Mechanochemical devulcanization of butadiene rubber with DPDS as a devulcanization aid

Bachelor Assignment Thesis

Stefan Flanderijn

Advanced Technology

Faculty of Science and Technology

Bachelor Assignment Committee

Chairman: prof. dr. ir. J.W.M. Noordermeer

Supervisor: MSc. S. Saiwari

External member: dr. B.A. Boukamp

July 27, 2012

Faculty of Engineering Technology

UNIVERSITY OF TWENTE.

ABSTRACT

Millions of used tires are generated each year. In order to reduce this incredible amount of post consumer waste, legislations are introduced. These also address the tire industry, where more recycled rubber has to be used. However, the devulcanization of rubber remains a challenge. Polybutadiene rubber (BR) is one type of rubber used in tire production. Due to its specific chemical structure, BR has been reported to be difficult to recycle; in reclamation or devulcanization. In this study, several conditions were tested for the devulcanization of BR with the use of DPDS in order to elaborate the best conditions for an efficient process. The results are described in terms of soluble fraction, cross link density and displayed in a Horikx plot.

The addition of DPDS leads to effective devulcanization: the sol fraction increases and the crosslink density decreases. When the devulcanization temperature is higher than 200 °C, the degree of devulcanization decreases. At 250 °C dumping of the devulcanizate immediately after devulcanization in liquid nitrogen is necessary to avoid oxidative degradation of the devulcanizates. Prolonging the devulcanization time reduces the degree of devulcanization, which implies recombination of the broken crosslinks.

CONTENTS

1. INTRODUCTION

1.1 Tires and end-of-life tires

The largest consumers of rubber are the automotive and transportation industries [1]. They use multiple kinds of rubber in different parts of tires. When the tires reach the end of their life, there are several destinations. It can be landfilled, burned with energy recovery, or it can be used for secundary applications, such as sandals [2, 3]. In the late seventies of the 20th century, around 70% of the used rubber, primarily tires, was landfilled. This is the least useful path, no material or energy is gained from the waste. In the 21st century this is no longer possible: the closure of sites for disposal and the environmental problems make it infeasible. Landfilling rubber isn't allowed anymore in the E.U. As for energy recovery, scrap tires have a higher heating value (HHV) of around 33 MJ/kg, whereas coal has a HHV between 18.6 and 27.9 MJ/kg [3]. Methods are developed to regain valuable fuels in an environmetal friendly process from waste rubber. The materials are treated in a closed oxidation process, emitting no hazardous byproducts [3].

The growing pile of used tires is, however, becoming a bigger problem every day [4]. In 2007, nearly 3.4 million tonnes of used tires were generated in the EU. For the USA this was 4.6 million tonnes and Japan and China each produced around 1 million tonnes of used tires [5]. New legislations starting in 2015 dictate that 95%

of the weight of the car needs to be recycled [6]. Improving the recyclability of tires is one of the pathways to reach these goals.

The difficulties of rubber recycling lie within the structure of the material. There are two types of polymers: thermoplastics and thermosetting materials. Thermoplastics can be shaped when they are heated, and stay in that shape when cooled. This process is, in principle, repeatable [3].

In contrast, rubber is a thermosetting material. The polymer chains are crosslinked, and the material can therefore not be softened and reshaped by reheating. The three-dimensional network has to be destroyed in order to achieve succesful recycling. This can be obtained by either scission of the crosslinks or by breaking of the polymer chains. Only scission of the crosslinks leaves the polymer intact, where breaking the polymer chains degrades the polymer and its properties. So in order to keep the quality of the rubber intact, crosslink scission is the preferred method. It is a global challenge to develop the best way to recycle and reuse used material.

1.2 Scope of the current research

Devulcanization of butadiene rubber (BR) is not yet very well documented. Several studies have been done on the devulcanization of natural rubber (NR) [7] and ethylene propylene diene rubber (EPDM) [6]. It is a challenge to study and understand the mechanism of BR devulcanization, since less research has been done on devulcanization of BR, compared to NR and EPDM.

In the present work, special attention will be devoted to the efficiency and mechanistic aspects of thermal and thermo-chemical devulcanization of sulfur cured BR.

Diphenyldisulfide has been used as the devulcanization aid. The influence of temperature, time, dumping conditions and amount of devulcanization aid on the devulcanizate is thoroughly investigated.

In this report, first the theory of rubber vulcanization and devulcanization is explained. This is followed by an explanation of the different steps performed in the research and an analysis of the data, followed by a discussion and conclusions.

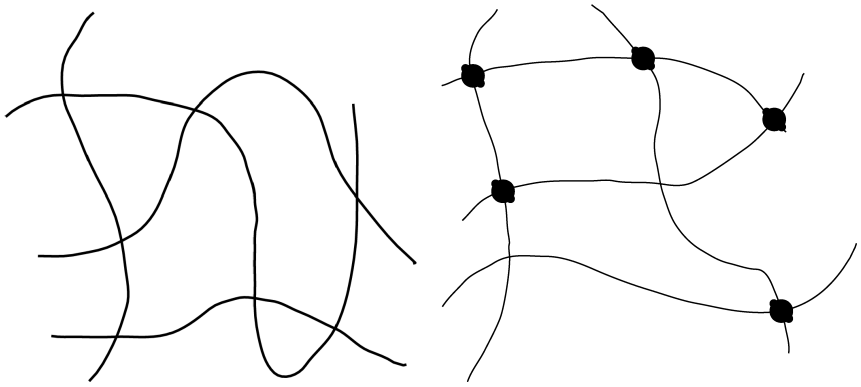
2. THEORETICAL BACKGROUND

2.1 Rubber network

2.1.1 Vulcanization

Vulcanization can be defined as ”the process by which rubber is changed form a plastic materical to an elastic or a hard material” [8]. This was discovered by Charles Goodyear in 1839, when he added sulfur and an inorganic accelerator to natural rubber and subjected it to the heat of a stove. During vulcanization chemical crosslinks are formed between the polymer chains of rubber. After vulcanization, the motion of the polymer chains is restricted which means that the chains cannot move anymore relatively to each other. This results in a decreased elongation and a higher resistance to deformation, as well as a higher strength of the material.

In Figure 2.1, a simplified polymer network is shown before and after vulcanization.



(a) Raw rubber (b) Vulcanized rubber

Fig. 2.1: Polymer chains in raw and vulcanized rubber; the crosslinks are indicated by bullets

2.1.2 Devulcanization and Reclamation

During reclamation, the sulfidic crosslinks as well as the carbon-carbon bonds of the polymer are cleaved. Devulcanization on the other hand is, literal, the reverese process of vulcanization, meaning that sulfidic crosslinks are cleaved, since only carbon-sulfur and sulfur-sulfur bonds are formed during vulcanization. However, according to ASTM, devulcanization is *a combination of depolymerization, oxidation and increased plasticity* [9] which conflicts with the literal meaning. In this perspective, the currently used methods of turning rubber into a reusable form are reclaiming rather than devulcanization.

One of the first methods for recycling of vulcanized rubber was also developed by Charles Goodyear [7]. This method consisted of grinding the scrap rubber into very small pieces and mix it with new rubber. This method sufficed for applications where the quality of the rubber wasn't the highest priority, but for shoes ,the main application of rubber at the time, the quality of the recycled rubber was too low.

