Influence of the Diene Monomer on Devulcanization of EPDM Rubber

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ABSTRACT: Ethylene–propylene–diene rubbers (EPDM) with 2-ethylidene-5-norbornene (ENB), dicyclopentadiene (DCPD), and 1,4-hexadiene (HD) as third monomers have been vulcanized with peroxide and with a conventional sulfur vulcanization recipe, and their devulcanization was subsequently investigated for recycling purposes. The behavior of these vulcanizates during pure thermal devulcanization depends on the EPDM third monomer and the crosslinker used. Peroxide vulcanizates of ENB-EPDM devulcanize only to a small extent and predominantly by random scission, whereas peroxide vulcanizates of HD-EPDM devulcanize by crosslink scission. In contrast, sulfur vulcanizates of ENB-EPDM, devulcanize mainly by crosslink scission. During devulcanization of sulfur-cured HD-EPDM, scission of both crosslinks and main chains occurs. Sulfur-cured DCPD-EPDM cannot be devulcanized but shows further crosslinking instead. In those cases, where purely thermal devulcanization is already effective to a certain extent, diphenyldisulfide as devulcanization agent increases the effectivity during thermochemical devulcanization. Hexadecylamine as an alternative devulcanization agent is effective for ENB-EPDM but does not contribute to thermochemical devulcanization of HD-EPDM. In summary, devulcanization proceeds by different mechanisms in ENB-EPDM, DCPD-EPDM, and HD-EPDM. Explanations are given in terms of the chemical structures of the third monomers, the corresponding crosslinks, and devulcanization agents. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 976–986, 2008

Key words: recycling; rubber; monomers

INTRODUCTION

Waste disposal is one of the more urgent present problems of society. For rubbers, recycling may provide a way of reducing the amount of rubber waste, while the fossil feedstock is saved.[1,2] Devulcanization of crosslinked rubber by converting the vulcanizate network into reusable, crosslinkable rubber again is a route toward rubber recycling, enabling the use in relatively high value end products. Because of its excellent resistance against oxygen, ozone and heat, and ethylene–propylene–diene rubber (EPDM) is one of the most used synthetic rubbers.[3] Devulcanization of crosslinked EPDM is therefore the subject of this study.

The thermochemical recycling of EPDM was the subject of an earlier paper.[4] EPDM with 2-ethylidene 5-norbornene (ENB) as the third monomer was studied. Diphenyldisulfide (DPDS) was used as devulcanization agent. A minimum temperature of around 265°C was needed to measure substantial devulcanization of EPDM sulfur vulcanizates. EPDM peroxide vulcanizates were less prone to devulcanize.

In commercial EPDMs, three types of diene were used until recently[5]: ENB, dicyclopentadiene (DCPD) and 1,4-hexadiene (HD). Their structures are shown in Figure 1; the asterix denotes the double bond that remains unaltered during copolymerization with ethylene and propylene and which is consequently used for crosslinking. The ethylidene unsaturation of ENB hardly reacts. The internal double bond of HD reacts to a small extent during copolymerization, and this is even more so for the cyclopentene double bond of DCPD, resulting in some degree of long-chain branching. For this reason, HD and DCPD are used less often than ENB. DCPD, however, offers some curing advantages and grades containing DCPD are therefore still on the market. In this study, all three dienes are included to demonstrate that the behavior of EPDM vulcanizates during devulcanization largely depends on the structure of the EPDM third monomer.

The peroxide cure of unsaturated elastomers is depicted in Scheme 1.[6] Peroxide crosslinking is initiated by thermal decomposition of the peroxide free-radical initiator. First, alkoxy radicals are formed, which react with EPDM via H-abstraction. The selec-
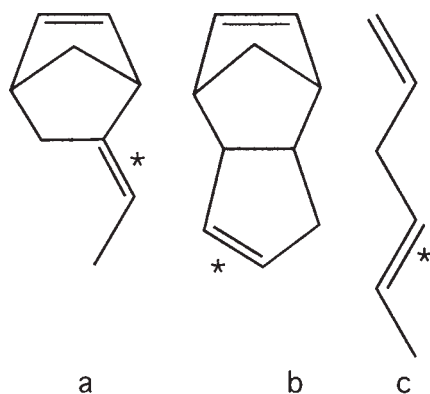
Figure 1 Diene monomer used in EPDM: ENB (a), DCPD (b), and HD (c). *: Double bond remaining after polymerization.

tivity of H-abstraction is dependent on the type and the concentration of the various H-atoms. Calculations for EPDM have shown that H-abstraction will mainly occur from the tertiary and secondary aliphatic C-atoms in the EPM backbone.[7] A recent ESR study has demonstrated selective H-abstraction at the allylic positions of the residual unsaturation in EPDM.[8]

