7

Regeneration and devulcanization

7.1

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7.1.1   Introduction

Material recycling of tire rubber is a well-known technology. Devulcanization is a rather new technology; most conventional technologies are based on grinding and regeneration. However, granulates and powders as well as regenerates face limitations in their application in terms of quality and quantity. The main reasons are:

1. Difference in modulus between matrix and (non-replasticized) recycled rubber particles results in stress concentrations at the interface between new and recycled rubber. As this interface is the weakest spot in such a blend, it is prone to early failure.
2. Breakdown of the polymer network during the regeneration process, which is not selective concerning the type of bonds to be broken, and shorter polymer chains imply lower strength properties.
3. Recombination of chain fragments, which results in uncontrolled network formation and thus a lower degree of devulcanization and reduced properties.

Devulcanization technologies are focused on shifting the balance of crosslink scission to polymer breakdown to the former process, implying that only sulfur-cured elastomers

can be devulcanized. As this is the case for tire rubber, devulcanization is a process that can be further developed for this material.

In this chapter, the following terms are used for the different types of recycled rubber:

1. Devulcanizate: The main breakdown mechanism is crosslink scission.
2. Regenerate: The main mechanism is random scission with a high percentage of polymer breakdown.
3. Replasticized rubber: The breakdown mechanism is not known; it comprises devulcanization as well as regeneration.

7.1.2 Analysis of the devulcanization mechanism

Replasticization of rubber granules occurs on different levels, on a molecular as well as macroscopic scale:

1. Molecular scale: Distinction between polymer and crosslink scission.
2. Macroscopic scale: Successive removal of devulcanized outer layers of the rubber granules versus homogenous devulcanization within the whole particle.

7.1.2.1 Selective crosslink scission versus random network breakdown

Whenever polymer chains are broken in the regeneration process, a decrease in mechanical properties results. As this is undesirable, a method to analyze the breakdown mechanism is needed. An estimation of the degree of crosslink to random scission is possible using the Horikx−Verbruggen analysis. This method is based on the theory of Horikx [1] on network degradation via two different routes:

1. Selective scission of sulfur crosslinks
2. Random network scission

Horikx based his work on the network theories of Charlesby [2,3]. With a few adjustments, this approach can be applied to devulcanization of sulfur-cured elastomer networks, as described by Verbruggen [4].

In this approach, the soluble fraction of the replasticized rubber − the sol content − is related to the decrease in crosslink density. Horikx derived a theoretical relationship between the soluble fraction generated after degradation of a polymer network and the relative decrease in crosslink density, as a result of either

main-chain scission or crosslink breakage. This treatment of polymer degradation can equally well be applied to rubber regeneration, in which a mix of main-chain scission and crosslink breakage also takes place. When main-chain scission takes place, the relative decrease in crosslink density is given by [5]:

$$1 - \frac{\nu_f}{\nu_i} = 1 - \left[\frac{\left(1 - s_f^{1/2}\right)^2}{\left(1 - s_i^{1/2}\right)^2}\right] \qquad (7.1.1)$$

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

$$1 - \frac{\nu_f}{\nu_i} = 1 - \left[\frac{\gamma_f \left(1 - s_f^{1/2}\right)^2}{\gamma_i \left(1 - s_i^{1/2}\right)^2}\right] \qquad (7.1.2)$$

where the parameters γ_f and γ_i are the average number of crosslinks per chain in the insoluble network after and before regeneration, respectively. The values for γ_f and γ_i are determined as described by Verbruggen [6]. Fig. 7.1.1 gives a graphical representation of Eqs. (7.1.1) and (7.1.2). The curves in the figure correspond to the situations when the network is randomly broken (solid curve) and when only crosslinks are broken (dashed curve). In the case of crosslink scission only, almost no sol is generated until most of the crosslinks are broken; only then the long chains can be removed from the network. In the case of
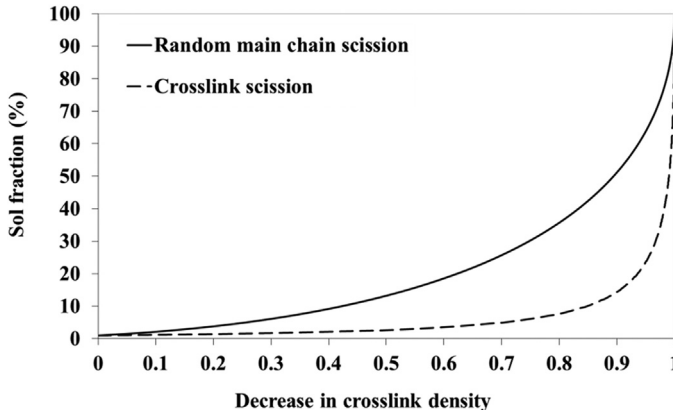
Figure 7.1.1 Horikx—Verbruggen graph to analyze the replasticizing process and determine the degree of crosslink versus random scission. Figure reproduced with permission of Kautschuk Gummi Kunststoffe.

main-chain scission, sol is produced at a much earlier stage, because random scission of the polymers in the network results in small loose network fragments, which can easily be removed [5]. When interpreting these graphs, it has to be taken into consideration that this method is based on a few assumptions and does not give exact percentages. It is a valid tool to show trends, but not precise enough to calculate percentages.

The soluble (sol) fraction of the replasticized materials as shown in the Horikx–Verbruggen plots are measured by Soxhlet extraction for 48 h in acetone to remove polar components followed by an extraction for 72 h in tetrahydrofurane to remove apolar parts. This fraction contains the soluble polymer released from the network by the replasticization process. The samples were dried under vacuum at 40°C. A correction for the oil contained in the original rubber has to be made. The gel fraction is calculated by:

$$\text{Sol fraction} = \frac{\text{weight of rubber dissolved}}{\text{weight of polymer in the compound}} \quad (7.1.3)$$

The crosslink density is in general determined by swelling in toluene for 72 h at room temperature. The weight of the swollen (de)vulcanizates was measured after removal of surface liquid with absorption paper. The crosslink density is calculated according to the Flory–Rehner equation [7], Eqs. (7.1.4) and (7.1.5) [5]:

$$\upsilon_e = \frac{V_r + \chi V_r^2 + \ln(1 - V_r)}{V_s\left(0.5V_r - V_r^{\frac{1}{3}}\right)} \quad (7.1.4)$$

with

$$V_r = \frac{m_r}{m_r + m_r\left(\rho_r/\rho_s\right)} \quad (7.1.5)$$

where ν_e = crosslink density per unit volume, V_r = polymer volume fraction of the swollen sample, V_s = solvent molar volume, m_r = mass of the rubber network, m_s = weight of solvent in the sample at equilibrium swelling, ρ_r = density of the rubber, ρ_s = density of the solvent, and χ = Flory–Huggins polymer–solvent interaction parameter.

This calculated crosslink density is based on the volume of gel in the rubber network after extraction. However, in order to compare these data with the Horikx theory, it has to be realized that the latter defines the crosslink density after devulcanization with the sol fraction still present. During the swelling test, this sol fraction is also extracted and thus needs to be included again in the calculation of the real crosslink density ν_{real} remaining after devulcanization but before extraction. Consequently, in order to obtain

the actual remaining crosslink density of the devulcanizate, the volume of total rubber must be taken into account. Correction for this real crosslink density is made according to [5]:

$$\nu_{\text{real}} = \frac{\text{Number of crosslinks}}{\text{Volume of total rubber}} = \nu_e \times (1 - \text{sol fraction}) \quad (7.1.6)$$

where ν_{real} = the final corrected crosslink density for the replasticized rubber.

The Flory–Rehner equation is strictly spoken only valid for non-filled systems. Therefore the Kraus [8] correction for filled compounds is used to give the correct values of the different crosslink densities. In its simplified form, the Kraus correction is given by [9]:

$$\nu_{\text{actual}} = \frac{\nu_{\text{apparent}}}{1 + K + \Phi} \quad (7.1.7)$$

with

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

$$(7.1.8)$$

where ν_{apparent} = measured chemical crosslink density, ν_{actual} = actual chemical crosslink density, K = constant for a given filler, Φ = calculated volume fraction of filler in the specimen, W_b = weight of the specimen before extraction, and W_a = weight of the specimen after extraction.

7.1.2.2 Homogeneity of network breakdown throughout the particles

Homogeneous breakdown of the polymer network results in a successive decrease of crosslink density throughout the particle. This will in first instance result in gel with a reduced crosslink density, but still all polymer chains attached to the network and no soluble part: the horizontal part of the crosslink scission line in Fig. 7.1.1. When the crosslink density further decreases, polymer chains are released from the network with a steep increase in sol content: the vertical part in Fig. 7.1.1. When the network is broken down randomly, sol is generated at an earlier stage, leading to the upper line. These two lines limit the generation of soluble network fragments in one case and polymer chains in the other. However, devulcanization does not occur in all cases according to this mechanism. For some polymers such as butyl rubber (IIR), an overproportioned amount of sol is generated in the early stages of network breakdown. In this case, the data points will be situated far above
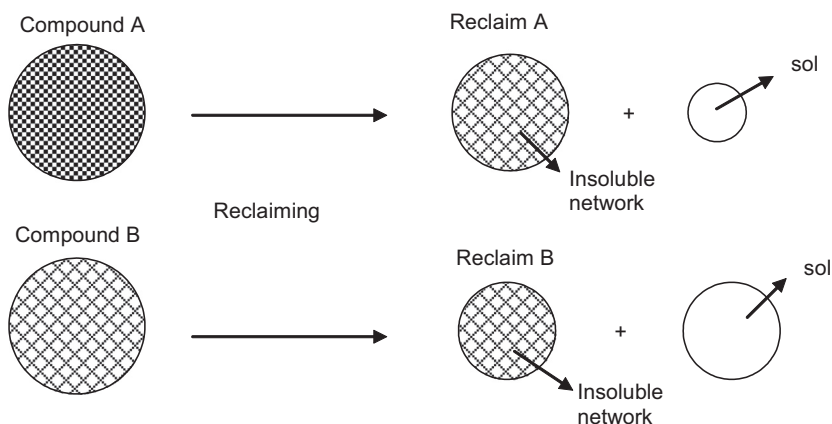
Figure 7.1.2 Schematic representation of homogeneous (top) and inhomogeneous (bottom) breakdown [10]. Figure reproduced with permission of Rubber Chemistry and Technology.

the random scission line. Fig. 7.1.2 shows the two ways of breakdown: In the upper schematic, the polymer network is homogeneously broken throughout the whole particle, resulting in a gel particle with a lower crosslink density over the whole diameter. In the lower case, a gradient in crosslink density is generated, leading to an onion-peeling effect: a lot of sol is generated, while the core of the particle still has a high crosslink density.

Another test method to indicate which type of network breakdown is occurring is the white rubber test (WRA): The replasticized material is blended with a white rubber compound at a concentration of 5 wt.%, and the number and size of remaining particles as well as the shade of gray give an indication to what extent the network within the particles is broken. If the particle size is reduced in parallel with generation of sol content but without significant reduction in crosslink density, an onion-peeling mechanism is predominant.

Fig. 7.1.3 illustrates the two extreme cases of none and complete breakdown of the network of the particles in the upper row, while the bottom row illustrates samples with a different degree of polymer breakdown.

The upper row shows reference samples without, with 10 wt.% ground rubber, and with 5 wt.% completely disintegrated replasticized rubber. The difference in gray-shade as well as size and number of particles is clearly distinguishable. In the bottom row, different samples with a low number of remaining large particles, with a higher number of large particles, and with only small particles and a darker shade of gray due to a more complete network breakdown are shown from left to right.

Reference samples

| White rubber compound | 10% ground rubber | 5% completely replasticized rubber |

Samples with 5% devulcanizate
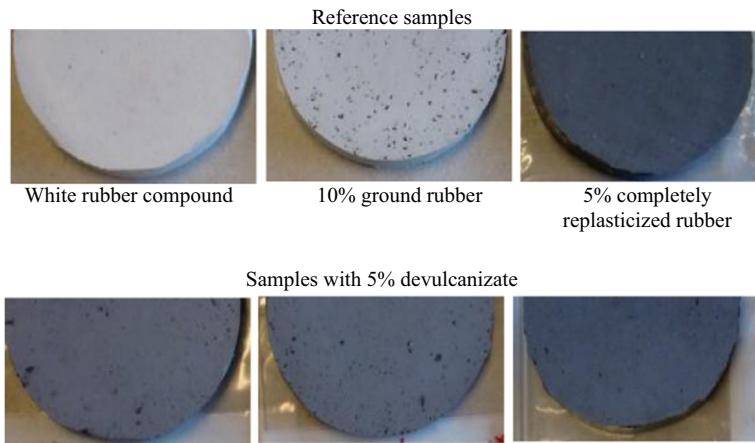
Figure 7.1.3 Samples of the white rubber test.

