

Best practice for the devulcanization of sulfur-cured SBR rubber

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Abstract

In the present paper, special attention will be devoted to thermo-chemical *devulcanization* of sulfur-cured styrene butadiene rubber (SBR) using diphenyldisulfide (DPDS) as devulcanization aid. SBR is the main component in whole passenger car tire rubber and, at the same time, the most critical one in terms of devulcanization. This study is the first step to realize an effective devulcanization process for whole passenger car tire rubber.

Diphenyldisulfide was found to be an effective agent for reclaiming of mainly natural rubber based sulfur-cured materials: DPDS acts as a radical scavenger and helps in preventing broken rubber chains to recombine. In this study, the effect of DPDS on the ratio of crosslink to polymer scission is investigated.

The most important process parameter is the temperature, at which the polymer network is broken down. A reduction of the crosslink density of the devulcanizate is observed with increasing devulcanization temperature from 180°C to 220°C. However, above a temperature threshold of 220°C, the crosslink density rises again. This is due to intramolecular rearrangements of chain fragments of butadiene moieties from uncontrolled degradation and oxidation effects.

Oxidation stabilizers are added during the devulcanization process in order to reduce the degradation and interrupt the oxidation cycles. Above a temperature threshold of 220°C, a further decrease in crosslink density without creating more sol fraction can be achieved this way. The combination of DPDS and oxidation stabilizers significantly enhances the devulcanization efficiency of SBR versus the one obtained when DPDS is used alone.

The results are interpreted in terms of mechanisms of main chain and sulfur bridge scissions and the degradative cycles triggered by the presence of oxygen.

Introduction

Synthetic styrene-butadiene rubber (SBR) is widely used in the rubber industry, especially in passenger car tire treads in which it provides a good balance of abrasion resistance, aging stability and dynamic properties. Solution-SBR (S-SBR) is used especially for silica-reinforced treads, as this combination reduces rolling resistance for about 30% compared to carbon black filled treads. [1]

Degradation of styrene-butadiene and butadiene based polymers follows a unique pathway due to the specific chemical structure of the polymer [2]. In degradation, polymer breakdown occurs, but at the same time recombination of chain segments takes place. In a thermal devulcanization process of sulfur-cured SBR, the occurrence of these two reactions, chain scission and formation of active chain segments, depends on the devulcanization conditions [3]. When working under non-optimized devulcanization

conditions, the active radicals are more likely to recombine to a new network, thereby reducing the sol fraction and increasing the crosslink density. This finally leads to inefficient devulcanization.

The combination of a chemical with a thermal devulcanization step is one of the alternatives to reach an efficient devulcanization. Using small amounts of a “devulcanization aid” during thermal treatment was reported to be a superior option [4-8]. It selectively breaks down the rubber network at crosslinking positions and creates sulfur-bridges during vulcanization thanks to the disulfide moiety in the molecule.

Disulfides are well-known devulcanization aids and used in rubber recycling as radical stabilizing agents. The efficiency of various disulfides as recycling agents for natural rubber (NR) [4-6] and ethylene propylene diene rubber (EPDM) [7-8] vulcanizates were reported. Diphenyldisulfide was found to be an effective reclaiming agent for natural rubber. Rajan et al. [4] observed that the reclaiming agent helped in preventing the broken rubber chains to recombine. A mechanism that is frequently proposed for the reaction of radical scavenger devulcanization agents like DPDS 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. An additional positive effect is expected when stabilizers are added: they suppress the reaction of radicals or other reactive species and interrupt the oxidation cycle due to the presence of oxygen-species during devulcanization.

Experimental

MATERIALS

The SBR type used in this investigation was SBR 1723, an oil extended emulsion-polymerized SBR containing 37.5 phr of Treated Distillate Aromatic Extract (TDAE) oil, obtained from Dow Chemical, Germany. The polymer contained 23.5 wt% styrene and 76.5 wt% butadiene, and its Mooney viscosity ML(1+4) measured at 100°C was 40 MU. Zinc oxide (ZnO) and stearic acid were obtained from Flexsys, the Netherlands. The curatives: sulfur and N-tert-butyl-2-benzothiazylsulfenamide (TBBS) were obtained from Merck. The solvents, acetone and tetrahydrofuran (THF), which were used for extractions, and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve. TDAE oil used as devulcanizing processing oil was supplied by Hansen & Rosenthal, Germany. The three types of disulfide as given in Table 1 and used as devulcanization aids were obtained from Sigma-Aldrich, Germany. The three types of oxidation stabilizers used were obtained from Ciba Specialty Chemicals Inc., Switzerland. Chemical names and structures of the stabilizers are given in Table 2.

Table 1 Chemical names and structures of the different disulfides

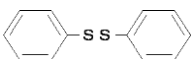
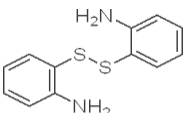
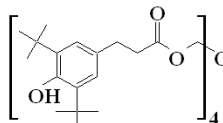
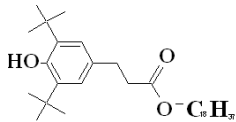
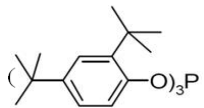
Chemical name	Chemical structure
Diphenyldisulfide, DPDS	
Dibutyldisulfide, DBDS	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Di(2-aminophenyl)disulfide, APDS	

Table 2 Chemical names and structures of thermal stabilizer investigated

Chemical name	Commercial name	Type	Chemical structure
Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)	Irganox 1010	Hindered Phenolic	
Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	Irganox 1076	Hindered Phenolic	
Tris(2,4-ditert-butylphenyl)phosphite	Irgafos 168	Phosphite	

PREPARATION OF DEVULCANIZED SBR

Compounding and mixing: The SBR was first compounded using a Brabender Plasticorder 350S mixer with a mixing chamber volume of 350 cm³. The compounding formulation is shown in Table 3. The mixer was operated at a rotor speed of 60 rpm; a fill factor of 0.75 and an initial temperature of 50°C were used. The final compound temperature before dumping was in the range of 70-90°C. The compound was tested for its cure characteristics using a RPA 2000 dynamic mechanical curemeter from Alpha Technologies at 170°C, 0.833 Hz and 0.2 degree strain, according to ISO 6502. The compounds were then vulcanized for $t_{c,90} + 5$ minutes in a Wickert WLP1600 laboratory compression molding press at 170°C and 100 bar, into 2 mm thick sheets.