Around the same period, thermal reclamation was introduced. The network breakdown was achieved by heating the rubber, which had usually lower concentrations of sulphur since the application (shoes) required little to no sulphur bloom, for a substantially longer time than the vulcanization time. The method was developed by Hiram L. Hall [10] in 1858. The low sulphur concentrations result in mostly monosulfidic and disulfidic crosslinks, which are more stable than polysulfidic crosslinks. This made it more difficult to devulcanize.

The dissociation energy for C−C bonds is 343 kJ/mol, for S−S bonds it is 226 kJ/mol and C−S bonds have an average dissociation energy of 272 kJ/mol. This means that if the devulcanization temperature is too high, also C−C bonds will break, thus the polymer chains will degrade and the quality of the rubber will decrease.

In both of the previous methods, reclamation is reached by the scission of the main chains of the polymer as well as the crosslinks. In the present study, thermochemical devulcanization is used. Different chemicals were used to devulcanize synthetic rubber. For example, in a study done by K. Dijkhuis [11], the effect of hexadexylamine, diphenyldisulfide and o'o'-dibenzamidodiphenyldisulfide on the devulcanization of EPDM was investigated.

The chosen devulcanization aid, DPDS, will initiate a radical reaction. First, heat and mechanical energy will split the disulfide into free radicals:

$$\begin{aligned} C_6H_5{-}S{-}S{-}C_6H_5 &\xrightarrow{\text{energy}} 2\,C_6H_5{-}S^{\cdot} \\ &\xrightarrow{\text{energy}} C_6H_5{-}S{-}S^{\cdot} + C_6H_5^{\cdot} \end{aligned} \tag{2.1}$$

The rubber is affected in the same way and main chain scission and crosslink scission is initiated. Before the crosslinks in the rubber can recombine, they should be

scavenged by a disulfide before bonding with a different polymer chain.

2.2 Devulcanization of butadiene rubber

2.2.1 Introduction

Butadiene rubber is largely used in tire compounding (trucks and passenger cars). It is always used in a blend, mainly with styrene-butadiene rubber (SBR), as this blend shows good wet traction properties.

BR is mainly produced using solution polymerization. Several catalyst systems are used and result in a specific microstructure. The BR used in this study was polymerized using Nickel as a catalyst. This results in a high (98%) cis oriented polymer. In Figure 2.2 the structure of butadiene rubber is given.

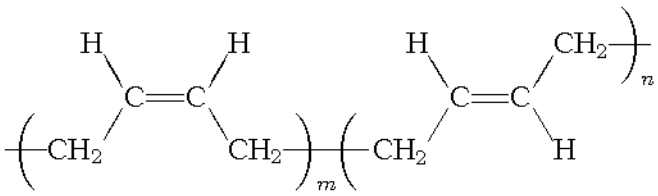


Fig. 2.2: 1-4-polybutadiene, cis-configuration on the left, trans-configuration on the right. The vinyl-configuration is not shown in this figure

2.2.2 Reclaiming of butadiene rubber

Reclamation of BR alone, i.e. not blended, is not extensively investigated. A study by Verbruggen [12] shows that BR is less reactive than natural rubber (NR) when a disulfide is used as a reclaiming agent. The study shows that an increase of devulcanization aid concentration decreases the crosslink density in the rubber.

Another study done by Oh and Isayev [13] investigates ultrasonic reclaiming of BR. A significant molecular weight reduction in the sol fraction of the devulcanizates was observed.

2.3 Tool to analyse devulcanizates: Horikx plot

The degree of devulcanization can be determined using a method developed by Horikx [14]. In this method, the rubber sol fraction of the devulcanizates and the crosslink density in the remaining gel are correlated. The relative decrease in crosslink density is related to the soluble fraction generated after polymer network degradation. This can be a result of either main-chain scission or crosslink scission. This method can be applied to rubber reclamation, where main-chain scission and crosslink scission occur. The relative decrease in crosslink density when only main-chain scission occurs, is given by:

$$1 - \left(\frac{\nu_f}{\nu_i}\right) = 1 - \left[\frac{\left(1 - {s_f}^{\frac{1}{2}}\right)^2}{\left(1 - {s_i}^{\frac{1}{2}}\right)^2}\right] \tag{2.2}$$

where:

ν_f = crosslink density of the devulcanizate

ν_i = crosslink density of the network prior to treatment

s_f = soluble fraction of the devulcanizate

s_i = soluble fraction of the network prior to treatment

When only crosslink scission occurs, the relative decrease in crosslink density is

given by:

$$1 - \left(\frac{\nu_f}{\nu_i}\right) = 1 - \left[\frac{\gamma_f \left(1 - {s_f}^{\frac{1}{2}}\right)^2}{\gamma_i \left(1 - {s_i}^{\frac{1}{2}}\right)^2}\right] \tag{2.3}$$

where:

γ_i = average number of crosslinks per chain in the gel prior to treatment

γ_f = average number of crosslinks per chain of the devulcanizate

The values for γ_i and γ_f are determined as described by Verbruggen [12]. In Figure 2.3 both curves for main-chain scission as well as crosslink scission are shown. The solid curve shows the situation of only main-chain scission, the dashed curve shows the situation of only crosslink scission. With crosslink scission, almost no sol is generated until a considerable decrease in crosslink density is reached, i.e. most crosslinks are broken. With main-chain scission, sol is generated at an earlier stage of decrease in crosslink density. The main-chain scission results in loose chains which are easily removed from the network.