Table 7.1.1 Energies of the different types of bonds in a sulfur-cured polymer network [11].

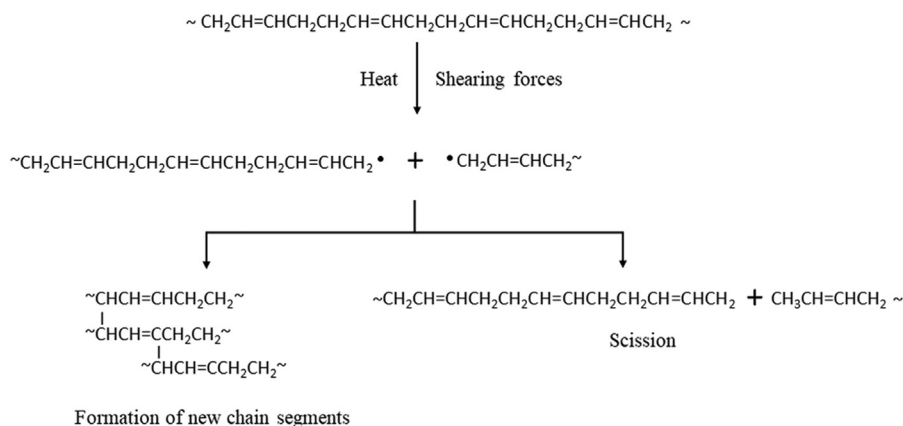|	Bonding energy [kJ/mol]
$R_3C{-}CR_3$	370
$R_3C{-}S{-}CR_3$	310
$R_3C{-}S{-}S{-}CR_3$	270

7.1.3   Devulcanization versus regeneration

Devulcanization in the strict sense of the word is the process of selectively breaking sulfur bonds. Within a sulfur-crosslinked elastomer network, different types of bonds are present as shown in Table 7.1.1.
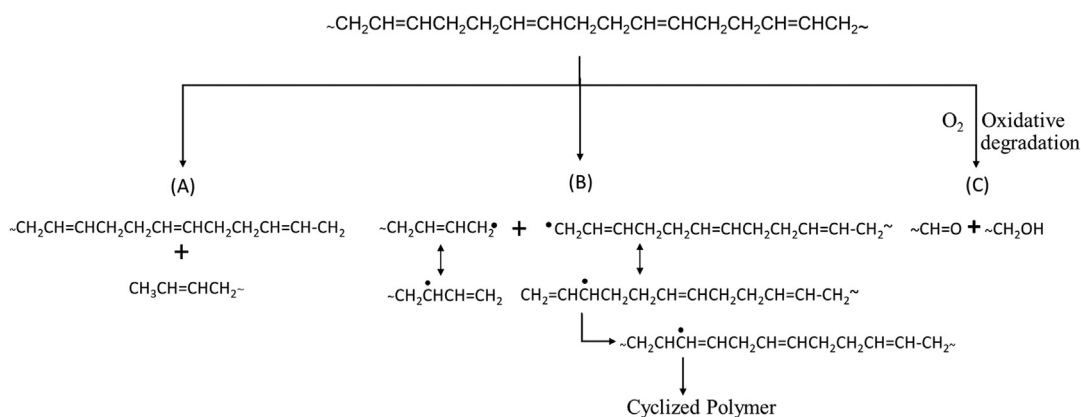
This difference in bond energy allows some selectivity in breaking of the polymer network. However, chemically attacking the sulfur bonds will have a much higher selectivity and is therefore the method of choice to achieve devulcanization. These chemical reactions require mechanical blending of the rubber with the devulcanization aid and a certain temperature level, but this will lead to mechanical and thermal breakdown of the polymer network as well. The challenge is to shift the balance of crosslink scission and polymer breaking toward the former one.

7.1.3.1   Devulcanization mechanisms

Polymer scission reactions are basically degradation reactions. Fig. 7.1.4 is a schematic depiction of the degradation of

~ CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$ ~

Heat | Shearing forces

~CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$• + •CH$_2$CH=CHCH$_2$~

~CHCH=CHCH$_2$CH$_2$~
|
~CHCH=CCH$_2$CH$_2$~
|
~CHCH=CCH$_2$CH$_2$~

~CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$ + CH$_3$CH=CHCH$_2$ ~

Scission

Formation of new chain segments

Figure 7.1.4 Simplified reaction scheme proposed for the degradation of polybutadiene and butadiene based polymers.

~CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$~

O$_2$ | Oxidative degradation

(A)   (B)   (C)

~CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CH-CH$_2$ ~CH$_2$CH=CHCH$_2$• + •CH$_2$CH=CHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CH-CH$_2$~   ~CH=O + ~CH$_2$OH

+

CH$_3$CH=CHCH$_2$~

~CH$_2$ĊHCH=CH$_2$ CH$_2$=CHĊHCH$_2$CH$_2$CH=CHCH$_2$CH$_2$CH=CH-CH$_2$~

└→ ~CH$_2$CHĊH=CHCH$_2$CH=CHCH$_2$CH$_2$CH=CH-CH$_2$~

Cyclized Polymer

Figure 7.1.5 Polymer scission (A), formation of active bond fragments (B), and oxidative degradation (C) in the specific degradation mechanism of polymers with a butadiene structure.

polybutadiene and butadiene based polymers. Basically, two reactions can occur during degradation of polybutadiene: chain scission and formation of active chain segments. Chain scission occurs when breaking of the C−C bonds (carbon−carbon bonds) in the polymer chains is accompanied by hydrogen transfer [12], and results in polymers with a lower molecular weight. Another reaction, the formation of radically active chain fragments, apparently takes place from three possible reactions as shown in Figs. 7.1.5 and 7.1.6. Reaction (A) in Fig. 7.1.5 is known as a hydrogen transfer reaction. It is initiated by breaking of the C−C bonds in the polymer chains due to physical forces: heat, light, and
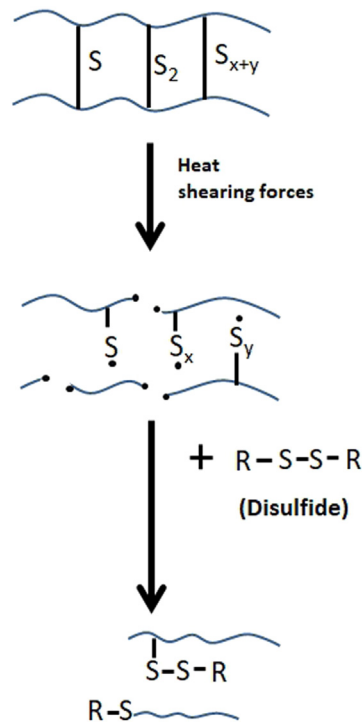
Figure 7.1.6 Simplified reaction scheme proposed for rubber devulcanization using additives with a disulfide moiety.

mechanical forces. It is accompanied by hydrogen transfer which also results in polymer chain scission. However, re-combination of unstable radicals to polymers could possibly take place when scission of C−C bonds in the chain is not accompanied by a hydrogen transfer [12]. It is reported that for degradation in air atmosphere, with the main active component oxygen, hydrogen transfer is less. Therefore the active radicals tend to recombine to a new polymer [5].

Reaction (B) in Fig. 7.1.5 is the transformation reaction. It is associated with thermal isomerization: cis-trans isomerization, cyclization, and volatilization of small fragments [13−15]. These chain rearrangements are enhanced by an increasing temperature and occur with the initial decomposition step of styrene-butadiene rubber (SBR) [5].

Reaction (C) in Fig. 7.1.5 involves generation of active groups derived from the presence of oxygen. The initial predominant attack of aerial oxygen (O_2) takes place at the double bonds. It continues with the generation of hydroperoxide radicals, which then

decompose to give carbonyl ($>C=O$) functionalities [16]. These reactions typically take place at high temperatures [5]. Accordingly, when carbonyl functionalities are generated, the possibility of creating a rubber soluble fraction is less: the bond energy of $C=O$ (799 kJ/mol) is considerably higher than that of $C-C$ (346 kJ/mol) or carbon hydrogen bonds, $C-H$ (411 kJ/mol) [17].

All three reactions as sketched in Fig. 7.1.5(A)−(C) can conjointly occur in the SBR devulcanization process, particularly at high temperatures. These result in reduction of the sol fraction and increase of the crosslink density above the threshold temperatures as stated above [5].

The degradation of rubber results in radical fragments, thus scavenging of these radicals is of crucial importance to suppress radical chain scission and shift the balance to crosslink scission. Various chemicals can act as radical stabilizing agents; examples are thiols, phenolic compounds and disulfides, which are the most common ones [18−22]. A mechanism that is frequently proposed for the reaction of radical scavengers in rubber replasticization is opening of crosslinks or scission of polymer chains by heat and shearing forces, and the reaction of fragments with disulfide based radicals, which prevent recombination. Okamato [23] suggested that when a vulcanized rubber compound is replasticized by using mechanical shear forces (i.e., milling), free radicals are produced that can further cause the formation of main chain radicals. Chemicals like thiols and disulfides react with these radicals, thus preventing their attack of the polymer chains and recombination [5].

Disulfides are well-known devulcanization aids especially for natural rubber (NR). These aids form radicals with increasing temperature. The radicals then combine with the polymer main chain radicals preventing their recombination. Studies of mechanochemical recycling processes of NR and other tire rubbers indicated that disulfides play an important role in the processes [24,25]. As a result, the mechanical properties (i.e., tensile strength, modulus, and tear strength) of revulcanized disulfide-containing rubber were higher than those of revulcanized rubber obtained without devulcanization aid.

A reaction scheme proposed for the devulcanization of rubber with disulfides based chemicals is shown in Fig. 7.1.6. A mechanism that is frequently proposed for the reaction of radical scavenger devulcanization aids like disulfides for the reaction with sulfur vulcanizates is the opening of crosslinks or the scission of polymer chains by heat and shearing forces, and the reaction of fragments with disulfide based radicals, which prevent recombination.

## 7.1.3.2   Devulcanization aids and processes

7.1.3.2.1   *Chemical devulcanization*

Many chemical compounds were considered and tested concerning their effectivity as devulcanization aids. The most common ones are amines and disulfides. In terms of amines, stronger nucleophiles are expected to be better devulcanization aids. Differences in amines that may influence the reclamation reaction are:

1. type of amines (primary, secondary or tertiary)
2. steric hindrance
3. basicity
4. presence of an α- hydrogen

Within the second category, diaryldisulfides (e.g., diphenydisulfide) are often applied [26]. A comparative study on the devulcanization efficiency of three different disulfides, diphenyldisulfide (DPDS), dibutyldisulfide (DBDS), and di(2-aminophenyl)disulfide [5], lead to the conclusion that DPDS and DBDS are even efficient, see Fig. 7.1.7. However, the choice of a devulcanization aid also includes the processing behavior; therefore DPDS is in general chosen. Besides odor, costs and availability have to be considered when choosing a devulcanization aid.

In this study [27], the presence of a stabilizer was also evaluated. A hindered phenolic stabilizer, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Ir1076), was used at a concentration of
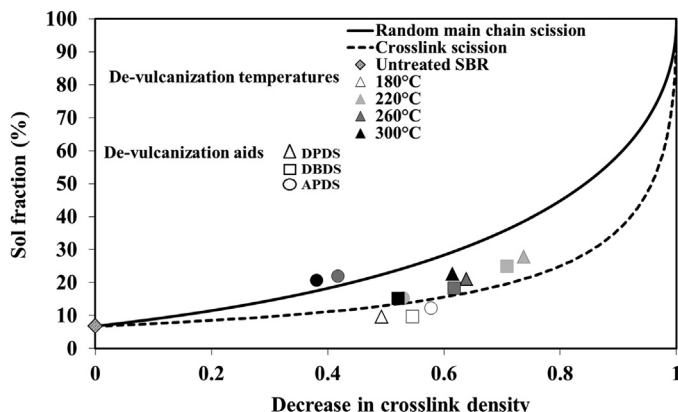
Figure 7.1.7 Devulcanization efficiency of different types of disulfides [diphenyldisulfide, dibutyldisulfide, and di(2-aminophenyl)disulfide]. Figure reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186—232.
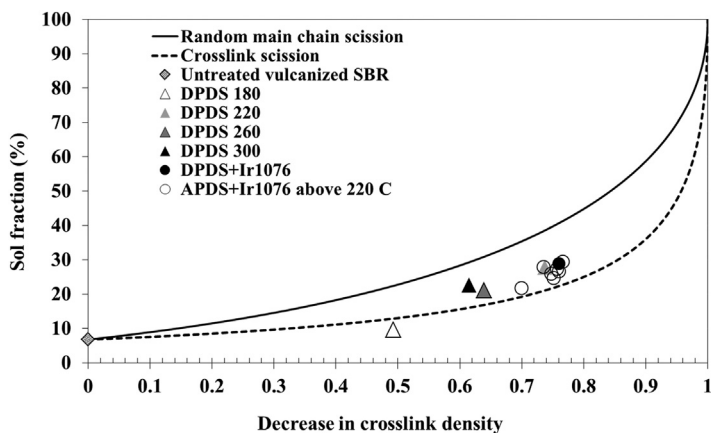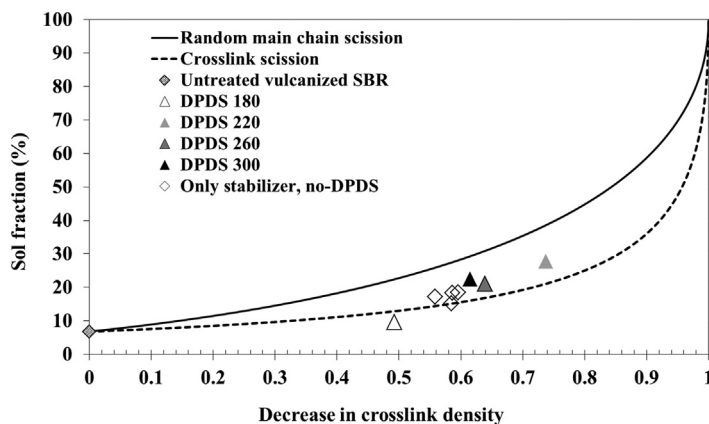
Figure 7.1.8 Devulcanization efficiency depending on temperature, presence of stabilizer (Ir1076), and devulcanization aid. Figure reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186–232.)

