25	555
50% non-treated EPDM + 50% fresh EPDM	17.5	385

Jiang et al. [65] researched the microbial desulphurization of SBR by *Sphingomonas* sp. Ground SBR was disinfected by 24h immersion in ethanol. *Sphingomonas* sp. was cultivated and subsequently 2.5% (w/v) rubber was added to the medium and desulphurization was allowed for ten days. The devulcanized SBR was subsequently incorporated into fresh NR and vulcanized. Incorporating 20% desulphurized SBR into the fresh NR led to retention of 99% of tensile strength and 100% of elongation at break, compared to 94% and 94% respectively for ground SBR. By FTIR-ATR and XPS a combination of C=C, S – C and S – S bond breakage was identified.

6 Energy recovery

In energy recovery the rubber is not directly used in other products. The high energy content of the rubber in the tyres can, however, be used for certain processes, or transformed into other energy carriers (e.g. oil and gas). These two approaches are briefly described below.

6.1 Incineration

Tyres are used as fuel source in incinerators, operated at high temperatures. Above 400°C, spontaneous combustion of the rubber takes place and the exothermic reaction maintains itself [66]. The process is focused on the production of heat, which can be used for the production of steam and subsequently electricity. Since sulphur oxide and nitrogen oxide are produced during incineration, a flue gas washing step may have to be introduced in order to remove these compounds.

Carrasco et al. [67] investigated the environmental impact of co-feeding scrap tyres in a cement kiln. Replacing 20 wt% coal by scrap tyres leads to an increase in particulate matter in the flue-gas of 7% and in the cooling units of 15%. The emissions remained, however, within the regulated quantities.

6.2 Pyrolysis

In pyrolysis the rubber waste is heated at moderate temperature (400 – 800°C) in absence of oxygen or presence of very little oxygen in order to thermally degrade the material [68]. This endothermic reaction produces a non-condensable gas fraction, a condensable liquid fraction and a solid residue. Emissions of sulphur oxide and nitrogen oxide are typically lower compared to incineration [66]. The non-condensable gas fraction is typically 20 wt% of the starting material and consists of hydrogen, hydrogen sulphide, carbon oxides and C1 – C6 hydrocarbons. This stream has a heat of combustion of 68 – 84 MJ m⁻³ and can be used for heating of the reactor. The condensable liquid fraction is typically 35 wt% of the starting material and contains C5 – C20 organic compounds, mainly polycyclic aromatic hydrocarbons (PAH's). Exact compositions of the streams, however, highly depend on the product composition and process parameters. The solid residue contains steel (if not removed before pyrolysis), char and carbon black and is typically 45 wt% of the starting material [68]. The obtained oil fraction may be used in furnaces and combustion engines, while the carbon black may be used for light absorption, the production of polymeric materials, the production of charcoal or in the production of tyres [68].

Chapter 2. Devulcanization of Carbon Black Filled Styrene Butadiene Rubber in a Batch reactor

In this chapter the developed devulcanization system for SBR is described and results obtained with this system are described. Furthermore, an empirical model predicting devulcanization in a certain range of the process parameters is developed.

1. Abstract

An empirical model investigating the effect of process parameters during devulcanization of carbon black (CB) filled Styrene butadiene rubber (SBR) with diphenyl disulphide (DPDS) in a batch reactor was created. Devulcanization temperature, time, and concentration devulcanization agent were varied and the sol fraction and crosslink density of the devulcanized rubber was studied. A concentration of 15 mmol/100g compound DA was found to be effective in combination with a temperature up to 270°C, in terms of sol fraction and crosslink density of the devulcanizate. CB was found to make the devulcanization of filled SBR more challenging than gum SBR, as the former is expected to accept radicals from SBR and subsequently supply them as well.

2. Methodology

This research focuses on chemical devulcanization of SBR with diphenyl disulphide (DPDS) in a batch reactor, where shear forces and heat are applied to the rubber. In order to obtain adequate devulcanization, optimization of process parameters (temperature, time, concentration DA) is required. A straightforward approach for optimization is the use of a statistical model. The model offers insight in the correlation between input and output parameters of the process, since physical reactions follow certain trends.

The devulcanization process can be viewed as a black box system (Figure 5). Input parameters are the temperature, the concentration DA, and the devulcanization time. The output of the system is characterized by its sol fraction and crosslink density. Another input parameter is rotational speed, however, this variable was kept constant at 50 RPM. The operating parameters (e.g. shear force, diffusive velocity, reaction rate) considered directly in a kinetic model, are influenced by the input parameters considered in this model and are therefore indirectly included. The obtained results are only representative for the ranges included in the model. The R^2_{PRESS} value, however, is an indication of the predictive capabilities of the model outside these ranges.

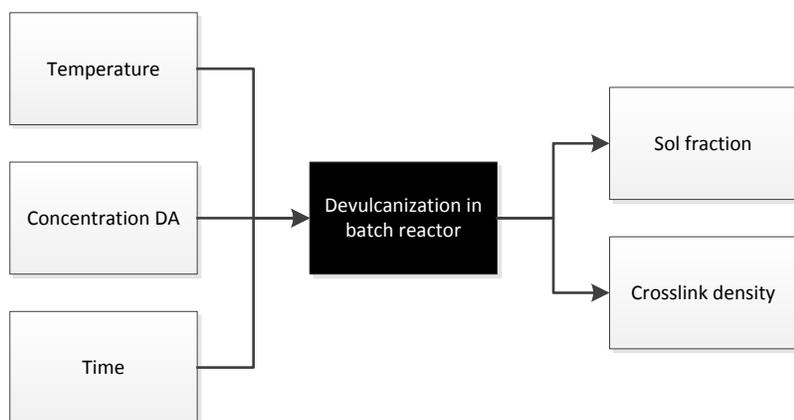


Figure 5. Black box model of devulcanization of SBR in a batch reactor

3. Materials and methods

3.1 Materials

A styrene butadiene rubber (SBR) masterbatch (sieve size 2 mm) was kindly produced by LANXESS (Geleen), according to recipe shown in Table 12.

Table 12. Vulcanization recipe of the masterbatch

SBR 1723 ²	137,5	phr
Carbon black N-326	70	phr
TBBS	2	phr
TMTD-80	1	phr
S-80 (R. S) 80 %	2,5	phr
ZnO (UM)	3	phr
Stearic acid	2	phr
CaO-80 (K. GR/DAB)	7,5	phr

Diphenyl disulphide (DPDS) (99%) was obtained from Acros and used as a devulcanization agent (DA). Treated Distillate Aromatic Extract (TDAE) oil obtained from Vredestein (Enschede) was used as a plasticizer. Acetone (pure) was obtained from Acros and used without further purification. Tetrahydrofuran (THF) (extra pure) was supplied Acros and used as obtained. Toluene (pure) was obtained from Acros and used without further purification.

² SBR 1723 contains 100 phr SBR and 37.5 phr processing oil

3.2 Equipment

3.2.1 *Brabender batch reactor*

A Brabender Plasti-Corder mixer, equipped with a 30 cc chamber was used for the devulcanization experiments. During experiments the torque and internal temperature of the mixture were monitored.

3.2.2 *Gel Permeation Chromatography (GPC)*

A HP Agilent 1100 series gel permeation chromatograph was used to measure the degree of degradation obtained during devulcanization. The chromatograph was equipped with three Polymer Laboratories gel 3 μ m MIXED-E columns. Eluent applied was THF at a flow of 1 ml/min. Refractive index was used to detect chains and PSS software was used to create a molecular weight distribution of the samples.

Further analyses of molecular weight distributions were conducted with a Spectra Physics AS 1000 LC-system. Eluent applied was THF at a flow of 1 ml/min. A Shodex RI-71 refractive index detector was used for detection of chains. Omniseq software was used to create a molecular weight distribution of the samples.

3.3 Rubber devulcanization

Samples of the rubber compound were treated on a Brabender batch mixer, according to a fill factor of 0.7. The compounds contained vulcanized, filled SBR and a mixture of TDAE oil and DPDS in case a DA was added. TDAE oil concentration was 5 wt% of the total amount of compound, DPDS was used in concentrations of 15 up to 45 mmol per 100g compound. The mixture of TDAE oil and DPDS was dispersed on the rubber particles and the compound was left to swell for a while. Thereafter, the compound was added to a preheated Brabender batch mixer, of which the chamber was depleted of oxygen by addition of nitrogen gas. The Brabender was operated at a rotational speed of 50 RPM and devulcanization time was varied between 6 and 15 minutes. After devulcanization, the mixer was opened and the treated rubber compound was collected and quenched with liquid nitrogen.

3.4 Carbon black experiments

SBR containing 37.5 phr processing oil was processed in the Brabender batch mixer, operated at 265 and 300°C, still at a fill factor of 0.7, rotating at 50 RPM. Samples containing carbon black (CB) were produced by adding 70 phr CB to the Brabender, along with 5 wt% oil (based on total amount of compound). DA was added in the same ratio to the SBR chains present in the blend as in the devulcanization experiments. DA concentration ranged from 0 to 30 mmol/100g compound. The compound was processed for 6 minutes and subsequently collected and quenched with liquid nitrogen. Hereafter, the product was extracted in order to determine the sol and gel fraction.

3.5 Analysis

Devulcanized rubber was analysed by sol fraction in acetone and THF and by crosslink density. The sol fraction in THF was further analysed by Gel Permeation Chromatography (GPC).

3.5.1 *Sol fraction*

Devulcanized rubber samples were extracted by a two-step Soxhlet extraction. During the first step, low molecular weight compounds (e.g. curatives, processing oil) were extracted with acetone for 48 h. THF

was used in the second step in order to extract dissolvable (devulcanized) rubber chains from the compound. The extractable fraction in THF with respect to the total amount of extractable rubber in THF was used as a measure of devulcanization, i.e. the sol fraction is compensated for bound rubber.

3.5.2 Crosslink density

Swelling of the gel fraction of the samples was used as a measure for their crosslink density. During swelling, rubber particles take up solvent in their network. The degree of swelling is limited by crosslinks. By calculating the weight increase due to swelling, the solvent uptake can be derived.

Rubber samples were immersed in toluene and shaken for 72 hours. The apparent crosslink density was calculated by the Flory-Rehner equation [69]. However, the Flory-Rehner equation is only valid for non-filled rubbers. Therefore the Kraus correction has to be applied in order to calculate the actual crosslink density [70].

The apparent crosslink density was calculated as follows:

$$X_{\text{apparent}} = \frac{\ln(1-V_R)+V_R+\chi V_R^2}{V_S(0.5V_R-V_R^{\frac{1}{3}})} \left(\frac{\text{mol}}{\text{cm}^3}\right) \quad (1)$$

Whereby V_R is the volume fraction rubber in the swollen sample, V_S is the molar volume of toluene, which is $106.2 \text{ cm}^3/\text{mol}$, and χ is the Flory-Rehner interaction parameter, which is $0.524 - 0.285V_R$ for Toluene/SBR [71].

In simplified form the Kraus correction is given by [72]:

$$X_{\text{actual}} = \frac{X_{\text{apparent}}}{1+C \times \phi} \quad (2)$$

Whereby C is constant for a certain filler and ϕ is the volume fraction of filler in the compound.

$$\phi = \frac{\text{weight fraction filler} \times \text{density of rubber compound} \times \text{sample weight before extraction}}{\text{density of filler} \times \text{weight of compound before swelling}} \quad (3)$$

$$C = 1.17 \text{ [73]} \quad (4)$$

3.5.3 Molecular weight of sol fraction

Molecular weight of the sol fraction was determined using GPC. Due to different interactions based on chain size with the column, separation based on molecular weight is possible. The applied column, however, is only reliable for molecular weights up to 40.000. Therefore, the calculated molecular weights are not representative of the actual molecular weight, however, the column still offered some resolution at higher molecular weights.

Evaluation of the molecular weight of the sol fraction of the CB experiments was conducted at a GPC equipped with two columns that are capable of measuring molecular weights up to 1.000.000.

3.6 Experimental setup

3.6.1 Determination of experimental range

Filled SBR was devulcanized by chemical devulcanization with DPDS as a DA. A Brabender batch mixer was used for generating shear stress by two rotating mixers and applying heat to the material. The standard conditions that were identified suitable for devulcanization of unfilled SBR by the University of Twente were used as a starting point. These conditions are regarded to as the default conditions and correspond with treatment for 6 minutes at 220°C and 50 RPM, with addition of 15 mmol DPDS per 100g rubber compound. Experiments were conducted at a mixing speed of 50 RPM and temperatures ranging from 200 to 270°C. Treatment times were varied between 6 and 15 minutes. DPDS content was varied between 15 and 45 mmol per 100g compound. In Table 14 an overview of the screening experiments is displayed. These results were used to formulate an empirical model for estimation of the devulcanization in a certain range.

3.6.2 Experimental design

Three input variables were incorporated in the research, namely temperature, devulcanization time, and DPDS concentration. For all variables a high value and a low value was indicated and all combinations were tested, leading to 8 distinguishable configurations. All experiments were executed in duplo, leading to 16 experiments. An overview of the conditions and the experiments is displayed in Table 13 and Table 14.

Table 13. Range of process variables for additional experiments

Factor	Lower value (-1)	Upper value (1)
Temperature (°C)	220	265
Time (s)	360	720
DA (mmol/100g)	15	30

Table 14. Overview of factors in experimental design

No	T (°C)	t (s)	DA (mmol/100g)
11	-1	-1	-1
12	-1	-1	1
13	-1	1	-1
14	-1	1	1
15	1	-1	-1
16	1	-1	1
17	1	1	-1
18	1	1	1

Table 15. Overview of screening experiments

Run	T (°C)	t (s)	DPDS (mmol/100 g rubber)	Purpose
1	220	360	15	default
2	200	360	15	determine T range
3	220	540	15	determine t range
4	220	720	15	determine t range
5	220	900	15	determine t range
6	270	360	15	determine T range
7	220	360	45	determine DPDS range
8	220	360	30	determine DPDS range
9	240	360	30	additional test
10	240	720	30	additional test

4. Results and discussion

In order to determine the range of experimental values for the experimental design, initial screening experiments (1 – 6) were conducted. Temperature was varied between 200 and 270°C, processing time between 6 and 9 minutes, rotational speed was set to 50 RPM, and the concentration DA was kept constant at 15 mmol per 100g compound. Results indicated a significant increase in sol fraction at higher temperature, while the effect of the processing time was found to have little effect on the sol fraction. Subsequently additional screening experiments were conducted, whereby the temperature was varied between 220 and 240°C and higher concentrations of DA were applied. Based on the initial results and visual inspection of the devulcanized SBR, a range of values for the variables was selected in the experimental design (Table 13). An overview of the experimental design is displayed in Table 14. An overview of all experiments related to the screening experiments and the subsequent sol fraction and crosslink density are displayed in Table 16. All combinations of the factors were tested in duplo, namely series 11 – 18 and 19 – 26. The results for the additional experiments related to the experimental model are displayed in Table 17.