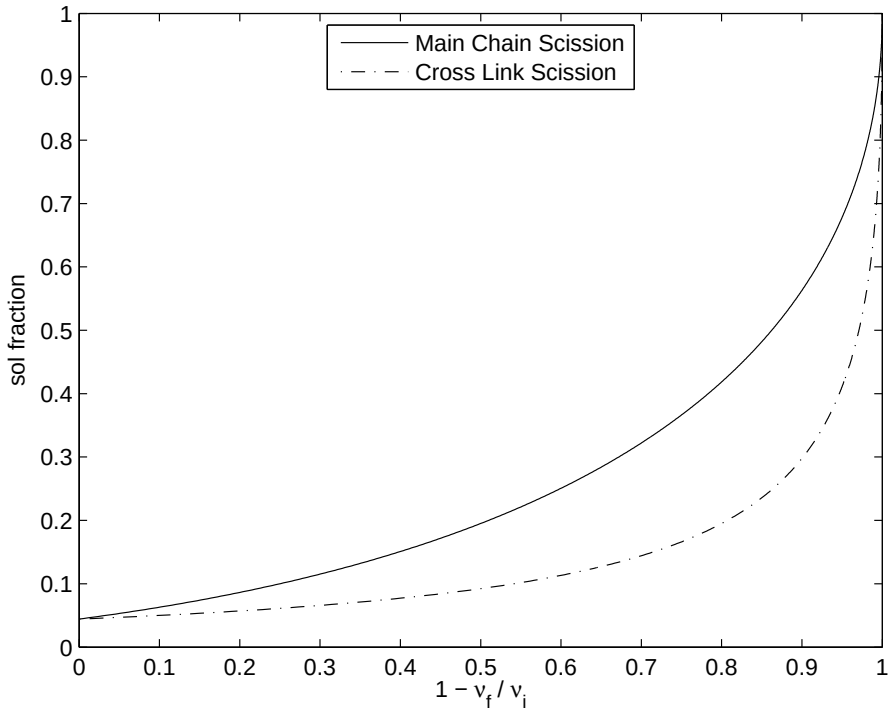


Fig. 2.3: Horikx plot for BR used in the present study

3. EXPERIMENTS

3.1 Materials

The BR (cis-1,4-polybutadiene) used in this investigation was Buna CIS 132, a stereospecific polybutadiene with high cis-1,4 content, obtained from Dow Chemical, Germany. The polymer is produced by nickel catalysis and its Mooney viscosity ML(1+4) measured at 100 °C is 45 MU. Zinc oxide (ZnO) and stearic acid were obtained from Flexsys, the Netherlands. The curatives, sulfur and N-tert-butylbenzothiazole sulfenamide (TBBS), were obtained from Merck. The solvents, acetone and tetrahydrofuran, which were used for extraction and toluene, which was used for equilibrium swelling measurements, were obtained from Biosolve. The diphenyldisulfide (DPDS) used as devulcanization aid was obtained from Sigma-Aldrich, Germany.

3.2 Preparation of (de)vulcanized BR

3.2.1 Mixing and vulcanization

BR was first compounded using a two-roll mill. The recipe for the compound can be found in Table 3.1. The compound was tested for its cure characteristics using a RPA2000 dynamic mechanical curemeter from Alpha Technologies at 170 °C.

The samples were then cured in a Wickert WLP1600 compression molding press at 170 °C and 100 bar into 2 mm thick sheets at T_{95}. T_{95} is the time required for the sample to reach 95% of the maximum torque.

Tab. 3.1: Compound recipe for BR compound

Compound	phr
BR [1]	100
ZnO	3
Stearic acid	2
Sulfur	2
TBBS [2]	0.9

[1] cis-1,4-polybutadiene rubber

[2] N-tert-butyl-benzothiazole sulfenamide

3.2.2 Grinding

The vulcanized BR sheets were ground in a Fritsch 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.

3.2.3 Devulcanization

The vulcanized rubber was devulcanized in a Brabender Plasticorder PL 2000 Internal Mixer. During devulcanization an amount of 5 phr of treated distillate aromatic extract (TDAE) oil was added. The mixer has a chamber volume of 35 cm^3 and has a tangential rotor geometry. The study is carried out in order to optimize the devulcanization parameters and the properties of the devulcanizate in respect to:

1. Effect of devulcanization aid concentration
2. Effect of devulcanization temperature
3. Effect of devulcanization time
4. Effect of dumping conditions

The parameters of devulcanization are given in Table 3.2.

Tab. 3.2: Devulcanization conditions

Factors	Varied conditions
Devulcanization aid concentration	DPDS[1] 10, 30 mmol/100 g compound
Devulcanization temperature	185, 200, 225, 250 (°C)
Devulcanization time	5, 10, 20 minutes
Dumping condition	In air, in liquid nitrogen

[1] Diphenyldisulfide

An overview of the tested samples can be seen in Table 3.3.

Tab. 3.3: Overview of experiments

Sample	D.A.[1]	D.A. conc. (mmol/100g)	Devulc. Time (minutes)	Temperature °C	Liquid nitrogen cooling
E0	-	-	-	-	
E1	DPDS[2]	10	5	200	
E2	DPDS	10	10	200	
E3	DPDS	10	20	200	
E4	-	-	5	200	
E5	-	-	5	250	yes
E6	-	-	20	200	
E7	-	-	20	250	
E8	-	-	20	170[3]	
E9	DPDS	10	5	250	yes
E10	DPDS	10	5	185	
E11	DPDS	10	5	225	
E12	DPDS	30	5	200	
E13	DPDS	30	5	225	
E14	DPDS	30	5	250	yes

[1] Devulcanization aid

[2] Diphenyldisulfide

[3] Control experiment for network breakdown at curing temperature

3.3 Analysis

The efficiency of the devulcanization process was evaluated by measuring the percentage of soluble material (sol fraction) and the crosslink density after the devulcanization process.

3.3.1 Rubber soluble fraction

The soluble (sol) and insoluble (gel) fractions of the devulcanized materials were determined by extraction in a Soxhlet apparatus. The vulcanized and devulcanized BR samples were extracted intially for 48 hours in acetone in order to remove low molecular substances like remains of accelerators and curatives, followed by an extraction for 72 hours in THF to remove the apolar components: oil and non-crosslinked polymer residues or soluble polymer released from the network by the devulcanization 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 gel fraction was calculated by the following equation:

$$\text{Gel fraction} = 1 - \frac{\text{Weight of rubber dissolved in solvents}}{\text{Weight of pure rubber in the compound}} \tag{3.1}$$

The sol fraction can then be calculated by the following equation:

$$\text{Sol fraction} = 1 - \text{gel fraction} \tag{3.2}$$

Since several additives have been added to the rubber, a correction needs to be made. The weight fraction of the TDAE oil and devulcanization agent must be substracted from the previously calculated value.

$$s_f = s - \frac{m_{TDAE} + m_{DA}}{m_r} \tag{3.3}$$

Where:

s_f = corrected sol fraction;

s = calculated sol fraction from equation 3.2;

m_{TDAE} = weight of TDAE added to the vulcanizate;

m_{DA} = weight of the devulcanization agent if added;

m_r = weight of the total compound, before devulcanization.

3.3.2 Crosslink density

The extracted BR samples were subsequently swollen in toluene for 72 hours at room temperature. The weight of the swollen vulcanizate and devulcanizates was measured after removal of surface liquid with absorption paper.

First the volume fraction of polymer at the maximum degree of swelling was calculated. This is done according to following relation:

$$v_r = \frac{m_r}{m_r + m_s \frac{\rho_r}{\rho_s}} \tag{3.4}$$

Where:

m_r = weight of the rubber before the swelling;

m_s = weight of the solvent in the rubber after swelling;

ρ_r = density of the rubber;

ρ_s = density of the solvent.

After v_r is calculated, the cross-link density, ν_e, can be determined using the Flory-Rehner relationship[15].

$$\nu_e = \frac{v_r + \chi v_r^2 + \ln(1 - v_r)}{V_S(\frac{1}{2}v_r - v_r^{\frac{1}{3}})} \tag{3.5}$$

Where:

v_r = volume fraction of polymer at the maximum degree of swelling;

χ = interaction parameter between BR and toluene;

V_S = molar volume of toluene.

χ is determined using the following relation[16].

$$\chi = 0.19 + 1.13 \cdot v_r \tag{3.6}$$

4. RESULTS AND DISCUSSION

4.1 Effect of devulcanization aid concentration

The sol fraction and crosslink density of the remaining gel as a function of devulcanzation aid concentration are depicted in Figures 4.1 and 4.2, respectively. Basically, the increase of the rubber sol fraction and decrease of crosslink density indicate the extent to which the rubber network is broken down.