Table 3 Formulation of the SBR compound

Ingredient	phr
SBR 1723	137.5
ZnO	4.13
Stearic acid	2.06
Sulfur	2.75
Accelerator (TBBS)	1.38

Grinding: The vulcanized SBR sheets were subsequently ground in a Universal Cutting Mill Pulverisette 19 (Fritsch, Germany) with a 2 mm screen. The particle size of the ground rubber was in the range of 0.85-2.00 mm.

Devulcanization: The thermo-chemical devulcanization was performed in a batch process in an internal mixer Brabender Plasticorder PL-2000, having a mixing chamber volume of 50 ml and a cam-type rotor. A fill factor of 0.7 and a constant rotor speed of 50 rpm were used. The devulcanization temperature was varied from 180 to 300°C and the devulcanization time was 5 minutes. The variations of the experimental conditions in this study are given Table 4.

Table 4 Devulcanization conditions

Factors	Varied conditions
Devulcanization aid	DPDS (30 mmol/100 g compound = 3.27 g/100 g compound)
Devulcanization temperatures	160, 180, 200, 220, 260, 300 (°C)
Oxidation stabilizers	Irganox 1010, Irganox 1076 and Irgafos 168 (1 g/100 g compound)

CHARACTERIZATION OF THE DEVULCANIZATES

Rubber soluble fraction: The soluble (sol) and insoluble (gel) fractions of the reclaimed materials were determined by extraction in a Soxhlet apparatus. The vulcanized and devulcanized SBR samples were extracted initially for 48 hrs in acetone in order to remove low molecular polar substances like remains of accelerators and curatives, followed by an extraction for 72 hrs in THF to remove the apolar components: oil and non-crosslinked polymer residues or soluble polymer released from the network by the de-vulcanization process. The extraction was followed by drying the samples in a vacuum oven at 40°C and determining the weight loss until constant weight. The sol fraction was defined as the sum of the soluble fractions in acetone and THF. The correction for the oil contained in the original SBR has been made. The gel fraction was calculated by the following equation:

$$\text{Gel fraction} = 1 - \frac{\text{weight of rubber dissolved in solvents}}{\text{weight of pure rubber in compound}} \quad (1)$$

Crosslink density: The extracted SBR samples were swollen in toluene for 72 hrs at room temperature. The weight of the swollen vulcanizates was measured after removal of

surface liquid with absorption paper. The crosslink density was calculated according to the Flory-Rehner equations [9], equations 2 and 3:

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

With

$$V_r = \frac{m_r}{m_r + m_s(\rho_r/\rho_s)} \quad (3)$$

where:

v_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;

χ = Flory-Huggins polymer-solvent interaction parameter
(0.37 for the system SBR/toluene [8])

This calculated crosslink density is based on the volume of gel rubber 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 de-vulcanization with the sol fraction still present. During the swelling test this sol fraction is also extracted, therefore needs to be included again in the calculation of the real crosslink density, remaining after the de-vulcanization but before the extraction. Consequently, to obtain the actual remaining crosslink density of the devulcanizate, the volume of total rubber is needed to be taken into account. Correction for this real crosslink density was made according to equation 4:

$$v_{real} = \frac{\text{Number of crosslinks}}{\text{Volume of total rubber}} = v_e \times (1\text{-sol fraction}) \quad (4)$$

where:

v_{real} = the final corrected crosslink density for the devulcanizate

Results and discussion

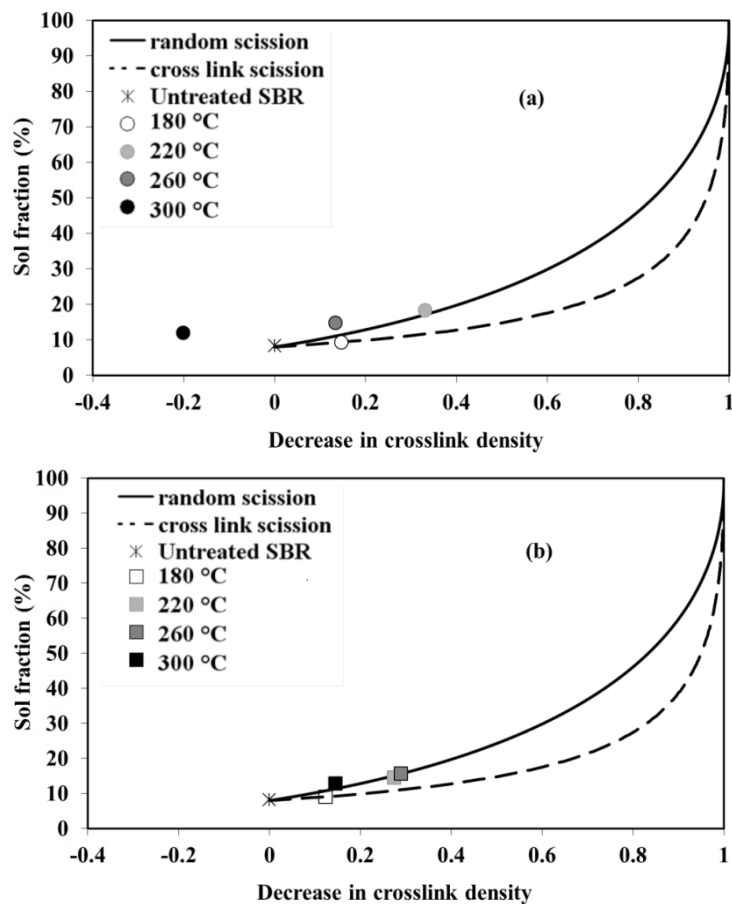
THERMAL DEVULCANIZATION

In this first part of the investigation, the rubber has undergone a 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 the extruder (TL), and under nitrogen atmosphere during devulcanization as well as after leaving the extruder (TN).