Table 16. Overview of Sol fraction and Crosslink Density as function of process temperature, process time and concentration of devulcanization agent (DA) for screening experiments

No	Temperature (°C)	Time (s)	DA ^b (mmol/100g)	RPM	Sol fraction ^c (%)	Xlink ^d (mol/cm ³)
1	220	360	15	50	25.60	1.27E-04
2	200	360	15	50	16.77	8.07E-05
3	220	540	15	50	27.24	1.50E-04
4	220	720	15	50	27.01	1.05E-04
5	220	900	15	50	28.48	1.14E-04
6	270	360	15	50	50.00	1.62E-04
7	220	360	45	50	31.04	1.23E-04
8	220	360	30	50	23.81	1.20E-04
9	240	360	30	50	43.72	1.60E-04
10	240	720	30	50	50.36	1.92E-04

^a DA = Devulcanization Agent. Concentration of DA in mmol per 100g rubber compound

^a Sol fraction = Sol fraction of the compound in THF (after extraction of low molecular weight compounds in acetone), calculated as fraction of total rubber and carbon black present in the compound and compensated for bound rubber

^a Crosslink density of the compound, number of crosslinks in mol per cubic centimeter

Table 17. Overview of Sol fraction and Crosslink Density as function of process temperature, process time and concentration of devulcanization agent (DA) for additional experiments

No	Temperature (°C)	Time (s)	DA (mmol/100g)	RPM	Sol fraction (%)	Xlink (mol/cm ³)
11	210	360	15	50	17.33	9.22E-05
12	210	360	30	50	21.18	1.14E-04
13	210	720	15	50	23.05	1.00E-04
14	210	720	30	50	25.81	1.18E-04
15	265	360	15	50	41.67	1.47E-04
16	265	360	30	50	52.19	3.16E-04
17	265	720	15	50	45.16	2.00E-04
18	265	720	30	50	61.78	3.61E-04
19	210	360	15	50	18.16	1.10E-04
20	210	360	30	50	24.46	1.11E-04
21	210	720	15	50	24.93	1.23E-04
22	210	720	30	50	30.24	1.25E-04
23	265	360	15	50	44.81	1.37E-04
24	265	360	30	50	55.52	2.27E-04
25	265	720	15	50	42.38	1.63E-04
26	265	720	30	50	42.32	3.11E-04

To study the effects of the process parameters (temperature, time, and concentration of DA) on the sol fraction in THF and the crosslink density, empirical models based on experimental results were developed according to Equation (5). Engineering calculation software Mathcad® was used for calculation of the intercept (a_0) and the regression coefficients. Based on the results of a t-test, non-significant regression coefficients were excluded from the model [74]. An overview of the calculated values for the regression coefficients is displayed in Table 18.

The results of the analysis of variance (ANOVA) are displayed in Table 19. The low P-values of 3.284×10^{-7} for sol fraction and 1.304×10^{-6} for Xlink illustrate the statistical significance of the models. The R^2 and R^2_{adjusted} values ranging from 0.91 – 0.95 indicate a proper fit of the empirical models with the experimental data. The R^2_{PRESS} values range from 0.79 to 0.86, indicating relatively good predictive capacity of the models. In Figure 6 the parity plots of the sol fraction and the crosslink density are shown. Both plots confirm the fit of the empirical models with the experimental data, since data points are present above and below the parity line.

$$y_k = a_0 + \sum_{i=1}^3 a_i x_i + \sum_{i=1}^3 a_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j>i}^3 a_{ij} x_i x_j \quad (5)$$

Table 18. Regression coefficients of Sol fraction and Xlink

Variable	Intercept (a ₀)	Sol fraction	Xlink
		Coefficients	Coefficients
Temperature (x ₁)	a ₁	1,256	-9,55E-06
time (x ₂)	a ₂	0,074	-
DA (x ₃)	a ₃	-1,817	-3,38E-05
x ₁ ²	a ₄	-1,74E-03	1,56E-08
x ₂ ²	a ₅	-	-2,82E-10
x ₁ .x ₂	a ₇	-2,88E-04	1,64E-09
x ₁ .x ₃	a ₈	9,47E-03	1,58E-07

Table 19. Analysis of variance of Sol fraction and Xlink

Sol fraction							
	SS	DF	MS	F	P-value	R ² values	
Model	2.69E+03	6	4.26E+02	39.371	3.284E-07	R ²	0.95
Error	1.30E+02	12	10.83			R ² _{adjusted}	0.93
Total	2.56E+03	18				R ² _{PRESS}	0.86
Xlink							
	SS	DF	MS	F	P-value	R ² values	
Model	6.44E-08	6	1.07E-08	30.75	1.304E-06	R ²	0.94
Error	4.19E-09	12	3.49E-10			R ² _{adjusted}	0.91
Total	6.86E-08	18				R ² _{PRESS}	0.79

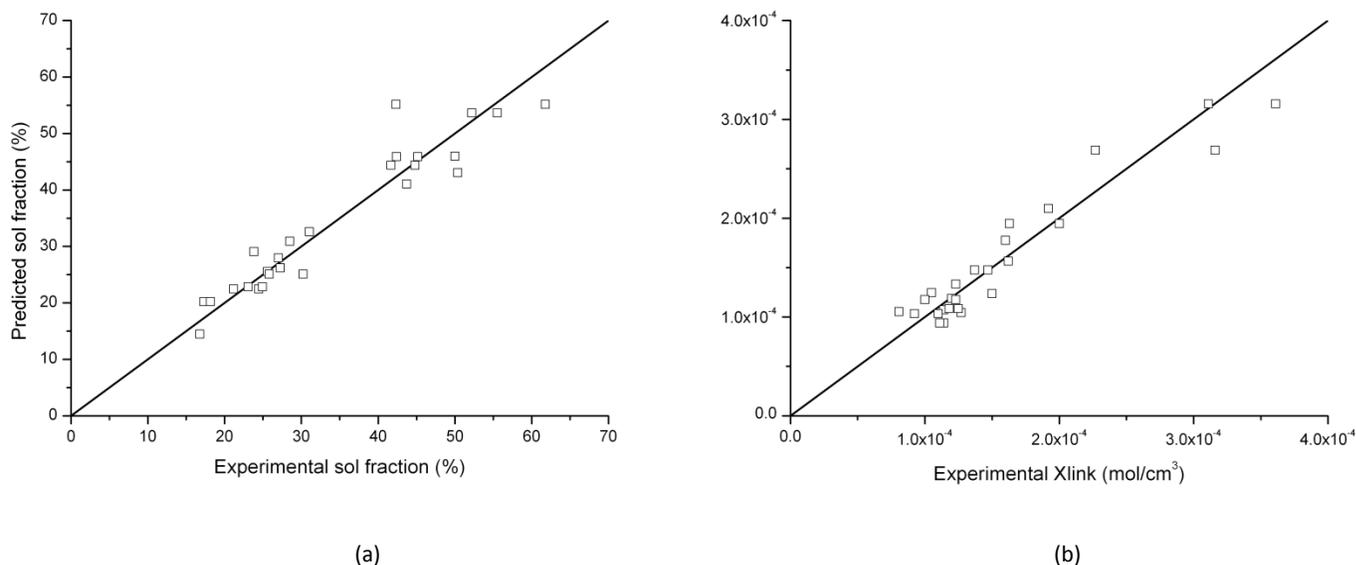


Figure 6. Parity plot between predicted and experimental values of sol fraction and Xlink

4.1 Sol fraction in THF

Based on model predictions graphs displaying the sol fraction as function of the processing time and temperature and as function of the processing time and the concentration DA were constructed. As displayed in Figure 7, temperature and DA content have a significant effect on the sol fraction. Increasing the processing temperature leads to higher sol fraction of the CB filled SBR. At low temperatures (200°C), increasing the DA concentration from 15 to 45 mmol/100g has no profound effect on the sol fraction. However, at high temperatures (270°C), the sol fraction increases significantly as function of the DA concentration. On the other hand, sol fraction only slightly increases with processing time. This effect is expected to be related to recombination of radical rubber chains. At shorter devulcanization times, recombination is expected to be less pronounced. The highest sol fraction (68.67%) is obtained at the shortest processing time (6 min), combined with the highest temperature (270°C), and the highest DA concentration (45 mmol/100g). In literature, no data on the sol fraction of SBR were found, however, sol fraction of NR was found to increase with milling time and DA concentration [75] [76]. Recently, Dijkhuis found the sol fraction of EPDM-rubber to increase with increasing temperature and DA concentration, while processing time was found to have only a marginal effect. The increase of the sol fraction of conventionally vulcanized EPDM-rubber with increasing the DA concentration was found to be more pronounced at higher temperatures, while this effect was not identified for efficiently vulcanized EPDM-rubber.

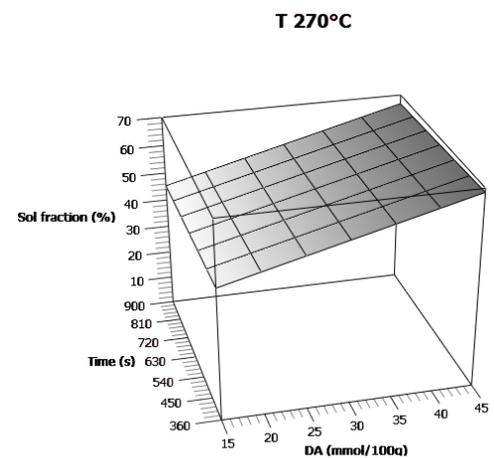
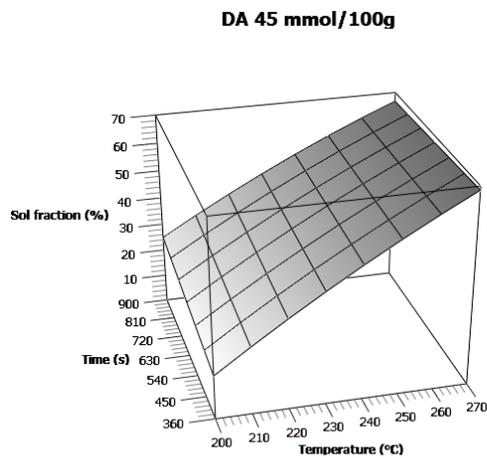
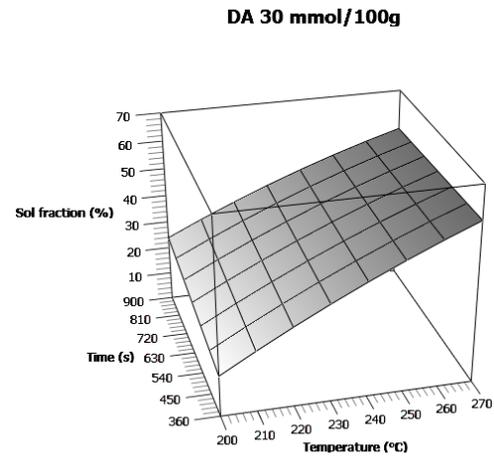
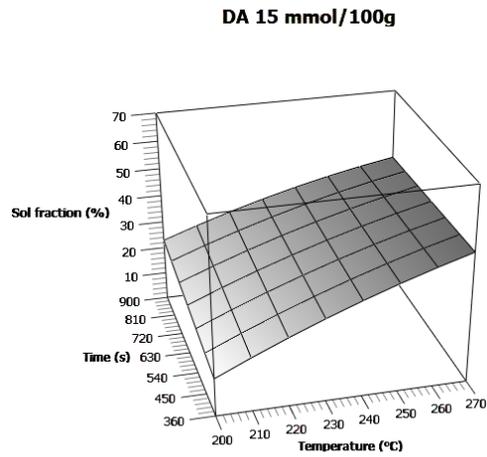


Figure 7. Prediction of sol fraction based on empirical model for devulcanization with 15 mmol/100g DA (a), 30 mmol/100g (b), and 45 mmol/100g (c), at 270°C (d).

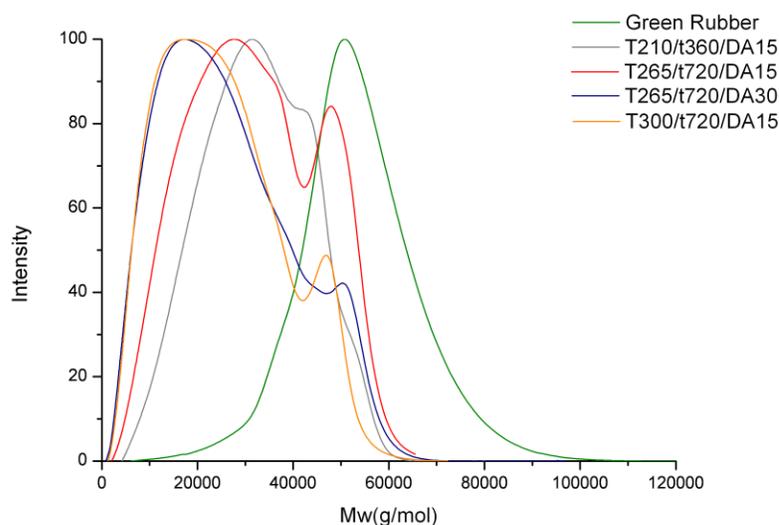


Figure 8. Indicative estimated molecular weight distribution of SBR chains based on GPC measurements of THF extracts of carbon black filled SBR devulcanized under various conditions

THF samples were subjected to GPC analysis in order to compare the composition of the sol fractions. In absence of main chain scission, GPC analysis is expected to display a similar pattern for green rubber (uncured rubber) samples and devulcanized samples, since only sulphur bridges are delinked. Based on the GPC results an estimation of the molecular weight of the samples is realized, however, due to the partial appropriateness of the column for high molecular weight compounds, the obtained values are too low, making the results only suitable for comparison between samples. An overview of GPC results for certain sol fractions and green rubber is displayed in Figure 8. In Figure 9 an overview of the estimated average molecular weights of the SBR chains present in the THF fractions is displayed.