1 wt.% in a SBR compound. DPDS was used as devulcanization aid. Fig. 7.1.8 shows that the devulcanization efficiency does not significantly change with temperature; even at high temperatures, when SBR otherwise tends to recombine, network recombination does not occur. Stabilizers thus allow to increase the devulcanization temperature, accelerating the reaction. It was also tested, if the stabilizer supports the devulcanization reaction. The results shown in Fig. 7.1.9 indicate that this hindered phenol does not have any effect on the network breakdown.

Table 7.1.2 gives an overview of different additives described as devulcanization aids.

7.1.3.2.2 Physical devulcanization

Supercritical gas like $spCO_2$ [16,50,51] is used as a medium to swell a devulcanization aid into the rubber particles. It is also used as the sole devulcanization additive [52]. Besides, the supercritical gas also results in mechanical breakdown of the rubber particles when the material exits the extruder by the sudden expansion due to the pressure loss.

Another approach to breakdown of crosslinked rubber is ultrasonic treatment [53]. This type of radiation is claimed to break by preference the sulfur bonds by cavitation within a few seconds, making it possible to use an extruder with the advantage of a continuous process. A detailed investigation on the extruder

Figure 7.1.9 Devulcanization efficiency with stabilizer and without devulcanization aid, compared to DPDS as devulcanization aid. Figure reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186—232.

Table 7.1.2 Different devulcanization aids.

Devulcanization aid	References
Ionic liquids	[28]
Nitric acid and benzoyl-peroxide	[29—31]
Thiobisphenols, e.g., 4,4-dithiobis(2,6-di-t-butylphenol)	[32]
Bis(3-triethoxysilyl propyl)tetrasulfide (TESPT)	[33,34]
N_2O in organic solvents	[35]
Benzoyl peroxide	[36]
Alcohols/amines and transition metal complex catalysts	[37]
Triphenylphosphine and 1,8-diazabicyclo[5.4.0]undec-7-ene	[38]
Photoactive substances (e.g., semiconducting nanocrystals) in combination with radiation treatment	[39]
Secondary imines	[40]
Amines or sulfides, organic acid or anhydride, oxidant and metal oxide	[41]
Proton donor, metal oxide, organic acid, vulcanization inhibitor and friction agent	[42]
Reactive hydrogen source and catalyst	[43]
Disulfides	[44]
Vegetable product with disulfide as major component	[45,46]
Tetramethyl thiuramdisulfide	[47—49]

settings for an efficient ultrasonic devulcanization is reported in [54]. Certain technologies additionally use devulcanization aids such as eutectic solvents based on, for example, blends of choline chloride and urea or zinc chloride [55].

Microwave treatment is another technique used to devulcanize elastomers. One example is the microwave treatment of a blend of whole-tire powder with a maximum particle size of 500 μm, 6 parts of 2-mercaptobenzothiazole (MBT), and 10 parts of virgin SBR. Prior to blending, the tire powder was oxidized with $KMnO_4$ and peroxide. This blend was irradiated for 150 s at 1000 W [56]. Gamma rays [57] and dielectric fields [58] are also described for physical devulcanization. For all these radiation devulcanization methods it is not well described whether it is indeed devulcanization rather than regeneration.

7.1.3.2.3 Biological devulcanization

Bacterial breakdown of sulfur bonds is another technology [59−61]; this is probably the only devulcanization process in the strict sense of the word. Bacteria that can transform bound sulfur into elemental sulfur and sulfuric acid are, for example, Sulfolobus acidocaldarius [62]. However, disadvantages of this process are that it is very time- and space-consuming, and the devulcanized material has to be dried after the devulcanization process.

7.1.3.3 Process technology

Many devulcanization processes are performed in an extruder with the advantage of a continuous process and a more homogeneous product. Extruder types used for this purpose are, for example, twin screw extruders (TSE), of which a typical setup is shown in Fig. 7.1.10. Planetary roller extruders (see Fig. 7.1.11) are also suitable machines for replasticization and devulcanization [63,64]. General rules for running an extruder in a mode to avoid polymer breakdown as much as possible are low temperatures and limited shearing forces. The critical parameter of an extruder process is the residence time, which generally is too short for complete devulcanization. This can be overcome by using a prolonged extruder die, for example.
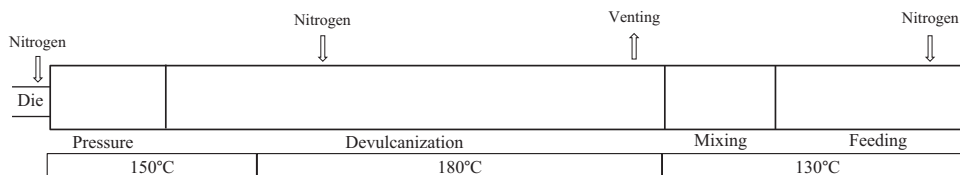
Figure 7.1.10 Twin-screw extruder setup for devulcanization using a devulcanization aid.
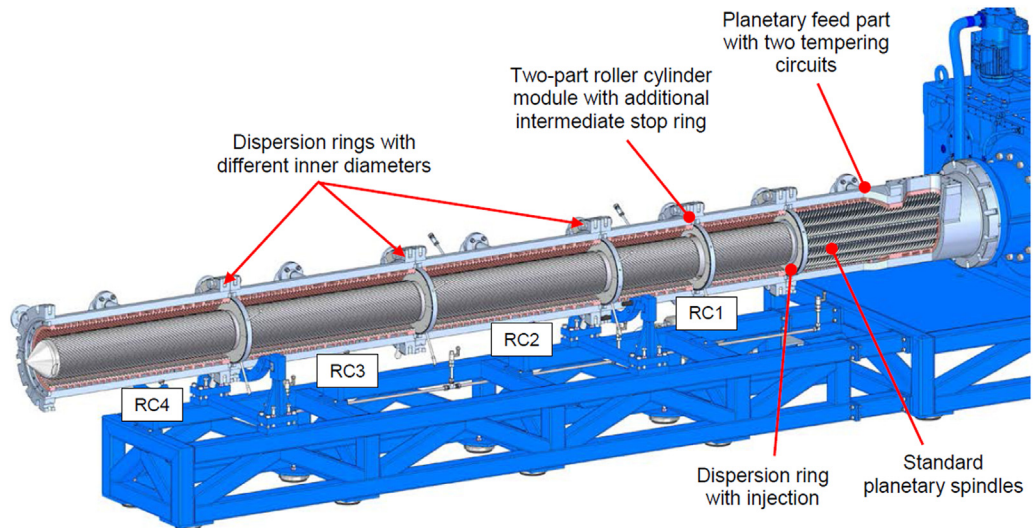
Figure 7.1.11 Planetary roller extruder. Figure reproduced with permission of Entex; Entex, Technical Information Issue 57: Process Technology Information for the Processing of Rubber With the Planetary Roller Extruder, Part 3: Devulcanising Extrusion Processes.

Table 7.1.3 Polymers in different tire parts.

	Apex	Bead	Belt	Cap-ply	Carcass	Innerliner	Sidewall	Tread
Natural rubber	X	X	X	X	X		X	X
Styrene-butadiene rubber	X				X			X
Butadiene rubber	X		X		X		X	X
Butyl rubber (IIR, CIIR, BIIR)						X		

7.1.4   Influence of rubber composition on the devulcanization efficiency: tire rubbers

Tires are an assembly of different type of compounds, which contain a blend of two or three polymers and different fillers, besides other additives such as, plasticizers, curatives and protecting agents. The main polymers used in tires are NR in larger size tires such as trucks and SBR in passenger car tires. Other polymers are butadiene rubber (BR) and butyl rubber (IIR). The latter can be modified with chlorine or bromine, chlorobutyl rubber (CIIR) and bromobutyl rubber (BIIR). Table 7.1.3 shows the presence of these polymers in different tire parts.

The polymers in the blends differ in structure, and - depending on the curing system - the blends differ in the type of crosslink network. The ratio of mono to di- and polysulfidic bonds significantly influences the devulcanization efficiency due to the differences in bond strength of the sulfur bridges and reactivity toward the devulcanization aid [65].

7.1.4.1   Devulcanization of styrene−butadiene rubber [5]

SBR is the most critical polymer in replasticization, as it is prone to recombination resulting in a branched structure and new links between the polymer chains. An extensive study first elaborated a devulcanization process for this polymer in an unfilled model compound, and applied this process to the other three polymers (BR, NR, CIIR) [66]. Fig. 7.1.12 shows the results of the thermochemical devulcanization of sulfur-cured SBR using DPDS as devulcanization aid. Temperature is a crucial parameter: At a temperature of 260°C, compared to the lower temperatures, a significant increase in crosslink density of the devulcanizate is observed. DPDS as devulcanization aid was added in order to scavenge radicals formed during the regeneration process and thus to avoid secondary reactions of the polymer parts; however, this works only at lower devulcanization temperatures. At high devulcanization temperatures, extensive generation of reactive radicals occurs. These lead to formation of new inter- and intramolecular bonds [12] resulting in a decrease of the rubber sol fraction and renewed increase in crosslink density, proving the abovementioned recrosslinking of the polymer during devulcanization at higher temperatures.

Figure 7.1.12 Relative decrease in crosslink density versus sol fraction of styrene-butadiene (SBR) devulcanizates (D-SBR: devulcanized SBR).

Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31−42.
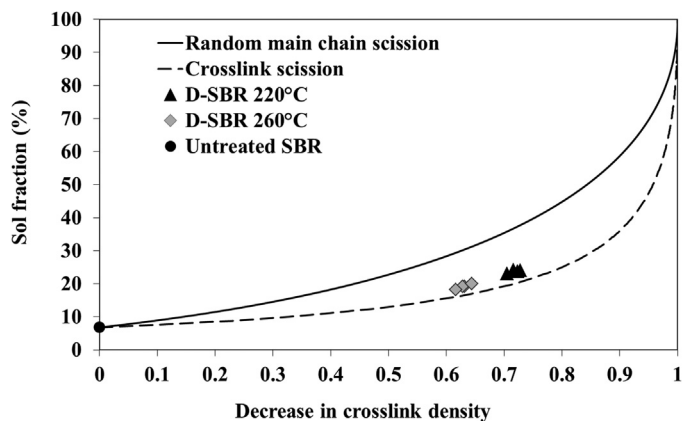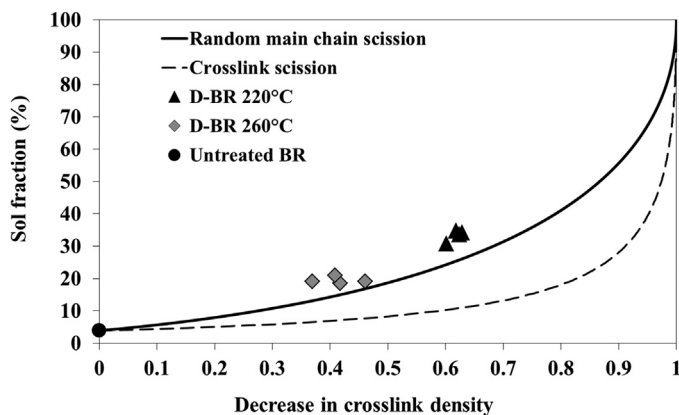
Figure 7.1.13 Relative decrease in crosslink density versus sol fraction of butadiene rubber (BR) devulcanizates (D-BR: devulcanized BR).
Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31—42.

