

Circular loops for tire rubber: chances and challenges

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## ABSTRACT

Tires are very sophisticated high-quality products and constantly improved in terms of efficiency, safety and environmental impact. Many of the improvements are material-based. Examples of these developments are the replacement of aromatic oils by Treated Distillate Aromatic Extract (TDAE) to eliminate polycyclic aromatic compounds, the introduction silica-silane reinforcing systems for a higher fuel efficiency, and currently the introduction of resins for improvement of the wet grip and rolling resistance balance.

Unfortunately, so far tires are not designed for recycling and material reuse. Rubber is a very durable material, and this hampers the re-processing and re-use of rubber. Nonetheless, there is a variety of recycled rubber products on the market: granulate, powder, reclaim and devulcanizate. The latter is expected to give the best properties as such and in a blend with virgin rubber, as devulcanization is the reversion of the vulcanization process: it aims at breaking the sulfur bonds and keeping the polymer chains intact.

However, the fact that tires are built from different types of compounds containing different polymers and fillers limits the quality of the recycled material, as our study showed. Besides, the influence of a silica-silane reinforcing system impedes the controlled scission of the sulfur network. This results in an insufficient degree of devulcanization and, as a consequence, difficult processing and a low level of properties. Ways to overcome these drawbacks in devulcanization efficiency will also be discussed.

## INTRODUCTION

Devulcanization of rubber is a challenging process; devulcanization of tire rubber even more due to the complicated structure of tires and the blend of different types of compounds and polymers. Tires based on mainly natural rubber (NR) such as truck- and bus-tires are rather easy to devulcanize. For passenger car tire rubber this is more difficult as the main polymer is styrene-butadiene rubber (SBR). This polymer tends to recombine in an uncontrolled manner, which decreases the quality of the material. Besides, the presence of silica results in an additional filler-polymer network. The sulfur-bonds in the latter and in the polymer-polymer network differ in length, and this implies that they require different devulcanization conditions.

Next to this, the fact that tires comprise a series of different compounds does make the best possible devulcanization process just a best compromise for the breakdown of each separate part. Furthermore, the separate tire parts consist of compounds containing different polymers, each with its own specific devulcanization characteristics. The properties of the devulcanizate finally are given by the properties of the lowest quality component.

Other problems are related to origin of the feedstock: post-consumer sources such as worn-out tires contain contaminations originating from the use of the tire on the road, as well as from the grinding process such as cord fibres and steel.

Devulcanization is based on a devulcanization aid. This aid has certain requirements in terms of compatibility, processability and sustainability. The devulcanization process has to be tailored in terms of shearing forces, temperature profile and reaction time for the different process steps. Last but not least, post-processing might be necessary to further improve the devulcanizate properties and processability. Once the devulcanizate is optimized regarding all these aspects, the application has to be tailored as well in terms of compounding and processing.

Another challenge is the analysis of the devulcanizate. The more practical approach is to cure the devulcanizate and judge the quality in terms of strength properties. For a rubber manufacturer this is the most important information. However, devulcanizate is barely used as such; it is in general blended with a virgin compound. This blend, once again, has to be optimized concerning curing behavior, reinforcing system, and processing. For the development of the devulcanization

process, an analysis method elucidating the devulcanization mechanism and the ratio of polymer to crosslink scission is required. Generally, a Horikx-Verbruggen plot is used for this purpose, showing the correlation between sol content and degree of devulcanization. However, for whole tire material containing different types of fillers, this method is might not be accurate enough even when corrections for the presence of fillers are made.

In spite of all these challenges, devulcanization is a promising way to broaden the application area of recycled rubber in terms of processing, quality of the final product and quantity of recycled rubber that can be re-used.

This study focuses on tailoring the devulcanization process for whole passenger car tire rubber, facing the challenges of the presence of SBR and silica, and getting an easy processable devulcanizate. This process needs to be continuous in order to provide a product as homogenous as possible. Parameters to be optimized within the devulcanization process are shearing forces, residence time, temperature profile, addition and concentration the devulcanization aid, and presence of oxygen. The main challenge is to find the a good compromise of all these parameters to get the best devulcanizate properties in spite of the problems mentioned above.

## 2 THEORETICAL CONSIDERATIONS CONCERNING DISTRIBUTION AND DIFFUSION OF DEVULCANIZATION AGENTS INTO RUBBER GRANULATE

In an earlier study, 2,2'-dibenzamidodiphenyldisulfide (DBD) was found to be an efficient devulcanization aid for ground tire rubber (GTR) based on whole passenger car tires. DBD is a solid with a melting point above 140°C, and this causes processing problems: the extruder configuration requires in first instance to thoroughly mechanically blend DBD with the GTR, and secondly to raise the temperature to a level that the DBD melts and is can migrate into the particles. These elements of physical transport might pose practical limitations and need special considerations:

- The concentration of the devulcanization aid relative to the volume of the particles depends on the surface to volume ratio of the granulate. When added to the granulate, oil and devulcanization aid are distributed over the surface of the particles, and then migrate into the particles;
- The migration of the devulcanization aid and oil into the particles creates a time-dependent concentration gradient from the surface to the core of the particle

- Heating up the particles to the devulcanization temperature will as well create a time dependent temperature gradient

### 2.1 CONCENTRATION OF THE DEVULCANIZATION AID IN PARTICLES OF DIFFERENT SIZES

Assuming spherical particles, the surface to volume ratio between the largest (3.5mm) and the smallest (1mm) particles in this study is a factor of 3.5. The effect of surface roughness is neglected. When mixing GTR with the processing oil and devulcanization aid, the additives will initially be distributed over the surface of the granulate particles. Due to the higher volume to surface ratio of the larger particles compared to the smaller ones, the concentration of oil and devulcanization aid will be roughly only one third for the largest granulate particles compared to the smallest ones. On an average, a concentration of 5wt% of processing oil will be added, resulting in a concentration of 9wt% for the smallest and 2wt% for the largest size particles. Similar differences in concentration of the devulcanization aid apply: after migration of the devulcanization aid into the particles, the largest ones will experience a considerably lower concentration than the smallest. This will lead to an inherent inhomogeneity of the degree of devulcanization of the various particles.

### 2.2 CONCENTRATION GRADIENT OF DEVULCANIZATION AID IN A PARTICLE

When mixing the devulcanization aid with the granulate, the latter 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 the particle is assumed to be fixed<sup>1</sup>. However, this assumption is not correct, as the amount of liquid at the surface of a the particle will decrease while it diffuses into the particle. Based on the requirement that devulcanization aid and oil have to migrate into the GTR, it takes much longer for a large particle until the center is reached.