As displayed, the peak caused by the rubber chains becomes broader with rubber devulcanized at higher temperatures. This wider chain length distribution is an indication for degradation of the main chain, since it results in the formation of smaller chains. However, in the THF sol fraction of rubber devulcanized at 300°C, long chains are still present. A similar broadening of the peaks by devulcanization was identified by ultrasonic devulcanization of unfilled butyl rubber [77]. On top of that, all devulcanized samples display a split-peak pattern to a certain degree. The peak on the right-hand side of the graph is related to higher molecular weight chains. This peak significantly decreases when increasing the devulcanization temperature from 265°C to 300°C, or increasing the DA concentration from 15 to 30 mmol/100g. Furthermore, incorporation of 30 mmol/100g DA instead of 15 mmol/100g seems to result in an even wider molecular weight distribution, however, more experiments are required in order to fully confirm this observation. The presence of rubber chains of smaller molecular weight at higher DA concentration might be related to capping of the rubber radicals by DPDS during the devulcanization, instead of recombination with other radical rubber chains. In order to obtain more insight in the process, additional experiments are conducted in paragraph 4.4.

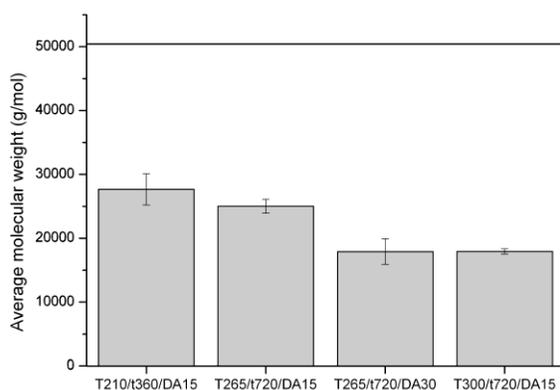


Figure 9. Indicative estimated average molecular weight of SBR chains based on GPC measurements of THF extracts of carbon black filled SBR devulcanized under various conditions

In order to enhance the understanding of the devulcanization process, a mechanism for the devulcanization is depicted in Figure 10, Figure 11, and Figure 12.

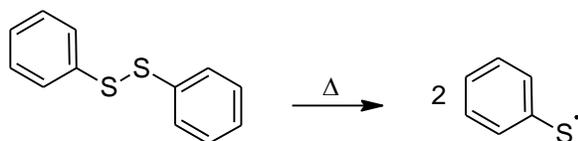


Figure 10. Dissociation of DPDS

Under heat, DPDS dissociates, leading to formation of thiophenol radicals. The SBR that is subjected to heat and shear stress, gives scission of crosslinks (Figure 11: 1.) and scission of the main chain (Figure 11: 2.). The thiophenol radicals can subsequently react with the radical chains. Furthermore, radical rubber chains can recombine with each other or with other chains, potentially leading to extension of the rubber chains. When DPDS penetrates into the rubber network, it can also directly react with sulphur bridges (Figure 12), transferring the radical to the rubber chain while creating sol.

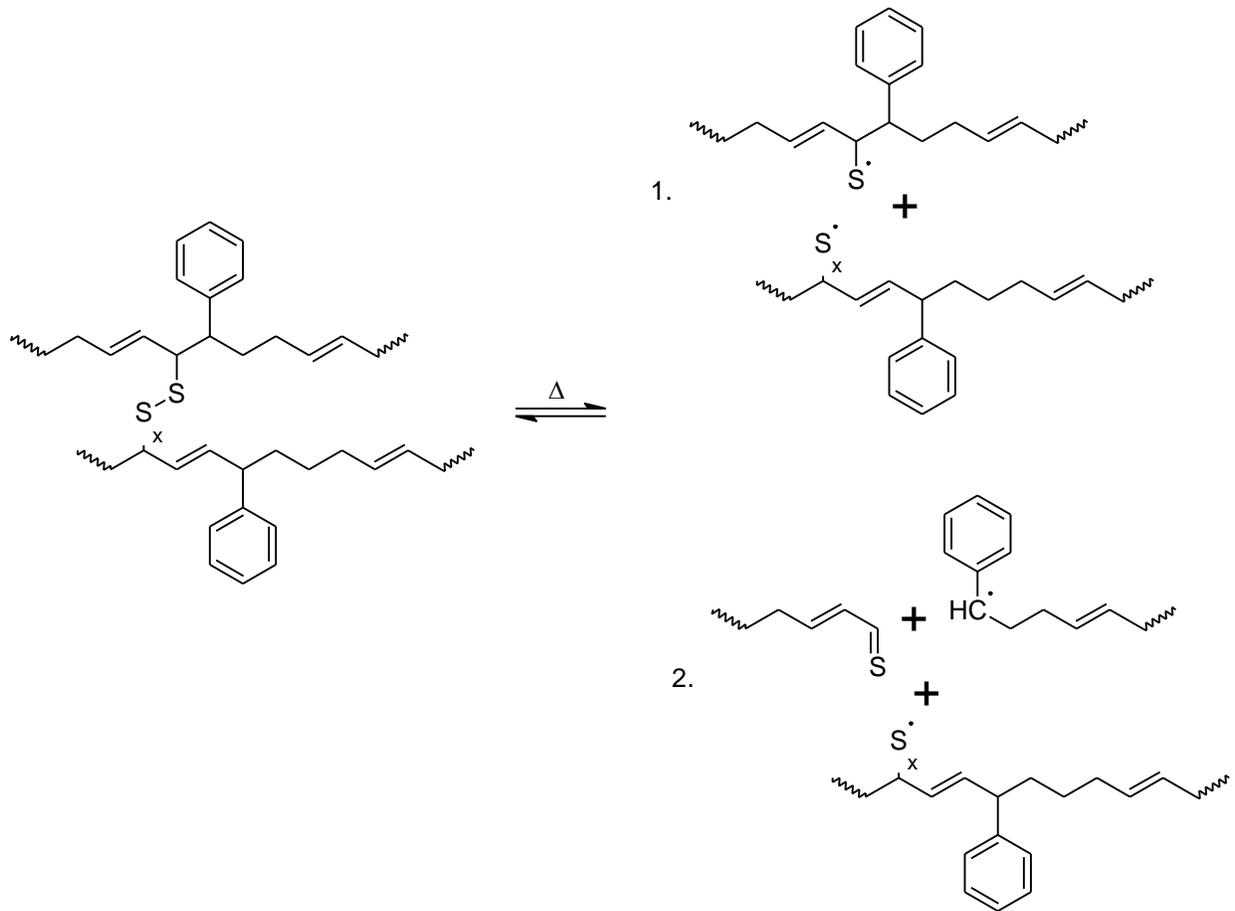


Figure 11. Scission of crosslinks (1.) versus a combination of crosslink scission and main chain scission (2.)

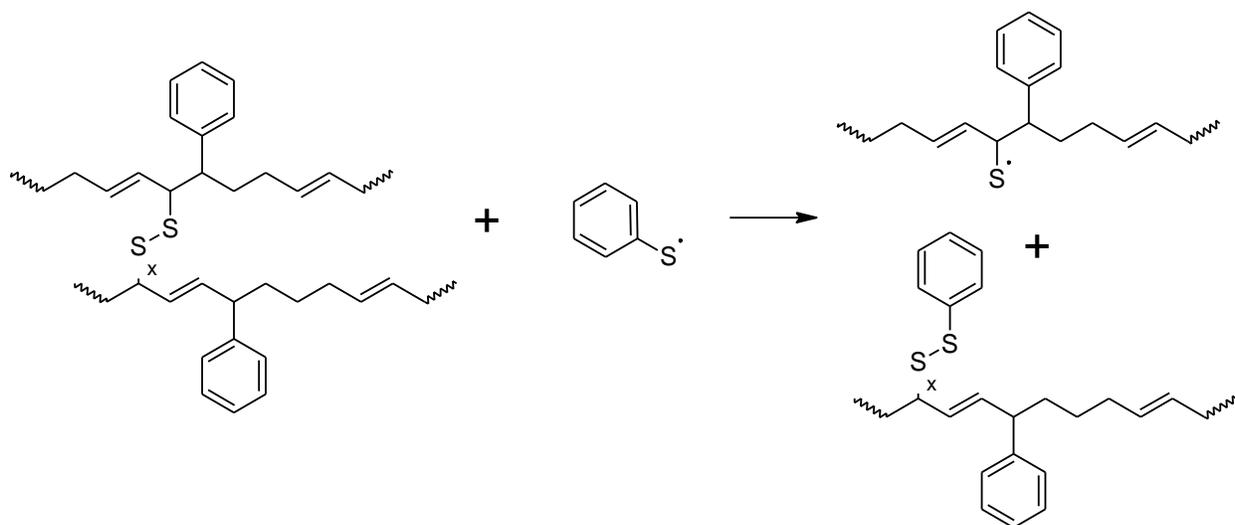


Figure 12. Devulcanization reaction of SBR by DPDS

4.2 Crosslink density

The crosslink density of the masterbatch was found to be $1.97\text{E-}4 \text{ mol/ cm}^3$. Figure 13 displays model predictions for the crosslink density of the devulcanized SBR for different DA concentrations. As shown, processing time has no significant effect on the crosslink density. Nevertheless, crosslink density increases with devulcanization temperature. This increasing effect becomes more pronounced at higher DA concentrations, leading to the highest crosslink density ($4.73\text{E-}4 \text{ mol/cm}^3$) at a processing time of 13 minutes, in combination with the highest temperature (270°C), and the highest concentration DA (45 mmol/100g). In Figure 14, model predictions of devulcanization at 200 and 270°C are displayed. As shown, a minor decrease in crosslink density with increasing DA concentration is obtained at 200°C , while at 270°C the opposite effect becomes apparent. At this higher temperature, the crosslink density increases linearly with the DA concentration. Contrarily to our findings, in literature crosslink density was found to decrease with increasing temperature and DA concentration for NR [76] and EPDM-rubber [78]. Dijkhuis [61] found that processing time of EPDM-rubber had no significant impact on the crosslink density of conventionally vulcanized EPDM-rubber, while a minor effect was identified for efficiently vulcanized samples. Moreover, conventionally vulcanized EPDM-rubber displayed a slight increase in crosslink density with increasing temperature at low DA concentration, as well as in absence of DA. However, at higher DA concentrations, the effect of temperature became unnoticeable. For the efficiently vulcanized EPDM-rubber, crosslink density was found to significantly increase with increasing DA concentration at high temperature (270°C). Contrarily, a decreasing trend was obtained at lower temperatures (230°C). Furthermore, crosslink density was found to increase with temperature at high DA concentrations (10 wt\%), while at low DA concentrations and in absence of DA, a slight decrease in crosslink density was obtained when increasing the temperature.

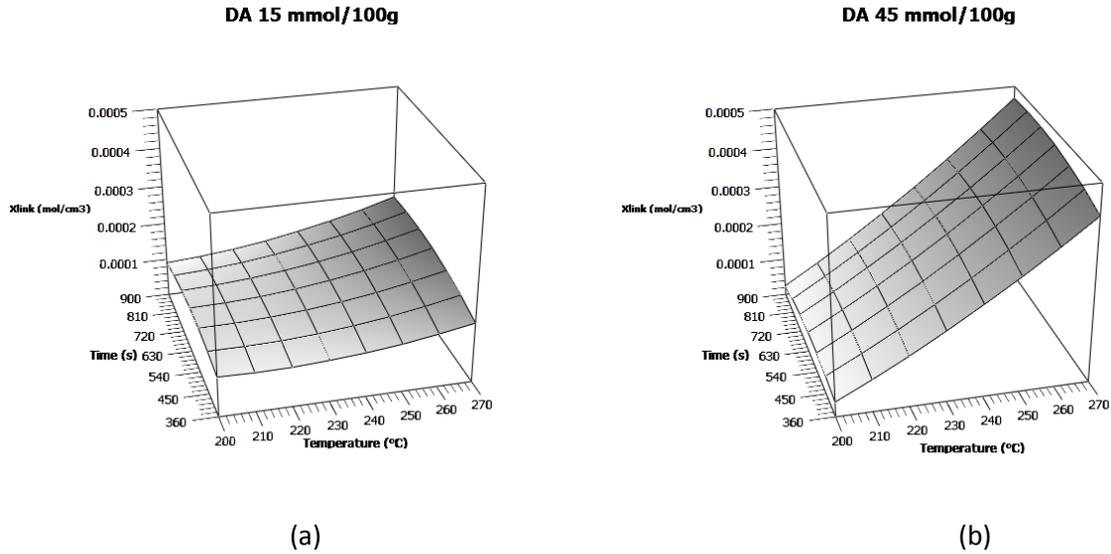


Figure 13. Prediction of crosslink density based on empirical model for devulcanization with 15 mmol/100g DA (a) and 45 mmol/100g (b).

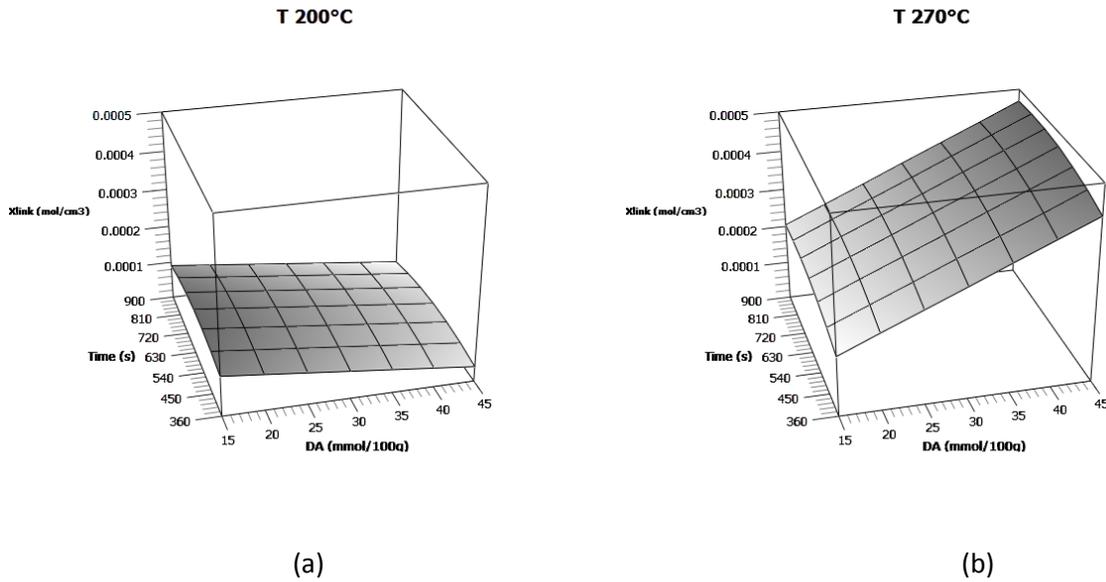


Figure 14. Prediction of crosslink density based on empirical model for devulcanization at 200°C (a), and 270°C (b).

