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Lifetime recycling loops for elastomer products

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Recycling of rubber worldwide is of growing importance because of increasing raw material costs, diminishing resources and growing awareness of environmental issues and sustainability.

A variety of different recycling processes for rubber have been investigated and developed throughout the years. Several in-depth reviews discussing the state-of-

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Edited by John Dick

the-art of rubber recycling were published in 1974, 2002 and 2012.¹⁻³ The main recycling methods hierarchically classified in the order of environmental and economic preference are shown in **Fig. 1**.

The lowest level is burning vulcanized rubber for energy recovery, and on the second level reside back-to-feedstock methods such as pyrolysis of used rubber to recover gas, oil and chemicals. The third method on the next level is material recycling by transforming used rubber into products with inferior quality compared to the original material or using recovered rubber for the production of new rubber products.

The most efficient rubber recycling route—or the highest level on the recycling ladder—is transforming used rubber into products of characteristics equal to that of the original materials; for example used tire rubber back into tires.

In the rubber recycling process, two types of rubber network breakdown simultaneously occur: reclamation and devulcanization, as shown in **Fig. 2**.

Reclaiming and devulcanization are often referred to as similar processes. In spite of the fact that they are similar in the procedure, they are fundamentally

Executive summary

With depletion of natural resources and growing awareness of the limited capabilities of the globe to cope with pollution, the need to design lifetime recycling loops for all types of products is steadily increasing. Rubber articles of all sorts and the need for a proper disposal of these at the end of their life cycle cannot escape this trend, and also come more and more into focus.

Most conspicuous in this context are tires, of which about 800 million are scrapped worldwide on a yearly basis. If piled up at a height of 25 centimeters each, it establishes a pile of 200,000 kilometers—two-thirds of the distance to the moon per year. Apart from the environmental problems which these scrap tires represent, they actually also are a source of valuable materials if they can be recycled and reused in proper ways.

This paper reviews the latest developments in recycling; devulcanization of rubber articles, including tires of various sorts; and the contribution which the research in the University of Twente has played in this field. It highlights what has been achieved for different major rubber types, but also what the hurdles are to be taken before rubber recycling is as obvious a technology as the manufacturing of first-use rubber articles.

different in the degree of rubber network breakdown and the molecular structure of the polymeric material. In other words, the difference between “reclaimed” and “devulcanized” rubber lies in different ratios of crosslink vs. polymer chain scission.

Devulcanization, the most ideal way of rubber recycling, is the process that aims to reverse vulcanization as far as possible without damaging the polymer. In sulfur vulcanization, formation of a rubber network by both carbon-sulfur bonds (C-S) and sulfur-sulfur bonds (S-S) takes place. Therefore only these bonds should be broken during devulcanization.

Devulcanization is the process of cleaving the monosulfidic (C-S-C), disulfidic (C-S-S-C) and polysulfidic (C-S_x-C) crosslinks of vulcanized rubber. An efficient devulcanization is needed in order to achieve a high-quality recycled rubber.

Reclamation is different from devulcanization due to the scission of the carbon-carbon bonds of the polymeric chains. Reclaiming is a process in which vulcanized rubber is converted into a state that

it can be mixed, processed and vulcanized again by using conventional processes.

Transforming the cured rubber into a re-processable material is done by breaking the links between and partly within the polymer chains. The general problem of the current reclaiming processes of rubber is the fact that apart from sulfur-crosslinks, the main polymer chains also are broken, and this influences the properties and reduces the quality of the recycled material. This technology is sometimes incorrectly referred to as devulcanization.

For reclaimed rubber, relatively poor mechanical properties are frequently reported, originating from changes of the molecular structure of the polymer that occur during the reclaiming process. Extensive polymer scission and a partly re-combination result in highly branched chain segments that differ greatly from virgin rubber.

In view of these arguments, the conversion of used rubber into a re-processable and re-usable form by the currently used physical/chemical processes should be called reclamation rather than devulcanization. The broken polymer chains generated in the reclaiming processes influence the properties and reduce the quality of the recycled material.

If the rubber is devulcanized, ideally only sulfur crosslinks are broken while the polymer chains remain intact. Consequently, the devulcanizate resembles the original material in structure and quality. An improvement of the properties of recycled rubber by developing a more selective breakdown process or “efficient devulcanization” is an important issue for the rubber recycling technology and a global challenge.

Devulcanization vs. reclamation: The Horikx-Verbruggen Model

Devulcanization efficiency can be analyzed by characterization of the creation or destruction of polymer networks. In rubber recycling processes, the rubber network is broken, causing main-chain scission and crosslink breakage.

There are two methods to investigate whether main-chain scission or crosslink breakage is the dominant process during devulcanization. The first method is based on the amount of soluble polymeric material generated during devulcanization—so-called sol-gel analysis. The second method is related to stress relaxation of the rubber network, which is based on the idea that the stress at any state of degradation is proportional to the network chain density.

The sol-gel analysis, developed by Charlesby in his study on the relationship between crosslinking, main-chain

The author

Jacques Noordermeer currently is a retired professor on part-time assignment at the University of Twente's Department of Elastomer Technology and Engineering in the Netherlands. He is a veteran of more than 40 years in the rubber and plastics industries.

He received his master's in biochemistry from Delft University of Technology in 1970, and received his doctorate from there in 1974. He followed that by being a post-doctoral research associate at the University of Wisconsin's Rheology Research Center.



