# Closing the Loop:
## Reuse of Devulcanized Rubber in New Tires

**Hans van Hoek**

# CLOSING THE LOOP: REUSE OF DEVULCANIZED RUBBER IN NEW TIRES

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*Dedicated to my late Dad, as I could accomplish what he never got a chance for.*

# Contents

# General Summary

## Motivation

Due to the very large number of produced and scrapped tires each year, and with the numbers still growing, end-of-life tires pose a huge environmental and societal challenge. Burning tires in the open air is not viable because of the environmental impact and new regulations, with rapidly growing piles of tires as a consequence. Dumping of tires is undesirable as tires hardly decompose, thus posing serious problems.

Tires are the largest application of vulcanized rubber. Any recycling technology that limits downgrading of vulcanized rubber materials should be explored to further increase the reuse of these materials. Devulcanization is such a technology. It is the reverse of vulcanization, the process of crosslinking mouldable green rubber to give them their shape and property profile. It produces re-mouldable rubber out of end-of-life material, which can be used for new applications. This technology is already proven for Ethylene-Propylene-Diene rubber (EPDM), which is typically used for foils for roofing, profiles or tubes; the devulcanized EPDM is actually already in use for new roof cladding. For truck tires, which mainly consist of Natural Rubber (NR), a process for high-quality recycled material is available. For passenger car tires mainly consisting of blends of Styrene-Butadiene Rubber (SBR) and Butadiene Rubber (BR) for the tread and a blend of NR and BR for the sidewall and other components of the tire, a process on laboratory scale was developed by Saiwari[1].

The present thesis describes the scaling up of the earlier developed lab process and transformation into a continuous process. In the next step, the influence of specific compounding additives and required process adjustments are elaborated. Last but not least, an application study for reuse of the devulcanizate in new passenger car tires is performed.

The objective of this study is to provide an important building block of circular economy. This comprises the reuse of rubber from end-of-life tires for new tires, as well as saving our resources.

## Summary of the requirements

### Literature review

In Chapter 2, "Sustainable recycling of passenger car tires", the most important factors, which can influence the quality and application of devulcanized passenger car tire rubber for new tires, are reviewed. The main factors are:

- Variations in composition of granulated passenger car tire rubber;

- New innovations in applied tire materials leading to changes in composition;

- The influence of devulcanizate on the production processes of new tires;

- Legislation.

The tire industry continuously develops new compounds to improve the properties of tires, for example the use of silica and resins to enhance tire performance. Each tire manufacturer uses his own proprietary formulations. As a result of both influences, the composition of whole tire granulate shows a wide variation, leading to the need for a detailed investigation into the properties of devulcanizate as a function of composition. Because of recent changes in legislation, it is important that tires are excluded that contains any carcinogenic chemicals when selecting the feedstock for devulcanization. These could still be present in older end of life tires and in imported tires from countries with a less severe legislation

For tire manufacturers, safety, fuel economy and wear resistance are important factors for tire design, driving performance improvements and product developments. Because of the expected variation in the composition of the worn-out tire granulates, which is the feedstock for devulcanization, the impact of using devulcanizates for new tires is a point of concern with respect to compound formulations and production processes.

It is mentioned that for both, ground tire rubber and devulcanized rubber, reuse of about $5 \, \text{wt}\%$ for new tires is a practical limit because of quality related aspects.

## Summary of the results

### Theoretical considerations and analysis methods

Chapter 4, "Theoretical considerations and analysis methods", describes the theoretical considerations with respect to transport phenomena in rubber, optimization of the Horikx-Verbruggen analysis method for the degree of devulcanization for different car tire rubbers, and the development of an analysis method for the size and amount of visible particles size distribution in devulcanizates. It is shown that:

- The size distribution of the tire granulate feedstock has a large influence on the amount and thus the concentration of the devulcanization agent and processing oil that is absorbed during the devulcanization process, for the applied ground passenger car tire rubber (GTR) in this study with granule sizes between $0.7 \, \text{mm}$ to $3.5 \, \text{mm}$ and an overall dosage of processing oil of $5 \, \text{wt}\%$, the actual concentration of the oil in the particles varied between $9 \, \text{wt}\%$ for the smallest and $2 \, \text{wt}\%$ for the largest particles. The devulcanization aid will show a similar distribution which leads to an inhomogeneous degree of devulcanisation of the particles.

- The estimated diffusion time of the processing oil into granulate particles of $3 \, \text{mm}$ at devulcanization temperatures of $180 \, °\text{C}$ to $200 \, °\text{C}$ is $11 \, \text{min}$ to $15 \, \text{min}$. This is within the same range as the devulcanization times. Hence, a concentration gradient of the devulcanization agent inside the

granulate particles during devulcanization can be expected, which will influence the homogeneity of the devulcanization.

- It is calculated that the heat transport inside the granulate particles is rather quick and therefore considered as of minor influence in this study.

- The accuracy of the Horikx-Verbruggen method to determine the decrease in network density by devulcanization and the ratio of crosslink to main chain scission can be increased for passenger car tire rubbers by only including the weight loss due to extraction of the dissolvable polar components before the calculations.

- The White Rubber Analysis method to quantify the size and number of particles remaining after devulcanization is introduced.

## Devulcanization process

In Chapter 5, "From batch to continuous processing using DPDS as devulcanization aid", the devulcanization process for passenger car tire rubber is scaled up from 15 g per batch to a few kg per hour, and transformed into a continuous process in a co-rotating twin-screw extruder. The devulcanization aid used in this study is DiPhenylDiSulfide (DPDS). Because SBR is rather sensitive to the devulcanization process conditions such as thermal and mechanical energy input, the screw is designed for relatively low shear, the low shear concept. The influence of the devulcanization conditions, extruder parameters and ancillary equipment on the devulcanization efficiency and the quality of the final product are studied. The size of the visible grains in the devulcanizate caused by insufficiently devulcanized particles can be reduced by adding some kneading elements midway of the screws. It is also shown that it is related to the size of the tire granulate used as feedstock. A best practice for continuous devulcanization using DPDS as devulcanization agent is found. The processing conditions defined for the Brabender batch reactor are also the optimized condition:

- A devulcanization temperature of 220 °C;
- A screw speed of 10 rpm, leading to a residence time of 6 minutes;
- A devulcanization aid concentration of 18 mmolDPDS/100g GTR;

With for the screw configuration:

- A screw with only a small number of kneading elements, Screw 3 in Figure 5.2, shows the best results in terms of devulcanization efficiency, quality and remaining visible grains size.

In Chapter 6, "Optimization of the continuous devulcanization process using DBD", a further improvement of the twin-screw extruder based devulcanization process is described with respect to the use of 2-2'-DiBenzamido-Diphenyldisulfide (DBD) as devulcanization aid. Because of its melting point of approximately 140 °C, this devulcanization aid is fed into the extruder as a powder after it is mixed with the passenger car tire rubber granulate, processing oil and anti-oxidant. Additional kneading elements have to be added for a thorough mixing. A low shear in the extruder, resulting from a limited amount of kneading elements in the devulcanization section, leads

to a devulcanizate with a coarse structure. Subsequent milling on a two roll mill at 60 °C with a very narrow nip width substantially shows to improve the homogeneity and the tensile strength of the devulcanizate after revulcanization.

This study also shows that the composition of passenger car tire granulate is too complex to use the Horikx-Verbruggen diagram as optimization method for the devulcanization process. Instead, tensile strength of the devulcanized and subsequently revulcanized rubber is chosen as an indicator for the quality of the devulcanizate. Best tensile strength values after revulcanization are obtained by using 4 wt% of devulcanization aid DBD, 2 wt% of processing oil and 1 wt% of anti-oxidant at a devulcanization temperature of 180 °C. It is concluded that for further upscaling, several processing steps viz mixing of the devulcanization aid with the granulate, the actual devulcanization process and milling of the devulcanizate, should be performed on dedicated equipment to optimize the capacity and effectiveness of the overall process.

### Influence of silica

The most prominent improvement in the recent past of the tire industry is the use of a silica-silane filler system in passenger car tire tread compounds instead of the traditionally used carbon black, to achieve improvements in rolling resistance and wet grip properties. In Chapter 7, "Implications of silica in GTR", the influence of silica present in passenger car tire granulate on both devulcanization and subsequent revulcanization, is investigated. The best tensile strength of the revulcanizate, using a carbon black based revulcanization formulation is 5 MPa. This can be improved to 6.5 MPa by adding 2.8 phr of 1,3-DiPhenylGuanidine (DPG) to the revulcanization formulation. By adding an extra silanization step during revulcanization by admixing 3.2 phr bis[3-(TriEthoxySilyl)Propyl] Tetrasulfide (TESPT) to the formulation, the tensile strength of the revulcanizates is further improved to 8 MPa: the silica in the granulate partly lost its reinforcing strength, but can be activated again by this silanization step and thus improvement of the revulcanization properties. By devulcanization and subsequent revulcanization of both a carbon black based and a silica based tread model compound, it is shown that a tensile strength of the revulcanizate of 13 MPa can be achieved in both cases. This shows the potential of devulcanized rubber when the various tire components are separated before the material is granulated for recycling purposes.

### Additional influences on the quality of the devulcanizate

In Chapter 8, "Additional influences on the quality of the devulcanizate and the tensile strength of the revulcanizate" are investigated and summarized below. In this and the following parts of the study, model compounds are used. The so called 'virgin compounds' before devulcanized and subsequently revulcanized and are used for reference for the properties of the devulcanized and subsequently revulcanized compounds.

Directly from the extruderline, the structure of the devulcanizate is a sticky and coarse granulate. Before this material can be handled, it needs an additional processing step, e.g. milling. This decreases the size of the

visible grains in the devulcanized and subsequently revulcanizedrubber. As mentioned before, tensile strength is taken as key property to evaluate the influence of blending of the devulcanized compounds with the virgin ones.

The tensile strength and the structure of the fracture surfaces of a carbon black reinforced tread model material does not change compared with those of the virgin compound after the devulcanization and subsequent revulcanization. For a silica-silane based tread model compound, on the other hand, both a significant drop in tensile strength as well as a rough and inhomogeneous fracture surface are observed. The tensile strength of the revulcanizate is similar to that of the carbon black based material.

In order to mimic whole tire material, a blend of granulates of a carbon black and of a silica based model compounds as well as mixed with a small amount of butyl rubber are investigated. These devulcanized and subsequently revulcanized blends show only a limited decrease in tensile strength compared with not blended. It is also found that the presence of a low percentage of 5 wt% of butyl rubber in the blend does not influence the tensile strength negatively. The fracture surfaces of the blends are comparable with that of the silica based compound after devulcanization and subsequent revulcanization. This shows that for a blend of carbon black and silica based tread model compounds and butyl rubber, an upper limit of about 11 MPa can be expected.

The homogeneity of the commercial grade of ground passenger car tire rubber granulate is investigated as well as the influence thereof on the reproducibility of the tensile properties of the revulcanizate. Also the reproducibility of the twin-screw extruder based thermo-mechanical chemical devulcanization process is estimated.

It is clearly shown that the silica content of the granulate is the most important factor for the reproducibility of the results after revulcanization. This indicates that separation of silica based compounds, i.e. the tread of the tire before granulation, will improve the reproducibility of the devulcanization and subsequent revulcanization process, as well as the tensile properties of the revulcanizate.

## Blends with devulcanizates

A more common approach to applying replasticized rubber is to use it in a blend with virgin rubber. A study of the influence of blending devulcanized GTR with three different compounds:

- A carbon black / natural rubber based undertread model compound (UT);

- A carbon black / styrene butadiene rubber model tread compound (CB);

- Another tread compound, but silica based (GT).
  (Because of the large improvement of the rolling resistance of car tires with a silica based tread compound, compared with the traditional carbon black based one, these are also indicated as "green tires".)

on the quality of the blends is described in Chapter 9, "The application of devulcanizate in tire compounds".

The devulcanized GTR is silanized (ds-GTR) prior to blending with the model compounds. All three blends react differently concerning cure behavior, tire performance indicators and aging. This suggests that the revulcanization formulation has to be optimized with respect to the virgin compound used for the blend.

The glass transition temperature ($T_g$) of the vulcanized blends containing devulcanizate is only marginally different from the $T_g$ of the virgin compounds, for up to 30 wt% of ds-GTR added to both carbon black based compounds and up to 20 wt% for the silica based one.

The tensile properties of the vulcanized blends are a tensile strength of 10 MPa to 12 MPa and a strain at break of 250 % to 300 % for 10 wt% to 30 wt% of ds-GTR in the blends: An acceptable decrease in tensile strength from 13 MPa for the original carbon black based tread compound CB, from 16 MPa for the original silica based tread compound GT and from 17.5 MPa for the original carbon black based undertread compound UT. The strain at break varies between 330 % to 350 % for all the original compounds.

With respect to aging the following influences are observed: ds-GTR has hardly any effect on the aging behavior of the tensile strength of the blends. For the rate of change of the strain at break during the first 9 days, the influence of blending with ds-GTR depends on the model compound: for the NR based UT/ rate of change decreases, while for the SBR/BR based model compounds CB/ and GT, the rate of change increases. For the CB blends it is the presence of ds-GTR while for the blends of GT the increase is more or less relative to the amount of ds-GTR. For the CB and GTcompound, M25 increases with the amount of ds-GTR, with a maximum of twice of the base level for 30 wt% ds-GTR. For the UT compound there is no significant influence on M25 for a blend with 10 wt%. M25 only increases up to 100 % for 30 wt% of ds-GTR. With respect to the hardness, for both carbon black filled compounds CB and UT, there is no influence of the amount of ds-GTR on the initial hardness, but a slight increase of the hardness in time. For the silica-silane filler based GT, the effect of ds-GTR is the opposite: an increase of the initial hardness relative to the amount of ds-GTR from 55 Shore A to 64 Shore A for the blend with 30 wt% ds-GTR but no increase in the rate of change compared to that of the compound without ds-GTR.

## Influence of resins

The use of resins in modern tire tread compounds has increased considerably in the previous years, to further improve tire performance. Based on the experience with silica-silane filler systems, which lead to a different network structure and a significantly changed devulcanization behavior, the influence of resin addition is investigated as well and is described in Chapter 10, "The influence of resins". The influence of 20 phr of resin in devulcanization and subsequent revulcanization of a silica-silane based tread compound is investigated with respect to processing behavior, curing, mechanical and dynamic properties. The resin-containing devulcanizates, which are prepared for revulcanization, show a difficult processing behavior due to stickiness. The tan$\delta$ at 0 °C shows a considerable increase, which indicates an improved wet grip of the tire. A marginal increase of tan$\delta$ at 60 °C is observed as well, which points to a minor increase in rolling resistance.

All other investigated parameters concerning the devulcanization and subsequent revulcanization process and the revulcanized material change according to expectations. This shows that the most important influence of the resins in the tire rubber can be expected in the processing of the devulcanizate, with the remark that the influence will be limited when the revulcanizate is used in a blend. Overall: the most prominent improvement is the positive influence on the wet grip indicator of the revulcanizates due to resin addition.

## Final remarks

The complexity and variety in composition of whole tire material and the influence on the devulcanization process was addressed in this study. It was shown that the separation of different parts of tires considerably improves the overall efficiency of the devulcanization process, consistency and quality of the devulcanizates. Furthermore it was demonstrated that it is possible to blend devulcanized whole passenger car tire rubber with virgin rubber up to 30 wt% with only a limited effect on aging properties.

As the main focus of the tire industry remains the continuous improvement of the magic triangle of safety, durability and fuel economy for tires through the use of structural integrity and production costs, the recycling market has to deal with the changes in chemical composition. That said, re-circulation of tire rubber into the main tire production is most desirable because of the sheer amount of produced tires. The potential of the recycling technology has for now made a step forward. With a technically viable solution to reuse passenger car tire rubber for new products, the legislation on design for circularity and limitation of waste can provide the final impulse to implement this technology on an industrial scale.

## References

[1] S. Saiwari, "Post-consumer tires back into new tires", PhD thesis (University of Twente, The Netherlands, 2013).

# Algehele samenvatting en conclusies

## Motivatie voor het onderzoek

Wegens het grote, en nog steeds toenemende, aantal jaarlijks geproduceerde en afgedankte autobanden, vormen de afgedankte autobanden een grote belasting voor het milieu en de maatschappij. Het in de open lucht verbranden van de banden wordt inmiddels steeds door regelgeving verboden vanwege de impact op het milieu, maar ook het dumpen van banden op stortplaatsen is niet gewenst vanwege de slechte composteerbaarheid. Met als gevolg het in een snel tempo vormen van grote stapels banden aan het einde van hun levensduur.

De grootste hoeveelheid gevulcaniseerd rubber wordt toegepast in autobanden. Van elke beschikbare techniek waarmee de eigenschappen van de samenstellende materialen zoveel als mogelijk behouden blijven, en daarmee het hergebruik hiervan in kwalitatief hoogwaardige toepassingen mogelijk maakt, moeten de mogelijkheden worden onderzocht. Devulcanizatie is er hier een van. Het is het omgekeerde proces van het vulcaniseren, waarmee vormbare materialen worden omgezet in een product met vastgelegde vorm en eigenschappen. Met het devulcaniseren worden weer vormbare materialen gemaakt van -rubberen- producten na het verstrijken van hun levensduur, waarmee het materiaal weer gebruikt kan worden voor nieuwe toepassingen. Dit is al een bewezen technologie voor Ethylene-Propylene-Diene rubber (EPDM), wat veel gebruikt wordt als dakbedekking, voor rubberen profielen en buizen; gedevulcaniseerd EPDM is inmiddels al in gebruik als grondstof voor nieuwe dakbedekkingen. Voor het devulcaniseren van vrachtwagenbanden, welke voor een groot deel bestaan uit Natuur Rubber (NR) is er inmiddels een proces beschikbaar waarmee kwalitatief hoogwaardig devulcanisaat geproduceerd wordt. Voor het devulcaniseren van personenwagenbanden, welke hoofdzakelijk bestaan uit mengsels van Styreen-Butadieën Rubber (SBR) and Butadieën Rubber (BR) voor het loopvlak, en NR en BR voor de zijwanden en andere onderdelen van de banden, is een proces op laboratoriumschaal ontwikkeld door S.Saiwari[1]... Deze studie beschrijft het omvormen van dit batch-gewijze laboratorium proces tot- en het opschalen hiervan naar een continue proces, het bepalen van de invloed van toevoegingen voor het compounderen en de daarbij behorende proces aanpassingen, alsmede de ontwikkeling van toepassingen van het devulcanisaat in nieuw te produceren banden. Het doel is om hiermee bij te dragen aan circulaire economie in de vorm van hergebruik van het rubber van banden aan het einde van hun levensduur, alsmede het verminderen van het gebruik van nieuwe materialen.

## Samenvatting van de vereisten voor het devulcanisatie proces

### Literatuur onderzoek

In Hoofdstuk 2, Sustainable recycling of passenger car tires, zijn de belangrijkste, in de literatur genoemde, aspecten samengevat die een invloed kunnen hebben op de herbruikbaarheid van gedevulcaniseerd personenwagenbanden rubber voor nieuwe banden. Deze zijn:

- Fluctuaties in de samenstelling personenwagenbanden granulaat.

- Ontwikkelingen in de voor banden toegepaste materialen, welke leiden tot een wijziging in samenstelling hiervan.

- Het effect van het devulcanizaat op de productieprocessen van autobanden.

- Wet- en regelgeving

In de banden industrie worden continue nieuwe rubber samenstellingen ontwikkeld om de eigenschappen van de banden te verbeteren, zoals bijvoorbeeld het gebruik van silica en harsen. Omdat ook elke bandenfabrikant zijn eigen, niet algemeen bekende, samenstellingen gebruikt, varieert de samenstelling van bandengranulaat sterk. En dit noodzaakt onderzoek naar eigenschappen van het devulcanizaat als functie van de samenstelling hiervan.

Vanwege recente ontwikkelingen in de wet- en regelgeving is het van belang dat uitgesloten wordt dat kankerverwekkende stoffen in het rubber granulaat aanwezig zijn wanneer dit als grondstof voor devulcanisatie gebruikt wordt. Deze stoffen zouden nog aanwezig kunnen zijn in oude banden of banden uit parallel import uit landen met een minder strenge regelgeving.

Veiligheid, brandstof gebruik en sluitvastheid zijn belangrijke eigenschappen bij het ontwikkkelen van banden en de rij-eigenschappen hiervan. De hierdoor te verwachten variaties in de samenstelling van banden granulaat, de grondstof voor het devulcanisatie proces, is een punt van aandacht bij het ontwikkelen van de hiermee samengestelde rubber formuleringen en te gebruiken productieprocessen.

Als practische grens voor het hergebruik van gemalen rubber zowel als voor reclaim rubber in nieuwe banden wordt een grens van $5\,\mathrm{wt\%}$ gehanteerd op grond van economische alswel kwaliteit-technische redenen.

## Samenvatting van de resultaten

### Theoretische overwegingen en analyse methodieken

In Hoofdstuk 4, Theoretical considerations and analysis methods, worden de theoretische aspecten van transport verschijnselen beschreven, een uitbreiding op- en een optimalisatie van de Horikx-Verbruggen analyse methodiek en een analyse methodiek voor het bepalen van de afmetingen en de distributie van nog aanwezige zichtbare deeltjes in het devulcanisaat. De Horikx-Verbruggen analyse wordt gebruikt voor het bepalen van de mate van devulcanisatie van rubber mengsels. Het is aangetoond dat:

- De variatie in afmetingen van het granulaat en de verdeling hiervan heeft een grote invloed op de hoeveelheid, en dus de concentratie, proces-olie dat is geabsorbeerd gedurende de eerste fase van het devulcanisatie proces. Voor het toegepaste granulaat (GTR), met afmetingen tussen 0,7 mm en 3,5 mm en een gemiddelde concentratie proces-olie van 5 gewichtsprocent, varieert de lokale concentratie tussen 9 gewichtsprocent voor de kleinste en 2 gewichtsprocent voor de grootste deeltjes. Eenzelfde verschil in concentratie kan verwacht worden voor de devulcanizatie middelen. Het gevolg hiervan is een niet-homogene devulcanisatie van de granulaat deeltjes.

- De geschatte diffusietijd van de proces olie in de granulaat deeltjes van 3 mm is 11 tot 15 minuten, berekend voor een devulcanisatie temperatuur van 180 to 200 °C. Dit is van eenzelfde orde van grootte als de devulcanisatietijd. Het mag daarom verwacht worden dat er een concentratie-gradient zal zijn binnen de granulaat deeltjes, hetgeen de homogeniteit van de devulcanisatie zal beïnvloeden.

- Volgens de berekeningen is de snelheid van het warmtetransport binnen de granulaat deeltjes dermate hoog dat dit geen invloed van belang zal hebben voor dit onderzoek.

- De nauwkeurigheid waarmee met de Horikx-Verbruggen analyse de afname van de netwerkdichtheid en de mate van ketenbreuk bepaald kan worden is verhoogd, door alleen de gewichtsafname gedurende de THF extractie te gebruiken.

- De Wit-Rubber Analyse methode is geïntroduceerd. Hiermee wordt het aantal, de maat en de verdeling van de zichtbare deeltjes in het devulcanisaat gekwantificeerd.

## Het devulcanizatie proces

In Hoofdstuk 5, From batch to continuous processing using DPDS as devulcanization aid, is beschreven hoe het devulcanisatie proces van het rubber van personenwagen banden is opgeschaald van 15 g per batch naar een paar kg per uur, en is omgezet naar een continue proces met gebruik van een co-rotating dubbelschroefs extruder. Daarbij is gebruik gemaakt van DiPhenyl-DiSulfide (DPDS) als hulpstof. Omdat SBR gemakkelijk degenereerd bij de proces condities bij het devulcanisatie proces, zoals thermische en mechanische energie toevoer, is de schroef geconfigureerd voor relatief lage afschuifkrachten, het "low shear concept". Tijdens het onderzoek zijn de invloeden van de devulcanisatie condities, extruder parameters en hulp apparatuur op de effectiviteit van de devulcanisatie en de kwaliteit van het uiteindelijke product bepaald. De afmetingen van de nog zichtbare deeltjes in het devulcanisaat, als gevolg van een niet volledige devulcanisatie, zijn gereduceerd door het toepassen van een beperkt aantal kneed elementen in het midden van de extruderschroeven. Er is ook aangetoond dat deze afmetingen samenhangen met de maat van het rubber granulaat dat als grondstof wordt gebruikt. De werkwijze voor het continu devulcaniseren met gebruik van DPDS is geoptimaliseerd. De proces condities zoals gebruikt voor het batch proces in de Brabender reactor, blijken te gelijkwaardig zijn aan de geoptimaliseerde condities voor het continu proces:

- Een devulcanisatie temperatuur van 220 °C.

- Een schroef toerental van 10 rpm, met een verblijfstijd van 6 minutes als gevolg.

- Een concentratie van de hulpstof van 18 mmolDPDS/100g GTR.

En voor de schroefopbouw:

- Een schroef met slechts een beperkt aantal kneed elementen, Screw 3 in Figure 5.2, gaf de beste resultaten gerelateerd aan de effectiviteit van de devulcanisatie, de kwaliteit van het devulcanisaat en de afmetingen van de zichtbare deeltjes.

Een verdere verbetering van het devulcanisatieproces met een dubbelschroef extruder is beschreven in Hoofdstuk 6, Optimization of the continuous devulcanization process
using DBD, waarbij gebruik gemaakt is van het poedervormige devulcanisatie hulpmiddel 2-2'-DiBenzamidoDiphenyldisulfide (DBD). Vanwege het smeltpunt van ongeveer 140 °C is het als poeder gemengd met het granulaat, proces olie en een anti-oxidant en in deze vorm als voeding voor de extruder gebruikt. Hierbij zijn extra kneedelementen nodig voor een verbeterd mengproces tijdens het smelten van het DBD in de extruder.

Het devulcanisaat heeft een grove structuur als gevolg van de relatief geringe afschuifkrachten in de extruder, door het gebruik van een beperkte hoeveelheid kneedelementen in het devulcanisatie gedeelte van de schroef. Door aansluitend het devulcanisaat bij 60 °C te walsen, met een zeer kleine opening tussen de walsrollen zijn zowel de homogeniteit als de treksterkte van het devulcanisaat na revulcanisatie aanzienlijk verbeterd.

De resultaten van dit onderzoek hebben ook laten zien dat de samenstelling van het granulaat te complex is om de Horikx-Verbruggen analyse methode te kunnen gebruiken voor de proces optimalisatie. In plaats daarvan is de treksterkte van het revulcanisaat gekozen als indicator voor de kwaliteit van het devulcanisaat. De hoogste waardes voor de treksterkte na revulcanisatie waren verkregen bij gebruik van 4 wt% devulcanisatie hulpmiddel DBD, 2 wt% proces olie en 1 wt% anti-oxidant, bij een devulcanisatie temperatuur van 180 °C.

Door de combinatie van proces eisen blijkt het niet mogelijk om de extruder bij optimale capaciteit in te kunnen zetten. Het wordt daarom aanbevolen om voor een verder opschaling van het proces voor de te onderscheiden proces stappen: het mengen van het devulcanisatie hulpmiddel, proces olie en anti-oxidant met het granulaat, de feitelijke devulcanisatie en het walsen van het devulcanisaat, meer geëigende apparatuur te gebruiken. Het overall proces kan daarmee worden geoptimaliseerd en kan er een hogere effectiviteit behaald worden.

## De invloed van silica op de kwaliteit van het devulcanizaat

De belangrijkste verbetering in het recente verleden van de banden industrie was het toepassen van het silica-silaan systeem als versterkende vulstof bij de loopvlak compounds voor personenwagenbanden, als vervanging van de meer traditioneel gebruikte carbon black. Hiermee zijn de rolweerstand

van de banden aanzienlijk verlaagd en de anti-slip eigenschappen onder natte condities sterk verbeterd. In Hoofdstuk 7, Implications of silica in GTR, is beschreven hoe het effect van de silica in het granulaat op zowel de devulcanisatie als de daarop volgende revulcanisatie is onderzocht. De beste treksterkte van het revulcanisaat was 5 MPa, verkregen met een op carbon black gebaseerde revulcanisatie formulering. Dit kan verbeterd worden tot 6.5 MPa bij toepassing van 2.8 phr 1,3-DiPhenylGuanidine (DPG) in de revulcanisatie formulering. Bij het uitbreiden van het revulcanisatie proces met een silanisatie stap en gebruik van 3.2 phr bis[3-(TriEthoxySilyl)Propyl] Tetrasulfide (TESPT) in de formulering, wordt de treksterkte verder verhoogt tot 8 MPa. De silica in het granulaat verliest kennelijk een deel van zijn versterkende eigenschappen tijdens het devulcaniseren, maar deze kunnen weer deels gereactiveerd worden met de toegepaste silanisatiestap en zorgen daarmee voor een verbetering van de eigenschappen van het revulcanisaat.

Met het de- en vervolgens weer revulcaniseren van zogenaamde loopvlak model compounds, een met carbon black als actieve vulstof en een andere met silica, zijn treksterktes van 13 MPa behaald voor beide compounds. Hiermee is het potentiëel van gedevulcaniseerd rubber van autobanden, waarvan de verschillende onderdelen zijn gescheiden alvorens deze te granuleren, aannemelijk gemaakt.

### Overige aspecten die de kwaliteit van het devulcanizaat beïnvloeden

In hoofdstuk 8, Additional influences on the quality of the devulcanizate and the tensile strength of the revulcanizate, een aantal andere invloeden op de kwaliteit van het devulcanisaat en de treksterkte hiervan na revulcanisatie zijn hier onderzocht. Deze invloeden worden hieronder nader benoemd. In dit hoofdstuk en de hierop volgende zijn model compounds gebruikt in plaats van banden granulaat. De als "virgin compounds" aangeduide materialen zijn niet gedevulcaniseerd en zijn een referentie voor de eigenschappen van de de- en revulcanizaten hiervan.

Het devulcanisaat zoals het uit de extruder komt is een plakkerig en nogal grof gekorreld materiaal, waar de structuur van het granulaat nog goed in te herkennen is. Het heeft nog een aanvullende bewerking nodig, bijvoorbeeld walsen, voordat het bruikbaar is voor verdere verwerking. Hiermee wordt de structuur van zowel het devulcanisaat alsmede het hieruit verkregen revulcanisaat fijner en de maat van de zichtbare deeltjes neemt af. Zoals reeds eerder is vermeld is de treksterkte gebruikt als eigenschap waarmee de invloed van het mengen van gerevulcanisaat met de "virgin compounds"wordt bepaald.

Zowel de treksterkte als de struktuur van het breukvlak van het met carbon black geproduceerde loopvlak model compound waren nauwelijks afwijkend van die van het virgin materiaal na devulcanisatie en opvolgende revulcanisatie. Dit was anders voor het met silica geproduceerde loopvlak model compound. Dit vertoonde een aanzienlijke daling in de treksterkte en een niet homogeen en ruw van structuur breukoppervlak. De treksterkte van het revulcanisaat was van eenzelfde orde van grootte als die van het op carbon black gebaseerde.

Om de invloed van mengsels van compounds te onderzoeken zoals deze voorkomen in het banden granulaat zijn mengsels van model compounds onderzocht: een op carbon black gebaseerd loopvlak model compound, een op silica gebaseerd en een butyl rubber binnenband compound. Er is slechts een geringe afname in treksterkte geconstateerd voor de revulcanizaten van de devulcanizaten van de mengsels van beide loopvlak compounds vergeleken met die van de niet gemengde. Toevoeging van 5 wt% butyl rubber aan het mengsel voor devulcanisatie had geen merkbare negatieve invloed op de treksterkte. De structuur van de breukvlakken van de trekstrookjes van de mengsels waren vergelijkbaar met die van het op silica gebaseerde compound na devulcanisatie en daaropvolgende revulcanisatie. Dit laat zien dat met een mengsel van op carbon black en silica gebaseerde loopvlak model compounds met 5 wt% butyl rubber een treksterkte van maximaal 11 MPa verwacht kan worden.

De homogeniteit van de samenstelling van het commerciële personenwagen-banden granulaat is onderzocht, alsmede de invloed hiervan op de reproduceerbaarheid van de treksterktes van de revulcanizaten. Verder is er een inschatting gemaakt van de reproduceerbaarheid van het op een dubbelschroefs extruder uitgevoerde thermisch-mechanisch chemische devulcanisatie proces: Er is duidelijk aangetoond dat de aanwezigheid van silica in het granulaat de meest belangrijke factor is voor de reproduceerbaarheid van de treksterkte van het revulcanisaat. Dit leidt tot de constatering dat het scheiden van de silica bevattende onderdelen van de banden voordat deze gegranuleerd worden, de loopvlakken, zal resulteren in een hogere reproduceerbaarheid van zowel het de- en revulcanizatie proces als de treksterkte van het revulcanisaat.

## Mengsels van model rubber compounds met devulcanizaten

Een meer gebruikelijke manier van toepassen van opnieuw kneedbaar gemaakt rubber is om het te gebruiken in een mengsel met nieuw rubber. Het onderzoek naar de invloed van het mengen van gedevulcaniseerd banden granulaat met drie verschillende model compounds:

- Een carbon black / natuur rubber gebaseerd onderloopvlak model compound (UT).

- Een carbon black / styreen butadiëen rubber model loopvlak compound (CB).

- Een tweede loopvlak compound, maar nu op silica gebaseerd (GT). (Vanwege de sterke verbetering van de rolweerstand van de banden met een op silica gebaseerd loopvlak compound vergeleken met de traditionele, op carbon black gebaseerde, worden deze eerste ook wel met "groene banden" (" green tires") aangeduid.)

op de kwaliteit van deze mengsels na vulcanisatie is beschreven in Hoofdstuk 9, The application of devulcanizate in tire compounds.

Het devulcanisaat is gesilaniseerd (ds-GTR) voordat het met de model compounds gemengd wordt. Alle drie de mengsels reageerden verschillend in vulcanisatie gedrag, indicatoren voor band eigenschappen en veroudering. Dit suggereert dat de revulcanisatie formules verder geoptimaliseerd kunnen worden op basis van het gebruikte virgin compound.

De glas overgangs temperatuur ($T_g$) wijkt voor de mengsels nauwelijks af van die van de virgin compounds, bij hoeveelheden tot 30 wt% devulcanisaat in de mengsels van de op carbon black gebaseerde compounds en tot 20 wt% voor het op silica gebaseerde.

De treksterkte van de gevulcaniseerde mengsels is 10 MPa tot 12 MPa bij een rek bij breuk van 250 % tot 300 %, voor 10 wt% tot 30 wt% ds-GTR. Dit is een acceptable afname treksterkte van 13 MPa voor het op carbon black gebaseerde loopvlak model compound CB, van 16 MPa voor het op silica gebaseerde loopvlak model compound GT en van 17.5 MPa voor het op carbon black gebaseerde onderloopvlak model compound UT. De rek bij breuk was voor alle virgin compounds tussen 330 - 350 %.

Met betrekking tot veroudering zijn de volgende invloeden waargenomen: toevoeging van ds-GTR heeft nauwelijks effect op het verouderingsgedrag van de treksterkte van de compounds. De invloed van ds-GTR op de snelheid van verandering van de rek bij breuk gedurende de eerste 9 dagen, hangt af van het gebruikte model compound: voor het op NR gebaseerde UT/ de snelheidsverandering vertraagt, terwijl deze voor de op SBR/BR gebaseerde model compounds CB/ en GT, versneld. Voor de CB compounds is het puur de aanwezigheid van ds-GTR, terwijl voor de compounds met GT de versnelling afhangt van de hoeveelheid. Bij de CB and GTcompounds, M25 neemt toe met de hoeveelheid ds-GTR, met een maximum van het dubbele van het basisniveau voor 30 wt% ds-GTR. Bij het UT compound is er geen significante invloed op M25 waargenomen tot 10 wt% ds-GTR. Een toename tot 100 % van M25 is waargnomen bij een hoeveelheid van 30 wt% ds-GTR. Voor beide op carbon black gebaseerde compounds CB and UT is er geen invloed van ds-GTR op de initiële hardheid, alleen een lichte toename in tijd. Bij het op silica gebaseerde GT is het effect van ds-GTR juist het tegenovergestelde: een toename van de initiële hardheid evenredig aan de hoeveelheid ds-GTR van 55 Shore A tot 64 Shore A voor 30 wt% ds-GTR, terwijl er geen versnelling is in toename van de hardheid, vergeleken met het compound zonder ds-GTR.

## De invloed van harsen

Het gebruik van harsen in moderne loopvlak compounds is in de afgelopen jaren aanzienlijk toegenomen om daarmee de eigenschappen van de banden nog verder te verbeteren. Met als achtergrond de ervaringen met het silica-silaan vulstof systeem, leidend tot een afwijkende netwerkstructuur in het loopvlak rubber, vergeleken met dat van de carbon black vulstof systemen. Omdat dit leidde tot een duidelijk veranderd devulcanisatie gedrag is ook de mogelijke invloed van de toevoeging van grotere concentraties harsen onderzocht. Dit is beschreven in het Hoofdstuk 10, The influence of resins.

De invloed van een concentratie van 20 phr hars is onderzocht op het devulcanisatie- en vervolgens revulcanisatiegedrag van een op een silica-silaan gebaseerd loopvlak compound. Daarbij zijn het gedrag bij het bewerken, bij het revulcaniseren en de invloed op de mechanische en dynamische eigenschappen bekeken.

De hars-houdende devulcanizaten waren lastig te walsen als onderdeel van het bewerken voor het revulcaniseren, omdat het materiaal zeer sterk aan de

walsrollen bleef kleven. De tan$\delta$ bij 0 °C was duidelijk verhoogt, hetgeen duidt op een verbeterde slipweerstand onder natte condities indien het revulcanisaat gebruikt wordt voor het loopvlak van een autoband. Verder was er een marginale verhoging van de tan$\delta$ bij 60 °C geconstateerd, hetgeen duidt op een licht verhoogde rolweerstand van een autoband waarin dit materiaal zou zijn verwerkt.

De overige onderzochte parameters betreffende het devulcanisatie- en vervolgens revulcanisatieproces en de eigenschappen van het gerevulcaniseerde materiaal veranderden vergelijkbaar met die van de materialen zonder hars. Dit laat zien dat de belangrijkste invloed van het hars in de bandencompounds verwacht kan worden tijdens het bewerken van het devulcanisaat voor revulcanisatie. Dit is uiteraard minder wanneer het devulcanisaat wordt toegepast in een mengsel met virgin compounds. Met betrekking tot de eigenschappen van harshoudende de- en revulcanizaten, vergelekem met die zonder hars, is de positieve invloed op de slipweerstand onder natte condities indien gebruikt in bandencompounds.

## Afsluitende opmerkingen

De complexiteit en variaties in de samenstelling van het banden materiaal, en de invloed daarvan op het devulcanisatie proces zijn onderdeel van deze studie. Verder is het aannemelijk gemaakt dat door het scheiden van de verschillende delen van autobanden alvorens deze te granuleren, zowel de effectiviteit van het devulcanisatie proces alsmede de kwaliteit van het devulcanisaat aanzienlijk verbeterd kunnen worden. Verder is gebleken dat het mogelijk is om tot 30 wt% van gedevulcaniseerd personenwagenbanden materiaal te mengen met virgin rubber met slechts een beperkte invloed op de eigenschappen na veroudering.

Omdat de aandacht van de bandenindustrie nog steeds uitgaat naar verder verbeteringen van de zgn. magische driehoek van veiligheid, duurzaamheid zoals slijtagegedrag en veiligheid, door beheersing van de structurele integriteit en de (productie) kosten, heeft men bij hergebruik van autobanden rubber maar om te gaan het de daarmee gepaard gaande veranderende chemische samenstelling. Desondanks is hergebruik van bandenrubber in nieuwe autobanden het meest gewenst, alleen al vanwege de zeer grote hoeveelheden geproduceerde banden. Met onderzoek is de mogelijkeid daartoie weer een stapje dichterbij gekomen. Met een haalbare techniek om het rubber van versleten personenwagen autobanden weer herbruikbaar te maken voor nieuwe producten, is het aan de wet- en regelgeving met betrekking op circular design en afvalbeperking om het zetje te geven naar het gebruik van deze technologie op industriële schaal.

## Referenties

[1] S. Saiwari, „Post-consumer tires back into new tires", proefschrift (University of Twente, The Netherlands, 2013).

# Chapter 1

# Introduction

Tires are important parts for most of moving equipments, specially for cars. Through the years, properties have improved with respect to reliability, safety, fuel economy and lifetime. The construction and rubbers used for the tires have been adapted to meet all the challenging demands, and the rubbers for each part of a tire have been fine-tuned to the specific needs. The materials are of high quality and the tires are made very durable. The latter, however, has several consequences, as every tire has a limited life-time: end-of-life tires are very difficult to disassemble and hardly decompose when disposed of. Especially because of the scale tires are used in, this poses a serious problem. One of the best solutions is to make the rubber reusable again, for instance by reversing the process of vulcanization, by which the rubbers got their special, application related properties, and return it to the so called virgin or green state. This process is called devulcanization.

At the Elastomer Technology and Engineering group of the University of Twente, there is extensive knowledge of devulcanization of sulfur crosslinked elastomers. Devulcanization processes of Ethylene-Propylene-Diene rubber (EPDM) and Natural Rubber (NR) proved to be successful. Saiwari developed a proof of concept for devulcanization of Styrene Butadiene Rubber (SBR) and other tire rubbers with a laboratory scale batch process, using a Brabender internal mixer[1]. She extended this process for devulcanization of end-of-life Ground passenger car Tire Rubber granulate (GTR), which contains, amongst all other components high amount of SBR. The next step towards an industrial and economical feasible process, is scaling up to a continuous devulcanization process based on the use of a twin-screw extruder, which is one of the topics of this thesis. A small scale processing line for continuous devulcanization of GTR has been developed and subsequently the implications the use of the devulcanizate for car tire compounds are investigated.The structure of the present thesis is as follows:

In Chapter 2, "Sustainable recycling of passenger car tires", developments in tires and consequences for feedstock composition are discussed. Developments in legislation concerning reuse and recycling end-of-life tire rubber and environmental aspects related to tire rubber are summarized.

In Chapter 3, "Materials and Equipment", all materials used for the present research are listed and specified. The setup of the continuous devulcanization line and all other equipment used in this research are described. As the following chapters all describe studies of different aspects of devulcanization

of GTR and their reuse, all formulations and preparatory procedures are detailed in this chapter.

In Chapter 4, "Theoretical considerations and analysis methods", the theoretical background of the implications of using coarse grade GTR is investigated. Adjustment of the method to analyze the quality of the devulcanizates, as developed by Verbruggen[2,3], is described. And further, an analysis method for quantification of remaining visible grains in devulcanized rubber is described in this chapter as well.

Scaling up of the laboratory scale devulcanization process in an internal mixer into a continuous process with a co-rotating twin-screw extruder, using DiPhenylDiSulfide (DPDS) as devulcanization aid, is described in Chapter 5, "From batch to continuous processing using DPDS as devulcanization aid".

In Chapter 6, "Optimization of the continuous devulcanization process using DBD", the reasons for and consequences of a change to devulcanization aid 2-2'-DiBenzamidoDiphenyldisulfide (DBD) are discussed. The necessary adaptations of the devulcanization process are described in detail. The use of tensile properties of the revulcanizates as optimizing criterion is introduced in this chapter.

A specific property of modern passenger car tires is the use of silica in the tread compound to improve fuel economy and safety. The implications of silica in GTR on the devulcanization process and material properties are discussed in Chapter 7, "Implications of silica in GTR". Further, a method to improve the properties of the silica-containing devulcanizate is introduced.

Chapter 8, "Additional influences on the quality of the devulcanizate and the tensile strength of the revulcanizate", covers several aspects related to the quality of de- and revulcanizates: The influence of additional milling of the devulcanizate to reduce the remaining visible grains, the differences in de- and revulcanization of carbon black and silica based model tread compounds, and the impact of butyl rubber (IIR) as one of the components in GTR on the tensile properties of the revulcanizates. The influence of variations in the composition of GTR on the reproducibility of the tensile properties of de- and revulcanizates is investigated.

Up to this point, 100 % pure devulcanizates were studied to achieve optimal tensile properties. However, in actual practice it is common to blend devulcanizates with virgin compounds. Therefore, in Chapter 9, "The application of devulcanizate in tire compounds", the properties of blends of devulcanizates with virgin rubber are investigated.

Although the use of silica in passenger car tires started already approximately 20 years ago, the implications on re-usability of GTR become now apparent and will more and more influence the composition of GTR. In Chapter 10, "The influence of resins", the consequences of a new development, the use of oligomeric resins in combination with processing oils in tread compounds on the devulcanization behavior, is investigated.

The stress and strain at break properties of typical revulcanizates in the present study are detailed in Appendix A, "Summary of tensile values", in Table A.1

# Chapter 2

# Sustainable recycling of passenger car tires

*Due to the very large number of car tires produced and deposited each year, with the numbers still growing, there is an urgent need for a sustainable solution to properly dispose of them. Although the amount of tires that are discarded in landfills is decreasing in Europe and the USA due to legislation on waste handling, the most important method still is incineration in kilns for the production of cement, only using the energy content of the tires, but not the valuable polymers or carbon black. Recovering the rubber for a second life, for example as rubber crumb for play grounds, is a first step to solving the waste problem, it generates some time before the rubber is to be discarded permanently. Reuse of powdered or reclaimed car tire rubber in new products appears to be limited to about $5\,wt\%$ of the rubber in certain parts of a new tire, due to a negative impact on the rubber properties. Devulcanized car tire rubber is promising as it allows to retain the rubber properties to a great extent, implying increased opportunities for reuse of this material in new car tires. However, by grinding whole car tires already at the beginning of the recycle process, tire components with distinctively different properties are mixed, limiting the re-use greatly. Separating these components before grinding increases the opportunities for reuse by devulcanization of these specific rubber materials.*

*Car tire properties are continuously improved, both in terms of construction and application of advanced compounding- and filler technologies. This implies varying feedstock compositions and, as a consequence, different material properties of devulcanized car tire rubbers. As car tire manufacturers require constant properties, the composition and quality of their base materials, improved quality-control and the consistency of devulcanized car tire rubber will increase its acceptance for its use in new car tires.*

*Due to legislation the amount of recycled car tires is increasing, but it also limits the reuse of the rubber of end-of-life car tires for new tires. End-of-life car tires produced before the relevant regulations, and even end-of-life tires from recent date but imported from outside the EC, might contain carcinogenic components which are not allowed anymore in the EC. This is another reason for sorting and selecting car tires before reuse. It is well conceivable because most of the modern car tires are identifiable by the use of imprinted or RFID labels.*

*The impact of e.g. a change in filler systems, fillers like silica for rubber, and of recent developments in vulcanization systems on the devulcanized and subsequently revulcanized of rubber is to be investigated. Rubbers and additives from renewable resources are continuously under investigation. The final properties of the resulting rubber must be close to those of conventional one's and no or only minor impacts on the prop[erties can be tolerated. Development of new and alternative additives, i.e. the use of resins for tread compounds is an ongoing process.*

## 2.1   Introduction

An important by-product of the transportation sector is the production of end-of-life tires. As early as 1974 this was noticed as an important aspect of the tire production and many possible, still valid, solutions were indicated by Beckman e.a[1], f.i. artificial reefs, highway abutment crash barriers and use as component for asphalt roads. The amount of end-of-life tires is growing annually: For 2008, the amount of end-of-life car tires was estimated to be equivalent to 17 million tonnes worldwide[2] and 3.2 million tonnes for Europe[3]: both are still increasing.

Initially, many end-of-life tires were discarded as landfill; however, the increased reuse of the tire material and the legislative limitations has decreased considerably. In Europe, discarding as landfill decreased from 62 million tonnes in 1992 to about 3 million tonnes in 2012 and 0.16 million tonnes in 2016[4]. Relative amounts are presented by the European Tyre Recycling Association (ETRA)[5] (see Figure 2.1). For Europe, the overall amount of end-of-life tires is about 3.4 million tonnes for 2017[6]. In the EU, countries are obliged to prohibit stock piling of whole and ground tires in landfills from 2006. It is shown that for countries that implemented Extended Producer Responsibility (EPR) a 100 % recovery can be achieved. Countries that implemented a tax based or a free market system have shown to be less effective[4]
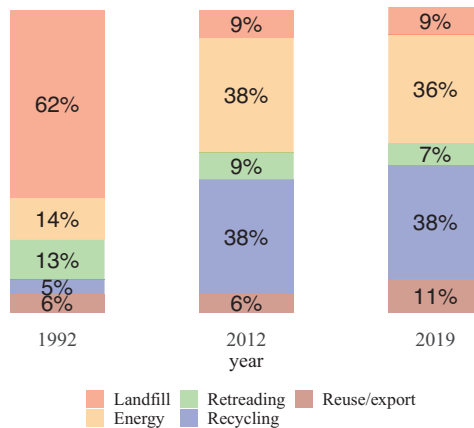


FIGURE 2.1: Tire recycling, Europe 1992 - 2019[2,5]

As the energy content of end-of-life tires is about $32\,\mathrm{MJ/kg_{tire}}$, burning such tires in energy plants or cement kilns is one solution, especially when the remaining ash and steel can be used for the production of cement or concrete. This saves conventional energy sources, such as coal. In Europe, in 2012 38% or 12,6 million tonnes of tire waste were used this way. A drawback of burning end-of-life tires is that only the energy content is used, while valuable raw materials are wasted. The good news is that, according to 'Global Recycling'[4], this decreased to less than 1 million tonnes for the EU in 2016. It is difficult to compare the figures of different sources as the groupings and the policies of different countries regarding end-of-life tires differ[4]. Nevertheless, 'Global Recycling' indicates an overall, global, increase of tire recycling in favour of burning[4]. Also a changing focus in China on responsible recycling of tires is noticeable, as a major producer and user of, mostly natural rubber[4]. Of the recycled tires in the EU, 57% is reused as granulate, 10% as whole tires[2]. Many applications are developed for this granulate from the tires: filler for sports fields, for road surfaces and others where the elasticity and durability of rubber are important attributions, see Figure 2.2 for percentages over 2015 for Europe and Figure 2.3 for 2020 for the Netherlands for small truck and car tires[7]
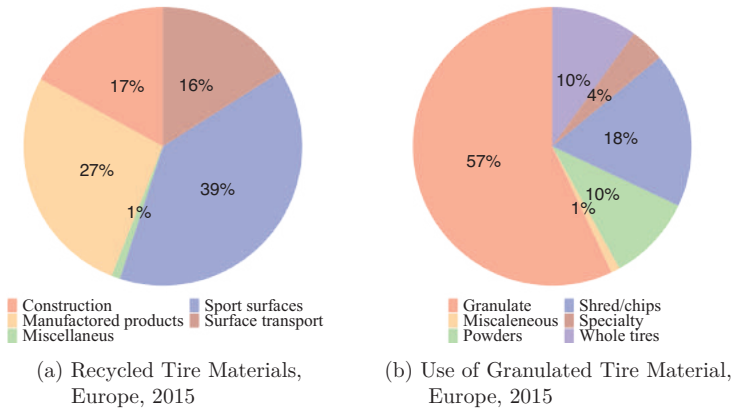


(a) Recycled Tire Materials, Europe, 2015

(b) Use of Granulated Tire Material, Europe, 2015

FIGURE 2.2: Recycled Tire Materials and the use of Granulated Tire Material in Europe (2015)[2]

With respect to recycling, all these applications lead to a downgrading of the properties of the original product and of lifetime; finally this rubber will still end up as waste and will be either used as a source of energy or dumped in landfills. Dumping of end-of-life tires in landfills is environmentally harmful: there is increasing evidence that tire waste leaches potentially harmful products such as zinc, lead from exhaust gasses and cadmium from the steel wires in the tires into the environment. Although many investigations are performed on harmful materials leaching from roads, due to that this represents the largest surface with possible remaining traffic related contaminations, most of the contaminations can be attributed to the wear of car components, like brakes (Marwood[8], Mohammed[9], Pysklo[10], Saeedi[11]). Research on tires in granulated form was performed by Kruger[12]. In this study, an overall ecotoxicity after leaching was estimated by growth inhibition or acute toxicity for Daphnia Magma or Pseudokirchneriella subcapitata. No
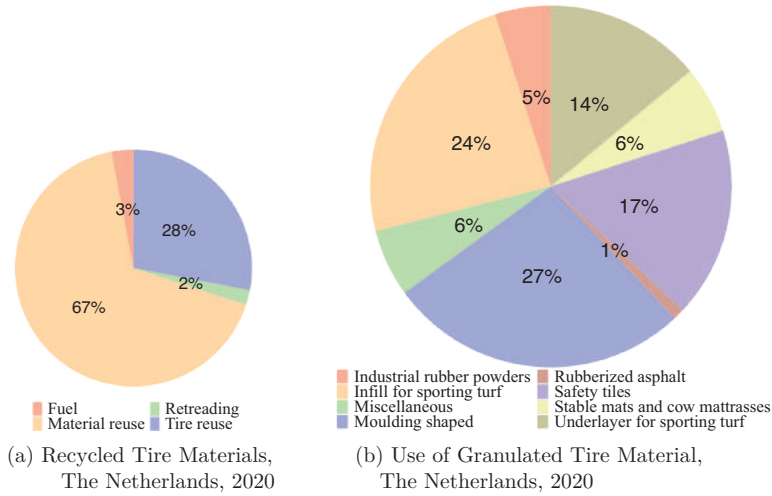
(a) Recycled Tire Materials,
The Netherlands, 2020

(b) Use of Granulated Tire Material,
The Netherlands, 2020

FIGURE 2.3: Granulated small truck and car tire materials
and the use of Granulated Tire Material in the Netherlands
(2020)[7]

detailed specifications are given. Horner[13] extracted car tire rubber with an acid rain simulation substance and found only zinc, but soil in the base of a tire dump in West London showed zinc, cadmium and lead with respective average concentrations of 1235 ppm, 22 ppm and 1160 ppm lead. Selbes[14] found iron and manganese when tire granulate was exposed to acid solutions, considered to be caused by the remaining metal in the rubber. Under basic pH conditions, dissolved organic carbon and dissolved nitrogen were indicated. The overall conclusion was that neutral pH conditions reduce the impact on the environment. Khoshgoftarmanesh[15] suggests that the zinc compounds in granulated tire rubber can act as a source of zinc, supporting plant growth.