The undesirable effect of an increasing in crosslink density when increasing the amount of DA is difficult to explain. This trend was not obtained for devulcanization experiments conducted at the University of Twente, with unfilled SBR. Assuming the onion model for devulcanization, i.e. devulcanization occurs on the surface area of rubber particles, it might be possible to explain a slight increase in crosslink density. A schematic representation of a rubber particle is shown in Figure 15. The darker colour of the core of the particle corresponds with a higher crosslink density. The crosslink density measurements are conducted with the gel fraction of the samples. Therefore, the outer layers of the rubber particles will be devulcanized and soluble, leaving the core of the particles for the crosslink density measurements.

The crosslink density of the core of the particles is expected to be higher, leading to higher obtained crosslink densities. In this case, a higher degree of devulcanization leads to an increase in sol fraction, leaving less of the outer shells of the particle intact. This might explain to a certain degree why an increase in crosslink density was obtained for devulcanized samples that were, based on visual inspection, found to have a structure that was better comparable to virgin rubber.

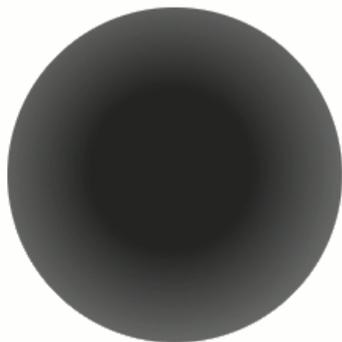


Figure 15. Rubber particle according to the onion model

Moreover, CB is known for its radical scavenging activities [79] and CB is found to trap peroxide radicals, leading to a crosslinked network structure [80]. Hirayama and Saron [81] measured the effect of CB loading on the crosslink density. The crosslink density was found to increase proportionally to the CB content. Samples devulcanized by microwave devulcanization displayed an increase in crosslink density, except for the highest CB loading (100 phr). The authors attributed this effect to a chemical equilibrium between formation and breakage of crosslinks. Heating of the material became more pronounced at higher CB content, due to the dielectric constant of CB. In Figure 16, a mechanism is proposed for the transfer of radicals between SBR chains and CB. Due to dissociation, incorporation of more DPDS into the process leads to the generation of more radicals. These radicals might be transferred to the CB, or to the SBR. The former is energetically favoured, however, if large quantities of radicals are present, the latter will occur simultaneously. Additionally, CB can supply the radicals to the SBR chains as well. Due to these transfers, SBR radicals have a shorter lifetime. This shorter lifetime might favour recombination of SBR chains instead of capping of SBR radicals by DPDS. This preliminary proposed mechanism indeed explains the increase in crosslink density obtained when increasing temperature on the one hand, and DPDS concentration on the other hand. In order to investigate whether the decomposition of the DA occurs at a significantly higher rate than its diffusion and whether recombination is favoured compared to capping, additional experiments with for instance rubber particles of different sizes have to be conducted. In order to gain some insight in the effect of CB during the devulcanization process, extra experiments with CB are conducted. The results are described in paragraph 4.4.

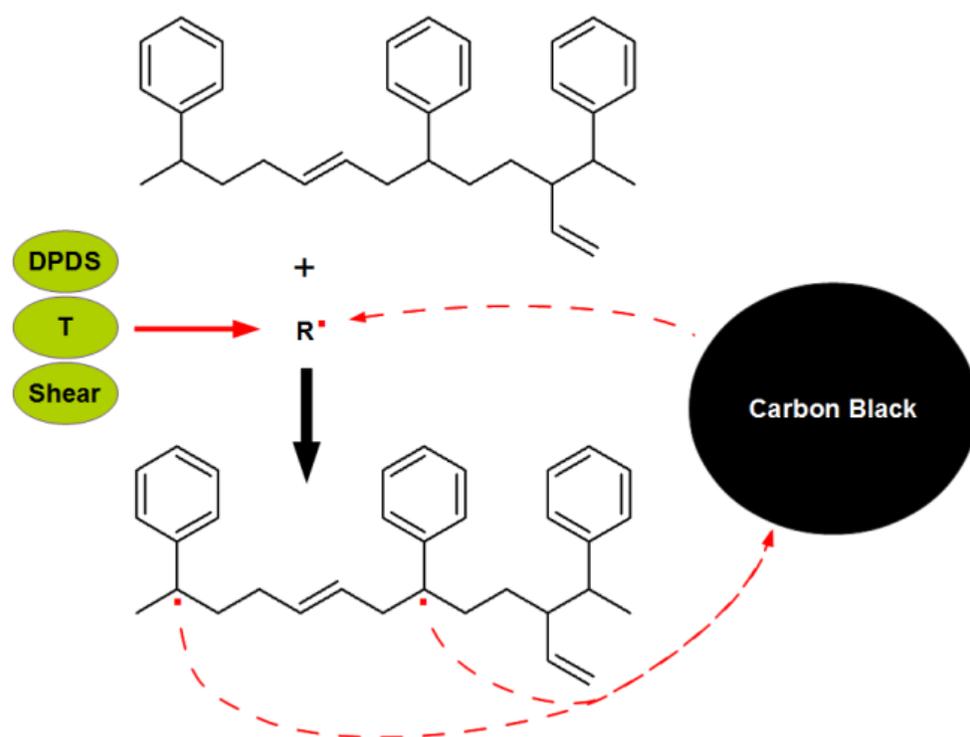


Figure 16. Radical transfer between SBR chains and CB

4.3 Accuracy of crosslink density measurements

In order to investigate the accuracy of the crosslink density experiments, samples that were devulcanized in duplo are used in some simple calculations. Crosslink density was measured by swelling of samples in toluene, whereby the solvent uptake was taken as a measure of the number of crosslinks per unit of volume. Several samples were used for the construction of an empirical model, however, the accuracy of these measurements was not directly considered. Since an increase in crosslink density was obtained as function of temperature, as well as DA concentration, experiments that were conducted in duplo are considered for additional analysis. The obtained crosslink densities are depicted in Table 20.

Table 20. Overview of crosslink density of samples used for additional analysis

	No	T	t	DA	W _{rubber} (g)	W _{toluene} (g)	V _R	χ	X _{apparent}	W _{0_rubber}	ϕ	X _{actual}
Series 1	11	210	360	15	0.3	0.93	0.22	0.46	1.19E-04	0.46	0.25	9.22E-05
	21	210	720	15	0.32	0.95	0.23	0.46	1.31E-04	0.5	0.26	1.00E-04
	31	210	360	30	0.32	0.9	0.24	0.46	1.48E-04	0.5	0.26	1.14E-04
	41	210	720	30	0.32	0.88	0.24	0.46	1.55E-04	0.52	0.27	1.18E-04
	51	265	720	0	0.34	0.95	0.24	0.46	1.47E-04	0.47	0.23	1.16E-04
	61	265	360	15	0.26	0.64	0.26	0.45	1.98E-04	0.46	0.29	1.47E-04
	71	265	720	15	0.24	0.52	0.29	0.44	2.68E-04	0.42	0.29	2.00E-04
	81	265	360	30	0.27	0.47	0.33	0.43	4.29E-04	0.5	0.31	3.16E-04
	91	265	720	30	0.25	0.42	0.35	0.43	4.97E-04	0.49	0.32	3.61E-04
Series 2	12	210	360	15	0.28	0.8	0.23	0.46	1.43E-04	0.43	0.25	1.10E-04
	22	210	720	15	0.3	0.81	0.24	0.45	1.61E-04	0.47	0.26	1.23E-04
	32	210	360	30	0.31	0.88	0.24	0.46	1.45E-04	0.5	0.27	1.11E-04
	42	210	720	30	0.29	0.78	0.25	0.45	1.65E-04	0.48	0.27	1.25E-04
	52	265	720	0	0.36	0.91	0.25	0.45	1.85E-04	0.49	0.23	1.46E-04
	62	265	360	15	0.3	0.76	0.25	0.45	1.84E-04	0.53	0.29	1.37E-04
	72	265	720	15	0.28	0.68	0.27	0.45	2.19E-04	0.5	0.29	1.63E-04
	82	265	360	30	0.28	0.57	0.3	0.44	3.11E-04	0.53	0.31	2.27E-04
	92	265	720	30	0.31	0.54	0.33	0.43	4.24E-04	0.57	0.31	3.11E-04

The error on the calculated crosslink density values would yield relevant information regarding differences in the actual crosslink densities of samples devulcanized under different conditions.

At first, a measure for the error on the toluene measurements has to be identified. Samples are weighed on a balance, of which the error is assumed to be 0. The error in the density of toluene and rubber, and the weight of the rubber is assumed to be 0 as well. V_R is a direct measure of the volume of rubber in the swollen samples, and is therefore highly depending on the crosslinking degree of the rubber. All samples devulcanized under similar conditions are paired and some calculations based on their respective V_R values are conducted. The results are shown in Table 21.

Table 21. Calculations based on volume fraction of rubber (V_R)

T	t (s)	DA	V_{Rx1}	V_{Rx2}	Average V_R	$V_{Rx1} - V_{Rx2}$	$abs(V_{Rx1} - V_{Rx2})$
210	360	15	0.22	0.23	0.23	-0.013	0.013
210	720	15	0.23	0.24	0.24	-0.015	0.015
210	360	30	0.24	0.24	0.24	0.002	0.002
210	720	30	0.24	0.25	0.24	-0.005	0.005
265	720	0	0.24	0.25	0.25	-0.018	0.018
265	360	15	0.26	0.25	0.26	0.006	0.006
265	720	15	0.29	0.27	0.28	0.018	0.018
265	360	30	0.33	0.30	0.32	0.032	0.032
265	720	30	0.35	0.33	0.34	0.017	0.017

St. dev. 0.0091

Average 0.0139

Since no relation is found for the absolute difference in the measurements as function of the weight of the rubber subjected to these measurements, normalizing the V_R has no beneficial effect on the results. The standard deviation and the average (AV) of the absolute difference of the V_R of both series were calculated.

In order to calculate the error on the calculated V_R values, a conservative assumption was made. Hereby, the error was assumed to equal the difference between the two calculated values for V_R . Two new series were created, one with V_{R_min} :

$$V_{R_min} = average (V_{Rx1} + V_{Rx2}) - AV \quad (6)$$

And one with V_{R_max} :

$$V_{R_max} = average (V_{Rx1} + V_{Rx2}) + AV \quad (7)$$

The V_R values are subsequently subjected to the Flory-Rehner equation, in order to calculate the apparent crosslink density. The resulting ranges of crosslink densities are displayed in table Table 22.

Table 22. Estimated range for the apparent crosslink density

T	t	DA	$X_{\text{apparent min}}$	$X_{\text{apparent max}}$
210	360	15	1.07E-04	1.57E-04
210	720	15	1.20E-04	1.74E-04
210	360	30	1.21E-04	1.76E-04
210	720	30	1.33E-04	1.91E-04
265	720	0	1.38E-04	1.97E-04
265	360	15	1.60E-04	2.25E-04
265	720	15	2.06E-04	2.83E-04
265	360	30	3.17E-04	4.21E-04
265	720	30	4.01E-04	5.23E-04

Since the rubber used in this research is a filled rubber, the Kraus correction has to be applied. The Kraus correction, however, considers the initial weight of the rubber in order to calculate the filler ratio. In order to stay conservative, measured weights are used to maximize the obtained range. Therefore, among the two samples devulcanized under similar conditions, for the lower range the value that results in the highest decrease in that range was chosen. Consequently, for the higher range the value that results in the highest increase in that very range was used. An overview of the resulting actual crosslink densities is shown in Table 23.

Table 23. Estimated range for the actual crosslink density

T	t	DA	Lower Xlink	Upper Xlink	Average	Δ
210	360	15	8.14E-05	1.23E-04	1.02E-04	2.10E-05
210	720	15	9.03E-05	1.33E-04	1.12E-04	2.16E-05
210	360	30	9.25E-05	1.37E-04	1.15E-04	2.21E-05
210	720	30	9.86E-05	1.48E-04	1.23E-04	2.47E-05
265	720	0	1.06E-04	1.58E-04	1.32E-04	2.60E-05
265	360	15	1.15E-04	1.70E-04	1.43E-04	2.77E-05
265	720	15	1.46E-04	2.20E-04	1.83E-04	3.69E-05
265	360	30	2.24E-04	3.13E-04	2.68E-04	4.44E-05
265	720	30	2.96E-04	4.12E-04	3.54E-04	5.77E-05

The Δ corresponds with the difference between the obtain crosslink density value and the average value. The results are plotted in Figure 17, and the average of the two samples is plotted as well, along with the standard deviation based on the two samples per condition. As shown, the error range that is estimated increases as function of the crosslink density. Furthermore, results indicate that samples devulcanized at 265°C with 30 mmol/100g DA display a higher crosslink density than the other samples, however, the latter was not verified statistically. The chance that the sample with the highest obtained crosslink density (T265/t360/DA30) actually has the same crosslink density as the sample with the

lowest obtained crosslink density (T210/t360/DA15) is negligible judging the difference between the conservatively estimated ranges.