Noordermeer

Noordermeer worked with General Electric Plastics from 1977-80. From 1981-99 he held various positions related to EPDM and rubber research and development at DSM Elastomers B.V. His positions included polymer development specialist; director of research and application technology; and R&D coordinator between DSM's global sites. He continued as an advisory consultant for DSM and then Lanxess from 2000-12.

He began his work in academia as a part-time professor of rubber technology at the University of Twente from 1995-2000. He was a full-time professor of Elastomer Technology and Engineering there from 2000-12, including time as head of the department. He retired and moved onto a part-time role at the school in 2013.

During his time at the University of Twente, his research focused on a variety of elements of rubber technology, including mechanisms of rubber reinforcement; crosslinking chemistry; rubber recycling/reuse; thermoplastic elastomers; and fiber/cord reinforcement.

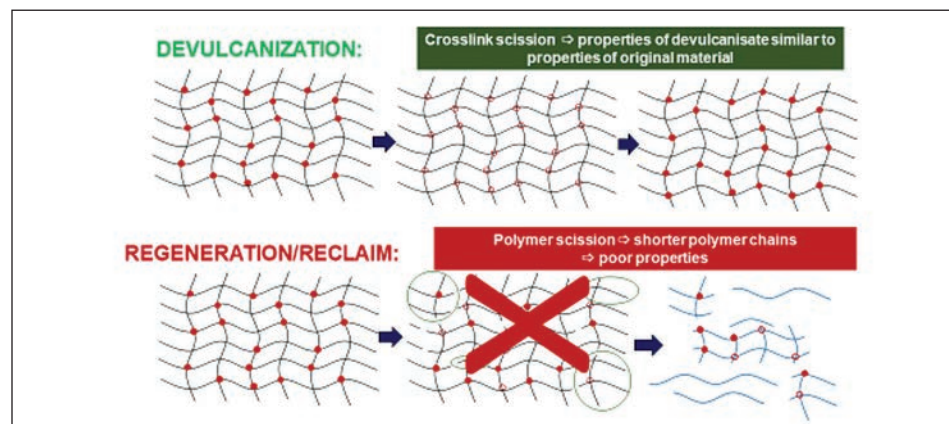
Noordermeer has won a variety of awards during his career, including: the technical award from the International Institute of Synthetic Rubber Producers; the gold medal of the International Rubber Conference Organization; the ACS Rubber Division's George Stafford Whitby Award; the Dutch Master of Materials; and the Lifetime Achievement Award of the Tire Technology International Organization. He also twice won best paper honors at Rubber Division meetings.

In addition, he is a member of numerous professional organizations. He currently is a member of Sigma Xi, the Scientific Research Society; the ACS Rubber Division; the Dutch Association of Rubber and Plastics Technologists; the International Rubber Conference Organizing Committee; and a board member of the Dutch Natural Rubber Foundation.

Fig. 1: Current recycling alternatives for scrap tires.



Fig. 2: Two types of network breakdown: Devulcanization vs. regeneration/reclamation.



scission and gel fraction in irradiated polymers, is based on the amount of soluble polymeric material generated.^{4,5}

Horikx assumed that these relations also were applicable to determine the sol fraction of a rubber sample undergoing network degradation by aging.⁶ Horikx used Charlesby's theory to develop a method in which a vulcanized rubber network is broken down again via two

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routes: main-chain scission and selective crosslink breakage.

This model was reworked by Verbruggen in her doctoral thesis, and recently published in Rubber Chemistry and Technology as a means to quantify the difference between the two mechanisms during network destruction.^{7,8}

Fig. 3 gives a graphical representation of the model. The curves in the figure correspond to the situation where only main chains are broken (solid curve) and where only crosslinks are broken (dashed curve). In the case of crosslink scission only, almost no sol is generated until all of the crosslinks are broken; only then the long

chains can be removed from the network.

In the case of 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. By measuring the amount of soluble polymer vs. decrease in crosslink density generated during network degradation, and correcting for the amounts of non-solubles in the rubber compounds,—such as fillers like carbon black, silica and mineral fillers—a reasonably good idea can be gained about the relative importance of the two mechanisms.

Only at the highest decrease of cross-

link density does the method cease to work due to the bound rubber: the amount of rubber physically or chemically fixed to the filler, which cannot be dissolved. See grey shaded area in Fig. 3.

Devulcanization of EPDM

Devulcanization: For EPDM rubber, α -hydrogen-containing aliphatic amines, such as HexaDecylAmine (HDA), were found to be very effective devulcanization aids.⁷⁻¹⁰ The relative decrease in the EPDM crosslink density was reported to be dependent on the concentration of the amines: a higher concentration of amines leads to a stronger decrease in crosslink density.

The use of HDA in a comparative study of two different vulcanization systems for carbon black-filled EPDM rubber was investigated, and HDA was found to be suitable as a devulcanization agent for both EPDM rubbers. Dijkhuis et al. stated that devulcanized rubber from conventionally vulcanized EPDM, mainly polysulfidic in

nature, shows a decrease in crosslink density with increasing HDA concentration and at low devulcanization temperatures.¹¹

After devulcanization at the lower limit of the experimental temperature window (i.e. 225°C), the concentration of remaining di- and polysulfidic crosslinks is higher than the concentration of monosulfidic bonds, while at the upper temperature level (i.e. 275°C), the concentration of monosulfidic bonds is highest, as shown in Fig. 4.