Two EPM macroradicals may combine, yielding a direct C—C crosslink between two chains. Furthermore, a macroradical may add to the unsaturation of another EPDM chain, yielding a crosslink macroradical, which, after H-transfer, yields the final crosslink

with a diene monomer moiety connecting two EPM chains. As a result, some double bonds are lost during peroxide curing.[9]

A third route is the combination of an allylic radical derived from the diene unsaturation with another radical. The chemical structure around the double bond determines the reactivity toward peroxide crosslinking.[6,10,11] On a molar basis, ENB and DCPD are equally reactive,[6,12] whereas HD is hardly reactive.

The contribution of the addition reaction is dependent on the structure of the residual unsaturation of the diene monomer. Propagation of the crosslink macroradical, that is, addition to a second unsaturation does not proceed.[6]

Although there is general agreement on the main course of accelerated sulfur vulcanization (Scheme 2), many details on the individual reaction steps are still under debate.[13] First, parts of the accelerator are linked to the rubber chain, yielding the so-called crosslink precursors. Under influence of accelerator-derived zinc salts, these crosslink precursors are converted into sulfur crosslinks with a relatively high sulfur rank, which at prolonged time and heating desulfurize.[13] For EPDM, the speed of this conversion varies with the kind of termonomer.[14] The final sulfur vulcanizate consists of elastomer chains linked by a mixture of mono- and oligosulfidic crosslinks. The sulfur crosslink is connected to the elastomer chains at the allylic position, that is, they consist of bisalkenylsulfides. The unsaturation activates the
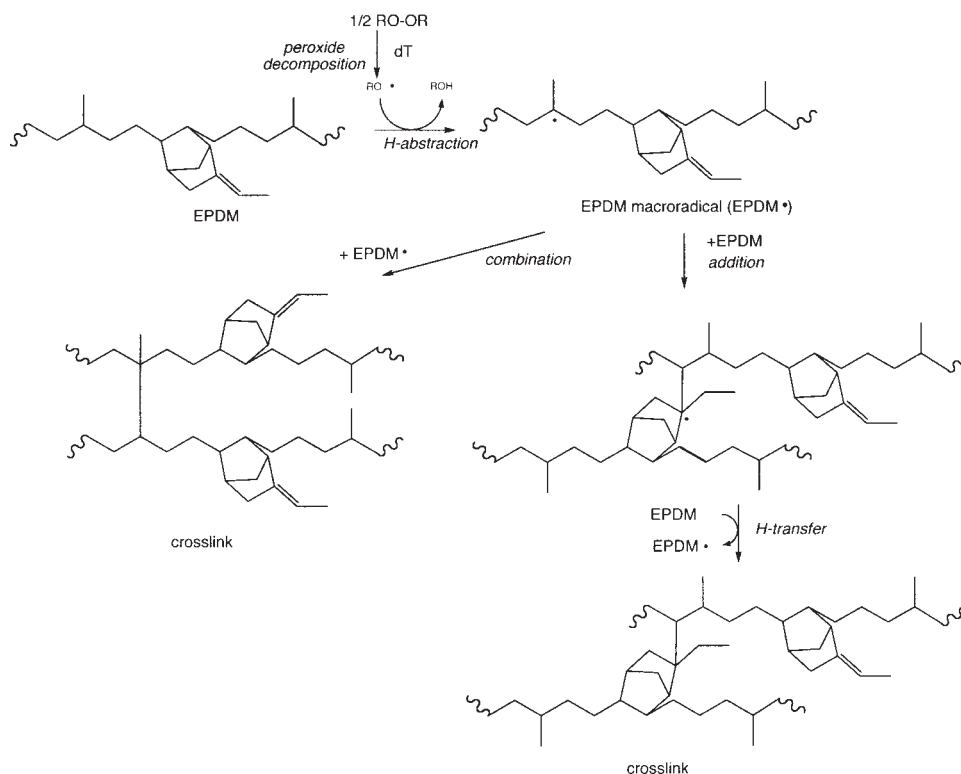
Scheme 1 Simplified scheme of the peroxide curing of ENB-EPDM.[6]
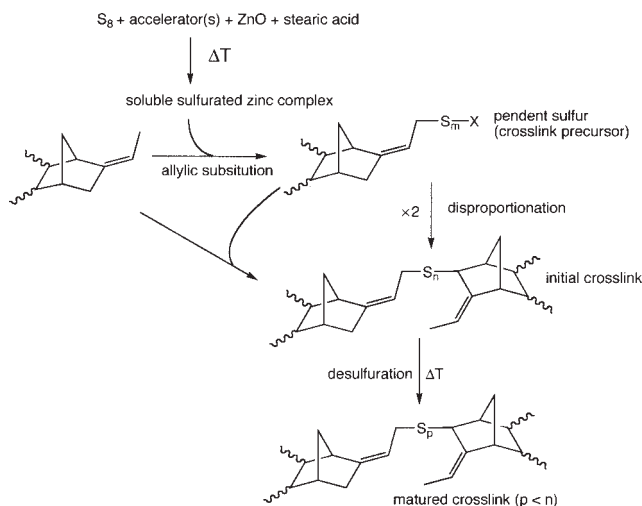
Scheme 2 Simplified scheme of the sulfur vulcanization of ENB-EPDM.

