MODEL COMPOUND STUDIES ON THE DEVULCANIZATION OF NATURAL RUBBER USING 2,3-DIMETHYL-2-BUTENE

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ABSTRACT

The mechanism of devulcanization of sulfur-vulcanized natural rubber with aromatic disulfides and aliphatic amines has been studied using 2,3-dimethyl-2-butene (C_6H_{12}) as a low-molecular weight model compound. First C_6H_{12} was vulcanized with a mixture of sulfur, zinc stearate and N-cyclohexyl-2-benzothiazylsulfenamide (CBS) as accelerator at 140 °C, resulting in a mixture of addition products (C_6H_{11}-S_x-C_6H_{11}). The compounds were isolated and identified by High Performance Liquid Chromatography (HPLC) with respect to their various sulfur ranks. In a second stage, the vulcanized products were devulcanized using the agents mentioned above at 200 °C. The kinetics and chemistry of the breakdown of the sulfur-bridges were monitored. Both devulcanization agents decompose sulfidic vulcanization products with sulfur ranks equal or higher than 3 quite effectively and with comparable speed. Diphenyldisulfide as devulcanization agent gives rise to a high amount of mono- and disulfidic compounds formed during the devulcanization, hexadecylamine, as devulcanization agent, prevents these lower sulfur ranks from being formed.

INTRODUCTION

In the present investigation a model compound study has been used to elucidate the mechanism of the devulcanization of natural rubber with an aromatic disulfide and an aliphatic amine. A model compound study instead of an in-rubber study has been chosen, because it gives a more detailed picture of the devulcanization characteristics of the various sulfur ranks of a vulcanizate. Model compound studies, in which the rubber polymer is replaced by a reactive low-molecular weight compound, have proven to be a suitable method for the study of vulcanization reactions and this technique has been extended in this paper for the study of devulcanization reactions as well. Model compounds are easier to analyze than their polymeric counterparts due to their low molecular weight. Nieuwenhuizen, Haasnoot and Reedijk have given a comprehensive review of the technique of Model Compound Vulcanization (MCV).[1]

The low molecular weight compound used should be representative of the reactive unit of the polymer, ensuring comparable chemical behavior during their reactions. Therefore, these compounds contain $C = C$ unsaturation. It is further essential, that the model compounds have at least one allylic hydrogen atom, since crosslink formation involves the substitution of an allylic hydrogen for a sulfur link. Tetrametylethylene (TME) is used as a model molecule for Natural Rubber in the present study, as a clear picture of the structure of the vulcanized and devulcanized products can be obtained. This compound is a general model for different types of rubber and commonly used for model compound studies. The advantage of TME is that it has only one type of allylic moiety and therefore, the reaction products have only few isomers. Furthermore, the crosslinked products can be separated by HPLC from the crosslink precursors and the unreacted TME. At a wavelength of 254 nanometers the crosslink precursors and the products can be detected.

An aromatic disulfide and an aliphatic amine were chosen as devulcanization agents for the

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present study, because historically these two have most prominently been used as devulcanization agents for natural rubber.[2] A mechanism that is often proposed for the reaction of disulphides with sulfur vulcanizates is the opening of crosslinks or the scission of chains by heat and shearing forces and their recombination with disulfides which prevents recombination via a radical reaction . Amines cleaves the sulfur crosslinks in the rubber vulcanizate by a nucleophilic reaction. [3,4]

EXPERIMENTAL

MATERIALS

TME (Aldrich, 98%) was used for the present study without further purification. Sulfur (Merck), N-cyclohexyl-2-benzothiazylsulfenamide (CBS, Flexsys B.V.) and zinc stearate (Merck) were the other chemicals used. The solvents used were of pro analysis quality; acetonitrile was HPLC quality (Merck).

MODEL VULCANIZATION AND DEVULCANIZATION

The recipes for the vulcanization and devulcanization experiments are given in Tables I and II. The reactions were carried out in thick walled glass ampoules. Before closing the ampoule by melting the glass neck, a flow of nitrogen was passed through the ampoule to remove oxygen, because the oxygen can oxidize the double bond in TME. The vulcanization was done by placing the vessel in a thermostatic oil bath kept at 140 °C and the devulcanization was carried out at 200 °C. The vulcanization reactions were carried out for 2, 5, 10, 15, 20, 30, 40, and 60 minutes. The devulcanization reactions were done for 5, 10, 20 and 30, minutes. For the devulcanization reactions separate ampoules were used and the vulcanized products and the devulcanization agents were added. During the reactions the model mixture was continuously stirred with a magnetic stirrer to assure its homogeneity. After the reactions the ampoules were quenched in an ice bath followed by a liquid nitrogen bath in order to stop the reaction.

TABLE I
MODEL COMPOUND VULCANIZATION RECIPE

Component	Amount (phr)
TME	100
S_8	2.3
CBS	0.6
Zinc steatate	5

TABLE II
DE-VULCANIZATION RECIPE

Component	Amount (phr)
Vulcanizate	100
Devulcanization agent	0, 1, 2

ANALYSIS OF THE REACTION PRODUCT

The ampoules were opened and a small portion (roughly 0.03 g) of the sample was weighed and dissolved into 2.5 ml of acetonitrile already containing an internal standard. 20µl of this sam-

ple was injected into the HPLC-column for analysis according to the conditions described in Table III. Before injecting into the HPLC, this mixture was filtered twice over a 0.45μm porous filter.