Bouvier<sup>2</sup> has investigated the migration of a heavy oil into SBR as a function of temperature. 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 to equilibrium  $t_{\mathbb{D}}$  as:

$$t_{\mathbb{D}} = R_0^2 / \mathbb{D} \quad (1)$$

with  $R_0$  the radius of the sphere.

With Equation 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 I.

Table I

Diffusion coefficients  $D$  and calculated diffusion times until equilibrium versus temperature for oil in styrene butadiene rubber (SBR) for particles of 2 and 3 mm.

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

The values in Table I show, that at a devulcanization temperature of about 200°C, the diffusion time till equilibrium for the larger particles is of the same order as the residence time in the extruder, about 6 minutes. At 163°C, still above the melting temperature of DBD, the diffusion would take up to 22 minutes, unacceptably long for an extruder process. Hence, although it is an estimation of the order of magnitude only, the migration times in the extruder have to be taken into consideration when tailoring the process parameters.

### 2.3 TEMPERATURE GRADIENT IN A PARTICLE

The temperature gradient in a sphere as a function of the time follows a similar relation as the concentration gradient<sup>1</sup>. An estimation can be made for the required time for the center of a particle of the granulate to reach a certain temperature, assuming the same spherical nature of the granulate. As an example, a calculation is made to reach a temperature of 200°C throughout the granulate, with an initial temperature of the granulate of 30°C and a temperature setting of the extruder of 220 °C. According to <sup>1</sup>, the following temperature ratio has to be calculated with Eq. 2:

$$\frac{T-T_0}{T_1-T_0} = 0.89 \quad (2)$$

with  $T_0$  the initial temperature of the granulate,  $T_1$  the temperature at the surface for  $t>0$ , and  $T$  the temperature at the center. Based on the master curves presented in<sup>1</sup>, 0.89 correlates with a

value of  $\alpha t/R^2 \approx 0.35$ , with  $\alpha$  the heat transfer coefficient,  $t$  being time and  $R$  the radius of the granulate.

For SBR, a major component of the granulate, it can be calculated that  $\alpha = \frac{\kappa}{\rho} \cdot c = 1.06 \cdot 10^{-7} \text{m}^2/\text{s}$ , with  $\kappa$  the thermal conductivity =  $0.2 \text{W}/\text{m} \cdot \text{K}$ ,  $\rho$  the density =  $940 \text{kg}/\text{m}^3$ ,  $c$  the specific heat capacity =  $2 \text{kJ}/\text{kgK}$ . For larger particles with a diameter  $2R$  of  $3 \text{mm}$ , the time until the center has reached a temperature of  $200^\circ\text{C}$  with the extruder set to  $220^\circ\text{C}$  can be calculated as:

$$\frac{\alpha t}{R^2} = 0.35 \rightarrow t \approx 7,5 \text{ seconds} \quad (3)$$

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

### 3 EXPERIMENTAL

#### 3.1 MATERIALS

The Ground passenger car Tire Rubber (GTR) used in this investigation was obtained from Genan, Dorsten, Germany. It is a commercial passenger car tire rubber granulate, medium grade in terms of granulometry, with a normal size distribution between 1 to 3.5 mm. After analysis with a set of laboratory sieves, a detailed size distribution is given in Table II. As it is a blend of different types of tires, the composition might vary, but it contains at least 45wt% polymer, of which 10-35wt% Natural Rubber (NR), and an ash content of at least 10wt%, according to the technical data sheet<sup>4</sup>. This GTR type was selected based on a low level of contaminations such as stones originating from

- contaminations adhering to the tires before granulating
- steel originating from both remaining steel of the bead wire of the tires and the grinding dust of the cutting and grinding equipment
- dust from the fibers in the tire carcass

The coarser grades usually contain higher levels of steel and fibers remaining in and adhering to the particles. The finer grades usually contain higher amounts of remaining steel and stone dust. By visual inspection, the selected granulate size contained a minimum amount of these contaminations. All other materials used in this study are listed in Table III.

Table II

Size distribution of the GTR after analysis with laboratory sieves.

Size Sieve mesh [mm <sup>2</sup> ]	Amount [wt%]
<0.85	negligible
0.85<...<2	80
2<...<3.5	19
>3.5	1

### 3.2 EQUIPMENT

The overall setup of the installation is shown in Figures 1 to 3. The 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-aeration positions between the supply funnel and outlet, as is shown in Figure 1. An elongated die was employed, with dimensions of a rounded rectangular slit of 20mm × 40mm and a length of 100mm, as can be seen in Figure 3. The extruder was operated with a screw speed of 10 to 30 rpm. At 20 rpm, the overall residence time of the devulcanizate in the combination of extruder and elongated die was approx. 12 minutes. At this speed, the pressure in the extruder just before the die reached a maximum of 5.3 MPa, depending on the temperature settings of 180 to 220°C in the devulcanization section, see Figure 1. The extruder was operated at 70 to 80% of the maximum torque. In order to minimize oxidative degradation during the devulcanization, the extruder was equipped with a nitrogen supply, placed in the supply funnel, at the end of the devulcanization section and at the end of the extruder just before the die, see Figures 1 and 2b. The devulcanizate was transferred to a specially constructed cooling calendar<sup>5</sup>, positioned directly behind the extruder, see Figure 2a. This calendar instantly cooled down the devulcanizate to 40 to 60°C to prevent oxidation. The capacity of this line was approximately 2kg/h at 20rpm.



Table III  
Materials.