7.1.4.2 Devulcanization of butadiene rubber

The sol fraction of BR devulcanizates as a function of the relative decrease in crosslink density according to Horikx–Verbruggen is shown in Fig. 7.1.13. With increasing temperature within this range, the crosslink density increases. This means that for this polymer, a devulcanization temperature of 220°C is more effective than a temperature of 260°C, as the percentage of soluble polymer is higher and the final crosslink density is lower. However, a considerable amount of main chain scission occurs in both cases, as the sol content is rather high. Degradation of polybutadiene and other butadiene-based polymers follows a unique pathway due to the specific chemical structure of the polymer [12]. In this degradation process, network breakdown occurs, but at the same time network recombination takes place. For this polymer as well, the devulcanization temperature should be as low as possible.

7.1.4.3 Devulcanization of natural rubber

NR is easily devulcanized as seen in Fig. 7.1.14, resulting in a material with relatively good properties. It is rather forgiving in the sense that the devulcanization conditions do not drastically influence the quality of the material.

For NR, the network density can strongly be decreased at temperatures above 170°C [67]. Moreover, DPDS was reported [68,69] to be an effective devulcanization aid for NR. Temperature is the main governing factor, and addition of DPDS can significantly enhance the effects. Using the process parameters as developed for SBR, the NR devulcanizate is completely soluble; not many network connections are remaining between the polymer

molecules. For this polymer, the devulcanization temperature is not critical within this temperature range, as long as the polymer chains do not thermally degrade to a large extent. However, the latter has to be taken into consideration, as NR starts to degrade in the presence of oxygen at about 150°C.

7.1.4.4 Devulcanization of chlorobutyl rubber (CIIR)

The relative decrease in crosslink density of a CIIR model compound is shown in Fig. 7.1.15. At a temperature of 220°C, the data points are far above the random scission line: In spite of a low decrease in crosslink density, the sol content is rather high. This is one example of the onion-peeling devulcanization mechanism discussed above. When the temperature is increased to 260°C, the polymer is degraded, as it is completely soluble.

Figure 7.1.14 Relative decrease in crosslink density versus sol fraction of natural rubber (NR) devulcanizates (D-NR: devulcanized NR).
Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31—42.
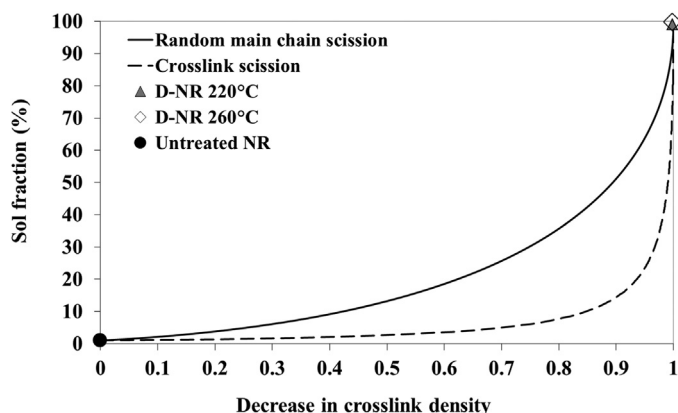
Figure 7.1.15 Relative decrease in crosslink density versus sol fraction of CIIR devulcanizates (D-CIIR: devulcanized CIIR).
Figure reproduced with permission of Rubber Chemistry and Technology; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Comparative investigation of the devulcanization parameters of tire rubbers. Rubber Chem. Technol., 87, (85), 2014, 31—42.
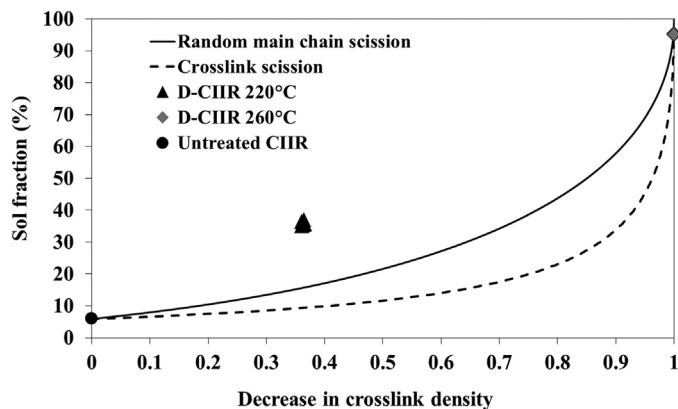
7.1.4.5 Devulcanization of whole-tire rubber

Many different techniques are applied for the devulcanization of ground tire rubber (GTR) from passenger car tires. The main characteristic of these processes is that they can only be a best compromise for the devulcanization efficiency and material quality. In Table 7.1.4, a few of these processes are summarized. Devulcanizates resulting from different processes are evaluated in a review [70].

7.1.4.5.1 Application studies of whole-tire devulcanizate

In general, devulcanized rubber is used to replace a part of a virgin compound. A few studies included such an application case.

The microwave treatment of a not further specified whole-tire powder resulted in a decrease of the crosslink density between 38.6% and 48.5%, depending on the additional treatment of the rubber powder: oxidation and/or MBT addition. According to a Horikx−Verbruggen analysis, the network breakdown was mainly caused by random scission, thus this process cannot be classified as devulcanization. The mechanical properties of a blend of 15 phr devulcanizate with a virgin SBR−silica compound without silane could slightly be improved by the additional treatment [56].

Cryogenically ground truck tire granulate with a maximum particle size of 0.4 mm was treated with supercritical carbon dioxide ($spCO_2$). Fig. 7.1.16 shows the stress−strain curves of blends of a virgin compound (Ref) with vulcanized rubber powder (GTR) and blends with $spCO_2$ devulcanized GTR (T−GTR) [51]. From this graph it can be concluded that the $spCO_2$ treatment does not result in significantly better properties than the untreated rubber powder.

Devulcanizates from different processes based on cryogenically ground whole tire rubber with a maximum particle size of 0.4 mm are compared in terms of mechanical and dynamic properties. The devulcanizates are tested in a NR compound (Ref−NR), to which 10 phr of devulcanizate was added. The fillers are 15 phr silica without silane, 37 phr carbon black in the reference compound, and 34 phr in the blends with recycled rubber. Compared were untreated ground rubber, $spCO_2$ and DPDS treated material, ultrasonically treated material, and samples prepared by bacterial breakdown [59]. Relative to the original compound, the mechanical properties of the blend are negatively influenced: strength is reduced by about 20%−25%, and the $spCO_2$-treated sample with the highest DPDS concentration gives the lowest value. The maximum strain is reduced by 10%. No further significant differences can be observed

Table 7.1.4 Overview of different devulcanization processes.

Process/Devulcanization aid	Process conditions	Properties of the cured vulcanizate as such[a]	Properties of a blend with devulcanizate[b]	References
Thermomechanical	220°C, 30 rpm	—	NR/SBR/15 phr[c] app. 14 MPa/ app. 350%	[71]
	180°C, 120 rpm	12.9 MPa/351%	—	[72]
	180°C, 250 rpm	app. 4.25 MPa/ app. 140%	NR/50/50 2.76 MPa/ 325%	[73]
Mechanochemical		10,9 MPa/289.4%	—	[74]
Mechanochemical/ pentachlorothiophenol hydrazine zinc chloride	150°C, 30 rpm	app. 3.1 MPa/ app. 350%	NR/70/30 14.7 MPa/ 450%	[75]
Ultrasonic	120°C, 20 rpm, 3000 W, 20 kHz	10.5 MPa/250%	—	[76]
	120°C, 20 rpm, 3000 W, 20 kHz	10.5 MPa/250%	—	[77]
	120°C, 20 rpm, 3000 W, 20 kHz	8.7 MPa/217%		[78]
Microwave/diphenyl disulfide	900 W, 3 min, 240°C, 2000 MHz	10 MPa/226%		[79]
Mechanochemical/thiobisphenols	200°C	5.85 MPa/app. 325%		[42]
Mechanochemical/1,8-Diazabicyclo (5.4.0)Undecene-7 (DBU)/ triphenylphosphine (PPh3)	30 rpm	13.6 MPa/390%		[39]
Mechanochemical/2-butanol	30°C, 40 min, 10 MPa	—	SBR/BR 85/15 15.4 MPa/738%	[80]
Mechanochemical/supercritical water/peroxide/alkylphenol polysulfide	200°C, 1.6 MPa	—	SBR app. 20.45 MPa/ app. 710%	[81]
Mechanochemical/supercritical water	200°C, 1.6 MPa	—	SBR app. 15 MPa/ app. 645%	

BR, butadiene rubber; NR, natural rubber; SBR, styrene-butadiene rubber.
[a]Tensile strength/elongation at break.
[b]Polymers in masterbatch/concentration devulcanizate tensile strength/elongation at break.
[c]Parts per hundred rubber.
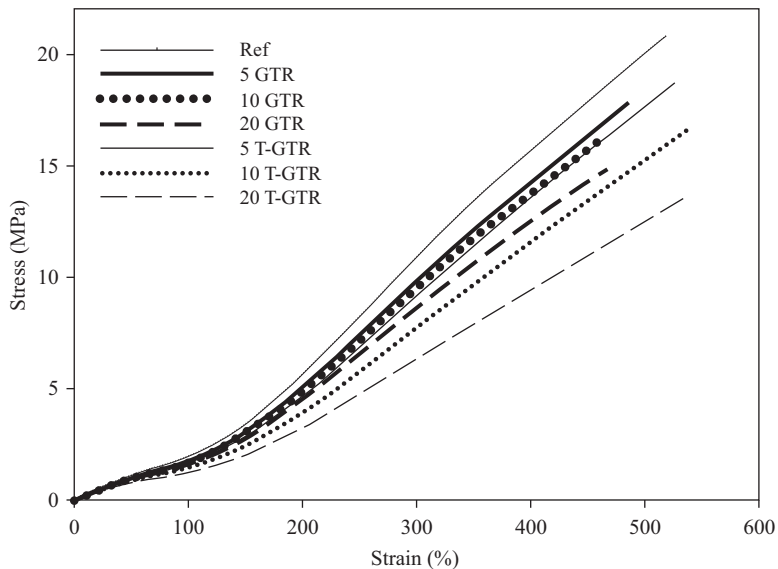
Figure 7.1.16 Stress−strain curves of blends of virgin rubber with rubber devulcanized using supercritical CO_2.
Figure reproduced with permission of Elsevier; I. Mangili, E.M. Collina, M. Anzano, D. Pitea, M. Lasagni. Characterization and supercritical CO_2 devulcanization of cryoground tire rubber: influence of devulcanization process on reclaimed material. Polym. Degrad. Stab., 102, 2014, 15−24.

between the different types of devulcanizates. Dynamic properties were also measured: tan δ as indication of rolling resistance showed an increase for all samples containing devulcanizate. The highest level was measured for the $spCO_2$−DPDS devulcanizate in the blend, the lowest for the bacteria-treated one [59].

In another study, devulcanized whole-tire rubber from different types of tires was treated in a microwave process at 800 W for 1−5 min. The material temperature after the microwave treatment was up to 370°C. The devulcanizates were added to a SBR compound in concentrations of 10, 30, and 50 phr. The only adjustment of the formulation was a reduction of the carbon black content from 67.75 to 63.25 phr. The trends given in Table 7.1.5 were measured on the blended materials [82].

7.1.5   Influence of rubber composition on the devulcanization efficiency: fillers

Devulcanization efficiency and material quality depend significantly on the type of tires used as feedstock, thus on the rubber composition. Besides the polymers discussed above, other ingredients also influence the devulcanization process and material properties. The most important ones are the filler systems.

Carbon black is often used as reinforcing filler in tires since it plays an important role in improvement of the mechanical

Table 7.1.5 Rheological and mechanical property changes by addition of microwave-devulcanized tire rubber to a virgin rubber compound.

	Increasing concentration of devulcanizate	Increasing degree of devulcanization by variation of treatment time
Delta torque (M_H-M_L)	↓	o
Scorch time t_{s2}	↓	o
Curing time t_{90}	↓	↓
Tensile strength	↓	o
Elongation at break	↓	o
Modulus at 100% elongation	o	o
Hardness	↑	o

o: no clear trend.

properties such as abrasion resistance, modulus, and fatigue life. A study of the influence of carbon black loading on the devulcanization of NR-based tire compounds using DPDS as devulcanization aid has shown that the presence of this filler resulted in a decrease in devulcanization efficiency [83]. Addition of carbon black to an elastomer causes adsorption of the polymer molecules onto the filler surface and anchoring in the carbon black structure, resulting in segmental mobility loss. The reactivity of the DPDS for trapping the sulfide radicals stemming from the network breakdown was decreased: these radicals have a high probability to be attached to carbon black and thus are inactivated.

