

Cradle-to-cradle devulcanization options for various elastomer types

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Recycling of rubber is of growing importance worldwide due to increasing raw material costs, diminishing resources and growing awareness of environmental issues and sustainability. Various different recycling processes for rubber have been investigated and developed throughout the years. Several in-depth reviews discussing the state-of-the-art of rubber recycling were published in 1974, 2002 and 2012 (refs. 1-3). The main recycling methods hierarchically classified in the order of

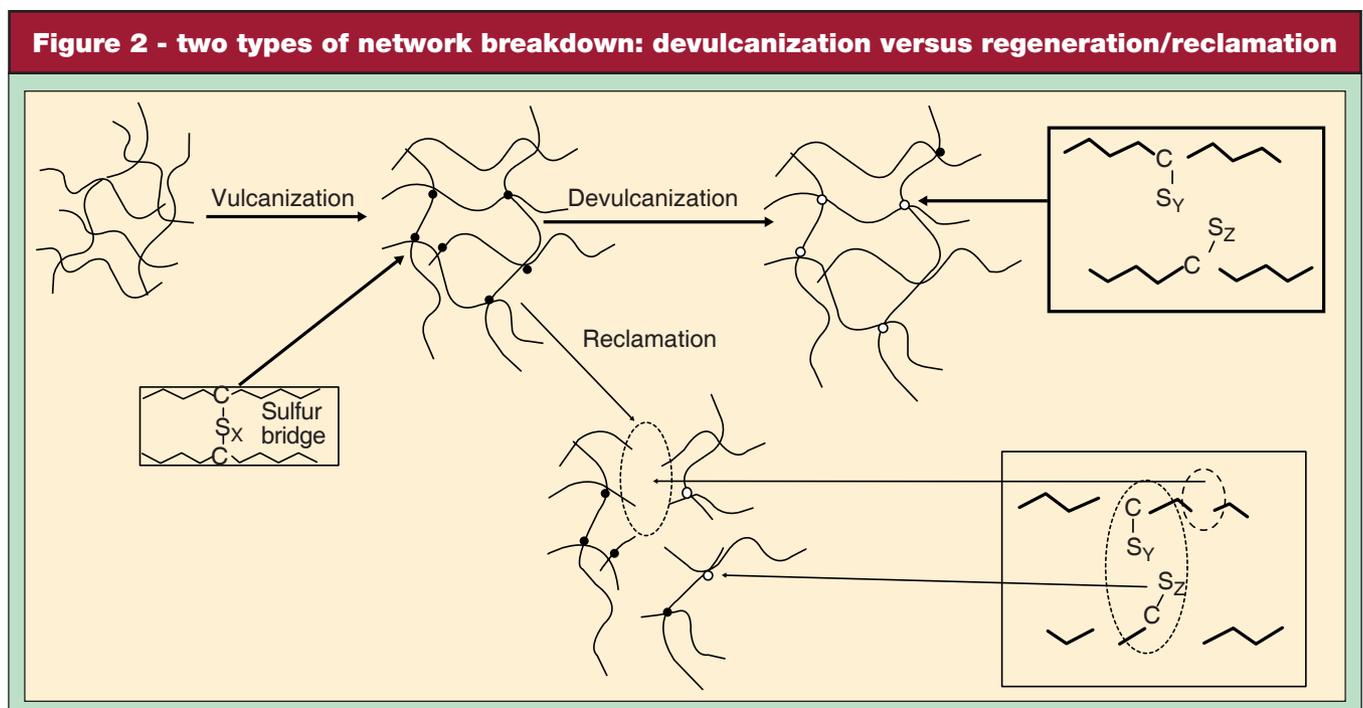
environmental and economic preference are shown in figure 1.

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 with characteristics equal to those of the original materials, e.g., used tire rubber back into tires.

In the rubber recycling process, two types of rubber network breakdown simultaneously occur, including reclamation and devulcanization, as shown in figure 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 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 versus polymer chain scission.

Devulcanization, the most ideal way of recycling rubber, 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), disul-



fidic (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 in which it can be mixed, processed and vulcanized again by using conventional processes. Transforming the cured rubber into a reprocessable 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 are also 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 partial recombination result in highly branched chain segments that differ greatly from virgin rubber.