Designation	Supplier
<u>Devulcanization agent:</u>	
DBD 2-2'-DiBenzamidoDiphenyldisulfide	Schill and Seilacher GmbH, Boeblingen, Germany
<u>Anti-oxidant:</u>	
TDTBP Tris(2,4-Di-Tert-Butylphenyl)Phosphite	Sigma Aldrich Cooperation, Zwijndrecht, The Netherlands
<u>Processing oil:</u>	
TDAE Treated Distillate Aromatic Extract, VIVATEC 500	Hansen & Rosenthal, Hamburg, Germany
<u>Solvents for Horikx analysis:</u>	
Acetone purity >99.5wt%	Atlas & Assink Chemie b.v., Enschede, The Netherlands
THF TetraHydroFuran, purity >99.8wt%	
Toluene purity >99.8wt%	
<u>Polymers and fillers:</u>	
BR Butadiene Rubber grade BUNA CB24	Arlanxeo Deutschland GmbH, Leverkusen, Germany
TiO <sub>2</sub> Titanium diOxide, Hombitan R210	Venator, Wynyard, UK
<u>Vulcanization system:</u>	
ZnO Zinc oxide	Merck KGaA, Darmstadt, Germany
St.A. Stearic acid	
S Sulfur	J.T.Baker
TBBS N-Tert-Butyl-2-BenzothiazoleSulfenamide	Lanxess Rhein Chemie GmbH, Cologne, Germany
MBTS 2,2'-DiBenzoThiazyl diSulphide	
DPG 1,3-DiPhenylGuanidine	
<u>Coupling agent:</u>	
TESPT bis[3-(TriEthoxySilyl)Propyl] Tetrasulfide	Evonik Industries AG, Essen, Germany
<u>Cleaning chemicals for the extruder ventilation:</u>	
NaOH technical quality	Sigma Aldrich Cooperation, Zwijndrecht, The Netherlands
NaHClO bleaching water, 2%	Household quality

Mixing of the GTR with the processing oil, DBD and an anti-oxidant was performed manually for a maximum batch size of 7 liters of GTR. A Brabender Plasticorder internal mixer with a chamber

volume of 50ml was used for compounding for de- and revulcanization. A Schwabenthan laboratory mill of 200mm length, a diameter of 80mm and a friction ratio of 1.13 was used at 22rpm for the final milling of the devulcanizate and for all milling after mixing. The cure characteristics were measured with a Rubber Process Analyzer, RPA Elite, from TA Instruments at 170°C, 0.833Hz, and 2.89% strain according to ISO 6502. For revulcanization of the devulcanizates, a Wickert WLP1600 laboratory compression moulding press was used at 170 °C for a period of  $t_{c,90} + 2$  minutes, using a mold of 100x100x2mm. Tensile testing was done with a Zwick BZ1.0/TH1S tensile tester.

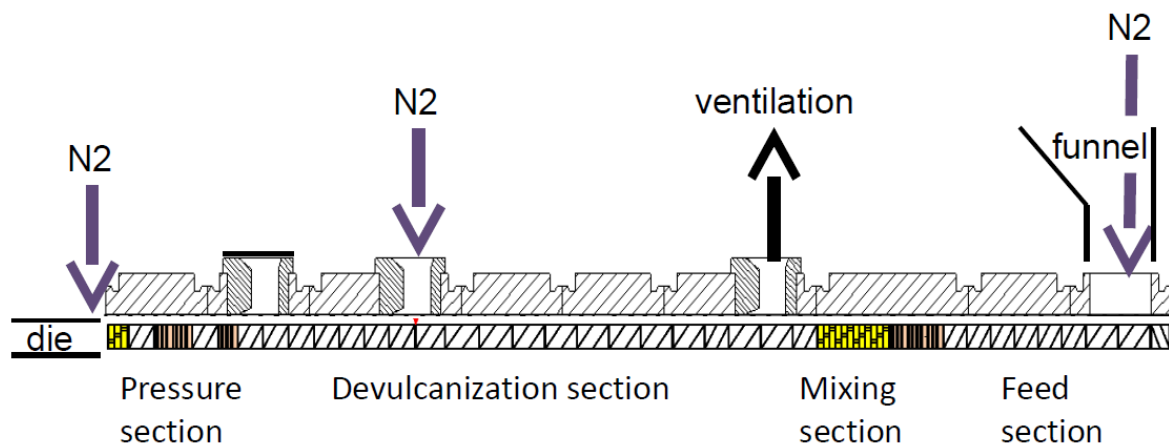


Figure 1: Layout of the extruder, from right to left, with an example of a low shear screw and nitrogen supply positions.

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.

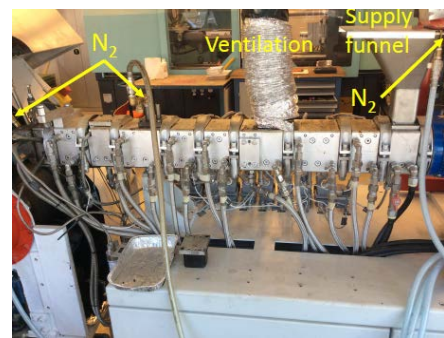


Figure 2: Extruder installation.

Left: extruder with calendar and ventilation, right: extruder with supply funnel, ventilation point and nitrogen supply.



Figure 3: Elongated die.

### 3.3 ANALYSIS METHODS FOR QUALITY OF DEVULCANIZATES

In order to quantify the amount of random polymer scission versus crosslink breakdown, the method of Verbruggen was employed, based on the Horikx<sup>6</sup> theory for polymer network breakdown by highly energetic radiation. This is based on plotting the amount of polymer that can be dissolved from the network versus the relative decrease in crosslink density after the treatment, see Figure 4. The network densities are calculated by the Flory-Rehner equation<sup>7</sup>, which was originally derived for unfilled polymer networks. Kraus<sup>8</sup> and Porter<sup>9</sup> have shown that this method is also applicable for carbon black filled rubber and derived a correction factor for the amount of filler. Verbruggen<sup>10</sup> has shown that the method can be applied for more complex single polymer networks as well such as EPDM for roofing applications. The soluble fraction, sol, was calculated by extraction of the samples with acetone and subsequently with THF in a Soxhlet, drying and weighing before and after the extraction. After swelling of the extracted samples in toluene, the crosslink density can be calculated from the amount of adsorbed liquid using the theory of Flory-Rehner, with the corrections derived by Kraus and Porter.

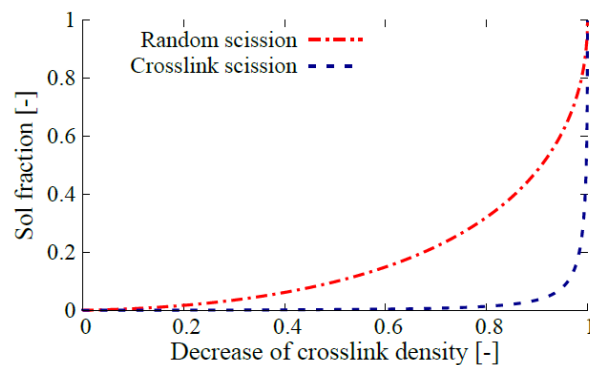


Figure 4: Horikx-Verbruggen diagram: correlation for random scission and crosslink scission.