TABLE III
HPLC MEASUREMENTS

Column	Nucleosil 100-5 C18 HD (reverse phase)
Mobile phase	97 Acetonitrile : 3 water (vol%)
Flow rate	1 ml/min.
Temperature	23 °C
Detector	UV
Wavelength	254 nm
Injected volume	20 μl
Length of the column	250 mm
Internal diameter of the column	4.6 mm

The internal standard is an extra component necessary for the quantitative analysis of the reaction mixture. It has a known response area with respect to the area of the other components. The internal standard used in this investigation is N-tert-butyl-2-benzothiazylsulfenamide (TBBS). TBBS is chosen because it has a retention time in the range of the retention times of the other components. Although it is a sulfur compound, it will not interfere with the sample, because it is added after vulcanization at room temperature just before injecting the sample into the HPLC.

For determining the amount of components in the sample, calibration lines were measured (Figure 1) and response factors were calculated. With use of the response factors the area of the HPLC chromatogram can be converted into concentrations. The response factor is calculated according to the following equation: [5]

$$R = \left(\frac{A_C}{A_{IS}} \right) \times \left(\frac{W_{IS}}{W_C} \right) \tag{1}$$

with R represents the response factor, A_C being the area of the component, A_{IS} being the area of the internal standard, W_{IS} representing the weight percentage of the internal standard and W_C is weight percentage of the component. The slope of the calibration line of a component, divided by the slope of the calibration line of TBBS (internal standard) results in the response factor. The response factors for the initial components measured at 254 nm are given in Table IV. Retention time and response factors of the pure ingredients were determined by injecting a solution of a single component into the HPLC device. TME does not have a retention time or a response factor, because it cannot be detected by UV light with a wavelength of 254 nanometer. The response factors are then used to calculate the weight percentage of the component in the vulcanized sample using the following equation: [5]

$$m_c = \left(\frac{A_C}{A_{IS}} \right) \times \left(\frac{W_{IS}}{R} \right) \tag{2}$$

with m_C being the mass of the component and m_{IS} is the mass of the internal standard. Since the initial masses are known, relative amounts can be calculated.

Whenever useful, ^{1}H-NMR spectroscopy (Bruker 300 MHz) was used to characterize the

structure of the reaction products. The solvent used for these experiments was $CDCl_3$.

TABLE IV
THE RETENTION TIME AND RESPONSE FACTOR OF THE INITIAL COMPONENTS

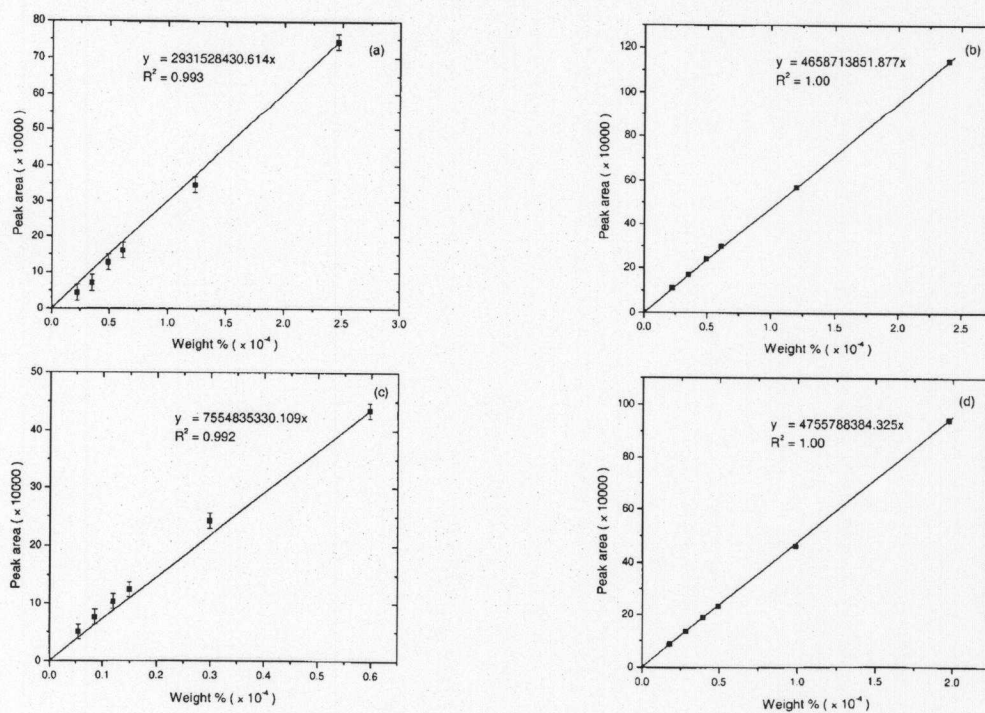| Component	Retention time (approx. min)	Response factor
CBS	5.6	10.92
TBBS	4.2	1.00
MBT	2.5	34.73
S_8	14.1	7.54

FIG. 1. — Calibration lines for (a) sulfur; (b) CBS; (c) MBT; and (d) TBBS; in terms of peak area vs. weight percentage.

RESULTS

The study is divided into two parts: The first part focuses on finding the optimum vulcanization time for TME and preparing the vulcanized TME. The second part covers the devulcanization of the vulcanizate using the aromatic disulfide and aliphatic amine as devulcanization agents.