For efficiently vulcanized EPDM with primarily monosulfidic crosslinks, HDA again has a positive effect on the devulcanization efficiency at low temperatures of maximum 225°C. At higher temperatures, the crosslink density increases with increasing concentrations of HDA.

A comparative study between two different vulcanization systems was done, and it was found that conventionally vulcanized EPDM devulcanizes to a larger extent by crosslink scission compared to HDA devulcanization.

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Fig. 3: Horikx-Verbruggen quantification of random main-chain scission vs. crosslink scission.

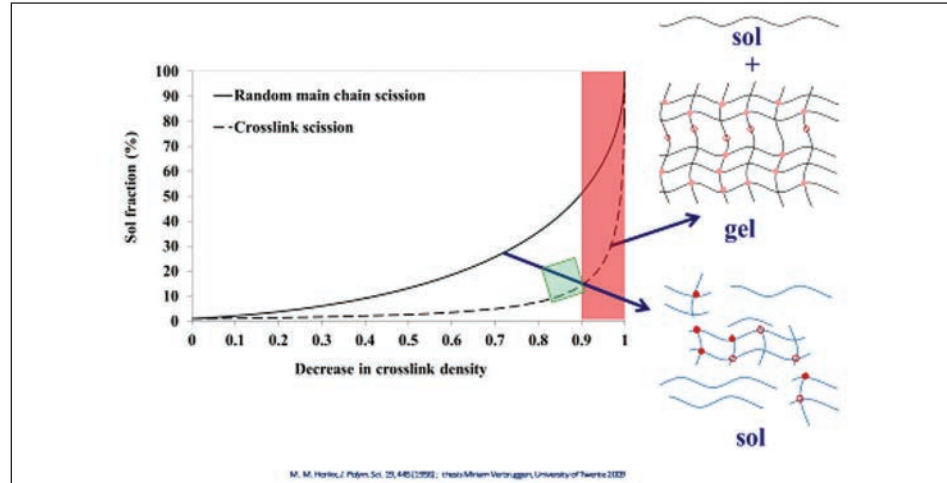


Fig. 4: Optimization of EPDM devulcanization: Influences of Concentration devulcanization aid (HDA) and mixer rotor speed on (a) Mooney viscosity of devulcanizate; (b) Insoluble fraction; (c) Overall crosslink density; (d) Monosulfidic crosslinks remaining.