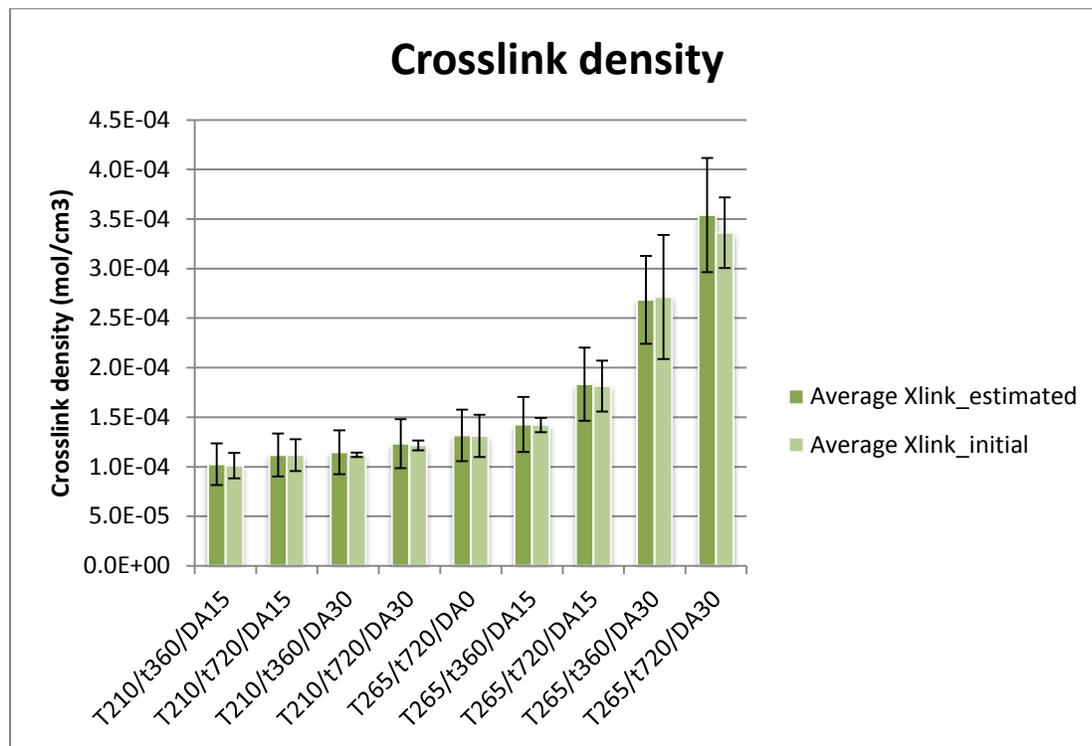


Figure 17. Estimated crosslink density range

4.4 Carbon black experiments

In order to investigate the effect of CB during devulcanization, additional experiments are conducted. Virgin SBR was processed in the Brabender batch reactor in presence and in absence of CB and DA. The product was subsequently extracted in order to determine the sol fraction and calculate bound rubber. On top of that, the sol fraction was subjected to GPC measurements on a column appropriate for measuring the molecular weight of the rubber in order to determine the molecular weight of the samples.

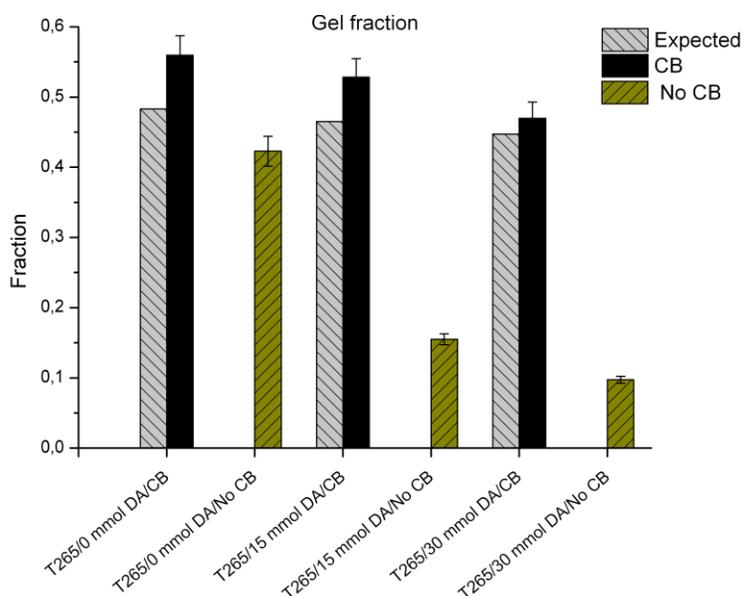


Figure 18. Effect of carbon black (CB) and concentration devulcanization agent (DA) on the gel fraction of unvulcanized SBR processed at 265°C. 'Expected' is calculated based on fraction of SBR chains, oil and DA, compensated for bound rubber.

In Figure 18, the gel fractions resulting of processing SBR in presence and absence of CB and in presence and absence of DA are displayed. SBR chains, processing oil, and DA are expected to be extractable. The grey bars are related to the expected unextractable fraction, namely CB along with bound rubber. Samples containing no CB are expected to yield no gel fraction. Samples processed in presence of CB display a slightly higher gel fraction than expected. Therefore, some recombination of radicals produced during the processing occurs, leading to the formation of very long chains that are not extractable in THF. At 265°C, a minor decrease in gel fraction was obtained for filled rubber when increasing the concentration DA from 0 to 30 mmol/100g. During the devulcanization experiments, a decrease in crosslink density with increasing DA concentration was only obtained at low temperatures (up to ca. 200°C). At higher temperatures, crosslink density was found to increase with increasing the DA concentration. The decrease in gel fraction in the CB experiments is obtained at 265°C, which might indicate that due to differences in exact composition of the blend, the temperature required to obtain an increase in crosslink density (or gel fraction) with increasing DA concentration is relatively higher compared to the devulcanization experiments. In absence of CB the effect of the concentration DA on the gel fraction is more pronounced. Increasing the DA concentration from 0 – 30 mmol led to a significant decrease in gel fraction. These results indicate that DPDS is a successful radical scavenger in gum rubber, however, in CB filled rubber the effectiveness of this scavenging reaction is decreased.

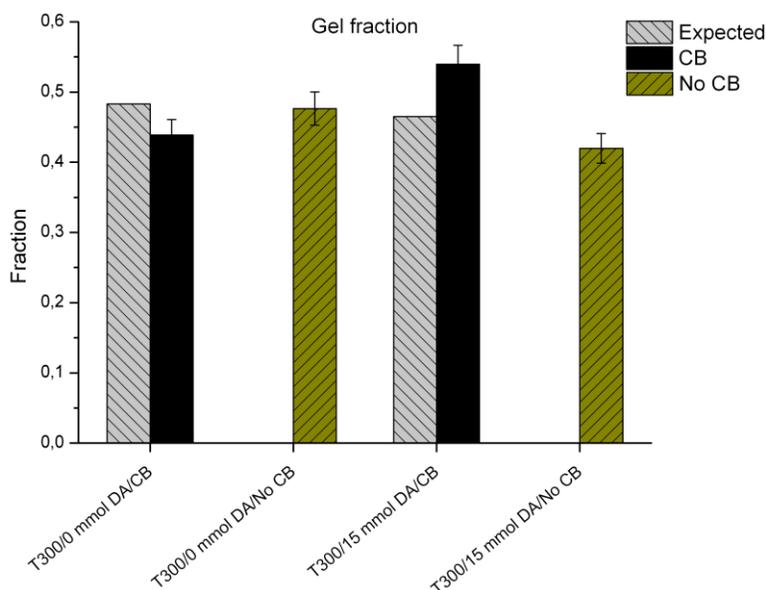


Figure 19. Effect of carbon black (CB) and concentration devulcanization agent (DA) on the gel fraction of unvulcanized SBR processed at 300°C. 'Expected' is calculated based on fraction of SBR chains, oil and DA, compensated for bound rubber.

In Figure 19, an overview of the gel fraction of samples of unvulcanized rubber processed at 300°C in presence and absence of CB and DA is displayed. The gel fraction was found to increase slightly when adding 15 mmol DA in presence of CB. This trend was also obtained during devulcanization experiments, however, already at lower temperatures an increase in crosslink density with increasing the DA concentration was obtained. In absence of CB, a minor decrease in gel fraction was identified. This effect however, was less pronounced than for experiments conducted at 265°C. The results seem to demonstrate that the DA is not an effective devulcanization agent at high temperatures (300°C). Furthermore, the results indicate that increasing the temperature from 265 to 300°C in absence of CB and DA leads to a slight increase in gel fraction, which is attributed to recombination of radical SBR chains, which becomes more pronounced at higher temperatures. In CB filled SBR, this effect turns around leading to a lower gel fraction at 300°C. This effect might be related to enhanced main chain degradation, leading to the formation of smaller fragments which adsorb at or react with CB. In presence of DA, however, gel fraction is found to increase at 300°C, attributed to recombination, enhanced by extra radicals in the system provided by the DA. These results correspond with the trend observed during devulcanization experiments, namely an increase in crosslink density when devulcanizing the rubber at high temperatures in presence of DA.

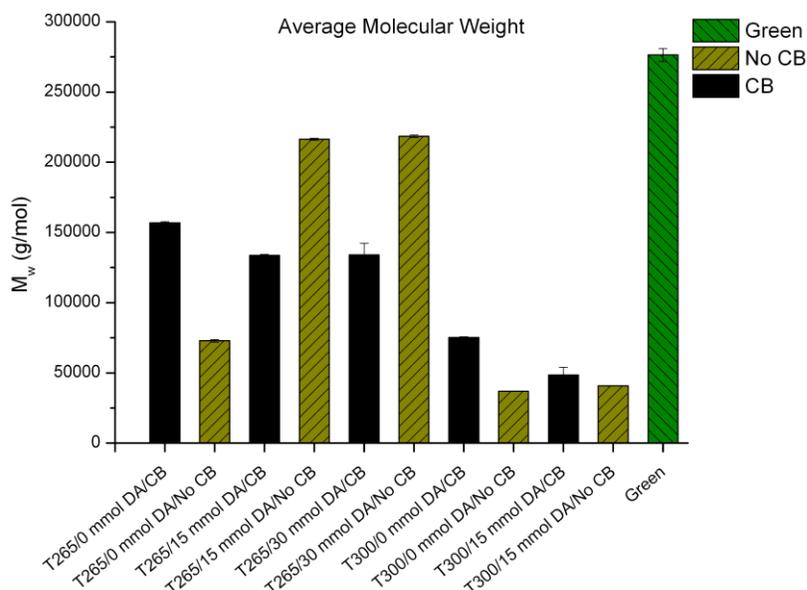


Figure 20. Average molecular weight of the sol fraction of unvulcanized SBR processed in presence and absence of carbon black (CB) and devulcanization agent (DA).

In Figure 20, an overview of the average molecular weight of the sol fraction of unvulcanized rubber treated in the Brabender batch reactor is displayed. The average molecular weight of green SBR is also shown for comparison. Samples treated at 265°C in presence of CB display a reduction in average molecular weight of approximately 50%, i.e. an average of one main chain scission per chain. The obtained decreases for the molecular weight of the extractable chains is higher than values obtained in literature, namely a decrease of 40% for EPDM devulcanized in a twin-screw extruder under various conditions [82]. Furthermore, samples devulcanized at 300°C were found to have an average molecular weight of 50% of the green rubber [83]. Similarly to our results, a broader molecular weight distribution was reported. In our research, filled samples processed at 265°C displayed a decrease in molecular weight of the sol fraction of 43 – 52%, while at 300°C, a decrease of 73 – 82% was found. In presence of CB, the concentration of DA was not found to have a strong effect at the degradation at 265°C. For gum SBR, however, incorporation of only 15 mmol/100g DA was found to prevent the majority of degradation of the molecular weight of the sol fraction at 265°C. Adding additional DA did not result in higher molecular weight of the sol fraction. Increasing the temperature from 265 to 300°C led to significantly higher degradation of the main chain. This indicates that a temperature of 300°C is too high for processing of SBR and devulcanization processes should be operated at lower temperatures. Again, CB was found to strongly affect the devulcanization process. In absence of DA, filled samples processed at 265°C displayed a higher molecular weight than gum rubber. This is expected to be related to crosslinking of SBR chains during processing. Gum rubber was found to crosslink during processing, mainly in absence of DA. The crosslinking leads to a three dimensional network, which is not extractable in THF. This corresponds with the high gel fraction for this sample found during the extraction. When 15 mmol/100g DA is incorporated into the mixture, the molecular weight of the sol fraction for gum rubber increases by a factor three, while the molecular weight of the CB filled rubber slightly decreases. SBR radicals are relatively stable and thus have a relatively long lifetime. In presence of DA, however, the

lifetime of radicals is reduced. In gum rubber, a large share of degradation is therefore prevented by DA. In filled rubber, radicals are expected to cycle between SBR chains and CB, leading to a shorter lifetime of SBR radicals, thereby influencing the ratio between capping by DPDS and recombination with other SBR radicals. Furthermore, longer chains might be more prone to physical and chemical adsorption onto CB, leaving shorter chains extractable. Again, these results indicate the radical scavenging capabilities of DPDS are mainly present in gum rubber.

5. Conclusions

SBR was devulcanized by DPDS in a batch reactor. An empirical model was created, which is capable of displaying the relation between process parameters and the resulting sol fraction and crosslink density of the SBR in the range studied. Sol fraction was found to increase with devulcanization temperature and DA, however, the effect of DA becomes more pronounced at higher temperatures. Crosslink density was found to increase with devulcanization temperature, however, DA was found to enhance this increasing trend at higher temperatures. Additional processing of gum rubber in presence and absence of CB and DA was conducted in order to determine their effect on the gel fraction and molecular weight of the sol fraction. In absence of CB, DA was found to be an effective radical scavenger. In filled SBR, however, DPDS was found to be less effected, which is attributed to a reduced lifetime of the SBR radicals. Furthermore, a temperature of 300°C was found to be too high for successful devulcanization of SBR.

Chapter 3. Revulcanization of Devulcanized Carbon Black Filled Styrene Butadiene Rubber

In this chapter, SBR that was devulcanized according to the method described in chapter 2 is blended with virgin rubber and curatives, and subsequently subjected to a revulcanization process.

1. Abstract

Carbon black (CB) filled styrene butadiene rubber (SBR) was devulcanized with diphenyl disulphide (DPDS) and subsequently blended with virgin SBR and revulcanized. Mechanical properties of revulcanizates containing 40 – 60% devulcanized rubber were measured. Temperature during the devulcanization process was not found to have a significant influence on the mechanical properties of the revulcanizates. As expected, mechanical properties of revulcanizates containing 40% devulcanized rubber were preferable over revulcanizates containing 60% devulcanized rubber. With the outlined method it was possible to vulcanize a revulcanizate containing 40% devulcanized SBR which retained 94% of tensile strength, 132% of elongation at break, and 81% of shore A hardness compared to a reference SBR sample.

2. Materials and methods

2.1 Materials

A Styrene Butadiene Rubber (SBR) masterbatch (sieve size 2 mm) was kindly produced by LANXESS (Geleen), according to the following recipe:

SBR 1723 ³	137.5	phr
Carbon black N-326	70	phr
TBBS	2	phr
TMTD-80	1	phr
S-80 (R. S) 80 %	2.5	phr
ZnO (UM)	3	phr
Stearic acid	2	phr
CaO-80 (K. GR/DAB)	7.5	phr

Diphenyl disulphide (DPDS) (99%) was obtained from Acros and used as a devulcanization agent (DA). Treated Distillate Aromatic Extract (TDAE) oil obtained from Vredestein (Enschede) was used as a plasticizer. Acetone (pure) was obtained from Acros and used without further purification. Toluene (pure) was obtained from Acros and used without further purification.