IDENTIFICATION OF PEAKS IN THE HPLC CHROMATOGRAM

An HPLC chromatogram for the vulcanization of TME with S_8 in the presence of zinc stearate and CBS at a reaction time of 30 minutes is shown in Figure 2. Basically two types of peaks can be distinguished in the chromatogram at different retention:

i)   The addition or crosslinked products with a general formula TME-S_x-TME (C_6H_{11}-S_x-

C_6H_{11}) but with a varying length of the sulfur chain (x = 1 to 6).

ii) The starting materials and/or the decomposition products of the starting material.
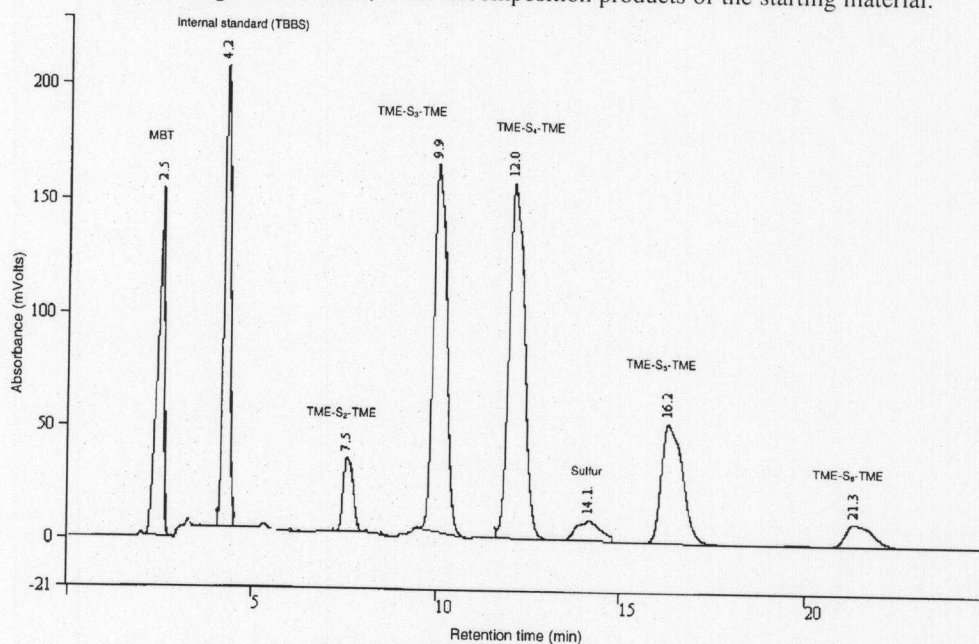

FIG. 2. — Analytical HPLC chromatogram of the reaction mixture from the vulcanization of TME with S_8 in the presence of zinc stearate and CBS at 140 °C for 30 minutes.

From Table IV, in which the retention times of the starting materials are given, it can be concluded that the peaks with retention times 2.5, 4.2, and 14.1 minutes correspond to MBT, being the decomposition product of CBS, TBBS (internal standard) and sulfur, respectively.[6] The so far unidentified peaks with retention times of 7.5, 9.9, 12.0, 16.2, and 21.3 minutes belong to the crosslinked products. The retention times of some of these products were determined by synthesizing the crosslinked products and making a chromatogram. As the separate synthesis of all the crosslinked products is not viable, only bis(2,3-dimethyl-2-butene-1-yl) monosulfide (TME-S_1-TME) and bis(2,3-dimethyl-2-butene-1-yl) disulfide (TME-S_2-TME) were synthesized and their structure characterized by ^{1}H-NMR spectroscopy. The monosulfide TME-S_1-TME has a retention time of 6.5 minutes and the disulfide TME-S_2-TME has a retention time of 7.6 minutes. According to Hann *et al.* there is a linear correlation between the sulphur rank and the logarithm of the retention time.[7] Figure 3 presents the sulfur rank as a function of the logarithm of the retention time of various crosslinked products. Since the retention times of the mono- and disulfidic crosslinks are known, the sulfur rank of the other crosslinked products can be extrapolated from Figure 3. The peak with retention time of 10.1 minutes is the trisulfide, the one with 12.2 minutes is the tetrasulfide, the one with 16.6 minutes is the pentasulfide and the peak with 21.8 minutes is the hexasulfide.
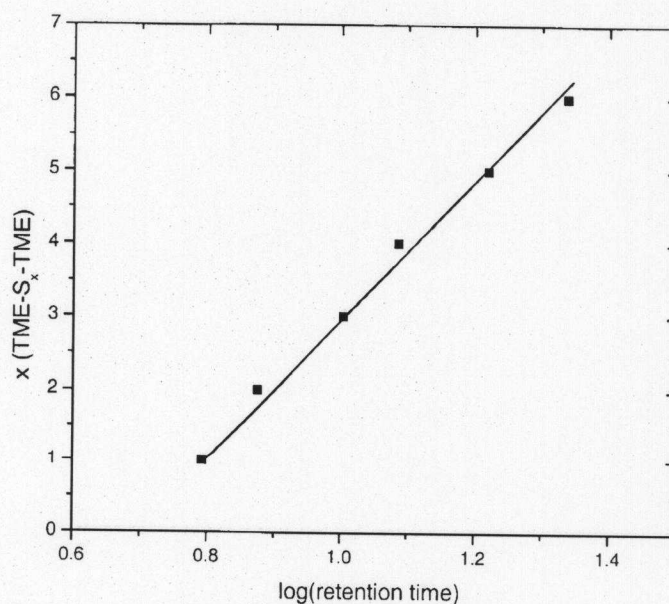
FIG. 3. — Sulfur rank of various crosslinked products as a function of the logarithm of their retention time.

DETERMINATION OF THE OPTIMUM VULCANIZATION TIME

In Figure 4, the relative amounts of CBS, sulfur and MBT for the model vulcanizate are displayed as a function of reaction time. During vulcanization the amount of elemental sulfur decreases to 38% of the initial amount for a reaction time of 5 minutes. This is an indication that the sulfur is partly inserted into the zinc complex.[8] Since initially there is no MBT present, the amount of MBT is related to the maximum that can be formed if all CBS would be transformed into MBT. CBS starts to decompose immediately after the start of the reaction, and at a reaction time of 10 minutes all CBS is decomposed. Correspondingly, the amount of MBT starts to increase and levels off after a reaction time of 15 minutes.