Figure 1 shows the experimentally determined sol fractions of the devulcanized SBR at various devulcanization temperatures as a function of the relative decrease in crosslink density, the Horikx plot. For the thermally treated material, TT in Figure 1 (a), an increase

of the devulcanization temperature to 220°C results in a shift of the data point to the upper right hand side of the graph, which indicates an increase of sol fraction and decrease of crosslink density. Nevertheless, 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. This reversion phenomenon is even more pronounced for devulcanization up to 300°C; for this temperature the data point is even found at the left hand side of the value for untreated SBR. The detrimental effect of the presence of oxygen in the devulcanization process causes inefficient devulcanization, in which the crosslink density of the devulcanized rubber is even higher than that of the untreated vulcanized one.

A suppression of the inefficient devulcanization is observed when oxygen is excluded; the results of the TL and TN sample are shown in Figure 1 (b) and (c), respectively. These figures illustrate that the experimental data for treatment at 180°C are situated at more or less the same position as the data for TT. An increase of the devulcanization temperature to 220°C exhibits the same trend as found for TT: the percentage of soluble polymer is increased and the crosslink density is decreased. 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 phenomenon 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 turn back to the left hand side for devulcanization temperatures of 260°C and 300°C.



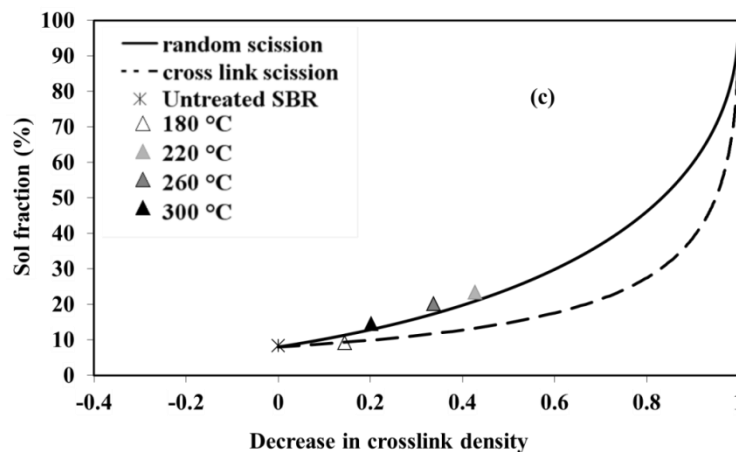


Figure 1 Sol fraction generated during devulcanization versus the relative decrease in crosslink density of devulcanized SBR.
a: TT; b: TL; c: TN.

The detrimental effect of the presence of oxygen in the devulcanization is smallest with nitrogen present during devulcanization and quenching in liquid nitrogen. The reversion phenomenon is less progressive in this case as the crosslink densities observed are still lower than the crosslink densities of devulcanized rubber treated at 180°C and untreated rubber. Thus, it must be concluded that working under exclusion of oxygen during and after devulcanization is a requirement for an efficient devulcanization process of SBR, and the temperature of 220°C is the optimum for devulcanization. Above 220°C reversion phenomena appear, whatever conditions are used. Based on these results, it is to be concluded that the devulcanization as obtained under the present conditions is primarily via the mechanism of main-chain scission. Theoretically, the scission of C-S and S-S bonds, which have lower bond strength than C-C bonds, should be the priority mechanism in network scission. However, practically, the data showed that main-chain scission mainly occurs. This is due to uncontrolled scission of the rubber network in a thermal process. As there is a majority of C-C bonds compared to C-S and S-S bonds, the probability of cleavage of the polymer backbone is higher.

THERMO-CHEMICAL DEVULCANIZATION

As thermal devulcanization turned out to be non-selective, the effect of a radical scavenger is studied. In this series of experiments, three disulfides were chosen as devulcanization aid, differing in chemical structure: an aliphatic one, dibutyldisulfide (DBDS), an aromatic one (diphenyldisulfide, DPDS), and an aliphatic one with an amine group (di(2-aminophenyl)disulfide, APDS), see Table 1.

The experimentally determined sol fractions of SBR devulcanized with DPDS at various temperatures as a function of the relative decrease in crosslink density are shown in Figure 2 (a): An increase of the devulcanization temperature up to 220°C results in a shift of the data points to the right hand side of the graph, which indicates an increase in sol fraction and a decrease of crosslink density. Nevertheless, a further increase of the devulcanization temperature above 220°C results in a back turn of the experimental data points to the left, which is the reverse of the expected decrease of crosslink density. This indicates inefficient devulcanization, in which the crosslink density of the devulcanized rubber is increased rather than decreased with increasing treatment temperature.