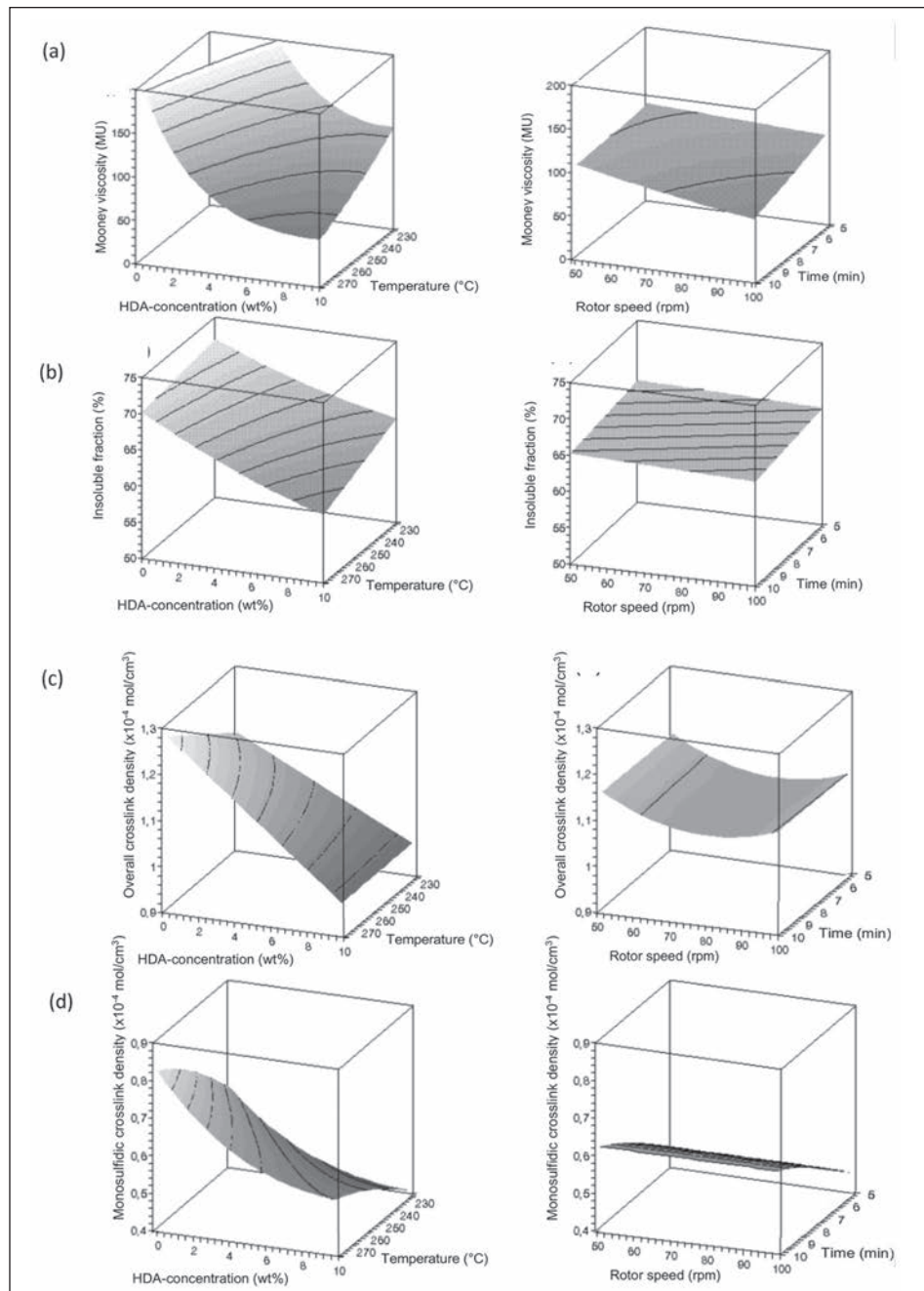
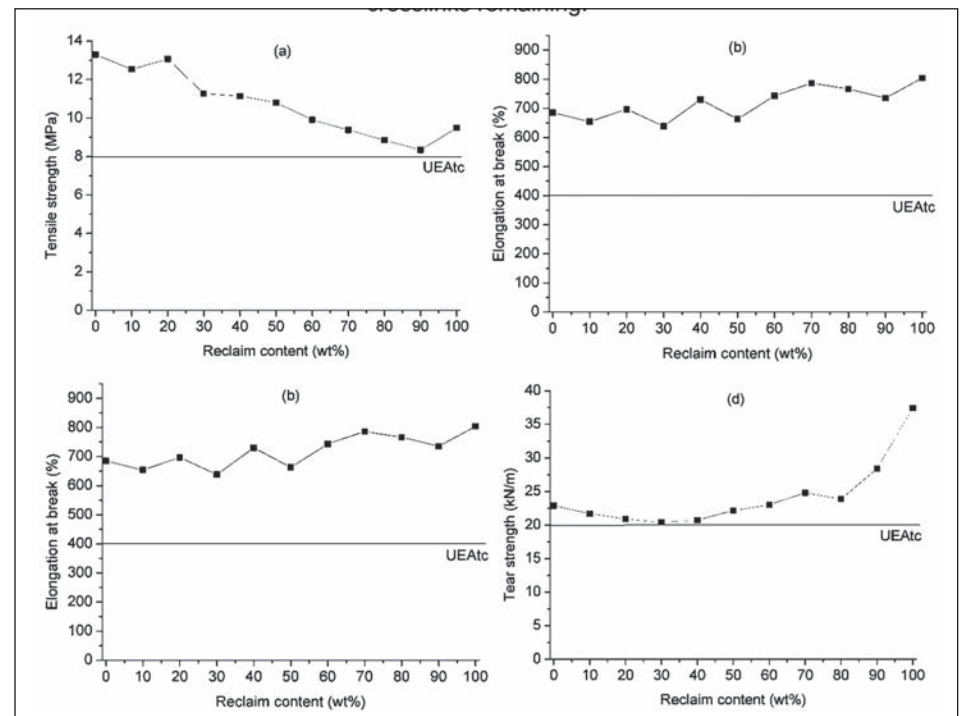
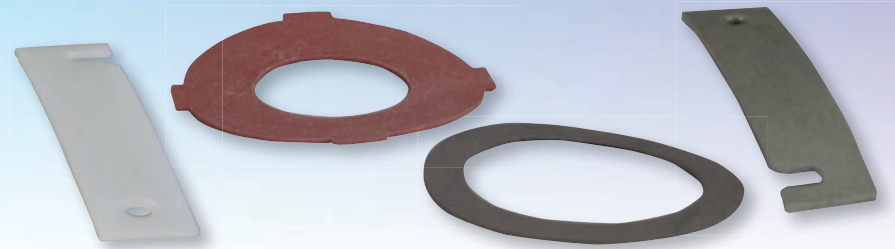


Fig. 5: EPDM-building profile devulcanizate mixed in various proportions into virgin EPDM roofsheeting compounds, compared with UEAtc-standard.



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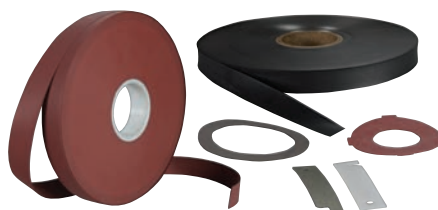


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pared to the efficiently vulcanized material, which primarily shows main-chain scission. The first does so because of the predominance of polysulfidic crosslinks, characterized by a low bond strength: 256 kJ/mol, vs. the second with a large amount of monosulfidic crosslinks with high bond-strength: 302 kJ/mol.

Comparison of the increasing or decreasing effects of the various variables in devulcanization show sometimes opposite effects in breaking polysulfidic vs. monosulfidic crosslinks: devulcanization temperature has the largest effect.

Re-use of devulcanized EPDM: Devulcanize of sulfur-cured EPDM building-profile scrap prepared in a co-rotating twin-screw extruder with HDA as devulcanization can be added to a virgin masterbatch in concentrations of more than 50 wt percent with a limited influence on the properties. (Fig. 5). This results in a qualitatively excellent material.¹¹

This is a high concentration of recycled rubber compared to the maximum loading of 10 to 15 wt percent, commonly known to be the practical limit. It can be blended in practically all proportions with a virgin EPDM roof-sheeting compound, where the resulting re-vulcanizates all fulfill the most stringent industri-

al UEAtc specifications.¹²

Increasing amounts of EPDM devulcanizate added to the virgin compound result in a decrease in vulcanization time and cure temperature for reversion-free vulcanization.

