

# TIRE RECYCLING TECHNOLOGIES: WHAT IS THE FUTURE?

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## ABSTRACT

Recycling is a heavily discussed topic nowadays, and recycled tire material to be re-used for the same application is one of the spear points of current R&D activities. Regarding the immense amount of used tires, more than just one outlet for the recycled material is needed. Besides the commonly used particulate and reclaimed rubbers, devulcanizates are another alternative currently under development.

As the name indicates, devulcanization is the reverse of the vulcanization step: mainly crosslinks are broken and the polymer remains intact. This leads to a recycled material with properties closer to the original ones compared to reclaim. The latter is produced in a non-selective process, in which the whole crosslinked polymer network is broken, including scission of the polymer chains.

A devulcanization process for passenger car tire rubber is developed step by step, starting with the single polymers contained in a tire, and finally finishing with whole tire granulate. The devulcanizate will be put in a broader frame of different recycling options for tire rubber and their potentials.

## INTRODUCTION

Rubber is a very durable material, in particular tire rubber, and this poses a major challenge for recycling. For end-of-life tires, incineration is currently the most important outlet, impeding the reuse of this valuable raw material in new rubber products. Other alternatives are back-to-feedstock methods such as pyrolysis: in this process, the aim is to recover the components of rubber such a gas, oil and carbon black. Material reuse is another, shorter loop: granulated or powdered rubber is reused for applications in products on a lower quality level. However, a considerable share of material recycling can be achieved only if tire material can be used in real recycling loops: tires back into tires.

The best practice to achieve a high quality and easy processable recycled rubber product is devulcanization, as shown in Fig. 1. The so far commonly available re-plasticized rubber is made in an uncontrolled degradation process, in which a considerable amount of polymer scission is occurring resulting in a low quality material. Fig. 2 summarizes the most important characteristics of devulcanizate versus reclaim.



*Fig. 1: Devulcanizate from an extruder process*

In a devulcanization process, the network of sulfur crosslinks will be broken while polymer chains will remain intact. The ratio of crosslink to main chain scission can be increased by the use of a devulcanization aid: a chemical compound which attacks the sulfur bridges and de-activates the reactive fragments from the devulcanization reaction. It can be measured by correlating sol content and crosslink density after devulcanization in a Horikx plot as shown in Fig. 3 <sup>1</sup>.

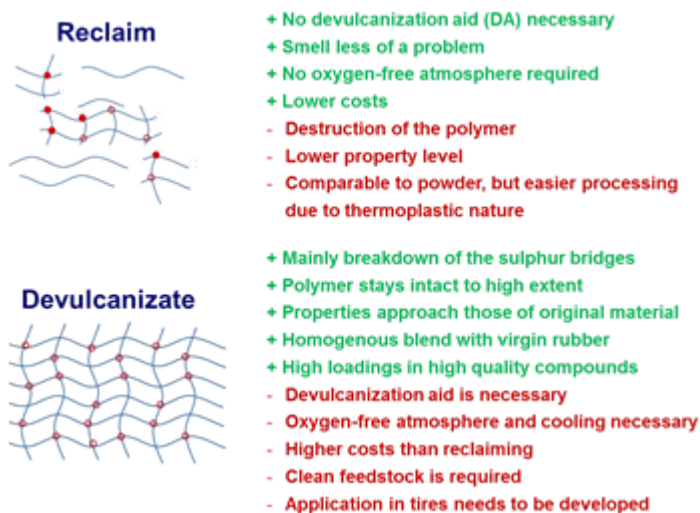


Fig. 2: Characteristics of devulcanizate and reclaim

Passenger car tire material is a blend of different polymers: styrene-butadiene rubber (SBR), butadiene rubber (BR), natural rubber (NR), and isobutylene-isoprene rubber (IIR), with the main component (40%) being SBR <sup>2</sup>. Each polymer has its own specific function in tires, and all show their own particular degradation and devulcanization characteristics. It is well-known that NR is rather easy to be re-plasticized, though from literature it is not clear whether the predominant mechanism is devulcanization or polymer scission. SBR and BR are more difficult to handle, as the network fragments tend to re-combine, resulting in an uncontrolled re-crosslinking of the polymer.