The devulcanizates were compounded according to the formulations in Table IV and revulcanized. Formulation 1 is based on a passenger car tire tread under the assumption that the devulcanizate is fully carbon black based. The corresponding compounding procedure is described in Table V. Formulation 2 is based on the assumption that there is also silica present to a large extent. The corresponding compounding procedure is given in Table VI. Subsequently, the compounds were vulcanized at 170°C under pressure in a Wickert press for  $t_{90}+2$  minutes, using a mold of 100\*100\*2mm. Modulus, tensile strength and elongation at break of revulcanizates were tested according to ISO 37 type II with a speed of 50mm/min.

Table IV  
Revulcanization formulations, values in phr.

Formulation nr.	1		2	
	DGTR re-vulcanizate(2)	DGTR re-vulcanizate(3)	A	B(4)
Component:				
Polymer (1)[x]	[100]	[100]	[100]	[100]
ZnO	3.0	2.5	2.5	
St.A.	2.0	1.0	1.0	
TDAE[x]	[42.7]	[42.7]	[42.7]	[42.7]
Carbon black[x]	[80]	[54]	[54]	[54]
Silica[x]		[42](5)	[42](5)	[42](5)
TESPT		3.2	3.2	
6PPD	1.0			
TMQ	2.0			
TBBS	1.5	1.64	4.64	
DPG		2.8	2.8	
Sulphur	1.5	1.64	4.64	

DGTR: Devulcanized Ground passenger car Tire Rubber

[x] Components present in devulcanizate

(1) Total polymer content of (D)GTR, a mix of mainly SBR, BR and NR

(2) Revulcanization formulation for a carbon black based tread formulation

(3) Revulcanization formulation for a silica based tread formulation

(4) Additional sulfur and TBBS for revulcanization

(5) Optimized in earlier experiments

Table V  
Compounding procedure for Formulation 1.

Time [minutes]	Mixer settings	Time [minutes]	Processing steps
	Brabender internal mixer	0	Mixer set at 50rpm,
	Chamber volume: 35ml	1	ZnO + stearic acid,
	Fill factor: 0.6	4	TBBS
	Initial mixer temperature of 80 °C.	4.5	Sulphur.
	Mixer set at 5rpm rotor speed.	5	Dump.
	<u>Addition of curatives.</u>		Thoroughly homogenized and sheeted off on the mill.
	Mixing order:		Relaxation for 24 hours.

Table VI  
Compounding procedure for Formulation 2.

Time [minutes]	Mixer settings and processing steps	Time [minutes]	Mixer settings and processing step
	Brabender internal mixer		Initial mixer temperature of 50 °C and 5rpm rotor speed.
	Chamber volume: 35ml		The silanized devulcanizate was added at 5rpm rotor speed.
	Fill factor 0.6		<u>Addition of curatives.</u>
	The mixer temperature was set to 145 °C.	0	Mixer set at 50rpm rotor speed.
	The devulcanizate was added at 5rpm rotor speed.	0.5	ZnO + stearic acid,
	<u>Silanization.</u>	1	TBBS + DPG,
0	Mixer set at 50rpm rotor speed.	1.5	Sulphur.
1	Silane.	2	Dump.
5	Dump at ±145 °C.		Thoroughly homogenized and sheeted off on the mill.
0	The devulcanizate was cooled down to 60 °C and milled with a gap-width of 0.1-0.5mm.		Relaxation for 24 hours.
5	Sheeted off at 2mm.		
	Relaxation for 72 hours.		

The White Rubber Analysis (WRA) is used to visualize the morphology of the devulcanizate. In the ideal case, the devulcanizate would be a smooth, homogenous material like virgin compounds. However, this is in actual practice barely achieved; the devulcanizate has a grainy structure. By blending it with a bright white compound, the remaining particles show as black grains in the matrix. The shade of grey of the matrix gives a qualitative indication of the devulcanization depth of the particles; it is the rubber that is easily sheared off the non-devulcanized cores.

## 4 RESULTS AND DISCUSSION

### 4.1 OPTIMIZATION OF THE SCREW CONFIGURATION FOR USE WITH DBD

With the use of DBD as devulcanization agent, the configuration of the screw had to be adjusted: the devulcanization aid had to be molten and thoroughly mixed with GTR in the mixing section of the extruder, see Figure 1: A more severe kneading in this section is required, hence Screw A, Figure 5, was assembled for a start. A configuration with elements with a negative flight, Screw B, to extend the residence time in the mixing section of the screw for a longer swelling time, turned out to be not a feasible concept: The extruder drive could not provide the required high 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, led to operational problems. Screw D appeared to be most appropriate with best results. This configuration was further used throughout the experiments. Additional intermediate screw configurations were tested too, but did not provide better results.

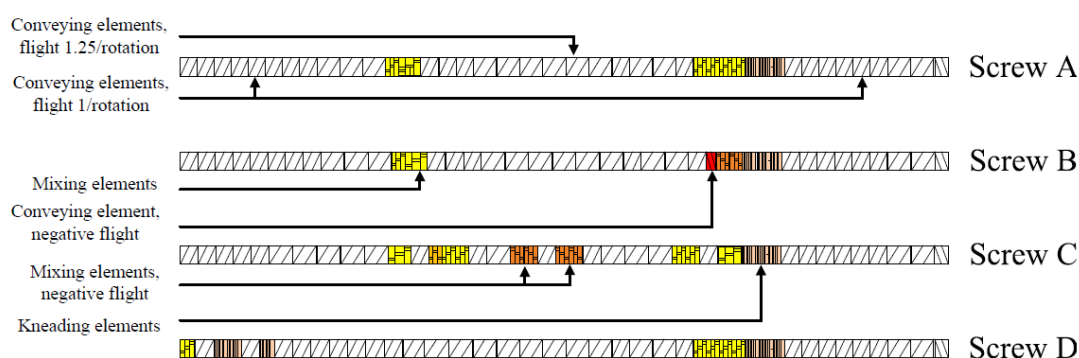


Figure 5: Screw configurations with different amounts of shear adapted for use with DBD.

Kneading elements are indicated in yellow, mixing elements in brown, kneading elements with negative flight in orange and a conveying element with negative flight in red.

### 4.2 SELECTION OF OPTIMIZATION CRITERIA

Providing a direct indication of the quality of the devulcanization process, the Horikx-Verbruggen procedure was firstly used for optimization. Secondly, the white rubber analysis was applied for remaining irregularities / visual grain. Using properties after revulcanization as optimization criteria for the devulcanization process has the disadvantage of being an indirect indication, as the revulcanization process is part of the measurement chain. However, it offers the opportunity to

adapt the devulcanization process and formulation to the specific characteristics of the devulcanizate. Therefore, this was used as a third method of characterization.