The most problematic component in tire rubber is a silica−silane filler system. This filler forms strong covalent bonds with the polymer by the silane, while carbon black forms physical bonds, which are rather easy to break. But as the additional silica−silane−polymer network results in a low hysteresis, thus lower rolling resistance, silica is more and more replacing carbon black in treads of passenger car tires.

The secondary filler−polymer network in silica-filled rubber is difficult to break, as it contains mainly monosulfidic bonds. Fig. 7.1.17 shows the devulcanization efficiency of a silica−silane-filled SBR compound. The devulcanization conditions were in first instance optimized for a nonfilled SBR rubber. For the latter compound, a devulcanization efficiency of 70%−80% was achieved; for the silica-filled rubber, the efficiency was about 20%−40%. This is caused by the monosulfidic bonds formed by the silane, bis-(3-triethoxysilylpropyl) disulfide.
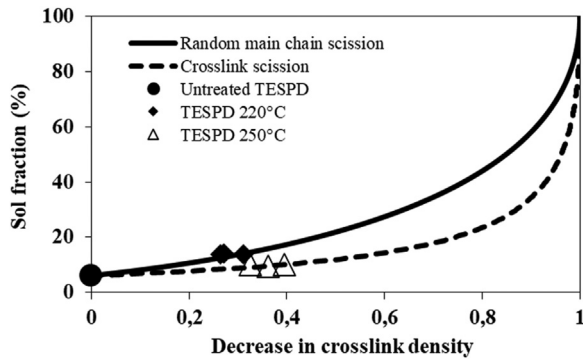
Figure 7.1.17 Devulcanization efficiency of silica—silane reinforced styrene-butadiene rubber.
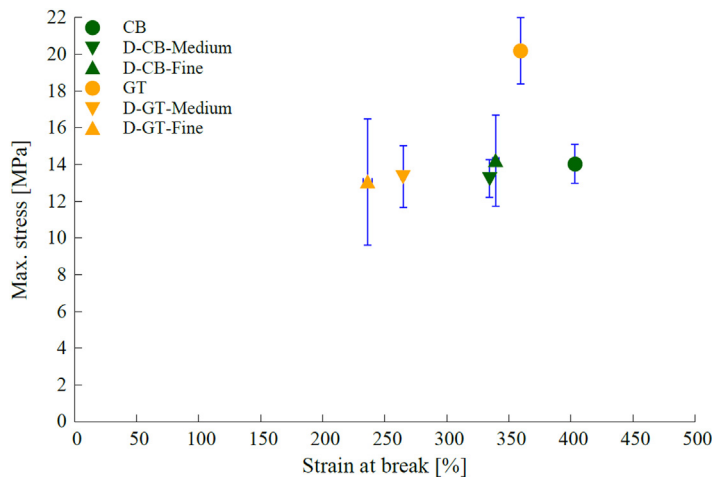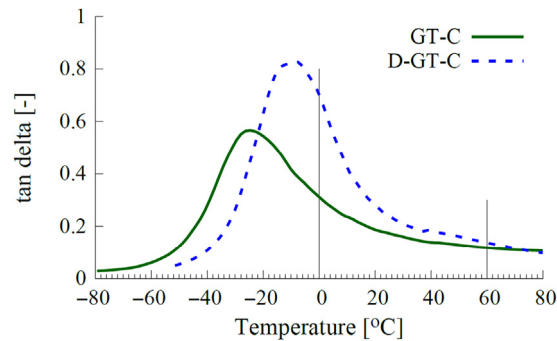

Figure 7.1.18 Stress—strain properties of a carbon black (CB) and silica (GT)-filled rubber before and after devulcanization and revulcanization (D—CB, D—GT) (medium and fine classify the granulometry of the feedstock).

Fig. 7.1.18 illustrates the difference between carbon black and silica filled rubber: the loss in properties after de- and revulcanization of the silica-filled rubber is significantly higher compared to the loss in properties of the carbon black filled material: the filler—polymer network in the latter is easier to be broken, as the filler—polymer bonds are rather weak.

Another new type of compounding ingredients are resins. They are added to mainly passenger car tread compounds in order to improve wet grip. The devulcanization study of this type of compounds was performed using 2-2'-dibenzamidodiphenyldisulfide as devulcanization aid. The resins were polyterpene- (resin A), hydrocarbon- (resin B), and terpene-phenol-(resin C) based. They were blended into a silica—silane passenger car tire tread formulation, in which 20 phr of oil was replaced by the same amount of resin. The
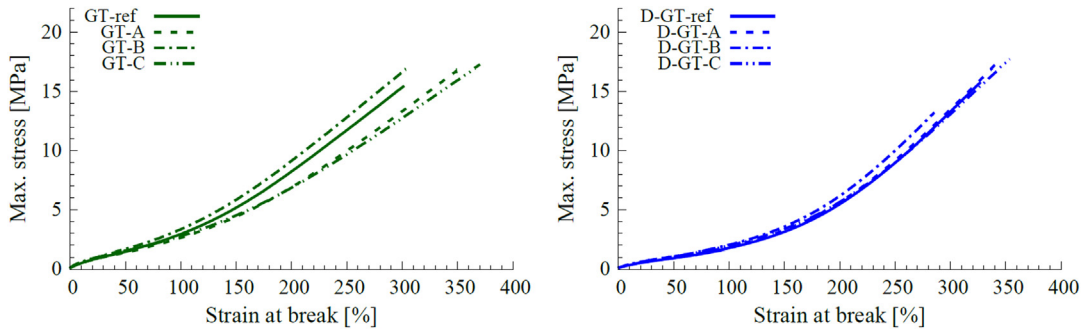
Figure 7.1.19 Stress−strain properties of a resin-containing rubber (left), and the properties of the same material after de- and revulcanization (right) (GT−ref: SBR−silica−silane reference compound; GT−x: SBR−silica−silane compound with resin x; D−GT−ref: reference compound after de- and revulcanization; D−GT−x: SBR−silica−silane compound with resin after de- and revulcanization).

Figure 7.1.20 The correlation between loss angle and temperature for a SBR-based silica-silane compound (GT−C: original compound; D−GT−C: compound with resin C after de- and revulcanization).

stress−strain properties of the original and the devulcanized and revulcanized rubber do barely differ: The presence of resins does not significantly influence the strength properties of the devulcanizate (see Fig. 7.1.19). In terms of tire performance indicators, the loss angle $0°C$ was increased significantly, while the value at $60°C$ was not influenced (see Fig. 7.1.20). The presence of resins thus has a positive influence on the wet grip properties when devulcanizate is added to the compound.

7.1.6 Process parameters affecting devulcanization efficiency

Not only the material composition and devulcanization aid, but also the processing parameters influence the devulcanization

efficiency. A study in an internal mixer on small scale in order to optimize the process conditions is reported [84]. This study shows that the time to swell process oil and devulcanization aid into granulate, concentration of the process oil, presence of oxygen as well as devulcanization time and temperature have an influence on the devulcanization efficiency. In this study, 30 mmol DPDS per 100 g compound were used, and a protective gas (nitrogen).

Fig. 7.1.21 shows that the concentration of the process oil, treated distillate aromatic oil (TDAE), has a considerable effect due to the plasticization of the material and thus less mechanical energy input in the internal mixer used in this study: higher concentrations reduce the devulcanization efficiency. Fig. 7.1.22 shows that an increasing devulcanization time beyond 6 min results in an increase in crosslink density, as the balance between chain scission and recombination of active chain segments shifts to the latter process. It is crucial to achieve a
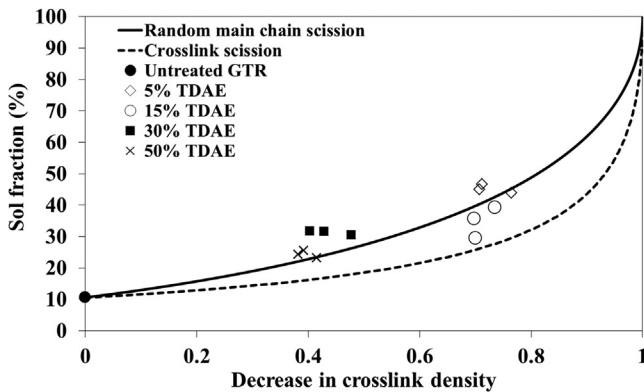
Figure 7.1.21 Influence of concentration of process oil on the devulcanization efficiency. Figure reproduced with permission of Kautschuk Gummi Kunststoffe; S. Saiwari, W. K. Dierkes, J.W.D. Noordermeer. Devulcanization of whole passenger car tire material. Kautsch. Gummi Kunstst., 66 (8), 2013, 20—25.
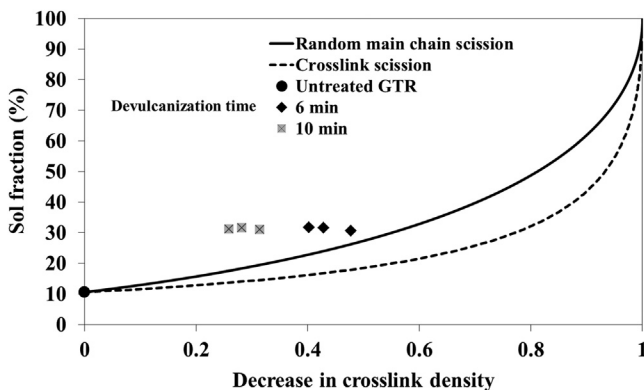
Figure 7.1.22 Influence of devulcanization time on the devulcanization efficiency. Figure reproduced with permission of Kautschuk Gummi Kunststoffe; S. Saiwari, W. K. Dierkes, J.W.D. Noordermeer. Devulcanization of whole passenger car tire material. Kautsch. Gummi Kunstst., 66 (8), 2013, 20—25.

breakdown of the network as far as possible before reformation of polymer−polymer bonds from active chain fragments becomes the prevailing reaction.

Fig. 7.1.23 illustrates the influence of oxygen during devulcanization and cooling of the sample. In this series of experiments, no devulcanization aid was used; therefore the degree of devulcanization is rather low. From Fig. 7.1.23(A) it is obvious that the combination of high temperatures with oxygen presence results in a high degree of recombination: the crosslink density of the material after devulcanization is even higher than the density of the starting material. This does not occur to such an extent when less oxygen is present; see Fig. 7.1.23(B) and (C): The absence of oxygen during devulcanization (B) and additionally during cooling (C) does reduce the degree of recombination, but does not significantly influence the final degree of devulcanization; to improve this, a devulcanization aid is needed. The stress−strain properties of the revulcanized rubber after devulcanization at 220°C for 6 min do not differ significantly depending on the presence of oxygen (Fig. 7.1.24).

Fig. 7.1.25 shows the influence of time, temperature, and screw speed on the devulcanization efficiency of passenger car tire rubber in a TSE using DPDS as devulcanization aid [85]. With increasing temperature, the data points move upward to the random scission line: higher temperatures result in a higher degree of nonselective thermal breakdown of the network. However, the recrosslinking seen in an internal mixer [Fig. 7.1.23 (A)] does not occur here, as the devulcanization was performed in a protective gas atmosphere. Residence time in the extruder also plays a role: when increasing the time from 1 to 3 min, the degree of network breakdown gets considerably higher. Another increase to 6 min enhances the devulcanization efficiency as well, but to a lesser extent. The influence of screw speed is not clear, as here the influence of the shearing forces on the temperature also plays a role.

A similar study [71] showed that the percentage of devulcanization was depending on shear stress, and that the barrel temperature was the most important parameter in changing the sol fraction.