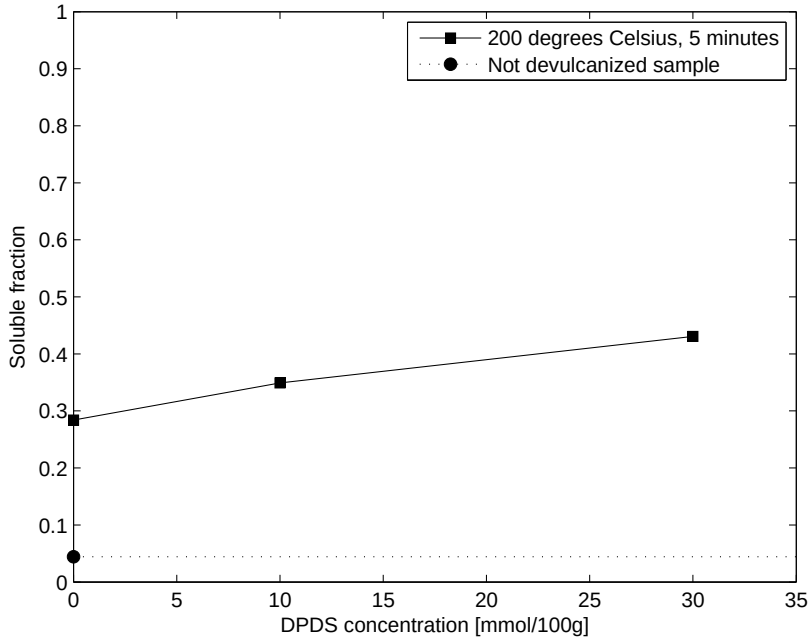


Fig. 4.1: Soluble fraction as a function of the concentration of active groups

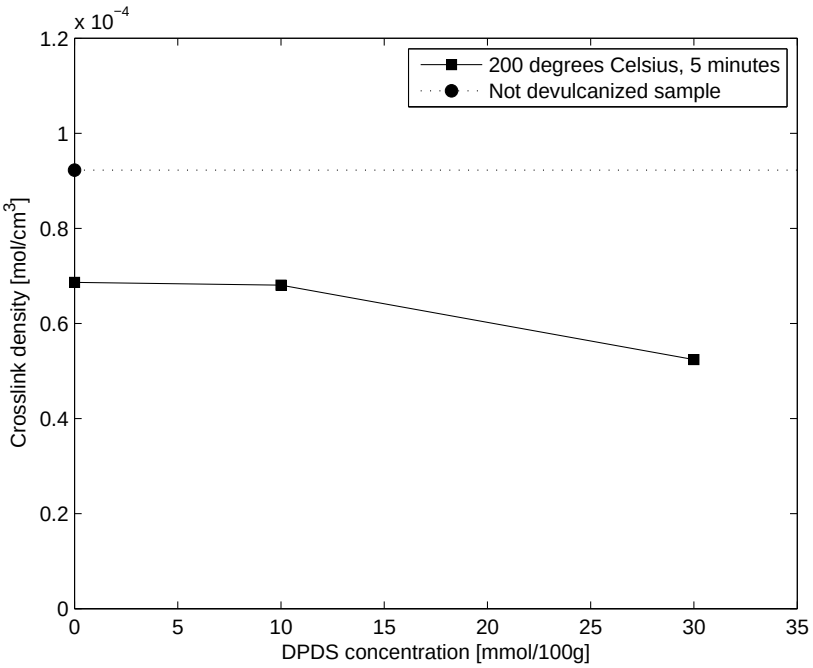


Fig. 4.2: Crosslink density as a function of the concentration of active groups

The soluble fraction increases with increasing DPDS concentration, as can be seen in Figure 4.1. In Figure 4.2, it can be seen that increasing the DPDS concentration to 10 mmol/100 g compound results in a slight decrease in crosslink density. Increasing the DPDS concentration further to 30 mmol/100 g compound, a significant decrease in crosslink density is observed.

DPDS as a devulcanization agent was added in order to scavenge radicals formed during the devulcanization process. Increasing the DPDS concentration leads to a more extensive generation of rubber sol fraction and reduction of crosslink density in the remaining gel. A simplified reaction scheme proposed for the rubber devulcanization with DPDS is given in Figure 4.3.

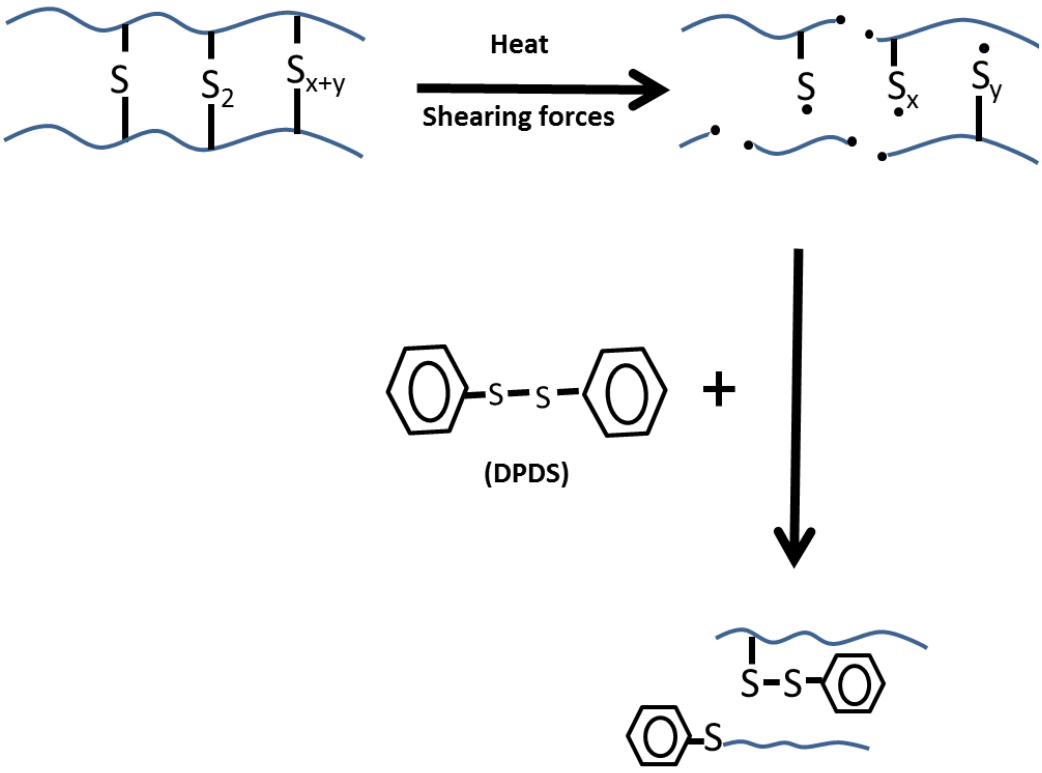


Fig. 4.3: Simplified reaction scheme proposed for rubber devulcanization using DPDS as devulcanization aid