The overall crosslink density shows a decrease with increasing devulcanizate content, while the ratio of mono- to di- and polysulfidic crosslinks increases. The insoluble fraction decreases with increasing devulcanizate content, indicating some loss of ability of the devulcanizate for re-vulcanization relative to the virgin compound. HDA also has an activating effect on crosslinking. Devulcanizate enhances the elasticity of uncured compounds, while it reduces the elasticity of the cured blends.

There is no general consensus about the temperature which should be taken to practically mimic the lifetime of EPDM roof-sheeting, as the service temperatures reach from sub-zero temperatures during winter times to temperatures as high as 80°C in the summer.

Aging tests were done to obtain an indication of the life-time expectancy of compounds containing increasing amounts of the EPDM devulcanizates, based on the time needed to reach 250 percent elongation at break at various elevated temperatures, and then extrapolated via an Arrhenius plot to 80°C. Even at full-time exposure of the roof-sheeting to a temperature of 80°C, the material still shows acceptable life-

times before reaching the threshold value of 250 percent elongation at break, taking into account that such high temperatures only occur on flat roofs during a limited period of time throughout the year.

The lifetime expectancy of virgin roof-sheeting compound with reclaim added is even extended relative to pure virgin compound. All blends perform well for very long periods of time before reaching the practical threshold value for elongation at break of 250 percent.

Devulcanization of SBR¹³

SBR is the main component in whole passenger car tire rubbers and, at the same time, the most critical one in terms of devulcanization. Devulcanization of styrene-butadiene and butadiene-based polymers follows a unique pathway due to the specific chemical structure of the polymer.¹⁴ In degradation, polymer breakdown occurs, but at the same time radical recombination of chain segments takes place.

In the present study, special attention was devoted to the investigation of the devulcanization efficiency under different conditions: thermal and thermo-chemical devulcanization of sulfur-vulcanized SBR. A positive effect was found when stabilizers were added. They suppress the reverse reaction by radicals or other reactive species and interrupt the oxidation cycle which may result from the presence of oxygen during devulcanization.

Thermomechanical treatment: In this first part of the investigation, the rubber was subjected to thermal treatment in an internal mixer under three different conditions: in presence of air at all stages (TT); with quenching of the devulcanizate in liquid nitrogen after devulcanization (TL); and under nitrogen atmosphere during devulcanization, as well as with quenching in liquid nitrogen (TN).¹⁵

Fig. 6 shows the experimentally determined sol fractions of the devulcanized SBRs at various devulcanization temperatures as a function of the relative decrease in crosslink density, the Horikx-Verbrug-

gen plot. For the thermally treated material, TT in Fig. 6(a), an increase of the devulcanization temperature to 220°C results in a shift of the data point to the right hand side of the graph, which indicates an increase of sol fraction and decrease of crosslink density.

A further increase of devulcanization temperature to 260°C results in a back turn of the experimental data point to the left, which is the reverse of the expected decrease of crosslink density; even more so for 300°C. For the latter temperature, the data point is even found at the left hand side of the value for untreated SBR. So some devulcanization is found only for a treatment temperature of 220°C.

Improved devulcanization is observed when oxygen is excluded; the results for the TL and TN samples are shown in Figs. 6(b) and 6(c). These illustrate a slight improvement relative to the TT data for treatment at higher temperatures than 180°C.

For TL, the values after treatment at 260°C are more or less at the same position as the values for the materials devulcanized at 220°C; however, the reversion phenomena still occur when the devulcanization temperature is further raised above 260°C. For TN, the data points first move to the right hand side for a treatment temperature of 220°C, but then also turn back to the left hand side for devulcanization temperatures of 260°C and 300°C.

Thus, it can be concluded that working under exclusion of oxygen during and after devulcanization is a requirement for efficient devulcanization of SBR, and a temperature of 220°C is the optimum for devulcanization. Above 220°C, reversion phenomena appear, whatever conditions are used.

Thermo-chemical treatment in presence of stabilizers and devulcanization aids: A more efficient devulcanization is observed for combinations of DiPhenylDi-Sulfide (DPDS) di(2-aminophenyl)disulfide (APDS) (3 percent w/w) and an oxidation stabilizer Irganox 1076 (1 per-

Fig. 6: Thermomechanical treatment of SBR: (a) TT, in air; (b) TL, in air atmosphere, with quenching in liquid nitrogen; (c) TN, under nitrogen blanket and quenching in liquid nitrogen.