The use of pyrolysis (heating without oxygen) of end-of-life tires to recover oil, gas and char is of increasing interest. Its economic feasibility has been indicated by WRAP[16], Peace[17] and Makitan[18], though Sienkiewicz[3] considers it too expensive. Jung[19] indicates that the char, mainly consisting of carbon black, can be produced nowadays with acceptable properties, comparable to the N600-N700 ranges of carbon black.

Despite all these developments in recycling of car tires, reusing end-of-life tires for new tires is hardly done. Investigations were performed into reuse of fine rubber crumb as a filler, but its concentration is limited to about 5 wt% of the tire weight[17], mainly because of the high costs of producing very fine rubber crumb. Another kind of reuse is using rubber crumb for thermo plastic rubbers. Drawback is the incompatibility of (recycled) polymers and GTR, which needs proper phase morphology and interfacial adhesion. This can be obtained by devulcanization of the GTR and dynamic vulcanization of the blend with the polymer. The use of additional compatibilizers might be necessary to improve the mechanical properties.[20]. With respect to replasticizing of vulcanized rubber to reuse it for revulcanization, both

reclaim and revulcanization processes are used. The main difference between both is the impact the process has on the chain length of the replasticized polymer(Saiwari[21]):

- because of high temperatures and shear rates used for reclaiming, the polymer chains as well as the crosslinks between the polymer chains are disrupted, with a material with relatively short polymer chains as a result, resulting in low tensile strengths and strains after revulcanization.

- for revulcanization, the process conditions are much milder and very often a devulcanization agent is used. The aim is to break only the crosslinks between the polymer chains and as least as possible the polymer chains itself, in order to maintain the tensile strength and strain at break after revulcanization as close as possible to those of the original polymer.

With the currently available methods often designated as 'devulcanization', the polymer is degraded to such an extent that reuse in car tire compounds is also limited to 5 %. This indicates that these are in fact reclaimed products. Reclaim is a better designation for these materials, to distinguish them from devulcanized rubbers. Despite this, Adhikari[22] already pointed to many positive aspects of using reclaimed rubber, like energy-savings, aging resistance and processing advantages during calendering and extrusion, because of a lower viscosity of reclaim rubber compared to virgin material. The latter, however, will mostly be less prominent for devulcanized rubber as the polymer chains will be much less deteriorated then of the reclaimed material.

Makitan[18] indicates that authors do not agree that recycling of end-of-life tires for replacing virgin rubber for new tires is energetically advantageous, but that economic feasibility largely depends on overall investments in equipment and processing costs, in particular on the logistics and the costs involved with acquiring the end-of-life tires.

Real devulcanization of rubber still remains under investigation, there are promising results: Sutanto[23] has successfully devulcanized EPDM rubber and Rajan[24] natural rubber for tire applications. Srinivasan[25] indicated that reclaiming of synthetic rubber is more challenging than of natural rubber (NR) based material: NR softens under heat and pressure, while synthetic rubbers harden. Saiwari[21] demonstrated that devulcanization of car tire rubber can successfully be done on laboratory scale. Schmidt[26] claims a devulcanization process using a planetary type extruder without addition of supporting chemicals, however those claims are very sparsely supported.

The aim of the present review is to make an inventory of the most important factors that can influence both, the quality and usability of devulcanized car tire rubber, and the further optimization of the re-use of the devulcanizate for car tire rubber.

## 2.2   Tires and their constructions

There are many kinds of tires such as truck, car, aircraft, tractor, and earth mover tires, and each of these kinds of tires have a different construction and more importantly, varying rubber compositions and properties, related to their specific use:

- Truck tires are produced for long mileage. The tread contains a relatively high amount of natural rubber[27] (NR).

- Aircraft tires must be resistant to very high forces and heat development in the tread due to the high acceleration during landing and high speeds while rolling. This requires very special compound properties[28] and a high amount of natural rubber[27].

- Tractor tires must transmit all forces in soft soil at low speed with special pads on the surface of the tread. They must be very resistant against punctures[29].

- Earthmover tires must be very resistant against punctures from e.g. sharp stones, and have to transmit high forces at low speeds[30].

- Passenger car tires must be wear resistant, but also need good wet grip and low rolling resistance properties. Typical tread compounds consist of Styrene-Butadiene rubber (SBR) and Butadiene rubber (BR) blends[27].

All these different properties with related constructions and compound compositions make it undesirable to mix them all together when the intention is to reuse the rubber in the same kind of applications. For truck and passenger car tires the overall material usage is described in Table 2.1. According to ISRI[31] "about 84 % of the scrap tires come from passenger car tires, 15 % from truck tires and the remaining 1 % from heavy equipment, aircraft and off-the-road tires" in the US.

**Table 2.1:  Materials used in tire manufacturing (in Europe and the USA)**

| Materials | In European Union Passenger | Truck | In USA Passenger | Truck |
|---|---|---|---|---|
| Natural rubber (%) | 22 | 30 | 14 | 27 |
| Synthetic rubber (%) | 23 | 15 | 27 | 14 |
| Carbon black (%) | 28 | 20 | 28 | 28 |
| Steel (%) | 13 | 25 | 14-15 | 14-15 |
| Fabric, other fillers, accelerators, antiozonants etc. (%) | 14 | 10 | 16-17 | 16-17 |
| Average weight new tire (kg) | 8.5 | 65 | 11 | 54 |
| Average weight scrap tire (kg) | 7 | 56 | 9 | 45 |

(%): According to the percentage of weight of the finished tire that each material class represents[3]

(a) Standard type tire
pixabay 961050

(b) Low aspect ratio type tire
pixabay 1492906

FIGURE 2.4: Example of different construction heights of
tires
both pictures under @ CC0 Public Domain license

### 2.2.1 Car tires

As shown in Figure 2.4 a and b, the absolute dimensions of car tires vary depending on car weight, engine power and torque, and the relative dimensions of sidewall to tread. Modern high-end cars tend to have lightweight wheels and high curve stability, leading to an increasing aspect ratio between tread vs. sidewall dimensions. As a consequence of this development, the relative amount of tread compound in the granulate increases and the sidewall compound decreases compared with the other compounds.

### 2.2.2 The various tire parts and their compositions
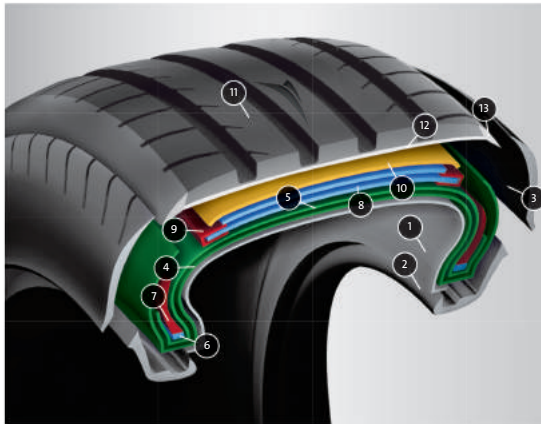


| 1. | Inner lioner |
| 2. | Rim cushion |
| 3. | Sidewall |
| 4. | Carcass layer 1 |
| 5. | Carcass layer 2 |
| 6. | Bead |
| 7. | Apex |
| 8. | Belt layers 1+2 |
| 9. | Gumedge |
| 10. | Nylon overhead |
| 11. | Tread |
| 12. | Undertread |
| 13. | Wingtip |

FIGURE 2.5: Construction of a car tire
Courtesy Apollo Vredestein

Basic requirements for all car tires are the opposing qualities of:

- high roadgrip to transmit the traction- and brake forces under dry, wet, hot and cold conditions,

- low rolling resistance for fuel economy,

- and long lifetime.

These are most commonly depicted as a triangle shaped diagram with rolling resistance, wet grip and wear/abrasion resistance on the corners: for better wear resistance, a higher hardness of the compound usually performs better, but this decreases the (wet) grip properties. Also, the rolling resistance is proportional with the resilience of the compound, while the (wet) grip needs lower resilience to improve energy dissipation in the contact layer of the compound with the road surface.

**Table 2.2: Polymers used in car tires[21]**

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

NR = Natural rubber; BR = Butadiene rubber; SBR = Styrene-butadiene rubber; IIR = Butyl rubber, mostly as chloro- or bromo-butyl rubber (CIIR or BIIR).

As a rule of thumb, it will take about four years before new developments in car tires will be found back in end-of-life car tires. Hence, when using devulcanized car tire rubber for new products, it is important to monitor these developments and to consider the potential impact on the quality of the devulcanizate. Modern car tires are complex and highly engineered products and comprise of about 12 components, each with their own mechanical properties and elastomer compositions, Figure 2.5.

Concerning devulcanization, the following tire components are most relevant:

- Tread (11): the most critical and severe loaded component, as all road contact is via this component. Wet grip, wear, traction, brake forces and rolling resistance are mainly determined by this part of the tire.

- Sidewall (3): the flexible link between bead and tread. It is also highly loaded due to the frequent deformation particularly for radial ply tires. Its dynamic properties are very important.

- Apex (7): the connection between the stiff rim and the highly flexible sidewall.

- Carcass-layers (4,5): support the belt (8) and the tread.

All the components are assembled and vulcanized together into one final car tire. Typical elastomer compositions for the various constructional entities are listed in Table 2.2.

As the normal recycling of end-of-life car tires starts with shredding the complete tire into granulate and cleaning from metal en fibres, the remaining granulate will be a mixture of all elastomers used in the car tires, including

fillers, processing chemicals and remaining vulcanisation additives. As the various components of the car tire are designed to result in a best balance of properties such as dynamic behavior, elasticity, damping, and hysteresis, it will be clear that the mix of components in the granulate will influence the final quality and re-usability of the devulcanized rubber. Both, the relative amount of the various polymers as well as the composition of each of the components, are relevant. Hence, the developments in dimensions of the tires as well as in the composition of the compounds are important. According to Rajan[24], the preferred use of reclaimed rubber in car, light truck and off-the-road tires is for carcass, sidewall and under-tread.

### 2.2.3 Other rubber additives influencing devulcanization

The properties of a rubber compound are to a great extent determined by the blend of polymers, the amounts and types of fillers, the vulcanization system and the vulcanization conditions. Hence, it is to be expected that changes in these conditions influence devulcanization processes and properties of the revulcanizates. Developments in compounding are most visible in tires designed for a range of operational conditions: e.g. summer, winter and all-season tires. Not only is the profile of the tread adjusted to the specific circumstances for which the tire is designed, but also the properties and compositions of the polymer compounds are optimized. All this is with the intention of improving fuel economy, wear resistance and dry, wet and sub-zero grip. Additionally, durability and decrease of environmental burden are in the focus of recent developments. An important development in car tires is the use of silica as an active filler, resulting in a considerable improvement of the overall properties.

*Silica:* At the end of the $20^{th}$ century, the performance of car tires was substantially improved by using silica as reinforcing filler, instead of or in combination with carbon black[32]. Developments in improving tire compounds with silica remain ongoing according to Reuvekamp[33] and Sarkawi[34], and include new silica types with optimized nano-structures as reported by Shan[35] and Saeed[36], as well as optimized coupling agents. Because of the considerable effects of these new silica types on the compound properties, the impact on the application of devulcanized tire rubber must be taken into account when using devulcanized rubber. One of the main differences of silica compared to carbon black is the chemical bond between the filler and the polymer in the former case compared to the physical bond between carbon black and the polymer. The implications for devulcanization and for the re-usability of the devulcanizate in new compounds is to be investigated.

*Zinc Oxide:* Heideman[37] and Byers[38] investigated the potential for reduction of the amount of zinc oxide and developed environmentally friendly alternatives. Due to the fact that the basic rubber network formation is still based on di- and polysulfidic bonds, it can be expected that the consequences for the devulcanization process and the re-usability of the devulcanizate will be limited.

*Vulcanization systems:* Vulcanization based on sulfur systems can be expected to remain the standard for tires. Contrary to peroxide curing, which leads to carbon-carbon bonds. Despite its good qualities for e.g.

high-temperature stability and low compression set, it is still inferior to sulfur based systems with respect to tensile, tear and flex properties and abrasion resistance. These are all very important for tires[27].

With respect to the other components of the sulfur-based vulcanization system, the primary and secondary accelerators, which are important for both the final properties of the rubber, and for the cure and for scorch (delay before curing) times, new products are developed. Hence, devulcanization systems based on de-crosslinking of the sulfur-sulfur bonds between the polymer chains can be expected to remain effective on the long run. For revulcanization of the devulcanizates, the need for continuous development may be expected due to the changes and improvements in the accelerators.

*Bio-based feedstocks:* From a sustainability point of view, bio-based plasticizers (Flanigan[39], Jayewardhana[40]) and alternative sources to overcome of agricultural problems of NR (van Beilen[41]) are important developments and the usability of these is promising. As bio-based materials in chemical compositions will be rather similar to the non-bio-based precursors, their basic properties should be similar and so the impact on devulcanization can be expected to be minimal. Because of the large scale on which car tires are produced, it is not to be expected that in the near future a significant portion of car tire compounds will be bio-based or from alternative sources for NR.

*Rubber crumb:* As mentioned previously, rubber crumb can still be used as an inactive filler up to 5 % of the rubber-compound with acceptable end-properties. Peace[17] mentions even concentrations up to 13 %, but only when a very fine, thus expensive grade of crumb is used (see Table 2.3 (b)), which is economically not feasible. Besides, agglomeration of ground rubber during shipment or storage might be a problem, as Baranwal and Klingensmith already indicated[42].

**Table 2.3: Types of recyclates and average prices**

| Type of recyclate | Size fraction | Size | Average price ($/ton) |
|---|---|---|---|
| Cut tires | >300 mm | > 25 mm | 27 |
| Shreds | 20-400 mm | 2-6 mm | 240 |
| Chips | 10-50 mm | 0.8 mm | 290 |
| Rubber Granulate | 0.8-20 mm | 0.6 mm | 340 |
| Rubber dust | <0.8 mm | 0.4 mm | 390 |
| | | 0.18 mm | 440 |
| | | 0.15-0.075 mm | 600 |
| | | <0.075 mm | 1240 |

(a) Classification of rubber recyclates obtained during the grinding of tires[3]   (b) Average Price of Crumb Rubber, Chips and Shreds in the USA, 2002[17]

Guzman[43] has explored the use of rubber crumb as activator in the vulcanization instead of of zinc oxide. Despite promising results in a model system, with a SBR / NR / BR compound the results fell short of expectations. However, it did indicate the impact that rubber crumb may have on vulcanization.

## 2.3   New trends

Passenger car tire technology is still improving. Due to increasing demands on wear, wet grip and fuel economy, environmental issues and regulations, new fillers and filler technology, improved polymers, new ways of protection against oxidation and aging, and alternative wheel-tire constructions are current topics[44]. However, some of these developments may have an impact on the re-usability of rubber of the end-of-life tires in renewed tire production:

*Airless tires*
> One development in which the tire is reduced to a tread only, connected to the axle with polymer spokes, is the non-pneumatic tire. This is, however, not a new idea as is shown by the tricycle of Millet of 1887, see Figure 2.6. Despite all the investigations into and developments of this type of tires, for example by Veeramurthy[45] on the effects of geometry on the performance, by Ju[46] on flexible cellular solid spokes and on the tread[47], by Heo[48] on the air resistance of the spokes and by Lee[49] on vibration analysis, it still cannot compete with the pneumatic tire for normal car operation. However, the research does indicate about the complexity of properties related to the sidewall. With respect to devulcanization, the non-pneumatic tire can be considered not to be relevant because of the low numbers used. But if this will be a success, there will be more. There is less rubber involved in such a tire, reducing the amount of rubber waste to be recycled. And it encompassed probably only one or two types of compounds, reducing the variety in the ground tire rubber.



Titre: Tricycle Millet

Inventaire n°: 14327-0000-

Tricycle à essence Millet, équipé d'un moteur rotatif en étoile, 1887

Félix Théodore Millet 1844-1929 Ingénieur mécanicien

© Musée des arts et métiers-Cnam/photo studio Cnam

FIGURE 2.6: Historic airless tire

*Short fibers:* Adding short aramid fibres up to 3 mm to the compound will reinforce the rubber matrix (Shirazi[50,51]), improve the adhesion between the rubber layers[52] and the wear properties of a tread[53]. Using short fibres in tire compounds is a recent development and it can be expected that large scale applications will influence the re-usability

of a devulcanizate. These short fibres cannot be removed from the compound anymore with existing technologies.

*EPDM rubber:* As an alternative method to prevent oxidation of the sidewall rubber up to 10 % EPDM can be added to the compound. Sahakaro[54], Ghosh[55] and Zhang[56] have investigated the effect of adding EPDM to a compound of SBR / BR. Although EPDM is easy to devulcanize, according to Sutanto[23], the overall effect on devulcanized tire rubber remains to be investigated.

## 2.4   Ground tire rubber as feedstock for recycling

The feedstock for granulated car tire rubber mainly consists of end-of-life tires. Part of it can also be off-spec tires from production.
Main resources for end-of-life tires are:

- tire replacement centers, garages and comparable organizations;

- after a second life, for example in agriculture, and disposed of at a later stage and entering the recycling chain;

- end-of-live tire recollection centers, for example municipal waste collection centers;

- car scrapyards.

These tires are collected by the tire recycling companies, sorted, coarsely cut in large shredders, and ground either under ambient or cryogenic conditions into finer grades. During this process steel and fibres are removed. A reasonable assumption is that the general feedstock consists of various tires of different ages, types, brands and constructions. From the resulting ground rubber, a mean composition can be determined but with deviations for each batch, see for example Figure 2.7. However, this composition is too general to be useful for determination of the characteristics of a devulcanizate.

| Properties | Test methods | Unit | Typical values |
|---|---|---|---|
| Specific gravity | ASTM D 1817 | kg/m$^3$ | 1,100-1,200 |
| Bulk density | EN 1097-3 | kg/m$^3$ | 420 ±6% |
| Particle size range | ISO 13322-2 | mm | 0.7-2.0 |
| Particle Size <0,5mm | ISO 13322-2 | % | < 1.0 |
| Total polymer content (RCH) | ISO 9924 | % | ≥ 45 |
| Natural rubber content | ASTM D 297, 52-53 | % | 10-35 |
| Ash content | ISO 9924 | % | < 10 |
| Moisture content (Loss 2h@105°C) | ASTM D 1509 | % | ≤ 1 |
| Free metal content | OA-698 [Note 1] | % | ≤ 0.002 |
| Free fibre content | OA-698 [Note 1] | % | ≤ 0.001 |
| Other contamination | OA-698 [Note 1] | % | ≤ 0.002 |
| EOX | DIN 38409-8 | mg/kg | ≤ 20 |
| DOC | EN 1484 | mg/l | ≤ 30 |
| Pb (in hydrous eluate) | EN 11885 | mg/l | ≤ 0.02 |
| Cd (in hydrous eluate) | EN 11885 | mg/l | ≤ 0.001 |
| Chrom total (in hydrous eluate) | EN 11885 | mg/l | ≤ 0.008 |
| Chrom VI (in hydrous eluate) | EN 11885 | mg/l | ≤ 0.008 |
| Hg (in hydrous eluate) | EN 1483 | mg/l | ≤ 0.001 |
| Sn (in hydrous eluate) | EN 11885 | mg/l | ≤ 0.02 |
| Zn (in hydrous eluate) | EN 11885 | mg/l | ≤ 0.2 |

FIGURE 2.7: Example of a composition of granulated car tire rubber[57].

Technical solutions are available to sort tires, based on a Radio Frequency Identification (RFID) label[58] to identify brand, type of tire and age. This is also possible by using the existing labeling system, and can be used to create more consistent batches. It is technologically also possible to separate parts of the tires, tread and sidewall, with waterjet cutting technology[59] with the opportunity to optimize the homogeneity inside a batch of granulated tire rubber.

### 2.4.1 Requirements on the feedstock

In the modern process industry, one of the important instruments to minimize production losses and optimize production quality is Statistical Process Control (SPC), with which the variation of production is minimized[60–62]. This is also a well known instrument in the tire manufacturing industry, indicated by Grossman[63] (1997) and Prajapati[64] (2012). As the focus of SPC is to keep production variations between pre-defined boundaries, any variation in the raw materials will have an impact on the final product quality. However, it is mandatory that variations in the properties of devulcanized material, when supplied to tire manufacturers, should be as minimal as possible. Within this framework it is worthwhile to note that in 2009 Srinivasan[25] remarked that, with the introduction of the radial tires, the 'uncompromising attitude towards quality control . . . has slowed down the reclaim industry'.

There are indications in literature that the quality of a devulcanizate depends on the batch of rubber granulate used. However, this has not yet been extensively investigated as such. Research is typically performed on material of a single batch, to minimize the uncertainty in results. Dijkhuis et al.[65] found large differences in behavior for various kinds of EPDM (roof sheeting and profile material, mainly differing in crosslinked network) and this might be true for granulated tire rubber as well.

To encourage tire manufacturers to accept substantial amounts of a new raw material, like devulcanized rubber as a replacement of the well-known natural and synthetic rubbers, it should meet at least the following criteria:

1. Consistent quality;

2. Known and constant impact on existing formulations and curing systems;

3. Defined impact on the properties of the resulting rubber compounds;

4. Relatively large scale availability.

This is evident as the rubber compounds for tire production are produced according to complex, material property dependent formulations and each change in the formulation requires extensive testing before being approved for large-scale production.

Hence, for large scale application of devulcanized rubber it is necessary to be able to characterize the material and its properties and fulfill the previously mentioned criteria. Vilaplana[20] has investigated these quality related issues for recycled polymeric materials in general. He states: "The main challenge for the recycling industry is to effectively combine the scientific knowledge about the degradation state and the quality properties of their recyclates,

and effectively design the upgrading process for each specific waste stream, in order to tailor the properties of the final recycled material and, thus, meet the requirements of the destined application".

This leads to an important question for the production of granulated tires. Overall, would it be most profitable to deliver a mix of whole granulated tires? This will consequentially produce devulcanizate with mean properties. Or to increase the quality of the devulcanizate by supplying granulate from selected parts of the tires, for instance by compound type as used for the treads and sidewalls of the tires, or sorted by manufacturer and type of tire, as each supplier has its specific formulation for each type of tire?

Because of the very strict environmental and health legislations, selection based on manufacturer and age of the tire might be the first necessary step, as that is the only warranty to process tires fulfilling this increasingly severe requirement. Especially older tires still may contain carcinogenic Polycyclic Aromatic Hydrocarbons (PAH) and / or N-nitrosamines, and this can even be the case for new tires which are produced under less severe regulations.

## 2.5   Legislation

Many developments in tire production and recycling are influenced by EU and other legislation. For instance, the EU management of used rubber is based on the 1999 Directive on the Landfill of Waste 1000/31/EC[3]. Furthermore, the ban on high polycyclic aromatic hydrocarbons containing processing oils in the 2010 European Directive 2005/69/EC (and its equivalent in Japan) have had a large impact: High Aromatic (HA) and Distillate Aromatic Extract (DAE) processing oils have been be replaced by Treated Distillate Aromatic Extract (TDAE) and other alternatives[66,67]. Other related European Union legislations are:

- Directive 2008/98/EC for waste policy;

- Directive 1999/31/EC on the landfill of waste;

- Directive 2000/53/EC on vehicles at the end of their useful life, including rules to prevent waste from vehicles such as tires;

- Directive 2000/76/EC on waste incineration that sets emission limits for all new cement kilns manufactured as of 2003.

REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) "is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risk that can be posed by chemicals"and "establishes procedures for collecting and assessing information on the properties and hazards of substances"[68]. REACH influences also the recycling of car tire rubber, as it considers reclaimed and revulcanized rubber as new feedstock, which implies that the producer has the responsibility to establish the compliance with applicable regulations. As the intended use of materials is part of the risk assessment, the situation for recycled rubber is rather complicated and goes beyond the scope of this overview.

## 2.6 Conclusions

The amount of end-of-life tire rubber is growing annually. Inspite of all alternative reuse options that are already available or under development, most of them are either only deferring the problem to the future for instance rubber crumb for playing grounds. Others are destroying valuable materials by using only the energetic value, for instance by incineration in cement kilns. Closing the loop by reusing the end-of-life tire rubber for new ones is at the moment only feasible for fine rubber powder, with a limit of 5 % of a tire. Devulcanized car tire rubber has the potential to be used in higher amounts in new tires.

However, many questions are still to be answered, apart from the upscaling of the devulcanization process to a continuous alternative, the topic of the present research:

- Is it possible to define a kind of average quality of the devulcanizate?

- What is the impact of fillers in general, but the use of silica more specifically on the devulcanization and reusability of the devulcanizate?

- What is the impact of the remaining vulcanization ingredients in the devulcanizate on revulcanization?

- Is it possible to reuse the devulcanizate "as is" or is it necessary to define a kind of generalized quality, requiring additional analysis and processing steps, before the remaining deviation from a kind of mean is acceptable for the tire manufacturers.

- Although the processing of devulcanized rubber requires only about 16 % of the energy that is needed to produce virgin rubber, is it possible to make the logistics and processing of devulcanization so efficient and effective that the overall costs are comparable to those of virgin compounds?

Due to all environmental safety and health regulations, reuse of a devulcanizate for new tires is only possible for PAH- and N-nitrosamines-free material. This requires that only recently produced end-of-life tires can be used for devulcanizates for the tire industry. Legislation has already influenced the recycling of rubber to a large extent by prohibiting landfills. Additional legislation can promote the reuse of end-of-life tires for new rubber products. In view of all the environmental problems related to the still growing amount of end-of-life tires, additional legislation can be expected.

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# Chapter 3

# Materials and Equipment

*Both the ground passenger car tire rubber and the twin-screw extruder setup are described in detail in this chapter. All other materials and equipment are introduced too, as well as the formulations and compounding procedures.*

## 3.1 Introduction

In this chapter, the two core elements of this study, the ground passenger car tire rubber (GTR) and the basic setup of the twin-screw extruder are introduced. All other materials used in this thesis are covered, as well as the specifications of the equipment. All compound formulations are specified in this chapter, paragraph Formulations. The compounding and mixing procedures are specified in the paragraph Procedures.

## 3.2 Materials

### 3.2.1 Ground passenger car tire rubber

The ground passenger car tire rubber used in this investigation was obtained from Genan, Dorsten, Germany. It is a commercial ground passenger car tire rubber granulate, medium grade in terms of granulometry, with a normal size distribution with dimensions ranging from 1 mm to 3.5 mm, see Figure 3.1a.



(a) Genan specifications (Granulat Mittel (M)3296.rdf[1]).

(b) After analysis with laboratory screens.
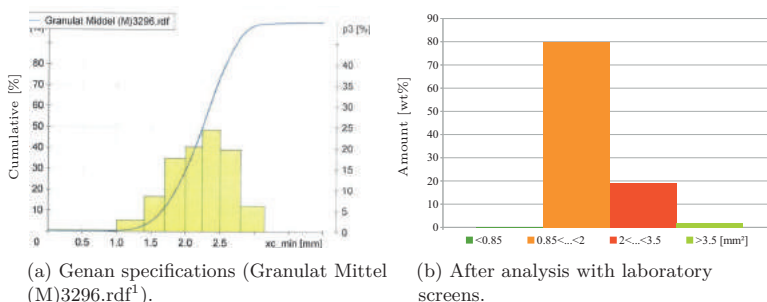
FIGURE 3.1: Size distribution of GRT.

It contains at least 45 wt% polymer, of which 10 wt% to 35 wt% Natural Rubber, and an ash content <10 wt%, according to the technical data sheet[1]. This GTR type is selected based on the low level of contaminations such as

stones, originating from dirt adhering to the tires before granulating; steel, coming from steel of the wires in the bead of the tires and the carcass, and abraded material from the cutting- and grinding equipment; and dust from fibres in the tire carcasses: The coarser grades usually contain higher levels of dust, steel and fibres remaining in and adhering to the granulate particles, the finer grades usually have higher amounts of steel- and stone contaminations. By visual inspection the selected grade contained a minimum amount of these contaminations. By Thermo-Gravimetric Analysis (TGA) the ash content, consisting of silica, ZnO and ZnS but also steel, stone dust and other contaminations, was determined as 20 phr to 40 phr, with 23 phr the overall mean value. Per hundred parts of rubber (phr) is a common unit in the rubber industry. This variation is because the granulates originate from different parts of a tire. After analysis with a laboratory set of screens, a slightly different weight distribution of GTR was found, see Figure 3.1b. Occasionally, an ambiently-ground whole car tire powder, supplied by Rubber Resources BV, Maastricht, the Netherlands, with a typical average particle size of 0.35 mm and a maximum particle size of 0.42 mm was used as a comparative material.

### 3.2.2   Other materials

All other materials are listed in Table 3.1:

**Table 3.1: Materials**

|  | Material | Supplier |
|---|---|---|
|  | Polymers: |  |
| NR | Natural rubber, grade SMR10 | Behn Meyer Holding AG, Hamburg , Germany |
| SBR | Styrene Butadiene Rubber. Grade: - SPRINTAN SLR 4601(50% vinyl, 25% styrene) - SPRINTAN SLR1732 (35phr oil) | Trinseo Deutschland GmbH, Schkopau, Germany |
| BR | High-cis Butadiene Rubber grade BUNA CB24 | Arlanxeo Deutschland GmbH, Leverkusen, Germany |
| IIR | Vulcanized Butyl rubber of end of life inner tubes | Rubber Resources, Maastricht, the Netherlands |
|  | Fillers: |  |
| CB | Carbon Black, grades N550, N375, N110 | Orion Carbon Black GmbH, Essen, Germany |
| Silica | Silica grade Zeosil 1165MP | Rhodia Silices, Lyon, France |
| $TiO_2$ | Titanium dioxide, Hombitan R210 | Venator, Wynyard, UK |
|  | Processing oil: |  |
| TDAE | Treated Distillate Aromatic Extract, VIVATEC 500 | Hansen & Rosenthal, Hamburg, Germany |
|  | Coupling agents: |  |
| TESPD | bis[3-(TriEthoxySilyl)Propyl] Disulfide | Evonik Industries AG, |
| TESPT | bis[3-(TriEthoxySilyl)Propyl] Tetrasulfide | Essen, Germany |

**Table 3.1: Materials, continued.**

| | Material | Supplier |
|---|---|---|
| | Vulcanization system: | |
| ZnO | Zinc oxide | Merck KGaA, |
| St.A. | Stearic acid | Darmstadt, Germany |
| S | Sulfur | |
| TBBS | N-Tert-Butyl-2-BenzothiazoleSulfenamide | Lanxess Rhein Chemie Gmbh, |
| MBTS | Mercapto BenzoThiazolediSulfide | Cologne, Germany |
| DPG | 1,3-DiPhenylGuanidine | |
| | Anti-oxidants, anti-ozonants: | |
| 6PPD | N-(1,3-dimethylbutyl)-N'-Phenyl-p-PhenyleneDiamine | Lanxess Rhein Chemie Gmbh, Cologne, Germany |
| TMQ | 2,2,4-Trimethyl-1,2-DihydroQuinoline | |
| | Processing stabilizer: | |
| TDTBP | Tris(2,4-Di-Tert-Butylphenyl)Phosphite | Sigma Aldrich Cooperation, Zwijndrecht, The Netherlands |
| | Devulcanization aids: | |
| DBD | 2-2'-DiBenzamidoDiphenylDisulfide | Schill and Seilacher GmbH, Hamburg, Germany |
| DPDS | DiPhenylDiSulfide | Sigma Aldrich Cooperation, Zwijndrecht, The Netherlands |
| | Solvents for Horikx-Verbruggen analysis: | |
| Acetone | purity >99.5 wt% | Atlas & Assink Chemie b.v., |
| THF | TetraHydroFuran, purity >99.8 wt% | Enschede, The Netherlands |
| Toluene | purity >99.8 wt% | |
| | Resins: | |
| A, B, C | See Table 3.2 | Kraton company, Almere, the Netherlands |
| | Cleaning chemicals for the extruder ventilation: | |
| NaOH | Pellets, technical quality | Sigma Aldrich Cooperation, Zwijndrecht, The Netherlands |
| NaHClO | bleaching water, 2% | Household quality |

**Table 3.2: Aromatic hydrocarbon resins properties**

| Resin | Type | Density [kg m$^{-3}$ @ 20 °C] | Softening point(*) [°C] | Flame point [°C] | $T_g$ [°C] |
|---|---|---|---|---|---|
| A | polyterpene (mostly $\alpha$-pinene) | 980 | 115 RB | 195 | 61 |
| B | hydrocarbon | 1060 | 85 RB | 207 | 39 |
| C | terpene-phenol | 1010 | 150 MCB | 246 | 97 |

(*) RB = Ring/ball; MCB = Mettler cup/ball
Resin B is best miscible with SBR, BR

## 3.3 Equipment

### 3.3.1 Extruder



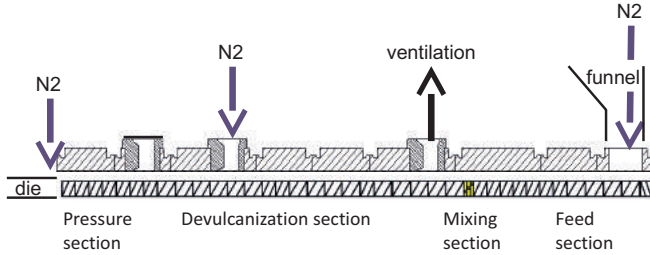FIGURE 3.2: Layout of the extruder, from right to left.



FIGURE 3.3: Elongated die.

Continuous devulcanization was performed in a KrausMaffei ZE 25 UTX co-rotating twin-screw extruder (KraussMaffei Technologies GmbH, München, Germany), length 42D with D = 25 mm, and equipped with 3 de-gassing positions between the hopper and outlet, of which one was used for nitrogen supply and one for venting, as shown in Figure 3.2. An elongated die, to increase the residence time, was employed, in the shape of a rectangular slit with rounded edges of 20 mm × 40 mm and a length of 100 mm, as can be seen in Figure 3.3. The design of the screw was part of the part of the study. This is described in detail in Chapters 5 and 6. The extruder was operated at a screw speed of 10 rpm to 30 rpm(rotations per minute). At 20 rpm the overall residence time of the devulcanizate in combination with the extruder and elongated die was approximate 12 min. At this speed, the pressure in the extruder before material entered the die reached a maximum of 5.3 MPa, depending on the temperature settings of 180 °C to 220 °C in the devulcanization section, see Figure 3.2. The extruder was operated at 70 % to 80 % of the maximally allowed drive-current, which indicates the applied torque.

In order to minimize oxidative degradation during devulcanization, the extruder was equipped with a nitrogen supply: in the hopper, at the end of the devulcanization section and at the end of the extruder just before the die, see Figures 3.2 and 3.4. The devulcanizate after the die was transferred to a specially constructed cooling calender[2], positioned directly following the extruder, see Figure 3.5. This calender instantly cooled the devulcanizate down to 40 °C to 60 °C to prevent oxidation. The capacity of this line is
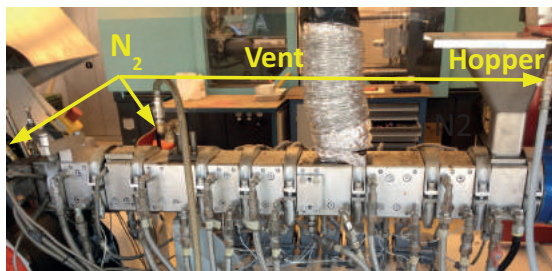
FIGURE 3.4: Extruder with the supply hopper, ventilation
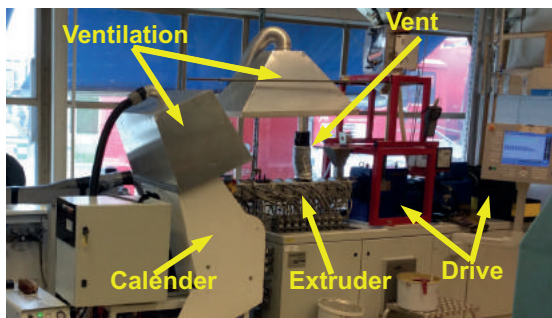point and nitrogen supplies.



FIGURE 3.5: Extruder with calender and ventilation.

approx. 2 kg/h at a screw speed of 20 rpm. Cleaning of the ventilation gasses
was performed by a home-made scrubber, using sodium hydroxide and sodium
hypo-chlorite as neutralizing agents.

Initially, DPDS was used as devulcanization aid. For mixing of the GTR with
the processing oil, DPDS and TDTPB, a Webac 2-roller-type heated sand
mixer (Webac Gesellschaft für Maschinenbau mbH, Euskirchen, Germany)
was used. When using DBD later on as devulcanization aid, a large amount
of processing oil, DBD and TDTBP stuck to the mixer wall. To achieve
homogeneous mixing of the GTR with the additives this was performed
manually with a maximum batch size of 7 L of GTR.

### 3.3.2 Other equipment

*Mixing:*

- A Brabender 350S internal mixer with a chamber volume of 390 mL
  was used for the preparation of the virgin compounds and the
  premix of a white rubber compound;

- A Brabender Plasti-corder internal mixer with a chamber volume
  of 50 mL was used for batch-wise devulcanization of small samples,
  for silanization of devulcanized materials prior to revulcanization
  and for compounding for revulcanization. A smaller chamber
  with a volume of 30 mL was used for the white rubber sample
  preparation.

*Milling:*

- A Schwabenthan laboratory mill with rolls of 200 mm in length, a diameter of 80 mm and a friction ratio of 1.13 was used at 22 rpm for the final milling of the devulcanizate and for all milling after mixing.

*Grinding and sieving:*

- A Fritz Pulverette with screen sizes of 0.7 mm and 2 mm was used for all grinding;

- A set of laboratory sieves with mesh sizes of $0.85\,mm^2$, $2\,mm^2$ and $3.5\,mm^2$ was used to separate ground materials into fractions;

- A Bosch PBS 75 AE belt sander with 120 grade sanding paper was used for sanding WRA samples.

*Dynamic properties:*

- A Rubber Process Analyzer, RPA Elite from TA Instruments was used at 0.833 Hz and 2.78 % strain, and at 1.667 Hz, and 2.98 % strain, both according to ISO 6502 for determination of cure characteristics and dynamic properties.

- A Dynamic Material Analyzer (DMA) VA 2000 from Metravib was used for measuring dynamic properties and analyzing the glas transition temperature ($T_g$).

*(Re)vulcanization:*

- A Wickert WLP1600 laboratory press was used with a mold of 100*100*2mm for tensile- and DMA test pieces. Temperatures are specified at the experimental descriptions. The white rubber blends were vulcanized at 170 °C for a period of 6 min, with a circular mould with a diameter of 50 mm and thickness of 5 mm. Rebound test pieces were vulcanized at 160 °C at $t_{c,90}$+10 min, using a circular mould of 20 mm and a thickness of 12 mm.

*Physical rubber properties:*

- Modulus, tensile strength and elongation at break were determined with a Zwick BZ1.0/TH1S tensile tester using dumbbell shaped samples according to ISO 37 type II with a crosshead speed of $50\,mm\,min^{-1}$;

- Hardness was tested with a Zwick Shore A tester according to ISO 868:2003;

- A Zwick-Roell 5109 tester was used for determination of rebound resilience according to ISO 4662.

*Chemical analysis:*

- For Thermo Gravimetric Analysis a TGA550 from TA Instruments was used. Temperature profiles are specified at the experimental descriptions.

- Fourier transform infrared spectrometric analysis (FTIR) was performed with a PerkinElmer Spectrum 100

- For Temperature Differential Scanning Calorimeter (DSC) a DSC 214 Polyma from Netzsch, with Proteus 70 software, was used.

- For Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX) analysis a Joel JSM 6400 SEM was used, with Jeol SemAforce digital Image acquisition software and a Noran Voyager energy Dispersive X-ray analyzer;

- For Gas Chromatography, a GC-2010 Plus ATF with an AOC-20i auto-injector from Shimadzu, equipped with a hydrogen generator, was used.

*Visual analysis:*

- For microscopy, a Keyence VHX 5000 was used, equipped with a VH-Z20R/Z20W/Z20T lens (20x-200x);

- Surface roughness and height measurements were done with a Keyence VK-0710 violet laser color 3D scanning microscope (Itasca, IL, USA). The surface roughness was determined according to ISO 4287[3]. The amplification factor was 10, and the sample size was $2 \times 2\,\mathrm{mm}^2$;

- Manual counting of visible particles was done on a surface area of $2\,\mathrm{cm}^2$;

- A standard camera with a wide angle lens was used for the white rubber analysis. For post processing of the pictures Matlab® scripts were developed;

- A CAT60 mobile phone equipped with a FLIR infrared camera and processing software was used for thermal pictures.

## 3.4 Formulations

The compounding formulations used in this manuscript are summarized in:

*Table 3.3,* for revulcanization of the whole tire base devulcanizate. To be able to revulcanize the devulcanized GTR, an estimation is made of a mean composition of the granulate. For the calculation of the amount of ingredients for revulcanization, all ingredients added during devulcanization are added to the base formulation of the compound. This formulation of the devulcanizate is used to calculate the revulcanization ingredients. Components that are supposed to be present already in the devulcanizate are marked,

*Table 3.4,* for vulcanization and revulcanization of the carbon black and silica based model compounds and devulcanizates hereof. For revulcanization, the active components of the formulations, zinc oxide, stearic acid, sulfur, accelerators and silane are consumed during vulcanization and need replenishment,

*Table 3.5,* for vulcanization and revulcanization of silica based compounds
   modified with 20 phr of resin and the reference compound without
   resin. Because of the higher temperatures to be expected during
   mixing as the softening point of the resins, TESPD is used instead of
   TESPT as TESPD is less sensitive for scorge. For revulcanization, the
   active components of the formulations, zinc oxide, stearic acid, sulfur,
   accelerators and silane are consumed during vulcanization and need
   replenishment,

*Table 3.6,* The compound for the White Rubber Analysis (WRA) as de-
   scribed in Chapter 4.

For blends of virgin compounds with devulcanized GTR, the weight ratio of
the components is used to deduct the formulation.

**Table 3.3: Revulcanization formulations for devul-
canized GTR**

|   | Formulation nr.: | **GTR-1** CB-based revulca- nization [phr] | **GTR-2** Si-based revulca- nization [phr] | **GTR-3** Si-based revulca- nization (1) [phr] |
|---|---|---|---|---|
| ↓ Component: | | | | |
| * | Polymer (2) | [100] | [100] | [100] |
|   | ZnO | 3.0 | 2.5 | 2.5 |
|   | Stearic acid | 2.0 | 1.0 | 1.0 |
| * | TDAE | [42.7] | [42.7] | [42.7] |
| * | Carbon black | [80] | [54] | [54] |
| * | Silica | | [42](3) | [42](3) |
|   | TESPT | | 3.2 | 3.2 |
|   | 6PPD | 1.0 | | |
|   | TMQ | 2.0 | | |
|   | TBBS | 1.5 | 1.64 | 4.64 |
|   | DPG | | 2.8 | 2.8 |
|   | Sulfur | 1.5 | 1.64 | 4.64 |

* Components already present in devulcanizate. The estimated amounts are
needed to calculate the formulation
(1) Revulcanization formulation with additional sulfur and TBBS;
(2) Total polymer content of (D)GTR, a mix of SBR, BR, NR and IIR;
(3) Based on TGA measurements.

**Table 3.4: Vulcanization and revulcanization formulations of carbon black and silica based model tread compounds**

| Formulations: | **CB** based tread compound [phr] | **UT** undertread compound(1) [phr] | **IIR** inner liner compound(2) [phr] | **Silica** based tread compound(3) [phr] |
|---|---|---|---|---|
| SBR (SPRINTAN SLR4601) | 65 | | 20 | 70 |
| BR | 35 | 60 | | 30 |
| NR | | 40 | 20 | |
| ClIIR | | | 60 | |
| * ZnO | 3.0 | 3.0 | 1.5 | 2.5 |
| * Stearic acid | 2.0 | 1.5 | 1.0 | 1.0 |
| TDAE | 35 | 20 | 10 | 32.5 |
| Carbon Black N550 | 80 | 80 | 60 | |
| Silica Zeosil | | | | 90 |
| * TESPT | | | | 7.2 |
| 6PPD | 1.0 | 2.0 | | 2.0 |
| TMQ | 2.0 | 2.0 | | 2.0 |
| Wax | | 2.0 | | |
| * TBBS | 1.5 | 1.7 | | 1.7 |
| * MBTS | | | 1.0 | 1.7 |
| * DPG | | | | 2.0 |
| * Sulfur | 1.5 | 1.7 | 1.0 | 1.4 |

(1) Based on the VanderBilt Rubber Handbook[4],
(2) Based on the VanderBilt Rubber Handbook[4], estimated composition of IIR, used for revulcanization only
(3) Based on the Green Tire Michelin patent[5],
* Components used for revulcanization.

**Table 3.5: Vulcanization and revulcanization formu-
lations for silica based tread compounds containing
resins**

| | Component | [phr] | |
|---|---|---|---|
| | SBR (SPRINTAN SLR4601) | 70 | |
| | BR | 30 | |
| (1,2) | Resin | - | 20 |
| (2) | TDAE | 32.5 | 12.5 |
| | Silica Zeosil | 90 | |
| * | TESPD | 7.2 | |
| * | ZnO | 2.5 | |
| * | Stearic acid | 1 | |
| | 6PPD | 2.0 | |
| | TMQ | 2.0 | |
| * | Sulfur | 1.7 | |
| * | TBBS | 1.7 | |
| * | DPG | 2.0 | |

(1) Resin A, B, C
(2) For resin containing compound, substitution
of oil by the same weight of resin.
*  Components used for revulcanization.

**Table 3.6: White rubber formulation.**

| Formulation: ↓ Component: | White rubber [phr] |
|---|---|
| BR | 100 |
| TiO$_2$ | 65 |
| ZnO | 5 |
| Stearic Acid | 1 |
| Sulfur | 5 |
| MBTS | 2.5 |

## 3.5   Procedures

The compounding procedures depend on the characteristics of both the
formulation and the mixer used. Compared with a carbon black based
compound a silica based formulation needs an additional silanization step.
Due to the difference in viscosity between processing oil and resins, the
mixing procedure for resin based compounds had to be adapted.

Throughout this thesis two Brabender internal mixers are employed, differing
in capacity: 50 ml vs. 390 ml chamber volume. Because of the small volume to
surface ratio of the 50 mL Brabender mixer and the corresponding ease of heat
removal, the temperature during mixing stays close to the set temperature of
the controller, which can be heated up to 240 °C. For the 390 mL Brabender
mixer, the volume to surface ratio is much larger, with the implication
that the rotor speed strongly influences the temperature development in
the compound. The initial mixer temperature is limited to 100 °C due to

the thermic oil used for the controller. Due to this difference, small scale devulcanization could only be performed in the 50 mL Brabender mixer.

An additional difference between both mixers is the pneumatic ram-based feed of the 390 mL Brabender, which allows for forced supply of the ingredients and thus pressure build-up in the mixing chamber. The manually operated feed opening of the 50 mL Brabender mixer limits the filling degree to about 0 6,with no substantial pressure build-up in the chamber. Because of these fundamental differences, compounding procedures are adapted for the formulation and mixer type used.

For blends of virgin compounds with devulcanized GTR which requires silanization, the recompounding procedure is adapted. This depend on the relative amount of the devulcanized GTR, as the viscosities of devulcanized GTR and the virgin compounds differ, which has an influence on the heat build-up during mixing in the 390 mL Brabender mixer.

The procedure for preparation of a resin containing compound, Table 3.9, is derived from a patent by Pille-Wolf[6].