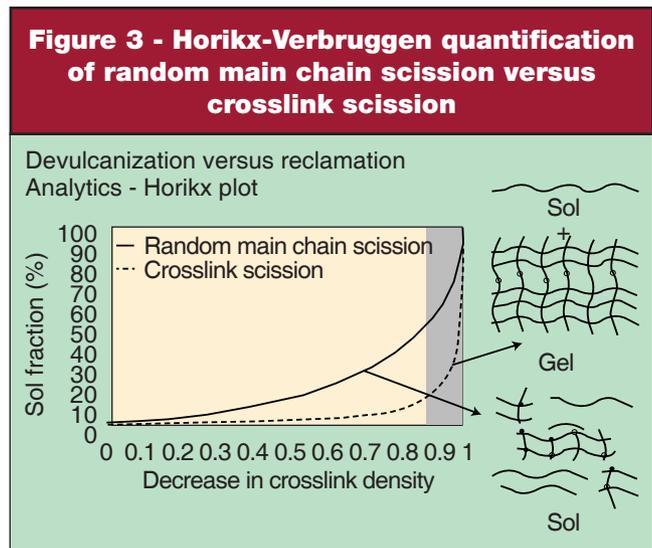
In view of these arguments, the conversion of used rubber into a reprocessable and reusable form by the currently used physical/chemical processes should be called reclamation rather than devulcanization. The broken polymer chains generated in the reclaiming processes influence the properties and reduce 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 rubber recycling technology and a global challenge.

Model for devulcanization versus 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 scission and gel fraction in irradiated polymers, is based on the amount of soluble polymeric material generated (refs. 4 and 5). Horikx assumed that these relations were also applicable to determine the sol fraction of a rubber sample undergoing network degradation by aging (ref. 6). Horikx used Charlesby’s theory to develop a method in which a vulcanized rubber network is broken down again via two routes: main chain scission and selective crosslink



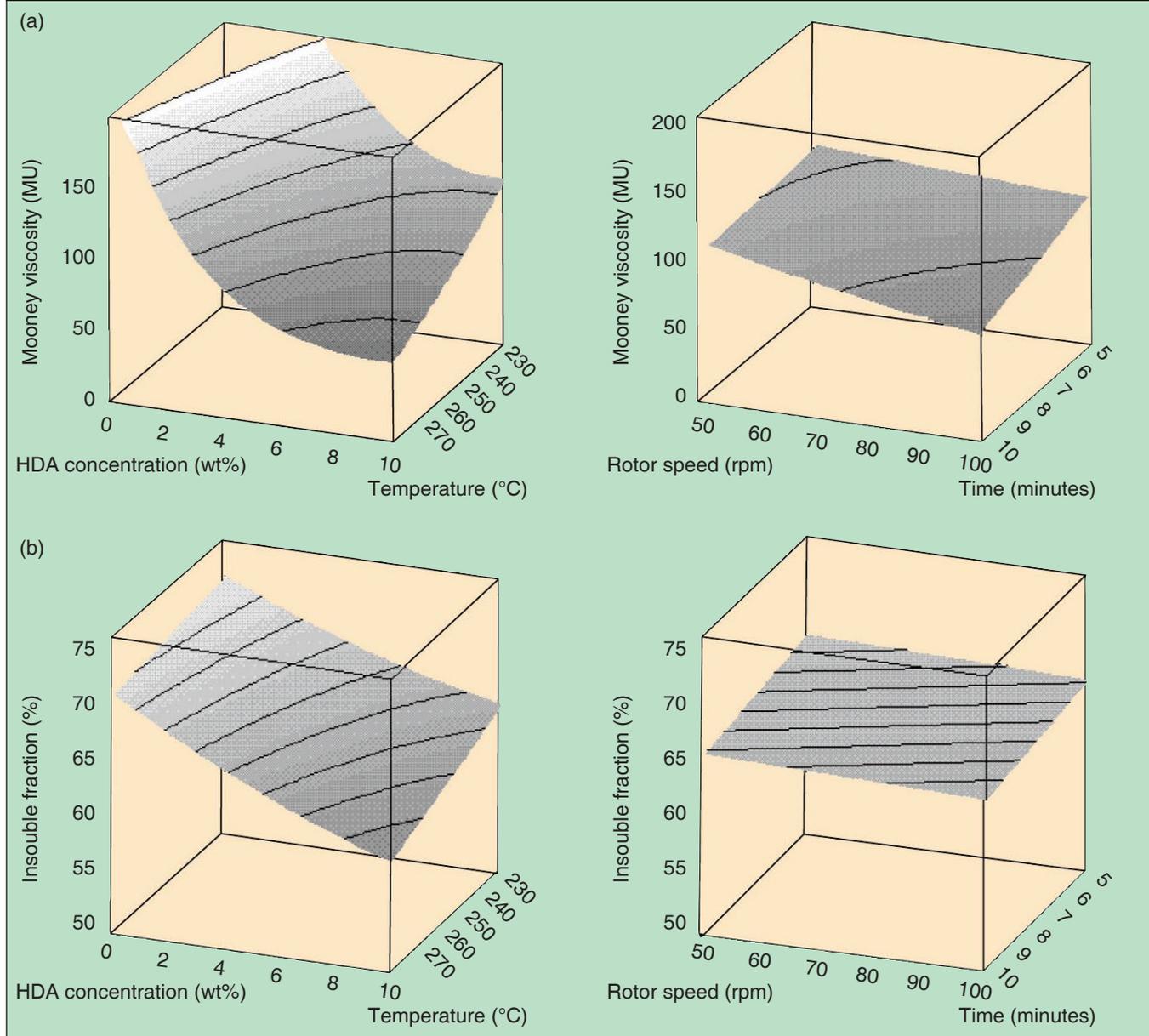
breakage. This model was reworked by Verbruggen in her Ph.D. thesis, and recently published in *Rubber Chemistry and Technology* as a means to quantify the difference between the two mechanisms during network destruction (refs. 7 and 8). Figure 3 gives a graphical representation of the model. The curves 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 can the long chains 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 versus decrease in crosslink density generated during network degradation, and correcting for the amounts of non-solubles in the rubber compounds, e.g., 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 crosslink 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 the gray shaded area in figure 3]).