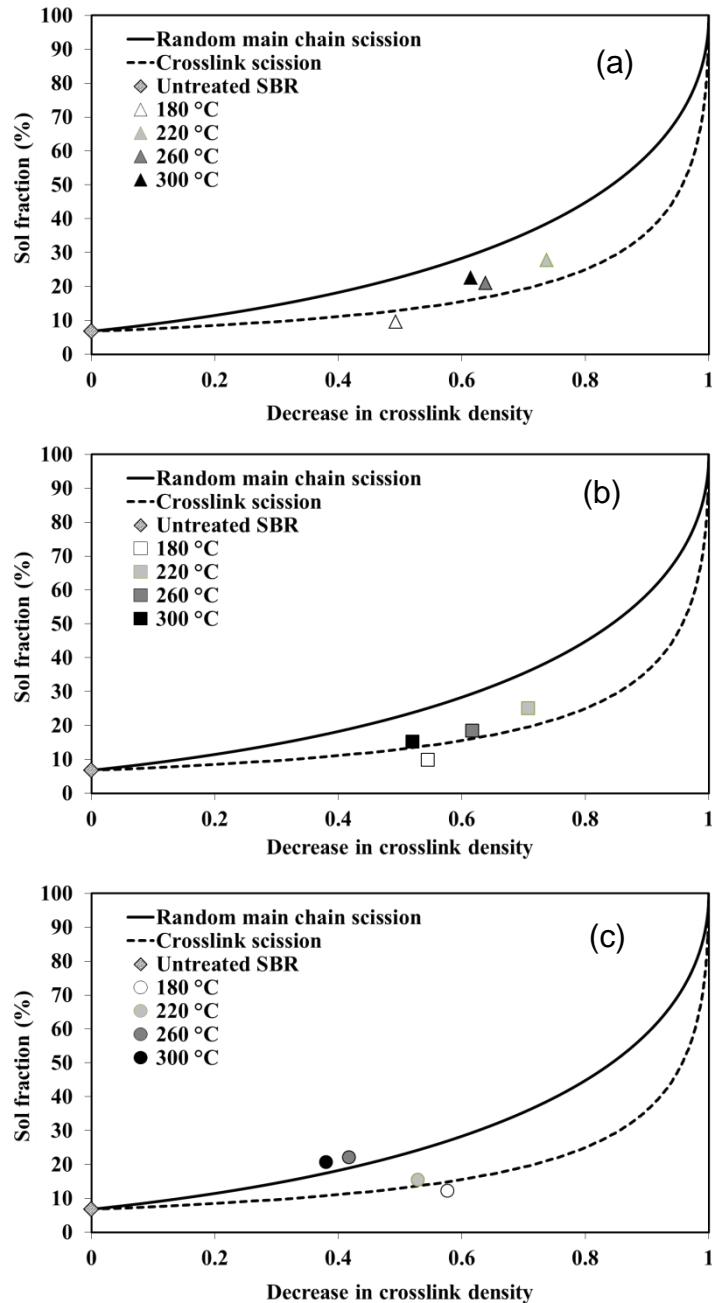


Figure 2 Sol fraction generated during devulcanization versus the relative decrease in crosslink density of devulcanized SBR
a: DPDS, b: DBDS and c: APDS as devulcanization aids

Figures 2 (b) and 2 (c) show the experimentally determined sol fractions as a function of the relative decrease in crosslink density at various devulcanization temperatures in presence of DBDS and APDS, respectively. In case of DBDS, an increase of the devulcanization temperature up to 220°C shows the same trend as found for DPDS as devulcanization aid: a shift of the data points to the upper right hand side of the graph while a further increase of devulcanization temperature to 260°C results in a back turn of the experimental data points to the left. However, in case of APDS devulcanized SBR, the back turn shifting occurs already at lower temperature of 180°C. The reversion phenomenon is most pronounced for devulcanization up to 300°C; for this temperature the data point is even moved to left hand side.

The sol fractions as a function of the relative decrease in crosslink density of SBR devulcanizates using all three types of devulcanization aids are gathered in Figure 3. It can clearly be seen that the reversion phenomenon occurs in all cases, but is more or less pronounced depending on the type of devulcanization aid. Each disulfide is effective till a different particular threshold temperature. Above this threshold temperature, devulcanization becomes inefficient. Degradation is more likely to occur at higher devulcanization temperatures, which is attributed to an excessive and uncontrolled generation of reactive radicals as mentioned before.

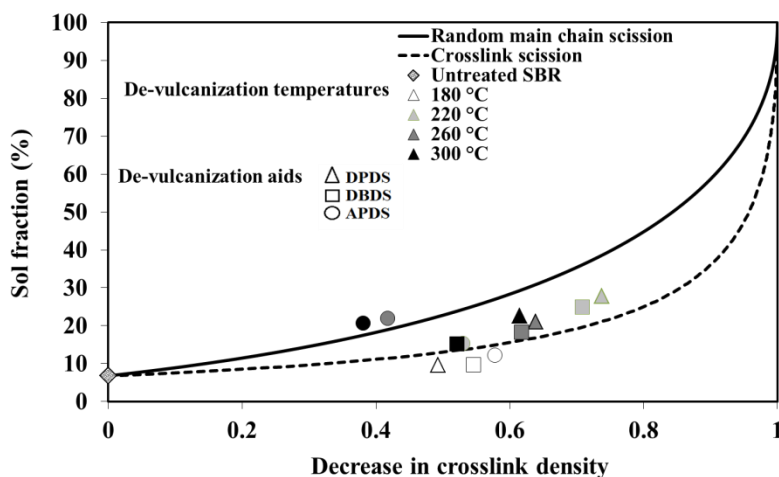


Figure 3 Sol fraction generated during devulcanization versus the relative decrease in crosslink density of devulcanized SBR using 3 different types of devulcanization aid: DPDS, DBDS and APDS

The efficiency for devulcanization of these three disulfides is related to their thermal reactivity. DBDS, a representative of aliphatic disulfides, was found to be an effective devulcanization aid only at low devulcanization temperatures up to 220°C. This is attributed to its thermal stability and a boiling temperature of 188°C. One of the aromatic disulfides, DPDS, with a higher boiling point than the previous one, was more effective in devulcanization at higher temperatures. APDS is an aromatic disulfide which was chosen to study the effect of a combination of a disulfide and an amine group. However, it turned out to be the least effective devulcanization aid, even though it has the highest boiling point of the three devulcanization aids. This is attributed to the presence of the amine group which reacts according to a nucleophilic mechanism [10] and has a positive effect on the devulcanization efficiency only at low treatment temperatures [7].