allylic substitution by sulfur, but it is not consumed itself.

As far as known, there are no studies on the chemical reactions occurring during devulcanization of peroxide-cured elastomers. As far as thermal devulcanization of sulfur-vulcanized elastomers is concerned, some useful insight may be obtained from studies on reversion and aging. Reversion is the process of desulfuration and decrosslinking when the vulcanization is continued for too long times and/or at too high temperatures.

The behavior of EPDM toward vulcanization[6,10] and reversion,[15,16] aging,[15] and oxidation[17,18] depends on the type of diene termonomer and therefore the devulcanization behavior may, among other factors, depend on the type of diene copolymerized into EPDM. This study compares the thermal and thermo-chemical devulcanization of sulfur- and peroxide-crosslinked EPDM with ENB, DCPD, and HD as termonomers. The aim is to establish whether the phenomena observed for ENB-EPDM are generally applicable to all types of EPDM, that is, with other sorts of third monomers.

Our previous study was also expanded with respect to the devulcanization agent used. Next to

disulfides, amines have for long been known as recycling agents for sulfur-vulcanized rubber.[19–21] Hexadecylamine (HDA) was chosen as a representative of this class of compounds, because of its high boiling point of 322°C and its good solubility in apolar EPDM rubber.

MATERIALS AND METHODS

Materials

EPDM polymers used are Keltan® 4802 (DSM Elastomers, 60.4 mol % ethylene, 1.2 mol % ENB: ENB-EPDM), Keltan 820 (DSM Elastomers, 66.3 mol % ethylene, 1.2 mol % DCPD: DCPD-EPDM) and Nordel® 1040 (Dupont, 64.5 mol % ethylene, 1.2 mol % HD: HD-EPDM). The following ingredients were used for compounding: zinc oxide (Merck), stearic acid (Merck), mercaptobenzothiazole (Perkacit MBT, Flexsys), tetramethylthiuram disulfide (Perkacit TMTD, Flexsys), sulfur (Merck) and dicumylperoxide (DCP, 100% pure, Schuchardt). Diphenyldisulfide (DPDS, Acros, 98%) and hexadecylamine (HDA, Acros, 99%) were used for thermochemical devulcanization.

Methods

The polymers were compounded according to the recipes in Table I on a laboratory size two-roll mill (Swabenthan) temperature controlled at 23°C. Samples of 0.3 mm thickness were vulcanized in a Lauffer press until the optimum cure time t_{90}, as derived from rheometer testing at 160°C in a Göttfert Elastograph 67.85. The sulfur formulation represents a typical conventional sulfur cure system for EPDM. Samples of ~ 0.5 g were subsequently used for the devulcanization experiments.

The research was not performed on postconsumer EPDM. Commercially used vulcanizates contain a variety of chemicals, antioxidants, accelerators, and fillers, as well as oxidized structures and shortened crosslinks resulting from aging reactions during use. This complicates the devulcanization reaction and analyses of the devulcanized products.

TABLE I
Compound Recipes (in phr)

	Peroxide	Peroxide	Sulfur	Sulfur	Sulfur
ENB-EPDM	100		100		
DCPD-EPDM				100	
HD-EPDM		100			100
DCP	2.7	2.7			
ZnO			5	5	5
Stearic acid			1	1	1
MBT			0.5	0.5	0.5
TMTD			1	1	1
Sulfur			1.5	1.5	1.5

The devulcanization agents were brought into the extracted vulcanizates by swelling the vulcanizates in solutions of these agents in tetrahydrofuran. Next, the tetrahydrofuran was removed from the vulcanizates by drying at room temperature in a vacuum oven until constant weight. The precise amount of absorbed devulcanization agent was determined by back weighing. Devulcanization experiments were performed in a mold, closed under nitrogen, and made gas tight by using two sheets of poly(tetrafluoroethylene). The system was heated to the devulcanization temperature of 200 or 265°C and kept under pressure for 2 h in a Lauffer press. The initial pressure was 7.6 MPa and increased during the reaction until a maximum of 15 MPa. After 2 h, the mold was cooled under pressure for 15 min to room temperature, before the samples were removed.