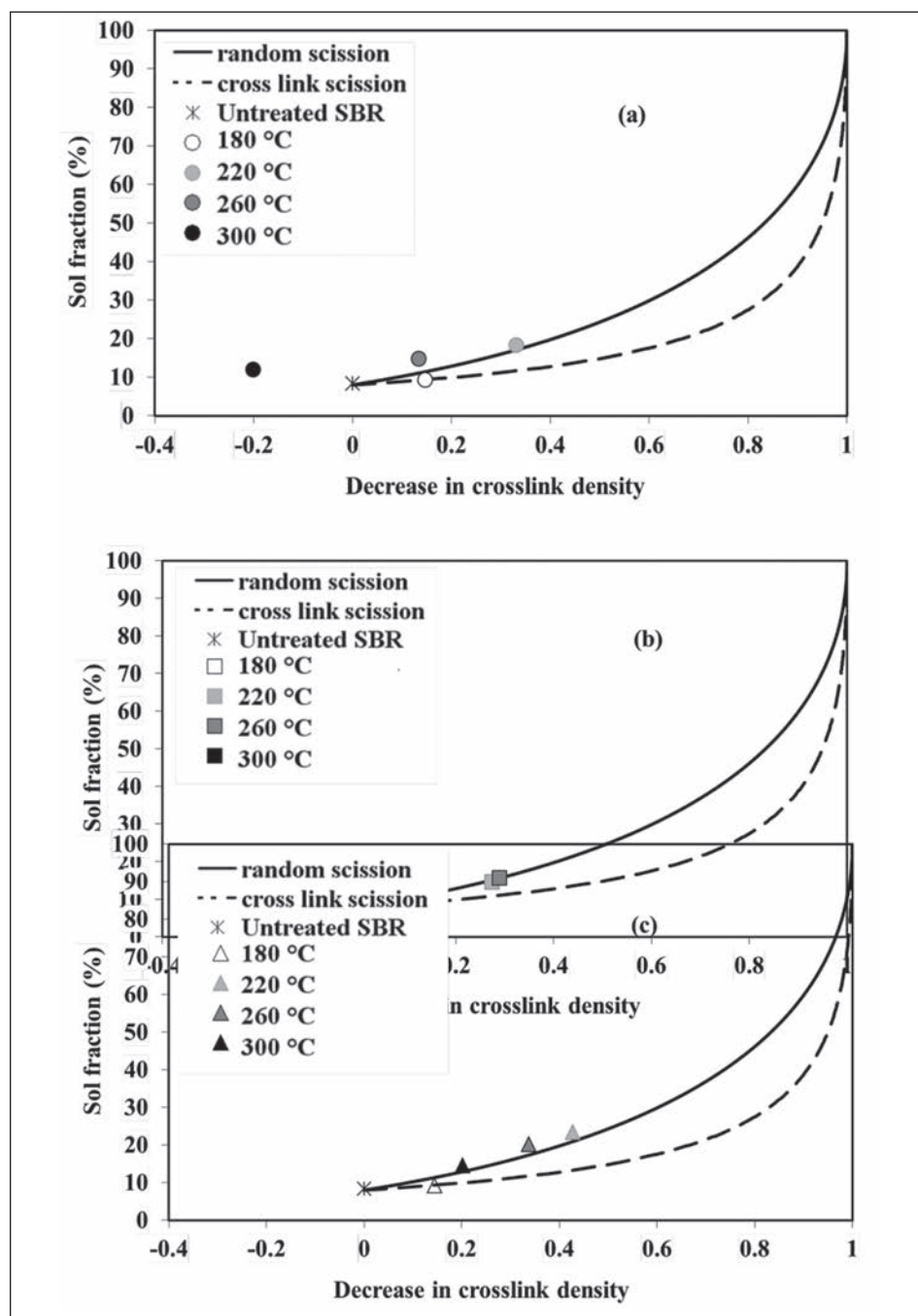


Fig. 7: Sol fraction generated during devulcanization of SBR vs. decrease in crosslink density using a combination of DPDS and stabilizer Irganox 1076.

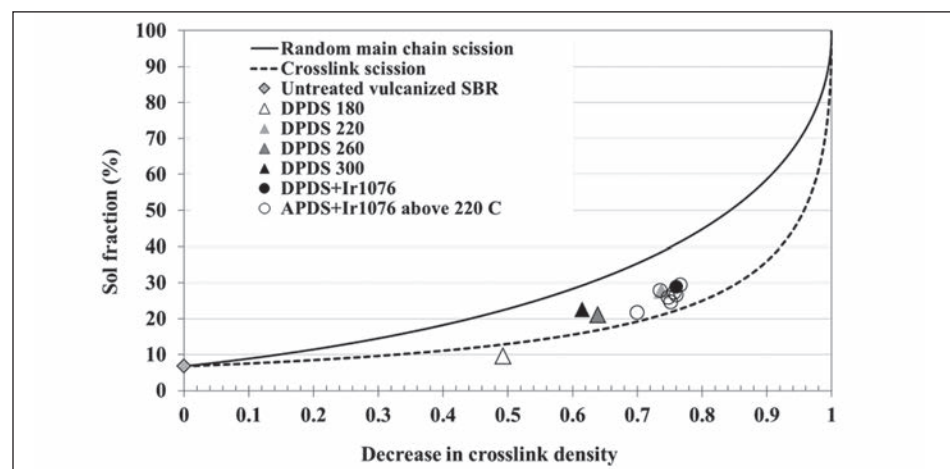
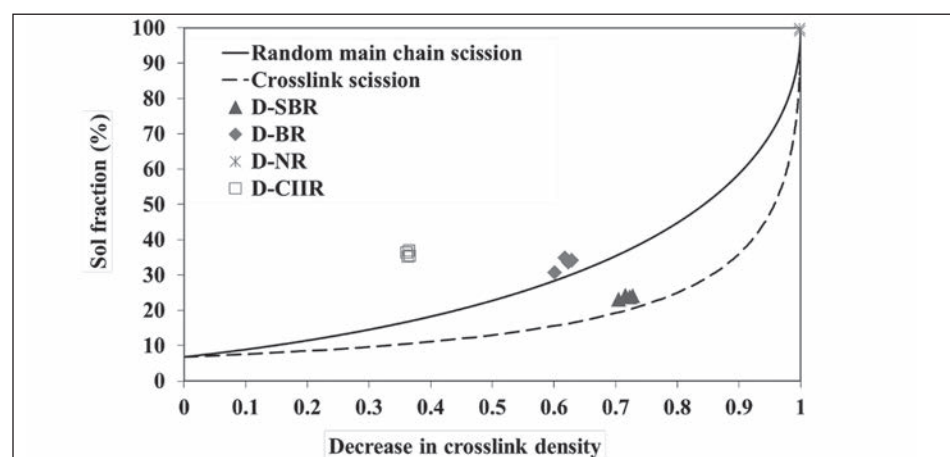


Fig. 8: Devulcanization results for various elastomers used in tires in presence of DPDS as devulcanization aid and 220°C.