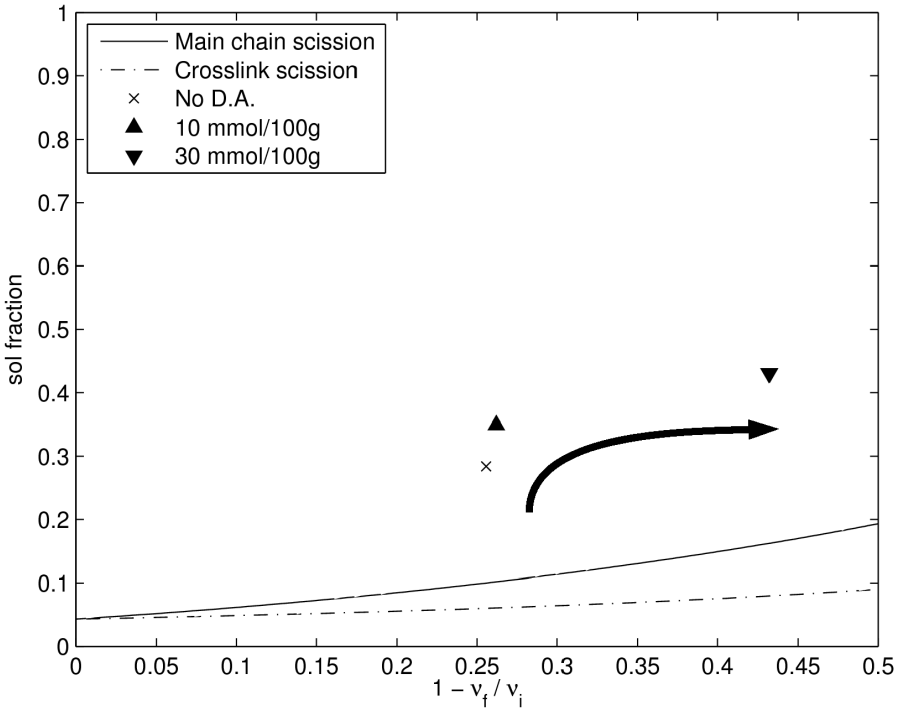


Fig. 4.4: Horikx-plot for different D.A. concentrations at 200°C

Figure 4.4 shows the Horikx-plot: fraction of sol generated during devulcanization, versus the relative decrease in crosslink density of the BR devulcanizate in presence of various concentrations of DPDS. As shown, addition of DPDS at 10 mmol/100 g compound results in a higher sol fraction, however, there is no significant decrease in crosslink density. This indicates that using DPDS at 10 mmol/100 g compound is not enough to prevent the recombination of active radicals as previously shown in Figure 4.3. Only a higher DPDS concentation, 30 mmol/100 g compound, leads to a higher devulcanization efficiency.

4.2 Effect of devulcanization temperature

The sol fraction and crosslink density of the remaining gel as a function of the devulcanization temperature are depicted in Figures 4.5 and 4.6, respectively.

Thermally treated BR devulcanizates show an increase of rubber sol fraction with increasing devulcanization temperature up to 200 °C; above this temperature the sol fraction decreases again. Furthermore, it can be seen from Figure 4.6 that above this temperature of 200 °C also a significant increase in crosslink density is observed again. This may be attributed to uncontrolled devulcanization at high devulcanization temperatures, i.e. above 200 °C. At these temperatures, an extensive generation of reactive radicals occurs, which leads to formation of new inter- and intramolecular bonds. This results in a decrease of the rubber sol fraction and renewed increase in crosslink density.

With addition of 30 mmol/100 g compound of DPDS, a more efficient devulcanization is observed. At the same devulcanization temperature, using a devulcanization aid shows an increase in sol fraction and a decrease in crosslink density compared to thermally treated BR devulcanizates. Furthermore, the decrease in sol fraction and increase in crosslink density with increasing devulcanization temperature above 200 °C is less pronounced with addition of DPDS. The positive effects of using DPDS as a devulcanization aid is clearly seen in Figure 4.7. In this figure the fraction of sol generated during devulcanization is plotted against the relative decrease in crosslink density for various devulcanization temperatures. In case of absence of DPDS, an increase of devulcanization temperature to 200 °C results in a shift of the data point to the right hand side of the graph, which indicates an increase in

sol fraction and a decrease of crosslink density. However, a further increase of the devulcanization temperature to 250 °C results in a back turn of the data points to the left, which indicates less efficient devulcanization.

To improve the devulcanization efficiency at high devulcanization temperatures: above 200 °C, a devulcanization aid has to be used. Figure 4.7 shows that the devulcanizates treated with DPDS are situated on the right side of the thermally treated devulcanizates for all temperatures. Nevertheless, at higher devulcanization temperatures, even with a devulcanization aid, the reversion phenomena still occurs.