In the study of Fig. 7.1.25, the following trends in terms of mechanical properties were found:

1. Temperature: Samples devulcanized at a maximum temperature of 180°C show higher tensile strength values than those devulcanized at 220°C.
2. Amount of the devulcanization aid (DPDS): There was no significant difference in tensile strength between samples
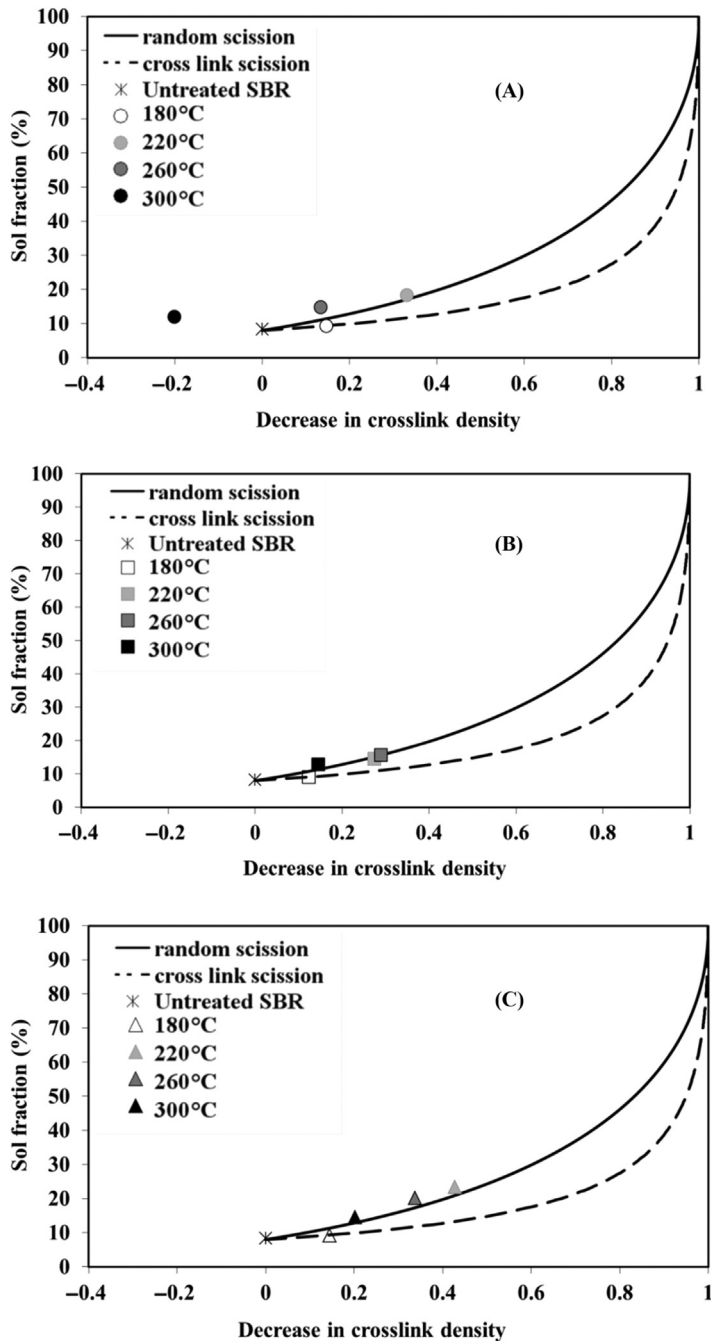
Figure 7.1.23 Influence of the presence of oxygen on the devulcanization efficiency [(A) with oxygen; (B) no oxygen during devulcanization; (C) no oxygen during devulcanization and cooling of the sample]. Figure is reproduced with permission of the Royal Society of Chemistry; S. Saiwari, W.K. Dierkes, J.W.M. Noordermeer. Recycling of individual waste rubber, in: J.K. Kim, P. Saha, S. Thomas, J.S. Haponiuk, M.K. Aswathi, (Eds.). Rubber Recycling: Challenges and Developments (Green Chemistry Series no.59), Croydon: The Royal Society of Chemistry, 2019. pp. 186–232.
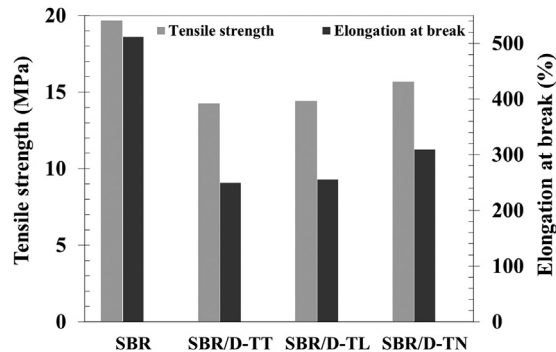
Figure 7.1.24 Stress–strain properties of styrene butadiene (SBR) rubber devulcanized with and without oxygen (SBR/D–TT: with oxygen; SBR/D–TL: no oxygen during devulcanization; SBR/D–TN: no oxygen during devulcanization and cooling of the sample).
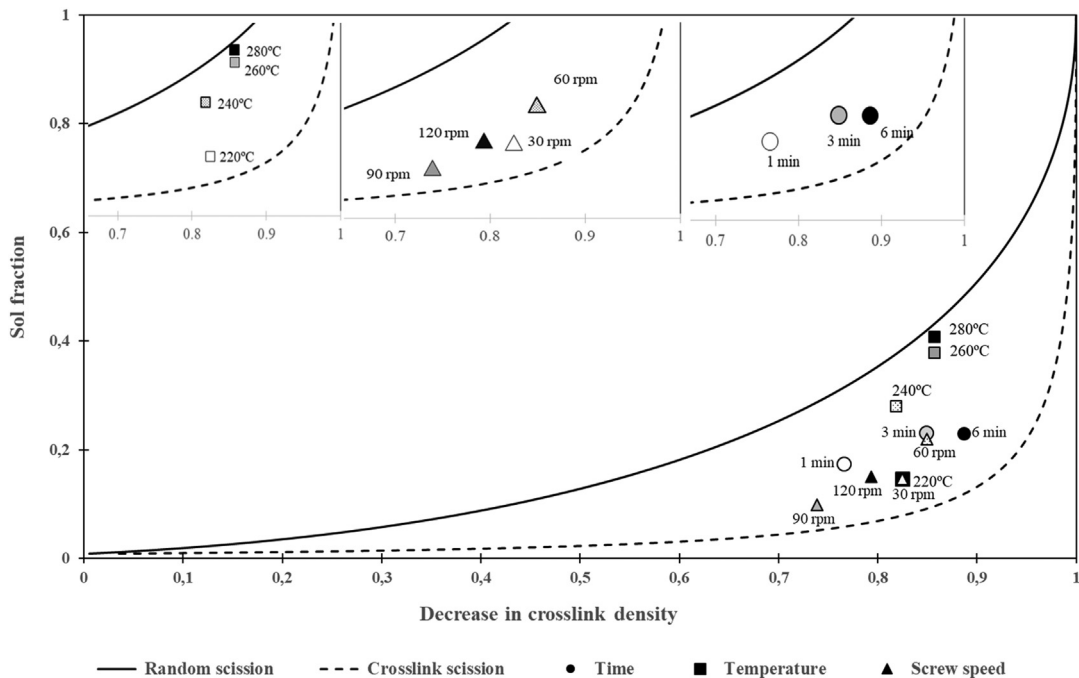
Figure 7.1.25 Influence of time, temperature, and screw speed on devulcanization efficiency in a twin-screw extruder.

devulcanized with 3.9 wt.% and with 6.85 wt.%. A higher amount of devulcanization aid is not necessarily beneficial.

3. Screw speed: As for the degree of devulcanization, the influence is not clear.

4. Amount of process oil: Combined with a low screw speed, high oil concentrations resulted in low tensile strength values.

From this study, it was concluded that the best conditions for the devulcanization of whole passenger car tire rubber in a twin-screw extruder are low shear forces and a devulcanization time of 6 to 7 min at a devulcanization temperature of 180°C. However, the relatively long residence time needed for the devulcanization limits the capacity of the extruder, as the length-to-diameter ratio needed 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, with limitations, an increase of the length-to-diameter ratio. A posttreatment on a mill with friction at a temperature of 60°C improves the morphology and properties of the devulcanizate.

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7.2

In-product-sorting end-of-life tires for effective recycling by devulcanization

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7.2.1 Introduction

The European Commission Directive of September 18, 2000 (Directive 2000/53/EC) deals with the management of end-of-life products. The purpose of this directive is to recover end-of-life waste in order to make a new raw material out of it.

In addition to the environmental issue caused by the storage of huge quantities of waste materials and the inevitable long-term shortage of certain raw materials, major economic developments such as the rapid development of certain countries (such as India and China) have caused an increasing demand and also tensions concerning waste materials.

End-of-life tires (ELTs) are a source of secondary materials for all countries with strong growth and especially for countries with few natural resources, such as European countries. Thus, End-of-Life tires (ELT) can constitute a strategic economic stake for raw material producers and rubber compounders.

However, as with the recycling of other used materials, the recycling of ELTs by devulcanization is generally difficult because of the association with other different materials that may be incompatible with each other. Therefore there is a need to study and improve existing sorting methods in order to provide the recycling industry with clean products that meet demanding specifications.

Currently, it is estimated that 49% of ELTs are incinerated mainly in cement plants and 46% are recycled as secondary material, mainly used in the manufacture of objects and recycled rubber. However, this mode of recycling is principally focused on the creation of objects bonded with polyurethane and only a small part is devulcanized for further processing and reuse after formulation and vulcanization.

The recycling of ELTs as new material by devulcanization involves four processing phases: collection, granulation, devulcanization, and marketing.

By using homogeneous and clean tire granulates ground tire rubber (GTRs) can be used to produce a higher quality devulcanized material. Efficient sorting and separation of ELT waste is therefore necessary, especially when it concerns waste composed of different gums whose formulas have different devulcanization kinetics, such as styrene butadiene (SBR), natural rubber (NR), and polybutadiene (BR).

Today, there are no separation technologies available that can separate rubber according to its nature or formula; it is impossible to separate, for example, SBR from NR or SBR from BR.

It has been found that the waste tire recycling industry by devulcanization is not in tune with the technical realities of the sorting processes used by ELT granulators. In order to further develop this industry, it is necessary to review and improve these sorting techniques by imposing further criteria and more relevant rules that should be defined.

7.2.2 Existing sorting criteria and their limits

ELTs are generally sorted before the shredding stage. For economic reasons, the only criterion applied in sorting ELTs is based on tire dimensions.

ELT granulation professional mainly classify tires according to their size. They can be divided into three categories: ELTs from passenger cars are all small tires, ELTs from trucks are those of larger sizes, and OTR (off-the-road) tires are even larger or tires from construction machinery and the agricultural world are mixed. However, this size criterion is completely subjective and does not ensure an effective, real, and optimal sorting (a sorting that takes into account the nature of the different elastomers composing each tire and not only the size of the tires.) so that the granulated material is destined for the devulcanization industry.

In fact, some large tires contain layers of rubber used in the manufacture of small tires (LV) such as SBR, for example, which can be found in some truck tires. Medium-size tires (e.g., light truck tires) are also sometimes listed with truck tires and other times with light truck tires. The criteria used so far have been satisfactory as long as the use of the GTR concerned sports fields or the manufacturing of objects using polyurethane

compounding. For these applications, transformers often use truck/light truck mixtures without any problems.

However, these criteria are no longer sufficient when it comes to developing good-quality recycled products (high added value). Indeed, devulcanization is much more sensitive to variations in the input material and this sensitivity manifests itself in several ways:

1. Heterogeneity of the devulcanized material: presence of devulcanized and nondevulcanized parts.
2. Variation in the mechanical characteristics of the devulcanized material.
3. Nonrepeatability of the devulcanization process.

This makes it difficult to integrate the devulcanized material into production processes, which limit its commercialization.

7.2.3 Mechanical characteristics of devulcanized materials according to the type of end-of-life tires

We can classify the devulcanized material in three categories (in terms of mechanical behavior) according to the source (the origin of the treated material):

- *Truck tread*: product composed mainly of NR and BR. Truck tread aggregates are generally clean and homogeneous because they are the result of selective sorting. Indeed, these aggregates are the result of retreading truck tires selected according to a more precise criteria. Generally, the mechanical characteristics of tire tread can reach maximum stresses of 14−15 MPa and strains up to 400%.
- *The whole truck tire*: when properly sorted, truck tires are relatively homogeneous because, as mentioned above, a truck tire is essentially made up of NR and BR. The heterogeneity of this product is greater than the previous category for two reasons: firstly, the formulae of the different parts of the same tire are different and secondly, the formulae differ from one range of tires to another and from one brand to another. The mechanical characteristics of devulcanized whole truck tire revulcanizates vary from 8 to 12 MPa for ultimate stresses and from 200 to 300% for ultimate deformations.
- *VL tires*: VL tires contain NR and SBR. These two products have very varied devulcanization kinetics, which cause problems during devulcanization. The mechanical characteristics obtained with this product fluctuate between 5 and

8 MPa at maximum stress and can reach up to 200% maximum deformation in the best of cases (Table 7.2.1).

The heterogeneity of granulates, when it is important, limits their use as feedstock (input material) for the devulcanization industry because the resulting products are often of very poor quality. In order to reduce these fluctuations, sorting will have to be further refined by finding other means and selection criteria in order to obtain the purest possible products.

7.2.4   Analysis of ground tire rubber samples available on the European market

This study was carried out at Phénix-Technologies located in Sancheville (France). Four big-bags of GTR produced from truck tires were purchased from five different European manufacturers, specialized in the granulation of ELTs.

A protocol was set up to statistically analyze the composition of the different GTRs. It was based on the assumption that the truck tires contained only NR and BR.