The procedures are grouped as follows:

*Section 3.5.1* Compounding procedures for virgin compounds, using the Brabender 390 mL mixer

*Section 3.5.2* Procedures for renewed compounding of blends with devulcanized GTR, using the Brabender 390 mL mixer

*Section 3.5.3* Recompounding procedures for devulcanizates, using the Brabender 50 mL mixer

*Section 3.5.4* Devulcanization procedures

*Section 3.5.5* White rubber preparation

### 3.5.1 Compounding procedures for virgin compounds, using the Brabender 390 mL mixer

**Table 3.7: 1-step compounding procedure for virgin carbon black-based formulations, using the Brabender internal mixer 390 mL**

| Time [min.] | Processing Step |
|---|---|
| | Set mixer temperature at 50 °C. |
| | Set rotor speed to 50 rpm. |
| | Fill factor: 0.7 |
| | |
| | Compounding: |
| 0 | Polymers |
| 1 | ZnO + stearic acid |
| 2 | 33% (CB and TDAE) |
| 3 | 33% (CB and TDAE) |
| 4 | 33% (CB and TDAE) |
| 5 | 6PPD and TMQ |
| 6 | TBBS |
| 6.5 | Sulfur |
| 7 | Discharge temperature max. 80 °C. |
| | Sheeted off on a mill to 2 mm thick slabs. |
| | Relaxation for 12 h. |

**Table 3.8: 2-step compounding procedure for virgin silica based formulations with TESPT, using the Brabender 390 mL mixer**

| Time [min.] | Processing Step | Time [min.] | Processing Step Cont. |
|---|---|---|---|
| | Set mixer temperature at 65 °C. | | Set mixer temperature at 50 °C. |
| | Set rotor speed to 100 rpm. | | Set rotor speed to 75 rpm. |
| | Fill factor: 0.7 | | |
| | | | |
| | Compounding | | Addition of curatives. |
| 0 | Polymers | 0 | Silanized compound |
| 1 | 33%(silica, silane and TDAE) | 1 | TBBS + DPG + sulfur, keep temp. below 90 °C |
| 2 | 33%(silica, silane and TDAE) | 3 | Discharge |
| 3 | 33%(silica, silane and TDAE) | | Cool down and sheet off on the mill to 2 mm thick slabs. |
| 4 | ZnO and stearic acid | | Relaxation for 12 h. |
| 5 | 6PPD and TMQ | | |
| | | | |
| 6 | Silanization. | | |
| | Keep speed at 100 rpm until 145 °C is reached | | |
| | Lower the speed to ±80 rpm to keep the temperature at 145 °C | | |
| | Discharge after 0.5 minutes mixing at 145 °C. | | |
| | Cool down and sheet off on the mill. | | |
| | Relaxation for 24 h. | | |

**Table 3.9: 2-step compounding procedure for virgin silica based formulations containing resins and using TESPD coupling agent, with the Brabender 390 mL mixer**

| Time [min.] | Processing Step | Time [min.] | Processing Step Cont. |
|---|---|---|---|
| | Set temperature at 65 °C. | 0 | Start silanization, keep temperature=155 °C by reducing speed |
| | Set rotor to 100 rpm. | | |
| | Fill factor: 0.7 | 4 | Discharge, cool, mill |
| | | | |
| | Compounding | | Set temperature to 60 °C. |
| 0 | Polymers | | Set rotor speed to 50 rpm. |
| 1 | ZnO, stearic acid, silica, silane, TDAE, resin, anti-oxidants | | Fill factor: 0.7 |
| | Mix until 155 °C | | Productive step |
| | Discharge and cool down, mill | 0 | Load compound |
| | | 1 | S, TBBS, DPG |
| | Set temperature to 65 °C. | | Keep temp. < 80 °C by reducing speed |
| | Set rotor to 100 rpm. | 2 | Discharge, mill |
| | | | Relaxation for 12 h. |
| | Silanization | | |
| | Add polymers | | |
| | Wait until temp.=155 °C | | |

## 3.5.2 Procedures for renewed compounding of blends with devulcanized GTR, using the Brabender 390 mL mixer

**Table 3.10: 1-step recompounding procedure for blends with devulcanized GTR, without silanization processing step, suited for carbon black-based formulations, using the Brabender 390 mL mixer**

| Time [min.] | Processing Step |
|---|---|
| | Set mixer temperature at 50 °C. |
| | Set rotor speed to 50 rpm. |
| | Fill factor 0.7 |
| | |
| | Compounding: |
| 0 | Polymers |
| 1 | ZnO and stearic acid |
| 5 | 6PPD and TMQ (*) |
| 6 | TBBS |
| 6.5 | Sulfur |
| 7 | Discharge temperature max. 80 °C. |
| | Sheeted off on a mill. |
| | Relaxation for 12 h. |

(*) if included in the formulation

**Table 3.11: 2-step recompounding procedure for GTR devulcanizates including silanization processing step suited for silica-based formulations, using TESPT coupling agent and with the Brabender 390 mL mixer**

| Time [min.] | Silanization | Time [min.] | Compounding |
|---|---|---|---|
| | Set mixer temperature at 95 °C. Set rotor speed to 110 rpm. Fill factor: 0.7 | | Set mixer temperature to 50 °C. Set rotor speed to 75 rpm |
| 0 | Silanization. Add devulcanizate in 4 portions: each portion when torque $\approx 85$ N m, add silane when temp.=130 °C | 0 | Addition of curatives. Silanized compound |
| | | 1 | ZnO and stearic acid |
| t | Wait until temp.=145 °C sweep, to limit temp. to 146 °C | 2 | TBBS, DPG and sulfur Keep temp. below 90 °C by decreasing rotor speed |
| t+1 | Discharge. Cool down on a mill Relaxation for 24 h. | 3 | Discharge, mill Relaxation for 12 h. |

**Table 3.12: 1-step recompounding procedure for carbon black-based formulations to be blended with 0 wt% to 30 wt% silanized GTR devulcanizate, using the Brabender 390 mL mixer**

| Time [min.] | Processing Step | Comments |
|---|---|---|
| | Set mixer temperature at 50 °C. Set rotor speed to 50 rpm. Fill factor: 0.7 | |
| | Compounding: | |
| 0 | Polymers + silanized GTR devulcanizate | |
| 2 | ZnO and stearic acid | |
| 3 | 6PPD and TMQ | |
| 4 | 50 % CB | 3 to 4 steps with sweep |
| 6 | 50 % TDAE | |
| 7 | 50 % CB | 3 to 4 steps with sweep |
| 9 | 50 % TDAE | |
| 10 | TBBS, DPG | use sweep to get the stuff down |
| | Ram open to cool down, set speed to 25 rpm until temp. <90 °C | |
| 11 | Sulfur | |
| 12 | Discharge | |
| | Sheeted off on a mill. Relaxation for 12 h. | |

Use GTR devulcanizate silanized according to silanization procedure in Table 3.11

**Table 3.13: 2-step recompounding procedure for blends with 0 wt% to 30 wt% devulcanized GTR, for silica based formulations with TESPT coupling agent, using the Brabender 390 mL mixer**

| Time [min.] | Processing Step | Comments |
|---|---|---|
| | Set mixer temperature at 65 °C | |
| | Set rotor speed to 100 rpm. | |
| | Fill factor: 0.7 | |
| | | |
| | Compounding | |
| 0 | Polymers | virgin and devulcanized GTR |
| 1 | 50 % silica, all silane | add in portions of 33 % with sweep |
| 3 | 50 % TDAE | |
| 5 | 50 % silica | add in portions of 33 % with sweep |
| 7 | 50 % TDAE | |
| | | |
| | Silanization | |
| t | When temperature is 145 °C | |
| t+1.5 | ZnO and St.A. | Keep ram open to cool down |
| t+3 | 6PPD + TMQ | Keep temperature <145 °C |
| t+4 | Discharge | |
| | Cool down on the mill | |
| | Relaxation for 24 h | |
| | | |
| | Set mixer temperature at 50 °C | |
| | Set rotor speed to 75 rpm. | |
| | | |
| | Addition of curatives | |
| 0 | Silanized compound | |
| 1 | TBBS, DPG and sulfur | Lower the speed to ±40 rpm to keep the temperature below 90 °C |
| 3 | Discharge. | |
| | Cool down on the mill | |
| | Relaxation for 24 hours | |

### 3.5.3  Recompounding procedures for devulcanizates, using the Brabender 50 mL mixer

**Table 3.14: 1-step compounding procedure for revulcanization formulations without silane, using the Brabender 50 mL mixer**

| Time [minutes] | Mixer settings |
|---|---|
|  | Set mixer temperature at 80 °C. |
|  | Set rotor speed set to 5 rpm. |
|  | Fill factor: 0.6 |
|  | Add polymers. |
| 0 | Set rotor speed to 50 rpm. |
| 1 | ZnO and stearic acid. |
| 2 | TDAE(*). |
| 4 | TBBS and DPG(*). |
| 4.5 | Sulfur. |
| 5 | Discharge. |
|  | Thoroughly homogenize and sheet off on the mill. |
|  | Relaxation for 24 h. |

(*) if included in the formulation

**Table 3.15: 2-step compounding procedure for revulcanization formulations with TESPT coupling agent, using the Brabender 50 mL mixer**

| Time [min.] | Processing Step | Time [min.] | Processing Step Cont. |
|---|---|---|---|
|  | Set mixer at 145 °C. |  | Set mixer at 50 °C. |
|  | Set rotor speed to 5 rpm. |  | Set rotor speed to 5 rpm. |
|  | Fill factor: 0.6 |  |  |
|  |  |  |  |
|  | Silanization. |  | Addition of curatives. |
|  | Add devulcanizate. |  | Add silanized devulcanizate. |
| 0 | Set rotor speed to 50 rpm. | 0 | Set rotor speed to 50 rpm. |
| 1 | Silane. | 0.5 | ZnO and stearic acid. |
| 5 | Discharge, cool down on a mill. | 1 | TBBS and DPG. |
|  |  | 1.5 | S |
|  | Relaxation for 72 hours. | 2 | Discharge. Mill for 5 min. |
|  |  |  | Relaxation for 24 hours. |

**Table 3.16: 2-step compounding procedure for revul-
canization formulations with TESPD coupling agent
and containing resins, using the Brabender 50 mL
mixer**

| Time [min.] | Processing Step | Time [min.] | Processing Step Cont. |
|---|---|---|---|
| | Set mixer at 155 °C. | | Set mixer at 60 °C. |
| | Set rotor speed to 5 rpm. | | Set rotor speed to 5 rpm. |
| | Fill factor: 0.6 | | |
| | | | |
| | Silanization | | Mixing |
| | Add devulcanizate. | | Add mixture. |
| 0 | Set rotor speed to 50 rpm. | 0 | Set rotor speed to 50 rpm. |
| 1 | Silane. | 1 | S, TBBS, DPG. |
| 5 | ZnO and stearic acid. | 2 | Discharge, mill for 5 min. |
| 6 | Discharge and cool down, mill. | | Relaxation for 24 h. |
| | Relaxation for 72 h. | | |

### 3.5.4 Devulcanization procedures

**Table 3.17: Preparation of mixtures for twin-screw
extruder based devulcanization**

| DPDS based | DBD based |
|---|---|
| Mix TDAE, DPDS and TDTBP(1). | Mix TDAE with cold* GTR(2). |
| Melt at 70 °C. | Add DBD and TDTBP. |
| Add to cold* GTR. | Mix until homogeneously distributed. |
| Mix until homogeneously distributed. | |
| Heat the mixture to 65 °C. | |
| Swell for 0.5 h(3). | |

    \*   Room temperature

    (1) Use the Webac sandmixer for large quantities.

    (2) Limit amount of GTR to 7 L per batch when mixing manually.
          The Webac sandmixer cannot be used as the devulcanization aid
          sticks to the mixer surfaces.

    (3) Unless otherwise specified.

**Table 3.18: Mixer based devulcanization procedure,
using the Brabender 50 mL mixer**

| | |
|---|---|
| | Set mixer temperature at 220 °C. |
| | Set rotor speed to 5 rpm. |
| | Fill factor: 0.6 |
| | |
| | Devulcanization: |
| | Load mixture*. |
| 0 | Set rotor speed to 50 rpm. |
| 6 | Discharge. |
| | Quench in liquid $N_2$. |
| | Mill with 0.1mm gap between rolls. |

   \*   Premix the granulated rubber with the devulcanization
     formulation prior to devulcanization, see Table 3.17

### 3.5.5   White rubber preparation

**Table 3.19:  White rubber compounding procedure, using the Brabender internal mixer 390 mL for the premix and 50 mL for the addition of the curatives**

| Time [minutes] | Processing steps | Time [minutes] | Processing steps |
|---|---|---|---|
| | Set mixer temperature at 60 °C. | | Set mixer temperature at 60 °C. |
| | Set rotor speed to 50 rpm. | | Set rotor speed to 50 rpm. |
| | Fill factor: 0.7 | | Fill factor: 0.6 |
| | | | |
| | Preparing premix | | Addition of curatives |
| 0 | Add BR. | 0 | Add premix. |
| 1 | ZnO and stearic acid. | 1 | MBTS. |
| 2 | TiO$_2$ in 4 portions. | 1.5 | Sulfur. |
| | mix for 2 min after last portion. | 2.5 | Discharge. |
| | Discharge, cool down. | | |

**Table 3.20:  White rubber sample preparation, using Brabender internal mixer 30 mL**

| Time [minutes] | Processing step |
|---|---|
| | Set mixer temperature at 60 °C. |
| | Set rotor speed to 5 rpm. |
| | Fill factor: 0.6 |
| | Add white compound (90 wt%) and de-vulcanizate (10 wt%) |
| | |
| | Preparing the blend |
| 0 | Set rotor speed to 50 rpm. |
| 4 | Discharge. |
| | Mill until homogeneous in color. |
| | Gap between rolls 0.15 mm to 0.2 mm |

The Brabender internal mixer 30 mL is used as this fits one sample size.

## References

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[3] *International Standard IS0 4287:1997(E/F)*, 2000.

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[5] R. Rauline, "Copolymer rubber composition with silica filler, tires having a base of said composition and method of preparing same", U.S. pat. 5227425A (Michelin, 1992).

[6]W. Pille-Wolf, "Resin-extended rubber composition and tire rubber compositions prepared therewith", U.S. pat. 2017/117578 (J. F. ( Arizona Chemical Company LLC, 2017).

# Chapter 4

# Theoretical considerations and analysis methods

*In this chapter, several topics are discussed: theoretical considerations with respect to transport phenomena in rubber, extension and optimization of the Horikx-Verbruggen analysis method for the degree of devulcanization for different car tire rubbers, and the development of an analysis method for the size and amount of visible grain distribution in devulcanizate.*

## 4.1   Introduction

In the present chapter three topics are covered:

- Theoretical considerations pertaining to transport phenomena related to the size of the granulate and migration of the devulcanization aid into the particles. The use of GTR with specific particle size about a factor of 10 larger than the material used in the previous study[1] and the use of devulcanization aid DBD: Chapter 6, made it necessary to consider the consequences. DBD, with a melting point of about 140 °C, has to be molten and mixed with the GTR in the extruder prior to the devulcanization process. These transport phenomena are described in detail in Section 4.2,

- To characterize the degree of devulcanization of EPDM, Verbruggen[2] developed an analysis method using the Flohry-Rehner theory of swelling a crosslinked network in a solvent and combined this with the Horikx theory for generation of soluble polymer material by either crosslink or main-chain scission. The Verbruggen approach uses the amount of extractable unbound polymer vs. the decrease of crosslink density, to represent the degree and quality of devulcanization graphically in a so called Horikx-Verbruggen diagram. Due to the complex nature of the GTR and its devulcanizate the procedure needs refinement to decrease the error margins. This is described in Section 4.3,

- The use of a medium sized granulate for devulcanization introduced a visible grain in the devulcanizate. A method is developed to create a contrast between the visible grains and the matrix material, using a white colorant. With the created contrast, a Matlab®script could be developed to quantify the grain. This is described in Section 4.4

## 4.2   Theoretical considerations concerning distribution and migration of devulcanization aids into rubber granulate

The consequence of using DBD as devulcanization aid is that an extruder configuration is required which thoroughly mixes the DBD mechanically with the GTR; and secondly raises the temperature to a level that the DBD melts and can migrate into the particles. The effect of physical transport should be considered in order to estimate the practical limitations. The use of a coarser granulate with a size of 1 mm to 3.5 mm diameter compared to 0.35 mm as was used by Saiwari[1], leads to the following considerations:

- The concentration of the devulcanization aid in relation to the volume of the particles depends on the surface to volume ratio of the granulate. The used oil and devulcanization aid is distributed over the surface of the granulate particles during the mixing, before they can migrate in;

- The migration time of the processing oil and devulcanization aid into the granulate particles creates a time dependent concentration gradient from the surface to the center;

- The time needed for uniformly heating the particles, and consequently a time dependent temperature gradient can exist;

### 4.2.1   Availability of devulcanization aid in relation to size differences in the granulate

Assuming spherical particles, the difference in the surface to volume ratio between the largest 3.5 mm and the smallest of 1mm particles is a factor of 3.5. The effect of surface roughness is neglected for the moment for the sake of simplicity.

When mixing the GTR with the processing oil and devulcanization aid, these will initially be distributed over the surface of the granulate particles. Because of the larger particles higher volume to surface ratio compared to the smaller ones, the amount of oil and devulcanization aid per unit weight of GTR will be only one third for the largest granulate particles compared to the smallest ones. Also, due to the relatively higher amount, the smaller granulate particles in the GTR will adsorb overall a disproportionally high amount of oil and devulcanization aid. For GTR, assuming ideal mixing and coverage of the surface, the ratio between oil versus GTR, with an overall amount of processing oil of 5 wt% added, will be about 9 wt% for the smallest vs. 2 wt% for the largest size particles. Similar differences in availability of the devulcanization aid apply. The overall conclusion is that, when migration of devulcanization aid and oil occurs to equilibrium into the particles, the largest ones will experience considerably lower concentrations than the smallest. This automatically means that this will lead to an inherent inhomogeneity of the devulcanization of the various particles.

### 4.2.2 Concentration gradient of devulcanization aid inside a granulate particle

When mixing the devulcanization aid with granulate, the aid needs to migrate into the particle in order to achieve an equilibrium concentration. For a model description of this situation, the concentration of a liquid outside a particle is assumed to be fixed[3]. Strictly speaking, this is not the case as the amount of liquid on the surface of the particles decreases while it migrates into the particle. The devulcanization aid and oil must migrate to the core of the particles of the GTR to function fully. As the migration time increases with larger distance, it takes much longer before the the core of a larger particle reaches a concentration high enough to initiate devulcanization compared to a smaller one.

Bouvier[4] has investigated the migration of a heavy oil in SBR as a function of temperature due to the initial concentration difference for spherical particles with a diameter of 5 mm. Although the concentration of oil outside the particle was kept constant, his results can be used for a first estimation of the time scale of the migration using Fick's law. For the system oil - SBR Bouvier measured the diffusion coefficient $\mathbb{D}$ as a function of temperature and defined the diffusion time $t_D$ to equilibrium as:

$$t_D = R_0^2/\mathbb{D} \tag{4.1}$$

were $R_0$ is the radius of the sphere.

With equation 4.1 and initial diameters of the particles of 2 and 3mm, an estimation of the time needed for migration of the processing oil into the particles till equilibrium can now be made, see Table 4.1.

**Table 4.1: Diffusion coefficients $\mathbb{D}$ and calculated diffusion times until equilibrium vs. temperature for oil in SBR[4] for particles of 2 mm and 3 mm.**

| Temperature [°C] | $\mathbb{D}$ [$\mu m^2\,s^{-1}$] | time d=2 mm | d=3 mm |
|---|---|---|---|
| 20 | 16 | 17 h | 39 h |
| 100 | 556 | 30 min | 67 min |
| 163 | 1690 | 10 min | 22 min |
| 180 | 2530 | 7 min | 15 min |
| 201 | 3390 | 5 min | 11 min |

At 200 °C, around which the devulcanization experiments will be performed, see Chapter 6, the diffusion time till equilibrium for the larger particles is of the same order as the residence time in the extruder, about 6 min. At 163 °C, still above the melting temperature of 125 °C of the devulcanization aid DBD, the diffusion time would take 22 min for the larger particles, is too long to be feasible. Hence, although it is an estimation of the order of magnitude only, the migration times are significantly longer than the available residence time in the extruder. It means that the concentration of the devulcanization aid in the core of the particles is lower than required for devulcanization. Therefore, experiments will be performed with various concentrations to find an optimum, see Chapters 5 and 6. Another option is to work with small particles and narrow size distributions of the granulate. This was pursuit for

one experiment only because of unavailability of sufficient quantities of this material: Chapter 5.

### 4.2.3   Temperature gradient inside a granulate particle

The temperature gradient inside a sphere as a function of the time follows a similar relation as for the concentration gradient[3]. An estimate can be made for the required time for the centre of a granulate particle to reach a certain temperature, assuming the same spherical nature of the granulate. For example, to reach 200 °C throughout the particle, and with the initial temperature of the granulate of 30 °C and the temperature setting of the extruder of 220 °C, then:

$$\frac{T - T_0}{T_1 - T_0} = 0.89 \tag{4.2}$$

with $T_0$ the initial temperature of the granulate, $T_1$ the temperature at the surface for time>0 and T the temperature at the center. Based on the master curves presented in Bird[3] chapter 11, 0.89 correlates with a value of $\alpha t / R^2 \approx 0.35$, were $\alpha$=the heat transfer coefficient, t=time and R=radius of the particle. For SBR, a major component of the granulate composition, it can be calculated[5] that:
$\alpha = \kappa / \rho c = 1.06 \times 10^{-7}\,\mathrm{m^2\,s^{-1}}$,
with $\kappa = $ thermal conductivity $= 0.2\,\mathrm{W\,m^{-1}\,K^{-1}}$,
$\rho = $ density $= 940\,\mathrm{kg\,m^{-3}}$,
c $= $ specific heat capacity $= 2\,\mathrm{kJ\,kg^{-1}\,K^{-1}}$.

For the larger particles with a diameter $2R_0$ of 3 mm, the time until the centre has reached a temperature of 200 °C with the extruder set at 220 °C can be calculated as:

$$\frac{\alpha t}{R_0^2} = 0.35 \longrightarrow t \approx 7.5\,\mathrm{s} \tag{4.3}$$

Hence, the heat transport inside the granulate particles is rather quick and therefore considered as a factor of minor influence in this study.

## 4.3   Optimization of the Horikx-Verbruggen analysis for use with car tire rubbers

In order to quantify the ratio between crosslink and main chain scission versus the degree of devulcanization in terms of decrease of crosslink density, the Horikx-Verbruggen methodology will be employed in this thesis.

Although the models of Flory-Rehner[6] and Horikx[7] were developed for unfilled polymer systems, it is indicated by Verbruggen[8] that these models can be combined to a method with acceptable accuracy for filled polymer systems. The Flory-Rehner relation is based on the volume fraction of polymer in a swollen sample $f_p$ as given by Eq.4.4:

$$f_p = \frac{m_r}{m_r + m_s \frac{\rho_r}{\rho_s}} \tag{4.4}$$

with $m_r$ the mass of the rubber in the sample, $m_s$ the mass of the solvent, $\rho_r$ the density of the pure polymer and $\rho_s$ the density of the solvent.

The crosslink density $\nu_e$ is calculated with the Flory-Rehner relation (Eq.4.5):

$$\nu_e = \frac{f_p + \chi f_p^2 + \ln\left(1 - f_p\right)}{V_{ms}\left(0.5 f_p - \sqrt[3]{f_p}\right)} \tag{4.5}$$

with $V_{ms}$ the solvent molar volume, $\chi$ the Flory-Huggins polymer/solvent interaction parameter. This parameter is 0.37 for SBR-Toluene[9]. For GTR - Toluene[1] it is estimated as 0.4.

Reinforcing fillers also have an interaction with the polymer network, hence influence the Flory-Rehner relationship. Porter[10] stated that a correction for carbon black, high abrasion furnace black (HAF), filled rubber can be described with Eq.4.6:

$$\nu_{chem,apparent}/\nu_{chem,actual} = 1 + K_{chem} * \phi \tag{4.6}$$

with $\phi$ the volume fraction of the filler and $K_{chem}$ a constant related to the interaction between polymer and filler.

$\phi$ can be calculated (before swelling) with Eq.4.7:

$$\phi = \frac{\text{volume of filler}}{\text{volume of filler + volume of polymer}} \tag{4.7}$$

The real crosslink density $\nu_{real}$ is then given by Eq.4.8:

$$\nu_{real} = \nu_e * \left(1 + K_{chem} * \phi\right) \tag{4.8}$$

, with $\nu_e$ according to the Flory-Rehner Equation (Eq.4.5). For a HAF carbon black filled system, Porter determined $K_{chem}$ to be 3.36.

As the Horikx theory is based on the total amount of polymer, sol + gel, $\nu_{real}$ is to be corrected with Eq.4.9:

$$\nu_{horikx} = \frac{\text{number of crosslinks}}{\text{total volume of rubber}} = \nu_{real}\left(\frac{m_{ps}}{m_p}\right) \tag{4.9}$$

with $m_{ps}$ the mass of the remaining polymer: the gel, after extraction and $m_p$ the original total mass of the polymer. To use the Horikx-Verbruggen representation, as given in Figure 4.1, the relation between $\gamma$ (average number of crosslinks) and s (sol fraction) according to Charlesby[11] (Eq.4.10) is required:

$$s = (1 + \gamma - \gamma * s)^{-2} \longrightarrow \gamma = \frac{1 - \sqrt{s}}{(1-s)\sqrt{s}} \tag{4.10}$$

The crosslink scission line is then given by Eq.4.11:

$$1 - \frac{\nu_f}{\nu_i} = 1 - \left[\frac{\gamma_f\left(1 - s_f^{1/2}\right)^2}{\gamma_i\left(1 - s_i^{1/2}\right)^2}\right] \tag{4.11}$$

and the random scission line by Eq.4.12:

$$1 - \frac{\nu_f}{\nu_i} = 1 - \left[\frac{\left(1 - s_f^{1/2}\right)^2}{\left(1 - s_i^{1/2}\right)^2}\right] \tag{4.12}$$

with $\nu$ = crosslink density, index i = initial value and index f = after devulcanization. See Figure 4.1
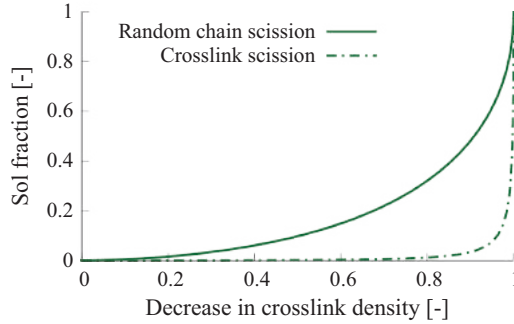


FIGURE 4.1: Horikx-Verbruggen basic diagram

With these analyses combined, two criteria for the quality of a devulcanization process can be derived:

  - The effectivity, by determination of the difference in crosslink density between the initial and the devulcanized material. This is indicated by the horizontal position of a data point.

  - The quality of the devulcanizanizate, by the ratio of random chain scission to crosslink scission. This is indicated by the vertical position of the sample between both scission lines.

Part of the formulations of rubber compounds are comprised of polar and non-polar components like plasticizers, waxes and additives for curing and protection against aging. These can be extracted by e.g. acetone for the polar and TetraHydroFuran, THF, for the non-polar components. For the extraction a Soxhlet apparatus is used. The duration of the acetone extraction is 2 days and for the THF extraction 3 days. Drying is employed until the sample weight is stable, after the acetone extraction for two days at $40\,^\circ\text{C}$ under vacuum and after THF extraction for 5 days. For the determination of the crosslink density, the extracted samples are swollen in toluene and the adsorbed amount is measured by gravimetry. The amount of fillers is determined by TGA, using a nitrogen atmosphere.
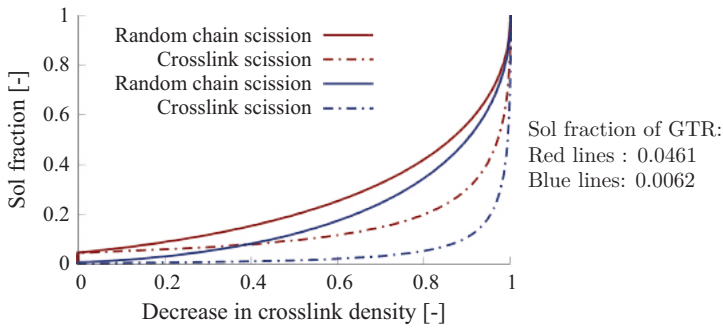
FIGURE 4.2: Influence of initial sol fraction on the shape of
the Horikx-Verbruggen diagram

The Horikx theory is based on the amount of sol directly related to the amount
of polymer released from the crosslinked network. However, in passenger car
tire rubber, about $10\,\text{wt}\%$ of the processing aids are additives for vulcanization
and others. These additives are extracted too when determining the initial
sol fraction $s_i$. As shown in Figure 4.2, the distance between the random and
crosslink scission lines is sensitive to the amount of sol, and the resolution
of the graph increases with an increasing distance between both lines. To
increase the resolution of the method, the sol of the GTR is to be separated
from the extractable additives. For devulcanization, processing oil and
devulcanization aids are added, which can be an amount of $10\,\text{wt}\%$ of the
GTR. In Figure 4.3 a schematic overview is presented of the composition of
the initial GTR (i), the mixture with devulcanization aids added (r) and the
rubber after devulcanization (f).



Legenda:
| | |
|---|---|
| DX De-crosslinked polymer | DA Additives for devulcanization |
| X (Crosslinked) polymer | OA All other additives |
| FA Fillers and activators: | UR Unbound rubber |
| CB, Si, ZnO, ZnS | |
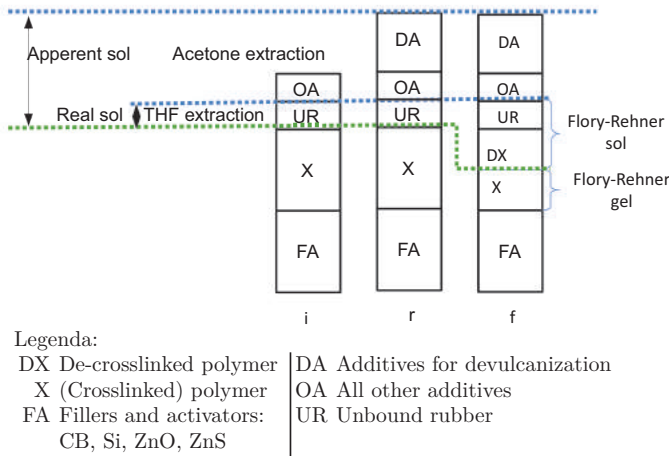
FIGURE 4.3: Definitions for the initial material(i), reference
material with devulcanization aids(r) and the devulcanized
material(f).

Because of the polar nature of most of the additives for both, GTR and devulcanizate, separation is required of the components extracted with acetone, in which the polar materials are dissolved, and with THF, in which the apolar materials like unbound polymers, are dissolved. Tire rubbers show a typical fingerprint in the derivative of the temperature - weightloss curve. By this, it can be concluded that hardly any rubber is present in the acetone extract, see Figure 4.4a. In contrast, the THF extract after acetone extraction, shows the rubber fingerprint, see Figure 4.4b. For a typical sample of GTR, the sol has decreased from initially 0.12 to 0.004 by this correction, see Table 4.2.



(a) Acetone extract, after extraction with acetone.



(b) THF extract, after extraction with acetone and THF.
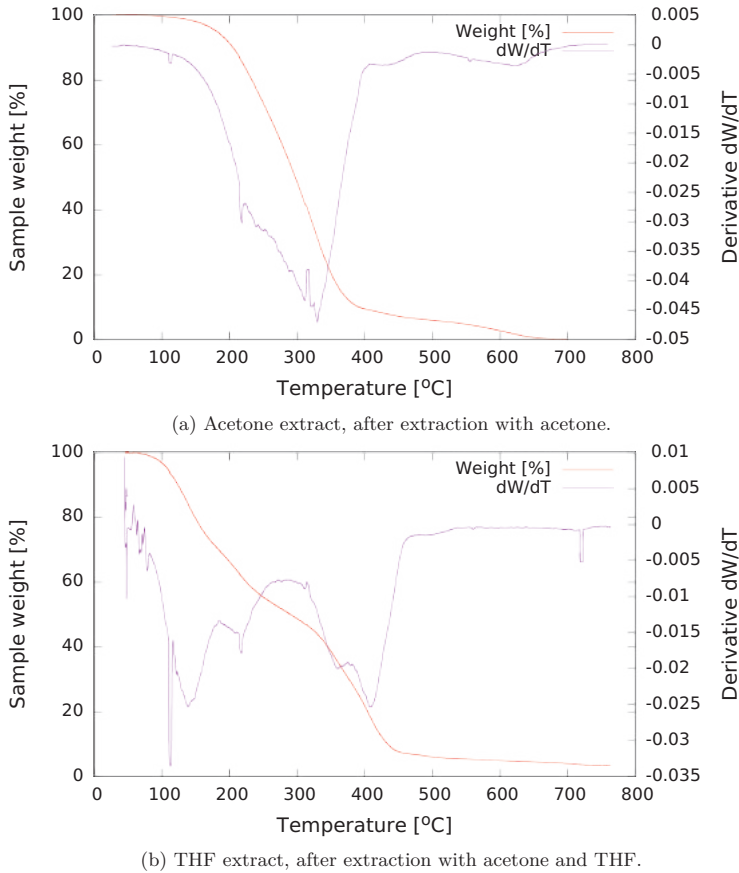
Figure 4.4: TGA of extracts of devulcanizate.
The sample weight (left axis) and the derivative dWeight/dT
(right axis) are given.

As the relative amount of the fillers in the samples of GTR changes after extraction and when adding devulcanization aids, as is indicated in Figure 4.3, a way to compensate for this is to analyse the amount of filler after THF extraction for GTR and the devulcanizate, using the insolublity of the fillers in both solvents.

The Horikx-Verbruggen method is based on the relative decrease of crosslink network density. Initial crosslink densities of materials of different sources

Table 4.2: Relative decrease in sample weights after extraction with acetone and with THF.

| Decrease after acetone extraction | Decrease after acetone and THF extraction | Difference between acetone extraction and THF extraction |
|---|---|---|
| [wt%] | [wt%] | [wt%]. |
| 11.9 plus/minus 0.74 | 12.3 plus/minus 0.72 | 0.39 plus/minus 0.24 |

Sample weights ≈0.5 g, average over 9 samples.

might differ considerably. This might as well influence the results and has to be taken into consideration.

## 4.4 White Rubber Analysis for quantifying size and amount of visible grains in the devulcanizates, which might have an influence on miscibility and revulcanizate properties

During the devulcanization experiments it appeared that a certain amount of visible grains remained in the devulcanizates, which might have an influence on miscibility and revulcanizate properties. These visible grains consist of particles with a decreasing degree of devulcanization towards the centre as discussed in section 4.2. To be able to analyze the amount and size of these visible grains, a new method needed to be developed as microscopy and manual counting was not appropriate. This will be called called the 'White Rubber Analysis' (WRA). For this analysis, a devulcanizate is blended with a butadiene (BR) based compound, with titanium dioxide as white pigment. As the main purpose of the compound is its whiteness, MBTS was chosen as accelerator because of its the non-staining property. For the same reason, processing oil was not used. BR was chosen as it mixes well without processing oil. For the formulation of the white rubber, see Table 3.6 and for the preparation Table 3.19. See Figure 4.5a for a pure white sample as a base.

10 wt% of the devulcanizate is blended with 90 wt% of the white rubber compound as described in Table 3.20, resulting in a light-gray compound in which remaining black particles are clearly visible. Subsequently, test pieces with a diameter of 50 mm and a thickness of 5 mm are vulcanized using the Wickert laboratory press at 170 °C for 10.5 min. The outer skin of one side of the sample is removed by sanding using a Bosch belt sander, to expose the inner structure, until a homogeneous inner structure is visible. To enhance the sanding, the samples are frozen in liquid nitrogen. Subsequently, a picture of the sanded sample is taken for analysis.

(a) pure white rubber          (b) with 20 wt% powder          (c) with 10 wt% reclaim



(d) with 10 wt%                      (e) with 10 wt%
devulcanizate                  devulcanizate (converted
                                    into black-white)
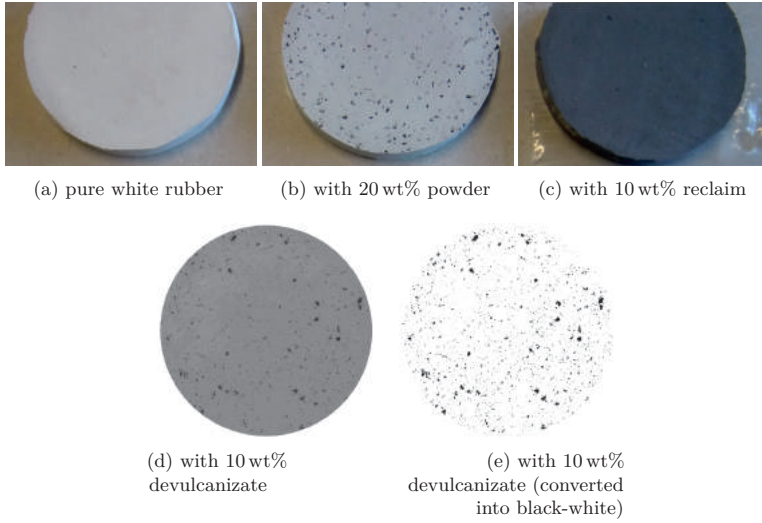
FIGURE 4.5: White Rubber Analysis test samples.

This weight ratio between devulcanizate and the white rubber compound was selected after a series of tests to obtain a substantial contrast for the whole range of hardly devulcanized until reclaimed rubber. To verify the accessible range of this method, it was tested with the following samples, representing the limits of the devulcanizates:

- A sample without any devulcanizate as reference: Figure 4.5a;

- A sample only containing 20 wt% of non-devulcanized powdered GTR to verify the amount of detectable particles: Figure 4.5b;

- A sample of reclaimed material, of which a blend of 10 wt% is used, to verify if the resulting color still allowed detection, assuming reclaimed rubber contains the highest amount of unbound polymer: Figure 4.5c;

With these samples it turned out that 20 wt% of particles, in Figure 4.5b 20 wt% powder, is still visible, also in the presence of 10 wt% reclaim: Figure 4.5c. The sample in Figure 4.5d is a randomly chosen devulcanizate, of which a 10 wt% blend was prepared. This clearly shows that grains in the devulcanizate can be distinguished in a blend using this concentration.

(a) Distribution of hard particles according to length in µm.

(b) Distribution of hard particles according to area in pixels (px), $1\,\mathrm{px} = 1156\,\mu\mathrm{m}^2$.

(c) Same as picture 4.6a, ordinate limited to 50.

(d) Same as picture 4.6b, ordinate limited to 20.
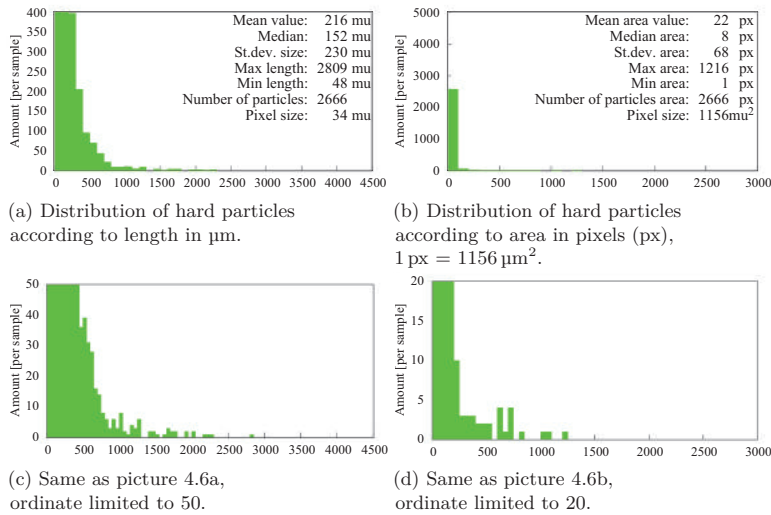
FIGURE 4.6: White Rubber Analysis: Statistics and histograms of sample in Figure 4.5e.

For a statistical analysis, the picture of Figure 4.5d was converted to black and white: Figure 4.5e, and analyzed with a MATLAB® script for connected areas. With this script, statistical data were obtained like the maximum size of the visible grains in the sample, the number of particles, mean, median and standard deviation. A histogram presentation of the frequency distribution for the size of the particles in Figures 4.6a and 4.6c, and for the surface area is shown in Figures 4.6b and 4.6d. For the size of the hard particles, the diagonal of the best fit rectangular is used, as this provides the most useful statistics instead of the computed surface. The pixel size of the original picture is used as basis for the sizes, but is not calibrated and therefore the dimensions can only be used for relative comparisons. The standard deviation of the mean value shows the best correlation with a visual evaluation of the sizes and amount of the grains, compared with both the mean value and median.

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# Chapter 5

# From batch to continuous processing using DPDS as devulcanization aid

*For ground passenger car tire rubber (GTR) with a relatively high percentage of SBR, a devulcanization process was developed in earlier work for a laboratory-scale internal mixer, using DiPhenylDiSulfide as devulcanization aid and GTR with a size of 0.35 mm to 0.42 mm. In the present study, the devulcanization process for passenger car tire rubber is upscaled from 15 g per batch and transformed into a continuous process in a co-rotating twin-screw extruder with a capacity of 2 kg h$^{-1}$. As SBR is rather sensitive to the devulcanization process conditions such as thermal and mechanical energy input, the screw design is based on a low shear concept. The influence of the devulcanization conditions, extruder parameters and ancillary equipment on the devulcanization efficiency and the quality of the final product are studied. The ratio of random to crosslink scission as determined by a Horikx-Verbruggen diagram is taken evaluate the process and material. A best practice for continuous devulcanization results.*

## 5.1  Introduction

Nowaday a significant part of end-of-life tires is recycled. However, the reuse in cradle-to-cradle loops (tires back into tires) is limited due to the low property profile of the recycled material. The decrease in the quality of the material is partly because the rubber already suffered a whole life cycle, but the recycling process itself also causes it: the end-of-life tire rubber is ground and re-plasticized in a process in which not only the crosslinks, but at the same time, the polymers are broken.

Compared to ground passenger car tire rubber (GTR) , the re-plasticized material has a different structure and properties. In order to achieve a quality of recycled rubber that is comparable to feedstock it needs to be devulcanized in such a way preferably only the sulfur crosslinks and hardly any of the polymers break down in the recycling process.

Saiwari[1] has shown that after thermo-chemical devulcanization of passenger car tire rubber using DiPhenylDiSulfide (DPDS) as devulcanization aid, the devulcanizate has the potential to be reused in tire production. As a follow-up to the batch devulcanization as developed by Saiwari, the present

study describes upscaling and transformation into a continuous process. A co-rotating twin-screw extruder was chosen for this purpose because of the good mixing properties and configuration flexibility. The influences of time, temperature and concentration of the devulcanization aid are studied with the optimal settings for the batch process as the starting point; respectively the extruder setup and screw configuration are investigated.

Styrene-butadiene rubber (SBR), a major component of GTR, is particularly sensitive to shear, as shown in the work of Saiwari[1]: during the devulcanization process it easily recombines due to its complex structure, resulting in the formation of inter- and intra-molecular chain fragment recombinations with an increase in crosslink density as result[2–5].

Some preliminary experiments with a high shear setup of a co-rotating twin-screw extruder, using the same optimal settings as for the batch process, conclude that the material was integrally broken down and the properties of the recycled material were rather poor due to the high shear[1]. Therefore, this study chose a low shear configuration of the same type of extruder as the starting point.

Additional equipment for the devulcanization process had to be developed: swelling equipment for the blend of the particulated rubber with the devulcanization aid and plasticizer, a nitrogen purging system and a cooling system for the devulcanizate. This introduced the possibility to study the effect of these process adjustments on the quality of the devulcanizate, however this was limited as it compares only trends during the experiments and no absolute values.

The main method for analyzing the devulcanization effect is the decrease of the crosslink density determined according to the Flory–Rehner method[1,6], combined with the Horikx-Verbruggen presentation of the results as described in Chapter 4. Another indication for the quality of the process and material is obtained from stress-strain properties and surface roughness analysis after renewed vulcanization of the devulcanizates.

## 5.2   Experimental

The GTR used in this investigation was specified in Section 3.2. All other materials are described in Table 3.1. The passenger car tire powder supplied by Rubber Resources, with a particle size of 0.35 mm to 0.42 mm, was used as comparative material for a study of the effect of the remaining visible grains, Section 3.2. It was devulcanized and subsequently revulcanized similar to the coarser GTR. As this powdery material behaves differently in the extruder compared to the 1.0 mm to 3.5 mm GTR, they cannot be compared other than the roughness of the revulcanized samples.

### 5.2.1   Pre-treatment for Devulcanization

Prior to mixing with GTR, TDAE, DPDS and TDTBP were molten and mixed at 70 °C. This blend was added to the GTR at room temperature, and subsequently heated to 65 °C during mixing for 0.5 h or 24 h (depending on the experiment) in a Webac 2-roller-type heated sand mixer.

### 5.2.2 Extruder Setup

The devulcanization was performed in a KrausMaffei ZE 25 UTX co-rotating twin-screw extruder as specified in Section 3.3, as well as all other equipment needed for additional handling of the devulcanizates. The configuration of the extruder screw can be divided into three sections: the supply and mixing section, the devulcanization section and the pressure section: Figure 5.1. The initial screw configuration was designed for minimal shear, as shown in Figure 5.2, Screw 1:

- In the supply and mixing section, a mixing element was installed with the necessary preceding pressure elements for flow control and the possibility to create a low shear zone thereafter;

- The devulcanization section is characterized by low shear forces by the design of the screw with small variations in flight: a mix of several kinds of transport and pressure elements was used. This create gentle mixing and shear due to varying degrees of filling of the screw;

- The pressure section is needed for building the extrusion pressure, hence by definition a high shear zone. At the discharge side of the screw, pressure elements were added to be able to discharge the devulcanized product.
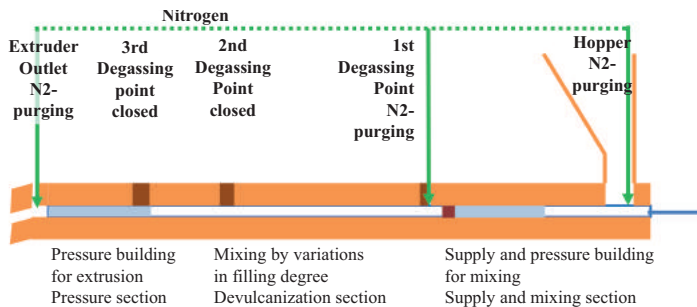


FIGURE 5.1: Low shear screw design and the positions of the degassing openings.
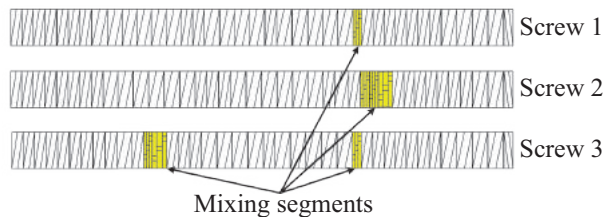


FIGURE 5.2: Overview of the three low shear screw designs.

The devulcanization conditions were extensively studied by Saiwari[1], and the optimal settings found for the internal mixer are given in Table 5.1. They provided the starting point for the determination of the parameter range for the extruder experiments, also given in this table. With visually checking the progress of the devulcanization in the extruder with Screw 1 via

the de-aeration openings in the barrel of the extruder, it appeared that the GTR kept its granulated shape up to halfway the extruder. Thereafter the consistency changed into a smaller sized granulate embedded in a plasticized matrix at the end of the middle section of the extruder.

Based on the observation in the internal mixer experiments that the devulcanization activity is decreasing considerably at temperatures below 180 °C, this is chosen as the lowest temperature limit for the supply and mixing section. This is to improve the migration of TDAE and DPDS by the elevated temperature into the GTR, but at the same time limit the chance of random polymer scission due to locally high concentrations of DPDS. This will be further elaborated in Section 5.3.1.

**Table 5.1: Devulcanization conditions, Brabender internal mixer vs. twin-screw extruder**

| Factors | Optimized Brabender Internal Mixer Conditions[+] | Extruder Conditions |
|---|---|---|
| Devulcanization aid | DPDS, 15mmol/100g GTR | DPDS 15, 18 to 30mmol/100g GTR |
| Devulcanization oil | TDAE 5 wt% | TDAE 5, 6.2 to 10 wt% |
| Anti-oxidant | TDTBP, 1 wt% | TDTBP 1 wt% |
| Swelling time | 30 min | **30 min** and 24 h |
| Swelling temperature | 65 °C | 65 °C |
| Devulcanization time | 6 min | $(<2)^*$, 2 to 6min |
| Rotor speed/screw speed | 50 rpm | 10 to 120 rpm |
| Rotor / Screw Configuration | High shear | Low shear screw with additional kneading elements in devulcanization section |
| Devulcanization temperature | 220 °C | 220 to 280 °C |
| Devulcanization atmosphere | Nitrogen gas purging | In air nitrogen gas purging |
| Swelling equipment | Hot air oven | **Heated mixer** |
| Extrudate handling | Quenched in liquid nitrogen | Cooling in air **Cooling in inert atmosphere** Cooling with cooling calander |
| Ventilation | - | Ventilation system with scrubber for cleaning and smell control |

Values in bold are the standard values used in the present investigations.
Underlined values are the settings with the best results.
* For experiments with screw speeds exceeding 30 rpm.
[+] As found by Saiwari[1].

It is important to realize that in the supply, mixing and devulcanization sections, the GTR is still present as particles. The behavior of these GTR particles in the extruder differs from the models concerning transport and mixing for highly viscous liquids, and these models are therefore not suitable for the design of alternative screw configurations[7–9]. Depending on the degree of devulcanization, the GTR can still be present to a certain extent in the pressure section as particles.

### 5.2.3 Additional Screw Designs

After the mixing step as described above, the material was milled on a two-roll mill with a nip-width of approximately 0.5 mm. During milling with this nip-width it was observed that the size of the visible grains decreased

considerably. However, the material did not become completely smooth during this after-treatment and this indicated that, although the material was partly devulcanized, it maintained a granular structure. Because of the amount and size of the visible grains still remaining in the devulcanizate, additional screws were designed: Figure 5.2: Screw 2 with additional mixing elements in the supply and mixing section and Screw 3 with some mixing elements in the devulcanization section.

### 5.2.4 Experimental Conditions

The temperature of the devulcanized material was measured at the outlet of the extruder with an integrated sensor in the extruder, which continuously measured the temperature close to the barrel. The temperature of the core of the extruded devulcanizate was measured sample-wise at the outlet of the extruder with an independent thermocouple-based contact thermometer. The core temperature was measured to be $2\,°C$ to $7\,°C$ above the set temperature of the last extruder sections, being an experiment setting.

By experimental setup the devulcanization temperature was optimized first, subsequently the residence time, the concentration of the devulcanization aid and the screw configuration. For screw 2 and screw 3, the residence times turned out to be similar to that of screw 1.

### 5.2.5 Surface Roughness

The devulcanizates were blended with a virgin SBR/BR compound in a ratio of 50/50 wt%, based on polymer content, and vulcanized according to the formulation in Table 5.2 in order to compare the amount and size of the remaining visible grains.

**Table 5.2: Formulation for revulcanizing the devulcanizates with virgin rubber.**

| Ingredients | Phr |
|---|---|
| Devulcanizate, | |
| based on polymer content | 50.0[*] |
| SBR (SPRINTAN SLR1732 (35phr oil) | 44.7[+] |
| BR | 17.5[+] |
| Carbon black: N375 | 80.0 |
| Plasticiser: TDAE | 9.8 |
| Zinc oxide | 3.0 |
| Stearic acid | 2.0 |
| Sulfur | 2.5 |
| TBBS | 1.5 |
| 6PPD | 1.0 |
| TMQ | 2.0 |

[*]: Not applicable for reference compound of virgin rubber only
[+]: Double amount for reference compound of virgin rubber only
Formulation as used by Saiwari[1]

## 5.3    Results and Discussion

### 5.3.1    Process Development
**Influence of Devulcanization Time**

In an extruder the devulcanization kinetics might be different compared to an internal mixer due to differences in heat transfer. The influence of the devulcanization time was studied. The devulcanization time in an internal mixer was earlier optimized[1] to 6 minutes. For the internal mixer, the devulcanization time was defined as the time interval between loading and unloading of the mixer, including the time to heat the GTR. In the extruder, the devulcanization will start when the minimum devulcanization temperature is reached; however, this point is difficult to determine. Therefore, the residence time was used: the time between entering the extruder screw and discharge at the die. In this series of experiments, the residence time of the rubber in the extruder was varied by adjusting the extruder screw speeds to 30 rpm, 20 rpm and 10 rpm, equivalent to residence times of 2, 3 and 6 minutes. Resulting variations in shear forces were accepted. Analysis of the devulcanizates was done by means of extraction and equilibrium swelling experiments as described in Chapter 4, and presented in Horikx-Verbruggen diagrams, as shown in Figure 5.3.
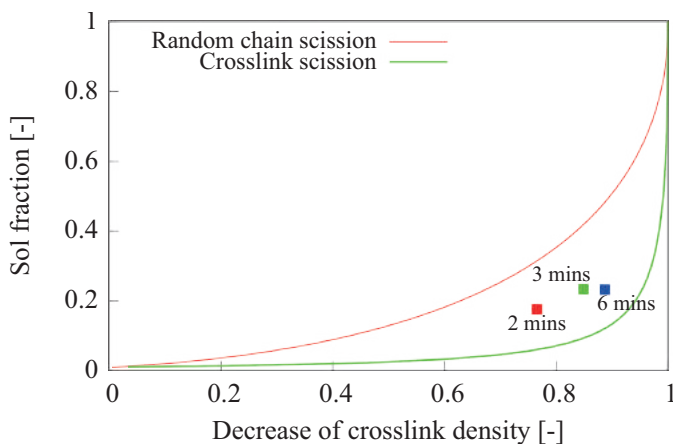


FIGURE 5.3: Influence of the residence time on the degree and quality of devulcanization.