An impression of the different components, polymers and reinforcing fillers in passenger car tires is shown in Table VII. These components are blended and are an integral part of GTR. Complicating factors arising from this broad composition are:

- SBR is well known for its tendency to recrosslink by radical mechanisms after being decrosslinked. Hereby the structure of the polymer is changed, which has a negative impact on the overall result of the devulcanization.
- Compounds based on silica as reinforcing filler are known to decrosslink only to a low degree, mainly because of their high amount of monosulfidic crosslinks, which cannot selectively be broken in this process.
- Carbon black based NR and BR compounds are known to decrosslink relatively easily.
- Remaining particles 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<sup>7</sup>, the swelling is to be corrected for the influence of active fillers on the swelling behavior of the sample. As it is doubtful whether the compensation, as proposed by Porter<sup>9</sup>, is similar for carbon black and silica-silane systems, the crosslink density calculation for a compound with both, carbon black and silica, might have some error.

Table VII

Most important elastomers and fillers in tire components.

Component	Polymer	Re-inforcing 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	IIR	Carbon black

With such a complex mixture of devulcanization reactions in the analyzed samples, the main conclusion is that the Horikx-Verbruggen analysis is of limited relevance. It allows to compare

different devulcanizates based on the same feedstock on a relative basis; when using whole tire rubber, the variable composition has to be taken into account when interpreting these charts.

As the granularity of the devulcanizates influences the tensile strength of the revulcanizates and thus the quality, the size and amount of the visual grain remaining in the devulcanizates was determined by the White Rubber Analysis. The smallest size particles were used as an optimization criterion for the devulcanization process as well.

As to revulcanization of the devulcanizates, this was based on pure devulcanizates, based on Formulation 1, Table IV, assuming carbon black as the only filler. It was not blended with a virgin elastomer. 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. Although in actual application practice, pure devulcanizate will not likely be used as such, but in a blend with a virgin elastomer.

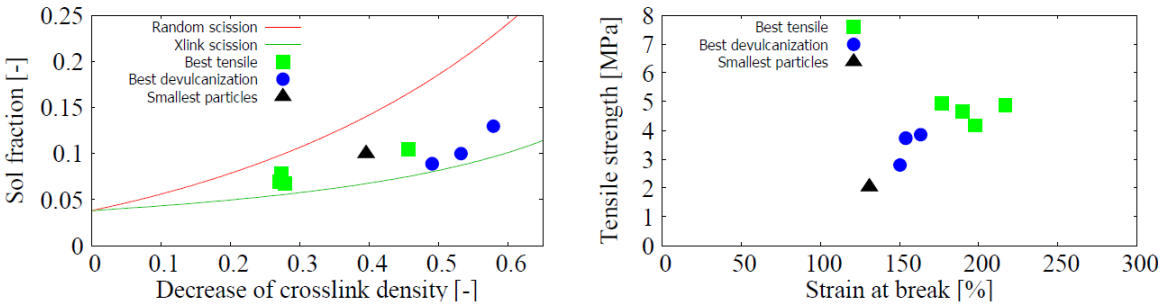
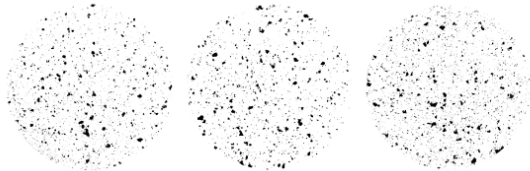
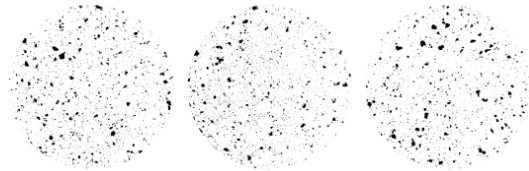


Figure 6: Materials with optimal decrease in crosslink density, smallest particle size and highest tensile strength in Horikx-Verbruggen cq. stress-strain diagrams.

(a) Horikx-Verbruggen diagram. (b) Stress-strain diagram.

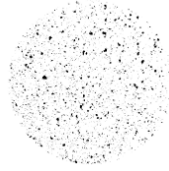


(a) Samples with optimal degree of de-crosslinking.



(b) Samples with highest tensile strength.





(c) Sample with smallest particles.

Figure 7: Comparison of remaining particle sizes of samples related to decrease in crosslink density, tensile strength and smallest particle size.

(Devulcanization aid: diphenyl disulfide)

After several series of experiments with variation of extruder speed, temperature profile of the extruder and concentration of the devulcanization aid, the best samples with respect to devulcanization quality as indicated by the Horikx-Verbruggen diagram, to tensile strength, and to the smallest remaining particle size are compared, see Figures 6 and 7: In contrast to the expectation, the devulcanization quality as judged by the Horikx-Verbruggen analysis, highest tensile strength and smallest particles, do not match. As shown in Figure 6, the samples with the best quality of devulcanization by virtue of the Horikx-Verbruggen analysis do not show the highest tensile strength after revulcanization. The samples with the lowest degree of devulcanization in the Horikx-Verbruggen analysis show the highest tensile strength. The sample with the smallest particle size shows an intermediate devulcanization quality in the Horikx-Verbruggen plot and the lowest tensile strength of all these samples, Figure 7c. Hardly any noticeable relation between the size and amount of the visual grains is observed for the samples with best devulcanization as indicated in the Horikx-Verbruggen diagram, Figure 7a, and those with the highest tensile strength as shown in the stress-strain diagram, Figure 7b. Together with the observation that the lowest tensile strength is shown for the sample with the smallest size and amount of visible particles, Figure 7c, it can be concluded that the differences in size and amount of the visual grains in the devulcanizates is not suitable as an optimization parameter.

The overall conclusion is, that the tensile strength of revulcanizates is the parameter of choice for optimization of the devulcanization process. Based on the present results and previous work<sup>11</sup>, the presence of silica in GTR is largely blamed for the low degree of devulcanization in the Horikx-Verbruggen analysis. Besides, when recompounding silica-containing devulcanizate, the presence of this particular filler has to be taken into consideration as done in Formulation 2 (A and B) in Table IV for a silica based tread formulation, respectively Table VI for the processing. As the size of the

remaining visual grains in the de- and revulcanizates is experienced as a quality issue, the White Rubber Analysis (WRA) is used as well to optimize the processing after devulcanization in the extruder for minimum amount and size.