Two examples of a successful and a more complicated devulcanization

Devulcanization of EPDM

Regarding devulcanization, for EPDM rubber, α -hydrogen-containing aliphatic amines, e.g., hexadecylamine (HDA), were found to be very effective devulcanization aids (refs. 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 de-vulcanized rubber from conventionally vulcanized EPDM, mainly polysulfidic in nature, shows a decrease in crosslink density with increasing HDA concentration

Figure 4 - optimization of EPDM devulcanization: Influences of concentration of devulcanization aid (HDA) and mixer rotor speed on (a) Mooney viscosity of devulcanizate and (b) insoluble fraction

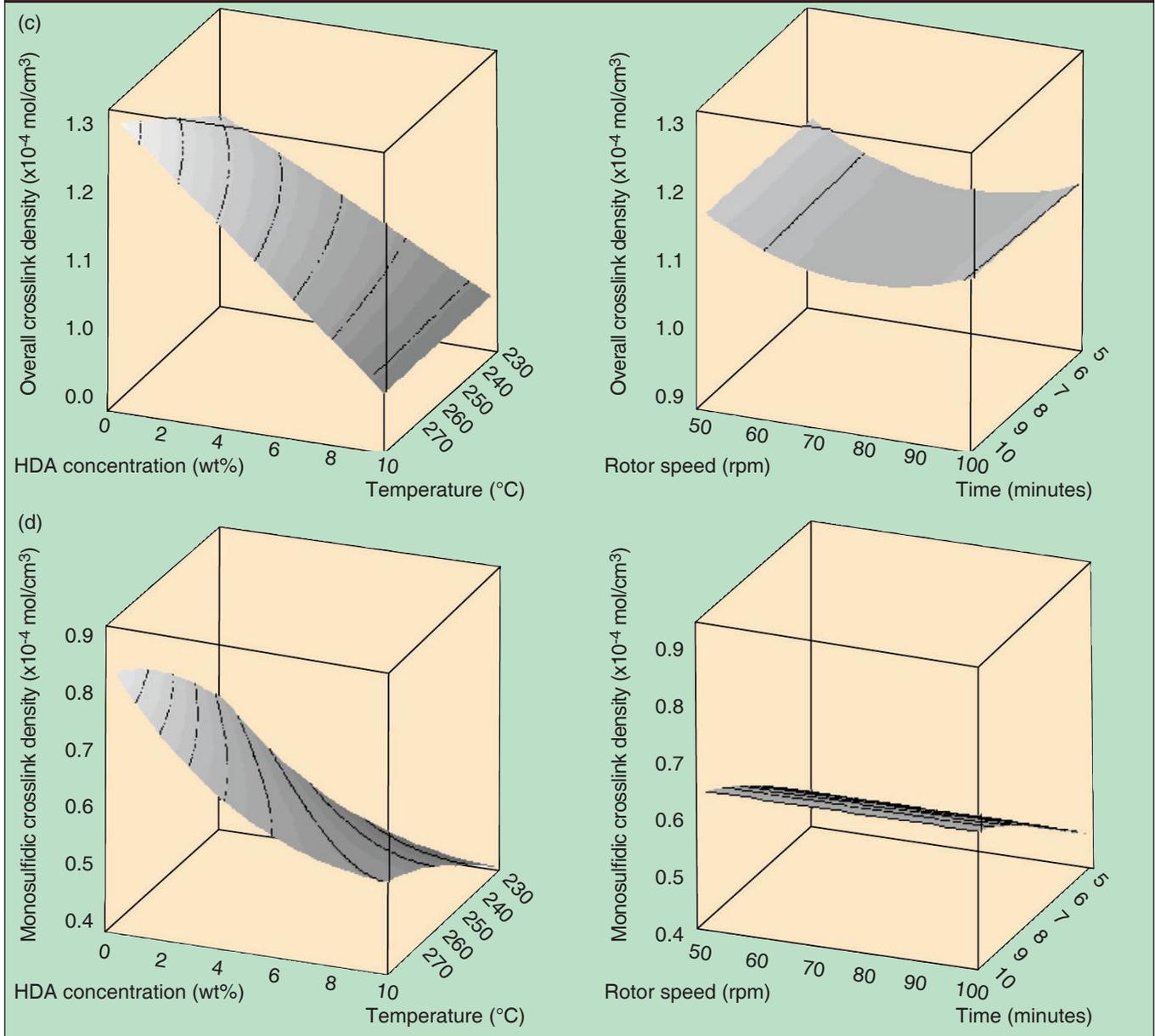


and at low devulcanization temperatures (ref. 11). After devulcanization at the lower limit of the experimental temperature window (i.e., 225°C), the concentration of remaining di- and polysulfidic crosslinks is higher than the concentration of monosulfidic bonds; while at the upper temperature level (i.e., 275°C), the concentration of monosulfidic bonds is highest, as shown in figures 4a and 4b. 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 the efficiently vulcanized material, which primarily shows main chain scission; the first because of the predominance of polysulfidic crosslinks, characterized by a low bond strength of 256 kJ/mol, versus the second with a large amount of monosulfidic crosslinks with high bond strength of 302 kJ/mol. Comparison of the increasing or decreasing effects of the various variables in devulcanization show sometimes opposite effects in breaking polysulfidic versus monosulfidic crosslinks: Devulcanization temperature has the largest effect.

Regarding reuse of devulcanized EPDM, devulcanizate 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% with a limited influence on the properties (figure 5). This

Figure 4 continued - optimization of EPDM devulcanization: Influences of concentration of devulcanization aid (HDA) and mixer rotor speed on (c) overall crosslink density and (d) monosulfidic crosslinks remaining