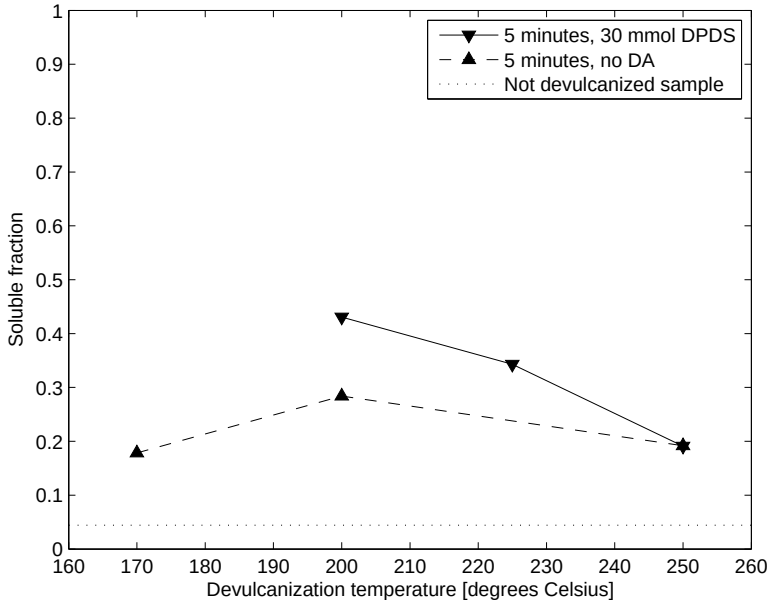


Fig. 4.5: Soluble fraction as a function of the devulcanization temperature

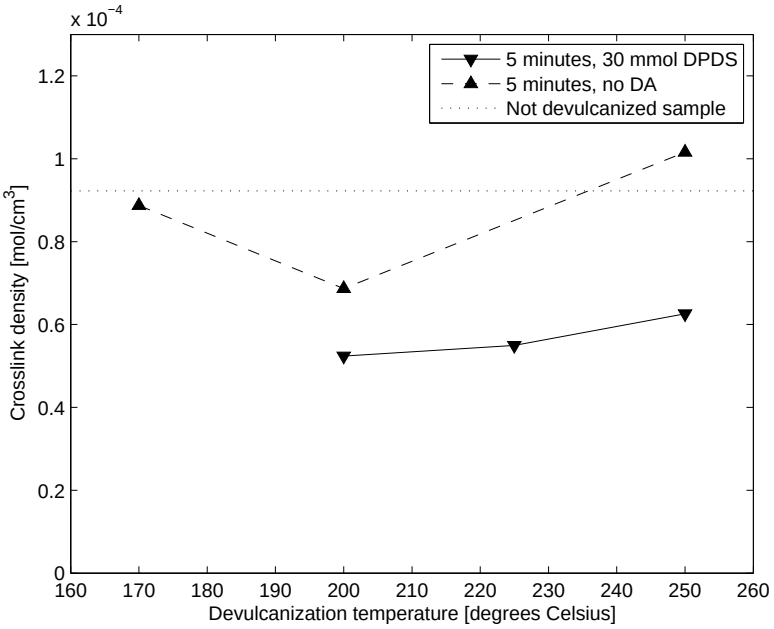


Fig. 4.6: Crosslink density as a function of the devulcanization temperature

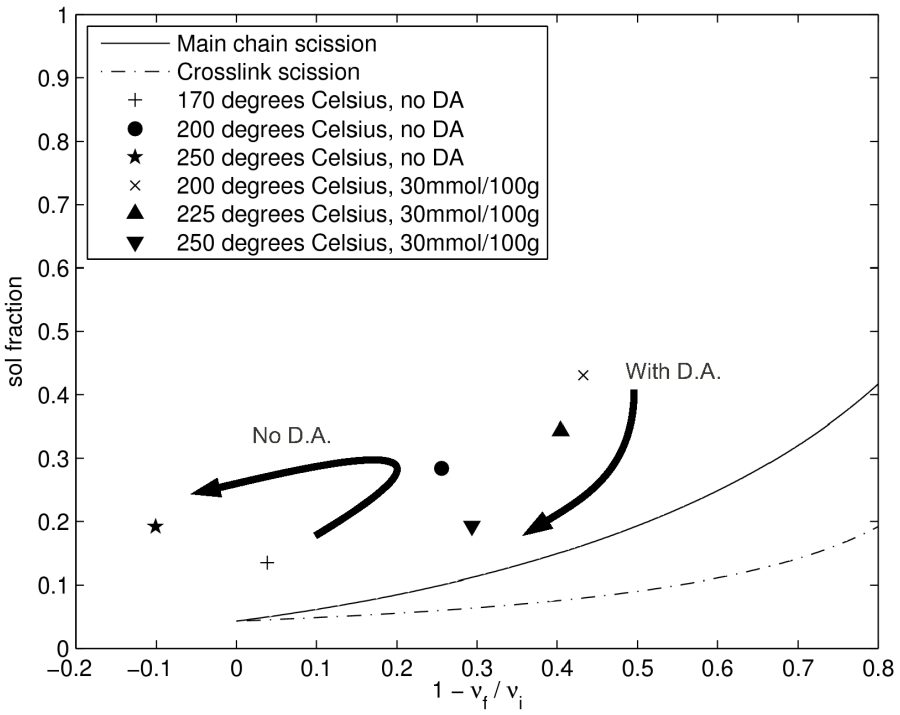


Fig. 4.7: Horikx-plot for different temperatures without D.A. and with a D.A. concentration of 30 mmol/100g

4.3 Effect of devulcanization time

The sol fraction and crosslink density of the remaining gel as a function of the devulcanization time of BR devulcanizates are depicted in Figures 4.8 and 4.9, respectively. In Figure 4.8 it is shown that a major increase in devulcanization time gives a marginal decrease in sol fraction, but at the same time an increase in crosslink density, as is shown in Figure 4.9. In Figure 4.10 it can be clearly seen that the experimental data points shift to the left hand side with increasing devulcanization time. From this it can be concluded that within the time frame of the experiments using a devulcanization time of 5 minutes is the optimal time.