This protocol is based on Fourier transform infrared (FTIR) analysis of granulate samples randomly recovered from each big-bag. Each sample is composed of approximately 500 granulates (five batches of one hundred grains each), the goal being to identify SBR-containing granules. Thermogravimetric analyses (TGA) were also conducted to identify the various components.

Three types of gums were identified by FTIR (Fig. 7.2.1). Two of the spectra (types 1 and 2) identified are those of NR and BR. The third spectrum is that of SBR (type 3), recognizable by its characteristic peaks, first at 967/cm, which corresponds to the vibration of the 1.4-trans, the peak at 911/cm corresponds to the vibration of the 1.2-Vinyl bond, and the peak at 699/cm, which corresponds to the vibration of the styrene bond [9].

At the same time, thermogravimetric analysis carried out under nitrogen, with a temperature ramp from 50°C to 550°C at 10°C/min, was performed on each type of granule identified by FTIR (Fig. 7.2.2).

The results of the thermogravimetric analyses (Fig. 7.2.2) confirm that the big-bags do contain three types of gum: natural rubber (degradation temperature under these conditions is 371°C); styrene-butadiene (degradation temperature of 413°C); and finally polybutadiene (degradation temperature of 453°C).

Table 7.2.1 Summarizes some examples of the mechanical characteristics obtained on revulcanizates of different types of used tires.

| Process	Type of end-of-life tyre	Process parameters	Properties of revulcanizate	References
Thermomechanical	50% Trucks 50% Passenger	*Screw speed*: 50, 100, 150, 200, and 250 rpm, feed rate: 5 kg/h, *T°*: 180°C	*Stress at break*: 3—6.5 MPa, strain at break: 110%—180%	[1]
	Undefined	*Screw speed*: 80, 100, 120, 140, and 160 rpm, *T°*C: 160°C, 180°C, 200°C, 220°C, 240°C, ratio feed rate/rpm = 1.4	*Stress at break*: 5.62—12.5 MPa, strain at break: 337%—356%	[2]
Microwave	Passenger	900 W for 3 min, *T°* = 240°C, diphenyldisulfide as devulcanization agent	*Stress at break*: 10 MPa, strain at break: 226%	[3]
Ultrasonic	Unclassified (mixed tread and side walls of passenger and trucks)	120°C 20 rpm 3000 W 20 KHZ	*Stress at break*: 3—8.7 MPa, strain at break: 110%—217%	[4]
			Stress at break: 10.5 MPa, strain at break 250%	[5]
			Stress at break: 4.38—7.74 MPa, strain at break 131%—183%	[6]
Mechanical chemical	Nonclassified	Chemical devulcanization agent	*Stress at break*: 12.3—13.6 Mpa, strain at break: 330%—390%	[7]
	Tread from tire of heavy trucks	Internal mixer: 45 rpm 180°C and 200°C	*Stress at break*: 4.2—6.5 MPa strain at break: 220%—340%	[8]

It should be noted that the three gums identified above were found on all the big-bags received. A statistical analysis to estimate the proportion of each gum was carried out on the 500 granules analyzed for each batch. The results of the distribution of these different gums according to each batch are shown in Fig. 7.2.3.
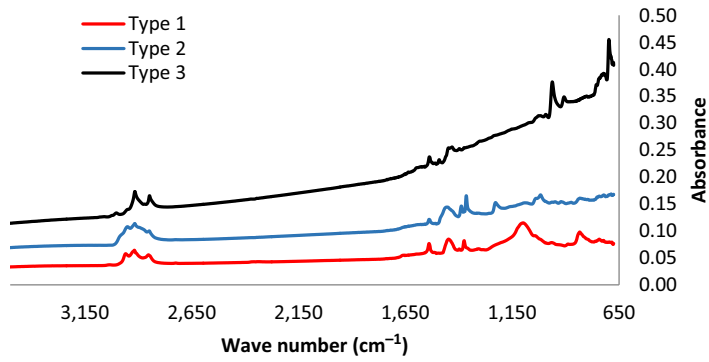
Figure 7.2.1 Fourier transform infrared spectra identified in the granules.
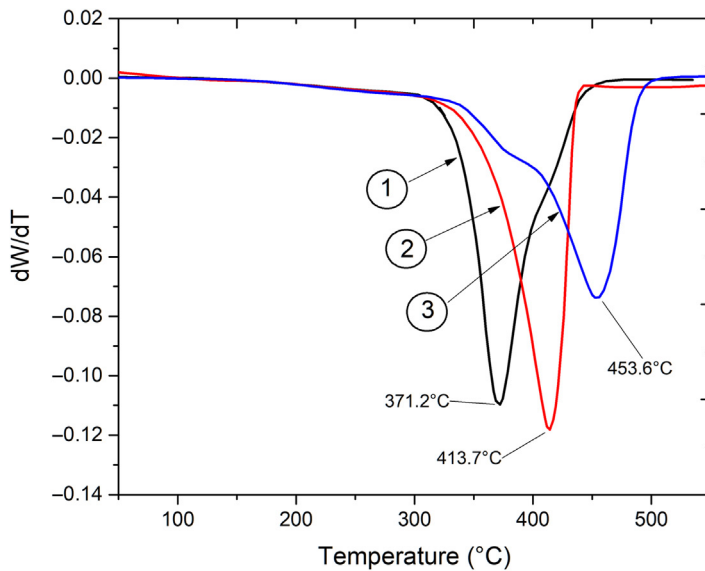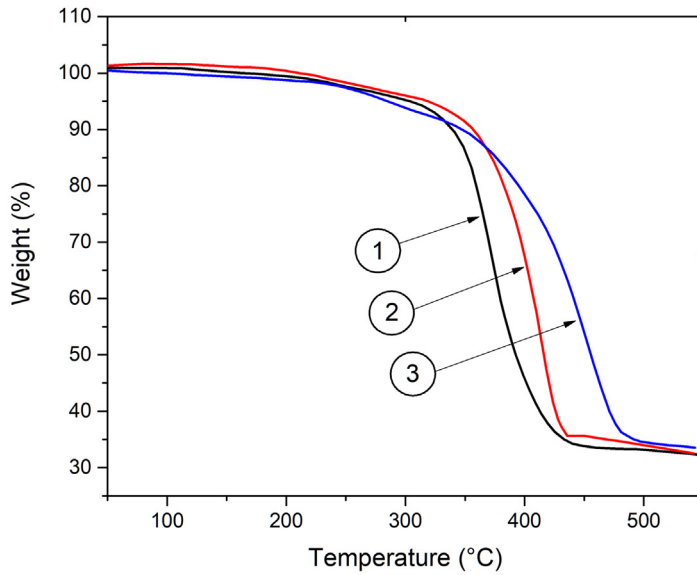
Figure 7.2.2 Thermogravimetric analyses of the three types of gums detected by Fourier transform infrared.
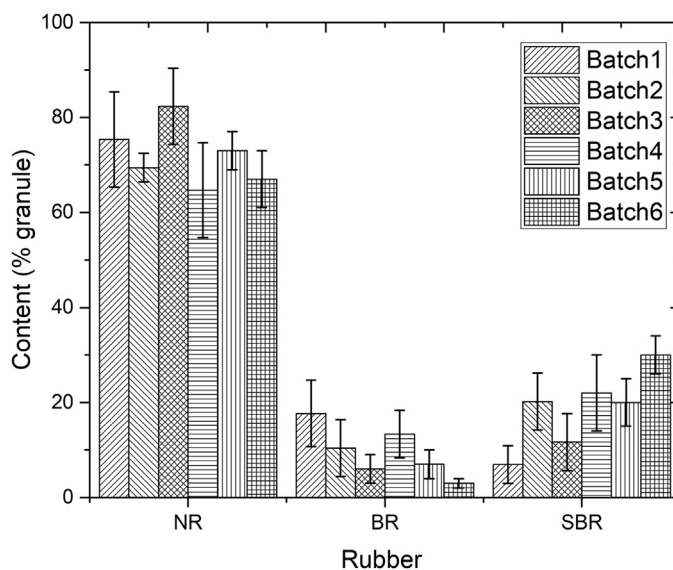
Figure 7.2.3 Distribution of the different gums by batches received and analyzed.

A very large dispersion of the proportion of SBR in each batch (Fig. 7.2.3) was observed, although truck tires are not supposed to contain this type of rubber. This proportion is estimated to be around 7% in batch 1 and 20% in batch 2, although the supplier is the same and the only difference is the delivery date of the two batches. In some cases, the proportion of SBR can be higher than 30%, as in the case of batch 6. What conclusion can be drawn from this situation?

### 7.2.5 Impact of ground tire rubber heterogeneities on the devulcanized material

In order to understand the effect of this dispersion on the quality of the devulcanized products, a sample from batch 1 and another sample from batch 2 were devulcanized and analyzed. To do so, the thermomechanical devulcanization process was used, under the same conditions, using a twin-screw extruder, corotating with a screw profile designed specifically for rubber devulcanization.

Visually, as can be seen, firstly, the strips extruded from the two batches (1 and 2) exhibit different morphologies (Fig. 7.2.4). Indeed, the strip obtained from batch 1 with an SBR proportion of about 7% is relatively smooth in appearance, in contrast to

Figure 7.2.4 Visual aspect of the two batches.
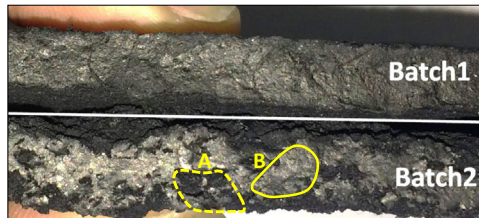

Figure 7.2.5 Extruded bands of two batches.

the aspect of the strip obtained from batch 2 with an SBR proportion of about 20%, which is more wrinkled and granular.

The cross-sectional view of two strips (batch 1 and 2) is shown in Fig. 7.2.5. Depending on the batch, the results showed significant material heterogeneities. Indeed, the general appearance of the band obtained from batch 1 is smooth, shiny, and homogeneous while that of the band from batch 2 is heterogeneous, with smooth domains resembling the smooth part of batch 1 (circled continuously – zone B) and granular domains (circled dashed – zone A).

Pieces of material were picked from both domains (A and B) of batch 2 and were analyzed according to the same procedure used for granule analysis (Fig. 7.2.1), using Fourier Transformed Infrared (Fig. 7.2.6) and Thermogravimetric analysis (Fig. 7.2.7).

FTIR analysis (Fig. 7.2.6) of the two domains observed on the faces of the two extruded bands (domain A and B) shows two very distinct spectra very similar to the spectra already obtained on the pellets.

In fact, the spectrum of zone A, corresponding to the granular domain, is characterized by three wave numbers, firstly that at 967/cm, which corresponds to the vibration of 1.4-trans; then the peak at 911/cm of the vibration of the 1.2-vinyl bond; and finally the peak at 699/cm, which corresponds to the vibration of the styrene bond. This spectrum indicates that this is the spectrum of the SBR. The smooth and devulcanized part, Part B, showed vibration peaks of natural rubber.
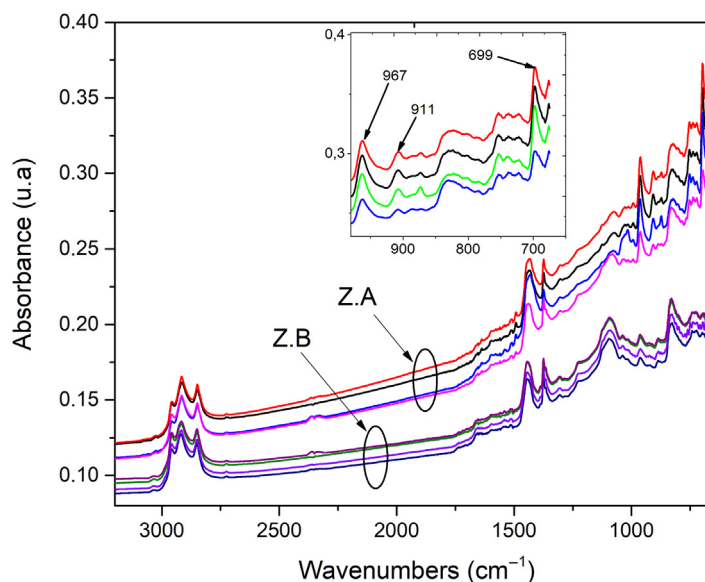
**Figure 7.2.6** Fourier transform infrared analysis of zones A and B.

These observations are confirmed by TGA analyses (Fig. 7.2.7), which also shows that the smooth and glossy material (Part B) degrades at 373.4°C, which corresponds to the degradation temperature of NR. Concerning the material from zone A, its degradation temperature is about 420.8°C, almost corresponding to the thermal degradation temperature of SBR.

The presence of the nondevulcanized material domains is probably related to the difference in the devulcanization kinetics of the two gums (NR and SBR) after thermomechanical devulcanization using extruders.