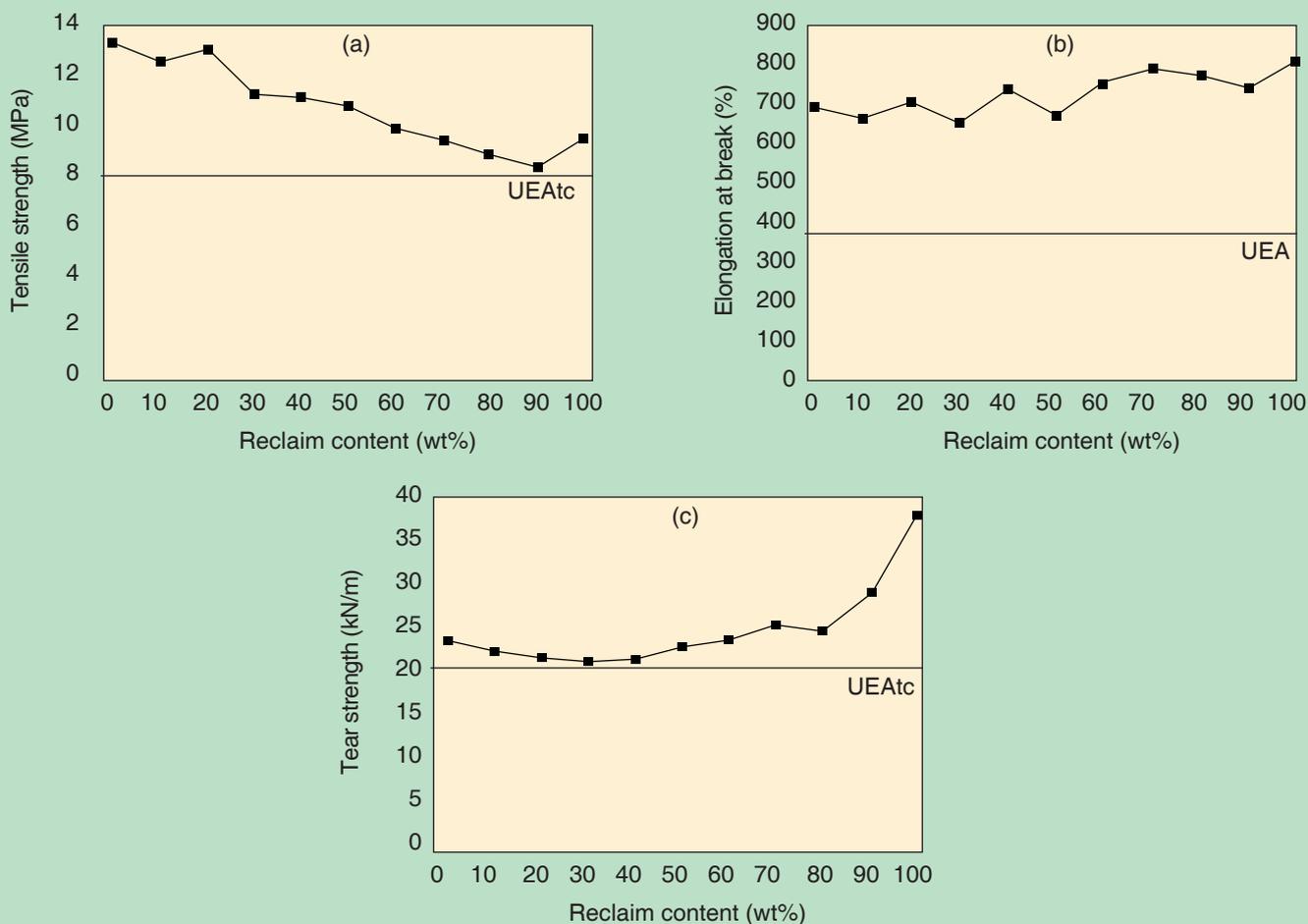


results in a qualitatively excellent material (ref. 11). This is a high concentration of recycled rubber compared to the maximum loading of 10 to 15 wt%, commonly known to be the practical limit. It can be blended in practically all proportions with a virgin EPDM roof sheeting compound, where the resulting revulcanizates all fulfill the most stringent industrial UEAtc specifications (ref. 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 revulcanization relative to the virgin com-

pound. HDA also has an activating effect on crosslinking. Devulcanization 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 wintertime to temperatures as high as 80°C in the summer. Aging tests were done to obtain an indication of the lifetime expectancy of compounds containing increasing amounts of the EPDM devulcanizates, based on the time needed to reach 250% 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 lifetimes

Figure 5 - EPDM building profile devulcanizate mixed in various proportions into virgin EPDM roof sheeting compounds compared with the UEAtc standard (a) tensile strength, (b) elongation and (c) tear strength



before reaching the threshold value of 250% 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%.