Another factor that can play a role in the efficiency of the devulcanization aids is the compatibility between rubber and the devulcanization aids, which can be estimated by their respective solubility parameters. The calculated values of the solubility parameters of SBR and the three disulfides are shown in Table 5. A larger difference in the solubility parameter results in a higher incompatibility of SBR with the devulcanization aids, which may affect the efficiency of devulcanization. The largest difference is found for the system APDS/SBR, which corresponds with the observation that APDS is the least effective devulcanization aid. DBDS and SBR have the closest solubility parameters, but here the low boiling point of DBDS prevails. DPDS is found to be the most effective devulcanization aid due to the high boiling point in spite of the differences in the solubility parameter compared to SBR.

Table 5 Solubility parameter

	Solubility (J/cm ³) ^{1/2}	parameter
SBR 1723	17.3	
Diphenyldisulfide	22.5	
Dibutyldisulfide	17.9	
Di (2-aminophenyl) disulfide	26.0	

Figure 4 is a schematic depiction of the degradation of 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 [11], 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 Figures 5 and 6. Reaction (A) in Figure 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 mechanical forces. It is accompanied by hydrogen transfer which results in polymer chain scission. However, re-formation 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 [11]. It is reported that for a 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.

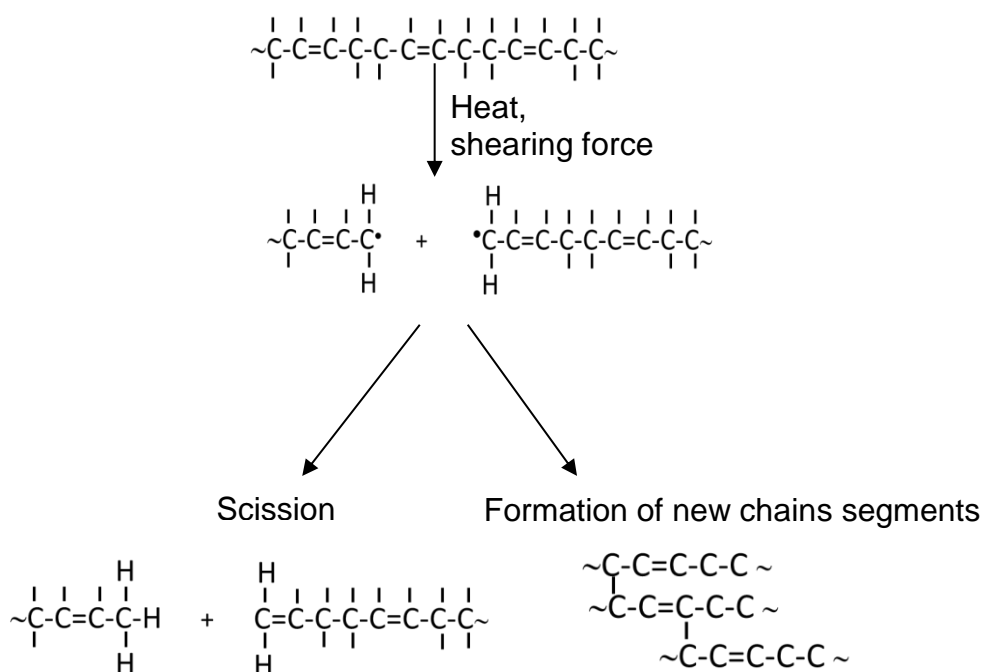


Figure 4 Simplified reaction scheme proposed for the degradation of polybutadiene and butadiene based polymers

Reaction (B) in Figure 5 is the chemical structure transformation reaction. It is associated with thermal isomerization: cis-trans isomerization, cyclization and volatilization of small fragments [12-14]. These chain rearrangements are undeniably enhanced with increasing temperature and occur at the initial decomposition step of SBR.

Reaction (C) in Figure 6 involves generation of active groups derived from the presence of oxygen. The initial predominant attack of aerial oxygen (O_2) takes place on the double bonds. It continues with the generation of hydroperoxide radicals which then decompose to give carbonyl ($>C=O$) functionalities [15]. These reactions typically take place at high temperature. Accordingly, when carbonyl functionalities are generated, the possibility of creating a rubber soluble fraction is less: the bond energy of $C=O$ (724 kJ/mol) is considerably higher than that of $C-C$ (410 kJ/mol) or carbon hydrogen bonds, $C-H$ (335 kJ/mol).

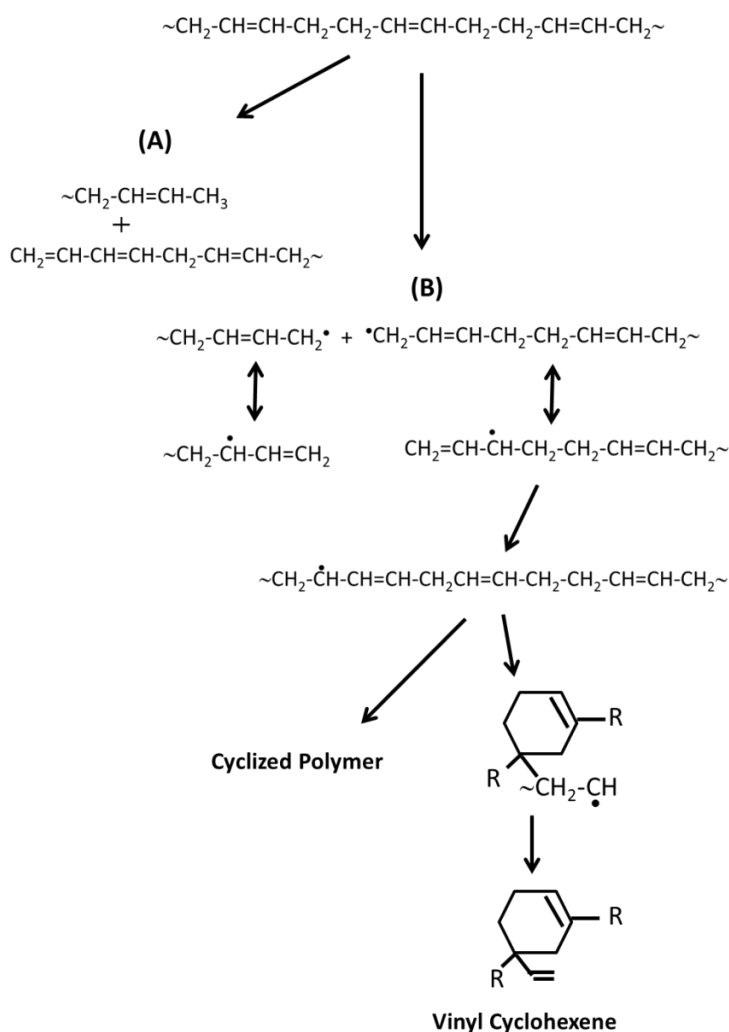


Figure 5 Reformation of active bond fragments in the specific degradation mechanism of polybutadiene and butadiene based polymers