It is therefore clear that the proportion of SBR plays a significant role in the devulcanization of NR/BR. Indeed, the increase of the SBR fraction from 6% to 20% changes the appearance of the devulcanized material, leading to the appearance of nonvulcanized material domains and reduces the mechanical characteristics (stress/strain).

Finally, a sample of each devulcanizate was formulated and then vulcanized to study their mechanical characteristics. For this purpose, the two samples were formulated with 4 phr ZnO (Zinc oxide), 2 phr stearic acid, 1 phr CBS (n-cyclohexyl -2-benzothiazole sulfenamide), and finally 1 phr sulfur (S). The mixture was processed on a cylinder mixer, then calendered (rolled), and finally vulcanized into a 2 mm thick plate.

The mechanical characteristics of the two products are very different. Indeed, a breaking stress of about 12 MPa and a
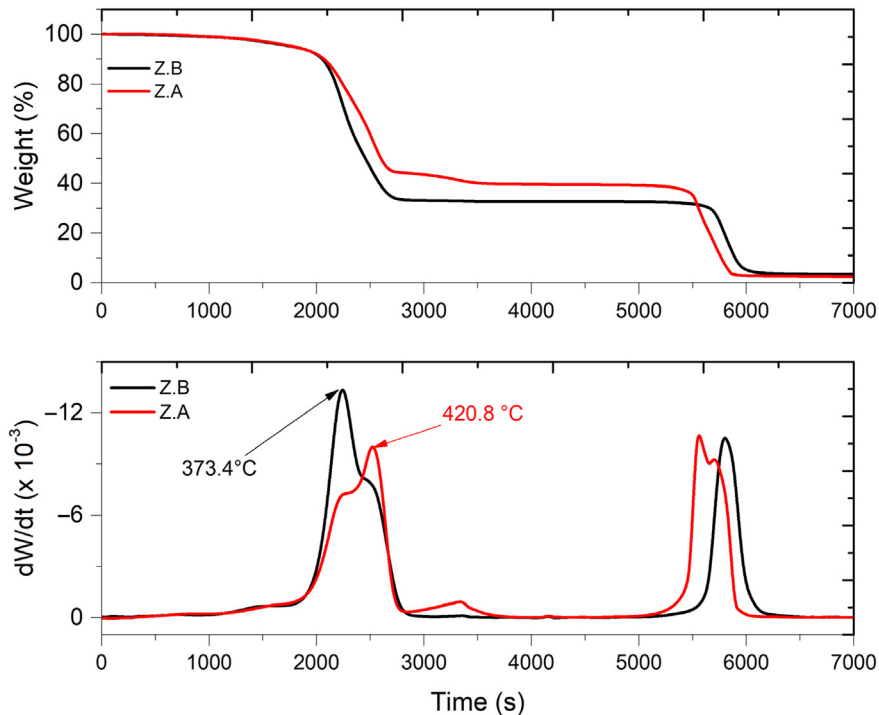
**Figure 7.2.7** Thermogravimetric analysis of Part A and B.

breaking deformation of about 350% were obtained on the devulcanized material from batch 1 in comparison to 7 MPa and about 150% deformation for the material obtained from batch 2.

7.2.6   Analysis of ground tire rubber at the industrial scale (case of industrial output)

7.2.6.1   Analysis of the incoming material (aggregate or feedstock)

The industrial-scale FTIR analysis of a delivery of GTR-truck tire was carried out on 18 tons of powder with a granular size of between 1 and 4 mm, delivered in a single batch and by the same granulator, in 18 big-bags of one ton each. An analysis following the protocol described above was carried out on all the big-bags received. Fig. 7.2.8 shows the SBR ratios measured in each big-bag.

The average of the percentage of FTIR spectra containing SBR measured over all big-bags is around 23%, however, there is quite a large dispersion from one big-bag to another. Indeed, this
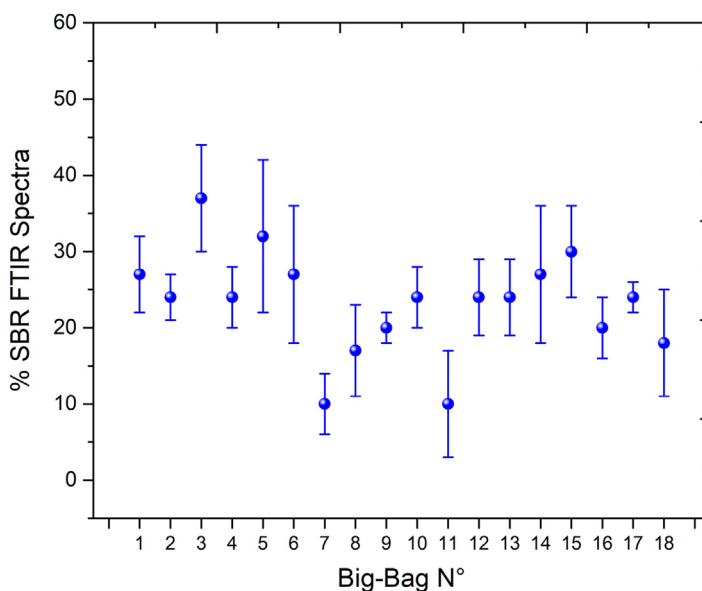
Figure 7.2.8 Statistical analysis of styrene butadiene in the different big-bags.

percentage varies from 10% in some cases to more than 30% in others. Moreover, the standard deviation measured in some cases in the same sample (i.e., in the same big-bags) is very large, which means that the protocol adopted is not very representative of the reality of a big-bag but only gives an idea of its heterogeneity.

Once the material was characterized, quantities of granules from each big-bag were devulcanized by the thermomechanical process using a 40 mm corporate twin-screw extruder (Leist Ritz Maxx40) with the same parameters for all the big-bags.

Devulcanization took five weeks at a rate of 70 kg/hour (i.e., approximately 700 kg/day). Three times a week (Monday–Wednesday and Friday of each week), samples were retrieved from the devulcanization line for analysis.

All samples recovered were analyzed; first to determine their viscosity, then to determine their mechanical characteristics after they were formulated and vulcanized (sulfur, zeno, CBS, and stearic acid).

7.2.6.2   Effect of the feedstock heterogeneity on the viscosity of obtained devulcanized rubber

Viscosity measurements were carried out throughout the production of the devulcanized material, which lasted almost a month. These measurements are shown in Fig. 7.2.9.
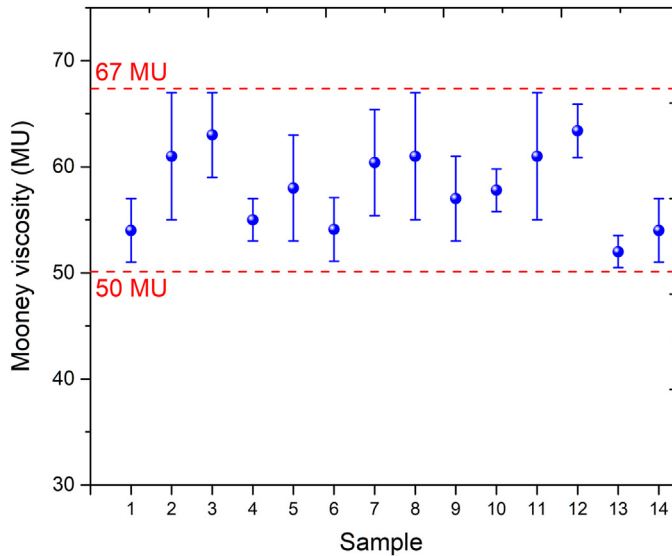
Figure 7.2.9 Viscosity of the different batches devulcanized along the production period.

The average viscosity over all samples is about 58 Mooney, however, it varies considerably from one big-bag to another. Indeed, the range of viscosity obtained varies from 50 to 67 Mooney. These variations are the consequence of the feedstock variation.

7.2.6.3   Effect of the feedstock heterogeneity on the mechanical properties

Throughout production, samples were collected, sulfur-accelerated, and vulcanized into 2 mm thick plates. H2 dumbbell type specimens were cut and tested according to the ISO37 standard and angular specimens were cut to perform tear tests according to the NFT 46-007 standard.

The results of these mechanical tests show the changes in stress at break (Fig. 7.2.10A), strain at break (Fig. 7.2.10B), and tear resistance (Fig. 7.2.10C).

As with viscosity, the mechanical characteristics of the devulcanized material vary greatly depending on the big-bags but also within the same big-bag. Variations ranging from 7.5−10.5 MPa are measured in terms of stress at break, from 150% to 245% in terms of deformation at break and finally from 16 to 22 N/mm in terms of tear resistance.

Again, the variation in the mechanical characteristics of the devulcanized material is strongly related to the variation in the homogeneity of the input material.
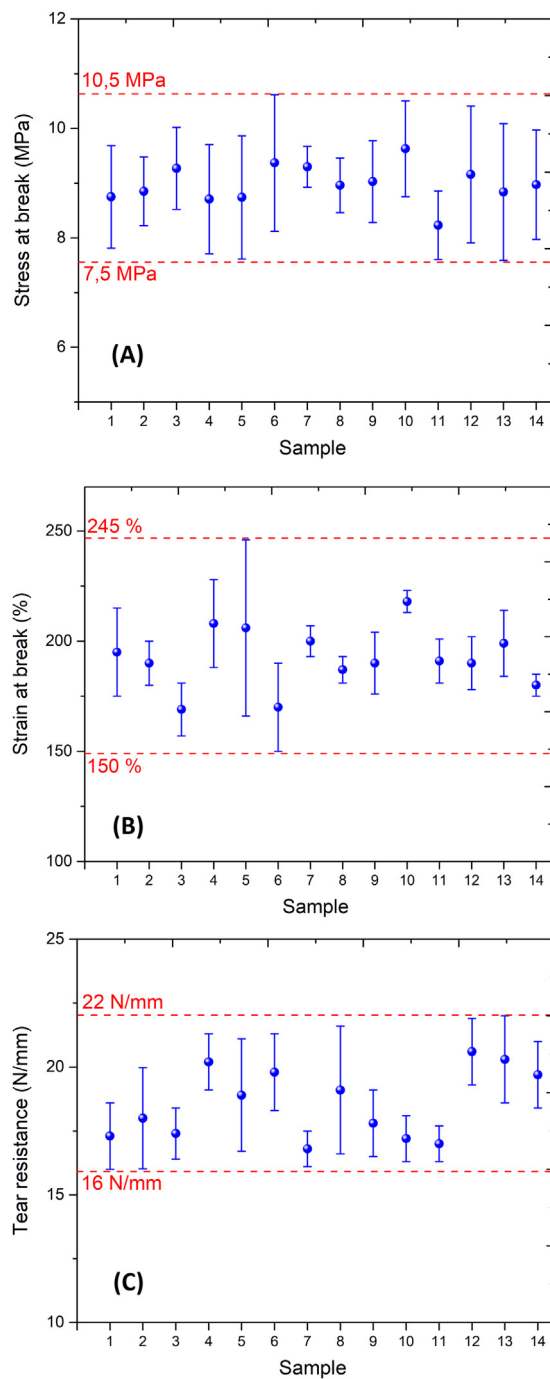
Figure 7.2.10 Stress at break (A), strain at break (B), and tear strength (C).

These variations have led some devulcanization manufacturers to provide only the minimum stress and minimal deformation on the technical data sheets of their products on sale; often, these characteristics are given with very wide standard deviations, a sign of very high dispersion.

7.2.7 Conclusion

New type of sorting other than the one existing or currently practiced must be implemented by used tire granulators to provide the devulcanization industry with cleaner, more homogeneous products. This would make it possible to avoid problems with the stability of the devulcanized material and also to stabilize and control the processes. These issues are a real obstacle to the development of the market for devulcanized material.

The improvement of the sorting condition should make it possible to reduce the heterogeneity of the GTR granules, thus reducing fluctuations in the characteristics of the devulcanized material and thus improving the mechanical characteristics once the material has been devulcanized, since the quality of the output material (devulcanized) depends essentially on the quality of the input material. This will enable the devulcanization industry to provide the rubber industry with more stable products with optimal mechanical characteristics.

Improving the homogeneity of the input material (feedstock) will also help the devulcanization industry to control the devulcanization processes because they will be more stable, more repeatable, and easily industrialized.

These conditions of process stability, repeatability, and ease of use are necessary for the devulcanization industry to produce a secondary raw material that can be valorized and for the rubber industry to be able to use it on a large scale in many industries.

The improvement of the sorting criteria will generate an additional cost for the granulation industry because it will require either additional investments or a larger and more qualified workforce. However, this additional cost can quickly impact on the devulcanization industry because it will allow them to have a more stable and easier to control process. Furthermore, they will also be able to offset part of this additional cost on their customers because they will be able to provide better quality and repeatable products.

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