## EXPERIMENTAL

The devulcanization process for whole passenger car tire material was elaborated using model compounds based on SBR, BR, NR, and CIIR. Recipes, mixing conditions and testing procedures are given in the thesis of S. Saiwari <sup>3</sup>. Based on the findings for these single rubber materials, the best devulcanization conditions for whole passenger car tire granulate were defined and tested in actual practice. Besides, the influence of the presence of silica and different coupling agents on the devulcanization efficiency was studied in model compounds. All details of these studies can be found in the same reference <sup>3</sup>.

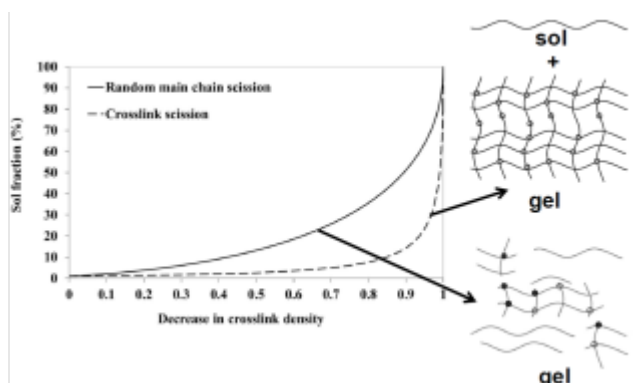


Fig. 3: Horikx plot for analysis of the ratio of crosslink to main chain scission.

## RESULTS AND DISCUSSION

Earlier work has shown that disulfides are the most effective chemical compounds for devulcanization of general purpose polymers like NR and SBR <sup>4,5</sup>. Based on this, a screening for the most efficient devulcanization of SBR was performed using different disulfides: diphenyldisulfide (DPDS), dibutyldisulfide (DBDS) and di(2-aminophenyl) disulfide (APDS). The addition of low concentrations of disulfides results in a significant increase in the soluble fraction and a decrease in crosslink density compared to untreated and just thermally treated SBR. When comparing the performance of the three different types of disulfides, the compatibility of the devulcanization aids with SBR turns out to play a major role for the properties of the devulcanizates. DPDS is found to be the most effective devulcanization aid, while APDS is the least effective as seen in Fig. 4, a conclusion that is supported by the difference in solubility parameters: it is the highest for the APDS/SBR combination. Even though DBDS has a solubility parameter close to SBR, the devulcanizate does not show satisfying

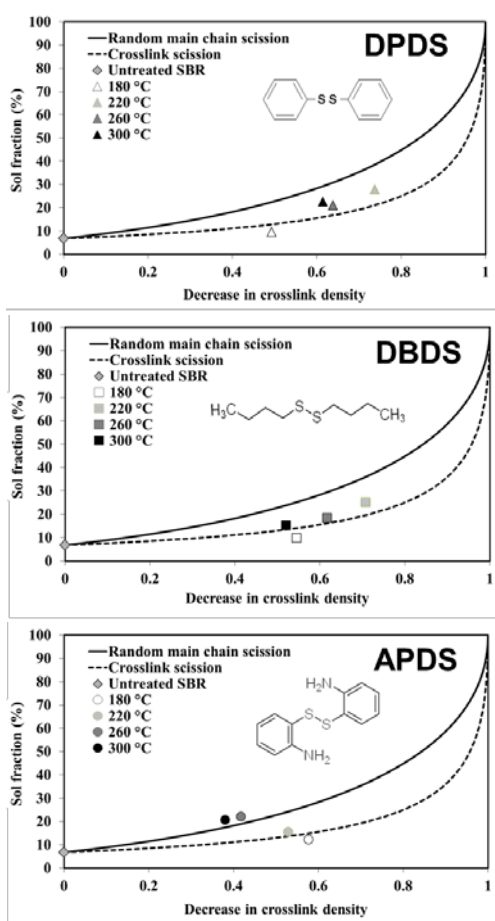


Fig. 4: Horikx plots for devulcanization with different disulfides.

The elaboration of the optimal devulcanization process for the blend of elastomers and other ingredients, the filler system in particular, is more complex than just finding the best compromise of the devulcanization parameters for the single types of elastomers used in a passenger car tire. In actual practice, the resulting inhomogeneity in devulcanization causes a reduced decrease in crosslink density at a particular sol fraction than would have been obtained from a homogeneous breakdown.