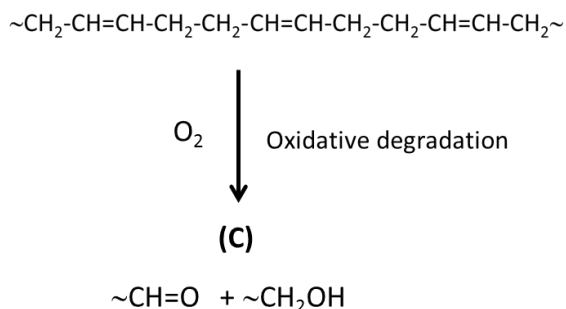


Figure 6 Simplified oxidative degradation mechanism of butadiene based polymers

CHEMICAL DEVULCANIZATION WITH THE AID OF STABILIZERS

In this series of experiments, stabilizers as specified in Tables 2 and 4 are additionally added to the devulcanization aid, DPDS. The experimentally determined sol fractions of DPDS devulcanized SBR at various devulcanization temperatures as a function of the relative decrease in crosslink density are shown in Figure 7. An increase of the devulcanization temperature to 220°C results in a shift of the data points to the right hand side of the graph, which indicates a small increase in sol fraction and large decrease of crosslink density. Nevertheless, a further increase of devulcanization temperature to 260°C results in a back turn of the experimental data points to the left, which is the reverse of the expected decrease of crosslink density. This reversion phenomenon is even more pronounced for devulcanization up to 300°C; for this temperature the data point is even found at the utmost left hand side. This indicates inefficient devulcanization, in which the crosslink density of the devulcanized rubber is increased rather than decreased with increasing treatment temperature.

A first attempt to improve the devulcanization efficiency at high devulcanization temperatures above 220°C was made by replacing DPDS with the oxidation stabilizers. However, it can be seen from Figures 7 and 8 that there is no significant improvement with switching to the stabilizers. Replacement of DPDS by the oxidation stabilizers shows lower soluble fractions and higher crosslink densities than obtained by using only DPDS. This indicates a more inefficient devulcanization, as can be seen in Figure 9, where the data points are shifted to the left hand side of the graph.

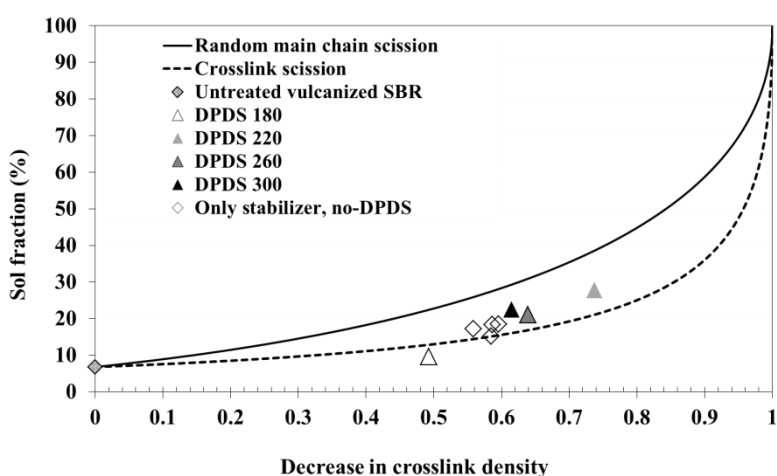


Figure 7 Sol fraction generated during devulcanization versus the relative decrease in crosslink density of devulcanized SBR

A more efficient devulcanization is observed for using combinations of DPDS and the oxidation stabilizers as devulcanization aids. The positive effect of using the combination of these two chemical species as devulcanization aid is clearly seen in Figure 8. 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.

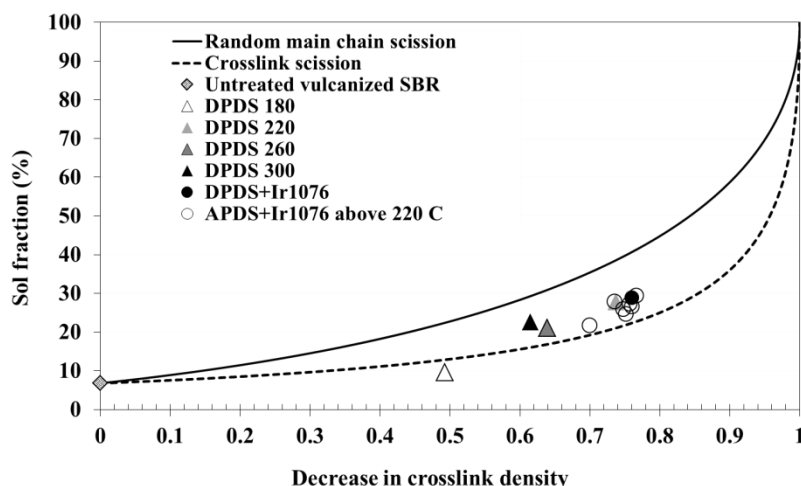


Figure 8 Sol fraction generated during devulcanization versus the relative decrease in crosslink density of devulcanized SBR using combination of DPDS and stabilizer as devulcanization aid

DPDS is reported to be an effective devulcanization aid. A mechanism that is frequently proposed for the reaction of radical scavenger devulcanization agents like DPDS 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. A simplified reaction scheme proposed for the rubber devulcanization with DPDS is given in Figure 9. Based on these results, it is to be concluded that DPDS is an effective devulcanization aid till a temperature up to 220°C. Above this threshold temperature inefficient devulcanization happens. This may be attributed to an excessive and uncontrolled generation of reactive radicals so that degradation is more likely to occur at the higher devulcanization temperature.