The peak areas of di-, tri- and polysulfidic crosslinks against the reaction time are given in Figure 5. For the crosslinked products it is not possible to plot relative amounts, because the response factors cannot be determined. Therefore, the mono-, di-, tri- and polysulfidic crosslinked products cannot be compared in terms of absolute quantities; only the trends can be compared. The tetra-, penta- and hexasulfidic crosslinked products are all combined, as they react similarly.

The polysulfidic compounds increase up to a reaction time of 30 minutes and tend to decrease with further increasing reaction time. A slight initial decrease of the amount of poly-sulfidic compounds is found for a reaction time of 10 minutes, but the concentration rapidly increases again up to 30 minutes. The formation of di- and trisulfides starts only after the same reaction time of 10 minutes. The polysulfidic crosslinks act as precursors for the shorter tri- and di-sulfidic crosslinks.[8] The breakdown of this precursor boosts the formation of shorter crosslinks. Apparently, no monosulfidic products are formed in the reaction mixture due to the fact that a conventional curing recipe with a high sulfur to accelerator ratio has been used.[6] The amount of disulfides levels off after a reaction time of 30 minutes, whereas the trisulfides further increase with reaction time.
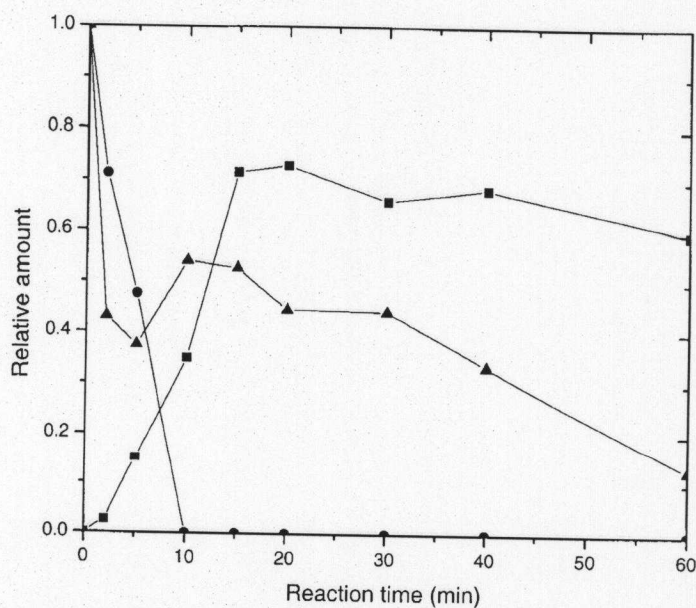
FIG. 4. — Relative amount of major compounds as a function of reaction time during the vulcanization of TME with S_8 in the presence of zinc stearate and CBS at 140 °C. (▲): Sulfur ; (●): CBS ; (■): MBT.
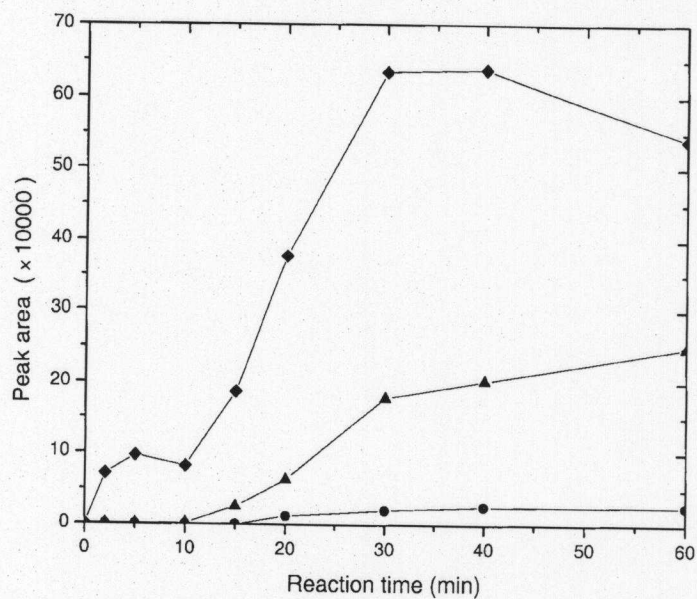

FIG. 5. — Peak areas of the crosslinked products as a function of reaction time during the vulcanization of TME with S_8 in the presence of zinc stearate and CBS at 140 °C. (●): disulfide; (▲): trisulfide ; (♦): polysulfide.

In analogy with the definition of the curing time for the vulcanization in real rubber systems, the time required for the formation of the maximum amount of crosslinks was taken as the optimum vulcanization time. Figure 5 shows that more or less around 30 minutes an optimum concentration of crosslinks is reached. This period was further chosen as the optimum vulcanization time in this study. The devulcanization experiments depicted in Figures 6, 7, 8, 9, 10, 11, and 12

are preceded by a curing step under the above mentioned conditions. The starting crosslink distributions were measured in each case to clearly define the system under investigation.