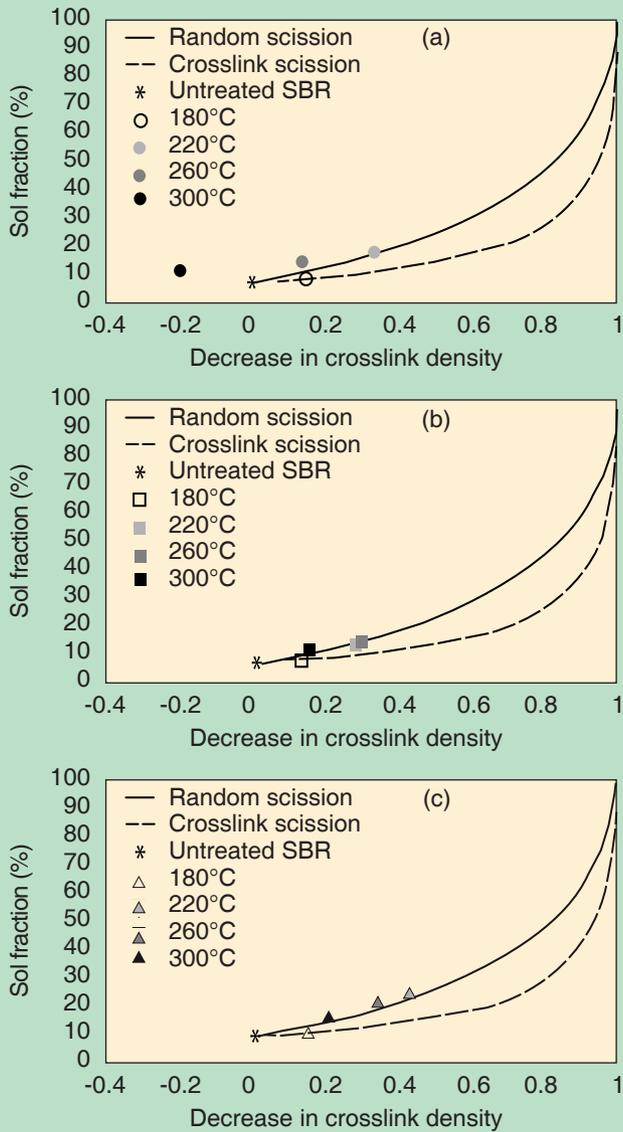
Devulcanization of SBR (ref. 13)

Styrene butadiene rubber (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 (ref. 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.

Regarding 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 the 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) (ref. 15). Figure 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-Verbruggen plot. For the thermally treated material, TT in figure 6a, 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 devul-

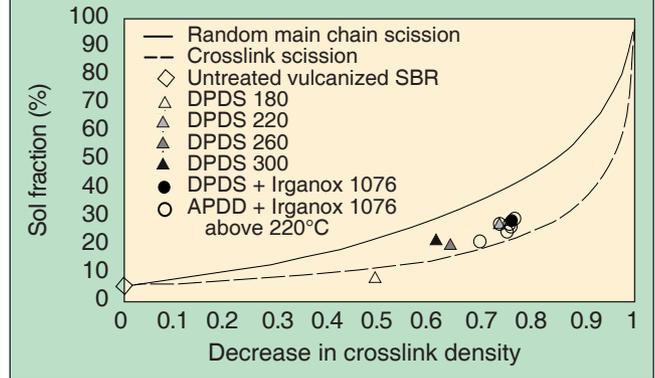
Figure 6 - thermomechanical treatment of SBR: (a) TT in air; (b) TL in air atmosphere, with quenching in liquid nitrogen; (c) TN under nitrogen blanket and quenching in liquid nitrogen



canization 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 figures 6b and 6c. 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 occurs 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

Figure 7 - sol fraction generated during devulcanization of SBR versus decrease in crosslink density using a combination of DPDS and Irganox 1076 stabilizer



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.