#### 4.3 OPTIMIZATION OF THE DEVULCANIZATION PROCESS BY TENSILE STRENGTH

The various process parameters, extruder section settings, screw speeds and devulcanization systems are summarized in Table VIII. For the samples with the highest obtained tensile strength after revulcanization, the configuration and settings are summarized in Table IX. The following observations can be made:

*Temperature:* The samples devulcanized at max. 180°C show better tensile strength values than those processed at 220°C.

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

*Screw speed:* The samples a up to and including d, with a good tensile strength, are 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 6.85wt% of DBD combined with a devulcanization temperature of 220°C.

*Amount of oil:* Samples a up to and including e are produced using 2wt% oil; for sample f, 6.2wt% oil was used. Combined with the lowest screw speed this 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 2wt% oil and revulcanized with Formulation 2B: samples d and e, compared with those revulcanized with formulation 2A: samples a and b.

Table VIII

Devulcanization formulations, screw configurations and extruder temperature settings used for the devulcanization.

Screw speed [rpm]	Used screw speeds:		
	10	20	30
<u>Variations in temperature profile of the extruder:</u>			
	[°C]		
Feed & mixing section*:	110	130	150 170 220
Devulcanization section*:		180	220
Pressure section*:	110	130	150 170 220
<u>Variations in devulcanization system:</u>			
Component	Amount, in wt% of GTR		
DBD:	3.9	6.85	
TDAE:	0	2	5 6.2
TDTBP:	1		
<u>Variations in revulcanization system (see Table 4)</u>			
Formulation 2-:	<b>A</b>		<b>B</b>
S and TBBS:	1.64phr		4.64phr

\* see Figure 1

Used screw configuration: D

Table IX

Comparison of processes with best tensile strength.

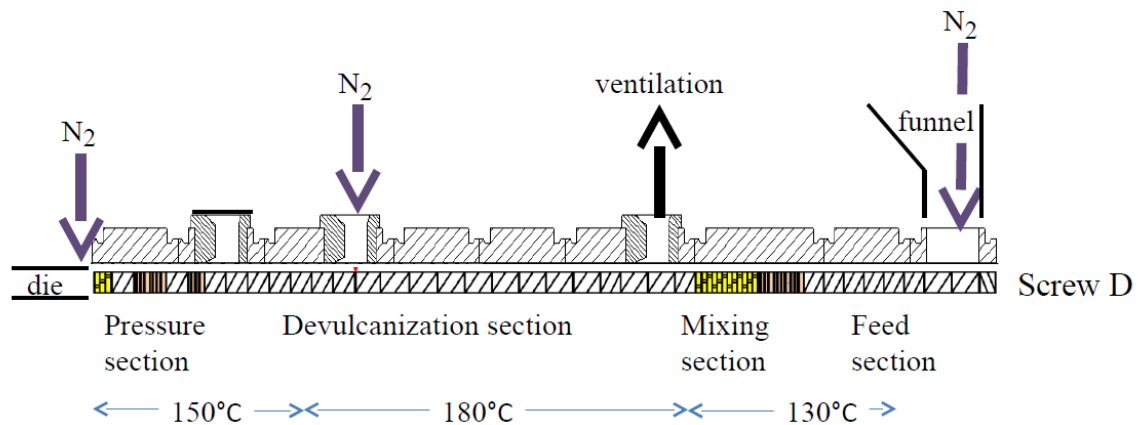
Sample	DA	temperature	speed	TDAE	Tensile	Strain	M100
	wt%	I-II-III*	rpm	wt%	stress	at break	MPa
					MPa	%	
Best samples after revulcanization with formulation 2A, Table 8							
a	6.85	130-180-170	20	2	8	176	3.8
b	3.9	130-220-150	20	2	7.6	131	5.2
c	5	130-220-150	20	2	7.5	140	4.7
Best samples after revulcanization with formulation 2B, Table 8							
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 1.

#### 4.4 SUMMARY OF THE BEST DEVULCANIZATION PROCESS SET-UP

These observations lead to the conclusion that a devulcanization temperature of 180°C, combined with screw configuration D and 2wt% oil, are the best settings for the devulcanization process. As there is no significant advantage of using 6.85wt% of DBD, 3.9wt% of DBD suffices. Revulcanization Formulation 2B was selected, as it gave slightly better strain at break. This is all summarized in Figure 8.



- Screw configuration: D
- Screw speed: 20rpm, residence time: 12minutes, throughput: 2kg/h
- Devulcanization system: DBD 3.9wt%, TDAE 2wt%, TDTBP 1wt%
- Post processing: mill, 0.1mm gap, 60°C
- Revulcanization system: S, TBBS 4.64phr, TESPT 3.2 phr, DPG 2.8 phr
- Revulcanization: compounding with silanization
- Tensile strength: 8.2MPa

Figure 8: Extruder configuration and devulcanization process for best tensile strength of revulcanizates.

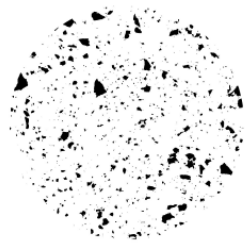
#### 4.5 POST-PROCESSING

The devulcanization process as developed in the present study is a thermo-chemical-mechanical treatment. The screw was chosen with focus on low shear; however, as a consequence the shear is too low to decrease the amount and size of visual grains in the devulcanizates. Screws configured for higher shear decreased the quality of the devulcanizates, as indicated by the tensile strength of the revulcanizates.

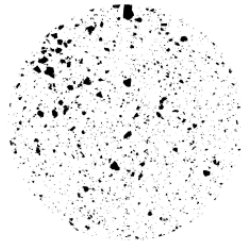
A clear positive effect was observed for additional milling as post-processing of the DGTR at 60°C with a gap width of 0.1mm. The positive influences of mixing and additional milling of the devulcanizates can be explained by free radicals created at the elevated temperatures due to crosslink scission, which are still active. These radicals cause undesired side effects in the polymer matrix, despite the presence of the devulcanization aid to neutralize them. At lower temperatures, the reactivity of the radicals decreases exponentially. This is shown in Figure 9 by comparing the size of the remaining visual grain after different treatments by WRA:

- A: Devulcanizate produced in twin screw extruder, followed by calendaring for cooling (Fig. 9a).
- B: Devulcanizate additionally milled at 60°C, with a gap width of 0.1mm and a friction ratio of 1.13 (Figure 9b).
- C: Devulcanizate as A, compounded for revulcanization at 80°C according to Formulation 1, Table V, including sheeting off on the mill, before revulcanization (Figure 9c).
- D: Devulcanizate as A, compounded for revulcanization at 145°C according to Formulation 2, Table 6, including sheeting off on the mill and before revulcanization (Figure 9d).
- E: The same treatment as B, followed by C, Figure 9e.
- F: The same treatment as B, followed by D, Figure 9f.