A shorter residence time results in a decrease of the devulcanization efficiency, indicated by a lower decreases in crosslink density. The longer the residence time, the more a shift towards crosslink versus random scission, is observed.

During the residence period migration of the devulcanization aid into the rubber, the transfer of heat into the rubber particles and the reaction of the devulcanization aid have to take place: after the scission of a crosslink, the devulcanization aid will react with the remaining highly-reactive radicals and neutralize these[10]. Only if all of these steps can be completed in the extruder, the devulcanization is complete, and a homogeneous devulcanizate can be achieved. A residence time of 6 minutes is the best choice for the extruder, as observed for the internal mixer.

**Influence of Devulcanization Temperature**

In a thermo-chemical-mechanical devulcanization process there are three main factors contributing to the efficiency of the devulcanization: thermal energy, the chemical reaction and shearing forces. Initially, a devulcanization temperature of 220 °C was used, which was the optimal temperature found for devulcanization in an internal mixer. The temperature in the extruder was set from 220 °C to 280 °C with the intention to optimize the devulcanization with respect to the reaction rate. Therefore, the screw speed for these experiments was kept constant at 30 rpm, resulting in a residence time of 2 minutes. The influence of the process temperature on the devulcanization efficiency of GTR is shown in Figure 5.4.
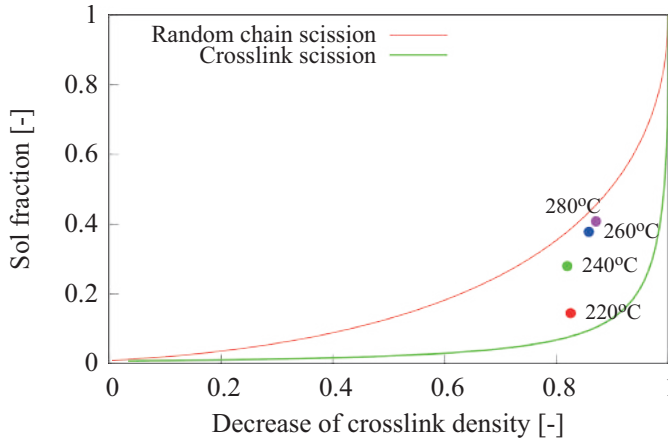


FIGURE 5.4: Influence of devulcanization temperature on the degree and quality of the devulcanization.

The expected trend, that an increasing temperature improves the devulcanization efficiency, indicated by an increasing 'decrease of crosslink density', is not found. The data points only show a tendency towards random scission, indicating that the quality of the devulcanizate decreases: at 280 °C nearly only random scission occurs.

In a thermo-chemical process like the present, the devulcanization aids are added in order to scavenge radicals formed during this process. However, a more intensive generation of reactive radicals occurs at very high devulcanization temperatures, i.e., above 220 °C. This threshold temperature indicates the optimum devulcanization temperature at which the rubber network can be broken in a controlled manner. The results clearly indicate that the most efficient temperature for devulcanization in the extruder is 220 °C, similar to the internal mixer.

**Influence of the Devulcanization Aid Concentration**

Compared to the material used in the earlier experiments[1] with a small and narrow particle size distribution, the GTR for the current experiments had relatively large particles with a size distribution of 1 mm to 3.5 mm. As discussed in Chapter 4, during the mixing of the GTR with the devulcanization

aid pre-dissolved in TDAE, it must first be distributed over the surface area of the GTR before migrating into the particles. The consequence is a size dependent concentration of the devulcanization aid. This results in a size dependent concentration of TDAE according to Figure 5.5b based on the size distribution of the granulate particles as shown in Figure 5.5a, and a similar distribution of the devulcanization aid.



(a) Size distribution of GTR

(b) Distribution of TDAE over fractions in wt% with average amount of 5 wt%
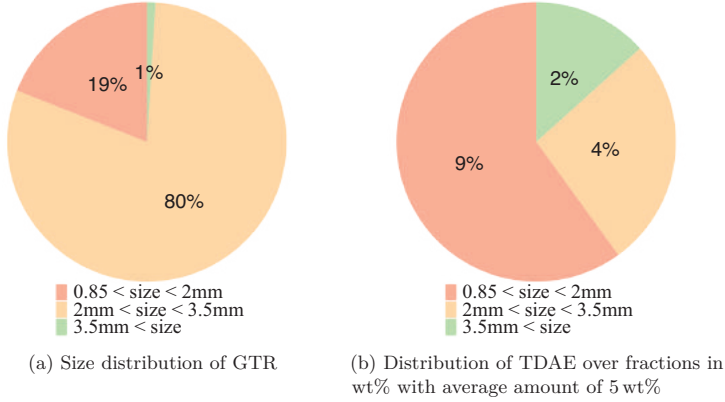
FIGURE 5.5: Size distribution of the GRT and the distribution of TDAE over the fractions.

The largest fraction of particles with a diameter of 2 mm to 3.5 mm absorbs 4 wt% of the TDAE at an average concentration of 5 wt% over the whole batch. The required amount of TDAE for a desired concentration in the main fraction can be calculated with equation 5.1

$$BRC_{TDAE} = MDC_{TDAE} * \frac{BAC_{TDAE}}{MAC_{TDAE}} \qquad (5.1)$$

With $BRC_{TDAE}$ the required concentration of TDAE over the whole batch, $MDC_{TDAE}$ the desired concentration of TDAE in the main fraction, $BAC_{TDAE}$ the actual concentration of TDAE in the batch and $MAC_{TDAE}$ the actual concentration in the main fraction.

For a TDAE concentration of 5 wt% in the main fraction, the mean concentration of TDAE over the whole batch should be increased to 6.25 wt%, rounded to 6.2 wt%; hence, with a factor of 1.2. As the DPDS is dissolved in the TDAE prior to mixing with the GTR, the same ratio is assumed. Most experiments are therefore performed with 18 ppm DPDS and 6.2 wt% TDAE instead of 15 ppm DPDS and 5 wt% TDAE. To account for this effect of particle size and the presence of remaining visible grains in the devulcanizate, experiments with a further increased amount of DPDS and TDAE were performed. Increasing the amount of TDAE might improve the migration of DPDS into the rubber matrix, but could also have other effects such as decreasing the shear in the extruder and influencing the processability of the devulcanizate. The results are shown in Figure 5.6.

The data point in the Horikx-Verbruggen diagram representing an increased amount of DPDS, TDAE/DPDS:1/2, has slightly moved to the right-hand side and closer to the main chain scission line. However, the change in
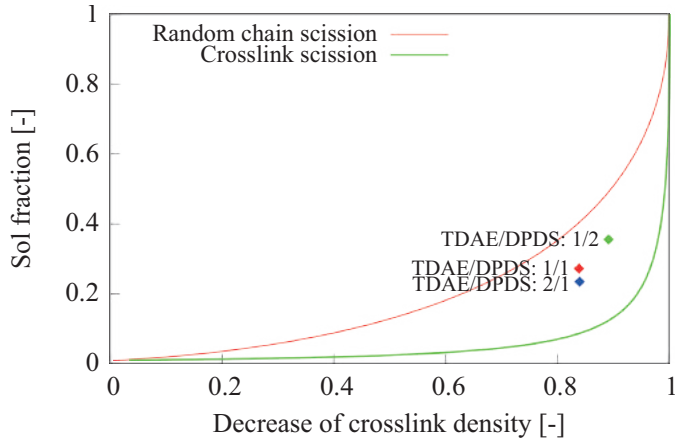
FIGURE 5.6: Influence of the varying concentrations of
devulcanization aid with a constant amount of processing oil
on the degree and quality of the devulcanization.

the decrease of crosslink density lies in the error range of the analysis and
is therefore not conclusive. Hence, the increasing amount of DPDS has a
decreasing effect on the quality of the devulcanizate, while the degree of
devulcanization remains more or less unchanged. Using a higher amount of
TDAE oil was expected to improve the migration of DPDS into the rubber
matrix resulting in a more efficient devulcanization. However, no difference in
effectivity or quality of the devulcanization was found; there is no significant
difference between both positions. A plausible explanation can be that the
shearing forces are reduced when the material has a lower viscosity due to
the added oil; this reduces the expected increase in network breakdown.

Increasing the concentration of DPDS from 18 to 30 mmol/100g GTR with
6.2 wt% TDAE results in an increase in the ratio of polymer to crosslink
scission and a slight decrease in crosslink density. This leads to the conclusion
that an increasing concentration for this material had only a minor effect on
the devulcanization efficiency and a negative effect on the quality. Hence, the
concentration of DPDS of 18 mmol/100g GTR with 6.2 wt% TDAE turned
out to be the optimal devulcanization mix.

### 5.3.2 Extruder Design and Parameter Optimization
**The Influence of Screw Speed**

In a twin-screw co-rotating extruder, an increase of the screw speed affects
several process parameters. These include temperature profiles, shear force
and residence time. In the experiments so far the screw speed was varied in
only a very narrow range of 10 rpm to 30 rpm assuming that the influence on
the other, parameters as mentioned above is negligible. In this part of the
experimental work, the intention was to study the actual effect of the screw
speed, while the variation of the related process parameters was neglected. In
the series of experiments described here, the screw speed was varied within
a wide range of 30 rpm, 60 rpm, 90 rpm and 120 rpm. The effects of screw

speed and related parameters on the devulcanization efficiency of the GTR are shown in Figure 5.7.
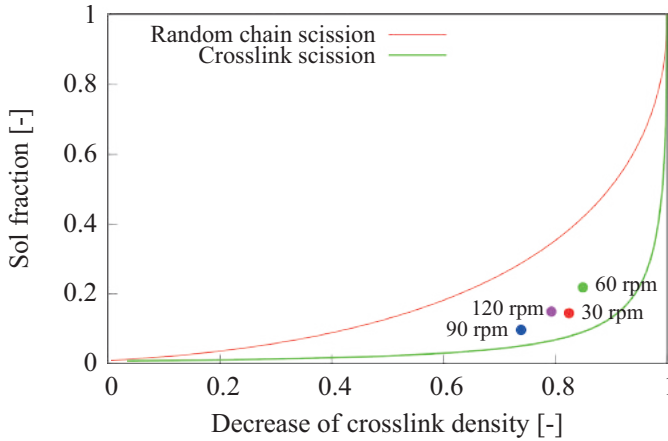


FIGURE 5.7:  Influence of the screw speed on the degree and quality of the devulcanization.

An increase of the screw speed from 30 rpm to 60 rpm causes the experimental data point in the Horikx-Verbruggen diagram to move upwards, representing the additional generation of a soluble fraction without significant reduction in crosslink density. This might be due to significantly higher shear forces at 60 rpm, leading to the uncontrolled breakdown of the polymer. The residence time was reduced by a factor of two; therefore, it was not expected and actually not found that the degree of devulcanization would be higher. However, when increasing the screw speed to 90 rpm and 120 rpm, the experimental data points in the Horikx-Verbruggen diagram moved backwards, indicating inefficient devulcanization.

These high screw speeds, thus low residence times of approximately 60 s and 30 s, respectively, resulted in low degrees of devulcanization as well as less polymer detached from the network. This is in contradiction with the expectation that high screw speeds create excessive shear forces and that therefore the soluble fraction should increase. However, the shear force is only one of the main parameters. The low residence times at high screw speeds might result in an inhomogeneous devulcanization due to a different devulcanization mechanism: devulcanization of the outer layers of the particles, while the inner cores remain more or less not devulcanized at the initial crosslink density. In practice, this inhomogeneity causes a lower average decrease in crosslink density at a particular sol fraction than would have been obtained with homogeneous break down.

The final conclusion from this part is that screw speed influences the devulcanization efficiency more by the change in residence time than by the variation of shear forces. Again the experiments indicate that a residence time of 6 minutes is necessary for completing the devulcanization reaction with this specific GTR, resulting in rather low screw speeds for this type of extruder.

**Influence of the Screw Configuration**

The initial extruder experiments by Saiwari[1] were done with a screw design that was optimized for Ethylene-Propylene-Diene rubber (EPDM) devulcanization[11]. Using this screw, a low devulcanization quality was found for the tire material; most probably due to the severity of the screw. In retrospect, this screw configuration may not have been the best choice, as GTR is very tough compared to the soft EPDM. Therefore, the development of a less severe screw for GTR was considered as the first step to improving the mechanical energy input. In this series of experiments, the screw was newly designed and assembled as shown in Figure 3.2 and screw 1 in Figure 5.2.
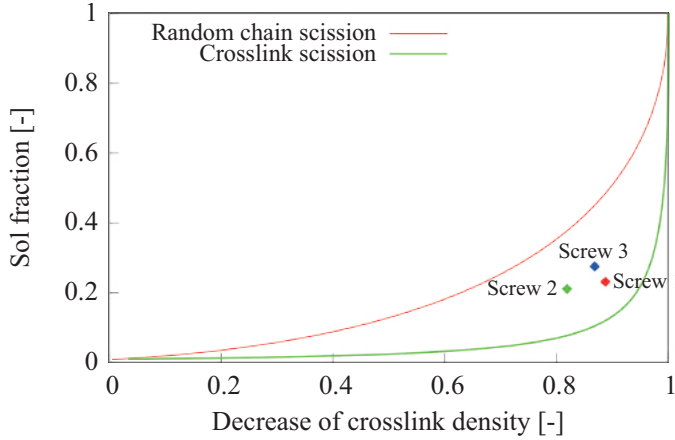


FIGURE 5.8: Influence of the screw configuration on the degree and quality of the devulcanization.

Considering that processing in the extruder can be divided into three sections (Figure 3.2): supply and mixing, devulcanization and pressure section, two alternative screw designs were designed, based on the hypothesis that the remaining visible grains mainly consist of non-devulcanized material:

- Screw 2 with additional mixing elements in the supply and mixing section, to improve the distribution of the devulcanization aids into the GTR particles.

- Screw 3 with mixing elements added to the devulcanization section, following the observations of high shear during the milling process reducing the grains in size. Besides, the inner non-devulcanized parts of the GTR particles must be exposed to a higher remaining concentration of devulcanization aids in the plasticized devulcanizate. The latter is implied by the distribution of devulcanization aids over the particles as discussed in Section 5.3.1. As discussed in Chapter 4, the migration of the devulcanization aid into the particles is a relatively slow process. This implies that the concentration of the devulcanization aid in the inner part of the larger particles might have been too low for an effective devulcanization in screw 1 and screw 2.

Pictures of the smoothest surface,          Pictures of most coarse surface,
          screw 3, 10 rpm.                            screw 1, 30 rpm.



(**a**) Devulcanized material mixed with      (**b**) Devulcanized material mixed with
50/50 wt% virgin rubber; visible grain.      50/50 wt% virgin rubber; visible grain.



(**c**) Devulcanized material;               (**d**) Devulcanized material;
       surface 2*2 mm$^2$.                           surface 2*2 mm$^2$.



(**e**) Surface roughness.                    (**f**) Surface roughness.
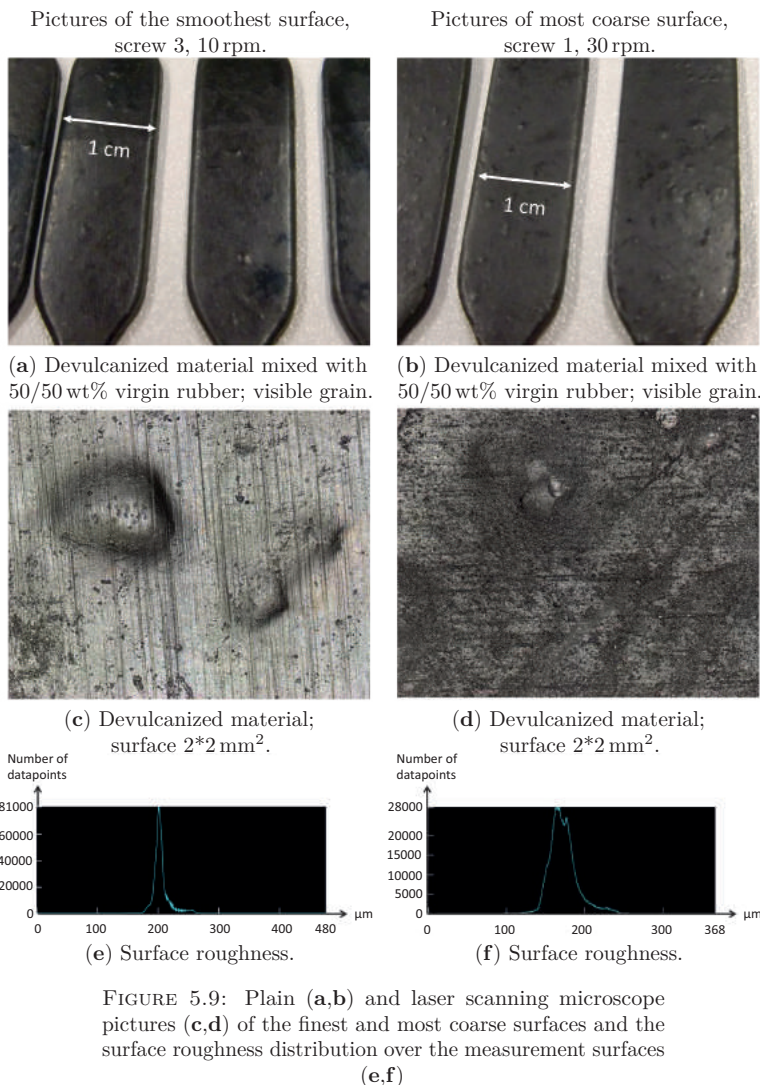
FIGURE 5.9:  Plain (**a**,**b**) and laser scanning microscope
pictures (**c**,**d**) of the finest and most coarse surfaces and the
surface roughness distribution over the measurement surfaces
(**e**,**f**)

The results for a devulcanization aid concentration of 18 mmol DPDS/100 g
are shown in Figure 5.8.  Changing the screw configuration appears to
influence the devulcanization rate and quality.

Devulcanization rate and quality: According to the Horikx-Verbruggen graph,
screw 1 shows the best results. Screw 3 shows a slight decrease in the quality
of the devulcanizate compared to screw 1, indicated by an increasing amount
of sol for a comparable decrease in crosslink density. With screw 2, both,
the quality and decrease in crosslink density are inferior: the results in the
Horikx-Verbruggen diagram show a decrease in devulcanization quality, as
indicated by a relative decrease in distance to the random scission line.

Visible grains: Investigation of the particle size of the devulcanizates was done

Table 5.3: Amount and size of the visible grains for the finest and most coarse material.

| Category (See Figure 5.10) | Material | Size | Amount |
|:---:|:---|:---:|:---:|
| 1 | Finest: (sample 1) | $\approx 1\,\mathrm{mm}$ $>0.1\,\mathrm{mm}, <1\,\mathrm{mm}$ | $2.5\,/\mathrm{cm}^2$ $5\,/\mathrm{cm}^2$ |
| 10 | Most coarse: (sample 17) | $\approx 1\,\mathrm{mm}$ $>0.1\,\mathrm{mm}, <1\,\mathrm{mm}$ | $8\,/\mathrm{cm}^2$ $22\,/\mathrm{cm}^2$ |

and evaluated by visual and microscopic inspection. Without instruments, it can already be clearly observed that there are large differences in the amount and size of remaining visible grains on the surface of the revulcanized rubber blends; see Figure 5.9. The pictures in Figure 5.9 show the most extreme cases: the most homogeneous blend of devulcanized and virgin rubber (Figure 5.9a), and the material with the coarsest surface morphology (Figure 5.9b). To further quantify the surface morphology of the materials, laser scanning microscopy pictures were used. Figures 5.9c, d show typical surface morphologies of a $2 \times 2\,\mathrm{mm}^2$ area: they visualize the quantity and size differences of the particles for the samples. Figures 5.9e, f show the quantitative evaluation of roughness of the surface: the more homogeneous sample has only a few, though still large particles with a height on the surface of $420\,\mu\mathrm{m}$; the distribution is rather narrow. The sample with the coarse surface has a broader distribution and a higher number of particles, Figure 5.9d. A manual count of the particles of the visible grains as given in Table 5.3 shows, that there is a significant difference in the number of large as well as small particles. The total number of particles increases by approximately a factor of four from Category 1 to 10. For further



Scale indication:
0 = virgin rubber,
1 = best material so far (see Figure 5.9a),
10 = most and largest visible grain (see Figure 5.9b).
* Material produced with screw 2.
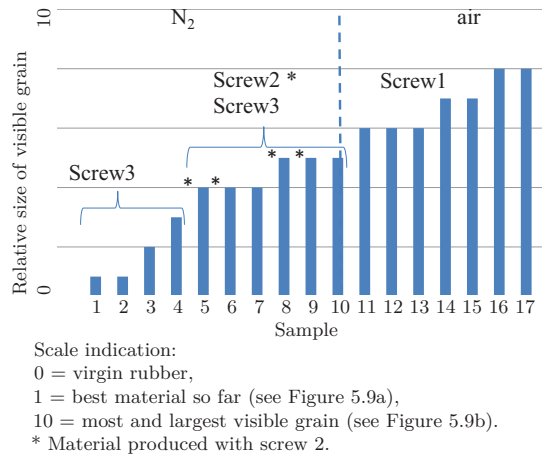
FIGURE 5.10: Relative order of the size and amount of the grain by visual inspection.

comparison of the sample morphology, the interval between Categories 1 and 10 is separated into nine steps of increasing size and number of visible particles. A clear relationship between screw configuration and the quality of the surface could be observed based on these characteristic numbers: with

screw 1, the particles were the largest and most numerous, as can be seen in Figures 5.9b and 5.10; with screw 3, the best material was produced with the smallest and lowest number of particles in the visible grain, as shown in Figures 5.9a and 5.10. Class 0 was assigned to a quality comparable to that of virgin non-vulcanized material. The results for screw 2 were in-between those of screw 1 and screw 3; see Figure 5.10.

The results of screw 2 indicate that the expected positive effect of the improved distribution of the devulcanization aid is hardly visible: there is only a minor decrease in the amount and size of the visible grains, and the quality of the devulcanizate decreases as well. The results of screw 3 show that a small increase of shear in the devulcanization section of the screw decreases the quality of the devulcanizate, but much less than expected. The decrease of the amount and size of the visible grains was as expected, so the overall results for screw 3 show a clear improvement compared with those of the other screw configurations.

The results indicated that a part of the visible grains consisted of non-devulcanized material. Additional TGA and FTIR analysis of these particles showed a high silica content as will be described in Chapter 7.

Overall, it can be concluded that screw 1 shows the best Horikx-Verbruggen representation, but also results in the highest amount and largest size of remaining visible grains. Therefore, screw 3, a low-shear screw with additional mixing elements in the devulcanization part of the extruder (see Figures 3.2 and 5.2), turns out to be most suitable in the present study for the devulcanization of GTR.

## 5.4   Conclusions

The previously established parameters for a devulcanization process in a small-scale discontinuous batch mixer with a capacity of 15 g per batch were transferred to a 40D 25 mm co-rotating twin-screw extruder with a capacity of 2 kg/h. Within this scale-up of the devulcanization the following parameters were fine-tuned for the extruder-based process:

- Devulcanization process conditions: The extruder conditions turned out to be comparable to the parameters determined for the Brabender internal mixer, as shown in Table 5.1:

  - Temperature profile: The main factor determining the devulcanizate quality is the temperature: if too low, devulcanization is too slow; if too high, the polymer degrades. The optimum is 220 °C.

  - Time: The residence time in the extruder is another important influencing factor for the product quality: shorter times caused by higher screw speeds result in insufficient devulcanization and uncontrolled breakdown of the polymer due to the higher shearing forces. The optimal condition for a screw configuration like screw 3 is resulting in a 6 minutes residence time.

  - Devulcanization aid concentration: The optimum concentration of DPDS was found to be 18 mmol/100 g GTR. Increasing the

concentration to 30 mmol/100g GTR decreased the quality of the devulcanizate.

The process conditions defined for the Brabender batch reactor were also valid for the extruder process. With respect to the degree of devulcanization, an extruder is more efficient than a batch mixer. While the maximum degree of devulcanization in the batch mixer was less than 80 %, the percentages found after extruder devulcanization were between 80 % and 90 %. Higher degrees of devulcanization cannot be analytically determined, as some polymer is bound to the filler and is therefore not soluble. Higher percentages than 90 % are not to be expected as the present devulcanization process is further not efficient for monosulfidic crosslinks.

- Extruder parameters: The extruder parameters are interdependent. The screw configuration determines the amount of shear and the residence time, at a certain screw speed. For a small speed range, both residence time and shear rate can be assumed to have a linear relation with the speed; however, this is not valid for larger differences in screw speed.

  - Screw speed: For this extruder and screw 3 10 rpm was optimal, leading to a residence time of 6 minutes.

  - Screw configuration: The low shear concept was proven to be a successful approach. From the three screw variations tested, screw 3, Figure 5.2, showed the best results in terms of devulcanization efficiency, quality and remaining visible grains. Despite the few additional mixing elements in the devulcanization section, this screw can still be considered as a low-shear type.

- Remaining visible grains: Depending on the devulcanization parameters, more or less large particles remain, mostly consisting of non-devulcanized material. However, even with the use of a small or very fine-passenger car tire powder, some visible grains. A first analysis indicates that bthis is due to a high amount of silica in these particles, for which additional investigations are required: Chapter 7

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# Chapter 6

# Optimization of the continuous devulcanization process using DBD

*The study in this chapter describes a further improvement of the twin-screw extruder based devulcanization process with respect to a low shear screw combined with the use of 2-2'-DiBenzamidoDiphenyldisulfide as devulcanization aid. Because of its melting point of approximately 140°C, it is fed into the extruder as powder after mixing with the passenger car tire rubber granulate, processing oil and anti-oxidant. As the low shear in the extruder leads to a mass with a coarse structure, subsequent milling on a two roll mill at 60°C with a very narrow nip width substantially improves the homogeneity, respectively the tensile strength of the devulcanizate after revulcanization. Passenger car tire granulate turns out too complex of composition for using the Horikx-Verbruggen diagram as optimization method for the devulcanization process. Instead, the tensile strength of the revulcanized devulcanizate is chosen as indicator for the quality of the devulcanizate. Best tensile strength values after revulcanization are obtained by using 4 wt% devulcanization aid, 2 wt% processing oil and 1 wt% anti-oxidant at 180°C operating temperature.*

## 6.1 Introduction

In Chapter 5 the upscaling of the earlier approach of Saiwari[1] using DPDS as devulcanization aid to a twin-screw extruder based devulcanization process was elaborated. The very limited availability of DPDS, which precludes industrial use on a large scale, was the first reason to step away from this additive. A second reason was the purgent smell, which persisted in the revulcanized material. And third, DPDS has the tendency to initiate main-chain scission of elastomers[2] which has a negative impact on the properties of the revulcanizates.

Because of these arguments an alternative devulcanization aid was used for the present study: 2-2'-DiBenzamidoDiphenyldisulfide (DBD). A major factor in the change from DPDS to DBD is the difference in melting point: DBD melts at 140 °C, while DPDS melts at 59 °C. In the previous approach, a pre-swelling of the tire granulate with a blend of molten DPDS and processing oil was employed; due to the high melting temperature of DBD, this approach was not feasible anymore: the rubber would start to degrade when kept at such high temperatures for the duration of the swelling process.

As a consequence the extruder screw had to be redesigned to include a mixing section to thoroughly mix the processing oil (TDAE), DBD and anti-oxidant (TDTBP) with the Ground Tire Rubber (GTR) prior to devulcanization. This introduced the temperature of the feed- and mixing section of the extruder screws as an additional parameter into the extruder configuration.

The Horikx-Verbruggen method for determination of the decrease in crosslink density and the ratio between random scission and crosslink scission[3] was used during the first optimization of the extruder temperature, screw configuration and speed in Chapter 5. However, as shown in the present study this method is not suitable for rubber containing both, carbon black and silica-silane as active filler systems. Instead, the tensile strength of the revulcanized devulcanizates is used for the optimization of the devulcanization process.

The method is employed in order to characterise the morphology of the devulcanizates, which may have an influence on miscibility and revulcanizate properties, as explained in Chapter 4.

## 6.2    Experimental

The Ground passenger car Tire Rubber (GTR) used in this chapter is specified in Section 3.2.1; all other materials are listed in Table 3.1. The twin-screw extruder used for devulcanization and all other equipment is described in Section 3.3. Formulations for revulcanization of devulcanizates are given in Table 3.3, and the procedures in Tables 3.14 and 3.15, using a Brabender mixer with 50 ml chamber. Formulations for White Rubber Compounds and blends are specified in Table 3.6, and processing is according to Tables 3.19 and 3.20.

## 6.3    Results and discussion

Based on the previous research[4] with DPDS, 18 mmol/100g GTR, 3.9 wt% of DBD was used as devulcanization aid, with 6.2 wt% TDAE oil and 1 wt% anti-oxidant, determined as the best formulation, see Chapter 5. This was used as starting point.The melting point of DBD is 140 °C and consequently it had to be melted in the extruder after being mixed with GTR, oil and anti-oxidant.

### 6.3.1    Optimization of the screw configuration for use with DBD

With the use of DBD, the configuration of the screws 1 to 3 as developed in Chapter 5 had to be adjusted: the devulcanization aid has to be molten and thoroughly mixed with the GTR in the mixing section of the extruder, see Figure 6.1 with the final screw configuration D. A more severe kneading in this section is required. Hence screw A, Figure 6.2, was assembled for a first series of experiments. A configuration with elements with a negative flight: Screw B to extent the residence time in the mixing section of the screw for a longer blending and swelling time, turned out to be a non-feasible concept: the extruder motor could not provide the required higher torque due to the additional friction at this point of the screw. The addition of more

kneading elements, partly with a negative flight, as shown in screw C, also led to operational problems. Screw D appeared to be the most appropriate with the best results. This configuration was further used throughout the experiments in this chapter. Additional intermediate screw configurations were tested too, but did not provide better results.



Screw with mixing (brown) and kneading (yellow) elements in the mixing section, variations in flight in the devulcanization section and some mixing and kneading elements in the pressure section.
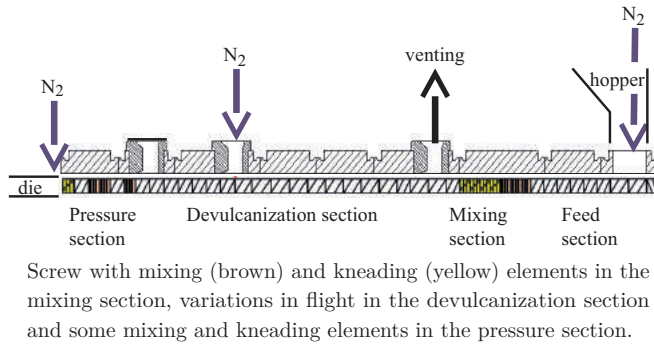
FIGURE 6.1: Layout of the extruder, from right to left, with final screw D and nitrogen purging positions.

### 6.3.2 Selection of optimization criterion

To Provide a direct indication of the quality of the devulcanization process, the Horikx-Verbruggen procedure was first used for optimization. Secondly, the White Rubber Analysis (WRA), as detailed in Chapter 4 was applied for remaining irregularities / visible grains. Third, stress-strain properties after revulcanization were used as optimization criterion for the devulcanization. This has the disadvantage of being an indirect characterization, as the revulcanization process is part of the measurement chain. However, it offers the opportunity to adapt the revulcanization process and the formulation to the specific characteristics of the devulcanizate.

Table 6.1: Most important elastomers and fillers applied in tire components

| Component | Polymer | Reinforcing filler |
|-----------|---------|--------------------|
| Tread | SBR, BR | Carbon black, silica-silane |
| Belt | NR | Carbon black |
| Sidewall | NR, BR | Carbon black |
| Carcass | SBR, NR, BR | Carbon black |
| Bead | NR | Carbon black |
| Apex | SBR, NR, BR | Carbon black |
| Cap-ply | NR, BR | Carbon black |
| Innerliner | CIIR, BIIR | Carbon black |

An impression of the mix of components, polymers and reinforcing fillers in passenger car tires is shown in Table 6.1[1]. These components are an integral part of GTR. Additional complicating factors are:

 Screw A

Conveying elements
(blank): EAZ-25/1/2————————EAZ-31.25/1/2———EAZ-25/1/2–AZ-31.25/1/2
Kneading elements
(yellow): —-EAZ-KB18,75/45/L–EAZ-KB31,25/5/45L—3*EAZ-KB18,75/45/L——
Mixing elements
(brown) : ——————————————————————3*AZ-ZB18,75/3/10L–

 Screw B

Conveying elements
(red) : ————————————————EAZ-25/0,5/2R————————
Kneading elements
(orange): ———————————————3*EAZ-KB18,75/45/R—————————
Mixing elements
(brown) : ——————————————————————3*AZ-ZB18,75/3/10L–

 Screw C

Kneading elements
(yellow): —EAZ-KB31,25/5/45L–2*EAZ-KB18,75/45/L——————————
Kneading elements
(yellow): ————————————2*EAZ-KB18,75/45/L–EAZ-KB31,25/5/45L—-
Kneading elements (dark
yellow): ————————EAZ-KB18,75/90————————————
Kneading elements
(orange): ———————————-2*EAZ-KB18,75/45/R——2*EAZ-KB18,75/45/R————
Mixing elements
(brown) : ——————————————————————3*AZ-ZB18,75/3/10L–

 Screw D

Kneading elements
(yellow): —-EAZ-KB18,75/45/L————————————3*EAZ-KB18,75/45/L——
Mixing elements
(brown) : —-2*AZ-ZB18,75/3/10L—AZ-ZB18,75/3/10L——3*AZ-ZB18,75/3/10L–

Element designation according to supplier system:
Length: 0.75L = 18.25, 1L = 25, 1.25L = 31.25
Pitch: 1 per unit element, except mixing elements; L = left, R = right handed
Kneading elements, staggering: 45 = 45 degrees, 90 = 90 degrees
Mixing elements: 3 = number of units
Conveying elements: EAZ = standard shape, AZ = increased volume
Conveying element configuration for all screws comparable with screw A

FIGURE 6.2: Screw configurations with different amounts
of shear adapted for use with DBD employed in the present
chapter.

- SBR is well known for its tendency to re-crosslink by radical mechanisms while and after being de-crosslinked. Hereby the structure of the polymer is changed, which has a negative impact on the overall result of the devulcanization and properties of the revulcanizate;

- Compounds based on silica as reinforcing filler are known to de-crosslink only to a low degree, mainly because of their high amount of mono-sulfidic crosslinks, which cannot selectively be broken in this process;

- Carbon black based NR and BR compounds are known to de-crosslink relatively easily;

- Remaining hard particles, visible grains in the samples, assumed to be devulcanized to a lower degree, offset the mean values of the crosslink density determination;

- For determination of the crosslink density by the Flory-Rehner method[5], swelling is to be corrected for the influence of fillers. As it is doubtful whether the compensation, as proposed by Porter[6] is similar to carbon black and silica-silane filler systems, the crosslink density calculation for a compound with both, carbon black and silica, will not be appropriate.

With such a complex mixture of devulcanization reactions in the analyzed samples, the main conclusion at this stage of the study must be that the Horikx-Verbruggen analysis is only of limited relevance.

As the remaining visible grains of the devulcanizates influence the tensile strength of revulcanizates and thus the quality, their size and amount remaining in the devulcanizates were determined by WRA. The number and dimensions of the smallest sized particles were used as an optimization criterion for the devulcanization process as well.

For the revulcanization pure devulcanizates were used, based on Formulation GTR-1, Table 3.3, assuming only carbon black as filler. It was not blended with virgin elastomer compound. The tensile strength and strain at break were taken as the optimization criteria in this context, as from an application perspective this is a prime property. It should be noticed that in actual application practice, pure devulcanizate will not likely be used as such, but only in a blend with virgin elastomers.

After several series of experiments with variations in extruder speed, temperature profile of the extruder and concentration of devulcanization aid, the best samples as indicated in the Horikx-Verbruggen diagram, tensile strength, and the smallest remaining particle size can be compared, see Figures 6.3 - 6.4: Opposite to what was expected, the degree of devulcanization as judged by the Horikx-Verbruggen analysis, highest tensile strength and smallest particles do not match. As shown in Figure 6.3, the samples with the highest degree of devulcanization by the Horikx-Verbruggen analysis (round, blue) do not show the highest tensile strength after revulcanization. The samples with the lowest degree of devulcanization (squares, green) show the highest tensile strength. The sample with the smallest particle size (triangle, black) shows an intermediate devulcanization degree by Horikx-Verbruggen and the lowest tensile strength of all samples, see Figure 6.4c. It can be concluded that the differences in size and amount of visible grains in the devulcanizates are not suitable as optimization parameter, neither is the position in the Horikx-Verbruggen plot.

The overall conclusion is, that despite the additional measurement error due to the revulcanization process, the tensile strength of revulcanizates is the best parameter for optimization of the devulcanization process. Based on the present results and previous work[7], it is the presence of silica in GTR which is assumed to be the cause of the poor results of the Horikx-Verbruggen analysis.
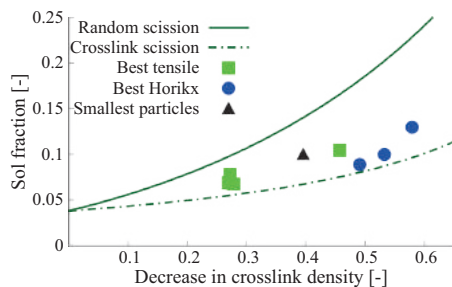
(a) Horikx-Verbruggen diagram
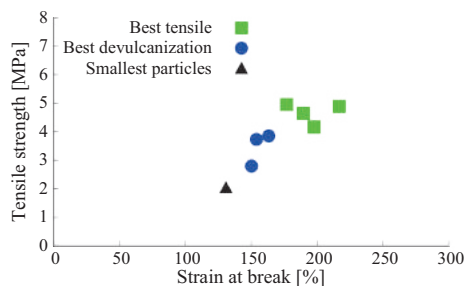


(b) Stress-strain diagram

FIGURE 6.3: Comparison of optimal decrease in crosslink density, smallest particle size and highest tensile strength in Horikx-Verbruggen cq. stress-strain diagram



(a) Samples with highest degree of de-crosslinking.



(b) Samples with highest tensile strength.



(c) Sample with smallest particles.
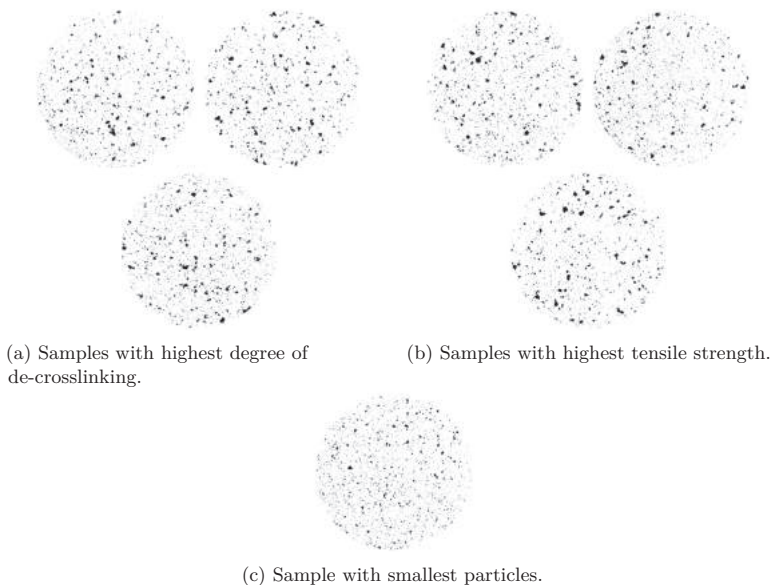
FIGURE 6.4: Comparison of remaining particle sizes of samples of Figure 6.3.

In the following paragraphs, the judgment of devulcanization quality will be based on tensile strength.

To take the presence of silica on the curing behavior during revulcanization into account, formulations GTR-2 and GTR-3 in Table 3.3 adapted for a silica based tread formulation, respectively Table 3.15 for processing are used. As the size of the remaining visible grains in the de- and revulcanizates is considered a quality issue, WRA is used as well to optimize processing after devulcanization in the extruder for minimum amount and size hereof.

### 6.3.3 Optimization of the devulcanization by tensile strength

The various process parameters, extruder section settings, screw speeds and devulcanization systems are summarized in Table 6.2.

**Table 6.2: Formulations, screw speed and extruder temperature settings used for devulcanization and revulcanization.**

| Screw speeds: | | | |
|---|---|---|---|
| Screw speed [rpm] | 10 | 20 | 30 |

| Variations in temperature profile of the extruder: | | | | | |
|---|---|---|---|---|---|
| | [°C] | | | | |
| Feed & mixing section*: | 110 | 130 | 150 | 170 | 220 |
| Devulcanization section*: | | 180 | | 220 | |
| Pressure section*: | 110 | 130 | 150 | 170 | 220 |

| Variations in the devulcanization system: | | | | |
|---|---|---|---|---|
| Component | Amount, in wt% of GTR | | | |
| DBD: | | 3.9 | 6.85 | |
| TDAE: | 0 | 2 | 5 | 6.2 |
| TDTBP: | | 1 | | |

| Variations in the revulcanization system (see Table 3.3) | | |
|---|---|---|
| Formulation : | **GTR-2** | **GTR-3** |
| S: | 1.64 phr | 4.64 phr |
| TBBS: | 1.64 phr | 4.64 phr |

* see Figure 6.1
Screw configuration: D in Figure 6.2

For the samples with the highest tensile strength after revulcanization, the settings and configuration are summarized in Table 6.3.

**Table 6.3:** **Comparison of processes resulting in materials with highest tensile strength**

| Sample | DA | Temperature | Screw speed | TDAE | Tensile stress | Strain at break | M100 |
|---|---|---|---|---|---|---|---|
| | wt% | I-II-III* | rpm | wt% | MPa | % | MPa |
| Best samples after revulcanization with formulation GTR-2, Table 6.2 ||||||||
| a | 6.85 | 130-180-170 | 20 | 2 | 8 | 176 | 3.8 |
| b | 3.9 | 130-220-150 | 20 | 2 | 7.6 | 131 | 5.2 |
| c | 5 | 130-220-150 | 20 | 2 | 7.5 | 140 | 4.7 |
| Best samples after revulcanization with formulation GTR-3, Table 6.2 ||||||||
| d | 3.9 | 130-180-170 | 20 | 2 | 8.2 | 158 | 4.4 |
| e | 6.85 | 130-220-150 | 30 | 2 | 7.8 | 161 | 4.1 |
| f | 6.85 | 100-220-100 | 10 | 6.2 | 6.9 | 179 | 3.1 |

DA : devulcanization aid DBD;
\* : I  = Feed& mixing section, II = Devulcanization section,
  III = Pressure section, see Figure 6.1.

The following observations can be summarized:

*Temperature:* The samples that are devulcanized at a maximum 180 °C show a better tensile strength than those devulcanized at 220 °C;

*Amount of DBD:* There is no significant difference in tensile strength between the samples devulcanized with 3.9 wt% DBD and those with 6.85 wt%;

*Screw speed:* Samples a up to and including d, with good tensile strengths, were obtained at a screw speed of 20 rpm. The tensile strength of sample f, produced at 10 rpm, is the lowest of this selection. Sample e, produced with a screw speed of 30 rpm, also has a reasonable tensile strength, but only with 6.85 wt% of DBD combined with a devulcanization temperature of 220 °C.

*Amount of oil:* Samples a up to and including e are produced using 2 wt% oil; for sample f, 6.2 wt% oil was used. Combined with the lowest screw speed, the high oil concentration resulted in the lowest tensile strength.

*Formulation:* As a secondary criterion, strain at break can be used. This is slightly better for the samples produced with 2 wt% oil and revulcanized with formulation GTR-3: samples d and e, compared to those revulcanized with formulation GTR-2: samples a and b.

### 6.3.4   Summary of the best devulcanization process set-up

These observations conclude that a devulcanization temperature of 180 °C, combined with screw D and 2 wt% oil is the best settings for the devulcanization process. Although for part of the experiments screw A was used, screw D gave better results. As there is no significant advantage of using 6.85 wt% of DBD, 3.9 wt% of DBD suffices. Revulcanization formulation GTR-3 gives a slightly better strain at break than formulation GTR-2. This is all summarized in Figure 6.5.

- Screw speed: 20 rpm, residence time $\approx$12 min, throughput $\approx$2 kg/h
- Devulcanization system: DBD 3.9 wt%, TDAE 2 wt%, TDTBP 1 wt%
- Post processing: mill, 0.1 mm gap, 60 °C
- Revulcanization system: S 4.64 phr, TBBS 4.64 phr, TESPT 3.2 phr, DPG 2.8 phr
- Compounding for revulcanization: with silanization

FIGURE 6.5: Extruder configuration and devulcanization process for best tensile strength of revulcanizates.

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### 6.3.5 Benefits of post processing steps

The devulcanization process as developed in the present study is a thermo-chemical-mechanical treatment. The shear created by the screw, however, is not sufficient to completely decrease the amount and size of the visible grains in the devulcanizates. Screws configured for higher shear showed a decrease in the quality of the devulcanizates, as indicated by the lower tensile strength of the revulcanizates.

A clear positive effect of additional post-devulcanization milling of the devulcanizate at 60 °C with a gap width of 0.1 mm was observed. At lower temperature, the shear forces to break crosslinks increase, but the reactivity of the free radicals decreases exponentially. An advantage of the post-process milling as an addition to the devulcanization process in the extruder, is that the devulcanizate gains coherency in spite of the remaining visible grains. A clear difference is observed during milling between the elastic nature of GTR, either as reference or as hardly devulcanized material, and the more plastic behavior of devulcanizate. This implies that the shear forces during milling do not destroy the rubber matrix, but only aid in shearing off the layers of devulcanized material from the particles. These observations are discussed in more detail in Chapter 8. Some experiments with replacing post-process milling by a single pass in a laboratory scale single screw extruder showed promising results as well, but was not further explored.

## 6.4 Conclusions

The difference in melting points of 59 °C for DPDS and 140 °C for DBD made adjustment of the devulcanization process necessary. So that DPDS could be melted, mixed with GTR and swollen into the GTR prior to devulcanization. DBD had to be mixed with GTR as a powder and melted in the extruder before the actual devulcanization. A major factor not further pursued in the switch from DPDS to DPD is the size and distribution of granulate dimensions as covered in Chapter 4. As the migration time of the devulcanization aid into the granular material is of the same order as the residence time in the

extruder, a lower concentration of devulcanization aid in the centre of the granulate particles might occur. In addition, as the devulcanization aid is distributed over the surface of the particles and has to migrate into their volume, larger granulate particles end up with a much lower concentration than needed at the center of the particles.

Unfortunately, granulated passenger car tire rubber is such a complex combination of materials that the degree and quality of devulcanization, indicated by the decrease in crosslink density and the ratio between random scission and pure crosslink scission by the Horikx-Verbruggen analysis, could not be used as a quality criterion. For optimization of the devulcanization processes therefor the tensile strength of revulcanizates was selected as criterion. A certain degree of still visible grains remaining in the devulcanizate did not influence the tensile strength after revulcanization, but had a minor influence on the strain at break.

The fact that GTR of recent date contains a substantial amount of silica raised a substantial problem: real devulcanization of granulate containing silica is very challenging. In addition, revulcanization formulations and procedures had to be adapted to compensate for the influence of silica on the curing and tensile properties. This will be elaborated on in more detail in Chapter 7.

The need to limit the material degradation by high shear forces in the twin-screw extruder was overcome by post-devulcanization milling at a temperature of about 60 °C. This improved the quality of the devulcanizate considerably: The size of the remaining visible grains in the devulcanizate decreased substantially, which decreased even more during mixing and milling for revulcanization.

## 6.5   Remarks on the devulcanization process scale-up

It is recommended for further upscaling to separate the processing steps due to the divergent requirements, which limits the capacity and effectiveness of the total process when all the needs are combined into one set for an extruder:

- The continuous twin-screw extruder set-up in the present study is limited by the time available to thoroughly mix the GTR with the devulcanization formulation, melt the devulcanization aid and allow adequate time for migration of DBD devulcanization aid into the granulate particles at a temperature of 140 °C. For further upscaling, it is more appropriate to use a separate process step prior to the devulcanization, e.g. a separate mixer step for swelling of the devulcanization aid;

- The limiting conditions for the devulcanization process are low shear forces during the devulcanization process and a devulcanization time of 6 minutes to 7 minutes at the devulcanization temperature of 180 °C: A twin-screw extruder is in principle suitable. However, the relatively long residence time needed for the devulcanization limits the capacity of the extruder, as the length to diameter ratio required for a reasonable throughput leads to impractically long screws. Due to the required low

shear, a delaying influence of additional mixing elements in the screw to increase residence times cannot be used in this devulcanization process. Possible adaptions are the use of an elongated die and/or an increased extruder volume by a decrease of the length to diameter ratio;

- Post-processing milling applying high shear at a temperature of 60 °C improved the structure and properties of the devulcanizate. However, this is not a practical solution for a continuous process. Some experiments with a laboratory scale single screw extruder instead showed promising results.

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# Chapter 7

# Implications of silica in Granulated passenger car Tire Rubber

*Tires are important vehicle components, as car handling, safety and fuel economy depend for a major part on the tire composition and construction. As a consequence, tires are improved continuously. The most prominent improvement in the recent past was using a silica-silane reinforcing filler system in passenger car tread compounds, instead of traditionally used carbon black. For recycling and re-use of end-of-life car tire rubber one of the most promising recycling methods is devulcanization: re-plasticizing the vulcanized rubber by selectively breaking the sulfur bridges between the polymer molecules. In the present chapter the influence of silica, present in the passenger car tires granulate, on both devulcanization and subsequent revulcanization, is investigated. The best tensile strength of the revulcanizate, using a carbon black based revulcanization formulation was 5 MPa. This could be improved to 6.5 MPa by using 2.8 phr of 1,3-DiPhenylGuanidine (DPG) in the revulcanization formulation. After addition of a silanization step during revulcanization by adding 3.2 phr bis[3-(TriEthoxySilyl)Propyl] Tetrasulfide (TESPT) silane to the formulation, the tensile strength of the revulcanizate was further improved to 8 MPa. With these results it is demonstrated that the silica in the granulate can be used to improve the revulcanization properties. By devulcanization and subsequent revulcanization of both a carbon black based and a silica based model tread compound, it is shown that a tensile strength of the revulcanizate of 13 MPa could be reached. This shows the potential of devulcanized rubber when the various tire components are separated before whole material is granulated at the beginning of the recycling procedure.*

## 7.1 Introduction

The performance of passenger car tires is continuously improved, supported by governmentally imposed labeling systems on relative performance in terms of safety and environmental aspects, noise and fuel economy. Due to the sheer amount of $10^9$ tires/year produced worldwide, end-of-life passenger car tires pose environmental problems when dumped because of their intrinsic resistance against decomposition, or when catching fire in the open air because of the soot, fumes and air pollution produced. These problems are addressed by the industry including academia as shown by the increasing number of

patents related to reuse of the materials of end of life tires by reclaiming, pyrolysis and related processes: Figure 7.1. Replasticizing end-of-life tire rubber, as done in reclaim processes, aims at the reuse of the valuable material for new products. However, due to the high shearing forces and processing temperatures applied in the conventional recycling processes, the reclaimed rubber is not readily reusable for high quality end products as scission of the polymer chains occurs.
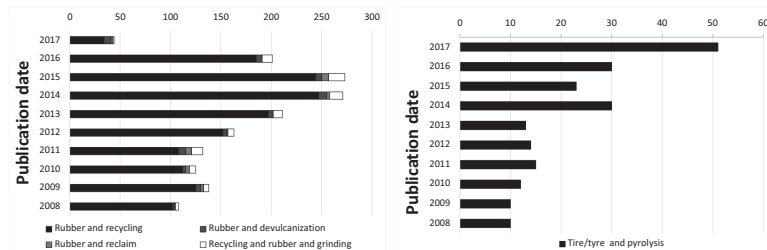


FIGURE 7.1: Number of patents on recycling of rubber.