One of the recent changes in passenger car tire tread compounding is the replacement of carbon black by a silica-silane filler system. The presence of the coupling agents in silica-filled rubber results in a chemical bond between the silica surface and the polymer, and the active moiety for the link to the polymer is a sulfidic group. The question arises how this sulfur-link will influence the devulcanization efficiency. Therefore, silica-filled SBR compounds with different types of coupling were devulcanized. The results as shown in Fig. 6 illustrate that still crosslink scission is the principal mechanism, but that the achievable reduction in crosslink density is 40%, compared to up to more than 70% for carbon black filled rubber.

An application study has shown, that adjustment of the curing system and the filler quantity results in a 60% increase of mechanical strength values compared to the non-adjusted 50/50 blend of virgin compound and devulcanizate. Taking these adjustments into consideration, addition of 30% devulcanizate to certain tire compounds is realistic; in contrast to a maximum of approximately 5% addition of the conventional reclaim qualities.

properties after devulcanization; however, the devulcanization temperature plays a major role in this case.

NR and CIIR show different behaviour than SBR. Breakdown of NR in this temperature range results in an almost complete destruction of the polymer network; crosslink density is reduced to almost zero and the sol fraction is close to 100%. At higher temperatures, the same result is found for CIIR, while at 220°C the reduction in crosslink density is lower compared to the other polymers, as seen in Fig. 5.

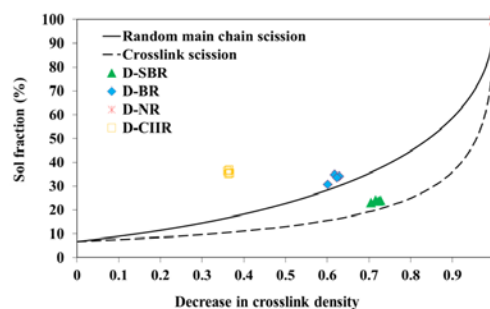


Fig. 5: Horikx plot for the devulcanization of the different tire polymers.

Devulcanization aid: DPDS 30 mmol; oil: TDAE 5%w/w, temperature: 220 °C, time: 6 minutes, atmosphere: with N<sub>2</sub> purging, dump conditions: in liquid nitrogen, drying: no

## SUMMARY

For the devulcanization of passenger car tire rubber, SBR is the most critical component. A screening study of different devulcanization aids based on different types of disulfides led to the conclusion that the most efficient devulcanization aid for this polymer is diphenyldisulfide, DPDS. BR acts similar to SBR and can be devulcanized efficiently with DPDS under comparable process conditions. NR is a non-critical component in the tire blend and will be devulcanized sufficiently under the chosen circumstances. The devulcanization behavior of CIIR is different: It will not effectively devulcanize in the temperature range of SBR and BR, but requires a higher temperature for a significant decrease in crosslink density. After fine-tuning the devulcanization process for whole passenger car tire rubber, this material can be devulcanized efficiently up to a degree of more than 70%. The presence of silica and silane hampers the reduction in crosslink density in the devulcanization process compared to carbon black filled tire rubbers.

Tailoring of compounding and processing is crucial for the application of devulcanizate; if both are adjusted properly, quantities of up to 30% of devulcanizate can be used in certain tire compounds.

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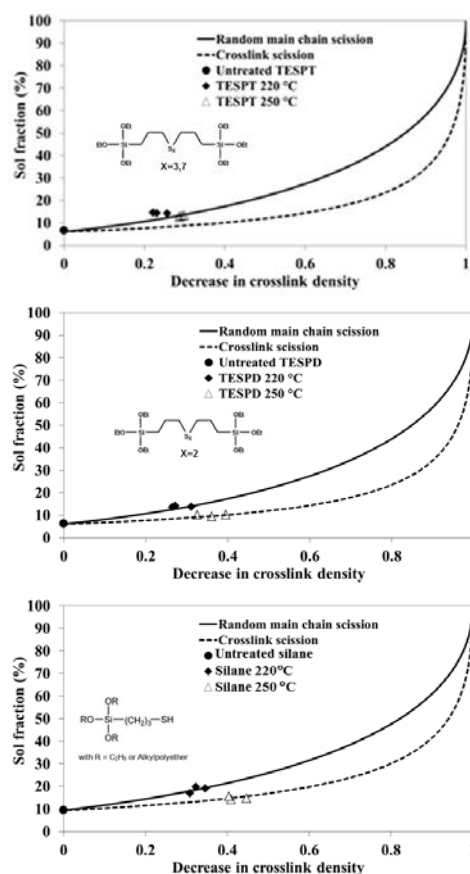


Fig. 6: Horikx plots of tread compounds with different silanes.