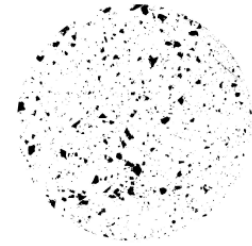
The material of sample A clearly contains visual grains which are reduced in size by the post-process milling, as is shown with sample B. When performing a processing step as compounding at either 80°C or 145°C, including sheeting off on the mill, the size of the visual grain is similar to those of Sample B, as is shown for samples C and D. When performing these process steps subsequently to a post-process milling step as for samples E and F, the size of the particles reduces noticeably. Post-process milling has by far the largest effect, while a small further improvement is found after compounding for revulcanization in an internal mixer including a light sheeting off on the mill. The temperature at which the compounding for revulcanization is performed has no clear effect. As derived above, a gradient in concentration of devulcanization aid in the GTR-particles can be expected due to both, size and size distribution of the virgin GTR. Thus a gradient in decrease in crosslink density in the particles of the devulcanizate can be expected. This implies a gradient in hardness and thus a decreasing onion peel or 'erosion'<sup>12</sup> effect of the devulcanized layers when applying high shear forces by post-process milling. An additional advantage of the post-process milling is that the devulcanizate gains coherency, in spite of the remaining visible grain.



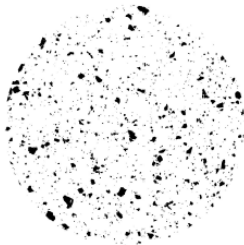
(a) Sample A, DGTR after TSE without post processing.



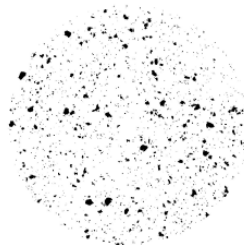
(b) Sample B, DGTR after TSE and post-process milling at 60°C, gap width 0.1mm.



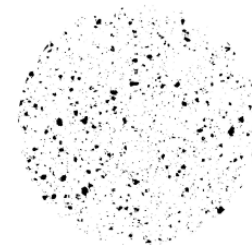
(c) Sample C, DGTR after TSE without post-process milling, followed by compounding according to Formulation 1.



(d) Sample D, DGTR after TSE without post-process milling, followed by compounding according to Formulation 2.



(e) Sample E: B + C.



(f) Sample F: B + D.

Figure 9: Influence of mill-post processing after twin screw extruder (TSE) devulcanization on size and amount of visible grains in DGTR.

Ahagon and Kirino<sup>13</sup> indicated that large deformations on a mill in SBR can decrease the crosslink density at first, while it can be increased later on. However, this is not observed in the present process during post-process milling of devulcanized GTR. Additionally it enhances the batch-coherence, which is another indication of a non-increasing crosslink density. A clear difference is observed during post-process milling between the elastic nature of the GTR which remains during milling, and the more plastic behavior of DGTR. This implies that shear forces during milling do not destroy the rubber matrix, but only aid in shearing off the layers of devulcanized material.

#### 4.6 CONCLUDING REMARKS ABOUT THE DEVULCANIZATION PROCESS SET-UP

This study is a first scale-up from a batch to a continuous operation for devulcanization of whole passenger car tire granulate: GTR. The fact that GTR of recent date contains a substantial amount

of silica compared to the older technology using carbon black as reinforcing filler raised substantial problems to be addressed:

- The continuous extruder set-up in the present study is limited in the time needed to thoroughly mix the GTR with the devulcanization additives, to melt the devulcanization aid and to allow adequate time for migration of DBD into the particles at a temperature of 130°C. For further upscaling it is appropriate to use a separate pre-processing step, e.g. a separate mixer step.
- A twin screw extruder is able to work at low shearing forces and a devulcanization time of 6 to 7 minutes at a temperature of 180°C. However, the relatively long residence time needed for devulcanization limits the capacity of the extruder, as the length to diameter ratio needed for a reasonable throughput leads to impractically long screw lengths. Due to the requirement of low shear, a delaying influence of additional mixing elements in the screw to increase residence times cannot be used in this devulcanization process.
- The post-processing milling step applying high shear at a temperature of 60°C is necessary for a smooth devulcanizate with small grains. However, this is not a practical solution for a continuous process. Some experiments with a laboratory scale single screw extruder showed as well promising results.

## 5 CONCLUSIONS

Effective devulcanization of whole passenger car tire rubber containing silica is very challenging. For a thermo-chemical-mechanical process, size and size distribution of the tire granulate is a major factor. As the migration time of the devulcanization aid into the granular material is rather long compared to the residence time in an extruder, a lower concentration of the devulcanization aid in the core of the particles can be expected. In addition, as the devulcanization aids is distributed over the surface of the particles and has to migrate into their volume, larger granulate particles end up with a much lower concentrations at the core. It is therefore recommended to separate mixing of the devulcanization aid into the granulate from the twin screw extruder process.

The need to limit material degradation due to high shear forces in the twin screw extruder was counterbalanced by a post-processing milling step at about 60°C. This improved the quality of the

devulcanize considerably. The size of the remaining visible particles in the devulcanizate decreased substantially.

The 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 crosslink scission in a Horikx-Verbruggen plot, could not be used as a quality criterion. To be able to optimize the devulcanization processes, the tensile strength of revulcanizates was selected as optimization criterion. Visible particles remaining in the devulcanizate did not influence the tensile strength after revulcanization, but had a minor influence on the strain at break.

#### ACKNOWLEDGEMENTS

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## FIGURE CAPTIONS

Figure 1: Layout of the extruder, from right to left, with an example of a low shear screw and nitrogen supply positions.

Figure 2: Extruder installation.

Figure 3: Elongated die.

Figure 4: Horikx-Verbruggen diagram: correlation for random scission and crosslink scission.

Figure 5: Screw configurations with different amounts of shear adapted for use with DBD.

Figure 6: Points of optimal decrease in crosslink density, smallest particle size and highest tensile strength in Horikx-Verbruggen cq. stress-strain diagram.