Finetuning of the process conditions leads to a shift towards devulcanization. It was shown that damage of the polymer chains could be limited considerably by tailoring the process conditions[1,2]. For EPDM[3] it has already been proven that devulcanization is possible with acceptable rubber properties of the revulcanized material. For end-of-life passenger car tire rubber this is still under development, mainly because of Styrene Butadiene Rubber (SBR), a main component of passenger car tires, which is more sensitive and prone to side reactions under the reclaiming process conditions.

An additional challenge is the production of a clean car tire granulate. During grinding, the rubber is separated from the remaining steel, fibres and contaminations. The particle size of the Granulated car Tire Rubber (GTR) is determined by the degree of purity required for the final application, and the costs. Besides, the granulate is a mixture of different rubber compounds from all tire components. An important, relatively recent change in passenger car tire tread compositions is the use of silica as reinforcing filler rather than the more common carbon black. This is because of the significant improvement of wet grip and rolling resistance of the tires, leading to improved safety and better fuel economy of vehicles. However, as earlier work has shown, devulcanization of silica based rubber is more difficult than of its carbon black counterpart, as indicated by a Horikx-Verbruggen analysis[4,5], which is used to determine the ratio of polymer to crosslink scission. This evaluation however has its shortcomings when applied to a blend of different compounds. Within the present study it was decided to use stress-strain properties after revulcanization as a measure for the quality of the devulcanizate.

The devulcanization process applied in this study is a thermo-chemical-mechanical twin-screw extruder based continuous process, scaled up from a small scale batch process, as described by Saiwari[5]. In the latter study, a low shear process at a low screwspeed was applied. The literature mentions both high and low shear processes using twin-screw extruders. However, most studies are based on a feedstock with a high Natural Rubber (NR) content,

like truck tires, or a mix of passenger car and truck tires, where NR is the main component of truck tires. The presence and content of silica are not mentioned[6–10].

In previous studies, the devulcanization aid DiPhenyl DiSulfide (DPDS) was used, but due to the smell of the final product and a reported scission of the polymer chains[11], an alternative had to be found: 2-2'-Di-Benzamido-Diphenyldisulfide (DBD). This devulcanization aid is used for most of the research described in this chapter. As a result of the use of DBD and corresponding optimization of the devulcanization process conditions, the physical properties of the devulcanizates changed from severely staining and smelling into a dry, sticky, coarse powder, that could be transformed into a coherent slab by milling. However, after mixing the pure devulcanizate with the revulcanization system, intensive homogenization on the mill was necessary as the material did not mix properly in the 50 ml Brabender mixer.

Because of a relatively low tensile strength of the first batch of revulcanized material, the devulcanization process had to be improved thoroughly. As the feedstock contained a considerable amount of silica, the revulcanization process and compound formulations need to be optimized.

To study the influence of a mixture of all kinds of compounds as can be found in passenger car tire granulate, both a silica based and a carbon black based model tread compound are prepared. The stress strain properties before and after devulcanization (and subsequent revulcanization) are measured. By microscopy of the fracture surfaces of the revulcanizates, the influence of silica on devulcanization is shown.

## 7.2 Experimental

The ground passenger car tire rubber (GTR) used in this investigation is specified in Section 3.2 and all other materials in Table 3.1. The twin screw extruder and all other equipment in Section 3.3.

## 7.3 Results and discussion

### 7.3.1 The presence of silica in GTR

The introduction of silica in passenger car tire treads started about 30 years ago; therefore, whole passenger car tire granulate of recent origin must contain a certain percentage of silica. By Thermo Gravimetric Analysis (TGA), Figure 7.2 and Table 7.1, the amount of silica in a compound can be determined: commonly the amount of polymers is defined to be equivalent to the weightloss of the sample between 300 °C and the point of a sharp decrease in weight at about 450 °C to 550 °C. In Figure 7.2, the amount of volatiles, which include mainly process oils, wax and other lightly evaporating components, ranges from $100\,wt\% \rightarrow 79\,wt\% = 21\,wt\%$, the polymers from $79\,wt\% \rightarrow 44\,wt\% = 35\,wt\%$, carbon black from $44\,wt\% \rightarrow 10\,wt\% = 34\,wt\%$ and silica + ash from $10\,wt\% \rightarrow 0\,wt\% = 10\,wt\%$. By setting the polymer content to 100, the amount of volatiles, carbon black and silica + ash can be easily converted into phr's (grams per hunderd gram polymer).
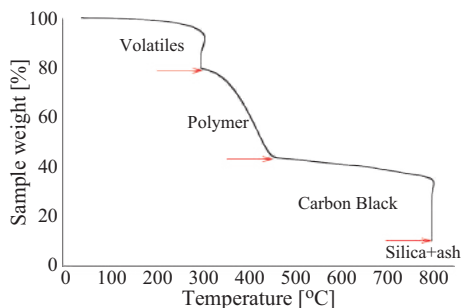
FIGURE 7.2: TGA analysis of the GTR.

Table 7.1: TGA program for determination of the amount of silica in GTR.

| Temperature | Action |
| --- | --- |
| | under nitrogen |
| $\longrightarrow 50\,^{\circ}$C | go to $50\,^{\circ}$C |
| keep at $50\,^{\circ}$C | for 2 minutes |
| $50\,^{\circ}$C$\longrightarrow 300\,^{\circ}$C | $100\,^{\circ}$C/min |
| keep at $300\,^{\circ}$C | for 15 minutes |
| $300\,^{\circ}$C$\longrightarrow 620\,^{\circ}$C | $20\,^{\circ}$C/min |
| $620\,^{\circ}$C | change to air |
| $620\,^{\circ}$C$\longrightarrow 800\,^{\circ}$C | $100\,^{\circ}$C/min |
| keep at $800\,^{\circ}$C | for 15 minutes |

With additional analysis it was shown that the silica content varies around an average of 23 phr. By Fourier Transform Infrared Spectroscopy (FTIR) analysis it was shown that the remaining GTR-ash after TGA, see Picture 7.3a, contains a certain amount of silica: curve C in Figure 7.4. In the ash, small hard particles were found, see Picture 7.3b, and FTIR showed that these particles consisted of silica only: curve A.



(a) Soft, gray ash.



(b) Hard, white particle.

FIGURE 7.3: Residues after TGA of devulcanizate.

By Scanning Electron Microscopy - Energy Dispersive X-ray analysis (SEM-EDX), the presence of silica particles up to 250 μm could be shown, see Figure 7.5. This can be explained by the use of earlier types of silica in the original tire compounds, with a dispersion not as good as that of the more modern types.
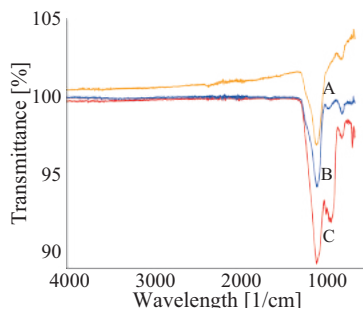
FIGURE 7.4: FTIR analysis of remaining particle in ash as in Figure 7.3b (A, orange) after TGA analysis of devulcanizate, of silica (B, blue) as reference and ash as in Figure 7.3a (C, red).
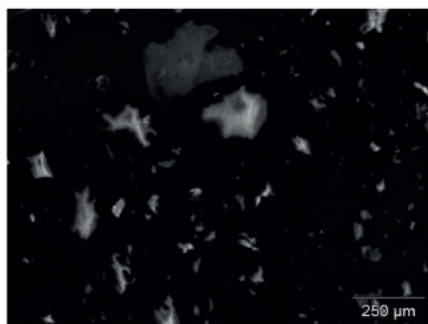


FIGURE 7.5: SEM-EDX picture of remaining particles from the devulcanizate after TGA. Pure silica is detected, 100-250$\mu$m, relevant for the visual granularity of the revulcanizate.

Although by TGA larger silica particles were found, see Figure 7.3b, it was shown by additional experiments that for a vulcanized compound with a high amount of silica, the latter will remain as a framework in the shape of the rubber granulate particles of which the polymer is degraded and evaporated during TGA.

## 7.3.2 Preparation of devulcanizates in the twin screw extruder

Devulcanization of GTR was done in a continuous process with the twin-screw extruder. The formulations as given in Table 7.2 were used. A disulfide concentration of 30 mmol/100g polymer, which is equivalent to 6.85 wt% DBD, was found by Saiwari[12] to be optimal. In another study of Saiwari[2,5], a concentration of 30 mmol/100g GTR was used. For DBD this is equivalent to 3.9 wt%. Both concentrations are used in this study. A concentration of TDAE of 6.2 wt% relatives to GTR was found by Saiwari[5] as the best performing. However, lower concentrations of TDAE were investigated with tensile strength as criterium instead of the Horikx-Verbruggen analysis. Also, a concentration of 1 wt% TDTBP was used, a similar concentration as used in the previous studies mentioned.

**Table 7.2: Devulcanization formulations used for continuous devulcanization.**

| Component | Amount in wt% of GTR | | | |
|---|---|---|---|---|
| DBD (2-2'-Di-Benzamido-Diphenyldisulfide) | | 3.9 | 6.85 | |
| TDAE (Treated Distillate Aromatic Extract) | 0 | 2 | 5 | 6.2 |
| TDTBP (Tris(2,4-Di-Tert-Butylphenyl)Phosphite) | | 1 | | |

All mutual combinations of the mentioned amounts are
used for continuous devulcanization.

Due to the melting point of DBD 140 °C, swelling before devulcanization was not possible. Because of the powdery consistency of the devulcanization aid, the GTR could be manually mixed with TDAE, TDTBP and DBD until the mixture was homogeneous. Mixing time was 5 min to 10 min at room temperature, depending on the amount of GTR. The functions of TDAE are multiple: it acts as a processing aid during devulcanization, as an additive to facilitate the migration of devulcanization aids into the GTR particles, and to prevent dust formation while dosing powdery devulcanization aid.

The screw design of the extruder was based on a minimal shear concept: minimized application of shear during the processing at high temperature and shear at lower temperatures after the chemical devulcanization, see Figure 7.6 and screw D in Figure 6.2. The extruder feed section was configured with conveying elements with a short flight to build some pressure, mix and knead elements, to mix the additives thoroughly with the GTR. The temperature of this section is just above the melting point of DBD to not start devulcanization already before the mixture enters the devulcanization section. In this section only small variations in screw-flight were applied but no kneading or mixing elements. The blend of rubber granulate, oil, stabilizer and devulcanization aid was gravity fed into the entrance section via a hopper. The hopper was always filled with the mixture to ensure that a constant flux of nitrogen could drive out trapped air. The extruder was operated under nitrogen atmosphere to prevent oxidation of the devulcanizate. Nitrogen was supplied through a dosage point midway of the extruder, just before the start of the compression section. To release the overpressure, a ventilation point was situated just behind the mixing section. Some mixing and kneading elements were used directly after the pressure section. The latter was configured with elements with a short flight to be able to supply the necessary discharge pressure. These elements did not add any improvement and will be left out when redesigning the screw setup. Also, nitrogen was supplied to the die, as shown in Figure 7.6. The devulcanizate was cooled down to approximate 60 °C directly after the extruder with the cooling calender. The devulcanizate was milled at 60 °C and a 0.1 mm gap between the rolls of the mill until a homogeneous slab was produced. Subsequently, the devulcanizate (DGTR) was stored at room temperature for at least 24 h before further processing.

### 7.3.3 Revulcanization of DGTR

Initially, revulcanization was done with formulation 1 of Table 7.3 and compounded as described in Table 3.14. Vulcanization was performed under pressure in a Wickert press for $t_{c,90}+2$ min at 170 °C. The formulation was derived from a common carbon black based tire tread compound. The best tensile strength obtained for this series of devulcanizates was 5 MPa.
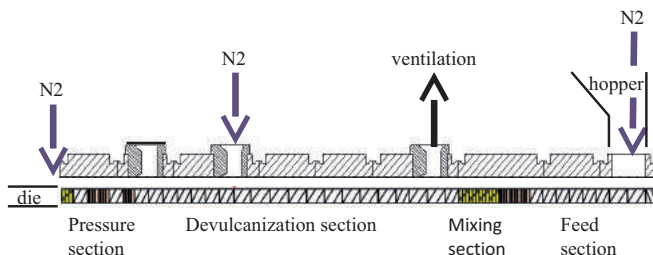


FIGURE 7.6: Nitrogen supply points at the extruder and screw

**Table 7.3: Revulcanization formulations, values in phr.**

| Formulation nr.<br>Component: | **1**<br>DGTR<br>re-vulca-<br>nizate(2) | **2**<br>DGTR<br>re-vulca-<br>nizate(3) | **3**<br>DGTR<br>re-vulca-<br>nizate(4) | **4**<br>DGTR<br>re-vulca-<br>nizate(5) |
|---|---|---|---|---|
| Polymer (1)[x] | [100] | [100] | [100] | [100] |
| ZnO | 3.0 | 2.5 | 2.5 | 2.5 |
| St.A. | 2.0 | 1.0 | 1.0 | 1.0 |
| TDAE[x] | [42.7] | [42.7] | [42.7] | [42.7] |
| Carbon black[x] | [80] | [54] | [54] | [54] |
| Silica[x] | | [42](7) | [42](7) | [42](7) |
| TESPT | | | | 3.2 |
| 6PPD | 1.0 | | | |
| TMQ | 2.0 | | | |
| TBBS | 1.5 | 1.7 | 1.7 + 3 (6) | 1.64 + 3 (6) |
| DPG | | 2.0 | 2.8 | 2.8 |
| Sulphur | 1.5 | 1.4 | 1.4 + 3 (6) | 1.64 + 3 (6) |

[x] Components already present in devulcanizate as measured by TGA, see Figure 7.2.
(1) Total polymer content of (D)GTR, a mix of mainly SBR, BR and NR;
(2) Revulcanization formulation, based on the carbon black based tread formulation in Table 3.4;
(3) DPG added because of the silica content. Amount derived from the silica based tread formulation in Table 3.4;
(4) Amount of DPG optimized;
(5) TESPT added for silanization of silica in GTR. Related to the amount of silica in the DGTR;
(6) Additional sulfur and TBBS added because of the revulcanization process;
(7) Based on preliminary experiments concerning the composition of GTR.

### 7.3.4   Influence of silica on de- and revulcanization of tire compounds

**Devulcanization of silica based tire compounds**

In a previous, unpublished, study the influence of a silica related vulcanization system on the performance of the devulcanization process was investigated by S.Saiwari[13] using the Horikx method, as developed by Verbruggen[4] for devulcanization. In this study a tire tread compound with formulation as in Table 7.4 and the compounding procedure in Table 3.8, was devulcanized using the previous DPDS.

**Table 7.4: Formulation of the silica based tire tread compound as used for the analysis of the devulcanizate as shown in the Horikx-Verbruggen diagram in Figure 7.7**

| Component | (phr) |
|---|---|
| SBR (SPRINTAN SLR1732 (35phr oil)) | 103 |
| BR | 25 |
| Silica Zeosil 1165MP | 80 |
| TESPT | 7.0 |
| TDAE | 5.0 |
| ZnO | 2.5 |
| Stearic acid | 2.5 |
| 6PPD | 2.0 |
| TMQ | 2.0 |
| Sulfur | 1.4 |
| TBBS | 1.7 |
| DPG | 2.0 |

While carbon black based compounds usually show a decrease in crosslink density of 60 % to 80 % and corresponding sol-fractions close to the crosslink scission line after devulcanization, as indicated in Figure 7.7 at position 2, silica based tread compounds showed a much lower decrease in crosslink density of 20 % to 40 % and corresponding sol-fractions on the random main chain scission line as shown in Figure 7.7, position 1.

This indicated that the amount of polymer that could be released from the polymer network of a silica reinforced compound by devulcanization was substantially lower than for a carbon black reinforced rubber. Possible explanations are, as illustrated in Figures 7.8a and 7.8b:

The applied devulcanization process does not break mono-sulfidic crosslinks, and the chemical bonds between silane and polymers are primarily monosulfidic, therefore a high percentage of these type of links survive. In addition to this, it was found during the experiments of the present thesis, that the degree of devulcanization of tire granulate was not corresponding to the tensile properties found after revulcanization. This can be due to the very complex composition of the devulcanized granulate with silica in it. Also, it is known that unsaturated elastomers in general and SBR in particular are sensitive to recombination during devulcanization, especially for temperatures above 200 °C, as were used in previously mentioned studies of Golub and Chen[14,15].

- The physical bonds between carbon black and the polymers as opposed to the chemical bonds between silica, silane and the polymers, which result in a different kind of network;

- The primarily monosulfidic nature of the chemical bonds present between the silane coupling agent and the polymers;
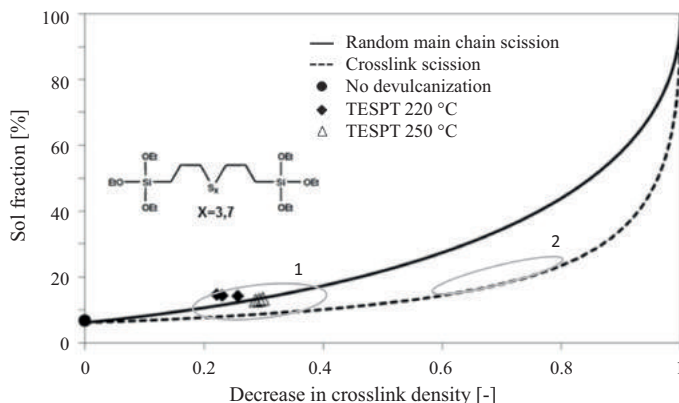


FIGURE 7.7: Degree of devulcanization of tire tread compounds as shown by a Horikx-Verbruggen diagram.
1=Measurements of silica-based devulcanizate,
2=Area of typical carbon black based devulcanizates.

This has a negative effect on the quality of revulcanized material. For reason of all these complicating factors caused by silica, the tensile strength of the revulcanizate was used furtheron as the prime parameter for optimization instead of the decrease in crosslink density.
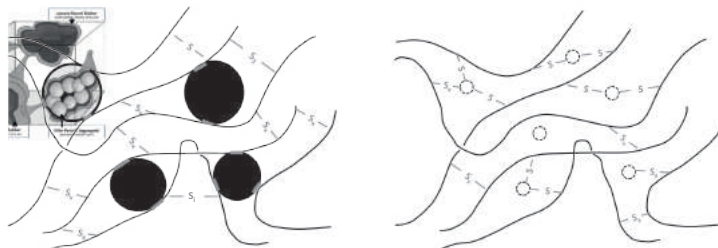


(a) Sulfide bonds in carbon black rubber. Insert bound rubber by Leblanc[16]: physical bonds between rubber and carbon black.

(b) Sulfide bonds in silica-silane based rubber. High amount of (mono)sulphidic bonds between silica and rubber.

FIGURE 7.8: Differences in network structure between carbon black based compounds and silica-silane based compounds

**Revulcanization of silica based compounds**

For silica it is known that the surface is covered with silanol moieties, as depicted schematically in Figure 7.9a with the consequence that it is acidic of nature which has a negative influence on vulcanization reactions. Furthermore,

to create a chemical bond with the polymer, a coupling agent is needed, mostly a silane, see Figure 7.9b[17]. As depicted in this figure, there are still free silanol moieties left on the silica surface after reaction with the coupling agent hindering vulcanization due to their acidic nature. In silica reinforcing technology DPG, a commonly used secondary accelerator in vulcanization[18], is required to shield these free remaining silanol moieties, with the advantage of neutralizing the acidic character of the silica and hence improve the vulcanization[19].

As the amount of silica in the GTR is considerable, as described before, the question may be raised if there are free silanol moieties left or regenerated after devulcanization. Therefore, DPG was added to the formulation to compensate for eventual acidity of the silica. The amount of DPG was set at 2 phr, similar to the concentration used in the silica based model compound, Table 7.3 formulation 2; but increased to 2.8 phr after optimization, formulation 3. Also, for better reproducibility of the tensile test results, an additional 3 phr of sulfur and of TBBS was added to the formulation, as shown in formulation 3 of Table 7.3. A reason to do so was the high viscosity of the 100 % revulcanizate compound which limits the the migration of sulfur in the compound during revulcanization[20]. Whether this is still needed when using this devulcanizate in blends with other elastomers is part of further research. With these optimizations, the best tensile strength value achieved increased to 6.5 MPa.



(a) Simplified schematics of the surface chemistry of silica.

(b) Silane bridges between silica and rubber. Part of the silanol moieties are still unoccupied.
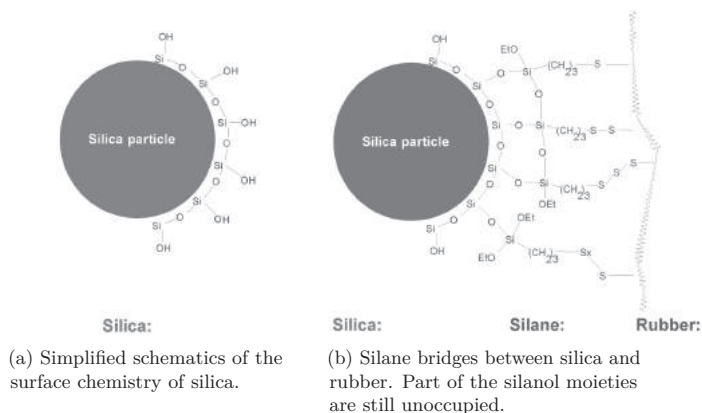
FIGURE 7.9: Chemical bonds between silica and rubber by silane bridges[17].

As the improved results due to the addition of DPG show, a certain amount of free silanol moieties is still available on the silica surface. To make use of these free moieties for building an additional network, a silanization step before the revulcanization process with coupling agent TESPT is required to improve further the tensile properties. By this secondary silanization, combined with a waiting time of 72 h, as shown in Table 3.15, the tensile strength improved to 8 MPa: see Figure 7.10, after vulcanization for $t_{c,90}+2$ min at 170 °C. These results demonstrate that the first improvement by the addition of DPG only remedied a certain acidity due to the silica in the GTR and hence in the devulcanizate. The second improvement by the silanization with

new TESPT indicates that the silica still has free silanol moieties left for a second silanization, enabling a further improvement of the properties of the material by re-silanization.
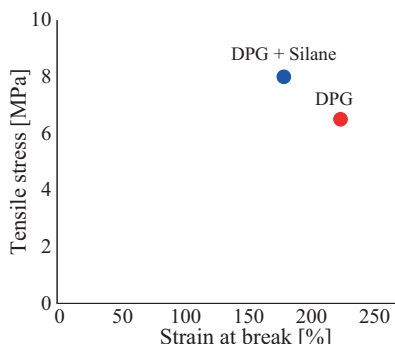


FIGURE 7.10: Tensile stress vs. strain at break of samples of DGTR after revulcanization with DPG only, Formulation 3 in Table 3.4; and with DPG and TESPT, Formulation 4 in Table 3.4.

**Comparison of carbon black- and silica-based tread compounds**

As discussed before, silica reinforced compounds are less prone to be devulcanized. However, in the earlier study[13] of Saiwari the devulcanized material was not analyzed in terms of stress-strain properties. To study the effect of silica as a reinforcing filler compared to carbon black with respect to devulcanization and tensile properties after revulcanization, two tread compounds with simplified formulations were prepared: one based on carbon black as filler, as reference; and another one based on silica. See Table 3.4, with formulation "CB" for carbon black and "Silica" for the silica based compound. These were mixed using the Brabender 350S tangential mixer according to the procedures in Table 3.7 for the carbon black based compound and Table 3.8 for the silica based. The compounds were vulcanized into sheets of 200*200*4 mm for $t_{c,90}+2$ min at 170 °C.

Both vulcanizates were ground at room temperature, sieved with the laboratory set of sieves to obtain a fraction of 2 mm to 3.5 mm and subsequently devulcanized. Devulcanization of these small batches was performed in the Brabender Plasti-corder mixer with a chamber volume of 50 ml. The mixer was preheated to a temperature of 220 °C, filled with a premix of the material to be devulcanized, using a fill factor of 0.6, and operated at 50 rpm for 5 min. The formulation used was DBD: 3.9 wt%, TDAE: 2 wt%, TDTBP 1 wt%. The devulcanizate was discharged into liquid nitrogen to quench and to prevent contact with oxygen. Afterward, it was post-treated on a mill in a similar way as the DGTR described before. The devulcanized compounds were revulcanized again using the same formulations as were used before for the initial vulcanization with respect to zinc oxide, stearic acid, sulfur, TBBS, DPG and TESPT. These ingredients were assumed to have been fully consumed during the initial vulcanization which turned out to be a usable approximation. For preparing the revulcanizates the procedures as described

in Tables 3.14 and 3.15 were used. The compounds were revulcanized for
$t_{c,90}$+2 min at 170 °C in the Wickert press into 2mm thick sheets like before.

Dumbbells were cut from all samples and tested for their stress strain proper-
ties according to ISO 37. Pictures were taken by microscopy of the fracture-
surfaces of the dumbbells after the tensile tests.

Tensile properties for both compounds, prior to devulcanization, were a tensile
strength of 20 MPa for the silica based compound at 380 % strain and 15 MPa
for the carbon black based at 400 % strain. After de- and revulcanization, the
revulcanizates showed a tensile strength of 13 MPa and a strain of 280 % for
the silica based and 14 MPa and 330 % for the carbon black based compound,
as shown in Figure 7.11.
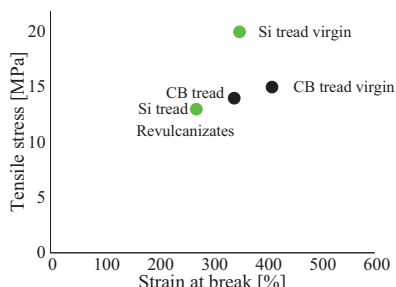


FIGURE 7.11: Tensile strength and strain at break of model
compounds with 80 phr CB and 90 phr silica, respectively before
and after devulcanization and subsequent revulcanization.
(Re)vulcanization of each compound with the same formulation,
see Table 3.4.

Hence, after revulcanization of the carbon black based compound about 95 %
of the tensile strength was recovered, but for the revulcanized silica compound
this was only about 70 %. Although this is significantly less compared to
the carbon black based compound, it is much better than would have been
expected from the decrease in crosslink density of similar compounds as shown
by the Horikx-Verbruggen diagrams in Figure 7.7 in area 1. By comparing the
fracture surfaces of the revulcanizates of both compounds, it appeared that
the carbon black based compound had a relatively smooth surface, as shown
in Figure 7.12a, indicating a homogeneous devulcanization. In contrast to
this, the fracture surface of the silica based material showed a rough surface,
as shown in Figure 7.12b.

(a) 80 phr carbon black.  (b) 90 phr silica.
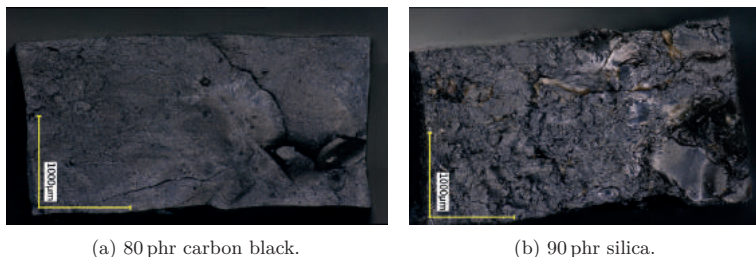
FIGURE 7.12: Microscopic pictures of fracture surfaces of
dumbbells of tensile tests of revulcanized, carbon black based
and silica based modelcompounds.

The latter implies a non-homogeneous devulcanization with remaining parts of
non-devulcanized rubber. This must be due to the fact that the silica-silane-
polymer bonds mainly consists of mono-sulfidic crosslinks which cannot
be broken by the devulcanization process, as shown in Figure 7.9. As
a consequence, the crosslinks that can be broken by the devulcanization
process are only di- and polysulfidic of nature, mostly found in the network
between the polymer chains.

## 7.4   Conclusions

GTR contains an increasing amount of silica over recent years, due to the
progressive use of this filler in modern tread compounds to improve tire
performance. It was shown that devulcanization of such silica containing
GTR is increasingly more difficult than of a carbon black based GTR. The
presence of silica in GTR has a double effect:

- It makes the rubber more difficult to devulcanize than GTR without
  silica, which leads to a coarser structure after revulcanization,

- It lowers the values of tensile strength.

With model tread compound studies with 80 phr carbon black or 90 phr
silica as filler, it was shown that it is possible to keep the decrease in tensile
properties of a revulcanizate of a devulcanized silica based compound to a
minimum by using additional DPG secondary accelerator and adding some
TESPT in the revulcanization formulation and implementing a silanization
step to the compounding procedure. The tensile strength could be largely
restored and limited to a decrease of 35 %, from 20 MPa to 13 MPa, while
for a carbon black based compound this was around 6 %, from 15 MPa to
14 MPa. However, when whole tire material was used, after adjusting the
revulcanization formulation and process for devulcanized GTR for the silica
content, an improvement in tensile strength from 5 MPa to only 8 MPa could
be obtained, with only a small decrease in strain at break relative to a virgin
compound, as is shown in Table 7.5.

**Table 7.5:** Summary of tensile properties of (re)vulcanizates,
[*] Ingredients for revulcanization only.

| Compound | Revulcanization formulation, Tables 7.3 and 3.4 | Tensile strength [MPa] | Strain @ break [%] |
|---|---|---|---|
| DGTR | 1 | 3.5 | 250 |
| ” | 2 | 5.0 | 180 - 230 |
| ” | 3 | 6.5 | 180 - 220 |
| ” | 4 | 8.0 | 140 - 170 |
| CB compound | 'CB' | 15 | 400 |
| Devulcanized CB compound | 'CB'[*] | 14 | 330 |
| Silica compound | 'Silica' | 20 | 360 |
| Devulcanized silica compound | 'Silica'[*] | 13 | 250 |

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# Chapter 8

# Additional influences on the quality of the devulcanizate and the tensile strength of the revulcanizate

*The devulcanized rubber from the extruder line needs further post-treatment, as the morphology is rather coarse. Milling considerably improves the handling of the material, while also decreasing the coarseness of the devulcanizate and revulcanizate. Applying this post-treatment, the tensile strength and the structure of the fracture surface of a carbon black-filled model rubber after devulcanization and subsequent revulcanization are comparable to the strength and morphology of the original rubber. For a silica-silane-based tread model compound, the tensile strength drops by 20 %, which is still less than the loss in mechanical properties experienced for use of ground tire rubber (GTR).*

*The influence of starting with a blend of different compounds, as present in the GTR, is studied using a model blend of granulates from a carbon black-filled compound with 28 wt% of a silica-based model rubber and 5 wt% of butyl rubber. After devulcanization and subsequent revulcanization, this blend results in a material with a tensile strength of 13 MPa, comparable to the strength of the individual model compounds with silica or carbon black. The fracture surface is similar to that of the silica-based model compound after revulcanization.*

*The homogeneity of the commercial grade of ground passenger car tire rubber granulate as used in this study is also investigated. The influence on the reproducibility of the twin screw extruder-based thermo-mechanical chemical devulcanization process and on the tensile properties of the revulcanizates is studied. It is shown that the silica content of the granulate is the most critical factor for the reproducibility of the results after revulcanization.*

## 8.1   Introduction

As shown in Chapter 6, the tensile strength of revulcanized GTR is less than that of the constituent virgin rubbers. The significant influence this has on the devulcanization and subsequent revulcanization processes was described in Chapter 7. In the present chapter, several other aspects are investigated

that could influence the quality of the devulcanizates and strength of the revulcanizates:

- The influence of the size and number of the remaining grains in the material after the extruder-based devulcanization process with a low shear screw configuration, and improvements by post-processing: Applying shear to the devulcanizate at a low temperature of 60 °C on a mill in order to improve the homogeneity and to inhibit any undesired chemical reactions of highly reactive polymer network fragments, which occur at higher devulcanization temperatures. This is described in Section 8.2.

- The influence of the particle size of the GTR on the structure and the tensile strength of the revulcanizate. In Chapter 4, it was indicated that a gradient of devulcanization can be expected due to the particle size and size distribution of GTR. The influence of particle size of the GTR on tensile strength and the morphology of the revulcanizate is investigated and described in Section 8.3.

- The influence of carbon black or silica on the degree of devulcanization and on the tensile properties and structure of revulcanizates is investigated and described in Section 8.4.

- The influence of blending of carbon black-filled and silica-filled tread rubber with butyl rubber (IIR) to mimic the composition of GTR, on tensile strength and morphology after revulcanization is described in Section 8.5.

- Variations in the composition of GTR from different sources and selections of passenger car tires is described in Section 8.6.

- The reproducibility of the twin screw extruder-based devulcanization process and its influence on the properties of the revulcanizate are described in Section 8.7.

For clarity, each section contains a short introduction, an experimental part, a results and discussion part, and conclusions. The conclusions are summarized at the end of this chapter.

## 8.2 The influence of the post-processing of GTR devulcanizate on the size of visible grains in the revulcanizate

### 8.2.1 Introduction

The number and size of visible grains in the devulcanizates influences the smoothness of the revulcanizates. This, in turn, influences the quality of the revulcanizates, especially for applications with a visible surface. This section investigates the influences of several processing steps after devulcanization in the extruder. The parameters used are the number and size of visible grains as indicated by white rubber analysis (WRA).

### 8.2.2 Experimental

GTR was devulcanized in the extruder with a pre-determined configuration, temperature setting, and devulcanization formulation as described in Chapter 6 and summarized in Table 8.1. All samples were taken from one production run.

**Table 8.1: Formulation and extruder parameters, optimized for devulcanization with DBD, as provided in Figure 6.5.**

| Devulcanization formulation [% of GTR] | | | Temperature profile [°C] | | | Speed [rpm] | Screw configuration [type] |
|---|---|---|---|---|---|---|---|
| TDAE | DBD | TDTBP | I | II | III | | |
| 2 | 3.9 | 1 | 130 | 180 | 170 | 20 | D |

I=mixing section, II=devulcanization section, III=pressure section

To study the influence of the processing before revulcanization on the remaining grains in the devulcanized and subsequently revulcanized GTR, several processing steps were performed after devulcanization in the extruder, as described below and summarized in Tables 8.2 and 8.3:

Post-devulcanization milling calendering for cooling:

| | |
|---|---|
| *Sample A:* | No additional processing. |
| *Samples B, E, F:* | Post-devulcanization milled on the Schwabenthan mill for 5 min at 60 °C and with a minimum gap size between the rolls of 0.1 mm. Because of this post-devulcanization milling, the granulate acquired consistency: from a slightly sticky powder to a coherent, non-sticky slab. |

Compounding with or without milling afterwards, comparable with preparation for revulcanization:

| | |
|---|---|
| *Samples A, B:* | No additional processing. |
| *Samples C, E:* | Prepared for revulcanization using formulation GTR-1 in Table 3.3 and procedure according to Table 3.14. |
| *Samples D, F:* | Prepared for revulcanization using formulation GTR-3 in Table 3.3 and procedure according to Table 3.15. |

The compounds for revulcanization were prepared using the Brabender Plasticorder 350S internal mixer. Vulcanization was done in the Wickert laboratory press. Samples of 2 mm thickness were produced at 160 °C and for $t_{c,90}+2$ min.

White Rubber Analysis (WRA) was performed on all samples according to the description in Chapter 4. This included revulcanization of the samples.

**Table 8.2: Sample preparation formulations as described in Table 3.3.**

| Sample | Revulcanization, formulation GTR-1 | Revulcanization, formulation GTR-2 |
|--------|------------------------------------|-------------------------------------|
| A | - | - |
| B | - | - |
| C | X | - |
| D | - | X |
| E | X | |
| F | - | X |

**Table 8.3: Differences in sample preparation after devulcanization for analysis of the influence of the size of the visible grains by WRA**

| Sample | Devulcanization in extruder | Calendering (cooling) | Milling(1) (60 °C) | Mixing (80 °C) | Mixing Silanization (145 °C) | Milling(2) (60 °C) | WRA Figure |
|--------|------------------------------|------------------------|---------------------|-----------------|-------------------------------|---------------------|------------|
| A | X | X | - | - | - | - | 8.1a |
| B | X | X | X | - | - | - | 8.1b |
| C | X | X | - | X | - | X | 8.1c |
| D | X | X | - | - | X | X | 8.1d |
| E | X | X | X | X | - | X | 8.1e |
| F | X | X | X | - | X | X | 8.1f |

(1) Post-devulcanization milling,
(2) Milling after compounding

### 8.2.3   Results and discussion

The devulcanization process under study is a thermochemical-mechanical treatment in an extruder. The shear created by the screw configured for a relatively low shear is not sufficient to reduce the number and size of visible grains in the devulcanizate. However, screws configured for higher shear reduce the quality of the devulcanizate due to extensive polymer damage, as indicated by the reduced tensile strength of the revulcanizate (see Chapter 6).

This negative effect could be suppressed by decreasing the temperature for mechanical shearing from 220 °C to about 60 °C when post-devulcanization milling of the devulcanizate of GTR (d-GTR) with a gap width of 0.1 mm. During the devulcanization process, highly active radicals are created. These radicals cause undesired side effects in the polymer matrix, such as recombination and the subsequent uncontrolled formation of a new network, despite the presence of devulcanization aids to neutralize these free radicals. At lower temperatures, the mechanical shear forces necessary to break the physical structure and crosslinks increase, but the reactivity of the free radicals decreases substantially. This is anticipated to lead to a lower remaining crosslink density due to less recrosslinking and a decrease in physical structure. This should be visible as a more homogeneous morphology of the devulcanizate. However, this is very hard to observe as the devulcanizate direct from the extruder has a slightly sticky granular structure. With the application of WRA,the homogeneous part of the devulcanizate is diluted with the white

compound into a grey blend and the grains become visible in the vulcanized samples. A combination of processing steps was performed to compare the influence of the mixing and milling steps performed on the devulcanizate on the size of the remaining visible grains, as summarized in Table 8.3. The results are shown in Figure 8.1. The visual comparison shows that the size of the visible grains are influenced by the different treatments. The material of sample A clearly contains visible grains that are made smaller by post-devulcanization milling, as is shown for sample B. Performing a mixing step as part of the preparation for revulcanization, mixing at either 80 °C or 145 °C, followed by milling after compounding, results in a visible grain size roughly similar to that of sample B: see samples C and D. When performing these mixing and milling as part of the compounding step after post-devulcanization milling, the size of the grain reduces noticeably, as is seen in samples E and F. The visible grains of both samples E and F are smaller than those of samples C and D: a post-devulcanization milling step before mixing and milling as part of the compounding therefore does decrease the grain size.

It was observed that the devulcanizate crumbled during the mixing compounding step in the Brabender internal mixer; therefore, hardly any shear forces during processing in the mixer occurred. Through subsequent milling after compounding on the Schwabenthan laboratory mill with a small gap between the rolls, coherence of the devulcanizate as obtained by post-devulcanization milling, was regained: the decrease in size of the visible grains can therefore be attributed to the combination of two milling steps, one before and the other after the Brabender mixing step, as part of the preparation for revulcanization. By visual observation, the impression is that the size of the visible grains and the number of larger particles in the samples decreases in the order A > B > C, D > E, F (see Figure 8.1).

As shown in Chapter 4, a decrease in concentration of the devulcanization aid towards the center of the GTR particles is expected due to migration limitations. Thus, a corresponding decrease in devulcanization, and an increase of crosslink density in the devulcanized particles towards the center results. This in turn implies an increase in hardness towards the center and thus decreasing erosion[1] of the devulcanized layers when high shear forces are applied in post-devulcanization milling, as illustrated in Figure 8.2a. However, as the devulcanizate gains coherency during post-devulcanization milling, there is a balance between an increasing amount of homogeneously devulcanized polymer and an increasing number of visible grains with decreasing size, as depicted in Figure 8.2b.

Ahagon and Kirino[2] have shown that large deformations in SBR rubber on a mill decrease the crosslink density at first, while increasing it again later on. However, this is not observed during post-devulcanization milling of the devulcanized GTR nor for a sample of GTR. This indicates that the deformations of the particles during the post-devulcanization milling process are not enough to decrease the crosslink density of still existing, not devulcanized, GTR. This indicates a shearing off of already decrosslinked material due to the prior devulcanization process.

As post-devulcanization milling is rather labor-intensive, tests were carried out to investigate whether the same effect can be reached by replacing this

(a) Sample A:
d-GTR after devulcanization in
extruder,
without post-processing

(b) Sample B:
d-GTR after devulcanization in extruder
after post-processing: milled(1) at 60 °C
and high shear forces; 0.1 mm gap
between rolls

(c) Sample C:
d-GTR after devulcanization in extruder
without milling(1), followed by
compounding at 80 °C (mixing -
milling(2))

(d) Sample D:
d-GTR after devulcanization in extruder
without milling(1), followed by
silanization at 145 °C and compounding
(mixing - milling(2))

(e) Sample E:
d-GTR after devulcanization in extruder
after post-processing: milled(1) at 60 °C,
followed by compounding at 80 °C
(mixing - milling(2))

(f) Sample F:
d-GTR after devulcanization in extruder
after post-processing: milled(1) at 60 °C,
followed by silanization at 145 °C and
compounding (mixing - milling(2))

(1) Post-devulcanization milling,
(2) Milling after compounding

FIGURE 8.1: Influence of post-processing on size of visible
particles in d-GTR

with a single pass in a laboratory-scale single screw extruder. This showed
promising results.

(a) Erosion model of Manas-Zloczower[1], adapted for a devulcanized particle, with in the center a low- to non-devulcanized remaining grain

(b) Model of low- to non-devulcanized grains, embedded in a matrix of homogenized devulcanizate
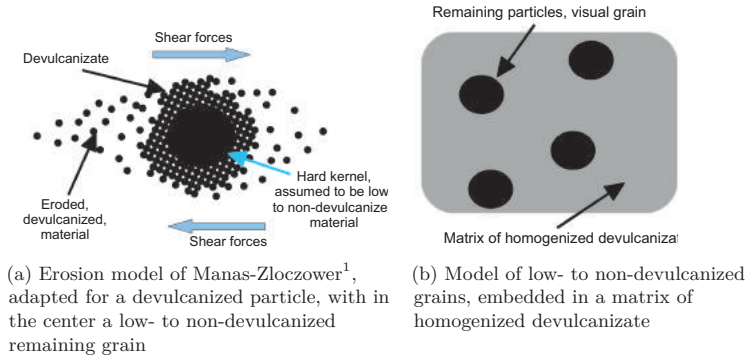
FIGURE 8.2: Erosion model and model of remaining visible grains in devulcanizate

To make the change in visible particle size and number more quantifiable, statistical analysis was performed on the WRA samples: for each sample, the distribution of the particle sizes was analyzed, the mean, median, and standard deviation were calculated, the maximum particle size for the samples was indicated and the number of visible particles counted, see Figure 8.3.



(a) Sample A,
d-GTR, no post-processing

(b) Sample B,
Milled only

(c) Sample C,
Mixed at 80 °C

(d) Sample D,
Mixed at 145 °C

(e) Sample E,
Mixed at 80 °C and milled

(f) Sample F,
Mixed at 145 °C and milled
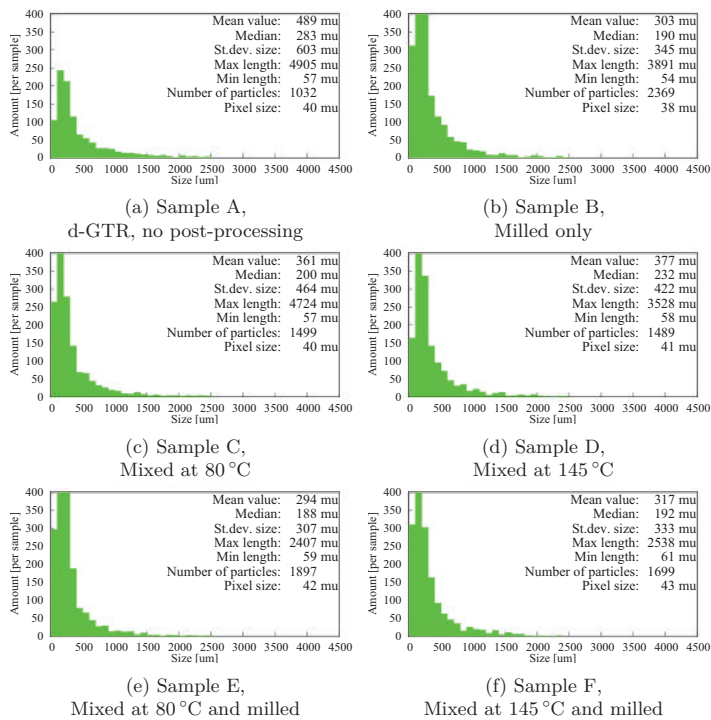
FIGURE 8.3: Influence of post-processing on the size of the visible particles in d-GTR

All samples, except sample A, show over 400 particles at minimum size.

As the minimum detection size is limited to the pixel size of the figures, calculated as 40 µm to 43 µm, smaller particles are not visible.

These parameters are shown relative to the highest value in Figure 8.4. The reference is sample A for all parameters, except for number of visible particles, where sample B has the highest value. For the median there is no clear pattern between the samples B to F that can easily be related to the observed order.
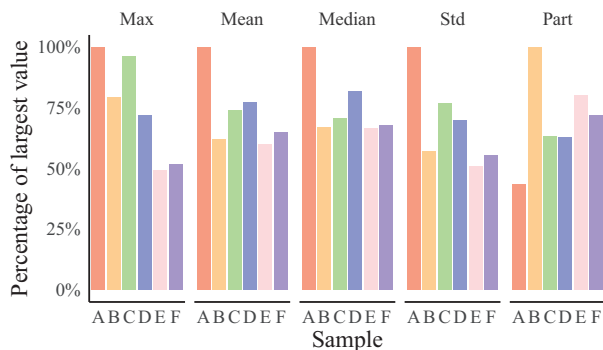


Legend:

| | |
|---|---|
| Max: | Maximum particle size in sample |
| Mean: | Mean value |
| Median: | Median value |
| Std: | Standard deviation |
| Part: | Number of particles in sample |

All values as percentage of the largest value

FIGURE 8.4: Influence of post-devulcanization milling on the distribution of the size of visible grains in d-GTR. Summary of Figure 8.3 as relative values

Both the mean value and the standard deviation, a measure of the broadness of the distribution of the particle sizes, show as order A > C, D > B, E, F, although it is more explicit for the standard deviation. For the maximum particle size, the order is A > C > B, D > E, F. For the parameters mean value, standard deviation, and maximum particle size, the positive influence of the post-devulcanization milling combined with the preparation for revulcanization on the decrease in particle size is shown. With respect to the number of particles, the decending order is B > E, F > C, D > A. The number of particles in sample B can only be explained by the higher temperatures of the processing of samples C to F, causing the size of the smallest particles to decrease below the detection value of the pixel size. Overall, both the maximum particle size and the standard deviation are useful parameters for quantification of the effect of milling and compounding on the particle size, although a difference in interpretation between visual observation and both parameters exists for sample B.

### 8.2.4   Conclusions

After devulcanization of GTR, in either a continuous extruder-based or batch mixer-based process, the remaining grains of the devulcanizates are rather coarse. Post-devulcanization milling of the devulcanizates at a lower

temperature of 60 °C with a gap of about 0.1 mm between the rolls decreases the size of the visible particles and improves the structure.

Although the size of the grains also decreases as a result of the preparation of the devulcanizate for revulcanization, which can be attributed to the milling after compounding step after mixing, the largest decrease in size of the visible particles in the revulcanizate (to about 50 % of the size after devulcanization) is attained by the combination of both milling steps: post-devulcanization milling and milling after compounding as part of the preparation for revulcanization.

Both the maximum particle size and the standard deviation of the particle size distribution, as derived by WRA, give a reasonable quantification of the change in particle size and number of particles as observed visually.

## 8.3 The influence of particle size of the GTR on the structure and strength of the revulcanizate

### 8.3.1 Introduction

As the particle size of the GTR is related to the extent of devulcanization of these particles, as explained in Chapter 4, the influence thereof on the structure and the strength of the revulcanizates is further investigated in this chapter.

### 8.3.2 Experimental

One sample of the originally obtained GTR was kept as reference, while the rest of the granulate was ground further under ambient conditions using the Fritz pulverette and screened using a set of laboratory sieves with sizes of 0.85 mm, 2 mm and 3.5 mm. Four batches, labeled GTR, Medium, Fine, and Xfine, were therefore created from the same base material, but with different particle sizes and limited size distributions:

*GTR:* Original size and distribution as presented in Chapter 3, Figure 3.1
*Medium:* 2 mm < size <3.5 mm
*Fine:* 0.85 mm < size <2 mm
*Xfine:* size < 0.85 mm

The Brabender Plasticorder mixer with a 50 ml chamber was used for devulcanization, with process parameters as described in Tables 3.17 and 3.18. The optimal formulation as given in Table 8.1 was used. The Schwabenthan mill was used to mill the devulcanizates. Unless stated otherwise, this post-devulcanization milling procedure was 5 min at 60 °C with a final gap size of 0.1 mm between the rolls.

The formulation GTR-3 in Table 3.3 and the procedure according to Table 3.15 were used for revulcanization, which includes milling after compounding. The compounds for revulcanization were prepared using the Brabender Plasticorder mixer. Vulcanization was done in the Wickert laboratory press. Samples of 2 mm thickness were produced at 160 °C and for $t_{c,90}$+2 min.

Tensile properties were analyzed using a Zwick-Roell tester, and microscopy of the fracture surfaces of the tensile test dumbbells was conducted using a Keyence VHX5000.

### 8.3.3   Results and discussion

The influence of the diffusion time of the devulcanization aid into the particles decreases with the decreasing particle size in the Medium, Fine, and Xfine samples, compared with those of the GTR. A time to the equilibrium of 11 min was calculated for particles with a diameter of 3 mm (see Table 4.1). This implies a large concentration gradient of the devulcanization aid in the larger particles and thus, as the devulcanization time was only 6 min for the Brabender mixer, an inhomogeneous devulcanization. For a particle size of 2 mm, the devulcanization time was 5 min, sufficient for a more homogeneous devulcanization. For sample Xfine, with a particle size <0.85 mm, a completely homogeneous devulcanization is expected. As an overall effect, it is expected that the homogeneiety of the devulcanization will increase the finer the samples are: from the coarser samples to finer ones. However, as shown in Figure 8.5, the tensile strength after revulcanization of all samples is 5 MPa, and the strain at break is similar for all samples.
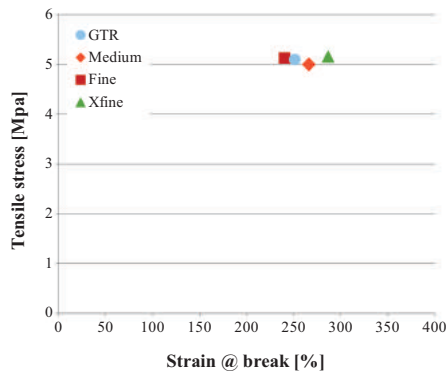


FIGURE 8.5: Influence of particle size of GTR granulate on tensile properties

The fracture surface of the tensile test samples of the GTR granulate after devulcanization and subsequent revulcanization was rather coarse (Figure 8.6a). The surfaces of the medium and fine samples (Figures 8.6b and 8.6c) look mutually rather similar and show a smooth area for about 30 % of the surface. The surface of the Xfine sample (Figure 8.6d) shows a relatively smooth area for about 50 % of the surface. This shows that the expected improved homogeneity with finer particle size feedstock can be seen, but to a lower degree than anticipated. Further, neither the improved morphology nor the expected degree of devulcanization correlate with an improvement in the tensile properties. This indicates that factors other than feedstock granulometry are influencing the structure of the material after devulcanization and the consequent tensile strengths of the revulcanizates.