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cent w/w): Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, added as devulcanization aids. DPDS and less so APDS are reported to be effective devulcanization aids.

A mechanism that is frequently proposed for the reaction of radical scavenger devulcanization two chemical species is clearly seen in **Fig. 7**. The experimental data for treatment above 220°C are situated at even slightly higher positions than the data for the devulcanizate treated at 220°C with only DPDS.

The reversion phenomenon is noticeably absent in this case as there is no move of the data points to the left hand side with increase of devulcanization temperature up to 300°C. Therefore, the utilization of the developed synergism of devulcanization aid with oxidation stabilizers results in a more efficient and controlled devulcanization.

Devulcanization of BR, NR, CIIR¹³

On a similar basis as for SBR, devulcanization was done for butadiene rubber (BR), natural rubber (NR) and chlorinated butyl rubber (CIIR), other elastomers most commonly applied in tire technology.

Clearly, the arguments presented before for the reversion of the butadiene-moieties in SBR apply even more for pure BR. It is even more difficult to achieve reasonable degrees of devulcanization for BR than for SBR, even with the use of DPDS and Irganox 1076, at 220°C, and at the cost of positioning itself on the chain-scission branch of the Horikx-Verbruggen plot (**Fig. 8**).

On the other hand, devulcanization of NR with DPDS is “proven technology” dating back many decades. With tem-

peratures of 220°C and 260°C, basically full devulcanization or reclaiming is achieved, related to the intrinsic “poor molecular integrity” of the polyisoprene polymer chain. With the position at the right top corner of the Horikx-Verbruggen plot, it is not possible anymore to distinguish whether main chain or crosslink scission has happened.

Thermochemical devulcanization of chlorinated butyl rubber was performed using DPDS as devulcanization aid. **Fig. 8** also shows the changes in sol fraction and crosslink density of CIIR devulcanizates at a devulcanization temperature of 220°C. Although a reasonably high sol-fraction is observed, there is still a very limited decrease of less than 40 percent in crosslink density at 220°C.

Furthermore, all experimental data are situated far above the line of main-chain scission. This can be attributed to a devulcanization mechanism which is not uniform and homogeneously distributed throughout the rubber particles, for which the validity of the Horikx-Verbruggen approach is limited. The two different devulcanization mechanisms, uniform and non-uniform, are schematically depicted in **Fig. 9**.¹⁷

A limitation of the Horikx-Verbruggen representation is that it assumes homogeneous breakdown of the vulcanized network throughout the particles (**Fig. 9A**). However, the results for devulcanized CIIR at 220°C indicate a different mechanism: peeling off of the outer layers of the particles, while the inner cores of the particles stay more or less untreated at constant crosslink density (**Fig. 9B**). This inhomogeneity causes in actual practice a lower decrease in crosslink density at a particu-

lar sol fraction than would have been obtained for homogeneous breakdown.

Use of whole tire devulcanizate

Making use of the more or less optimized devulcanization conditions, a series of application studies were executed for a passenger tire tread, an undertread, a carcass compound and a tire apex.¹⁶ The experiments represent first shots, without formulation adjustments, with 10, 30 and 50 percent whole tire devulcanizate added to the virgin compounds. The results are presented in **Fig. 10**.

A decrease in tensile strength is observed up to 55 percent for some of the 50/50 blends, accompanied by an increase in elongation at break for the undertread, carcass and apex. The main reason seems to be indicated as under-vulcanization.

Compound adjustments with curatives as if the devulcanizates need as much curatives as the virgin compounds, allowed for an increase in tensile strength of 60 percent in the 50-50 blend for the apex, as indicated by the grey block. For the other compounds, slightly lower improvements were obtained. For the 30/70 blends, generally the original tensile values could be obtained, except for the undertread compound. Again it needs to be emphasized that these were only preliminary, first-shot experiments.

Limitations and challenges

In spite of the positive results obtained with devulcanization of tires, the technology still faces quite some challenges. The main challenge is the steady increase in use of silica instead of carbon black as reinforcing filler. On a molecular scale, the main difference is the presence of chemical coupling of the silica filler particles to the elastomer via silane coupling agents, like commonly used bis-(Tri-Ethoxy-Silyl-Propyl)Tetra sulfide (TESPT) or the disulfide equivalent TESPD; versus the physical interaction between the elastomers and carbon black.

As mono-sulfidic crosslinks are among the hardest to break during devulcanization because of their highest bond energy for sulfur-bridges, it is primarily such mono-sulfidic bridges which link the silica-fillers and the elastomers via the coupling agents. An example of the poor devulcanization of such a silica-based tread-compound containing TESPT as a coupling agent, at 220°C and 250°C is given in **Fig. 11**.