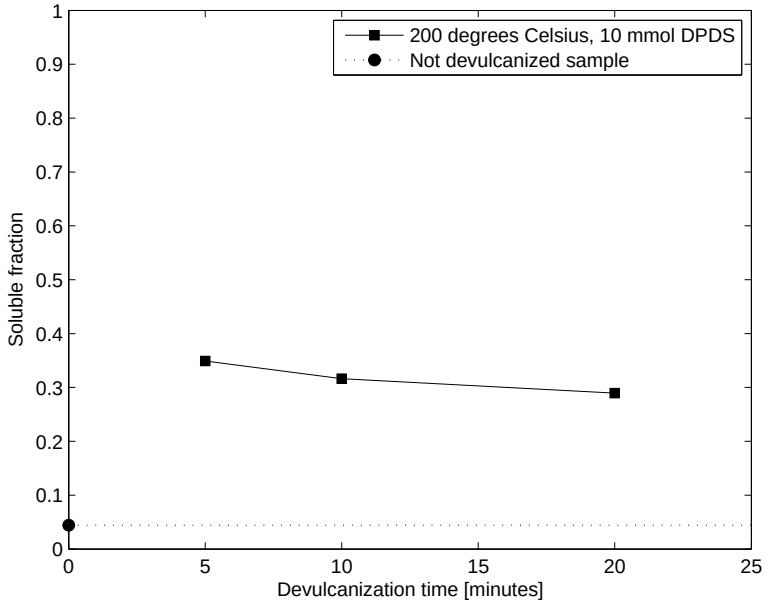


Fig. 4.8: Soluble fraction as a function of the devulcanization time

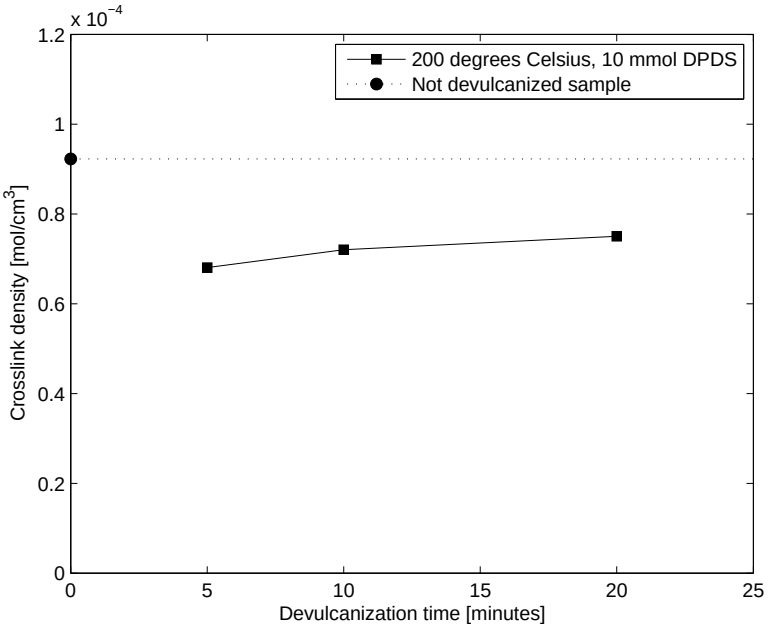


Fig. 4.9: Cross link density as a function of the devulcanization time

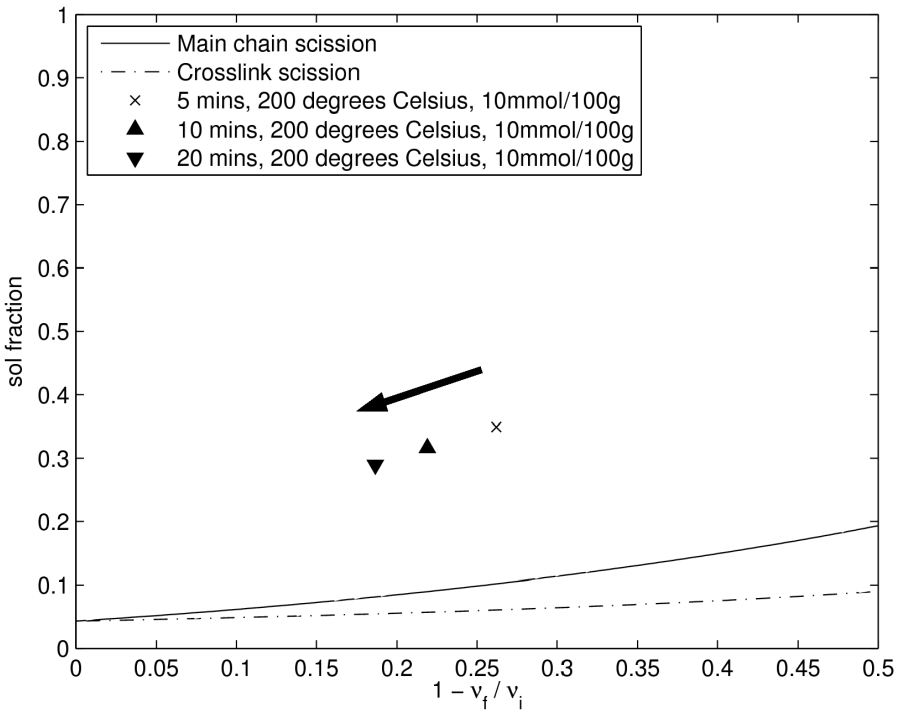


Fig. 4.10: Horikx-plot for different devulcanization times with a D.A. concentration of 10 mmol/100g at 200 Celsius

4.4 Effect of dumping conditions

Figures 4.11a and 4.11b show the physical characteristics of BR devulcanized at 250 °C with different dumping conditions. From Figure 4.11a it can be seen that the devulcanizates got burned after devulcanization using the normal dumping conditions, dumping in air. The burned devulcanizates were not suitable for further processing and analysis. An attempt was made to overcome this drawback by changing the dumping conditions. The devulcanizate was quenched directly in liquid nitrogen after devulcanization. There is a significant improvement in devulcanizate quality due to dumping in liquid nitrogen, as can be seen in Figure 4.11b.

(a) without liquid nitrogen quenching (b) with liquid nitrogen quenching

Fig. 4.11: Samples devulcanized at 250 °C

4.5 Mechanistic considerations

The experimentally determined sol fractions of DPDS devulcanized BR at various devulcanization conditions as a function of the relative decrease in crosslink density are shown in Figure 4.12. Basically, the highest devulcanization efficiency is reached when the experimental data points are situated at the most upper and right hand side of the graph, as this combines a high degree of reduction of crosslink density with a high sol fraction, meaning rather intact polymer chains. The blue arrow shows the shift of the experimental data to the left hand side when the devulcanization time is increased. The red arrow shows the shift of the data points to the right hand side when the devulcanization aid concentration is increased. The green arrow shows the shift of the data points to the left when the devulcanization temperature is increased. From these observations, the optimal devulcanization conditions can be obtained.

The optimal results found in this study reach a sol fraction of 40% and a relative decrease in crosslink density of 45% which is the limit for BR. This can be attributed to the complexity of the degradation of BR [17]. Degradation of polybutadiene and butadiene based polymers follows a unique pathway due to the specific chemical structure of the polymer. In degradation, network breakdown occurs, but at the same time network recombination takes place. The degradation mechanisms are schematically depicted in Figure 4.13. 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 and is accompanied by hydrogen transfer [18], 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 the presence of oxygen, the hydrogen transfer reaction is less likely [17]. Therefore, the active radicals are more likely to recombine to a new network, thereby reducing the sol fraction and increasing the gel-level. Both, the hydrogen transfer as well as the radical scavenging by the devulcanization aid of the active chain fragments are more effective at low devulcanization temperatures. This leads to a higher sol fraction and a lower crosslink density in case of a devulcanization temperature of 200 °C. Therefore, the temperature should be as low as possible.