DEVULCANIZATION OF CROSSLINKED PRODUCTS WITH DISULFIDE AND AMINE

Figures 6 and 7 show the peak areas of mono-, di-, tri-, and polysulfidic crosslinks after devulcanization with 1 phr of diphenyldisulfide and hexadecylamine at 200 °C, respectively. The peak area at 0 minutes corresponds to the amount of sulfidic products originally present before devulcanization. The amount of polysulfides decreases exponentially with reaction time. A small amount remains even after 30 minutes, for devulcanization with diphenyldisulfide as well as with hexadecylamine. Both systems react similarly with respect to the decrease of polysulfides. The trisulfide increases during the first 5 minutes and then decreases again with increasing reaction time, in a similar manner for both systems. The amount of disulfide first increases and then decreases for devulcanization with diphenyldisulfide. Further, a large amount of monosulfides is formed right from the beginning of the devulcanization with diphenyldisulfide. On the other hand, for the devulcanization with hexadecylamine only minor amounts of di- and monosulfides are formed. This conspicuous difference between the two systems triggered a more detailed study into the concentration-dependences of the devulcanization with both types of compounds.
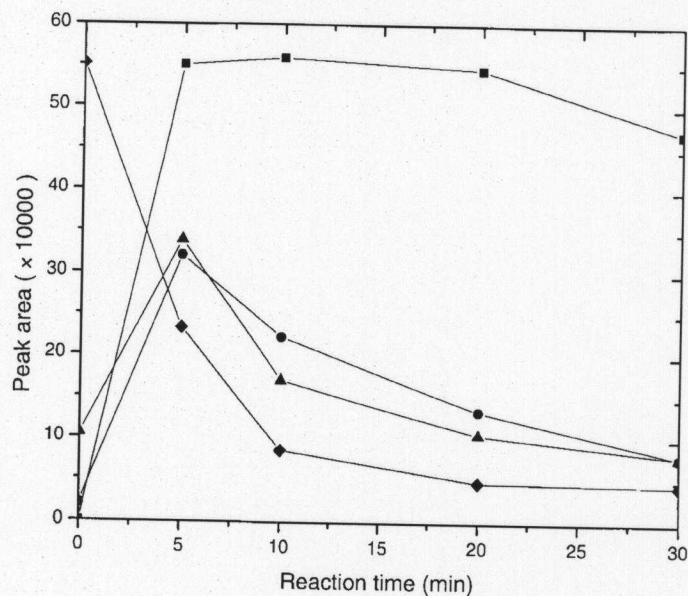

FIG. 6. — Peak areas of the crosslinked products as a function of reaction time during the devulcanization of the vulcanizate with 1 phr of diphenyldisulfide at 200 °C. (■): monosulfide ; (●): disulfide ; (▲): trisulfide ; (◆): polysulfide.
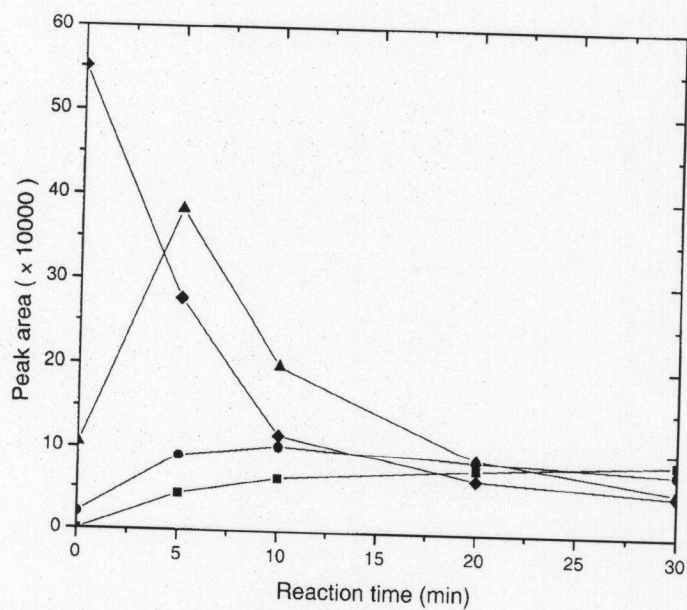
FIG. 7. — Peak areas of the crosslinked products as a function of reaction time during the devulcanization of the vulcanizate with 1 phr of hexadecylamine at 200 °C. (■): monosulfide ; (●): disulfide ; (▲): trisulfide ; (◆): polysulfide.

EFFECT OF CONCENTRATION OF DEVULCANIZATION AGENTS

In Figure 8 the peak areas of the monosulfidic compounds are shown against reaction time of devulcanization at 200 °C, for various concentrations of diphenyldisulfide and hexadecylamine, respectively, after thermal devulcanization. The latter indicates the absence of devulcanization agent. In all cases monosulfides are formed, but again the large difference between diphenyldisulfide and hexadecylamine is conspicuous. The higher the amount of diphenyldisulfide added, the more monosulfidic compound is formed. For hexadecylamine the opposite applies: the more added, the less monosulfidic compound is formed. The thermal treatment, without either of the two devulcanization agents present, clearly falls in between. Once formed, there is little decrease of the monosulfidic compound anymore, later on in the process.
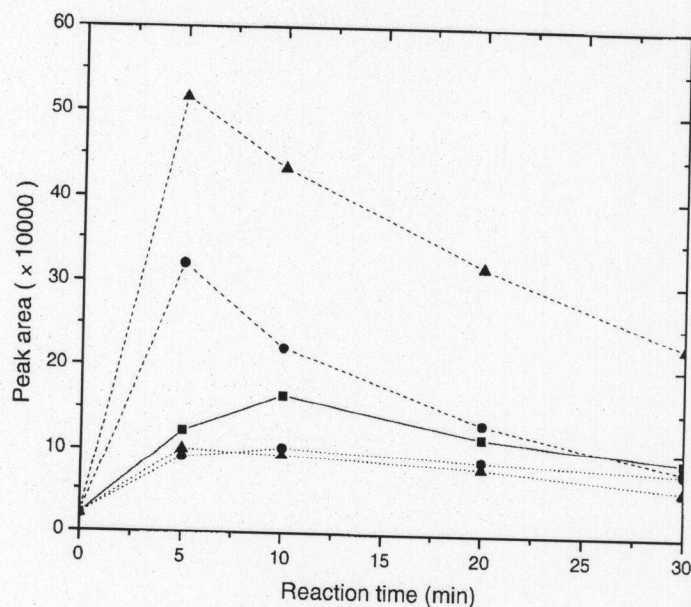
FIG. 8. — Peak areas of monosulfide crosslinks devulcanized with diphenyldisulfide (------), hexadecylamine (.......) and thermally (————) at various concentrations of devulcanization agents as a function of reaction time at 200 °C. (■): 0 phr ; (●):1 phr; (▲): 2 phr.