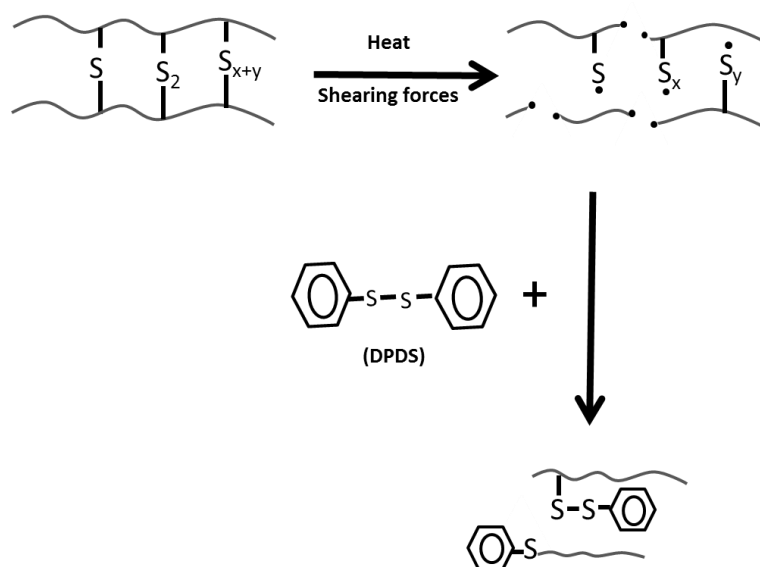


Figure 9 Simplified reaction scheme proposed for rubber devulcanization using diphenyldisulfide as devulcanization aid

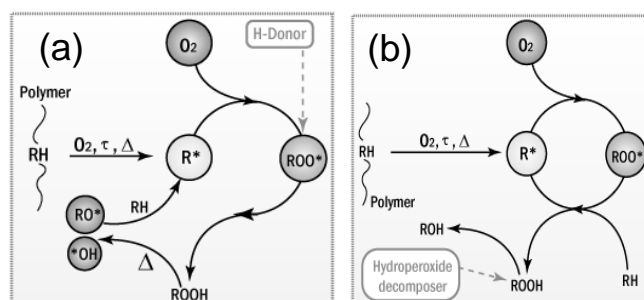


Figure 10 Preventing degradation by an oxidation stabilizer [16]:
 a) Hindered phenolic stabilizer; b) phosphite compound

Generally, polymer degradation is initiated by breaking C-H and C-C bonds along the polymer chains. Consequently, unstable carbon radicals (R^{\bullet}) are formed. These radicals readily react with oxygen (if present) to form peroxy radicals (ROO^{\bullet}) which subsequently abstract a hydrogen atom from other polymer molecules to form hydroperoxides ($ROOH$) and propagate in an oxidative degradation cycle [17]. Once oxidation starts, it sets off a chain reaction which accelerates degradation unless an oxidation stabilizer is present to interrupt the cycle. The principle mechanism of degradation and the effect of an oxidation stabilizer is shown in Figure 10 [18]. Oxidation stabilizers are capable of scavenging or destroying these chain propagation species: alkoxy radicals (RO^{\bullet}), hydroxy radicals (HO^{\bullet}) and peroxy radicals (ROO^{\bullet}). Therefore, the oxidative degradation cycle can be prevented either by using an oxidation stabilizer or by totally eliminating oxygen in the devulcanization process. Two types of oxidation stabilizers were used in this present work: hindered phenolic and phosphite compounds. Hindered phenolic stabilizers act as hydrogen donor. The stabilizer reacts with peroxy radicals to form hydroperoxides and prevents the abstraction of the hydrogen from polymer molecules. Phosphite compounds function as hydroperoxide decomposers, the stabilizer prevents the split of hydroperoxide into extremely active radicals: alkoxy and hydroxyl [19-21].

Degradation of polybutadiene and butadiene based polymers follows a unique pathway due to the specific chemical structure of the polymer [22]. In degradation, network breakdown occurs, but at the same time network recombination takes place. The degradation mechanisms are schematically depicted in Figure 5. Basically, two reactions can occur during degradation of polybutadiene:

- Chain scission and formation of inactive molecules;
- Formation of active chain segments.

Chain scission occurs when breaking of the C-C bonds in the polymer chains is accompanied by hydrogen transfer [23], and results in polymers with a lower molecular weight. The formation of active bond fragments presumably takes place when hydrogen transfer is not possible. In presence of oxygen, the hydrogen transfer reaction is less likely [22]. Therefore, the active radicals are more likely to recombine to a new network, thereby reducing the sol fraction and increasing the gel-level.

Efficient devulcanization is observed with using a combination of DPDS and oxidation stabilizers as devulcanization aids. Combination of two different functional chemicals frequently gives better protection against polymer degradation than would be expected from each compound alone, commonly called synergism. A decrease in crosslink density

without creating more sol fraction is found for the combination of an oxidation stabilizer and DPDS. Figure 11 emphasizes the importance of the developed “synergistic devulcanization aid”.