Before devulcanization, a two-step extraction method with acetone and tetrahydrofuran was used to remove low-molecular weight products, including soluble vulcanization chemicals, and soluble noncrosslinked polymer, the fraction S_i, from the vulcanized samples.[4] The samples were first extracted in a Soxhlet apparatus for 48 h with acetone to remove residues of the vulcanization ingredients. After drying in a vacuum oven until constant weight, they were extracted for 72 h with tetrahydrofuran to remove uncrosslinked polymer. S_i was calculated as the percentage of soluble polymer in the sample before extraction with tetrahydrofuran. S_f is the fraction of soluble polymer, obtained after devulcanization of the extracted samples. It is obtained in the same way as S_i, by a two-step extraction method, removing low-molecular weight products of the devulcanization reaction and residual devulcanization agent with acetone and debound polymer with tetrahydrofuran.

The elastically active network chain densities before and after devulcanization, v_i and v_f, were determined by equilibrium swelling for 72 h in decaline, using the Flory-Rehner equation for tetrafunctional crosslinks:[22]

$$v_e = -\frac{\ln(1-v_r) + v_r + \chi v_r^2}{V_s(v_r^{1/3} - \frac{1}{2}v_r)}$$

where v_e is the elastically active network chain density, v_r is the volume fraction of polymer in the swollen gel, V_s is the molar volume of the solvent, and χ is the interaction parameter for the solvent-polymer system. The polymer-solvent interaction parameter was taken from literature:[23] $0.121 + 0.278v_r$, where v_r is the volume fraction of the rubber in the swollen sample. The relative decrease in network chain density is calculated from the values of v_e before and after devulcanization, v_i and v_f, respectively.

Horikx[24] distinguished two ways of network degradation: random scission and crosslink scission. For both cases, relationships between S_f and $(1 - v_f/v_i)$ were derived. The equations used to calculate the data for random and crosslink scission are those derived by Horikx with a slight adjustment for the extraction of S_i before devulcanization:[25]

$$1 - \frac{v_f}{v_i} = 1 - \frac{\gamma_f\left(1 - \sqrt{S_f + S_i}\right)^2}{\gamma_i\left(1 - \sqrt{S_i}\right)^2}$$

for crosslink scission and

$$1 - \frac{v_f}{v_i} = 1 - \frac{\left(1 - \sqrt{S_f + S_i}\right)^2}{\left(1 - \sqrt{S_i}\right)^2}$$

for random scission.

The lines for crosslink and random scission were constructed by taking decreasing values for v_i and corresponding γ_f for each vulcanizate and calculating the corresponding values for $(1 - v_f/v_i)$ and S_f using the experimentally determined values for S_i and γ_i. In the case of crosslink scission, one also has to take the effect of entanglements on v_i, as derived from equilibrium swelling, into account.[25]

The distribution of mono-, di-, and polysulfidic crosslinks was determined with thiol-amine chemical probe reagents in combination with equilibrium swelling.[26,27] The reaction conditions were experimentally optimized for EPDM. All vulcanizates were preswollen for 72 h in toluene. For cleaving only polysulfidic crosslinks, 30 mL per gram vulcanizate of 0.4M 2-propanethiol and 1M piperidine in toluene and a reaction time of 2 h was used. For cleaving both di- and polysulfidic crosslinks, 30 mL per gram vulcanizate of 1M 1-dodecanethiol and 3M piperidine in toluene and a reaction time of 168 h were used.

RESULTS

The values for t_{90} for the peroxide cure of ENB-EPDM and HD-EPDM as derived from testing with the cure rheometer were 15 and 22 min, respectively. The values for t_{90} for sulfur vulcanization were 15, 20, and 25 min for ENB-EPDM, HD-EPDM, and DCPD-EPDM, respectively. The sulfur vulcanization rates of EPDM decrease in the order: ENB > HD > DCPD in agreement with literature.[5,15] For sulfur vulcanization of DCPD-EPDM, the torque keeps increasing over time ("marching modulus"), and a value of t_{90} cannot be accurately determined. Vulcanization for the latter was continued until the first derivative of the rheometer curve approached zero;

TABLE II
Sol Fractions, Network Chain Densities, and Crosslink Distribution of EPDM Vulcanizates