Figure 9 shows the peak areas of the disulfidic compound after the thermal devulcanization with diphenyldisulfide or hexadecylamine, resp. thermally at 200 °C, for various concentrations of devulcanization agents. Again, large differences are seen between the use of diphenyldisulfide and hexadecylamine. For diphenyldisulfide the concentration of disulfidic crosslinks reaches a maximum after approximately 5 minutes and then decreases with increase of time: all at a level higher than for the case where no devulcanization agent has been used at all. However, only a relatively small amount of disulfide compounds is formed for the amine as devulcanization agent, more or less irrespective of its concentration, at a level below the thermal devulcanization.

The peak areas of trisulfidic compounds obtained for devulcanization are shown in Figure 10. All curves now show the same trend of an initial increase, followed by a decrease in time. The curves for diphenyldisulfide as well as for hexadecylamine all fall below the line for thermal treatment. Diphenyldisulfide forms the least amount of trisulfides, and the amount decreases slightly with increasing concentration, whereas for hexadecylamine little effect of concentration is seen. Thermal devulcanization leads to the maximum amount of trisulfides. There is not much difference in rate of decomposition of trisulfides after the initial increase, for both diphenyldisulfide and hexadecylamine.
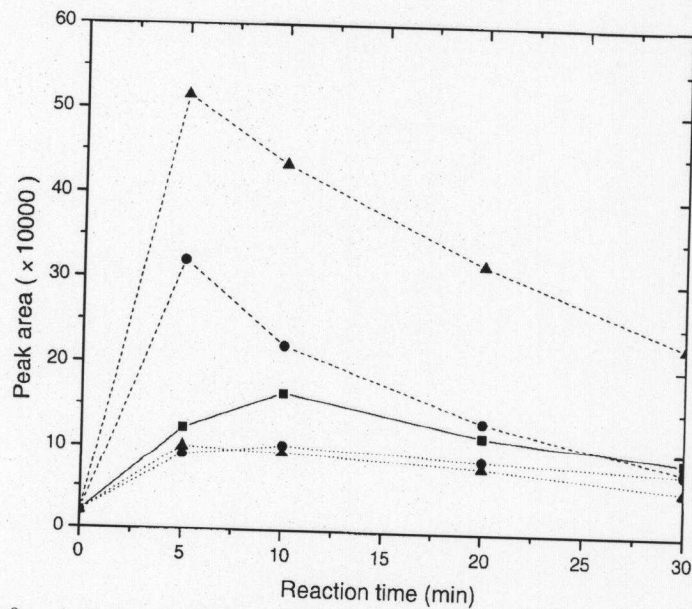
FIG. 9. — Peak areas of disulfide crosslinks devulcanized with diphenyldisulfide (---------),
hexadecylamine (.......) and thermally (———————) at various concentrations of devulcanization agents
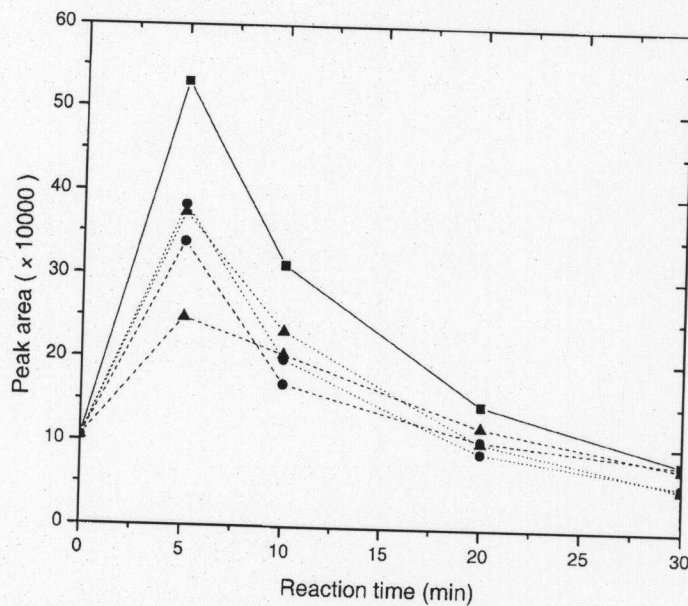as a function of reaction time at 200 °C. (■): 0 phr ; (●): 1 phr; (▲): 2 phr.

FIG. 10. — Peak areas of trisulfide crosslinks devulcanized with diphenyldisulfide (---------),
hexadecylamine (.......) and thermally (———————) at various concentrations of devulcanization agents
as a function of reaction time at 200 °C. (■): 0 phr ; (●): 1 phr; (▲): 2 phr.