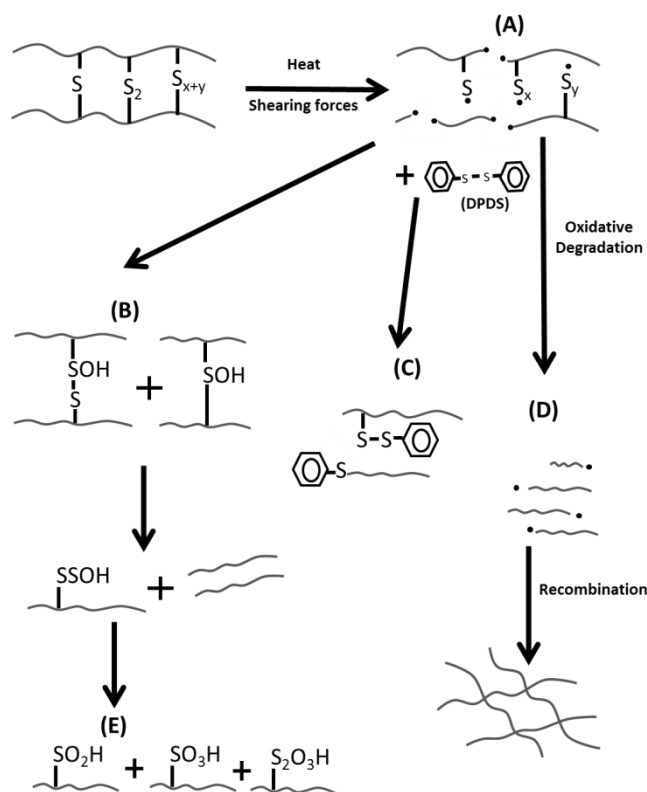


Figure 11 Simplified reaction scheme proposed for thermo-chemical devulcanization

Reaction (A): The initial step is opening of crosslinks or the scission of polymer chains by heat and shearing forces. Unstable radicals are formed. Generally, this happens to a small extent at low temperatures, but is of greater importance with increasing temperature [23]. Subsequently, these unstable radicals further react in secondary reaction steps in the presence of oxygen: (B), (C) and (D). These three reactions can jointly occur depending on the devulcanization conditions [22-25].

Reaction (B): As hydroperoxide is formed in subsequent oxidative aging of the vulcanizate, a variety of oxidized organic sulfur groups will result from reaction of the various mono-, di- as well as polysulfide groups with hydroperoxides. The sulfenic acids (RSOH) and thiosulfoxylic acids (RSSOH) formed from the oxidized sulfur network, are expected to react with hydroperoxides to form sulfinic (RSO₂H), sulfonic (RSO₃H) and thiosulfuric (RS₂O₃H) acids. All of these acids can contribute to the destruction of hydroperoxides to non-radical products and thus function as preventive antioxidants [24].

Reaction (C): The reaction of active radical fragments with disulfide based radicals, which prevent recombination of rubber molecules. In addition to this, the diffusion speed of the disulfide into the polymer matrix increases at high temperatures, enhancing the chance of combination of one radical with another rubber radical [26].

Reaction (D): Main-chain scission is caused by degradation. At higher treatment temperatures further activating the developing reactions, the probability of the generated reactive groups to undergo oxidative degradation increases. The number of radical products formed during the high treatment temperature, that may participate in chain transfer, is increased. This results in severe main chain scission of the rubber network and leads to a high degree of network recombination as previously shown in Figure 11. This reaction needs an oxidation stabilizer to prevent the uncontrolled breakage of the rubber network.

At low temperature, the occurrence of reactions (B) and (C) is predominant; therefore DPDS functions satisfactorily under these circumstances. However, uncontrolled generation of reactive groups occurs at higher temperatures, which leads to the predominant occurrence of reaction (D). The stabilizers prevent this to a large extent.

Conclusions

In thermal devulcanization of sulfur-cured SBR, intra-molecular rearrangements of chain fragments due to uncontrolled degradation and oxidation affect the properties of the material. Interestingly, an increase of the devulcanization temperature results in a decrease of the crosslink density in first instance, but it increases again above a temperature threshold of 220°C. This effect occurs independently of the presence of oxygen during the devulcanization process, but it is most pronounced for a thermal treatment without exclusion of oxygen. Optimal properties of devulcanized SBR are achieved by working at an optimized temperature of 220 °C and in an oxygen-free atmosphere. FT-IR spectra showed that the presence of oxygen during devulcanization causes molecular rearrangements during breakdown of the polymer network.

In thermo-chemical devulcanization of SBR using disulfides as devulcanization aids, an increase of the devulcanization temperature results in a reduction of the crosslink density in first instance, but it increases again above a certain temperature threshold. Although the network breakdown is enhanced by increasing the temperature, it is necessary to keep the devulcanization temperature as low as possible to prevent uncontrollable reactions. Particularly at high devulcanization temperatures, i.e. above the threshold temperature, three possible reactions can jointly occur. These lead to reformation of partially crosslinked or branched polymers from unstable chain segments, which results in a reduction of the sol fraction and increase of the crosslink density above the stated threshold temperature. The optimal devulcanization temperature for SBR is 220 °C, and DPDS is found to be the most effective devulcanization aid. These devulcanization conditions result in a maximum increase in the soluble fraction from 6.8 % to 27.8 %, and a decrease in crosslink density from 0.92 to $0.24 \times 10^{-4} \text{ mol/cm}^3$.

The devulcanization efficiency of SBR is affected by uncontrolled degradation and oxidation during thermo-chemical devulcanization. Using only DPDS as devulcanization aid, an increase of the devulcanization temperature results in a decrease of the crosslink density in first instance, but an increase again above a temperature threshold of 220°C.

Using a combination of DPDS and one or more oxidation stabilizers results in a more efficient devulcanization, especially at high devulcanization temperatures. A decrease in crosslink density without creating more sol fraction is found for a combination of an oxidation stabilizer and DPDS. DPDS scavenges formed reactive radicals, preventing

recombination of the rubber network. The stabilizers suppress the reaction of oxygen, which accelerates the degradation of the polymers and recombination into new crosslinks. The synergistic function of these two chemicals results in the most efficient devulcanization for SBR.

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