(a) GTR  (b) Medium, $2\,\mathrm{mm}<...<3.5\,\mathrm{mm}$

(c) Fine, $0.85\,\mathrm{mm}<...<2\,\mathrm{mm}$  (d) Xfine, $<0.85\,\mathrm{mm}$
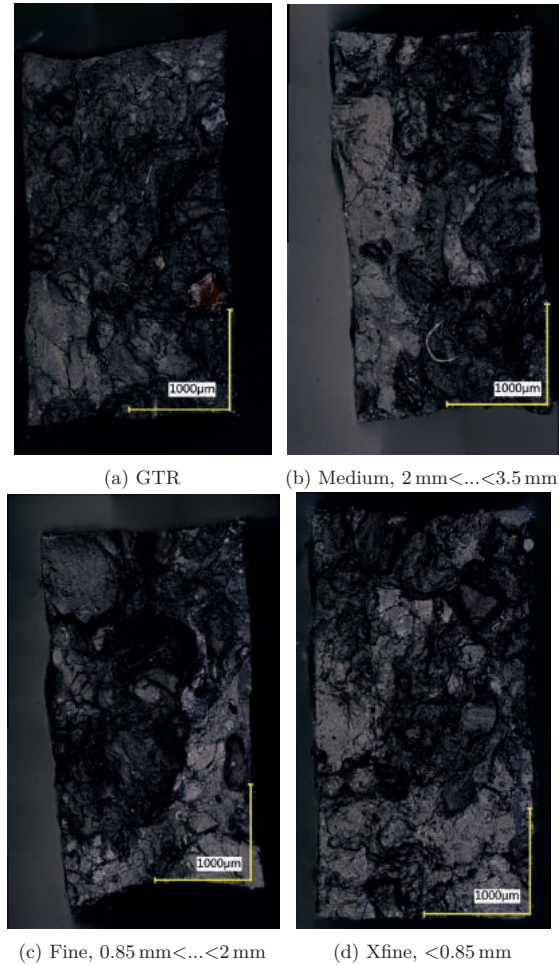
FIGURE 8.6: Influence of the size of the granulate before devulcanization on the fracture surfaces of revulcanizates.

### 8.3.4 Conclusions

Decreasing the size and size distribution of the GTR by milling before devulcanization, to reduce the influence of devulcanization time and concentration gradient of the devulcanization aids on the homogeneity of the devulcanization as described in Chapter 4, did not improve the tensile properties of revulcanizates and only slightly improved the structure of the fracture surfaces. This indicates that factors other than the homogeneity of devulcanization influence the tensile properties after revulcanization and the homogeneity of the fracture surfaces of the tensile test samples.

## 8.4   Influence of feedstock granulometry of carbon black-based and silica-based tread model compounds on the homogeneity of fracture surfaces and the tensile strength of revulcanizates

### 8.4.1   Introduction

As shown in Section 8.3, the influence of the particle size of vulcanizates before devulcanization on the tensile strength of the revulcanizates is, within the investigated range, negligible. The influence on the structure of the fracture surfaces is also limited. To investigate the influence of the type of compound, a carbon black-based and a silica-based tread model compound were produced, devulcanized and subsequently revulcanized.

### 8.4.2   Experimental

For the model compounds, the formulations "CB" for the carbon black-based and "Silica" for the silica-based, as given in Table 3.4 were used and prepared as described in Table 3.7 for the carbon black-based and Table 3.8 for the silica-based. The samples were devulcanized using the devulcanization formulation as described in Table 8.1 and the procedure according to Table 3.18. Vulcanization, grinding of the vulcanizates, devulcanization and subsequent revulcanization were carried out as described in Section 8.3.2. The vulcanized tread model compounds were ground and two fractions were created from each compound:

*Medium:* 2 mm < size <3.5 mm
*Fine:*     0.85 mm < size <2 mm.

For revulcanization, the formulations from Table 3.4 were used and the procedures from Tables 3.14 and 3.15.

### 8.4.3   Results and discussion

As discussed in Chapter 7, a considerable decrease in tensile properties and increase in the number of inhomogeneities in the fracture surface are seen in a silica-silane-based tread model compound compared with a carbon black-based one, as shown in Figures 7.11 and 7.12. This section considers the influence of the filler type and the feedstock granulometry, as discussed in Section 8.3.

As can be seen in Figures 8.7b and 8.7c, both revulcanizates of the silica-based compound of different gtanular size show a surface full of inhomogeneities compared with the surface of the original vulcanized compound (Figure 8.7a). For the carbon black-based compounds, the fracture surfaces of the revulcanized samples look similar to the original vulcanized sample (see Figures 8.7d, 8.7e and 8.7f). Little difference can be seen between the tensile fracture surfaces of the medium and the fine devulcanized and subsequently revulcanized samples, neither for the silica-based nor for the carbon black-based compounds. As discussed before in Chapter 7, a clear difference between the fracture surfaces of the devulcanized and subsequently revulcanized samples of the carbon black-based and the silica-based compounds can be seen again.

(a) GT     (b) rd-GT, Medium     (c) rd-GT, Fine

(d) CB     (e) rd-CB, Medium     (f) rd-CB, Fine
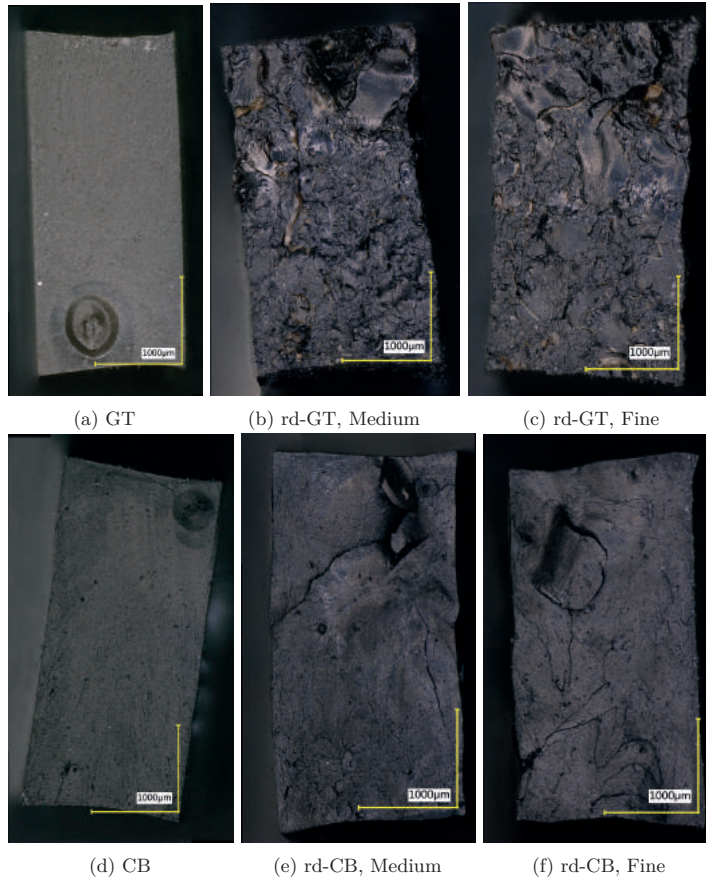
Legend:
GT: Silica-based tread model compound
CB: Carbon black-based tread model compound

Treatment:
CB, GT: vulcanized only
rd-CB, rd-GT: devulcanized and subsequently revulcanized

Size:
Medium: $2\,\text{mm}<...<3.5\,\text{mm}$
Fine: $0.85\,\text{mm}<...<2\,\text{mm}$

FIGURE 8.7: Influence of filler type and size of granulate before devulcanization on the fracture surfaces of revulcanizates.

The differences between the tensile fracture surfaces are reflected in the tensile stress and strain of the compounds (see Figure 8.8). Mutually, no significant differences in tensile strength or strain are observed between the revulcanizates of the fine and medium samples of the silica-based compounds ($13\,\text{MPa}$ and $260\,\% \pm 10\,\%$ strain) nor for the carbon black-based compounds

(14 MPa and 350 % strain). This indicates that the differences in the size of the granulates before devulcanization are not reflected in the structure of the revulcanizates or the strength properties, despite the relatively short devulcanization time of 6 min in the internal mixer.



Error bars: plus/minus $2\sigma$
Medium: 2 mm<...<3.5 mm
Fine: 0.85 mm<...<2 mm
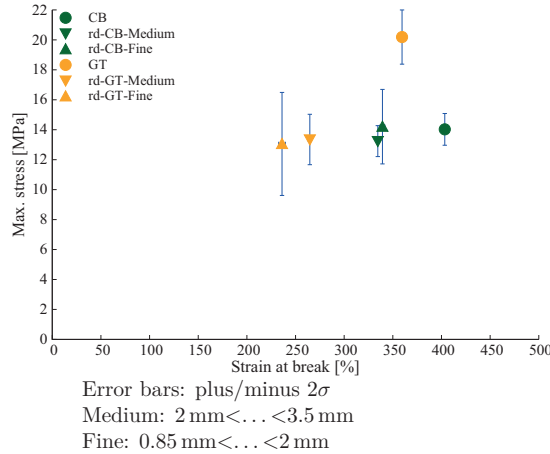
FIGURE 8.8: Tensile properties of carbon black and silica-based model compounds after vulcanization and devulcanization and subsequent revulcanization

These results show again that the particle size of the granulate has only a minor influence on the homogeneity of the devulcanizates and revulcanizates. As shown in Section 8.3 and this present section, the coarse morphology in revulcanizates of the silica-containing compounds correlates with a decrease in tensile properties. Unexpectedly, differences in the granulometry of the feedstock have almost no effect on the tensile properties of the revulcanizates within the measurement variations. The influence of the silica on the morphology of the devulcanizates was discussed already in Chapter 7.

### 8.4.4   Conclusions

The tensile strength of a devulcanized and subsequently revulcanized carbon black-based SBR-BR tread model compound was roughly similar to the strength of the compound before devulcanization and subsequent revulcanization, independent of the granular size of this compound before devulcanization, while 85 % of the strain at break was retained. Only a slight decrease in smoothness of the fracture surfaces was observed, and no significant influence of the grains in the compound before devulcanization and subsequent revulcanizationwas seen.

The tensile strength of a revulcanized silica-based SBR-BR tread model compound was about 65 % of that of the compound before devulcanization and subsequent revulcanization, independent of the grains' size in the compound before devulcanization. However, a significant decrease in smoothness and homogeneity of the fracture surface compared to the rubber before devulcanization and subsequent revulcanization was observed. No significant influence of the grain size of the compound before devulcanization on the

tensile properties of the devulcanized and subsequently revulcanized samples was observed.

## 8.5 The influence of blending carbon black-based and silica-based tread compounds with a butyl rubber compound on the tensile properties of the revulcanizate

### 8.5.1 Introduction

As the tensile strength of the devulcanized and subsequently revulcanized carbon black-based and silica-based model tread compounds are, as observed in this chapter, 13 MPa to 14 MPa, the question arises whether it is the blend of both compounds with IIR that reduces the tensile strength of the GTR to 8.2 MPa, as found in Chapter 6. Therefore, the influence of blending the model tread compounds with IIR on the tensile strengths of the devulcanized and subsequently revulcanized compounds are investigated in this section.

### 8.5.2 Experimental

Carbon black-based and a silica-based model tread compounds were prepared as described in Section 8.4.2, except that the procedure in Table 3.9 was used for the silica compound, and the silanization temperatures were adjusted to 145 °C for use with TESPT. The model tread compounds were vulcanized in the Wickert press at 160 °C for $t_{c,90}+2$ min into 100*100*2mm plaques. Post-consumer butyl rubber (IIR) was obtained from Rubber Resources (see Table 3.1). The model tread plaques and the IIR cuttings were then ground using the Fritz pulverette to a size between 0.85 mm and 2 mm. These granulates were mixed according to their estimated weight ratio in a tire. Based on the silica content of GTR, these mixtures contained 28 wt% silica-based compound, 0 wt%, 5 wt% and 10 wt% IIR compound, and the remainder was the carbon black-based compound. The amount of IIR in end-of-life passenger car tires was estimated to be around 5 wt%.

These blends of granulates were devulcanized using the devulcanization formulation as described in Table 8.1 and the procedure according to Table 3.18. For revulcanization, the devulcanizates were treated in a similar way as those of passenger car tire granulate: the overall formulation was estimated based on the contribution of each component in wt% and the revulcanization formulation was adapted accordingly: the formulations "CB" for the carbon black-based rubber, "Silica" for the silica-based tread compounds, and "IIR" for an innerliner compound as given in Table 3.4 were used for the revulcanization. See Table 3.15 for the revulcanization procedure. Prefixes used are "d-" for devulcanized, "ad-" for devulcanized and subsequent addition of the curing formulation and "rd-" for devulcanized and subsequently revulcanized.

To assess processability, the viscosities of the devulcanized samples and the samples mixed with the revulcanization formulation were measured in a temperature sweep between 40 °C to 160 °C using the RPA2000 (Alpha Technolgies). Due to lack of material, the cure curve for the sample of carbon

black-based model tread compound was not measured; instead, a previously derived value for vulcanization was used.

### 8.5.3   Results and discussion

Comparing the cure curves of the for revulcanization prepared devulcanizates of the silica-based and carbon black-based model compounds and the blends with 0 wt%, 5 wt% and 10 wt% butyl rubber added, it was observed that this did not have any influence on the torque (Figure 8.9). The blend of silica-based and carbon black-based compound, however, shows a much lower torque compared with the cure curves of the revulcanizates of the pure compounds (Figure 8.9).
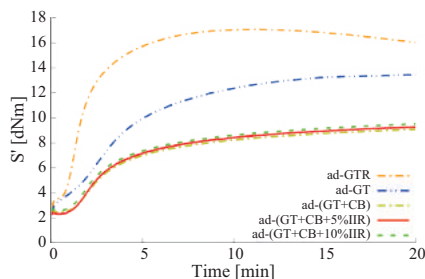


All compounds are devulcanized and prepared for revulcanization (ad-). ad-GTR car tire granulate added as reference.

FIGURE 8.9:  Cure curves of devulcanizates of blends of carbon black-based and silica-silane-based tread compounds and butyl rubber.

The composition of the blend had little influence on the tensile properties after revulcanization (Figure 8.10): 14 MPa for the pure silica-based compound, 13 MPa for the pure carbon black-based compound, and 12 MPa for the mix of both compounds and for the blend with 5 wt% butyl rubber. Only for the blend with 10 wt% butyl rubber was there a small decrease in tensile strength to 11 MPa observed. For the devulcanized and subsequently revulcanized GTR however, the tensile strength was 8 MPa at about half of the strain at break of the other compounds.

The structures of the tensile fracture surfaces of the mixes (Figures 8.12a, 8.12b, 8.12c) are comparable with the silica-based compound in Figure 8.7b, but show a slight decrease in smoothness when compared with the surface of the pure silica-based model compound in Figure 8.11. This indicates that it is the influence of the silica-based compounds in the GTR that is the main cause of the low homogeneity of the fracture surfaces of the devulcanized and subsequently revulcanized GTR.

The main conclusion is that silica-based and carbon black-based model compounds do not blend very well during devulcanization. Despite this, the tensile strengths are similar within the accuracy range Up to 5 wt% of butyl rubber does not influence the tensile strength of the blend revulcanizate. The relatively large difference of 5 MPa between the tensile strength of the devulcanized and subsequently revulcanized pure GTR (7 MPa), shown as

Error bars: plus/minus $2\sigma$
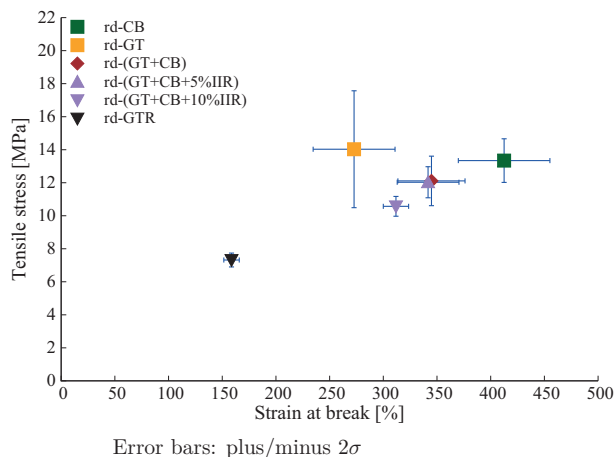
FIGURE 8.10: Tensile properties of pure and blends of carbon black-based and silica-based model compounds with and without butyl rubber additions after vulcanization and devulcanization and subsequent revulcanization (rd-). rd-GTR added as reference.



FIGURE 8.11: Fracture surface of devulcanized and subsequently revulcanized pure silica-based tread model compound

reference in Figure 8.10, and the blend of these model compounds (12 MPa) can be ascribed to the influence of all other variations in compound composition, contamination of the material and the influence of aging. An additional observation supports the latter conclusion: the viscosities (measured as complex viscosities in temperature sweep) of the devulcanizates of the model compounds are not significantly influenced by the mixing step for addition of the curatives, as shown in Figure 8.13. The decrease with temperature is similar for all compounds, and the increase at temperatures above 100 °C is the onset of vulcanization. Hoiwever, the difference between the viscosity of d-GTR and the viscosity of the devulcanizate after blending with the revulcanization additives (ad-GTR) is remarkable. As the mixing

(a) rd-(GT+CB+0 %IIR)          (b) rd-(GT+CB+5 %IIR)          (c) rd-(GT+CB+10 %IIR)
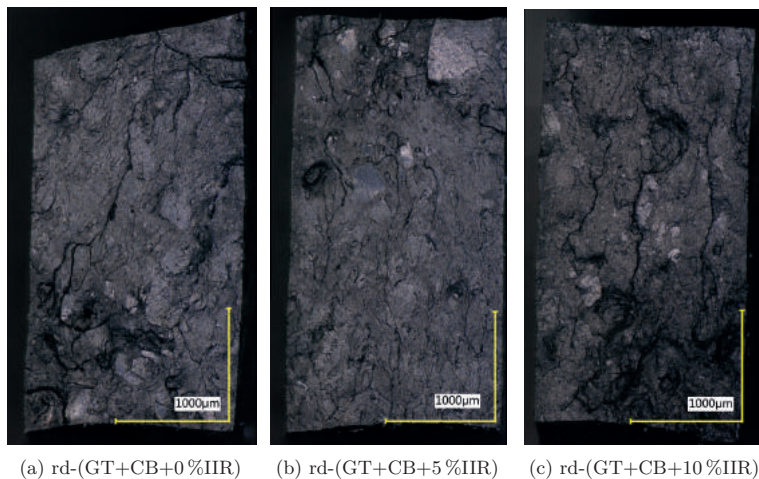
FIGURE 8.12:  Influence of devulcanization and subsequent
revulcanization of a mix of granulates of carbon black-based
and silica-based tread model compounds with butyl rubber
on the tensile fracture surface.

procedure for revulcanization includes a silanization process step at 145 °C
(see Table 3.15), it cannot be excluded that additional reactions occur due
to the complex composition of GTR that are not observed for the model
compounds.
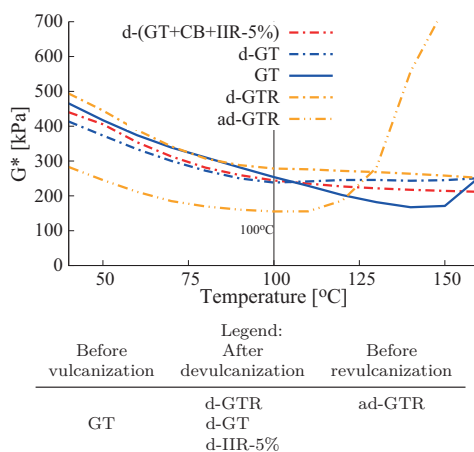


FIGURE 8.13:  Viscosity of uncured tread compounds

### 8.5.4   Conclusions

The tensile strength of a blend of 72 wt% ground carbon black-based and
28 wt% silica-based tread model compound was approximately 12 MPa after
devulcanization and subsequent revulcanization.  This is comparable to
the strength of the revulcanizates of the single pure rubbers.  The strain

of approximately 350 % is the average of the values for both revulcanized compounds. The roughness/inhomogeneity of the tensile fracture surfaces of the blends was similar to that of the silica compound after revulcanization, while the fracture surface of a carbon black-based compound is rather smooth, as shown in Figure 8.7e.

Adding up to 5 wt% of butyl granulate to the mixture of carbon black-based and silica-based granulates did not change the tensile properties of the revulcanizates, compared to the mixtures without butyl rubber.

## 8.6 Evaluation of the variation in composition of GTR feedstock

### 8.6.1 Introduction

Due to its origin, whole ground passenger car tire rubber is a mix of:

- different kinds of elastomers: Natural Rubber (NR), different types of Styrene Butadiene Rubber (SBR), Butadiene Rubber (BR), and Butyl Rubber (IIR) in varying amounts;

- compounds produced with wide variations in formulations;

- compounds prepared with different kinds of active fillers: carbon black or silica-silane, which can vary in specification and concentration;

- remaining contaminants, fibers and steel.

To study the homogeneity of GTR, extraction and thermogravimetric analyses (TGA) were performed. Extraction with a polar solvent (acetone) allows the separation of polar additives (curatives, antioxidants, and antiozonants), while the non-polar solvent (THF) dissolves a non-polar components such as oils and unbound polymer. TGA makes it possible to estimate the composition in terms of volatile components, polymer, carbon black, silica, and zinc compounds.

The homogeneity within the same stock and between different, additional stocks of GTR was studied using extraction. These additional stocks of GTR were comprised of selected passenger car tires, either discarded after the production process or were less than six years old, and from different suppliers. A sample was also taken from a reference batch, which was taken immediately from the stock after production, and therefore differs from the present GTR. The homogeneity within the same stock was also studied using TGA.

### 8.6.2 Experimental

The following variations of the feedstock were used for this study:

*Batches A to D:* GTR as detailed in Section 3.2.1;

| *Batch E:* | A sample of the base stock of GTR that was kept as reference; |
| *Batch F:* | Ground passenger car tires supplied by Rumal B.V., the Netherlands; |

| | |
|---|---|
| *Batch G:* | Granulate of tires younger than six years supplied by Granuband B.V., the Netherlands; |
| *Batch H:* | Granulate of off-spec tires, discarded from the production process, supplied by Granuband B.V., the Netherlands. |

All of these grades had a similar size distribution.

For Batches A to D, a sample of the regular GTR stock was taken. To minimize the influence of variations within the GTR, small samples were randomly taken from the stock and combined into batches of 20 l each. Of all batches A to H, three samples were extracted in acetone and THF, using a Soxhlet extraction device according to the method described in Chapter 4.3. TGA was then performed on all samples.

As an indication of the homogeneity of the GTR within one batch, extra attention was paid to the homogenization of the samples for TGA: 500 ml of the GTR was taken from the 20 l and ground in the Fritz pulverette until it passed the $0.7 \, mm^2$ laboratory sieve. From this powder, five samples (1 to 5) of about 10 mg each was taken randomly.

The temperature was held at 300 °C for the TGA procedure until no further weight loss occurred. The weight loss that takes place up to 300 °C is commonly described as "volatiles". The weight loss from 300 °C to 500 °C is indicative of the amount of polymers, and the weight at 500 °C under nitrogen atmosphere is indicative of the amount of carbon black, zinc oxide or zinc sulfide, and silica in the samples. The remaining weight at 800 °C after a change to air instead of nitrogen and after allowing the weight to stabilize, is the amount of zinc oxide or zinc sulfide and silica.

### 8.6.3   Results and discussion

**Analysis of GTR variation in composition by extraction analysis**

*a. Analysis of variation within the same stock*   Figure 8.14a shows the extraction data for GTR for batches A to E. The weight after acetone extraction varies from 88 wt% to 90 wt%, and after additional THF extraction the total weight is close to 88 wt% for all samples, as shown in Figure 8.14b. This shows that the ratio of polar and non-polar extractable additives varies, even between the relatively large samples of 500 mg used for Soxhlet extraction, and that the composition of GTR varies even between the samples from one feedstock. The differences between the three extractions per sample are indicated by error bars.

*b. Analysis of variation between stocks*   For comparison, extraction data were obtained for GTR composed of a selected mix of tires as specified for batches E to G (see Figure 8.15). After acetone extraction, the remaining weight was 88 wt% to 90 wt%, and after THF extraction 83.5 wt% to 88.5 wt%. This shows that the composition of GTR differs considerably, depending on the composition of the used tires, although the differences between stocks with a mixed contribution of a wide range of tires will not be as large as those between the batches of selected tires.

(a) Amount of residue for extraction of polar components after extraction with acetone

(b) Total amount of residue after extraction with acetone and THF
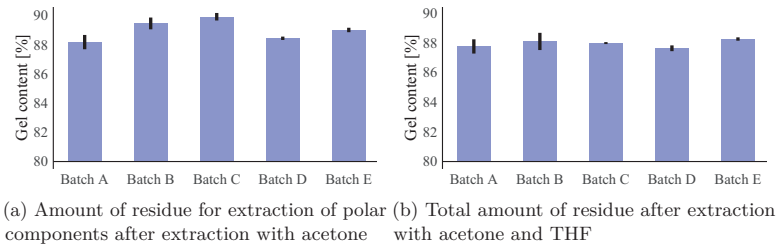
FIGURE 8.14: Extraction data GTR (batches A to D and the reference batch E)
Note: The ordinate starts at 80%



(a) Amount of residue of selected tires after extraction with acetone

(b) Amount of residue of selected tires after extraction with acetone and THF
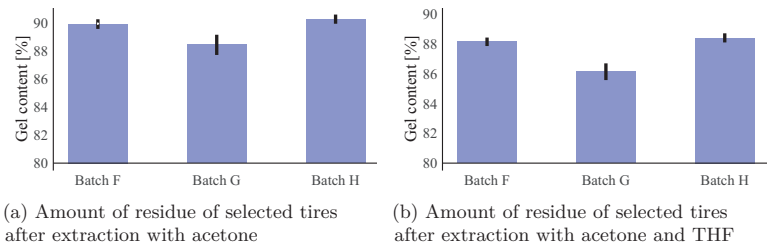
FIGURE 8.15: Extraction data GTR (batches E, F, and G)
Note: The ordinate starts at 80%

## Analysis of variation in GTR composition by TGA

As can be seen in Figure 8.16, the weight loss up to $300\,°C$ varies between $16\,wt\%$ and $20\,wt\%$ for the five samples, and the weight loss from $300\,°C$ to $500\,°C$ varies between $35\,wt\%$ and $45\,wt\%$, indicative of large differences in polymer contents. The amount of ash, the remaining matter at $800\,°C$, varies between $9\,wt\%$ and $10\,wt\%$, with relatively small differences. The amount of non-volatile material (polymers, fillers, zinc oxide, and zinc sulfide) is shown in Figure 8.17a. In Figure 8.17b, this is converted into amounts of carbon black and silica with zinc oxide and zinc sulfide relative to the amount of polymers, expressed in "parts per hundred rubber" (phr). The amount of carbon black varies between 68phr and 103phr and of silica and zinc oxide and zinc sulfide between 20phr and 29phr. The amount of zinc oxide and zinc sulfide is generally 2phr to 4phr for tire rubbers.

The results of the extraction analysis and TGA indicate that the composition of GTR varies considerably: mostly between batches of different compositions, but also within batches.
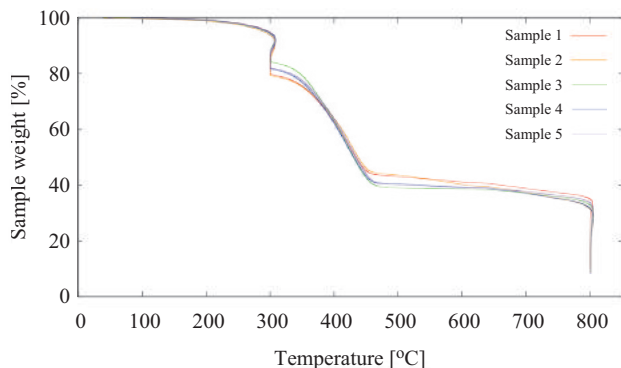
FIGURE 8.16:  TGA analysis of randomized homogenized
samples of GTR of batches A to D



(a) Amount of polymers, fillers, and zinc
oxide by weight [wt%]

(b) Amount of fillers and zinc oxide relative
to amount of polymers [phr]
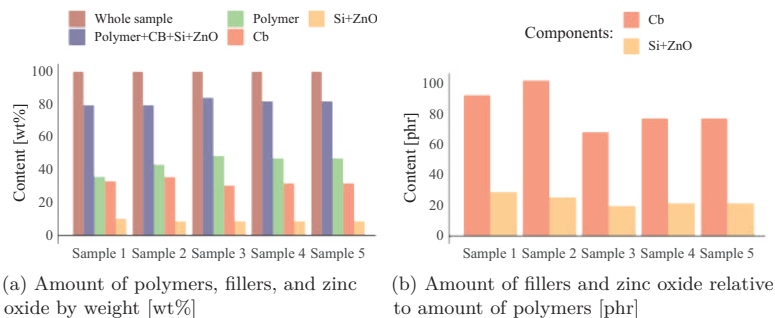
FIGURE 8.17:  TGA analysis of GTR (batch D) to indicate
the amount of carbon black and silica relative to the amount
of polymer

### 8.6.4   Conclusions

Overall, this evaluation shows that commercially available GTR is inherently
inhomogeneous at the macro level between different producers and types of
tires and at the micro level between samples of 10mg of powdered GTR of
the same batch. This is due to the fact that whole tires consist of a mix of
compounds which not only contain different polymers (NR, BR, SBR, and
IIR) and various active fillers (carbon black and silica), but also differ in
formulations.

## 8.7   Evaluation of the variation in tensile strength of the devulcanized and subsequently revulcanized GTR as an indication of variations in feedstock and process reproducibility

To verify the influences of the devulcanization and subsequent revulcanization
processes on the tensile strength, GTR was devulcanized using a twin screw

extruder. Variations in tensile strength are expected due to variations in the preparation of the mixture of GTR with the devulcanization additives, in the process conditions of the extruder, and in the preparation for revulcanization.

### 8.7.1 Experimental

GTR from batch D was used, as detailed in Section 3.2.1. It was manually blended with the devulcanization additives in total batches of 5 l to 7 l, which experience showed is the maximum amount that can be mixed manually in a homogeneous manner. First, oil was added to the GTR. Secondly, the devulcanization aid and antioxidant were added. After both additions, the blend was mixed until the oil and the powdery additives were homogeneously distributed, judged by color. Subsequently, this material was devulcanized using the optimal devulcanization parameters and the extruder settings and devulcanization formulation described in Chapter 6 and summarized in Table 8.1. Variations in extruder conditions, such as a cold or warm start and a change of extruder settings (a change of temperature or screw speed from the original setpoint and back) were applied to mimic experimental conditions. A total of six experiments were carried out (batch 1 to 6) to study these influences.

Contamination between extruder batches was prevented by discarding changeover material for the residence time of one extruder filling when changing formulations or after temperature profile and pressure changes, counted from the moment of stabilization. Each of these batches was further processed on the mill as the final part of the devulcanization process, and subsequently revulcanized in three different samples numbered 1 to 3. The tensile strength was measured five times per sample. For revulcanization, the formulation GTR-3 in Table 3.3 and the procedure according to Table 3.15 were used.

### 8.7.2 Results and discussion

The resulting tensile strengths are presented in Figure 8.18. Variation in the mean tensile strength per batch and variation in the standard deviation (s) for the tensile strength test for each sample can be seen. The error bars of +/- 2s denote a 90% reliability interval.
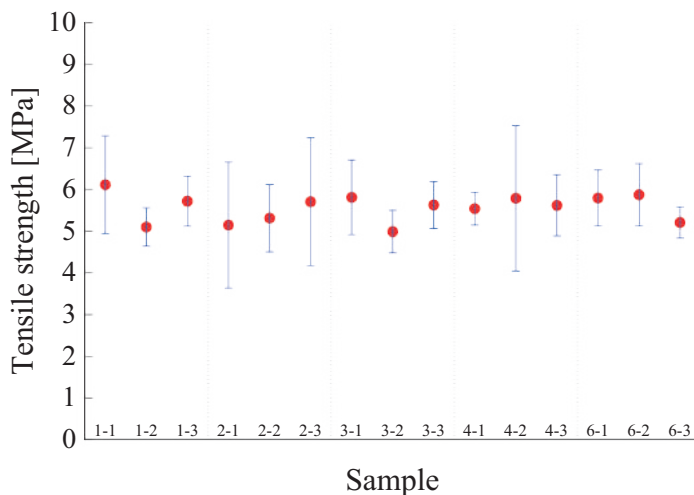
x-1, x-2 and x-3: tensile results of the revulcanized samples of one batch;
Mean value of five measurements of the tensile strength of one sample;
Error bars: plus/minus 2s (s = standard deviation).

FIGURE 8.18: Tensile strength after revulcanization of the
devulcanizates of batch D, produced with identical extruder
settings and devulcanization formulation
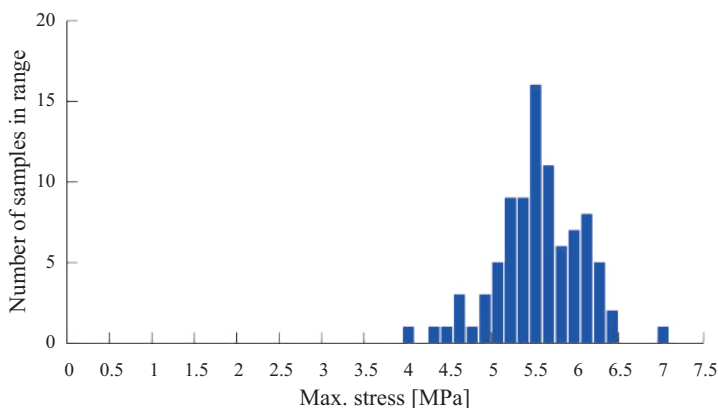


Mean value = 5.6 MPa, standard deviation = 0.5 MPa

FIGURE 8.19: Distribution of all tensile strength values of
all measurements of Figure 8.18

Hence, the variation in the mean values of the three samples per batch is in
these cases larger than the reliability interval of the tensile measurements per
sample suggests. The reliability intervals of the samples 2-1, 2-3, and 4-2 are
also considerably larger than those of the other samples. This indicates large
variations in the homogeneity of the revulcanized compounds per sample
and per batch. The histogram of all measurements of batches 1 to 6 (see
Figure 8.19) shows a normal-like distribution. Applying the Shapiro-Wilk

normality test for the tensile strength gives the parameters $W = 0.98$ and p-value $= 0.39$; the p-value $> 0.05$, implying that the distribution of the data is not significantly different from a normal distribution[3].

Thus, the devulcanization and revulcanization circumstances of batches 1 to 6 are sufficiently equal to combine them in one histogram. The mean value of the tensile strength is 5.6 MPa, with a standard deviation of 0.5 MPa.

**Table 8.4: Standard deviation of revulcanizates**

| Revulcanizate of compound: | TS Mean value [MPa] | Value of s min. mean max. [MPa] | | | s/TS min. mean max. [-] | | |
|---|---|---|---|---|---|---|---|
| Carbon black-based tread (1) | 14 | 0.16 | 0.34 | 0.52 | 0.01 | 0.02 | 0.04 |
| Silica-based tread (1) | 13 | 0.80 | 1.27 | 1.70 | 0.06 | 0.10 | 0.13 |
| GTR | 5.6 | 0.16 | 0.5 | 0.88 | 0.03 | 0.09 | 0.16 |

s = standard deviation, TS = Tensile strength
s/TS = standard deviation / tensile strength
(1): See Section 8.4

Comparing the ratio between s and the tensile strength (s/TS) for the revulcanizates of a carbon black-based compound, a silica-based compound, and GTR as shown in Table 8.4, the smallest value is found for the carbon black-based compound. For both the silica-based compound and GTR, these ratios are comparable and about five times higher than for the carbon black tread. This is consistent with the smoother structure of the fracture surfaces of tensile test pieces of the carbon black-based compound and the coarser structure of the others, as discussed earlier.



Error bars are plus/minus 3s
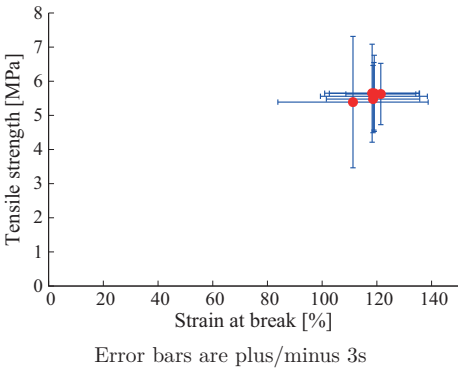
FIGURE 8.20: Reproducibility of the devulcanization process, indicated by the mean tensile strength and strain at break after revulcanization for batches 1 to 6.

This also indicates that the silica-based compounds influence the variation in the tensile strength of the GTR the most. The value of s/TS $= 0.02$ for the carbon black-based compound indicates the overall variation in tensile strength due to all processing variations. It is not unreasonable to expect that the variations due to the extruder-based devulcanization and subsequent revulcanization will be in a similar range. This leads to the conclusion that

the influence of the silica-based compounds in the GTR on the variation in tensile strength after devulcanization and subsequent revulcanizationis about five times higher than the process variations (s/TS = 0.1 versus 0.02).

It also indicates that a standard deviation in the tensile strength of 0.09*5.6 MPa = 0.513 MPa can be expected for GTR. For a reliability interval of 99 %, ≡ 3s, this is approximately 1.5 MPa. This is consistent with the real error bars as shown in Figure 8.20 for the mean values of the tensile strength per batch. This can be interpreted as the combined reproducibility of the process of devulcanization and subsequent revulcanization and the influence of silica-based compounds in GTR.

Overall, the evaluation of these results and those in Section 8.6 shows that commercially available GTR is inherently inhomogeneous at both the macro level (between different producers and type of tires) and the micro level (between samples of 10mg of powdered GTR of the same batch). This is because whole tires consist of a mix of compounds, which not only contain different polymers: NR, BR, SBR, and IIR, various active fillers, carbon black, and silica, but also differ in formulations. This inhomogeneity contributes to a relatively large standard deviation in tensile strength of devulcanized and subsequently revulcanized GTR. Variations are also found between experiments with the same devulcanization parameters between different series and within the same series. It can therefore be concluded that the silica-based compounds in the GTR contribute to a large extent to these inhomogeneities.

The use of the tensile strength of devulcanized and subsequently revulcanized samples as a selection criterion, led to values between 7 MPa and 8.2 MPa. The mean value of the tensile strength within the optimal processing window was 5.5 MPa with a standard deviation of 0.5 MPa.

### 8.7.3   Conclusions

The variance in tensile strength, expressed as standard deviation per tensile strength, $\sigma/TS$, is 0.1 for revulcanizates of the silica-based tread model compound and GTR, and 0.02 for revulcanizates of carbon black-based tread model compounds. This combines variations due to the devulcanization and subsequent revulcanization process.

From these results, it can be derived that most of the variance in tensile strength of the devulcanized and subsequently revulcanized GTR is due to the influence of the silica-based compounds in the GTR.

A standard deviation of 0.5 MPa and mean tensile strength of 5.5 MPa for the devulcanized and subsequently revulcanized GTR implies a reliability interval of 99 % of 4 MPa to 7 MPa under very controlled conditions. For samples of devulcanized and subsequently revulcanized GTR under comparable conditions, a tensile strength of 8.3 MPa is measured, as described in Chapter 6. This suggests an even larger variation in tensile strength under operational conditions than derived in this section.

## 8.8 Overall conclusions

The following overall conclusions can be drawn from this study:

- The particle size of the compounds or the GTR before devulcanization has only a minor influence on the tensile strength or the fracture surface of the tensile test pieces after devulcanization and subsequent revulcanization for particle sizes between 0.7 mm and 3.5 mm.

- There is a large difference in the composition of GTR from different sources. Even between samples of the same batch, there are relatively large differences, resulting in a standard deviation of 0.5 MPa and a mean value of 5.5 MPa for the tensile strength of samples of GTR that are devulcanized and subsequently revulcanized under similar conditions.

- Devulcanization and subsequent revulcanization deteriorate the internal structure of silica-based tread model compounds, but a tensile strength of 14 MPa can still be obtained with an optimized revulcanization formulation.

- Mixing a silica-based tread model compound with a carbon black-based tread model compound and up to 5 % butyl rubber before devulcanization gives a tensile strength of 12 MPa.

- A mean tensile strength of 5.5 MPa and a maximum tensile strength of 8.3 MPa, see Chapter 6, were found for devulcanized and subsequently revulcanized GTR. Compared with a tensile strength of 12 MPa for the devulcanized and subsequently revulcanized mixture of model tread compounds as obtained in the present chapter, this implies that the difference of about 5 MPa is due to the complexity of the GTR material and other influences.

- As to the complexity of the GTR material it would be highly beneficial if some sort of separation of the various main components of used tires: treads, undertreads, sidewalls and innerliners could be implemented in order to create sort-specific feed stocks for the devulcanization.

- As to other influences there may be effects involved of dynamic fatigue or aging of the used tires during their operation which play a role here. However difficult it is to quantify these effects, they would justify deeper studies not further pursued in the context of the present thesis.

## References

[1] D. L. Manas-Zloczower, Ica Feke, "Dispersive Mixing of Solid Additives", in *Mix. compd. polym. theory pract.* Edited by I. Manas-Zloczower, 2nd editio (Hanser Publications., München, 2009) Chap. 4, pp. 181–215.

[2] A. Ahagon and Y. Kirino, "Mechanochemical Reactions in Black-Filled SBR Vulcanizates under Large Deformation", Rubber Chem. Technol. **80**, 265–278 (2007).

[3] A. Ghasemi and S. Zahediasl, "Normality tests for statistical analysis: A guide for non-statisticians", Int. J. Endocrinol. Metab. **10**, 486–489 (2012).

# Chapter 9

# The application of devulcanizate in tire compounds

*The effects of blending devulcanizate with virgin, not-devulcanized, compounds on tire performance indicators and on accelerated aging of these materials are investigated in this chapter. The devulcanizate was blended with a carbon black- and a silica-based SBR-BR tire tread model compound and a carbon black-based NR-BR undertread model compound, with contents of up to 50 wt% of devulcanized passenger car ground tire rubber (GTR), containing an average of 20 wt% silica. Prior to blending with the virgin compounds, the silica present in the devulcanized GTR (d-GTR) was silanized (ds-GTR), which considerably improved the tensile strength of revulcanized rubber in earlier experiments (see Chapter 7).*

*The influence of ds-GTR varied a lot, depending on the type of model compound. For tread and undertread carbon black-based compounds, vulcanization was accelerated, and the torque increase during curing was reduced by adding up to 20 wt% of ds-GTR. For silica-filled compounds, no acceleration was observed, and the delta torque during curing increased with the addition of a maximum of 40 wt% devulcanizate ds-GTR. The addition of up to 30 wt% of ds-GTR resulted in a tensile strength of 10 MPa to 12 MPa, independent of the initial strength of the virgin compound.*

*In terms of dynamic properties, the rebound resilience at room temperature decreased with the addition of ds-GTR, indicating better wet grip behavior. The loss angle (tanδ) versus temperature curves of the SBR-BR tread compounds did not change with ds-GTR concentrations up to 30 wt%, while the tanδ value at the glass transition temperature ($T_g$) decreased. $T_g$ increased for the carbon black-filled compounds, while it decreased for the silica-filled compound.*

*The aging behavior of compounds was affected by the presence of ds-GTR: the stress at 25 % (M25) increased up to 100 % for concentrations up to 30 wt% of ds-GTR, the influence on the hardness and tensile stress was limited. The influence on the rate of change of the strain at break was limited to the first 9 days of the 130 days of the aging measurements and increased or decreased by + or - 30 wt%, depending on the base compound.*

# 9.1   Introduction

In the previous chapters, the pure devulcanizate (100 % d-GTR) was used to optimize the devulcanization process, the revulcanization formulation and procedure, as well as to compare the influence of the fillers carbon black and silica on the properties of devulcanizates and revulcanizates. There is a plethora of literature on the use of blends of virgin rubbers with reclaimed / devulcanized rubbers, without an explicit focus on the ratio of crosslink scission to main chain scission or the silica content, as detailed in this thesis. This will be further explored in the present chapter. For practical applications, blends with virgin, not-devulcanized, rubber are more common. For an impression of the influences of d-GTR on the properties of blends, different kinds of compounds were chosen: SBR-BR-based tread model compounds with carbon black or silica-silane as active fillers, and a NR-BR-based undertread model compound, also with carbon black as active filler. The emphasis is on the influence of the addition of d-GTR on the following properties of the above mentioned compounds.

**Curing behavior**

According to literature, one limiting factor of the use of reclaimed rubber is that it increases the risk of scorch, and at the same time accelerates the curing behavior of a blend with virgin rubbers[1]. For this reason, the influence of devulcanizate on the curing kinetics is investigated in Section 9.3.1. De and De[2], for example, compared the cure rate and optimal cure time of an SBR compound with 40 phr carbon black with a blend of 80 wt% SBR, 20 wt% reclaimed GTR and the same amount of carbon black. They showed that the optimal cure time decreased from 10 min to 4.5 min.

**Mechanical properties**

Another aspect of using reclaimed GTR in a blend is that it lowers the tensile strength relative to the virgin compounds. This limits the acceptable amount of reclaim, especially for applications where a high tensile strength is required[3]. However, both are general claims and are not detailed with respect to either the composition of the GTR in terms of polymer content or concentration of silica, nor the specific reclaiming process used. Therefore, the influence of the addition of devulcanizate on tensile properties and rebound resilience is investigated in Sections 9.3.2 and 9.3.3.

Rattanasom et al.[4] investigated the influence of reclaimed rubber (RR) in a blend with an NR-based compound and showed that the hardness and modulus at 100 % strain increased, and that tensile strength and strain at break decreased, all more or less linear with the concentration of RR.

**Tan$\delta$-temperature relationship and glass transition temperatures**

Devulcanized GTR is a blend of different compounds, which has implications for the glass transition temperature ($T_g$) of the revulcanizates and of a blend with virgin rubber. Due to the chemical and mechanical treatment of the rubber during devulcanization, an effect on the molecular weight distribution of the polymers and the overall mobility of the polymer chains is expected,

which influences the tan$\delta$ versus temperature relation. Hence, the influence of devulcanizate on T$_g$ and tan$\delta$-temperature relation of above mentioned compounds is investigated in Section 9.3.4.

**Aging**

Unsaturated hydrocarbon rubbers are prone to aging. Shelton[5] published an extensive review paper on the very complex mechanisms involved in the aging of these materials. A concise summary, based on the descriptions by Huntink[6] and Naskar[7], is presented below. It is focused on measurable influences of blending devulcanizate with virgin rubber on the tensile properties of vulcanizates after aging. As a first estimate, Rattanasom et al.[4] found for a blend of a NR-based compound with 50 wt% Reclaimed Rubber, without further specification, that the tensile strength decreased to about 80 % when aged for 22 h at 100 °C in air.

Oxygen in the form of $O_2$ or ozone: $O_3$, is the primary factor in the deterioration of elastomers by aging. The degradation mechanism of a hydrocarbon polymer by ozone is different from the deterioration by atmospheric oxygen involving hydroperoxides:

*Oxidation by ozone ($O_3$)* Oxidation by ozone is the most severe aging attack on rubbers under dynamic loading. It is limited to a surface layer of 10 to 40 molecular layers, as long as the layers are not disrupted by dynamic deformations of the rubber[8]. A commonly used anti-degradant is 6PPD (N-(1,3-dimethylbutyl)-N'-Phenyl-p-PhenyleneDiamine), which provides protection from oxidation and the influence of ozone for one to five years[8].

*Oxidation by oxygen ($O_2$)* An oxidation mechanism derived for simple mono-olefins indicates that the primary product of oxidation is hydroperoxide. The following free-radical chain reactions Schemes (R1) to (R11) describing the initiation, propagation and termination stages, is generally accepted[5,6] (with RH = rubber hydrocarbon):

Initiation:
Both thermal and light-initiated oxidation proceed by similar free-radical chain mechanisms involving the formation of hydroperoxides.

$$RH \rightarrow R \cdot + H \cdot \tag{R1}$$

$$R - R \rightarrow 2R \cdot \tag{R2}$$

Equations R1 and R2 are initiated by heat, shear or light. For carbon black filled rubbers the light-initiation commonly plays a minor role, as each light-quant is immediately transformed into heat by the carbon black.

$$R \cdot + O_2 \rightarrow ROO \cdot \tag{R3}$$
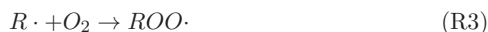
R3 is initiated by existing radicals in the polymer.

Propagation:
$$ROO \cdot + RH \rightarrow R \cdot + ROOH \tag{R4}$$
$$ROOH \rightarrow RO \cdot + OH \cdot \tag{R5}$$
$$ROOH + RH \rightarrow RO \cdot + R \cdot + H_2O \tag{R6}$$

$$RO \cdot + RH \rightarrow ROH + R\cdot \tag{R7}$$
$$OH \cdot + RH \rightarrow HOH + R\cdot \tag{R8}$$
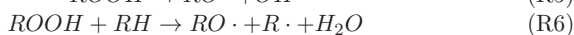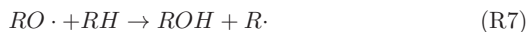
Termination:
Bimolecular combination of radicals rendering inactive products:

$$2R\cdot \rightarrow RR \tag{R9}$$
$$R \cdot + RO\cdot \rightarrow ROR \tag{R10}$$
$$R \cdot + RO_2\cdot \rightarrow ROOR \tag{R11}$$
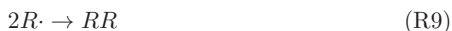
In literature, chain scission and chain recombination are major factors for the change in mechanical properties of rubber products in time[5]. Chain scission can be understood as a result of the initiation and propagation reactions, while the termination reactions are the source of the recombination in the rubber network. Chain recombination results in an uncontrolled increase of network density, hence an increase in stiffness, while the effect of chain scission is the overall shortening of the polymer chains with a decrease of tensile strength. Shakiba and Najmeddine[9] have shown that by using chain scission and chain recombination as major factors for a constitutive equation, the change in tensile stress-strain response in time by ageing could be simulated.

*Effect of temperature on oxidation*   Temperature is an important factor for the initiation of radicals, as expressed by Equations. R1 and R2, and has an effect on the overall reaction rate. The accelerating effect of temperature on oxidation and aging is well known, as is the formation of radicals by the thermal scission of bonds. Although the same mechanisms extend over the whole temperature range, from $50\,°C$ to $110\,°C$, the additional oxygen absorbed at higher temperatures causes more extensive deterioration of physical properties. However, the ratio of chain scission to crosslinking is of greater relative importance at lower temperatures. For SBR, it means that the ratio of recrosslinking to chain scission increases with rising temperatures, while for NR the amount of recrosslinking is so low that chain scission is dominant at higher temperatures[10].