Carbon black (CB N-375), N-tertbutyl-2-benzothiazole (TBBS), and Tetramethylthiuram Disulphide (TMTD-100) were used as received. Sulphur (S-100), zinc oxide (ZnO), and stearic acid were obtained from Sigma-Aldrich. SBR 1723 (containing 37.5 phr processing oil) was obtained from LANXESS.

³ SBR 1723 contains 100 phr SBR and 37.5 phr processing oil

2.2 Equipment

A Brabender Plasti-Corder mixer, equipped with a 370cc chamber was used for the devulcanization experiments. Compounding of the devulcanized rubber with curatives and fresh rubber was executed on a Brabender Plasti-Corder mixer (PL2000), equipped with a 35cc chamber. A two-roll mill was used for additional compounding of this rubber blend. Cure time was measured on an Alpha RPA. A Wickert WLP1600 press was used to (re)vulcanize samples. Shore A Hardness of the vulcanizates was measured with a Zwick Hardness-tester. A Tinius Olsen H25KT tensile testing apparatus equipped with a 1kN loadcell was used for measuring the tensile strength and elongation at break of the vulcanizates. Extraction of low molecular weight compounds from the vulcanized samples was realized with a Soxtec type 2043 extraction unit.

2.3 Rubber devulcanization

Samples of the rubber compound were treated in a Brabender batch mixer, according to a fill factor of 0.7. The compounds consisted of vulcanized, filled SBR and a mixture of TDAE oil and DPDS. TDAE oil concentration was 5 wt% of the total amount of compound, DPDS was used in concentrations of 15 up to 30 mmol per 100g compound. The mixture of TDAE oil and DPDS was dispersed on the rubber particles and the compound was left to swell for a while. Thereafter, the compound was added to a preheated Brabender batch mixer, of which the chamber was depleted of oxygen by addition of nitrogen gas. The Brabender was operated at a rotational speed of 50 RPM and devulcanization time was kept constant at 6 minutes. After devulcanization, the mixer was opened and the treated rubber compound was collected and quenched with liquid nitrogen.

2.4 Rubber revulcanization

Devulcanized SBR compound and fresh SBR were added to a Brabender batch mixer, operated at 60°C and 60 RPM. After 1 minute of blending, ZnO and stearic acid were added. After one additional minute, carbon black (CB) and TDAE oil were added to the mixture. Three minutes later TBBS and TMTD-100 were appended, followed 1 minute later by sulfur. The compound was blended for two additional minutes and subsequently transferred to a two-roll mill in order to process it for a couple of minutes until a uniform slab of rubber was obtained.

Samples were left to rest overnight before the cure characteristics were determined. Samples were pressed at 170°C at 100 bar for t_{95} (time to reach 95% of maximum viscosity) + 5 minutes.

2.5 Revulcanization recipes

All curatives in the devulcanized blend were assumed to be deactivated and were added freshly to the compound to be revulcanized. Calcium oxide, which is used for drying of the rubber, was not added to the compounds. The adjusted recipes are depicted in Table 24. It has to be mentioned, the master batch used in the revulcanization was compounded over a year before the actual vulcanization.

Table 24. (Re-)vulcanization recipes

	Master batch	Reference	D-60	D-40	
D-compound	0	0	147.5	98.33	phr
SBR	100	100	40	60	phr
ZnO	3	3	3	3	phr
Stearic acid	2	2	2	2	phr
CB N-375	0	70	28	42	phr
CB N-326	70	0	0	0	phr
TDAE	37.5	37.5	15	22.5	phr
TBBS	2	2	2	2	phr
TMTD-80	1	0	0	0	phr
TMTD-100	0	0.8	0.8	0.8	phr
S-80	2.5	0	0	0	phr
S-100	0	2	2	2	phr
CaO-80	7.5	0	0	0	phr

2.6 Analysis

The revulcanized samples were analyzed by crosslink density, shore A hardness, tensile strength, and elongation at break.

2.6.1 Crosslink density

Revulcanized rubber was extracted in a Soxhlet apparatus by boiling for 4 hours with acetone followed by 4 hours of rinsing. The remaining rubber was immersed in toluene and shaken for 72 hours. The samples were dried in a vacuum stove until constant weight. The apparent crosslink density was calculated by the Flory-Rehner equation [69]. However, the Flory-Rehner equation is only valid for non-filled rubbers. Therefore the Kraus correction has to be applied in order to calculate the actual crosslink density [70].

The apparent crosslink density was calculated as follows:

$$X_{\text{apparent}} = \frac{\ln(1-V_R)+V_R+\chi V_R^2}{V_S(0.5V_R-V_R^{\frac{1}{3}})} \left(\frac{\text{mol}}{\text{cm}^3}\right) \quad (8)$$

Whereby V_R is the volume fraction rubber in the swollen sample, V_S is the molar volume of toluene, which is $106.2 \text{ cm}^3/\text{mol}$, and χ is the Flory-Rehner interaction parameter, which is $0.524 - 0.285V_R$ for Toluene/SBR [71].

In simplified form the Kraus correction is given by [72]:

$$X_{\text{actual}} = \frac{X_{\text{apparent}}}{1+C \times \phi} \quad (9)$$

Whereby C is constant for a certain filler and ϕ is the volume fraction of filler in the compound.

$$\phi = \frac{\text{weight fraction filler} \times \text{density of rubber compound} \times \text{sample weight before extraction}}{\text{density of filler} \times \text{weight of compound before swelling}} \quad (10)$$

$$C = 1.17 [73] \quad (11)$$

2.6.2 Shore A Hardness

Shore A hardness of piles containing four layers vulcanized rubber slab was measured. The samples were tested at a Zwick Hardness-tester Shore A type according to DIN 53503. Samples were tested in three-fold and the average hardness and standard deviation were calculated.

2.6.3 Tensile strength and elongation at break

Dumb-bell shaped specimens were cut from the vulcanized rubber sheet according to ISO 37 (type 2). A Tinius Olsen H25KT tensile testing apparatus equipped with a 1kN loadcell was used for measuring the tensile strength and elongation at break of the vulcanizates, at a crosshead speed of 500 mm/min. Tensile strength and elongation at break were calculated based on the results of 3 up to 7 samples, depending of the successfulness of the measurements (samples tended to break inside the clamp).

3. Results and discussion

Based on visual inspection, all revulcanizates containing rubber devulcanized at 270 and 300°C displayed a homogenous structure. The revulcanizates containing SBR devulcanized at 220°C showed a granular structure, indicating only partial compatibility of the revulcanized rubber with the fresh rubber matrix. An overview of the mechanical properties of these samples is displayed in Table 25.

Table 25. Overview of mechanical properties of revulcanizates produced according to the adjusted recipe

Sample	Tensile strength (Mpa)	Retention (%)	Elongation at break (%)	Retention (%)	Shore A Hardness	Retention (%)	Crosslink density (mol/cm ³)
Reference	19.0	100%	495	100%	66	100%	3.89E-04
40 % T220/15 mmol DA	17.6	93%	609	123%	54	82%	2.71E-04
60 % T220/15 mmol DA	13.4	71%	558	113%	49	74%	2.67E-04
40 % T270/15 mmol DA	18.0	94%	656	132%	54	81%	2.26E-04
60 % T270/15 mmol DA	13.2	70%	597	121%	47	72%	2.20E-04
40 % T300/15 mmol DA	17.5	92%	538	109%	55	83%	2.46E-04

3.1 Crosslink density

In Figure 21, an overview of the crosslink density of (re-)vulcanized samples is displayed. Samples containing devulcanized rubber were found to have a lower crosslink density compared to the reference sample containing solely fresh rubber. The exact quantity of devulcanized rubber incorporated into the revulcanizates in the range of 40 – 60%, and the temperature at which the rubber was devulcanized were not found to have a significant impact on the crosslink density of revulcanizates. Jalilvand et al. studied the devulcanization of unfilled EPDM rubber with diphenyl disulphide in a co-rotating twin screw extruder [84]. The devulcanized rubber was blended with curatives and subsequently revulcanized. Samples displayed in general lower crosslink density than the virgin sample, except for samples devulcanized under the mildest conditions (lowest temperature and rotational speed).

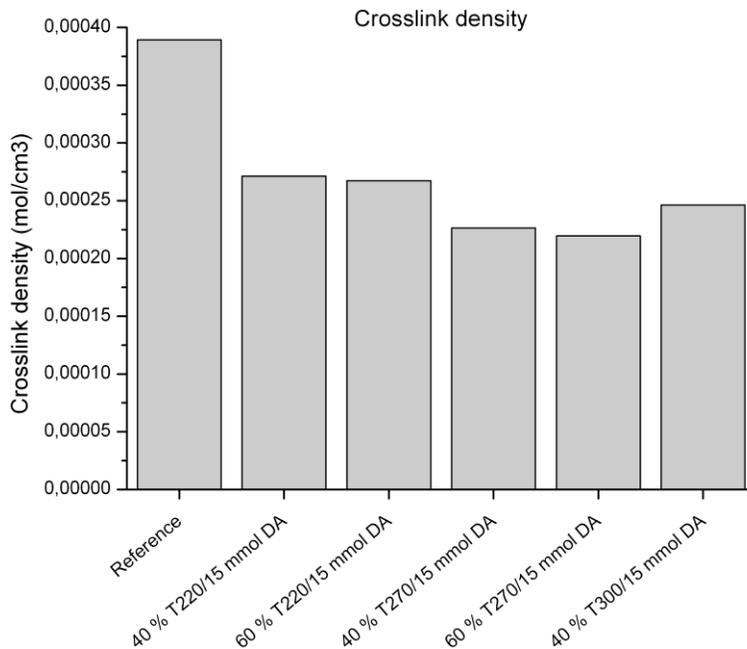


Figure 21. Crosslink density of (re-)vulcanizates

3.2 Shore A Hardness

The shore A hardness of (re-)vulcanizates was found to decrease compared to the freshly vulcanized sample. Furthermore, hardness was found to decrease with incorporating more devulcanized rubber into the revulcanizates. The decreasing trend when incorporating more devulcanized rubber into the revulcanizates was found to correspond with their respective decreasing crosslink densities.

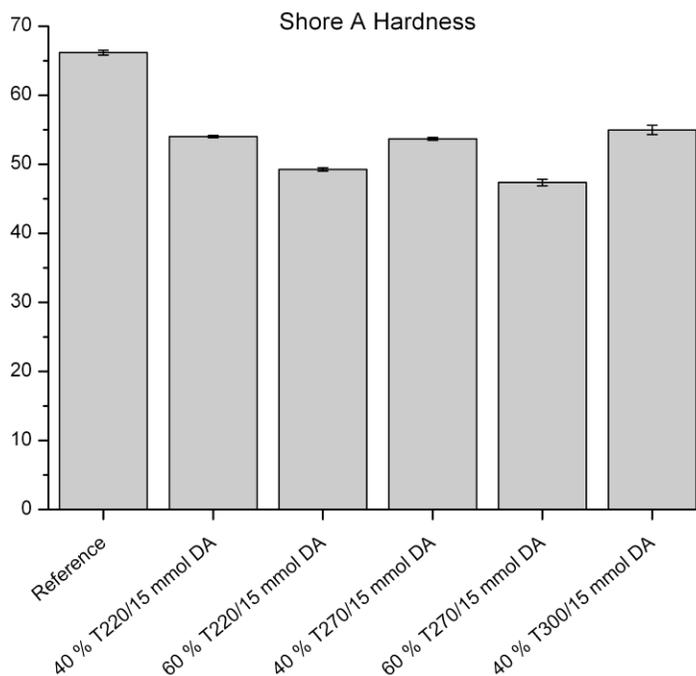


Figure 22. Shore A Hardness of (re-)vulcanizates

In literature, shore A hardness of revulcanizates containing 15% devulcanized rubber was found to be higher than that of a reference virgin sample, however, corresponding crosslink densities were higher for revulcanizates as well [85]. This higher crosslink density is expected to be related to overcuring of revulcanizates, leading to formation of more crosslinks and thus higher hardness of the rubber. Jalilvand et al. obtained a lower shore A hardness for revulcanized, unfilled, EPDM rubber [84]. A slightly decreasing trend was obtained for hardness when increasing the devulcanization temperature and increasing devulcanization agent content.

3.3 Tensile Strength

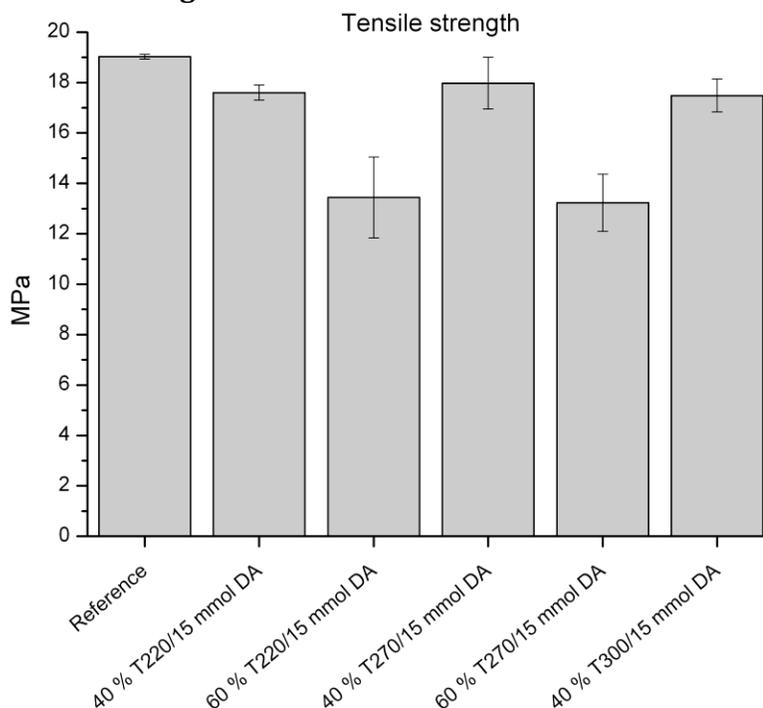


Figure 23. Tensile strength of (re-)vulcanizates

In Figure 23, the elongation at break of revulcanizates containing devulcanized rubber is shown. Devulcanization temperature was not found to have a noticeable effect on the tensile strength of the samples. The degree of incorporated devulcanized rubber on the other hand, was found to have a profound effect. Samples containing 60% devulcanized rubber instead of 40% displayed a tensile strength which was approximately 20 – 25% lower. Samples containing 40% devulcanized rubber displayed a tensile strength slightly lower than the reference sample. The revulcanizate with the best mechanical properties (containing rubber devulcanized at 270°C), displayed 94% retention of tensile strength compared to the reference sample.