Figure 11 shows the peak areas of the polysulfidic compounds against reaction time. The
amounts of polysulfides decrease with increasing concentration of both diphenyldisulfide and
hexadecylamine. Both devulcanization agents decompose the polysulfides in the same fashion;

both have a similar reactivity towards the polysulfide crosslinks. The decomposition of the poly-sulfide in the thermal treatment is much slower, particularly in the beginning.
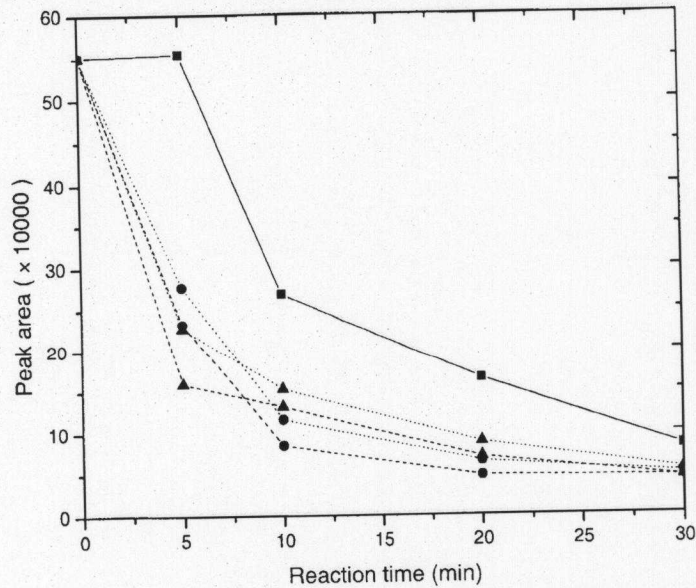

FIG. 11. — Peak areas of polysulfide crosslinks devulcanized with diphenyldisulfide (--------), hexadecylamine (.......) and thermally (————————) at various concentrations of devulcanization agents as a function of reaction time at 200 °C. (■): 0 phr ; (●): 1 phr; (▲): 2 phr.

FIG. 12. — Cumulative peak areas of all crosslinks devulcanized with diphenyldisulfide (-----------), hexadecylamine (.......) and thermally (————————) at various concentrations of devulcanization agents as a function of reaction time at 200 °C. (■): 0 phr ; (●): 1 phr; (▲): 2 phr.
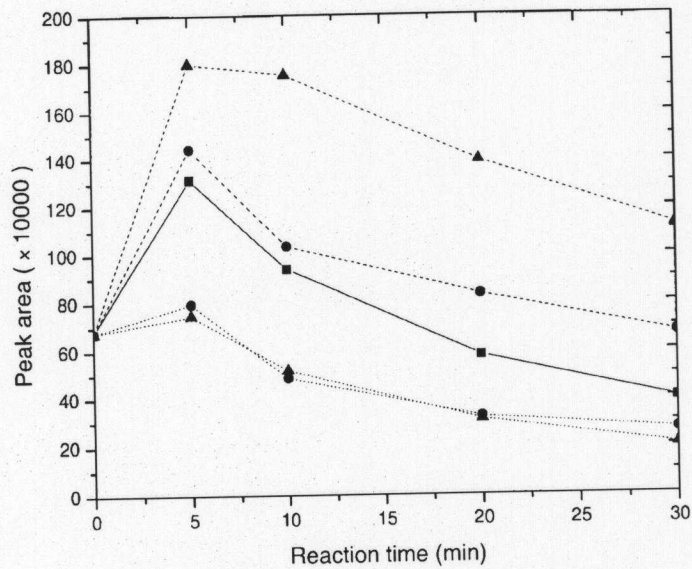
The cumulative peak areas of all crosslinks of the compound as a function of reaction time are presented in Figure 12. The cumulative areas representing the sum of all crosslinks increase in the initial 5 minutes of the reaction time and then decrease in all cases for devulcanization with diphenyldisulfide or hexadecylamine and, thermal devulcanization resp. at 200 °C, for the various concentrations of devulcanization agents. Samples devulcanized with diphenyldisulfide show the highest values, with an increasing trend for higher concentrations of diphenyldisulfide. On the other hand, the hexadecylamine devulcanized products have lower values, decrease, compared to thermally devulcanized material. No influence of the concentration of the amine is found.

In order to further investigate the particular behavior of diphenyldisulfide in interaction with the vulcanization chemicals, experiments were conducted with the recipes A, B and C given in Table V at 200 °C for a short incubation period of 5 minutes. In these recipes, the accelerator CBS is replaced by diphenyldisulfide: recipe B; in recipe C, CBS and diphenyldisulfide are jointly added to the curing reaction mixture. Peak areas of the mono-and disulfide crosslinked compounds are given in Figure 13. Large amounts of monosulfides and disulfides are formed whenever diphenyldisulfide is used in the reaction, with or without CBS present.

TABLE V
CURING RECIPES WITH CBS REPLACED BY DIPHENYLDISULFIDE (phr)

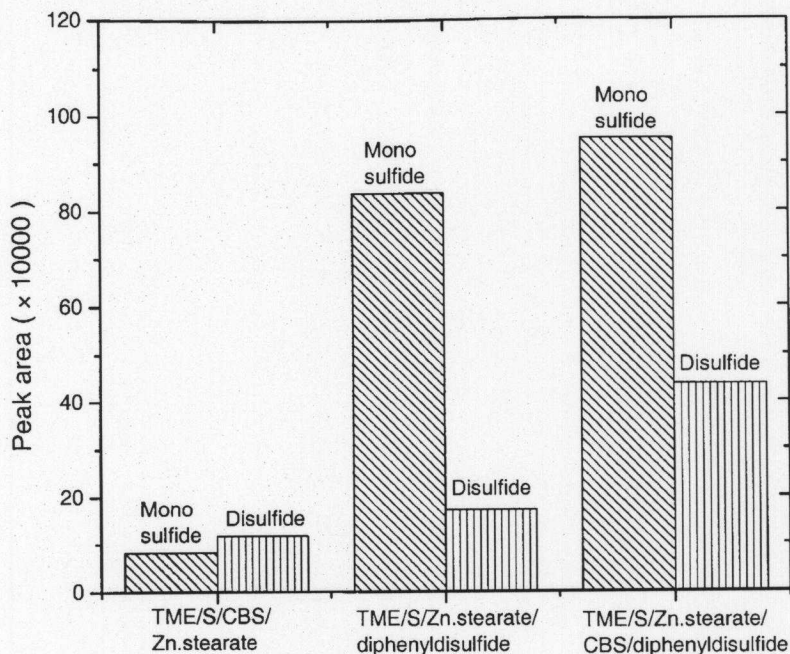| Component	A	B	C
TME	100	100	100
S_8	2.3	2.3	2.3
CBS	0.6	-	0.6
Zinc stearate	5	5	5
Diphenyldisulfide	-	0.6	2

FIG. 13. — Peak areas of the mono- and disulfidic crosslinks as a function of different reaction mixtures at 200 °C for 5 minutes.