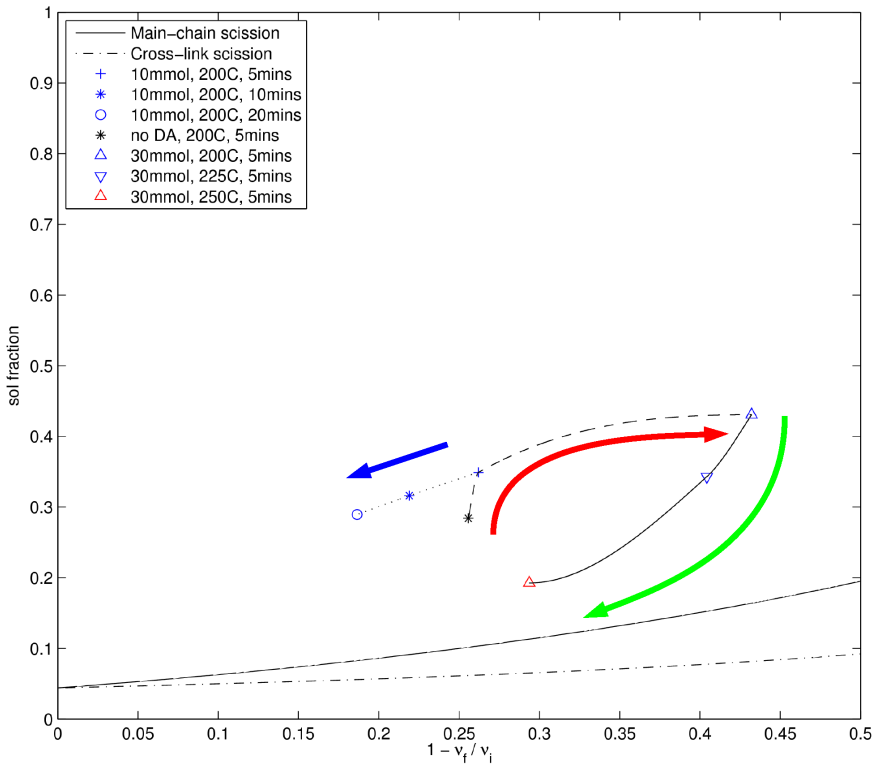


Fig. 4.12: Horikx plot for the three tested variables

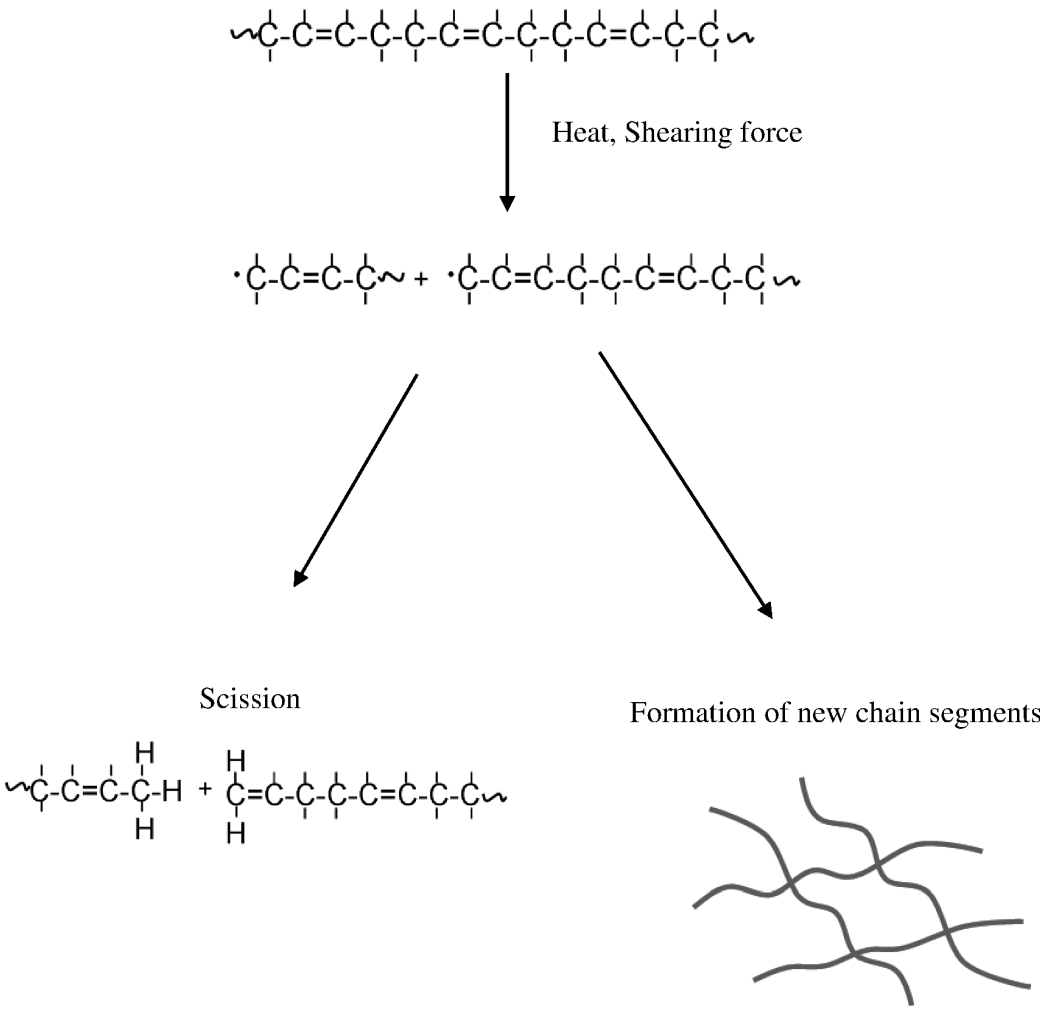


Fig. 4.13: Simplified reaction scheme proposed for the degradation of polybutadiene and butadiene based polymers

5. CONCLUSIONS

DPDS is found to be an effective devulcanization aid for BR. An increase in rubber sol fraction and a decrease in crosslink density in the BR devulcanizates are observed with an increase in DPDS concentration. Thermally treated BR devulcanizates show an increase of rubber sol fraction and a decrease in crosslink density with increasing devulcanization temperature up to 200°C. Above this temperature the sol fraction decreases again. This indictaes inefficient devulcanization. With addition of 30 mmol/100 g compound DPDS, a more efficient devulcanization is observed. The decrease in sol fraction and increase in crosslink density with further increasing devulcanization temperature above 200°C is less with the addition of DPDS.

An efficient devulcanization can be reached by using a good compromise of devulcanization conditions: low temperatures and presence of a devulcanization aid. Longer devulcanization times even had an adverse effect. With devulcanization at temperatures of 250°C and higher, quenching in liquid nitrogen immediately after the process results in higher quality devulcanizates.

BIBLIOGRAPHY

[1] H.H. Greve. *Ullmann's Encyclopedia of Industrial Chemistry*, chapter Rubber, 2. Natural, pages 583–594. Wiley-VCH Verlag GmbH & Co. KGaA, 2000.

[2] G.C.C. Yang. Recycling of discarded tires in Taiwan. *Resources, Conservation and Recycling*, 9(3):191 – 199, 1993.

[3] B. Adhikari, D. De, and S. Maiti. Reclamation and recycling of waste rubber. *Progress in Polymer Science*, 25(7):909 – 948, 2000.

[4] M.B. Rodgers. *in: Encyclopedia of Materials: Science and Technology*, chapter Rubber Tires, page 8237–8242. Elsevier Science Ltd, Oxford, 2001.

[5] P.T. Williams, I.F. Elbaba, C. Wu, and J.A. Onwudili. High yield hydrogen from the pyrolysis-catalytic gasification of waste tyres. In *Proceedings of the Third International Symposium on Energy from Biomass and Waste*, 2010.

[6] K.A.J. Dijkhuis. *Recycling of vulcanized EPDM-Rubber*. PhD thesis, University of Twente, the Netherlands, 2008.

[7] V.V. Rajan, W.K. Dierkes, R. Joseph, and J.W.M. Noordermeer. Science and technology of rubber reclamation with special attention to NR-based waste latex products. *Progress in Polymer Science*, 31:811–834, 2006.

[8] K.C. Baranwal and H.L. Stephens, editors. *Basic Elastomer Technology*, pages 1–8,165–190. The Rubber Division, ACS, 2001.

[9] American Society for Testing and Materials. Glossary of terms relating to rubber and rubber technology. In *Special Technical Publication N1814A*. 1987. Version 29.

[10] C.M. Blow and C. Hepburn, editors. *Rubber technology and manufacture*, chapter Ground vulcanized rubber and reclaimed rubber. Butterworths Scientific London, 1982.

[11] K.A.J. Dijkhuis, I. Babu, J.S. Lopulissa, J.W.M. Noordermeer, and W.K. Dierkes. A mechanistic approach to EPDM devulcanization. *Rubber Chemistry and Technology*, 81:190–208, 2008.

[12] M.A.L. Verbruggen. *Devulcanization of EPDM rubber*. PhD thesis, University of Twente, the Netherlands, 2007.

[13] J.S. Oh, A.I. Isayev, and E. von Meerwall. Molecular mobility in ultrasonically devulcanized unfilled butadiene rubber. *Rubber Chemistry and Technology*, 77(4):745–758, 2004.

[14] M.M. Horikx. Chain scissions in a polymer network. *Journal of Polymer Science*, 19:445–454, 1956.

[15] P.J. Flory. Statistical mechanics of swelling network structures. *Journal of Chemical Physics*, 18:108–111, 1950.

[16] A.J. Marzocca, A.L. Rodriguez Garraza, P. Sorichetti, and H.O. Mosca. Cure

kinetics and swelling behaviour in polybutadiene rubber. *Polymer Testing*, 29:477–482, 2010.

[17] M.D. Sarkar, P.G. Mukunda, P.P. De, and A.K. Bhowmick. Degradation of hydrogenated styrene–butadiene rubber at high temperature. *Rubber Chemistry and Technology*, 70:855–870, 1997.

[18] S.L. Madorsky. *Thermal degradation of organic polymers*. Polymer reviews. Interscience Publishers, 1964.