*Influence of metal-ions*   The effect of catalysis by metal ions (e.g., iron, copper or chromium ions) results in an increase in the rate of oxidation initiation by peroxide decomposition.

*Effect of carbon black*   The influence of carbon black on oxygen adsorption is quite complex and is a result of several competing effects. It has both accelerating and inhibiting effects. An accelerating effect is due to:

- a catalytic effect on the oxidation reaction;

- catalysis of peroxide decomposition to free radicals;

- adsorption of antioxidant onto the surface of the carbon black; or

- an increased solubility of oxygen when carbon black is present[5].

The accelerating effect is commonly reflected in a stronger modulus increase during aging. Inhibition may be attributed to several factors, including:

- the activity of the carbon black surface as a free radical acceptor;

- interaction of the carbon with metal ions with a mutual reduction in the catalytic effect of both; or

- the effect of carbon black on the decomposition of peroxides into stable products.

The observed behavior in any given case will depend on the relative contributions of these individual mechanisms.

*Effect of silica*   Guo et al.[11] showed that silica reduces the thermal oxidative aging of SBR. However, the exact silica content of GTR is not known. It is therefore not possible conclude about the effect of silica in GTR devulcanizate on aging. The influences of aging on different material properties of blends with d-GTR as studied here are described in Section 9.3.5.

## 9.2   Experimental

### 9.2.1   Experimental choices

The age of the rubber in GTR is unknown: it can originate directly from the factory as production waste and rejected tires, or from scrap tires at the end of their lifetime. Aging also depends on temperature, which can vary greatly in a tire's life. Degradation of rubber can be expected due to converting of poly- to di- and monosulfidic crosslinks, scission of the polymer chains due to oxidation, and recrosslinking[10]. In the present study, the devulcanization process is not expected to contribute to oxidative aging of the rubber because of the inert atmosphere during processing.

From a recycling point of view, reusing devulcanized GTR (d-GTR) for new tires is a very interesting application as described in Chapter 2. Therefore, three tire formulations were chosen in the present study for blending with devulcanizate which represent three common rubber/filler combinations in car tires: a carbon black-reinforced SBR-BR-based tread model compound (CB), a silica-silane SBR-BR-based "green" tread model compound (GT) and a carbon black NR-BR-based undertread compound (UT). The choice of these types of compounds, variations in filler type and base rubber, and the influence of d-GTR on curing, physical properties, and aging are covered. As described in the preceding chapters (see Chapters 7 and 8), improved tensile strength properties of revulcanizates were obtained by silanization of the devulcanizates and by using a silica-based revulcanization formulation. In the present study, this silanized devulcanizate (ds-GTR) is used for blending with the virgin tread model compounds (thus the not-devulcanized model compounds).

For a first impression of the influence of blending devulcanizate with virgin compounds, a static aging test at a constant temperature of 80 °C was chosen. A static test was chosen so that the integrity of the surface layers is not compromised by dynamic loading of the samples, and so that there is no

influence on the initiation and propagation of cracks in the polymer, which due to ozone in the air increase the effects of aging.

Bevilacqua and Wenisch[10] showed that the migration of oxygen into test pieces does not limit the rate of oxidation up to 80 °C. To mimic a lifetime of 5 years, testing was performed for 130 days. This was based on a rough estimate of a doubling of the chemical reaction rate for each 10 °C increase in temperature, and assuming about 40 °C as a mean value of all operating and non-operating conditions of a tire. Based on earlier investigations, up to 50 wt% of ds-GTR is used for the carbon black-based compounds, while the amount was limited to 30 wt% for the silica-based compound. Surpassing these concentrations of ds-GTR showed a decrease in tensile strength that was considered too severe for reuse.

### 9.2.2   Experimental setup

The Brabender 350S mixer was used for all mixing and the Schwabenthan mill was chosen for milling. Unless stated otherwise, the milling procedure was 5 min at 60 °C. Vulcanization was carried out using the Wickert laboratory press and cure characteristics were measured using an RPA Elite from TA Instruments. Samples of 2mm thickness were vulcanized for $t_{c,90}+2$ min at 160 °C. Stress-strain properties were analyzed with a Zwick-Roell tensile tester, and the Zwick-Roell 5109 was used to measure rebound resistance. Hardness was measured using a Zwick Shore A tester, and a DMA VA2000 from Metravib was used for the $\tan\delta$-temperature sweeps. Microscopy of the fracture surfaces of the tensile dumb-bells was carried out with the aid of a Keyence VHX5000. More details are provided in Chapter 3.

Virgin compounds were produced according to the formulations in Table 3.4: 'CB' for carbon black, 'Silica' for silica-based tread compounds, and 'UT' for the undertread model compounds. The carbon black-based tread and undertread model compounds were mixed according to the procedure given in Table 3.7, and the silica-based tread model compound as described in Table 3.8.

Devulcanized GTR was produced in one batch with the best settings as specified in Figure 6.5 and subsequently milled with a minimum gap size of 0.1 mm, then silanized according to the 'Silanization' procedure in Table 3.11 using the formulation for GTR-3 as specified in Table 3.3.

**Table 9.1: Blends of virgin compounds with devul-canized GTR.**

| Compound | Amount of ds-GTR[1] [wt%] | | | | | | |
|---|---|---|---|---|---|---|---|
| GT[2] | 0 | 10 | 20 | 30 | | | |
| CB | 0 | 10 | | 30 | 50 | 70[3] | 90[3] | 100[3] |
| UT | 0 | 10 | | 30 | 50 | | |

[1] devulcanized silanized GTR (ds-GTR).
[2] "Green" tire Tread, because of the fuel economy properties of tires with a silica based tread compound.
[3] For cure behavior only.

The blending ratios for the virgin compounds with ds-GTR are summarized in Table 9.1, and the 'Compounding' procedure in Table 3.11 was used. For preparation for revulcanization all compounds and ds-GTR are prepared as indicated before blending the compounds with ds-GTR. For aging, eight vulcanized test sheets of each blend were prepared and kept freely hanging at 80 °C in an air circulating oven. After the planned time intervals, the samples were kept at 5 °C until testing.

## 9.3 Results and discussion

### 9.3.1 Curing behavior

The addition of ds-GTR to the three virgin rubber compounds shows very different influences on the curing properties of the blends, as shown in Figures 9.1 till 9.3. The differences in the concentration of TBBS between the formulation of ds-GTR and the virgin compounds, as given in Table 9.2, can explain the increase in the cure rate, as seen most prominently in Figures 9.1 and 9.3. De and De[2] noticed a similar increase in cure rate for a carbon black-based SBR compound and a blend with d-GTR. The decrease in scorch time also indicates that active accelerators of the original curing systems remain in the GTR. This is also shown by the scorch time of the 100 % ds-GTR, which is the shortest of all compounds.

**Table 9.2: Added amount of sulfur and TBBS to the compounds, extract of Tables 3.3 and 3.4.**

| | Compound | | | |
|---|---|---|---|---|
| | CB | UT | GT | ds-GTR |
| Sulfur [phr] | 1.5 | 1.7 | 1.4 | 4.64 |
| TBBS [phr] | 1.5 | 1.7 | 1.7 | 4.64 |

For the CB compound, adding 10 wt% to 30 wt% of ds-GTR results in a significant acceleration of the curing reaction. The scorch time decreases rapidly from about 5 min for the virgin compound to 1 min for 30 wt% ds-GTR blend. For higher amounts of ds-GTR, the scorch time still decreased, but at a lower rate. Despite the considerable differences in the
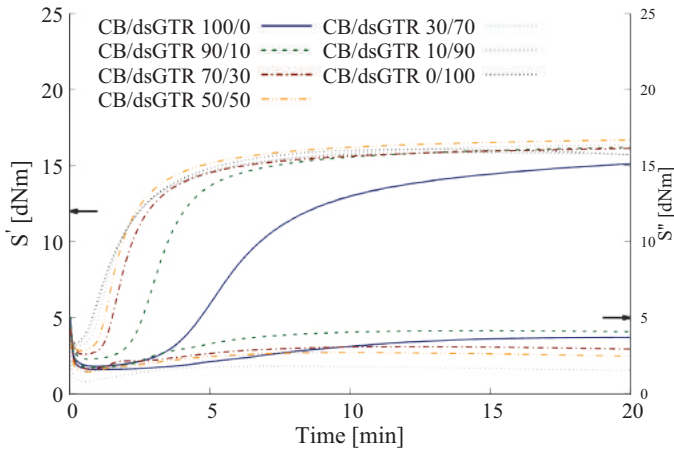
FIGURE 9.1: Cure curves of blends of virgin carbon black
based tread compounds (CB) with ds-GTR.

amount of sulfur and TBBS in the formulations of CB and ds-GTR, the
increase in delta torque, which is a measure of the degree of network
formation during vulcanization, is similar for all ratios. The 100 % CB
material shows a marching modulus curve at the timescale presented, and
the delta torque (S') is about 90 % of that of the blends when measured at
20 min, where the curve is nearly flat. For the viscous response (S"), it can
be seen that the level decreases with an increasing amount of ds-GTR.
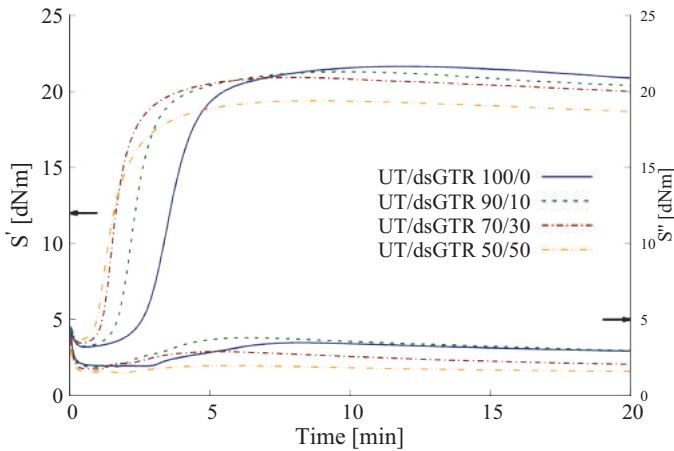


FIGURE 9.2: Cure curves of blends of the virgin carbon black
based undertread compound (UT) with **ds-GTR**.

For the blends of the UT compound the influence of ds-GTR on the curing
behavior, as shown in Figure 9.2, shows a slight decrease in delta torque
with an increasing concentration of ds-GTR. A decrease in scorch time from
3 min to 1 min, with increasing amounts of ds-GTR is seen. This can again

be attributed to the still active accelerators in the GTR. No influence can be seen on the differences in concentrations of sulfur and TBBS in the formulations of UT with ds-GTR. The viscous response shows a similar pattern as that for the CB compound, although the levels are slightly lower.
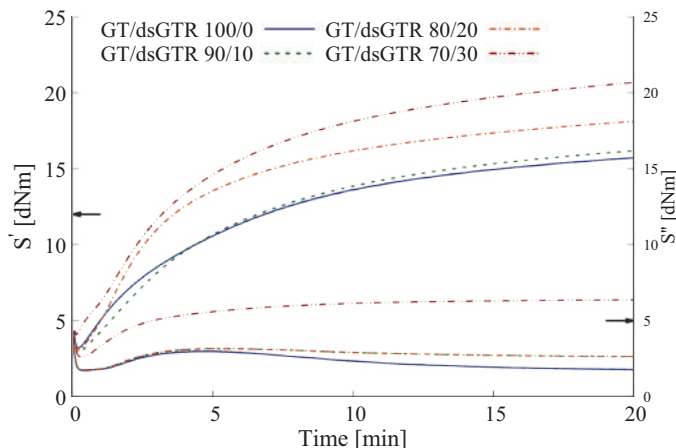


FIGURE 9.3: Cure curves of blends of the virgin silica based tread compound (GT) with ds-GTR.

The cure curves of the blends with the GT compound are shown in Figure 9.3. The pure (100/0)GT compound shows very slow curing and a strong marching modulus. The latter is a well-known problem for silica compounds, while the former characteristic is unexpected, as a common formulation was used. It might be caused by an incomplete silanization during mixing caused by too low silanization temperature and time. An incomplete silanization leaves silanol groups unreacted, with an acidic character influencing the curing kinetics.

The influence of ds-GTR on the curing behavior shows a completely different picture compared to both carbon black compounds earlier. Adding 10 wt% ds-GTR to the compound has hardly any influence. Larger influences on delta torque are noted for an increasing amount of ds-GTR of up to 30 wt%, but the shape of the curves hardly changes: there was no indication of an accelerated curing, all curves are marching and scorch times are very short. This suggests that the amount of silica in ds-GTR has more influence on the curing kinetics than the amount of remaining curatives in GTR and thus ds-GTR. The viscous response also shows a different picture compared to the response of both carbon black-based compounds, and the model GT compound with 0 wt% ds-GTR has the lowest S". The relative increase in S" for the blend with 30 wt% ds-GTR is rather high, while for the blends with 10 wt% and 20 wt% ds-GTR the viscous modulus is only slightly higher than for the virgin compound.

These results indicate that there is no general trend in the influence of ds-GTR on the curing behavior: each combination reacts differently.

### 9.3.2   Stress-strain properties

As can be observed in Figure 9.4, the tensile strength (TS) and strain at break (SB)of all the blends with 10 wt% to 30 wt% ds-GTR are 10 MPa to 12 MPa at 250 % to 300 % elongation, independent of the original strength of the pure, not blended compounds. They decrease from 9 MPa to 10 MPa and 220 % for a further increasing amount of ds-GTR up to 50 wt%. This decrease in strength values may be attributed to the inhomogeneous structure of the revulcanized ds-GTR, caused by the silica content, as discussed in the previous chapters. Figure 9.5 shows an example of the morphology of a blend of 50 wt% virgin carbon black-based tread compound with 50 wt% devulcanizate.
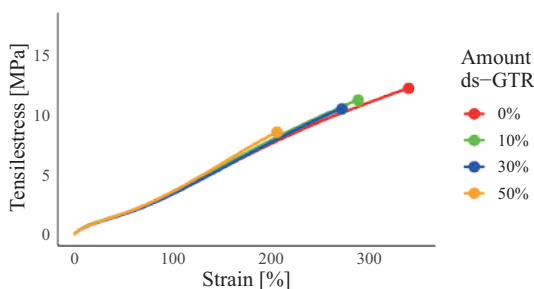


(a) CB blends
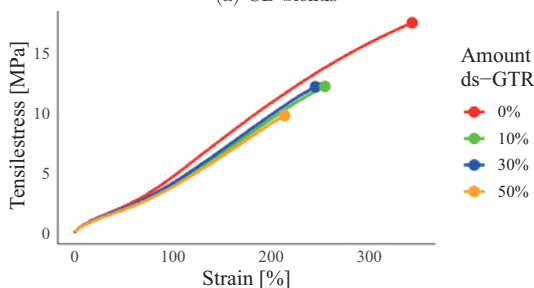


(b) UT blends
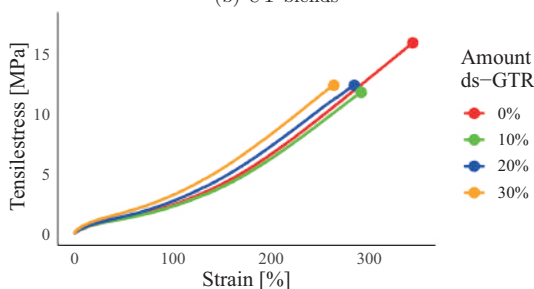


(c) GT blends

FIGURE 9.4: Tensile strength and strain at break for blends of virgin compounds with ds-GTR.

(a) Virgin CB tread compound



(b) Blend of 50 wt% of virgin tread compound and 50 wt% of devulcanizate
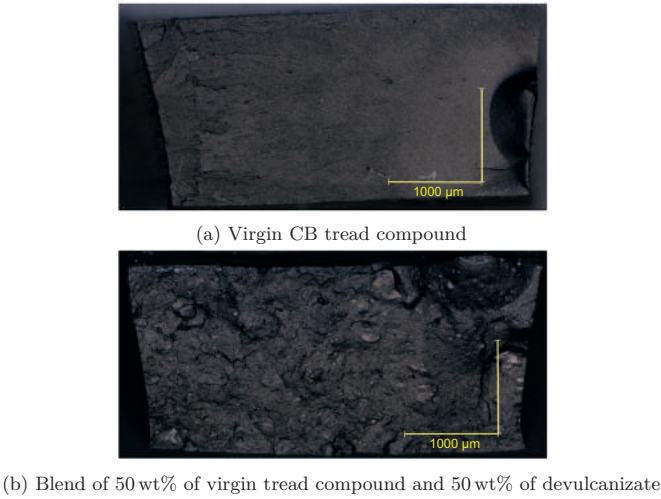
FIGURE 9.5: Microscopic pictures of the surface fracture of tensile test samples of a blend of a carbon black based tread compound with 50 wt% devulcanizate.

The trends in both moduli, M25 at 25 % strain and M100 at 100 % strain, as displayed in Figure 9.6, show an increase as more ds-GTR is added for



(a) Modulus at 25 % strain (M25)



(b) Modulus at 100 % strain (M100)
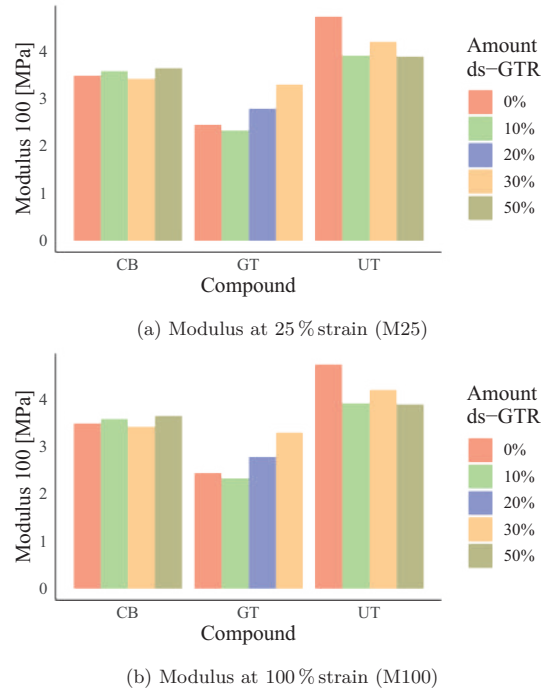
FIGURE 9.6: Moduli of blends of virgin CB compounds with ds-GTR.

the GT compound, hardly any effect for the CB compound and a decrease for the UT compound, but none reflect the pattern of the torque differences in the cure curves, as indications of the crosslink density. The crosslink densities of the blends of the compounds with ds-GTR are not homogeneous due to the presence of incompletely devulcanized grains in the devulcanizate. Therefore, the relation between the moduli and the crosslink densities is not as commonly seen for homogeneous compounds.

### 9.3.3   Rebound resilience

The rebound resilience values given in Figure 9.7 show a slight decrease for an increasing amount of ds-GTR in the blends. This is as expected, due to inhomogeneities in the revulcanized ds-GTR, as shown in Chapters 7 and 8.
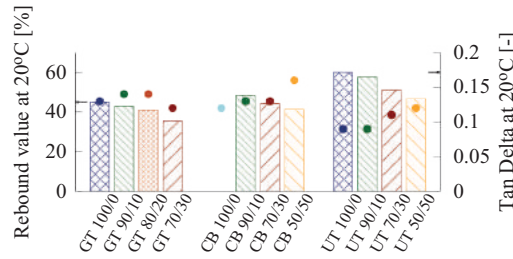


FIGURE 9.7: Rebound and tan$\delta$ values for blends of virgin compound with gtr (Rebound values as bars, tan$\delta$ values as dots, both measured at 20 °C.)

The domains with different crosslink densities and interfaces between virgin matrix and devulcanizate particles are a source of energy dissipation and thus decrease the recovered energy. The viscoelasticity depends on the crosslink network, which is different in the virgin model compound compared to the devulcanizate. The changes in rebound resilience values for increasing concentrations of ds-GTR are inversely related to the differences in tan$\delta$ at 20 °C, as indicated in Figure 9.7. For all compounds, the rebound resilience decreases with an increasing amount of ds-GTR, while tan$\delta$ increases for both carbon black compounds, as expected. The trend of the tan$\delta$ values for the silica compound is not conclusive. Both properties indicate the same trend of higher viscoelastic damping with more ds-GTR added.

### Table 9.3: Tan$\delta$ at T$_g$ for all compounds.

| | | | Compound[†] | | | | | | | | | | |
| | CB | | | | UT | | | | GT | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 100/0 | 90/10 | 70/30 | 50/50 | 100/0 | 90/10 | 70/30 | 50/50 | 100/0 | 90/10 | 80/20 | 70/30 |
| $T_g$ [°C] | -42 | -44 | -42 | -28 | -63 | -58 | -56 | -52 | -33 | -34 | -34 | -38 |
| $\Delta T_g$* [°C] | 0 | -2 | 0 | +14 | 0 | +5 | +7 | +11 | 0 | -1 | -1 | -5 |
| Tan$\delta$ [-] | 0.75 | 0.69 | 0.66 | 0.63 | 0.51 | 0.54 | 0.51 | 0.48 | 0.78 | 0.66 | 0.64 | 0.52 |
| Tg$\delta$ rel[+] [%] | 100 | 92 | 88 | 84 | 100 | 106 | 100 | 94 | 100 | 85 | 82 | 67 |

[†]: values for revulcanized ds-GTR (rds-GTR): Tan$\delta$ = 0.6 at T$_g$ = $-30$ °C
*: $\Delta T_g$ = T$_{g\text{-compound}}$ - T$_{g\text{-}100/0}$
[+]: Tan$\delta$ rel = 100% (tan$\delta$)/(tan$\delta_{100/0}$)

### 9.3.4 Tan$\delta$ versus temperature

In this section the influences of the concentration of ds-GTR in the blends with CB, UT, and GT compounds on the glass transition temperatures ($T_g$) are discussed. For comparison, the curve for revulcanized ds-GTR (rds-GTR) is added to the figures for all compounds. For rds-GTR, $T_g$ is $-30\,^{\circ}$C and the tan$\delta$ curve shows a broad peak around $T_g$. This suggests a wide distribution of molar masses of the polymer chains, which can be expected from devulcanized materials, for which random chain scission cannot be fully prevented. Branching of the polymers during the devulcanization process is also likely to occur, especially in the case of SBR, and can increase the broadening of the curve at $T_g$: see Table 9.3 and Figures 9.8 to 9.10.

The curves of unblended CB and GT compounds show a $10\,^{\circ}$C difference between $T_g$. As these compounds have a similar polymer composition and a similar amount of processing oil, this difference must be caused by a different network structure and modified interaction of the polymers with the carbon black and the silica-silane filler system. This indicates that the silica-silane network in the GT compound has a larger influence on $T_g$ than the carbon black network of the CB compound. When comparing $T_g$ of the rds-GTR compound of $-30\,^{\circ}$C with $T_g$ of the CB and GT pure virgin compounds, the former temperature is very close to the $T_g$ of the GT compound ($-33\,^{\circ}$C), while the $T_g$ of the CB compound ($-42\,^{\circ}$C) is much lower. This indicates that the silica-silane network in rds-GTR has a larger influence on $T_g$ than the carbon black network. As the rds-GTR and the GT compound shows a $T_g$ in the same range, the silica-silane network is the main responsible factor for the mobility in the network.

For the blends with the CB compound, there are only minor differences in $T_g$ and in the shape of the curves of tan$\delta$ versus temperature up to $30\,\text{wt}\%$ of ds-GTR, as shown in Figure 9.8 and Table 9.3. For the 50/50 blend, the height, width and shape of the curve are similar to those of the curve of rds-GTR. However, when adding ds-GTR to the CB compound, $T_g$ shifts from $-42\,^{\circ}$C to $-28\,^{\circ}$C and tan$\delta$ decreases from 0.75 to 0.63. This signifies a decreasing mobility of the polymers in the blend due to the increasing influence of the silica-silane network. This is in contrast to the characteristics of the blends with lower concentrations of rds-GTR, for which the carbon black-based network prevails. A gradual shift in $T_g$ would be expected instead of the large shift that is shown between the 70/30 and 50/50 blends.

The large increase in tan$\delta$ at $0\,^{\circ}$C for the blend with $50\,\text{wt}\%$ ds-GTR indicates an improvement in the wet grip for such compounds used for tire applications, while the tan$\delta$ values at $60\,^{\circ}$C, as indication of rolling resistance, remains almost unchanged. All curves of the blends show a single peak value at $T_g$, which indicates the compatibility of the components in the blend. This is because the polymers in the compounds and in GTR, and thus in rds-GTR, are similar.
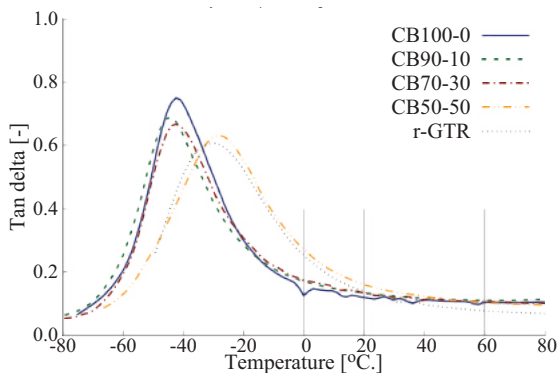
FIGURE 9.8: Tan$\delta$ against temperature for blends of a carbon black based tread compound (CB) with ds-GTR.

For the blends with the UT compound, the level of tan$\delta$ at $T_g$ does not change much for concentrations up to 30 wt% ds-GTR, but the maximum shifts upwards between $-63\,°C$ to $-52\,°C$, as shown in Figure 9.9 and Table 9.3. For the 50/50 blend, the peak broadens considerably. This indicates an increasing range in the mobility of the polymer network, caused by the higher amount of devulcanizate in the blend. An increase in tan$\delta$ at $0\,°C$ and only a minor rise in tan$\delta$ at $60\,°C$ are observed on the addition of ds-GTR.
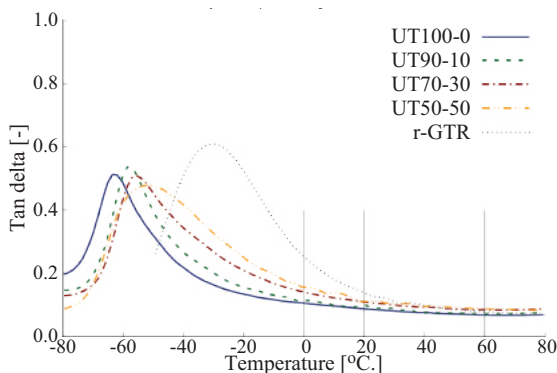


FIGURE 9.9: Tan$\delta$ against temperature for a blend of carbon black based undertread compound (UT) with ds-GTR.

For the blends with the GT compound, $T_g$ does not change considerably: from $-33\,°C$ to $-34\,°C$ for blends up to 20 wt% of ds-GTR. The maximum tan$\delta$ decreases from 0.78 to 0.64 and the peak of the curve at $T_g$ broadens, as seen in Figure 9.10 and Table 9.3. The mobility of the polymer network is unchanged but the energy absorption decreases, suggesting a relatively tighter network. For the blend with 30 wt% ds-GTR, there is only a minor additional shift in $T_g$ from $-33\,°C$ to $-38\,°C$. However, the maximum tan$\delta$ decreases significantly, from 0.78 to 0.52. This signifies an even larger increase in the tightness of the network. As the amounts of sulfur and TBBS

in the vulcanization system for the GT compound are lower than in the rds-GTR rubber, an overall increase in the tightness of the network due to an increase in the amount of ds-GTR must be the cause.
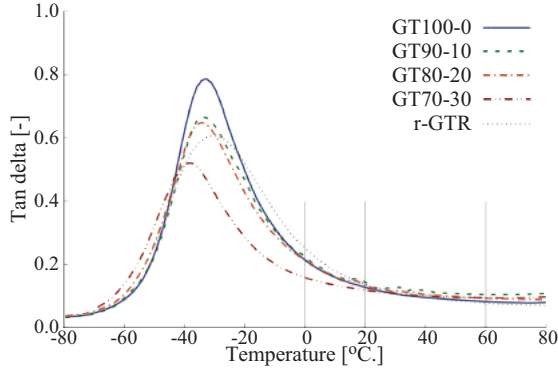


FIGURE 9.10: Tan$\delta$ against temperature for a blend of silica based tread compound (GT) with ds-GTR.

For blends up to 20 wt% of ds-GTR, only minor changes in tan$\delta$ are seen at 0 °C and 60 °C, but for 30 wt% ds-GTR, tan$\delta$ at 0 °C decreases from 0.21 to 0.18, due to the shift of $T_g$ to a lower value and a reduced tan$\delta$ peak at $T_g$. As the silica SBR-BR-based compounds are optimized for a low rolling resistance combined with a high wet grip, a decrease in the wet grip parameter is expected as a result of blending with ds-GTR, this in contrast to the carbon black based UT and CB compounds which are per definition not optimized for wet grip. Although the rolling resistance indicator tan$\delta$ at 60 °C is better for rds-GTR, the tensile properties are much lower, as seen in Figures 9.4c and 9.6.

The very different influences on $T_g$, tan$\delta$ at $T_g$ and tan$\delta$ versus temperature for the blends of the different compounds with ds-GTR show again the complex interaction between fillers, virgin polymers, ds-GTR, chosen formulations, and processing. This, combined with the different curing kinetics, signifies that there is room for optimization of the formulations and processing for each separate compound.

As the CB and the GT compounds only differ in the active filler system, carbon black respectively silica-silane, the difference in $T_g$ between both compounds can be attributed to this. Hence it indicates the influence on the $T_g$ of the amount of silica-silane based compounds in the rd-GTR. It also shows the impact of the amount of silica in the ds-GTR on the usefulness of GTR as a recyclate in a blend with a specific compound.

### 9.3.5   Aging

The aging related processes, most importantly chain scission, decrosslinking, and recrosslinking, are very complex chemical processes[5]. The influence on the rate of change of aging-related indicators such as tensile properties are difficult to predict for blends with devulcanizate compared to the virgin compounds:

- The feed stock for the devulcanizate has already undergone aging during its service life. The amount of poly-sulfidic cross-links between the rubber chains has been reduced already, which decreases at least one source of free radicals, in addition to the sources mentioned in Equations R1 to R3.

- Also, the amount of available RR-bonds will have been decreased by the aging, hence according to Eq. R2, the possibility of initiation of radicals will be lowered.

A rising amount of d-GTR in a blend will decrease the rate of change of aging related indicators. On the other hand:

- (Tire) rubbers are usually protected by anti-oxidants and anti-ozonants, for a lifetime of about 5 years[1]. A certain amount of these protectors will be consumed, so the remaining protection time will be decreased, which should be visible in an increasing rate of change related parameters,

After an overview of all stress-strain curves for all combinations of base compounds, amounts of ds-GTR and aging times, the influences of aging on the stress at 25 % (M25), the rate of change of the tensile stress and strain at break, and the hardness is discussed. To compare the stress-strain behavior of the compounds at aging, normalized data is used, as discussed in section 'Rates of change of tensile strength and strain at break'.

**Tensile strength and strain at break**

In Figures 9.11, 9.12 and 9.13 the stress strain curves of all compounds are shown, with a separate curve for each measurement time. For the pure virgin NR based UT compound both the tensile strength and strain decrease, although for the blend with 50 wt% ds-GTR the decrease in tensile strength is limited. For the CB compound, the decrease in tensile strength seems to be less than for the strain at break. For the GT compound the decrease in tensile strength is again more severe, similar to the decrease in strain at break. This indicates a different influence of the carbon black filler on the aging compared to the silica-silane filler system.

**Modulus 25 %**

Modulus 25 (tensile stress at 25 % strain, M25) was chosen as many blends did not reach 100 % strain over the whole aging experiment. The M25 increases for all blends during the aging time, and for nearly all blends the increase is larger with increasing amount of ds-GTR. There is a clear difference between the NR based UT and the SBR/BR based CB and GT compounds (Figure 9.14).

*Undertread compound*   For the UT compounds, the curves of the blends with 0 wt% and 10 wt% ds-GTR are very similar and only at the end of the experiments an influence of the ds-GTR can be observed: After a small but steep increase over the first days, M25 increases with an almost steady slope to 3.6 MPa for 0 wt% ds-GTR and to 3.8 MPa for a blend with 10 wt%. For both blends with 30 wt% and 50 wt%, the slope of the increase of M25 over

(a) Stress - strain for UT 0 wt% ds-GTR

(b) Stress - strain for UT 10 wt% ds-GTR

(c) Stress - strain for UT 30 wt% ds-GTR

(d) Stress - strain for UT 50 wt% ds-GTR

Legend: Days — 0 — 7 — 26 — 45 — 89 — 130 .
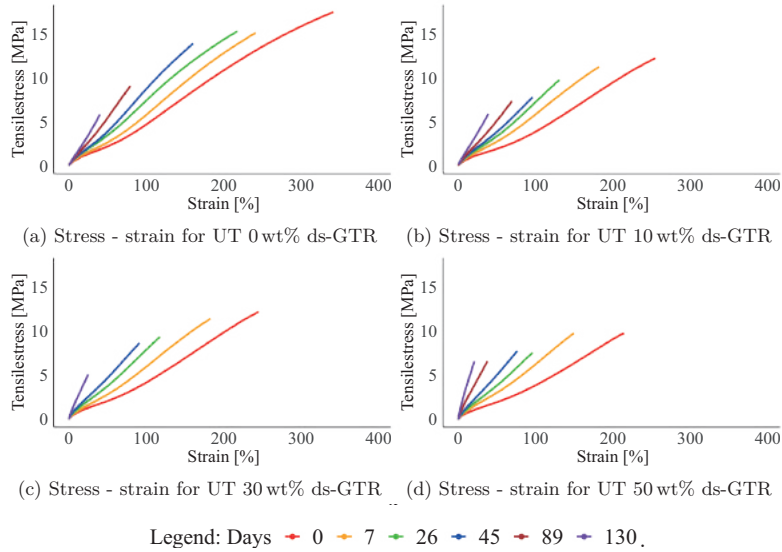
FIGURE 9.11: Tensile stress against strain for blends of UT compound with ds-GTR during static aging at 80 °C, over the indicated time-period.



(a) Stress - strain for CB 0 wt% ds-GTR

(b) Stress - strain for CB 10 wt% ds-GTR

(c) Stress - strain for CB 30 wt% ds-GTR

(d) Stress - strain for CB 50 wt% ds-GTR

Legend: Days — 0 — 7 — 26 — 45 — 89 — 130 .
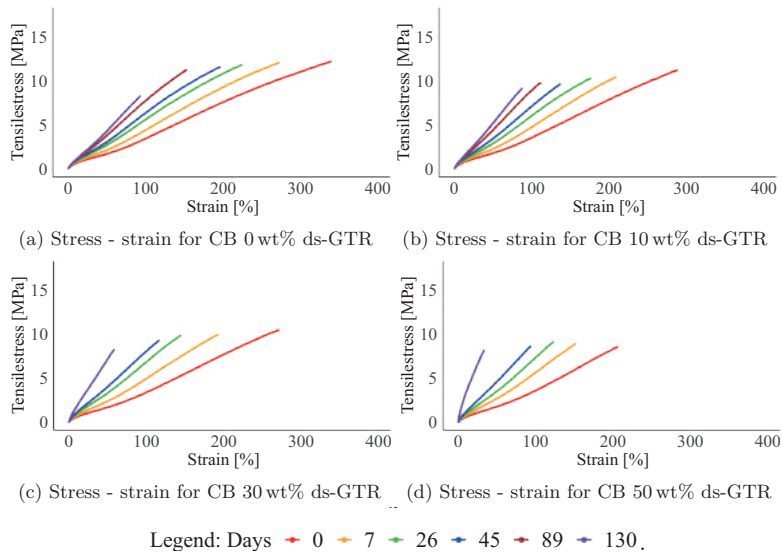
FIGURE 9.12: Tensile stress against strain for blends of CB compound with ds-GTR during static aging at 80 °C, over the indicated time-period.

time is much steeper than the previous ones. The samples fail before the end of the test at 2.6 MPa for a blend with 30 wt% ds-GTR after 45 days and at 4.6 MPa for a blend with 50 wt% after 89 days. So, for up to 10 wt% ds-GTR there is hardly any influence on M25 of UT while from 30 wt% and

(a) Stress - strain for GT 0 wt% ds-GTR



(b) Stress - strain for GT 10 wt% ds-GTR



(c) Stress - strain for GT 20 wt% ds-GTR



(d) Stress - strain for GT 30 wt% ds-GTR

Legend: Days ✦ 0 ✦ 7 ✦ 26 ✦ 45 ✦ 89 ✦ 130 .
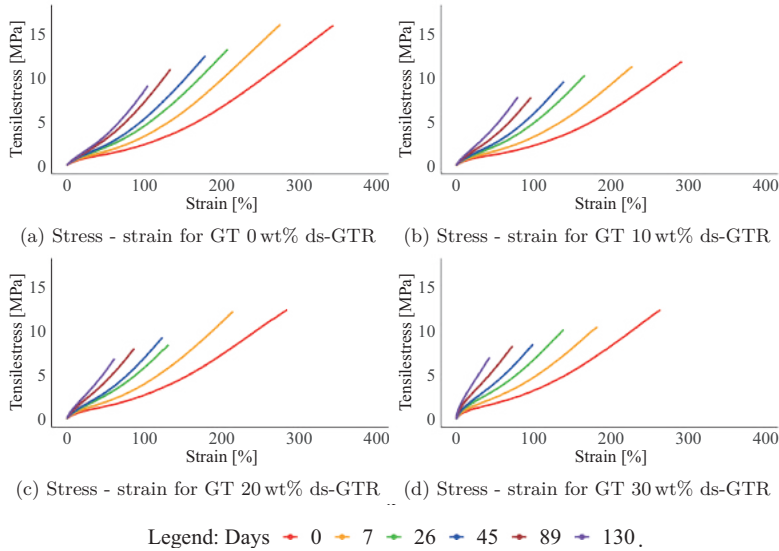
FIGURE 9.13: Tensile stress against strain for blends of GT
compound with ds-GTR during static aging at 80 °C, over
the indicated time-period.

more the influence is significant: Figure 9.14a.

*Carbon black compound*  For the CB compound, after a short but steep
increase of M25, it rises steadily with the duration of the test, where the
increase of the compound with 0 wt% ds-GTR the smallest. M25 of the
samples with 0 %, 10 %, 30 % and 50 % are 2.3 MPa, 2.7 MPa, 3.9 MPa and
6.7 MPa respectively. After 49 days, the slope of M25 of the sample with
50 wt% becomes clearly steeper: Figure 9.14b.

*Green tire compound*  For the GT compound, contrary to the other two
compounds, there is no short but steep increase of M25, but the value at day
zero increases slightly for an increasing amount of ds-GTR, and the slope is
about constant throughout the test, increasing with the amount of ds-GTR.
M25 of the samples with 0 wt%, 10 wt%, 20 wt% and 30 wt% are 1.8 MPa,
2.4 MPa, 2.9 MPa and 4.6 MPa respectively: Figure 9.14c.

The slope of the line for CB with 0 wt% ds-GTR is slightly steeper then the
line for GT. As both are for SBR/BR blends, the difference in slope
indicates a difference in sensitivity for oxidation, which is to be attributed to
the influence of carbon black compared to the silica-silane filler system. As
according to Shelton[5] carbon black has an inhibiting effect on the oxidation
reactions under the test conditions, the effect is even stronger for the
silica-silane filler system.

As the slope of increase of M25 per unit time is steeper for both CB and GT
blends with an increasing amount of ds-GTR, this influences the amount
and rate of increase of the network density and thus the sensitivity of the
blend for oxidation.

(a) UT: M25 versus time

(b) CB: M25 versus time

(c) GT: M25 versus time
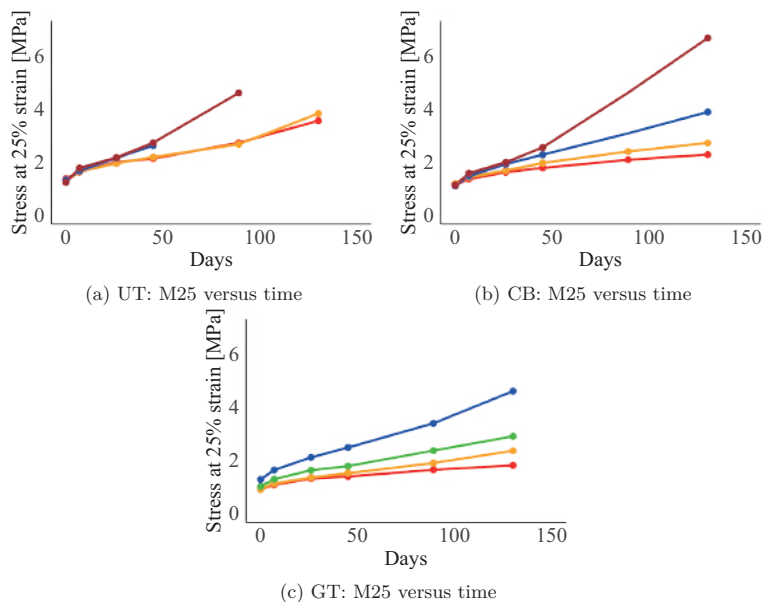
Legend: Amount ds−GTR — 0% — 10% — 20% — 30% — 50%
(CB, UT 0%, 10%, 30% and 50%, GT 0%, 10%, 20% and 30%).

FIGURE 9.14: Modulus 25 against time for blends with ds-GTR during static aging at 80 °C.

A most likely reason is the relative decrease of the amount in the protection systems for oxidation per amount of rubber: the rise of M25 as shown for CB with 50 wt% ds-GTR is more to be expected, where a depletion of the oxidation protection system is shown by an increase in the rate of oxidation after 50 days.

The NR based UT shows an oxygen absorption capacity for up to 10 wt% ds-GTR without a clear influence on the increase of the network density. However, the rate of increase of M25 for UT with 0 wt% ds-GTR is already at the level of the SBR/BR compounds with 10 wt% ds-GTR.

The slope of increase of M25 per unit time for both UT blends with 30 wt% and 50 wt% ds-GTR looks rather similar to that of the CB blend with 50 wt% ds-GTR, although the samples fail after a shorter time. This indicates that the NR based UT blend is more sensitive to higher amounts of ds-GTR.

As indicated by Shelton[5], the balance between chain scission and recrosslinking depends on temperature and the kind of polymer. An increase in modulus indicates an increase in network density due to a high degree of recombination of polymer chain fragments. The lines for 0 wt% ds-GTR show that the balance shifts toward scission-recrosslinking at the aging temperature, and more so for the NR-based UT compound than for the SBR-based CB and GT compounds.

As the modulus 25 % is more or less linearly related to the network density in rubber[12], this shows that the network density of the UT compound increases faster than that of the other virgin compounds. This indicates that the NR based UT blend is more sensitive towards higher amounts of ds-GTR where ds-GTR increases of the network density.

**Rates of change of tensile strength and strain at break**

To compare changes in parameters of different scales, e.g. tensile strength or strain, the parameters can be normalized or standardized by dividing them by a characteristic dimension, so the critical dimensions are of the same magnitude[13]. In the present case, the maximum values of the tensile strength and the strain at break for each compound and blend at day 0 are chosen to divide by, so all values of the normalized tensile strength or strain at break are dimensionless and a fraction of the maximum value, in the range of $0\,[-]$ to $1\,[-]$:

$$TSnorm_{c,a} = \frac{TS_{c,a}}{max(TS_{day=0,c,a})} \qquad (9\text{--}12)$$

and similar for the strain at break:

$$SBnorm_{c,a} = \frac{SB_{c,a}}{max(SB_{day=0,c,a})} \qquad (9\text{--}13)$$

with TSnorm the normalized strength, SBnorm the normalized strain at break, with index "c" = compound code in the range of CB, UT and GT, and index "a" = amount of ds-GTR in the blend, in the range of 0%, 10%, 20% (for GT only), 30% and 50% (for CB, UT).

To estimate the rate of change of these parameters, the change of the parameter in a certain time interval is to be divided by the length of the interval:

$$TSchangerate_{day(x),c,a} = \frac{(TS_{day(x),c,a} - TS_{day(x-1),c,a})}{(day(x) - day(x-1))}$$
$$\text{and}$$
$$TSchangerate_{day(0),c,a} = 0 \qquad (9\text{--}14)$$

$$SBchangerate_{day(x),c,a} = \frac{(SB_{day(x),c,a} - SB_{day(x-1),c,a})}{(day(x) - day(x-1))}$$
$$\text{and}$$
$$SBchangerate_{day(0),c,a} = 0 \qquad (9\text{--}15)$$

with TSchangerate is the rate of change of the normalized tensile strength, SBchangerate the change of rate of the normalized strain at break, with dimension 1/day and "x" = the index from 1 to 6 for the range of measurement days of (0, 7, 26, 45, 89, 130), with the index of day(0) = 0.

*Rate of change of normalized tensile strength v.s. time*   For the variations of the rate of change of the tensile strength over time, all compounds and blends show the overall tendency of large variations at the beginning to

small variations at the end of the aging, but no pattern can be distinguished in the influence of the amount of ds-GTR. For each type of compound however, there are clear differences for the instability of the rate of change and the duration of these, see Figure 9.15.



(a) CB blends

(b) UT blends

(c) GT blends
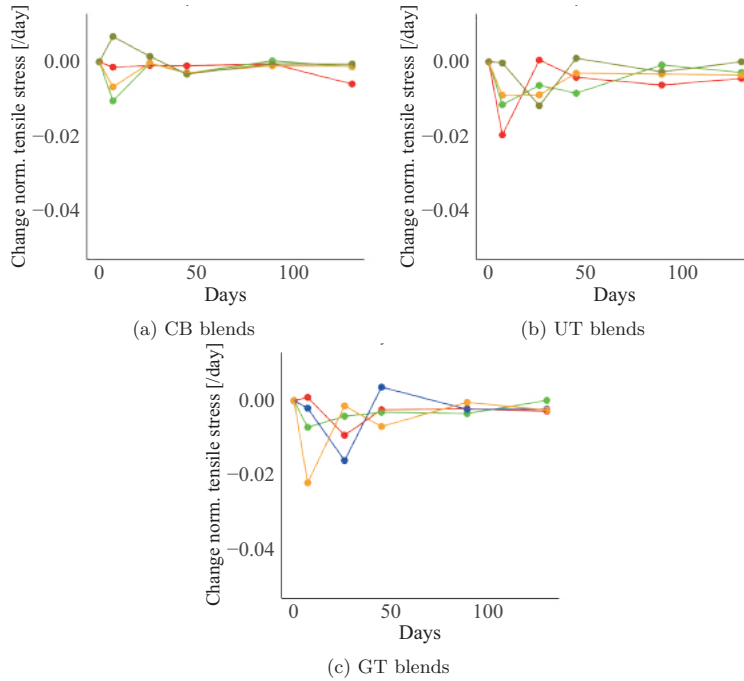
Legend: Amount ds−GTR ● 0% ● 10% ● 20% ● 30% ● 50%
(CB, UT 0 %, 10 %, 30 % and 50 %, GT 0 %, 10 % and 30 %).

FIGURE 9.15: Rate of change of normalized tensile strength for blends of the compounds with ds-GTR during static aging at 80 °C.

*Rate of change of normalized strain at break v.s. time* As for the variation of the rate of change of the strain at break over time, a clear pattern is shown: all compounds and blends show the overall tendency of large, consistent variations up to 26 days, reducing to the end of the measurements: Figure 9.16.

For the CB and GT compounds, at 9 days the change of rate for the blends is larger than the compound without ds-GTR and relative to the amount. On the contrary, for the UT compound, the variation of the rate of change is less prominent and not consistent with the amount of ds-GTR.

For all three compounds and their blends, the presence of ds-GTR after 26 days has hardly any influence, the decrease in strain at break is concentrated in the first 9 days to 26 days. Both SBR/BR based tread model compounds CB and GT are sensitive to the amount of ds-GTR: it increases the initial speed of hardening. For the NR based UT model

compound there is no clear, consistent, influence of the amount of ds-GTR on the initial speed of hardening: the tendency is to decrease it.



(a) CB blends



(b) UT blends



(c) GT blends
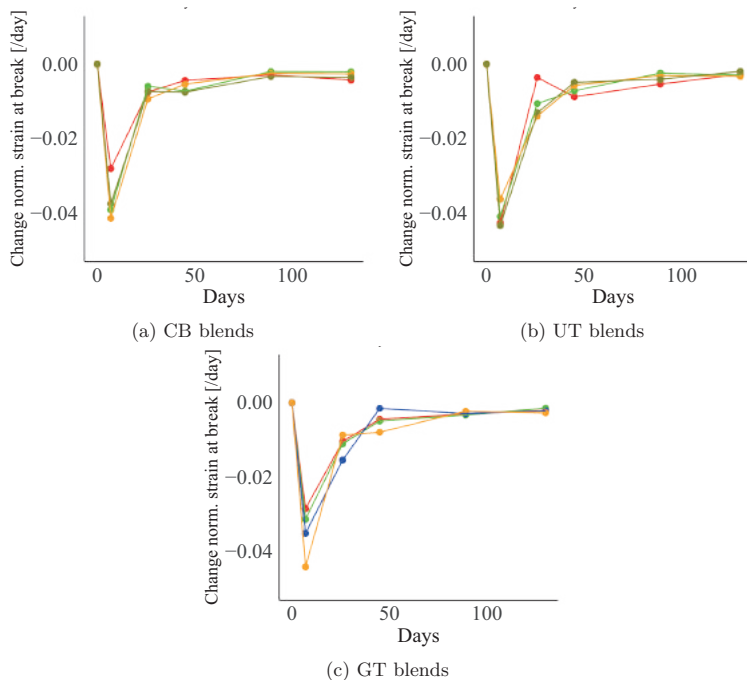
Legend: Amount ds−GTR  ● 0%  ● 10%  ● 20%  ● 30%  ● 50%
(CB, UT 0 %, 10 %, 30 % and 50 %, GT 0 %, 10 %, 20 % and 30 %).

FIGURE 9.16:  Rate of change of normalized tensile strain at break for blends of the compounds with ds-GTR during static aging at 80 °C.

**Hardness**

After an initial steep increase in hardness, for all compounds and the blends, the hardness keeps increasing, but at a lower pace. For the CB and UT compound, the initial hardness is not influenced by the amount of ds-GTR. For the GT compound however, the initial hardness increases with the amount of ds-GTR. For the CB and UT compounds, the increase of hardness becomes faster with the amount of ds-GTR. For the GT compound, there is hardly any influence of the amount of ds-GTR on the speed of the hardness increase . (Figure 9.17).

In one case, for the tensile strength of the virgin CB compound, the influence of the depletion of antioxidants could be observed.

In most other cases, however, the initial aging of the blends with ds-GTR outpaces that of the virgin compounds, indicating that ds-GTR is more susceptible to thermal oxidation than the virgin compounds, though it may also be due to a difference in the initial amount of antioxidants. After the initial stage, the blends age more slowly than the virgin compounds, as is

shown for the tensile strengths and strain at break of the UT and CB compounds. The prior aging of the GTR feedstock during service life for the ds-GTR might be the main cause of this. Interestingly, this is not observed for the modulus 25 or for the hardness, which is an indication of the different influences of aging on recrosslinking, shortening of the sulfur bonds, and chain scission.