Vulcanizate	Sol fraction (%)	Crosslink density (10^{-4} mol/cm^3) (%)						
		Total crosslinks	Monosulfidic crosslinks		Disulfidic crosslinks		Polysulfidic crosslinks	
Peroxide								
ENB-EPDM	1 ± 0.1	3.09 ± 0.06						
HD-EPDM	7.92 ± 0.09	1.52 ± 0.07						
Sulfur								
ENB-EPDM	0.97 ± 0.05	3.1 ± 0.1	0.4 ± 0.1	12	1.5 ± 0.4	47	1.28 ± 0.08	41
DCPD-EPDM	5.1 ± 0.2	2.0 ± 0.1	0.86 ± 0.07	44	0.98 ± 0.09	50	0.118 ± 0.009	6
HD-EPDM	7 ± 1	1.85 ± 0.07	0.17 ± 0.07	9	0.16 ± 0.07	9	1.5 ± 0.2	82

t_{90} was taken relative to the torque at that time point.

The initial sol fractions, S_i, the initial network chain densities, ν_i, and the crosslink sulfur-ranks of the vulcanizates are summarized in Table II. These were the starting values for the devulcanization experiments. For peroxide crosslinking, the HD-EPDM provides a lower ν_i than ENB-EPDM, which is explained by the lower degree of substitution of the residual HD versus ENB unsaturation.[7] For sulfur vulcanization, HD-EPDM provides the lowest ν_i, whereas ENB-EPDM gives the highest state of cure in agreement with previous investigations.[5] The percentage of polysulfidic crosslinks is very high for the HD-EPDM sulfur vulcanizate. The DCPD-EPDM vulcanizate provides the highest percentage of monosulfidic crosslinks.

Devulcanization of peroxide-cured ENB-EPDM and HD-EPDM without and with the aid of DPDS devulcanization agent

The results of the devulcanization of peroxide-cured ENB-EPDM and HD-EPDM at 200 and 265°C in the absence of DPDS, that is, a simple thermal treatment,

are graphically depicted in Figure 2. The sol fractions after devulcanization, S_f, are plotted against (1 − ν_f/ν_i), where ν_f is the network chain density after the devulcanization step and (1 − ν_f/ν_i) the decrease in network chain density, relative to the network chain density before devulcanization. The lines drawn in Figure 2 represent the two extreme cases of crosslink scission and random scission, corresponding to the method developed by Horikx. Figure 2 shows that thermal devulcanization of peroxide-cured ENB-EPDM proceeds via random scission, whereas HD-EPDM appears to devulcanize by crosslink scission. This is somewhat surprising, because in both cases carbon–carbon bonds are broken. Because of the relatively high ν_i of ENB-EPDM peroxide vulcanizates, S_f is small, even though random scission generates more sol than crosslink scission.

A comparison of the (1 − ν_f/ν_i) values in Figure 2 shows that the final level of thermal devulcanization for HD-EPDM peroxide vulcanizates is somewhat higher than for ENB-EPDM peroxide vulcanizates, DCPD-EPDM peroxide vulcanizates were not studied because, as stated earlier, the crosslink density of such vulcanizates kept increasing during curing, as it does as well with aging,[28] which precludes the
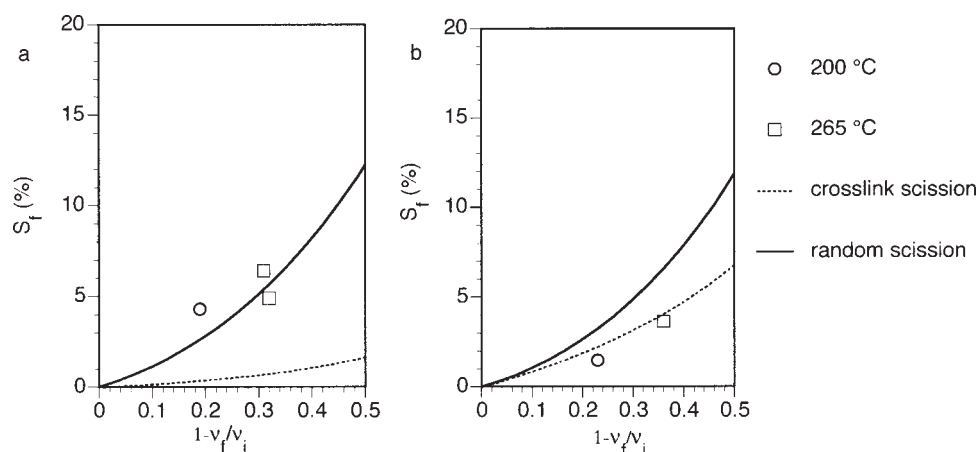