Samples containing rubber devulcanized at 220°C were expected to yield lower mechanical properties due to their granular structure. Their performance, however, is comparable to the samples with a more homogenous structure. Due to the slightly higher crosslink density of the former, it is expected that the devulcanization process was to a greater extent a surface treatment, leading to devulcanization of the outer shells of the granules. These granules apparently display proper adhesion to the fresh rubber,

which is expected to be related to entangling of fresh rubber chains with devulcanized chains on the surface of the recycled rubber, along with formation of new sulphur bonds between the devulcanized chains and the fresh rubber.

Tensile strength of revulcanizates containing 15% devulcanized rubber (NR/SBR blend) was found to be lower than the virgin reference sample [85]. The applied conditions (temperature and screw speed) were found to have a significant influence on the crosslink density and the sol fraction of devulcanizates. Contrarily to our findings, the devulcanization conditions were found to have a profound effect on the tensile strength of revulcanizates, however, no general trend was obtained.

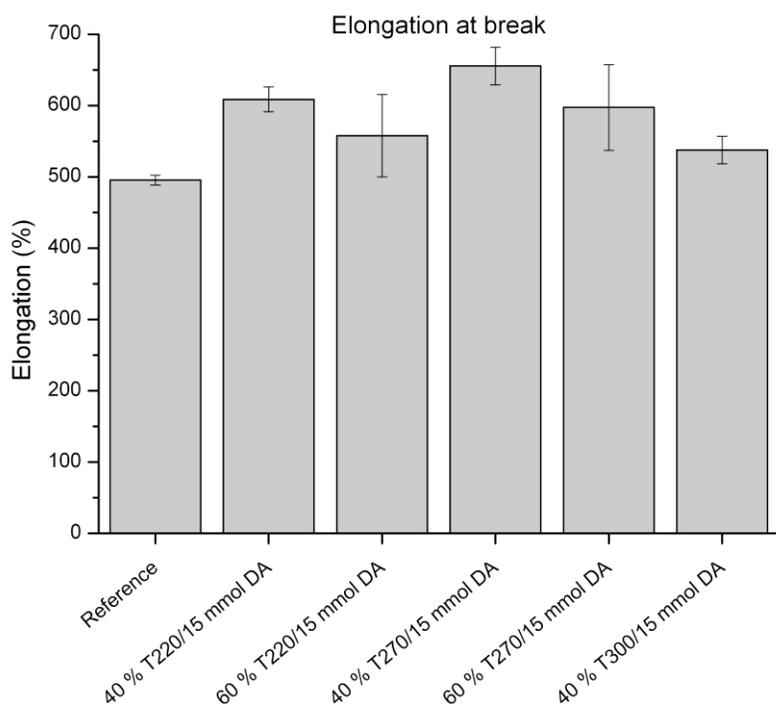


Figure 24. Elongation at break of (re-)vulcanizates

In Figure 24, an overview of the elongation at break of (re-)vulcanized samples is displayed. As shown, revulcanized samples display higher elongation at break than the reference sample. Samples containing 60% devulcanized SBR displayed a slightly lower elongation at break compared to sample containing 40% recycled rubber. This is an unexpected trend, since no continuous pattern is obtained when increasing the devulcanized rubber content from 0%. The obtained pattern, however, might be a coincidence and judging the error bars, the actual elongation at break values might be not significantly different. The revulcanizate containing rubber devulcanized at 270°C, displayed 132% retention of elongation at break.

In literature, NR/SBR blends containing CB were devulcanized in a twin-screw extruder [85]. In general, elongation at break of revulcanizates containing 15% devulcanized rubber was found to be higher than the reference virgin sample.

4. Conclusions

Re vulcanizates containing 40 – 60% devulcanized filled SBR were fabricated. Crosslink density, shore A hardness, tensile strength, and elongation at break of the samples were measured. The exact devulcanization temperature was found to have only a minor influence on the mechanical properties of revulcanizates, however, samples containing rubber devulcanized at 300°C were found to display lower elongation at break than samples containing rubber devulcanized at 220 – 270°C. With the applied devulcanization and revulcanization method it was possible to prepare a revulcanizate containing 40% devulcanized rubber which retained 94% of tensile strength, 132% of elongation at break, and 81% of shore A hardness compared to a reference SBR sample.

5. Acknowledgements

The presented work benefited from the University of Twente, who provided chemicals required for the (re-)vulcanization process and equipment in order to produce the (re-)vulcanizates.

Chapter 5. Applications

The devulcanized SBR according to the method described in this report has properties that make the rubber suitable to be revulcanized. A compound consisting of 40% devulcanized SBR and 60% fresh SBR has a hardness that is regarded to as 'soft – medium', a tensile strength regarded to as 'high', and elongation at break above the minimum of 400% [86].

According to 'cradle-to-cradle' recycling, the rubber should be incorporated into products comparable to the product from which the rubber originated. Assuming full potential for the described method regarding passenger car tyre rubber, the rubber should be incorporated into new tyres.

This incorporation of the devulcanized rubber into new tyres is possible. However, to what degree is it possible? Granulated waste rubber also has some potential to be incorporated into new tyres, nonetheless, the recycled rubber does not attribute to the strength of the new product. Therefore, the amount of incorporated rubber is very low and cannot exceed 5 – 10%. Since the SBR revulcanized in this research yields good results, namely retention of 94% of tensile strength, 132% of elongation at break, and 81% of shore A hardness, incorporating 40% of devulcanized rubber is expected to be possible into the majority of the parts of the tyre. Due to the decrease in hardness, incorporation of the devulcanized rubber into the tread might be limited, attributable to its critical requirements.

However, considering the lower shore A hardness of the devulcanized SBR compared to vulcanized virgin SBR, the devulcanized SBR might have potential to be applied in the tread of snow tyres. The tread, however, has the most critical requirements regarding mechanical properties of all the parts of a tyre, since the tread is the link between the car and the road. Therefore, exact tread compositions are highly important and significantly affect the performance of a passenger car (e.g. stopping distance, grip). In order to gain more insight in the potential of incorporating the devulcanized rubber into the tread of tyres, studies by tyre manufacturers have to be conducted.

The devulcanized SBR has potential in other applications as well. Automotive parts apart from tyres, e.g. window rubbers, oil seals, footrests, mud protectors, and several other components, have less strict requirements, which makes it possible to incorporate a larger share of devulcanized rubber into the products.

Furthermore, several lower value products have potential to incorporate devulcanized rubber into. For instance conveyor belts, mats, shoe soles, floor tiles, roofing, flooring, paddings, pipes [87]. Production of these products is not desirable from a recycling point of view, since the material is 'down-cycled'. On top of that, the expected cost related to the devulcanization process is expected to be too high to make incorporation of devulcanized SBR in these applications economically viable.

Chapter 6. Conclusions and Recommendations

1. Conclusions

Regarding devulcanization of rubber, three approaches are identified, namely physical devulcanization, chemical devulcanization, and biological devulcanization.

In physical devulcanization, external energy is applied to the rubber. The majority of the processes are conducted at elevated temperatures, along with increased pressure in order to separate bonds. Rubber is only slightly devulcanized by this process and therefore seems to behave as non-reinforcing filler in revulcanizates. In order to increase the surface area of the rubber particles and thus enhance the devulcanization during this surface treatment, cryomechanical milling was introduced. Results are identified to be superior compared to rubber treated at ambient conditions. In microwave devulcanization, microwave radiation is used to heat the rubber. Polarity of the material is required in the transformation process of radiation to heat, however, polar carbon black is present in tyre rubber. The rubber is typically treated for a couple of minutes and can subsequently be revulcanized or blended with fresh rubber to be vulcanized. Properties of these revulcanizates are better compared to untreated rubber crumb, however, not comparable to a compound consisting of 100% fresh rubber. In ultrasonic devulcanization, ultrasonic waves are applied to the rubber, typically in presence of heat and pressure. Contrarily to other methods ultrasonic and microwave devulcanization occurs throughout the rubber particles and is not limited to the surface. The results for ultrasonic devulcanization are comparable to results obtained by microwave devulcanization. Revulcanizates display a decrease in mechanical properties, which is expected to be related to main chain scission of the rubber.

In chemical devulcanization, a chemical or a mixture of chemicals is added to the rubber and the compound is subsequently devulcanized (typically at elevated temperature and pressure). Several chemicals are used in this devulcanization process and results vary widely. The majority of the methods is described in patents that are written purposefully vague. Furthermore, results obtained by the application of these methods are regularly absent in the patents. Organic disulphides and mercaptans are used in swelling processes, which have typical residence times of 4 – 10 hours at temperatures up to 200°C. Available results, however, indicate poor mechanical properties for pure revulcanizates, leading to the expectation that main chain scission is an important factor in this process. Furthermore, long processing times make these processes unattractive from a business point of view. Compounds using salts (inorganic compounds) are also widely used in rubber devulcanization. Reasonable mechanical properties are obtained by the Delink mixture, however, properties are not comparable to that of fresh vulcanized rubber.

In biological devulcanization, microorganisms are used for selective breakage of sulphur bonds in rubber. The process typically takes several days up to a month. Revulcanizates are identified to be superior compared to untreated rubber crumb, and results ranging from poor to quite well (especially for EPDM) are obtained. Due to the very long processing times, biological devulcanization is very difficult to apply industrially.

In this research, CB filled SBR was devulcanized by DPDS in a batch reactor. The sol fraction and the crosslink density of the gel fraction were studied as function of the devulcanization temperature, processing time, and concentration DA. The sol fraction was found to increase with devulcanization temperature and concentration DA. The effect of DA on the sol fraction was identified to become more pronounced at higher temperatures. Crosslink density was found to increase with devulcanization temperature. This increase was observed to be enhanced at higher DA concentrations. The latter is explained using the 'onion model' of devulcanization. Additional experiments led to the conclusion that in absence of CB, DA is an effective radical scavenger. In presence of CB, the effectiveness of the DA is reduced, which is expected to be related to radical transfer to CB.

Subsequently, devulcanized SBR was compounded with fresh SBR and revulcanized. The temperature to which the rubber was subjected during devulcanization in the range of 220 – 300°C, was not found to have a large effect on the mechanical properties of revulcanizates. Revulcanizates containing 40% devulcanized rubber were found to yield higher mechanical properties than samples containing 60%. Blending 40 % SBR subjected to the described method, with 60% fresh SBR led to retention of 94% of tensile strength, 132% of elongation at break, and 81% of shore A hardness. Due to its high mechanical properties, revulcanizates containing 40% devulcanized SBR can be used in the production of high-value products.

2. Recommendations and further research

The rubber devulcanized in this research was not subjected to a harsh useful life. In reality, rubber products will be endlessly used before being discarded, thereby degrading to some extent. The effect of this degradation on the potential of devulcanizing and subsequently revulcanizing the material is very crucial for industrial application of the process, since otherwise only manufacturing scrap is suitable to be subjected to the revulcanization process. Therefore, additional experiments with degraded or aged rubber have to be conducted.

The mechanism behind the devulcanization is only understood to a certain degree. In order to increase understanding, additional experiments investigating for instance the diffusion rate of DPDS by subjecting SBR of different particle sizes to the devulcanization process have to be conducted.

In order to widen the potential for the devulcanization process, its potential for devulcanization of passenger car tyre rubber has to be investigated. The latter contains several types of rubber, as well as several types of carbon blacks and curatives, all in varying ratios. Devulcanization of tyre rubber is therefore far more challenging than regular SBR. Since SBR is the most strenuous compound in the passenger car tyre rubber blend, expectations are that the process will be suitable for tyre rubber as well. Application of the method on the one hand on other pure types of rubber has to be investigated. On the other hand, blends of discarded passenger car tyre rubber have to be subjected to the process.

Finally, certain tyres contain a silica filler instead of a CB filler. The effect of the presence of silica in the blend should be investigated, in order to make the process more durable and suitable for the devulcanization of all types of passenger car tyre rubber.

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Appendix A: Mass balance

In order to check whether the extractions with acetone and THF are successful, it is important to check if the compounds that are expected in the extracts are present, and if the fractions of weight extracted correspond with the expectation.

In the acetone extract, it is expected that all low molecular weight compounds will be extracted. An overview of the compounds is displayed below:

- N-tertbutyl-2-benzothiazole (TBBS)
- Tetramethylthiuram Disulfide (TMTD)
- Sulphur (S)
- Zinc Oxide (ZnO)
- Stearic acid
- Calcium Oxide (CaO)
- Devulcanization agent
- Processing oil (TDAE)

Sulphur consumed during the vulcanization process, as well as devulcanization agent that has combined with rubber chains will not be extracted in acetone, however, this is assumed to correspond to a low amount and thus a low fraction. In Figure 25, the FT-IR spectra of the acetone extract of devulcanized rubber, SBR containing oil, and the oil are displayed. TDAE oil can be clearly recognized in the FT-IR spectrum of the devulcanized rubber. SBR, on the other hand, was not found to be present in noticeable quantities in the acetone extract of the devulcanized rubber. The pronounced SBR absorbance at 698, 909, and 965 cm^{-1} was not identified in the acetone extract of the devulcanized samples. Furthermore, a peak at 1702 cm^{-1} resulting from the presence of stearic acid was found in the spectrum of the devulcanized rubber (Figure 26). The other rubber additives are present in low quantities, making them difficult to detect and distinguish with FT-IR.