(a) CB

(b) UT

(c) GT
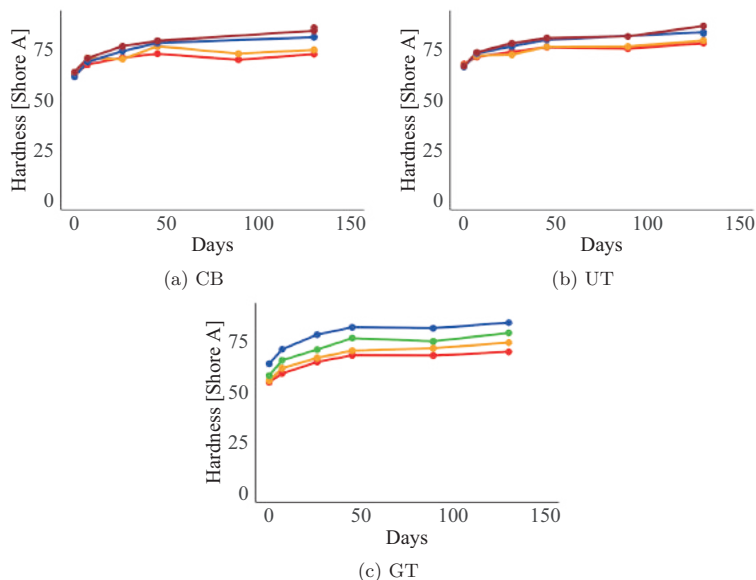
Legend: Amount ds−GTR ◆ 0% ◆ 10% ◆ 20% ◆ 30% ◆ 50%
(CB, UT 0 %, 10 %, 30 % and 50 %, GT 0 %, 10 %, 20 % and 30 %).

FIGURE 9.17: Hardness against time for a blend of compounds with ds-GTR for static aging at 80 °C.

It shows that the aging reactions are very diverse and depend highly on the composition of the virgin compounds. As mentioned by Shelton[5], the balance between chain scission and recrosslinking depends on the base rubber (NR or SBR) and on temperature. Because of the static nature of the test, influences of ozone on the aging processes can be considered to be negligible, as the oxidized surface layer is undisturbed[8].

It must be noted that, compared with other studies on aging, the chosen interval is relatively long. This has the advantage of emphasizing the differences, but the remaining properties of the compounds and blends are far beyond having any practical value.

## 9.4 Summary

In this chapter the application of silanized devulcanizate of whole passenger car tire rubber (ds-GTR) in blends with a carbon black SBR-BR-based tread model compound (CB), a carbon black NR-BR-based undertread model compound (UT), and a silica SBR-BR-based tread model compound

(GT) is investigated. The Non-aging related results are summarized in section 9.4.1 and those of Aging related results in section 9.4.2:

## 9.4.1   Non-aging related results

*Vulcanization* The influence on the curing behavior depends on the virgin compound: it strongly accelerates the curing of the carbon black-based tread compound, shows a slight acceleration of the carbon black-based undertread compound, and increases the torque difference for the silica-based tread compound.

*Morphology* The morphologies of the blends after vulcanization are similar to those of the devulcanized and subsequently revulcanized GTR, due to the amount of the silica-silane filler system related rubber components here in.

*Tensile strength* The blends with up to 30 wt% ds-GTR shows a tensile strength of 10 MPa to 12 MPa, almost independent of the tensile strength of the original blend.
For blends with 50 wt% this decreases to a tensile strength of 9 MPa to 10 MPa.

*Strain at break* Similar to the tensile strength: 250 % to 300 % for the blends with up to 30 wt% ds-GTR. This decreases to 220 % for a blend with 50 wt%.

*Rebound* The blends show a decrease of about 15 % in the rebound for the highest ds-GTR concentrations. The GT compound is most sensitive.

*Glass transition temperature* Both SBR-BR-based compounds, CB and GT, show a decrease in tan$\delta$ at $T_g$, but no shift in $T_g$ for blends with up to 30 wt%. For the UT compound, the influence on tan$\delta$ is small, and $T_g$ shifts from $-60\,°C$ to $-50\,°C$ for 50 wt% of ds-GTR.

## 9.4.2   Aging related results

The aging behavior of the CB, GT and UT compounds is very different. The influence of ds-GTR is strongly related to the type of compound, SBR/BR or NR based, but also of the filler system, carbon black or silica-silane based. Most of the aging, with the largest change in properties, is concentrated in the first 9 days of the experiments. This indicates that not the amount of oxidation protectors, but the relative availability of oxidizable molecular bonds and - groups is the more relevant parameter.

*Modulus 25:* For the CB and GTcompound, M25 increases with the amount of ds-GTR, with a maximum of twice of the base level for 30 % ds-GTR. For the blend of GT with 50 wt% ds-GTR M25 increases to 200 %.
For the UT compound there is no significant influence on M25 for a blend with 10 %. M25 only increases up to 100 % for an amount of 30 wt% to 50 wt% of ds-GTR, with the remark that the samples with 50 % ds-GTR failed at 89 days.

*Tensile strength:* For the rate of change of the normalized tensile strength it is shown that there is no pattern in the influence of the amount of

ds-GTR. However, the variation in results is rather high for the first 50 days. See Figure 9.15. This indicates that small inhomogeneities in the compounds and blends have a relatively large influence on the aging behavior of the tensile strength.

*Strain at break:* Apart from the high rate of change of the strain at break during the first 9 days, the values clearly show the influence of the model compound on the effect of blending with ds-GTR: for the NR based UT/ ds-GTR the rate of change decreases, see Figure 9.16b, while for the SBR/BR based model compounds CB/ ds-GTR and GT/ ds-GTR, the rate of change increases. For the CB blends it is the presence of ds-GTR while for the blends of GT the increase is more or less relative to the amount of ds-GTR, see Figures 9.16a and 9.16c.

*Hardness:* Concerning the hardness, for both carbon black filled compound CB and UT, there is no influence of the amount of ds-GTR on the initial hardness, but it is on the increase of the hardness in time. See Figures 9.17a and 9.17b. For the silica-silane filler based GT, the effect of ds-GTR is the opposite: an increase in the initial hardness relative to the amount of ds-GTR but no increase in the rate of change compared to that of the compound without ds-GTR. See Figure 9.17c

## 9.5   Conclusions

Overall: The addition of ds-GTR up to 30 wt% for CB and UT and 20 wt% for the GT compound has a limited influence on most properties of the blend. As each compound reacts differently to blending with ds-GTR, each blend of a compound with ds-GTR needs to be optimized to achieve the best properties. With respect to aging, the effect of the addition of ds-GTR is best to describe by that it increases the rate of recrosslinking during the first 9 days of the 130 days of the measurements.

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# Chapter 10

# The influence of resins on the devulcanization and revulcanization of tread compounds

*Recently, the use of oligomeric resins in modern tire tread compounds has become customary to improve tire performance further. Therefore, based on the experience with the change from carbon black to silica-silane filler reinforcement which led to a different network structure and a significantly changed devulcanization behavior, the influence of resin addition also deserves an extra look.*

*The influences on devulcanization and subsequent revulcanization is studied of a silica-silane-based tread compound with 20 phr resin are studied with respect to processing, curing and the mechanical and dynamic properties of revulcanizates. The resin-containing devulcanizates show difficult processing behavior for the reason of tackiness. Tanδ at 0°C of the revulcanizates increase considerably compared to the original material; indicating improved wet grip when used in a tire tread. A marginal increase in tanδ at 60°C is also observed, which is an indication of a slight increase in rolling resistance. All other investigated parameters concerning the devulcanization and revulcanization processes and the properties of the revulcanized material change in a comparable manner as for a compound without resin.*

## 10.1   Introduction

A new development in passenger car tire manufacturing is the use of oligomeric resins in silica-containing tread compounds, to improve the durability of the tire, wet grip, and rolling resistance of the tire over a broader temperature range[1–7]. However, this might introduce similar effects on the reusability of end-of-life tires by devulcanization and subsequent revulcanization as were introduced by the use of silica for car tires: Considerable improvements in tire safety and driving economy. The silica car technology was introduced in the market about 25 years ago. The end-of-life passenger car tires produced according to these new formulations are now a substantial part of the shredded tire granulates as confirmed by the amount of silica in the granulates used in the present study and was discussed in Chapter 7. This is of increasing

importance due to the growing interest in the reusability of tire rubbers for new applications instead of incineration of the shredded tires.

An aspect of using resins in tire compounds is an increased $\tan\delta$ at $0\,°C$, an indicator of wet grip properties of tire compounds. $\text{Tan}\delta$ at $60\,°C$ is an indication of the rolling resistance of tire tread compounds. The increased use of resins is confirmed by resin suppliers[8], but not yet reflected in the literature on this topic. The basic characteristics on which the application of resins in rubber compounds are based, are the relatively high $T_g$ and the influence thereof on the compounds. The relatively high softening point and the influence on rolling properties of tires when replacing a part of the plasticisers in the compounds is another relevant parameter[9]. Further, commonly up to $1\,\text{wt}\%$ resins are used as a tackifier in green tread and undertread compounds for tires[10].

The topic studied in the present chapter is the influence of resins on the devulcanization and subsequent revulcanization properties of silica-reinforced tread compounds. Considering the presence of silica in GTR and the implications for reusability, the possible influences of resin containing compounds concerning processing during devulcanization and subsequent revulcanization, and mechanical and dynamical properties. For revulcanization $100\,\%$ devulcanizate was used.

## 10.2   Experiment

Four silica-silane-based tread model compounds were prepared: a reference compound (ref) and three resin-containing compounds, each with a different kind of resin: Resin A, Resin B and Resin C (see Table 3.2 for the specifications). Formulations and compounding procedures were based on the patent of Pille-Wolf[11]: The formulations for devulcanization and subsequent revulcanization are specified in Table 3.5, and processing for vulcanization took place according to the procedure in Table 3.9. The basic differences between the amount of plasticiser and resins is summarized in Table 10.1

**Table 10.1: Amounts of plasticiser and resins in the compounds without and with resin.**

| Compound | GT-ref [phr] | GT-A, B, C [phr] |
|---|---|---|
| Resin A, B, C | - | 20 |
| TDAE | 32.5 | 12.5 |

Substitution of oil by the same weight of resin.

All compounds were mixed using a Brabender 350S internal mixer and subsequently milled on a two-roll mill. . The compounds were vulcanized in $2\,\text{mm}$ thick sheets at $160\,°C$ for $t_{c,90}+2\,\text{min}$ using a Wickert laboratory press. For devulcanization, the test pieces were ground using a Fritz pulverette with a screen of $2\,\text{mm}$, and the fraction between $0.85\,\text{mm}$ and $2\,\text{mm}$ was separated using laboratory sieves. The granulate was devulcanization and subsequent revulcanization using a Brabender Plasticorder with a $50\,\text{ml}$ chamber. For devulcanization, the formulation mentioned in Figure 6.5 was used, and the

procedure as described in Table 3.18. The procedure for revulcanization was according to Table 3.16.

An RPA Elite from TA was used to measure the shear modulus of the devulcanizates at processing temperatures, for the analysis of the cure behavior, and subsequently to measure tan$\delta$ at 60 °C as an indicator of the rolling resistance for a tire tread compound based thereon. A Zwick tensile tester was used to measure tensile properties, a Zwick Shore A tester to measure hardness, a Zwick-Roell 5109 tester to measure rebound resilience, and a DMA VA 200 from Metravib to determine T$_g$ and tan$\delta$ between $-80$ °C and 80 °C. The morphology of the fracture surfaces of the tensile test samples was studied with a Keyence VHX 5000 microscope. A CAT60-FLIR infrared camera was used for thermal pictures. All equipment is further specified in Chapter 3.

## 10.3   Results and discussion

### 10.3.1   Processing

A definition of the different intermediate products from virgin rubber to revulcanized rubber is given below, and distinguished by green marking in Figure 10.1:

*Compound:* The composition of polymers, fillers, and all other ingredients after compounding, before vulcanization.

*Devulcanizate:* The material after devulcanization of the rubber granulate and post-processing.

*Compound for revulcanization:* The devulcanized material after compounding as preparation for revulcanization.

As an indicator of the processing properties of these intermediate products, the complex shear modulus versus temperature is measured using the RPA (see Figure 10.2). The results of the three intermediate products are discussed below.

**Compounds:** Figure 10.2a shows that the complex shear modulus decreases almost linearly with temperature. At about 150 °C, the onset of curing can be observed by a steep rise in the shear modulus. The shear modulus of the resin-containing compounds is slightly higher than for the reference, and from 100 °C onwards the shear modulus starts to deviate more because the softening points of the resins. The shear modulus of the compound with Resin A, with a softening point of 115 °C, is the highest. The softening point for Resin B is 85 °C and for Resin C it is 150 °C. As no significant change in shear modulus is observed at these temperatures, the softening point is of minor influence. Considering the measurement time of 30 min, the low mass of approximately 7 g and the large ratio between the surface and volume of the disc-like samples, it can be assumed that the shear modulus of the resins will decrease quickly after passing the softening temperature.

**Devulcanizates:** Figure 10.2b shows a similar pattern to the compounds, except:
- A steady decrease in shear modulus levels off at 100 °C, after which it does not decrease any further. The horizontal lines might result from
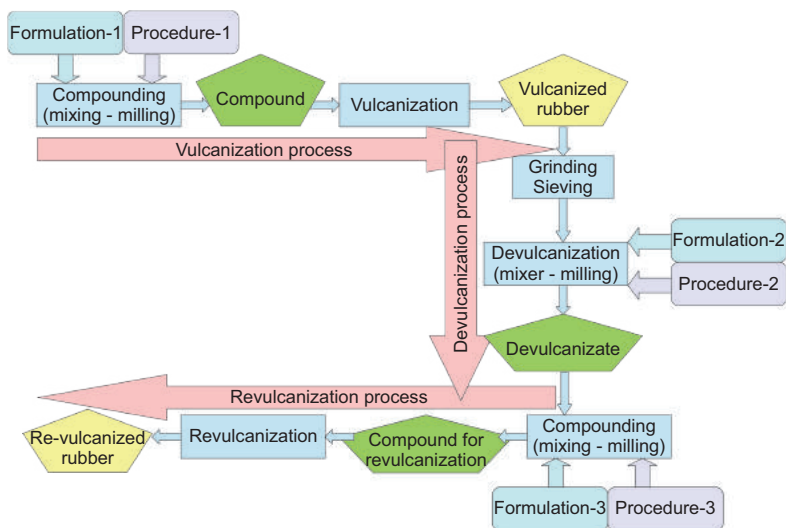
Definition of intermediate products in green pentagons:
For formulation 1, see Table 3.5, and for procedure 1, Table 3.9;
for formulation 2, see Figure 6.5, and for procedure 2, see Table 3.18;
and for formulation 3, see Table 3.5, and for procedure 3, see Table 3.16.

FIGURE 10.1: Devulcanization - revulcanization processes.

friction between the not fully devulcanized particles which increases with
temperature and at a certain point compensates for the temperature-
related decrease in modulus.

- No increase of the complex shear modulus at curing temperatures, which
  indicates that no remaining activity of the original curing system is left.
  This dictates the requirement curing formulation for revulcanization
  i.e. similar to the vulcanization formulation in the first curing before
  devulcanization.

**Compounds for revulcanization:** Figure 10.2c shows hardly any difference
between the curves for resins A and C. The onset of curing at about $140\,°C$
is clearly visible and the modulus shows a similar flattening at $100\,°C$ as was
seen for the devulcanizates. The overall level of the complex shear modulus
is lower than that for the devulcanizates. This is consistent with the decrease
in the size of the visible grains due to the further processing, as shown in
Chapter 8. It is also another indication that friction between the remaining
particles might play a role, as stated above.

As is shown for the compounds with Resin A in Figure 10.2d. The complex
shear modulus of the devulcanizate is not significantly lower than for the
compound. However, a large decrease in modulus is measured between these
two materials and the compound for revulcanization, as observed for the
devulcanized GTR (see Figure 8.13). This is due to the processing steps
that this material has undergone: silanization, compounding and the milling
steps. This indicates a decrease in size of the grains in the devulcanized
compounp before revulcanization compared with the devulcanizate. The

(a) Resin compounds

(b) Devulcanizates

(c) Compounds before revulcanization

(d) Resin A, all

Legend:
A, B, C, ref:     Resin type and reference without resin
GT:               Silica-silane based tread compounds
d-GT:             Devulcanizates
ad-GT:            Compounds before revulcanization
                  Compounds d- and ad-GT-B are missing due to lack of material
                  .
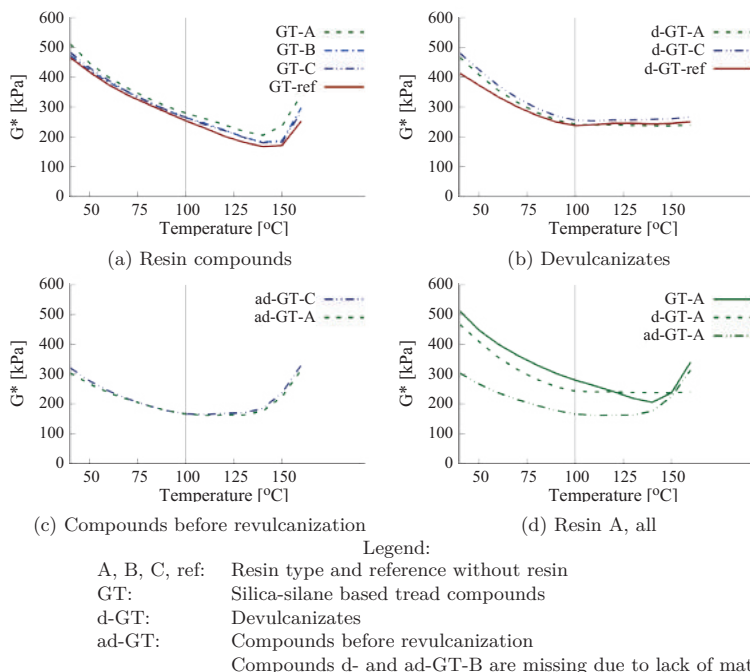
FIGURE 10.2: Complex shear modulus vs. temperature for
the silica-silane resin based tread compounds before vulcan-
ization, after devulcanization and before revulcanization, see
Figure 10.1

latter is already discussed in Chapter 8 (see Figures 8.1b and 8.1f). It can indicate a decrease in shear during the compounding procedure due to the lower viscosity of the devulcanizate. This is because of the increasing ratio devulcanizate vs. amount of rubber in the grains.

With respect to processing, the optimal milling temperature of the resin containing compounds for revulcanization, approximate room temperature, is lower than the $60\,°C$ for the reference compound. The tack of the compounds containing Resin A and Resin C was noticeable as the material sticks to the rolls of the mill. For the compound with Resin B, this was noticed at elevated temperatures, $40\,°C$ and higher. This tackiness to the rolls of the mill., combined with a decreased cohesive nature of the devulcanizates and hence the same for the compound for revulcanization, leads to difficulties in milling of the resins containing compounds for revulcanization; see Figure 10.3b for Resin C.

### 10.3.2   Curing

The cure curves of the compounds for first vulcanization show marching modulus for the first vulcanization, as is frequently seen for silica-silane-based compounds (see Figures 10.4a and 10.5a). The minimum torque of the compounds with resins is slightly higher than for the reference, as also corresponds with Figure 10.2a. This is due to the higher viscosity of the
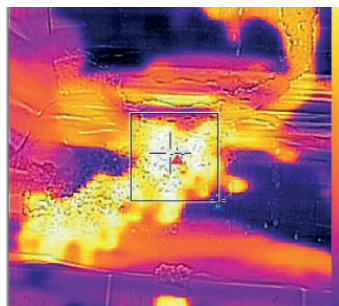
| Measurements [°C] | | | |
| --- | --- | --- | --- |
|  | Min | Mean | Max |
| Square: | 22.3 | 38.0 | 43.0 |
| Cross: | 42.7 | | |

(a) Thermo image of milling of
revulcanizate with Resin C.

(b) Milling of devulcanized compound
with Resin C as part of compounding for
revulcanization.

FIGURE 10.3: Processing on a mill of silica-silane based
devulcanized tread compounds with resins as part of the
compounding before revulcanization.

resins compared to the plasticizing oil. The torque differences at the end of
the measurement at 30 minutes indicate an effect of the resins on the crosslink
density or filler dispersion.

For the revulcanizates (see Figure 10.4b), the minimum torque is similar
for all compounds. The scorch time has decreased for all revulcanizates
compared to the first compounds. This indicates that some ingredients still
play an accelerating role in the revulcanization process. The cure curves
for vulcanization of the silica containing virgin compounds all show strong
marching modulus, Figure 10.4a. Those for the revulcanizates reach a
constant level, with the exception of the compounds with resins A and C,
which show reversion, while the curves for the revulcanizates of the reference
and the compound with Resin B still show marching modulus. It indicates
that resins A and C have a negative effect on the crosslinking process after
devulcanization, which is opposite to the influence on crosslinking in a virgin
compound, Figure 10.4b. All revulcanizates showed a decreased increment
between the minimum and maximum torque during curing compared with
the first compounds (Figure 10.5b). The decrease for the resins containing
revulcanizates is higher than for the reference. This indicates a negative
effect of the resins on the crosslinking of revulcanizates (see Figure 10.5b).

### 10.3.3   Morphology of the vulcanizate

As shown in Chapter 7, silica as an active filler causes a rather coarse
morphology of the revulcanizates. As is shown in Figure 10.6 of the fracture
surfaces of the tensile test pieces of the vulcanizates and revulcanizates, there
is no is clear difference seen between the morphologies of the resin-containing
revulcanizates and the reference: the morphology of the revulcanizates is
mainly determined by the silica rather than by the resins in the revulcanizates.

(a) Vulcanization

(b) Revulcanization

The legend is ordered from highest to lowest final torque

Curing at 160 °C
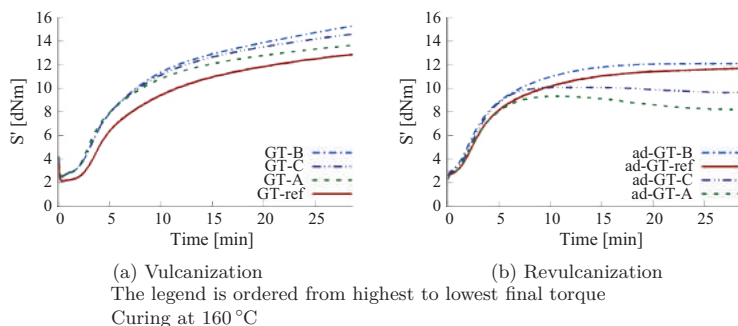
FIGURE 10.4: Cure curves of silica-silane based tread compounds with resins.



(a) Min. torque
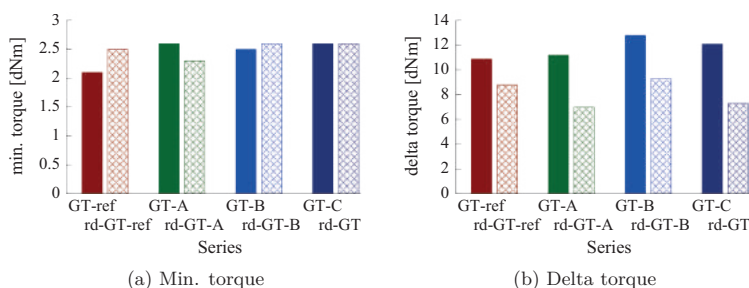
(b) Delta torque

FIGURE 10.5: Min. torque and delta torque values of cure curves of silica-silane based tread materials with resins.

## 10.3.4 Mechanical properties

Devulcanization and subsequent revulcanization seem to have hardly any influence on the tensile strength and strain at break (Figures 10.7 and 10.8). For all compounds, the differences are within error margins, even for the two compounds with Resin B, which show a large difference in tensile strength. The mutual differences between the compounds are also within error margins. Compared with the decreased tensile properties for silica-based revulcanizates relative to those of the virgin compounds, as described in Chapters 7 and 8 the data suggest a slightly positive influence of resins A and C on the tensile strength and strain at break of the revulcanizates compared with the first compounds: see Figure 10.7. Despite the tackiness of the compounds for revulcanization, the homogeneity in terms of stress-strain behavior of these revulcanizates turns out to be better than that of the compounds, see Figure 10.8. As seen in Figure 10.3b the presence of the resins in the compounds meant for revulcanizations causes tackiness to the mill rolls. This leaves the impression of inhomogeneity. But the reproducibility of the stress-strain results turned out to be real good anyway, see Figure 10.8

The hardness of all of the revulcanizates decreased by approximately 5 % compared to the original compound (Figure 10.9). The initial hardness of the compounds with resins B and C was slightly higher than that of the other compounds, but the reduction in hardness was similar to that of the other revulcanizates. This is similar to the reduction in delta torque for the

(a) Vulcanized ref compound

(b) Vulcanized compound Resin A

(c) Vulcanized compound Resin B

(d) Vulcanized compound Resin C

(e) Revulcanized ref compound

(f) Revulcanized compound Resin A

(g) Revulcanized compound Resin B

(h) Revulcanized compound Resin C
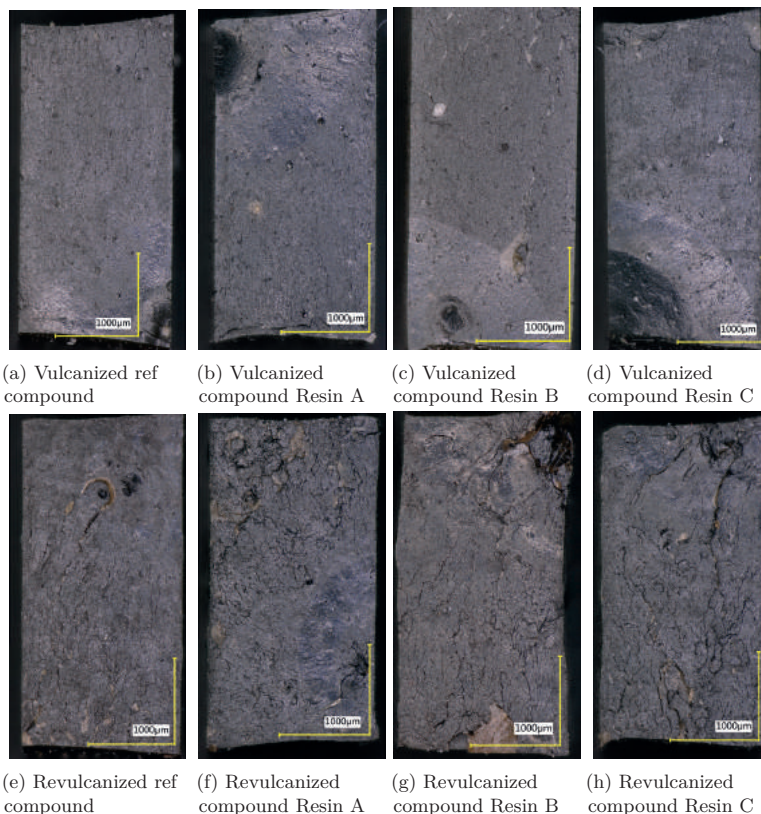
FIGURE 10.6: Morphology of resin containing compounds before and after devulcanization. Fracture surfaces of tensile test samples of vulcanized (a-d) and revulcanized (e-h) compounds.

revulcanizates, as indicated in Figure 10.5b.

## 10.3.5 Dynamic properties

As to the dynamic properties, all of the revulcanizates show a clear increase in the peak of tan$\delta$ at $T_g$ ( Figure 10.10). This is due to the recrosslinking reactions during devulcanization. This results in a more complex structure of the revulcanizates than the first compounds at a molecular level. It implies more energy dissipation, also indicated by an increased $T_g$: the revulcanized reference sample shows an increase in $T_g$ of 8 °C, the compound with Resin A an increase of 5.5 °C, the sample with Resin B only a minor change of 8 °C, and the material with Resin C an increase of 17 °C. This suggests differences in the homogeneity of the samples, most probably due to a difference in miscibility of the compounds and devulcanizates. As a consequence, tan$\delta$ at 0 °C increased for all of the revulcanized samples, indicating of improved wet grip for compounds based thereon. The resin containing revulcanizates showed a slightly increased tan$\delta$ at 60 °C compared with the reference without

Mean values of 5 samples; Error bars are plus/minus $2\sigma$
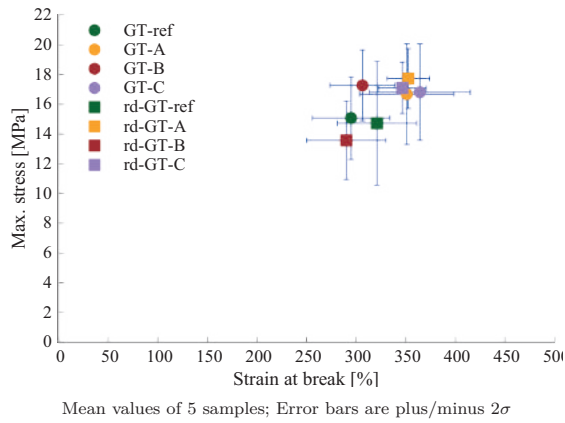
FIGURE 10.7: Tensile properties of silica based model compounds with resins after vulcanization and devulcanization-revulcanization



(a) Virgin compounds                    (b) Revulcanizates

One sample of each compound
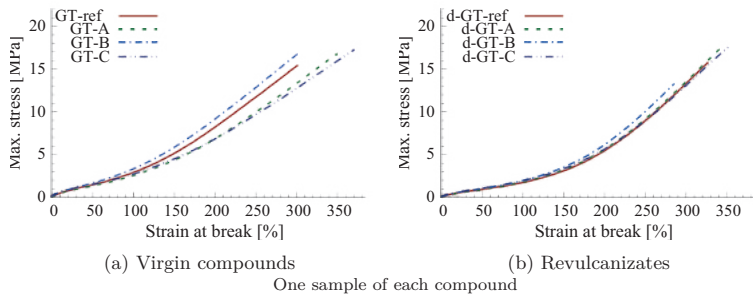
FIGURE 10.8: Tensile properties as graph of silica based model compounds with resins after vulcanization and devulcanization-revulcanization
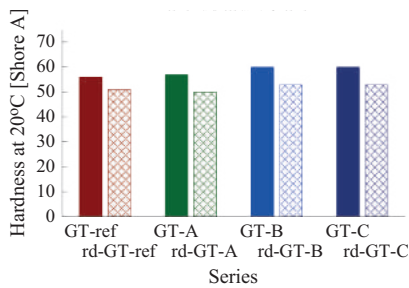


FIGURE 10.9: Hardness of silica-silane based tread compounds with resins before and after devulcanization

resin and the original vulcanizates with resin (see Figure 10.11 and Table 10.2), indicating slightly improved rolling resistance for compounds based on these.

The rebound test provides a fast indication of the energy losses during dynamic load. As is shown in Figure 10.12, the rebound values of the resin
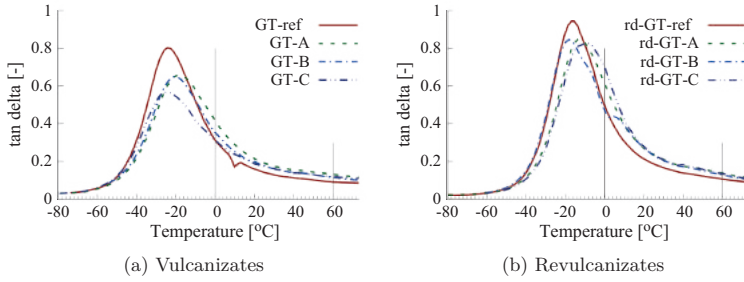
FIGURE 10.10: Tan$\delta$ vs. temperature of silica-silane based
tread compounds with resins, vulcanizates vs. revulcanizates
for all compounds
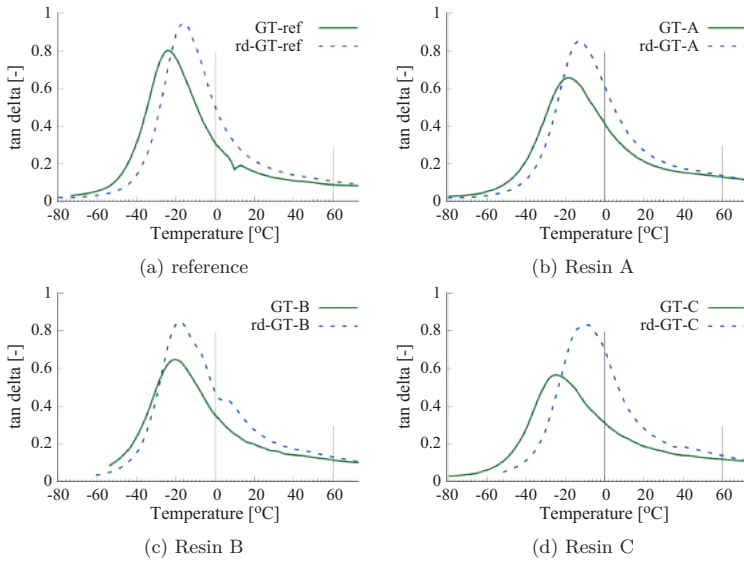


FIGURE 10.11: Tan$\delta$ vs. temperature of silica-silane based
tread compounds with resins, vulcanizates vs. revulcanizates,
for each compound separated.

containing vulcanizates are generally lower than the values for the reference.
This is consistent with the higher tan$\delta$ values at 20 °C, as shown in Figure
Figure 10.10a. A similar pattern is shown for the revulcanizates, with a slight
decrease in rebound values compared with the primary vulcanizates. This is
again consistent with the tan$\delta$ values at 20 °C as shown in Figure 10.10b.

Overall, the effect of resins on the dynamic properties of devulcanization
and subsequent revulcanization compounds is minimal. Only the wet grip
parameter is far better for the resin containing revulcanizates than the
reference.

**Table 10.2: Tan$\delta$ at T$_g$ of silica-silane based tread compounds with resins: vulcanizates vs. revulcanizates.**

| Resin | Vulcanizates | | | | Revulcanizates | | | | |
| | T$_g$[°C] | tan$\delta$ at: | | | T$_g$[°C] | tan$\delta$ at: | | | $\Delta$T$_g$[°C] |
| | | T$_g$ | 0 °C | 60 °C | | T$_g$ | 0 °C | 60 °C | |
|---|---|---|---|---|---|---|---|---|---|
| Ref. | −24 | 0.8 | 0.31 | 0.09 | −16 | 0.94 | 0.50 | 0.11 | 8 |
| A | −18 | 0.65 | 0.42 | 0.13 | −12.5 | 0.85 | 0.62 | 0.135 | 5.5 |
| B | −21 | 0.65 | 0.35 | 0.11 | −18 | 0.84 | 0.48 | 0.13 | 3 |
| C | −25 | 0.56 | 0.31 | 0.12 | −8 | 0.83 | 0.7 | 0.135 | 17 |

$$\Delta T_g = T_{g-revulcanizate} - T_{g-vulcanizate}$$
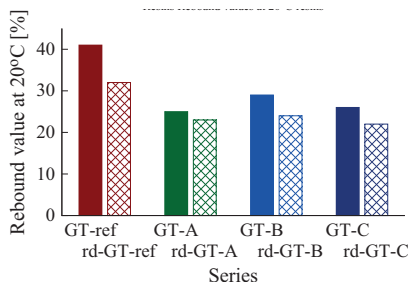


FIGURE 10.12: Rebound at 20 °C of silica-silane based tread compounds with resins before and after devulcanization.

## 10.4   Conclusions

Devulcanization and subsequent revulcanization of a compound influence the curing and the mechanical and dynamic properties, especially for a silica-containing rubber. Additional effects of resins in the compounds are listed below:

*Processing:* Milling of the devulcanizates after silanization and of the compounds before revulcanization all containing resins A and C, requires special attention because of tackiness to the rolls of the mill.

*Curing:* The cure curves for the virgin silica containing compounds with or without resins all show a strong marching modulus. Those for revulcanizates reach a constant level except of resin A and C, which even lead to reversion.

*Tensile properties:* Hardly any difference was noticed between the tensile properties of the compounds with resin and the revulcanizates.

*Hardness:* No additional increase in hardness was found compared to the reference revulcanizate.

*T$_g$:* A shift in T$_g$ by 3 °C to 17 °C between the vulcanized and devulcanized and subsequently revulcanized compounds is measured, depending on the resin type. The shift for the reference compound was 8 °C. This difference in T$_g$ shift is due to different structures of the networks.

*Tanδ at $T_g$:* The tanδ values at $T_g$ increase to a higher extent when the material is revulcanized for the compounds with resin, compared to the reference compound without resin.

*Wet grip:* The wet grip indicator, tanδ at 0 °C, indicates a considerable increase for the devulcanization and subsequent revulcanization compounds containing resin compared to the original material.

*Rolling resistance:* The rolling resistance indicator (tanδ at 60 °C) and the rebound values indicate a slight increase in this property.

*Processing:* The most important influence of the presence of 20 phr resins on the devulcanization process is the increased tackiness during the milling of the devulcanizate as part of the renewed compounding before revulcanization.

Although there are some additional influences on tanδ and $T_g$, the influences on the properties of the revulcanizates are relatively small, when compared with the impact of silica

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# List of Abbreviations

|        | prefixes as used for de- and revulcanizates |
|--------|---------------------------------------------|
| ad-    | devulcanized and subsequently addition of revulcanization materials |
| d-     | devulcanized |
| ds-    | devulcanized and subsequently silanized |
| rd-    | devulcanized and subsequently revulcanized |
| rds-   | devulcanized and subsequently silanized and revulcanized |

| | |
|--------|---------------------------------------------|
| **BAC**   | **Actual concentration in the main fraction** |
| **BIIR**  | **Bromo-isoprene** |
| **BR**    | **Butadiene Rubber** |
| **BRC**   | **Required concentration over the whole batch** |
| **B.V.**  | **Besloten Vennootschap, similar to Ltd or Inc.** |
| **CB**    | **Carbon Black, carbon black based model tread compound** |
| **CIIR**  | **Chloro-isoprene** |
| **DAE**   | **Distillate Aromatic Extract, processing oil** |
| **DBD**   | **2-2'-DiBenzamidoDiphenyldisulfide , anti-oxidant, devulcanization aid** |
| **DMA**   | **Dynamic Material Analyzer** |
| **DPDS**  | **DiPhenylDiSulfide , devulcanization aid** |
| **d-GTR** | **Devulcanized Granulated passenger car Tire Rubber** |
| **DPG**   | **1,3-Diphenylguanidine** |
| **DSC**   | **Temperature Differential Scanning Calorimeter** |
| **ds-GTR**| **devulcanized silanized Granulated passenger car Tire Rubber** |
| **ECHA**  | **European Chemicals Agency** |
| **ELT**   | **End of Life Tires** |
| **EPDM**  | **Ethylene-Propylene-Diene rubber** |
| **FTIR**  | **Fourier Transform Infrared Spectroscopy** |
| **GT**    | **Silica-silane based model tread compound ('Green tread')** |
| **GTR**   | **Granulated passenger car Tire Rubber** |
| **HA**    | **Highly Aromatic processing oil** |
| **HAF**   | **high abrasion furnace black, type of carbon black** |
| **IIR**   | **Butylene rubber** |
| **M25**   | **Modulus at 25 % elongation** |
| **M100**  | **Modulus at 100 % elongation** |
| **MBTS**  | **Mercapto BenzoTiazolediSulfide, curative** |
| **MDC**   | **Desired concentration in the main fraction** |
| **NaHClO**| **Sodium hypochlorite, active component of bleaching water** |
| **NaOH**  | **Sodium hydroxide** |
| **NR**    | **Natural Rubber** |
| **NWO**   | **Nederlandse Organisatie voor Wetenschappelijk Onderzoek, the Netherlands Organization for Scientific Research** |
| **PAH**   | **Polycyclic Aromatic Hydrocarbons** |
| **phr**   | **per hunderd rubber** |

| | |
|---|---|
| **px** | Area in pixels |
| **rd-GTR** | revulcanized devulcanized Granulated passenger car Tire Rubber |
| **SBR** | Styrene-Butadiene Rubber |
| **SPC** | Statistical Process Control |
| **TBBS** | N-tert-Butyl-2-BenzothiazoleSulfenamide, curative |
| **TDAE** | Treated Distillate Aromatic Extract, processing oil |
| **TDTBP** | Tris(2,4-Di-Tert-Butylphenyl)Phosphite, antioxidant |
| **TESPD** | bis[3-(TriEthoxySilyl)Propyl]Disulfide, coupling agent |
| **TESPT** | bis[3-(TriEthoxySilyl)Propyl]Tetrasulfide, coupling agent |
| **THF** | TetraHydroFuran, solvent |
| **TMQ** | 2,2,4-TriMethyl-1,2-Dihydroquinoline, antioxidant |
| **REACH** | A regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. |
| **RFID** | Radio Frequency Identification, used for product labeling |
| **RIVM** | Dutch National Institute for Public Health and the Environment |
| **RPA** | Rubber Process Analyzer |
| **S** | Sulfur |
| **SEM-EDX** | Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis |
| **St.A.** | Stearic Acid |
| **std** | standard deviation |
| **$T_g$** | Glass transition temperature |
| **TGA** | Thermo-Gravimetric Analysis |
| **$TiO_2$** | Titanium di-oxide |
| **TSE** | Twin Screw Extruder |
| **UT** | Undertread model compound |
| **WRA** | White Rubber Analysis |
| **ZnO** | Zinc oxide |
| **6PPD** | N-(1,3-Dimethylbutyl)-N'-Phenyl-p-Phenylenediamine, antiozonant |

# List of Figures

# List of Tables

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## Curriculum Vitea

Hans van Hoek was born in Amsterdam on 28th of Februari, 1956. He attended high school at the "Ignatius college" in Amsterdam. He continued education at the "Hogere scheepvaartschool voor scheepswerktuigkundigen" in Amsterdam and was employed as marine engineer for Shell Tankers from 1978 to 1980. Subsequently he obtained a masters degree in mechanical engineering, specialization measurement and control engineering, at the Technical University of Delft in 1986. He worked as a control engineer for Stork Amsterdam, department Food and Diaries industries, and for Stork Wärtsila. Here he continued as manager software engineering for the development of the control system of the Wärtsila diesel engines. In 2005 he got a position at the University of Applied Sciences Windesheim, Zwolle, as a teacher in mechanical engineering. In 2014 he joined the professorship for Polymer Engineering at Windesheim as teacher / researcher. This groups focuses on the sustainable use of raw materials and sustainable production processes. Recycling, environmental impact and energy savings are important areas of research. In October 2014 he started his PhD study on recycling of passenger car tire rubber by devulcanization in the Sustainable Elastomer Systems group, SES, at the University of Enschede, with Associate Professor W. Dierkes as promotor. SES as part of the Elastomer Technology and Engineering group, ETE, has a long standing expertise on devulcanization technology of rubber.

"*For every complicated problem there is a solution that is simple, direct and understandable...*

*but wrong.*"

H.L.Mencken

"*What makes us human is not that we influence our environment, like all living beings do,*
*but that we reflect on it.*"

Free to Adam Rutherford

"*An alternative way of defining gravity:*
*Everything likes to live where it ages the most slowly, and gravity pulls it there.*"

Prof. Kip Thorn, theoretical physicist

"*Science is like throwing stones into the water.*
*The best part is to make a postulate that leads to another one.*"

Free to Prof. Michal Ernée, pre-historian

# *Acknowledgements*

The start of this PhD traject is a story on its own, and it shows the team effort which has made this project successful:

This whole project would have been impossible if not for the policy of the Dutch government to promote the number of teachers with a doctoral degree at the Universities of Applied Sciences. Ineke van der Wal, then managing director of the school of Engineering and Design of Windesheim University, with her sound sense of politics, asked me my thoughts about a PhD traject. And so it started. Geert Heideman, associate lector of the professorship for Polymer Engineering still keeping a working relationship with then professor Jacques Noordermeer and dr. Wilma Dierkes of the Elastomer Technology and Engineering department (ETE) of the Tniversity of Twente, after taking his doctoral degree there, suggested I should meet Jacques and Wilma. Some weeks later they visited Windesheim, and to make the story short, Jacques asked me why I wanted to opt for a PhD study, as my hair was almost as grey as his. Anyhow, Wilma had a follow up project on tire recycling and the rest is history.

The second part of the story is even more important, as Windesheim could not supply all financial support. I do not know who all were involved in arranging the financial support, but Wilma, Geert, Margie Topp, lector of the professorship for Polymer engineering, were key players in writing the project proposal for the NWO scholarship for teachers. It was granted by NWO for 2 days per week, which was estimated to be insufficient for a study with so many practical experiments as the proposed topic would involve. I also should mention Alexander Jansen, managing director of Tech for Future TFF, and Herbert Schulze, then connected with Schill and Seilacher, for their efforts to make this project possible by additional support. And of course Sietse Dijkstra, manager of Engineering and Design, who made this project possible by rearranging my activities. Without this team effort, this project would have stranded before it even had started, I have to express my gratitude to everyone involved.

As Jacques accepted me as his PhD student, he was assigned as my promotor. However, soon he retired and Anke Blume, as the new professor of ETE, became assigned as my promotor. In the mean time, Wilme was appointed as associate professor at ETE and thus, the promotorship went over to Wilma. I must admit, it gave a sense of importance, being appointed to three promotors.

The members of the project team, Jacques, Anke, Wilma, Geert, Herbert, Alexander, Margie, Rikus Eising, former Dean of the department of Engineering Technology and now also connected to TFF, and Louis Reuvekamp, then appointed as staff member of ETE, they have seen me stumble, supported me, asked questions, and so on.

With the twin-screw extruder at the premises of the Polymer Science Park in Zwolle, the close working relationships with the colleagues there contributed to the success of the project too: Tonny van Dijk, then managing director, introduced me to then DSM-resins, now Alliancys-Zwolle, which proved itself a valuable contact. Mireille Kinket, Manita van der Ploeg, Gydo Willemsen,

all from PSP, with whom it was possible to organize working procedures and practical support in such a way, that operation of the extruder was possible, that not every time the building had to be evacuated because of smoke alarms, the occupants of the PSP building were not forced to wear gas masks because of the smell, etc.

Siti Saiwari who investigated the devulcanization of passenger car tires in the preceding project and whom's thesis I used as bible for my project, stayed for half a year in Enschede. Together we performed the first extruder experiments, published a paper and operated as a team. I still consider the offer to visit Thailand and revive their extruder. . .

Another group of important persons connected with this project are the students: the seven bachelor students, the four premaster students and the seventy-two students of the minor "polymer engineering", who performed a three day practical workshop on devulcanization and rubber vulcanization. I have learned a lot from them and their questions forced me to find answers on not expected problems. Two students I like to mention by name: Peter-Bas Schelling, who designed and built a calander for his final practical work to obtain his bachelor's degree in engineering at Windesheim, which proved to be an invaluable piece of equipment for the project; and Jiska Schuring, teacher at the University of Applied Sciences Hogeschool Utrecht and performing her practical work for her master's degree of education in chemistry at ETE. Professional and serious as chemists, we had a lot of fun by designing the setup of the glovebox for experiments with very smelly and very toxic chemicals. And it was a pleasure to see her working with the motley collection of glassware, containers, chemicals, cleaning stuff etc, as once the glovebox was closed, it could not be opened anymore before all experiments were done. Unfortunately her results did not made it as part of the present thesis.

There are many more people who made a valuable contribution to my project. First of all Nadia Vleugels, who learned me the basics of rubber processing, introduced me to the informal structure at the university and showed me the coffee-room in the basement. Jacob Lopulissa, former technical assistent of ETE, who teached me that an observation without a picture is scientifically not valid; Dries van Swaaij, later technical assistent of ETE, who became a good friend and with whom I had a pleasant working relationship as engineers among ourselves, and a walking encyclopedia for all kind of practical questions. And all Phd-students, PDIng-students and master students at ETE as colleagues, with whom we created a nice atmosphere in the group. Too many to mention, but with two of them there was a special relationship: Marzieh Salehi, joined ETE just after me and whom I could tease so nicely about the necessity of safety shoes, and Dorota Kokot, who supplied me a wall picture of a view at nature, when I could not occupy my favorite window seat anymore after an internal reorganisation. It are those small things that made life pleasant.

And of course Ceciel ter Horst-Strootman, department secretary of ETE and Wendy van Schooten-Delnay and Annechien Dijkstra administrative support for the professorship of Polymer Engineering, necessary for all those things that are to be dealt in order to get things going smoothly.

And last but not least, all my colleagues at Windesheim. The nice contacts I still could maintain, the interest in the progression of the project, it all made it possible to keep my attention focused.

After this long list of persons who contributed to the project, I have to mention some persons again: Jacques, as top dog quality controller, for the final finishing touch of all papers and the thesis; Margie, for her straight forward comments on the presentations and, above all, both my daily supervisors, Wilma and Geert. Invaluable for the progress and quality of the project.

This list is not complete without mentioning Geert, Wilma and Anke again for their support and continuing belief in me after my short but intense stay in the hospital. Anke to take me to Kuala Lumpur for the presentation at the IRC, after just being released from the hospital, and Wilma and Geert, never complaining but accepting my slow revalidation.

I thank you all.

# Appendices

# Appendix A

# Summary of tensile values

**Table A.1: Summary of tensile properties of revulcanizates**

| Revulcanizates of: | Revulcanization formulation, | Tensile strength [MPa] | Strain @ break [%] |
|---|---|---|---|
| **Devulcanization optimized for DBD** | | | |
| Blends of modelcompounds and ds-GTR | | | |
| Virgin GT compounds with | | | |
| 0 wt% to 20 wt% ds-GTR | 4 | 12 | 270-300 |
| Virgin UT and CB compounds | | | |
| with 0 wt% to 30 wt% ds-GTR | 4 | 11-13 | 270-290 |
| | | | |
| Blends of modelcompounds | | | |
| Blend of CB and GT with up to | | | |
| 5 wt% IIR | 4 | 12 | 350 |
| | | | |
| Modelcompounds | | | |
| d-GT compound with 20 phr resin | 3 | 13-18 | 300-370 |
| d-GT | 3 | 13 | 250 |
| d-CB | 1 | 14 | 330 |
| | | | |
| Revulcanization formulation with DGP and silane | | | |
| ds-GTR, best value | 3 | 8.5 | 140 - 170 |
| ds-GTR, mean value over 75 | | | |
| measurements | 3 | 5.5 | |
| | | | |
| Revulcanization formulation with DPG | | | |
| d-GTR , produced with DBD, | | | |
| best value | 2 | 6.5 | 180 - 220 |
| | | | |
| Revulcanization formulation based on carbon black based compound | | | |
| DGTR, produced with DBD, | | | |
| best value | 1 | 5.0 | 180 - 230 |
| | | | |
| **Devulcanization optimized for DPDS** | | | |
| Revulcanization formulation based on carbon black based compound | | | |
| d-GTR, produced with DPDS, | | | |
| best value | 1 | 3.5 | 250 |

Legend:

Revulcanization formulations:
- 1:        Carbon black based
- 2:        Carbon black based with DPG
- 3:        Silica based, with DPG and silane
- 4:        Mix of formulations in ratio of constituent compounds of the blend

| CB | Carbon black based model tread compound |
|---|---|
| UT | Carbon black based model undertread compound |
| GT | Silica based based model tread compound |
| IIR | Butyl rubber |
| d-CB | Devulcanized carbon black based model tread compound |
| d-GT | Devulcanized silica based based model tread compound |
| d-GTR | Devulcanized GTR |
| ds-GTR | Devulcanized and silanized GTR |

*Devulcanization is, with respect to recycling of rubbers, a promising technique. For passenger car tires, mainly consisting of blends of Styrene-Butadiene Rubber, Butadiene Rubber and Natural Rubber, a process on laboratory scale was developed by S.Saiwari in 2013.*

*The present thesis describes the scaling up of the earlier developed small scale process, the influence of specific compounding additives and required process adjustments, transformation into a continuous process and application development into newly produced tires.*

*Most important conclusion is that by separation of the silica containing tread compound from the remainder of the tire before shredding, the formulations and procedures for revulcanization can be tailored to the specific compounds. This results in better stress-strain properties compared to the revulcanized devulcanizate based on whole tire granulate.*

*With these results, reusing the rubber of end-of-life tires for qualitative demanding applications is at hand.*