Regarding thermo-chemical treatment in the presence of stabilizers and devulcanization aids, a more efficient devulcanization is observed for combinations of diphenyldisulfide (DPDS) and di(2-aminophenyl)disulfide (APDS) (3% w/w), and an oxidation stabilizer Irganox 1076 (1% w/w) or 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 of two chemical species is clearly seen in figure 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 an 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.

Figure 8 - devulcanization results for various elastomers used in tires in the presence of DPDS as a devulcanization aid at 220°C

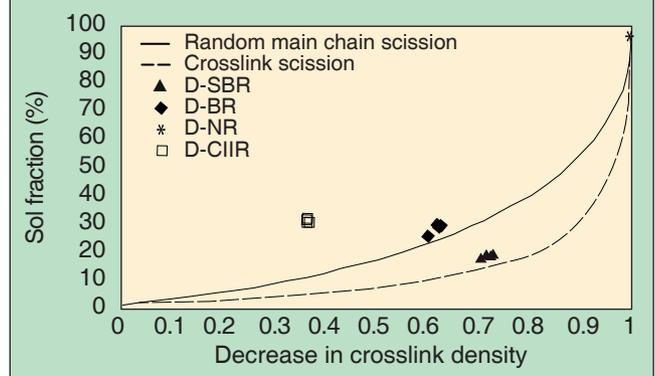
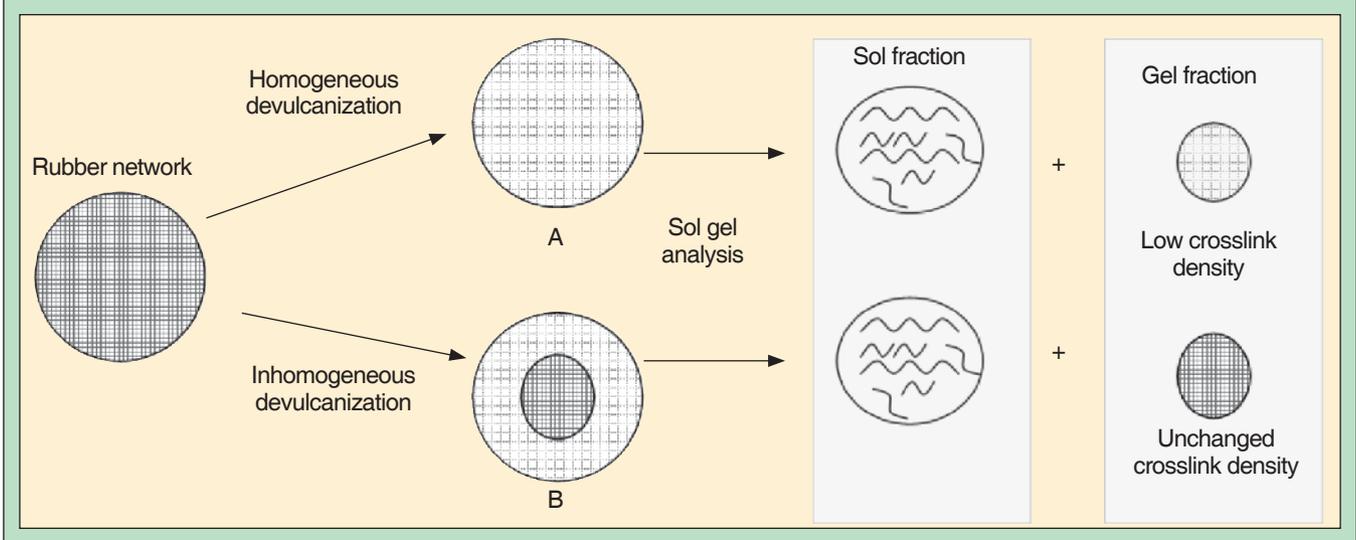


Figure 9 - homogeneous versus inhomogeneous devulcanization



Devulcanization of BR, NR and CIIR (ref. 13)

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 (figure 8).

On the other hand, devulcanization of NR with DPDS is “proven technology” dating back many decades. With temperatures 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 (CIIR) was performed using DPDS as the devulcanization aid. Figure 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% 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 figure 9 (ref. 16).