DISCUSSION

It has become clear from the results presented, that the two devulcanization agents, diphenyldisulfide and hexadecylamine, act by different mechanisms. For diphenyldisulfide as devulcanization agent there is a clear increase in the amount of mono- and disulfides observed, and the amounts increase with increasing concentration of the diphenyldisulfide. For hexadecylamine, an increase in concentration of the devulcanization agent results in a decrease of the amounts of mono- and disulfidic crosslinks relative to the case where no devulcanization agent is present at all. The amine retards the formation of mono- and disulfides during the devulcanization reaction.

The process of disulfidic crosslink formation already starts to a limited extent during the vulcanization step: Figure 5. Bis-(2,3-dimethyl-2-butene-1-yl)-polysulfide, TME-S_x-TME, is known to undergo further reactions after formation, described as maturation of the vulcanizate.[9] The most important reactions are:

(i)   disproportionation or S-S bond interchange reactions;

(ii) decomposition reactions; and

(iii) desulfuration reactions.

The disproportionation reactions may occur by a free radical mechanism[9-12] or by an ionic mechanism.[13] In polar media the reactions are unlikely to proceed rapidly. The disproportionation reactions do not yield any new carbon-sulfur bonds and will therefore not change the total number of crosslinks. The decomposition of a polysulfide can lead to the liberation of elemental sulfur and to modification of the olefinic fragment. The de-sulfuration reactions are of a much greater influence on the product distribution than the other two reactions. In the presence of a zinc-accelerator complex the extracted sulfur can even be used for additional crosslink formation. The formation of these new crosslinks is then accompanied by a shortening of the average length of the sulfur bridges.[14] This may explain the initial decrease of the polysulfidic curve in Figure 5: the first amounts of polysulfides formed are quickly used for the beginning of the formation of tri- and di-sulfides, after which the polysulfides really start to become formed in large quantities. The vulcanization step does not reach the point of monosulfidic crosslinks in the time-span allocated to the vulcanization step.

The most conspicuous result is, that during the devulcanization reaction with diphenyldisulfide large amounts of mono- and to a lesser extent disulfides are formed: Figures 6 and 7, resp. 8 and 9. Crosslinked products with higher sulfur ranks decompose to a large extent into di- and monosulfides. The monosulfides do not disintegrate further under these circumstances due to the high bond energy of the carbon-sulfur bond.[15,16]

In the opposite case, with hexadecylamine present, the amounts of di- and monosulfides is reduced relative to the thermal treatment where no devulcanization agent is used: Figures 6 and 7, resp. 8 and 9. Hexadecylamine stabilizes the reaction mixture against these short sulfides formation.

The fundamentally different behavior between the two devulcanization agents can be explained by side reactions, which diphenyldisulfide provokes by virtue of its sulfur-content. Besides the breakdown of diphenyldisulfide into sulfide radicals (thiyl radicals), it may decompose into diphenylmonosulfide and sulfur: it acts as a sulfur-donor. The sulfur can react with still unreacted TME to form mono- and disulfidic crosslinked products. Another mechanism is, that diphenyldisulfide – itself being a disulfidic compound exchanges its sulfur moiety – via thiyl-radicals with polysulfidic crosslinks to preferably form short crosslinks. The experiments in Table V and Figure 12 confirm the outcome of these reactions, but without allowing a conclusion which one is the prevailing one. Further research is necessary to clear the mechanism.

Once large amounts of mono- and – to a lesser extent – di-sulfides are formed, they are not broken anymore under the conditions of devulcanization. The high bonding energy of monosul-

fidic crosslinks compared to the bonding energies of poly- or disulfidic crosslinks prevents this from happening. In that perspective, hexadecylamine and diphenyldisulfide perform equally well as devulcanization agents for the higher sulfide ranks: 3 and more. But hexadecylamine is greatly preferred, because it prevents the formation of large amounts of di- and mono-sulfides, which eventually survive the devulcanization and lower the efficiency of the process.

CONCLUSIONS

Model compound studies in combination with HPLC measurements are an effective tool to study the reactions during vulcanization and devulcanization of sulfur vulcanized compounds. All crosslinked products with sulfur ranks from 1 to 6 can be identified in the HPLC chromatogram. Both devulcanization agents, diphenyldisulfide and hexadecylamine, are effective agents in breaking polysulfidic and trisulfidic crosslinks at 200 °C. Large amounts of mono- and disulfidic crosslinks are formed when diphenyldisulfide is used as devulcanization agent and the amount of mono- and disulfides increases with increasing concentration of diphenyldisulfide. With increasing concentrations of hexadecylamine as devulcanization agent the amount of mono- and disulfidic crosslinks formed is significantly reduced, relative to the case where no devulcanization agent is used. Monosulfides formed during the devulcanization reaction cannot be decomposed any further under the conditions of devulcanization, neither by diphenyldisulfide nor by hexadecylamine, due to the high bonding energy of monosulfidic crosslinks. Therefore, the formation of monosulfides is to be limited as much as possible and hexadecylamine is greatly preferred over diphenyldisulfide as devulcanization agent.

ACKNOWLEDGEMENT

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