Figure 7: Comparison of remaining particle sizes of samples by decrease in crosslink density, tensile strength and smallest particle size. (Devulcanization aid: diphenyl disulfide)

Figure 8: Extruder configuration and devulcanization process for best tensile strength of revulcanizates.

Figure 9: Influence of mill-post processing after twin screw extruder (TSE) devulcanization on size and amount of visible grains in DGTR.

Table I

Diffusion coefficients  $\mathbb{D}$  and calculated diffusion times until equilibrium versus temperature for oil in styrene butadiene rubber (SBR) for particles of 2 and 3 mm.

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

Table II

Size distribution of the GTR after analysis with laboratory sieves.

Size Sieve mesh [mm <sup>2</sup> ]	Amount [wt%]
<0.85	negligible
0.85<...<2	80
2<...<3.5	19
>3.5	1

Table III  
Materials.

Designation	Supplier
<u>Devulcanization agent:</u>	
DBD 2-2'-DiBenzamidoDiphenyldisulfide	Schill and Seilacher GmbH, Boeblingen, Germany
<u>Anti-oxidant:</u>	
TDTBP Tris(2,4-Di-Tert-Butylphenyl)Phosphite	Sigma Aldrich Cooperation, Zwijndrecht, The Netherlands
<u>Processing oil:</u>	
TDAE Treated Distillate Aromatic Extract, VIVATEC 500	Hansen & Rosenthal, Hamburg, Germany
<u>Solvents for Horikx analysis:</u>	
Acetone purity >99.5wt%	Atlas & Assink Chemie b.v., Enschede, The Netherlands
THF TetraHydroFuran, purity >99.8wt%	
Toluene purity >99.8wt%	
<u>Polymers and fillers:</u>	
BR Butadiene Rubber grade BUNA CB24	Arlanxeo Deutschland GmbH, Leverkusen, Germany
TiO <sub>2</sub> Titanium diOxide, Hombitan R210	Venator, Wynyard, UK
<u>Vulcanization system:</u>	
ZnO Zinc oxide	Merck KGaA, Darmstadt, Germany
St.A. Stearic acid	
S Sulfur	J.T.Baker
TBBS N-Tert-Butyl-2-BenzothiazoleSulfenamide	Lanxess Rhein Chemie GmbH, Cologne, Germany
MBTS 2,2'-DiBenzoThiazyl diSulphide	
DPG 1,3-DiPhenylGuanidine	
<u>Coupling agent:</u>	
TESPT bis[3-(TriEthoxySilyl)Propyl] Tetrasulfide	Evonik Industries AG, Essen, Germany
<u>Cleaning chemicals for the extruder ventilation:</u>	
NaOH technical quality	Sigma Aldrich Cooperation, Zwijndrecht, The Netherlands
NaHClO bleaching water, 2%	Household quality

Table IV

Revulcanization formulations, values in phr.

Formulation nr.	<b>1</b>	<b>2</b>	
	DGTR	DGTR	
Component:	re-vulcanizate(2)	re-vulcanizate(3)	
		<b>A</b>	<b>B(4)</b>
Polymer (1)[x]	[100]	[100]	[100]
ZnO	3.0	2.5	2.5
St.A.	2.0	1.0	1.0
TDAE[x]	[42.7]	[42.7]	[42.7]
Carbon black[x]	[80]	[54]	[54]
Silica[x]		[42](5)	[42](5)
TESPT		3.2	3.2
6PPD	1.0		
TMQ	2.0		
TBBS	1.5	1.64	4.64
DPG		2.8	2.8
Sulphur	1.5	1.64	4.64

Table V

Compounding procedure for Formulation 1.

Time [minutes]	Mixer settings	Time [minutes]	Processing steps
	Brabender internal mixer	0	Mixer set at 50rpm,
	Chamber volume: 35ml	1	ZnO + stearic acid,
	Fill factor: 0.6	4	TBBS
	Initial mixer temperature of 80 °C.	4.5	Sulphur.
	Mixer set at 5rpm rotor speed.	5	Dump.
	<u>Addition of curatives.</u>		Thoroughly homogenized and
	Mixing order:		sheeted off on the mill.
			Relaxation for 24 hours.

Table VI  
Compounding procedure for Formulation 2.

Time [minutes]	Mixer settings and processing steps	Time [minutes]	Mixer settings and processing step
	Brabender internal mixer Chamber volume: 35ml Fill factor 0.6 The mixer temperature was set to 145 °C. The devulcanizate was added at 5rpm rotor speed.		Initial mixer temperature of 50 °C and 5rpm rotor speed. The silanized devulcanizate was added at 5rpm rotor speed.
	<u>Silanization.</u>		<u>Addition of curatives.</u>
0	Mixer set at 50rpm rotor speed.	0	Mixer set at 50rpm rotor speed.
1	Silane.	0.5	ZnO + stearic acid,
5	Dump at ±145 °C.	1	TBBS + DPG,
0	The devulcanizate was cooled down to 60 °C and milled with a gap-width of 0.1-0.5mm.	1.5	Sulphur.
5	Sheeted off at 2mm.	2	Dump.
	Relaxation for 72 hours.		Thoroughly homogenized and sheeted off on the mill. Relaxation for 24 hours.



Table VII

Most important elastomers and fillers in tire components.

Component	Polymer	Re-inforcing 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	IIR	Carbon black

Table VIII

Devulcanization formulations, screw configurations and extruder temperature settings used for the devulcanization

Screw speed [rpm]	Used screw speeds:		
	10	20	30
<u>Variations in temperature profile of the extruder:</u>			
	[°C]		
Feed & mixing section*:	110	130	150 170 220
Devulcanization section*:		180	220
Pressure section*:	110	130	150 170 220
<u>Variations in devulcanization system:</u>			
<u>Component</u>	<u>Amount, in wt% of GTR</u>		
DBD:		3.9	6.85
TDAE:	0	2	5 6.2
TD/TBP:			1
<u>Variations in revulcanization system (see Table 4)</u>			
Formulation 2-:	<b>A</b>	<b>B</b>	
S and TBBS:	1.64phr	4.64phr	

Table IX

Comparison of processes with best tensile strength.

Sample	DA wt%	temperature I-II-III*	speed rpm	TDAE wt%	Tensile stress MPa	Strain at break %	M100 MPa
Best samples after revulcanization with formulation 2A, Table 8							
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 2B, Table 8							
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 1.