Conclusions

Recycling and in particular devulcanization pose quite some challenges to the rubber world at large. There are cases where devulcanization is relatively easily achieved, such as EPDM, while for butadiene-containing elastomers like SBR and BR, devulcanization is accompanied by radical crosslinking, so that the end-effect may be disappointing.

For EPDM, devulcanization strongly depends on the network structure: better for polysulfidic crosslinks than for mono-sulfidic crosslinks (and obviously even worse for peroxide-vulcanized EPDM). The best devulcanization is achieved with amines as de-vulcanization aids. The risk of recombination of network fragments or polymer strands at high concentrations of devulcanization aids and temperatures are limited.

Shear and devulcanization time have a minor influence compared to devulcanization temperature. Dependent on the application, 50 percent and more virgin rubber can be replaced by devulcanizate.

For butadiene-containing elastomers like SBR and BR, the devulcanization temperature <220°C is the most critical parameter, as well as a protective atmosphere by exclusion of oxygen and low shear, resp. fast and efficient cooling after the devulcanization—all to prevent radical re-combinations of devulcanized chains and network fragments.

Under these optimized conditions degrees of devulcanization up to 80-90 percent can be reached, limited by the monosulfidic crosslinks and limitations imposed upon the Horikx-Verbruggen analysis by the bound rubber.

Lots of challenges remain, in particular the use of silica instead of carbon black for rubber reinforcement and the primarily monosulfidic bonds between the elastomers and the silica particles via the silane coupling agents, most difficult to break with devulcanization.

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Fig. 9: Homogeneous vs. inhomogeneous devulcanization.

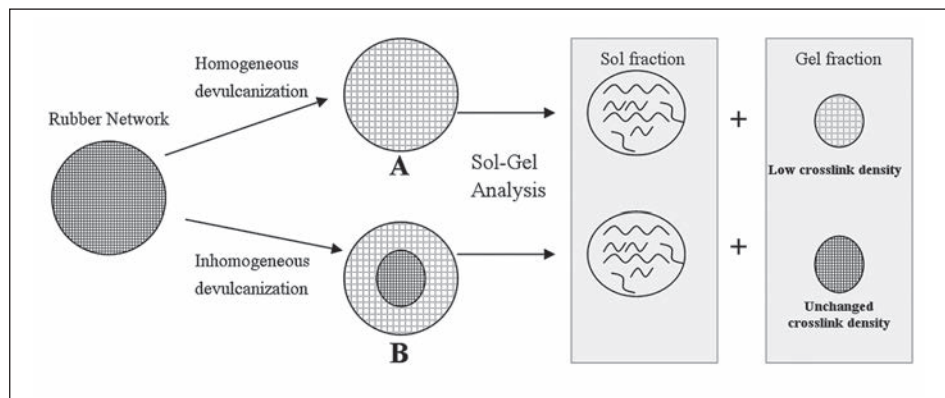


Fig. 10: Application study of whole tire devulcanizate in various passenger tire components.

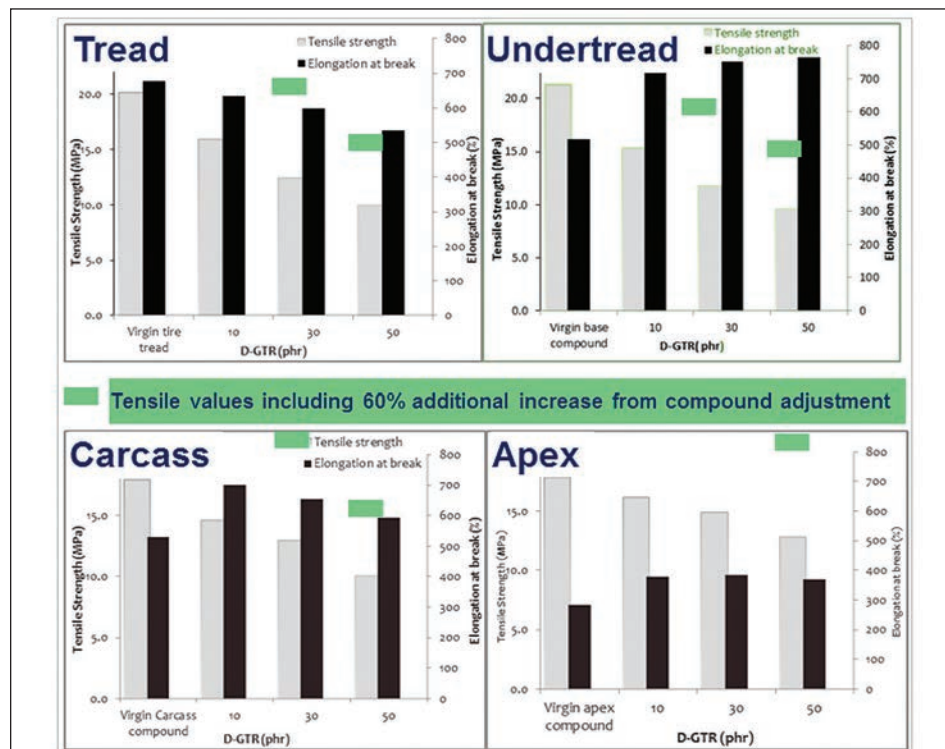


Fig. 11: Limited success with devulcanization of a silica-containing TESPT-coupled SBR at 220°C and 250°C.