Figure 2 Rubber sol fraction versus relative decrease of network chain density for thermal devulcanization of peroxide vulcanizates: (a) ENB-EPDM and (b) HD-EPDM.
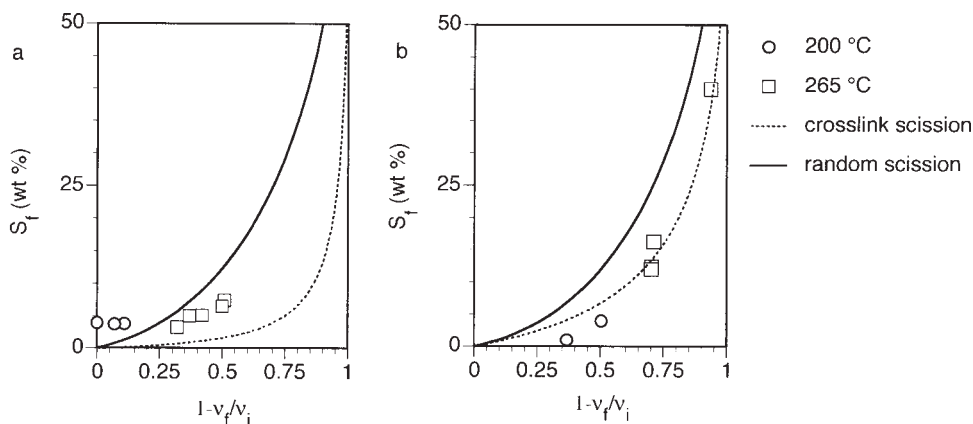
Figure 3 Rubber sol fraction versus relative decrease of network chain density for devulcanization of peroxide-cured EPDM with amounts of DPDS ranging (a) from 0.86–1.97 $\times$ 10^{-4} mol/cm^3 for ENB-EPDM and (b) from 0.95 to 1.96 $\times$ 10^{-4} mol/cm^3 for HD-EPDM.

possibility to devulcanize with thermal treatment only.

In Figure 3, the results of the peroxide devulcanization of ENB-EPDM and HD-EPDM in the presence of DPDS are graphically depicted according to the method developed by Horikx. Figure 3 shows that during devulcanization in the presence of DPDS, peroxide-cured ENB-EPDM still devulcanizes mainly by random scission and peroxide-cured HD-EPDM still reacts by crosslink scission, similar to purely thermal devulcanization in the absence of DPDS. In Figure 4, the network chain densities remaining after devulcanization for peroxide-cured ENB and HD-EPDM vulcanizates are plotted versus the concentration of DPDS. It shows that at 200°C, DPDS suppresses the devulcanization of ENB-EPDM peroxide vulcanizates, that is, higher v_f values are determined than for thermal devulcanization. Actually, no devulcanization is observed at all at 200°C and 1.75 $\times$ 10^{-4} mol/cm^3 DPDS. DPDS, however, does aid in the devulcanization of HD-EPDM peroxide vulcanizates at 200°C. At 265°C, DPDS is approximately equally effective in absolute terms in aiding the devulcanization of both ENB-EPDM and HD-EPDM peroxide vulcanizates. Peroxide-cured HD-EPDM turns out to be almost completely devulcanized at 265°C with a high concentration of DPDS. This is explained by a combination of the low value of v_i, compared to peroxide-cured ENB-EPDM and the susceptibility for devulcanization of peroxide-cured HD-EPDM, as already seen for devulcanization in the absence of DPDS.

Thermal devulcanization of sulfur vulcanizates

Figure 5 shows the differences between the sulfur-vulcanized EPDM with three different dienes during thermal devulcanization, that is, in the absence of

devulcanization agents. Little or no random scission takes place for ENB-EPDM sulfur vulcanizates at 200 and 265°C; crosslink scission predominantly occurs. For HD-EPDM, the decrease in network chain density is higher than for ENB-EPDM sulfur vulcanizates, as for peroxide cure. However, HD-EPDM sulfur vulcanizates do not fully devulcanize by crosslink scission, as was the case for the corresponding peroxide vulcanizates. The values of S_f are in between the two extreme cases of crosslink scission and random scission. There are two possible explanations: devulcanization of sulfur-vulcanized HD-EPDM proceeds via a combination of crosslink scission and random scission, or alternatively, main-chain scission occurs in the neighborhood of the crosslink sites, which was called "directed scission" by Horikx.[24]