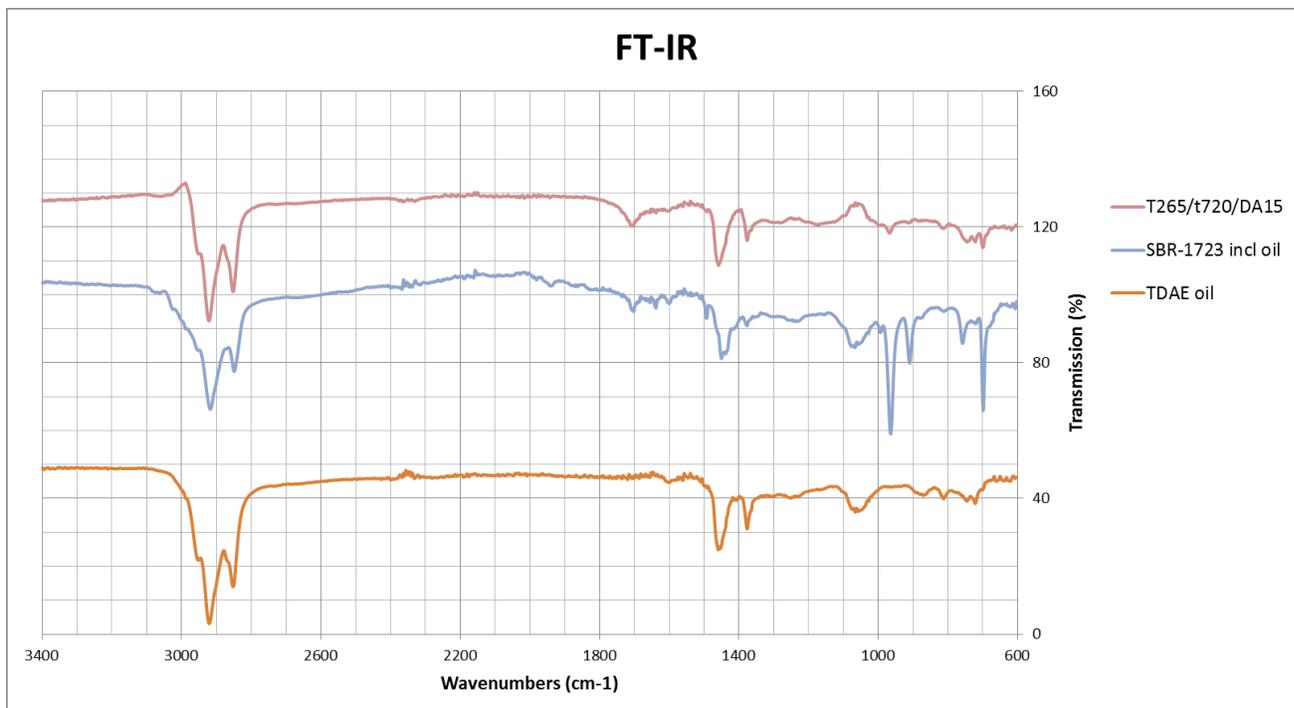


Figure 25. FT-IR of acetone extract of devulcanized rubber compared with FT-IR of TDAE oil and SBR-1723 containing TDAE oil

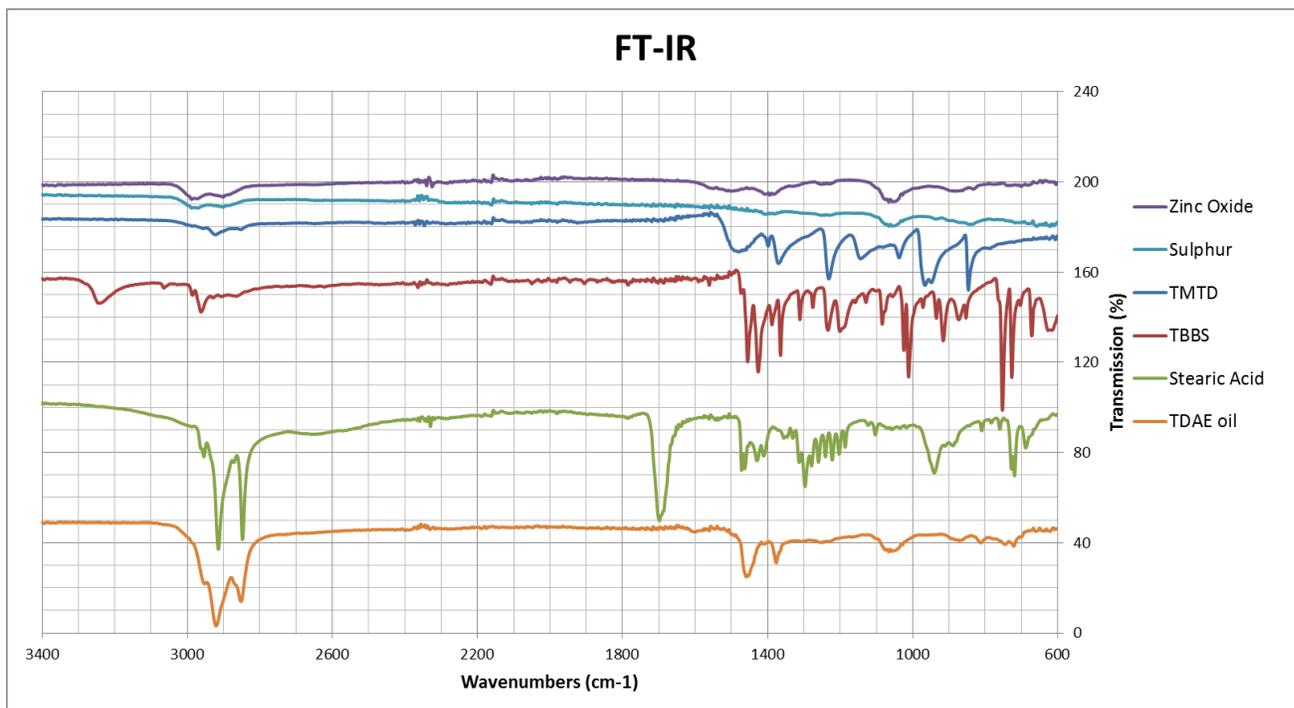


Figure 26. FT-IR spectra of low molecular weight compounds expected to be extracted with acetone

During the THF extraction, uncrosslinked rubber chains will be extracted. In green (unvulcanized rubber), this corresponds with all rubber chains present, excluding the bound rubber (rubber chains adsorbed at the CB surface). In devulcanized samples, SBR chains that are disconnected from the network will be extracted in THF.

The remaining fraction is crosslinked compound. This fraction contains the carbon black, bound rubber, and the SBR chains that are (still) crosslinked.

Bound rubber is calculated based on extraction results of green rubber samples. The fraction of rubber chains that was not extractable in THF is used as the fraction of SBR chains that will be present as bound rubber. This fraction (0.355) is applied to all extracted samples.

In Figure 27, mass balances for green rubber are displayed. As shown, quite some variation exists between the two measured samples. This variation, however, is within the margins of extraction processes, where 5% deviations can occur.

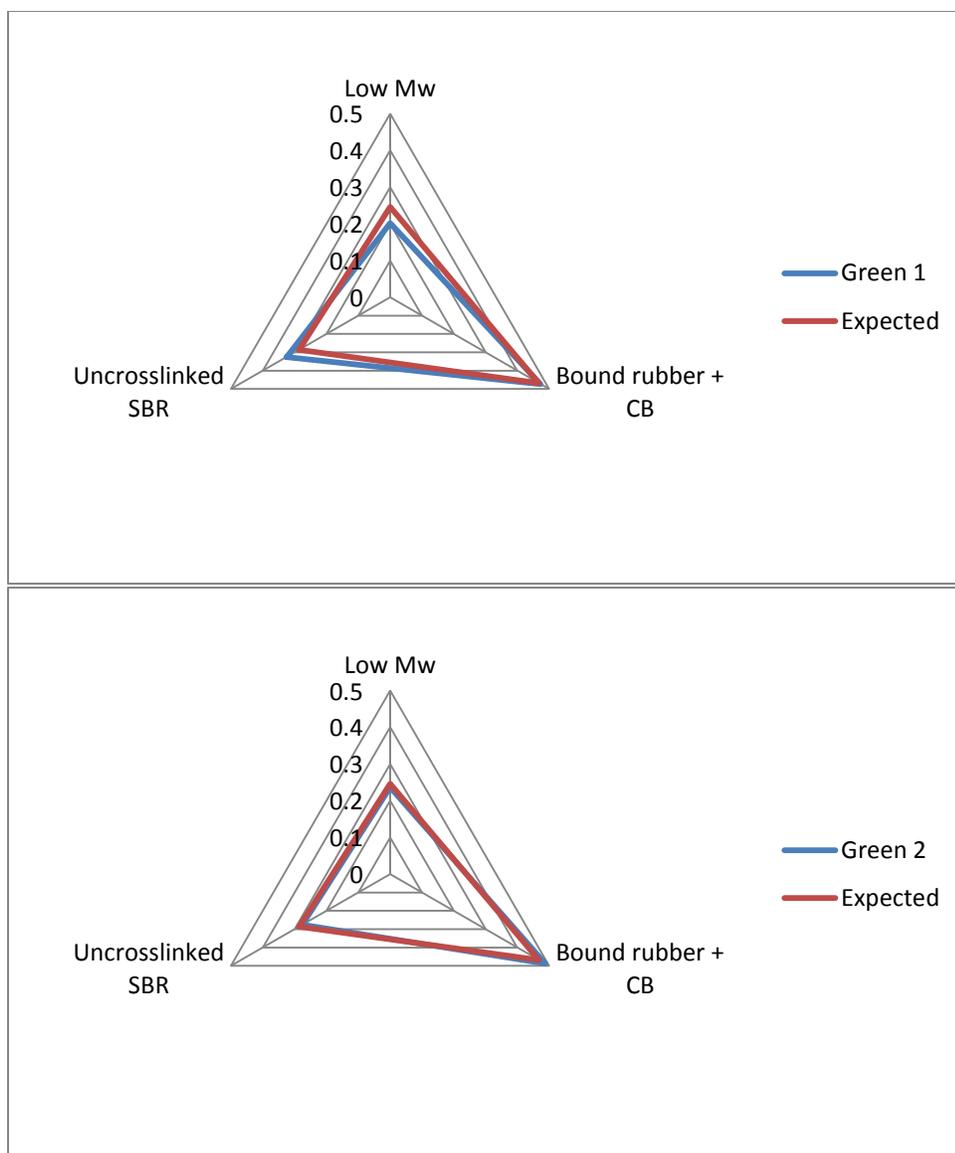


Figure 27. Mass balance of green rubber (expected and two measured samples)

In Figure 28, the mass balance of a sample devulcanized for 6 minutes at 240°C with 30 mmol/100g DPDS is shown. As shown, the fraction of low molecular weight compounds corresponds with the fraction extracted in acetone. Furthermore, at least the bound rubber + CB fraction is expected to exist as crosslinked compound. As shown, more rubber remains crosslinked, i.e. no full devulcanization is reached during the process. Remaining rubber is the amount of rubber that is devulcanized and which can be extracted in THF. The red line corresponds with the expected fraction in case of 100% devulcanization. As displayed, nearly half of the potentially extractable rubber was extracted from sample 10, which corresponds with the 44.1% sol fraction compensated for bound rubber which was calculated.

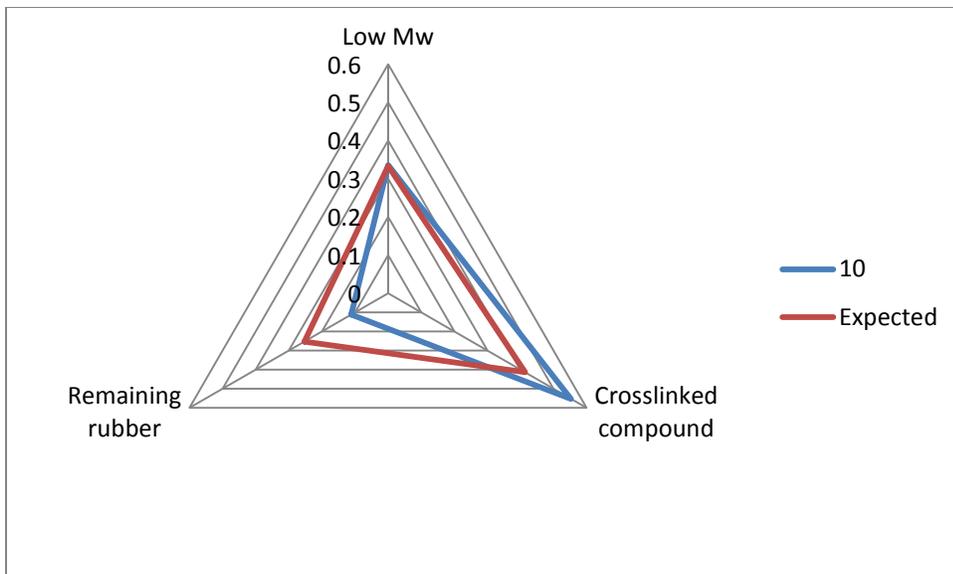


Figure 28. Mass balance of sample 10 (expected and measured values)

In Figure 29, the mass balance of a vulcanized masterbatch sample is displayed. As shown, the low molecular weight compounds are indeed extracted with acetone. Furthermore, the rubber was found to be fully crosslinked (nearly 100%), no rubber chains were soluble in THF.

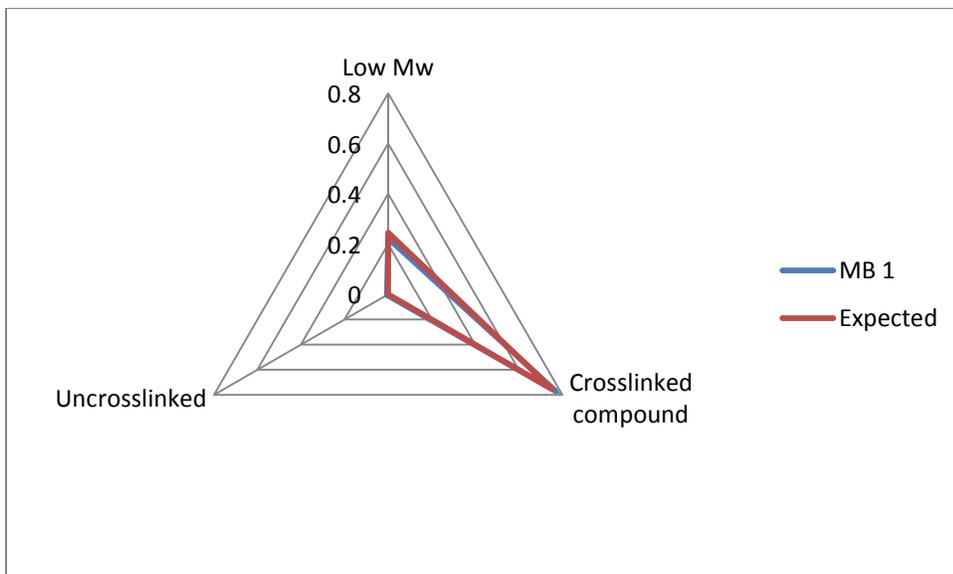


Figure 29. Mass balance of master batch (sample 1) (expected and measured values)