A limitation of the Horikx-Verbruggen representation is that it assumes homogeneous breakdown of the vulcanized network throughout the particles (A). 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 (B). This inhomogeneity causes in actual practice a lower decrease in crosslink density at a particular sol fraction than would have been obtained for homogeneous breakdown.

Application of whole tire devulcanizate in various tire components

Making use of the more or less optimized devulcanization conditions, a series of application studies was executed for a passenger tire tread, an undertread, a carcass compound and a tire apex (ref. 17). The experiments represent first shots, without formulation adjustments, with 10%, 30% and 50% whole tire devulcanizate added to the virgin compounds. The results are presented in figure 10.

A decrease in tensile strength is observed up to 55% 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 indicate under-vulcanization. Compound adjustments with curatives, as if the devulcanizates need as much curative as the virgin compounds, allowed for an increase in tensile strength of 60% in the 50/50 blend for the apex, as indicated by the black blocks. 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 some challenges. The main challenge is the steady increase in the use of silica instead of carbon black as a 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)tetrasulfide (TESPT), or the disulfide equivalent (TESPD), versus the

Figure 10 - application study of whole tire devulcanizate in various passenger tire components

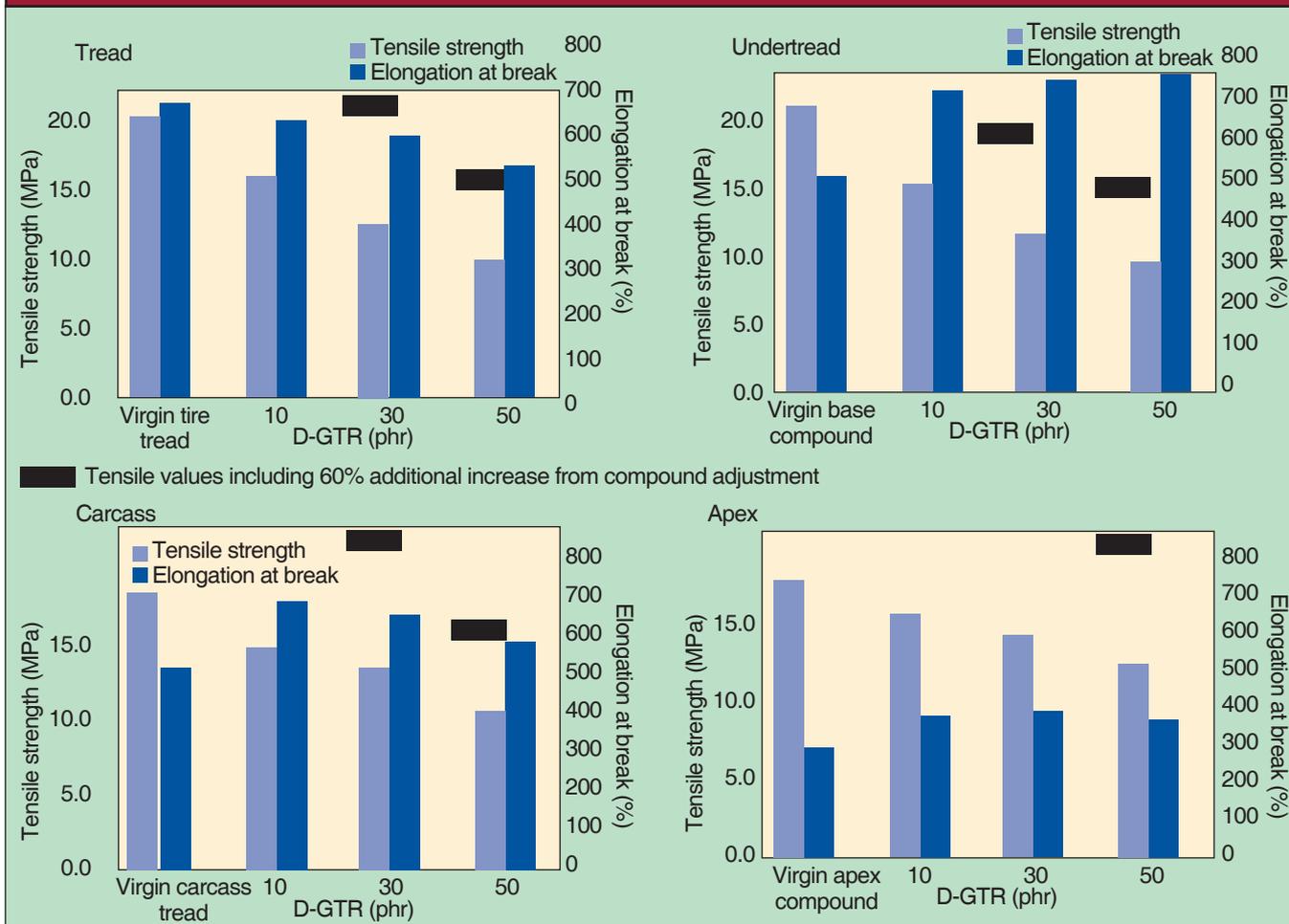
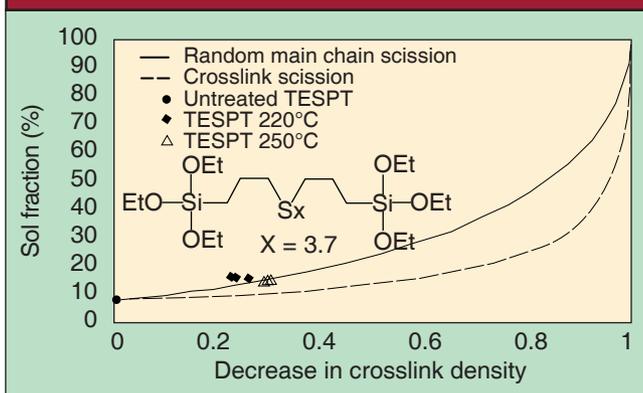