During thermal devulcanization of DCPD-EPDM sulfur vulcanizates an increase in crosslink density was found at both temperatures instead of the
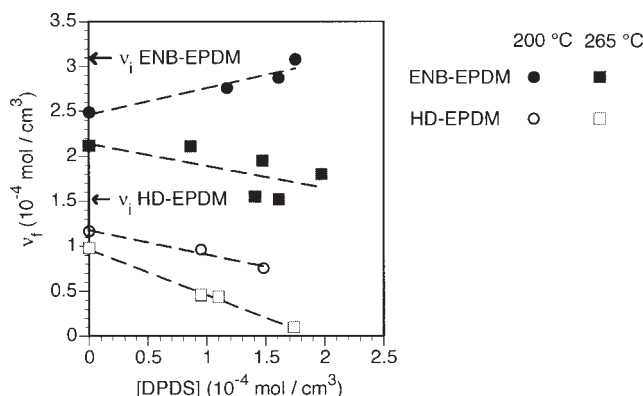

Figure 4 Network chain densities remaining after devulcanization versus concentration of DPDS for peroxide-cured ENB and HD-EPDM vulcanizates.
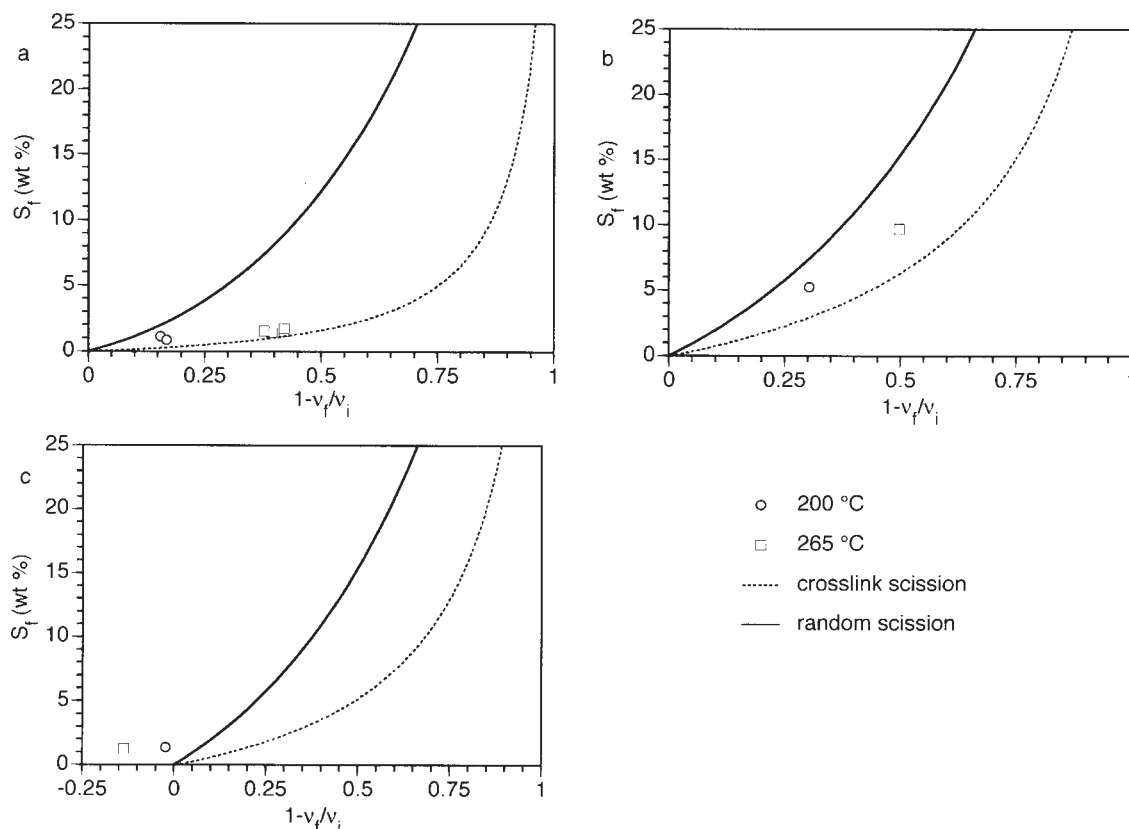
Figure 5 Rubber sol fraction versus relative decrease of network chain density for thermal devulcanization of EPDM sulfur vulcanizates: (a) ENB-EPDM, (b) HD-EPDM, and (c) DCPD-EPDM.

expected decrease, resulting in a negative value for $1 - v_f/v_i$ in Figure 5(c). This is probably related to the marching cure as observed in the rheometer experiments. Although the crosslink density increases, a very small amount of soluble product is still formed during devulcanization. This indicates that while new crosslinks are formed, some random scission occurs at the same time and small branched fragments are detached from the network. Overall, crosslinking prevails over scission during thermal treatment of sulfur-vulcanized DCPD-EPDM.