Figure 11 - limited success with devulcanization of a silica-containing TESPT coupled SBR at 220°C and 250°C



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 figure 11. A recent study has shed more light on the intricate influence of silica on the quality of devulcanization, degradation of the rubber and decrease in tensile properties after revulcanization, as compared to carbon black based tire tread compounds.

Conclusions

Recycling and, in particular, devulcanization pose quite some challenges to the rubber industry 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, so is 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 devulcanization aids. The risk of recombination of network fragments or polymer strands at high concentrations of devulcanization aids and temperatures is limited. Shear and devulcanization time have a minor influence compared to devulcanization temperature. Dependent on the application, 50% and more virgin rubber can be replaced by devulcanizate.

For butadiene containing elastomers like SBR and BR, the

devulcanization temperature <math><220^{\circ}\text{C}</math> is the most critical parameter, as well as a protective atmosphere by exclusion of oxygen and low shear; respectively, fast and efficient cooling after the devulcanization, all to prevent radical recombinations of devulcanized chains and network fragments. Under these optimized conditions, degrees of devulcanization up to 80-90% can be reached, limited by the monosulfidic crosslinks and limitations imposed upon the Horikx-Verbruggen analysis by the bound rubber.

Many challenges remain, including the use of silica instead of carbon black for rubber reinforcement, and the monosulfidic bonds between the elastomers and the silica particles via the silane coupling agents. These appear to be the most difficult to break with devulcanization.

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References

1. J.A. Beckman, G. Crane, E.I. Kay and J.R. Laman, *Rubber Chemistry and Technology*, 47, 597 (1974).
2. M. Myhre and D.A. MacKillop, *Rubber Chemistry and Technology*, 75, 429 (2002).
3. M. Myhre, S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, *Rubber Chemistry and Technology*, 85, 408 (2012).
4. A. Charlesby, *Proc. R. Soc. London, Ser. A*, 222, 60 (1954).
5. A. Charlesby, *J. Polym. Sci.*, 11, 513 (1953).
6. M.M. Horikx, *J. Polym. Sci.*, 19, 445 (1956).

7. M.A.L. Verbruggen, Ph.D. Thesis, University of Twente, Enschede, The Netherlands (2007).

8. M.A.L. Verbruggen, L. van der Does, W.K. Dierkes and J.W.M. Noordermeer, *Rubber Chemistry and Technology*, 89 (4), 671 (2016).

9. M.A.L. Verbruggen, L. van der Does, J.W.M., Noordermeer; M. van Duin and H.J. Manuel, *Rubber Chemistry and Technology*, 72, 731 (1999).

10. M. van Duin, J.W.M. Noordermeer, M.A.L. Verbruggen and L. van der Does, U.S. Patent 6,956, 065 (to DSM) (2005).

11. K.A.J. Dijkhuis, J.W.M. Noordermeer and W.K. Dierkes, presented at a meeting of the Rubber Division, ACS, October 2008, Louisville, KY.

12. Union Européenne Pour l'Agrément Technique Dans la Construction (1988).

13. S.S. Saiwari, Ph.D. Thesis, University of Twente, Enschede, The Netherlands (2013).

14. R.N. Hader and D.S. le Beau, *Ind. Eng. Chem.*, 43 (2), 250 (1951).

15. S. Saiwari, W.K. Dierkes and J.W.M. Noordermeer, *Rubber Chemistry and Technology*, 87, 31 (2014).

16. K.A.J. Dijkhuis, I. Babu, J.S. Lopullissa, J.W.M. Noordermeer and W.K. Dierkes, *Rubber Chemistry and Technology*, 81, 190 (2008).

17. J.W. van Hoek, G. Heideman, J.W.M. Noordermeer; W.K. Dierkes and A. Blume, *Materials*, 12, 5 (2019).

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