Devulcanization of sulfur vulcanizates in the presence of DPDS and HDA

The use of DPDS does not affect the relative contribution of crosslink versus random scission to the devulcanization, as can be seen in Figure 6. In the presence of DPDS, HD-EPDM sulfur vulcanizates devulcanize almost completely at a temperature as low as 200°C. As indicated by a $1 - v_f/v_i$ value of unity, at 265°C, complete devulcanization is achieved at a concentration of $\sim 2 \times 10^{-4}$ mol/cm^3 DPDS. Again, an increase in crosslink density is observed for sulfur-vulcanized DCPD-EPDM.

In Figures 7 and 8, the network chain densities for EPDM sulfur vulcanizates, devulcanized at 200 and

265°C, respectively, are plotted versus the concentration of DPDS. The figures show that in the presence of DPDS chemical devulcanization adds to thermal devulcanization for sulfur vulcanized ENB- and HD-EPDM. For HD-EPDM, the addition of small amounts of DPDS $\geq 10^{-5}$ mol/cm^3 leads to a completely devulcanized product. In contrast, DPDS does not significantly enhance the devulcanization of DCPD-EPDM sulfur vulcanizates, neither at 200°C nor at 265°C. At 265°C, the use of DPDS does lower the network chain density, but as a result of simultaneous crosslinking, the decrease in network chain density is still very limited. Only at higher concentrations of DPDS $\geq 10^{-4}$ mol/cm^3 some significant devulcanization is observed.

The effect of HDA on the devulcanization of the sulfur vulcanizates of HD-EPDM and ENB-EPDM at 265°C is shown in Figure 9. The devulcanization of HD-EPDM sulfur vulcanizates is only marginally improved by the addition of HDA. On the other hand, HDA has a beneficial effect on the devulcanization of ENB-EPDM, comparable to that of DPDS.

DISCUSSION

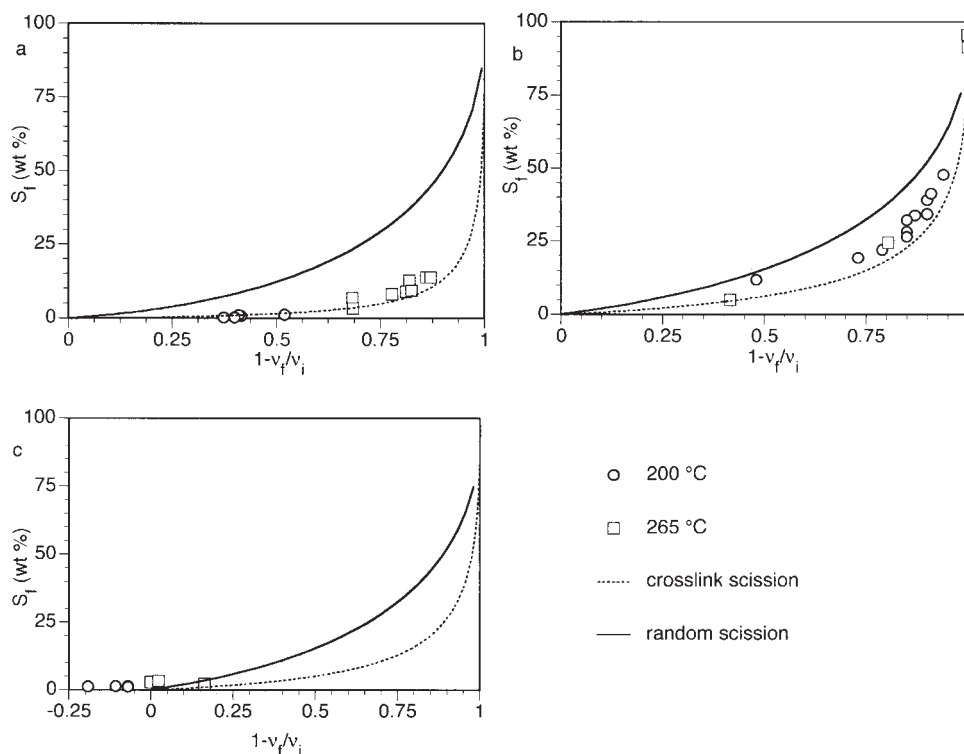The results of the various series of devulcanization experiments for crosslinked EPDM with different

Figure 6 Rubber sol fraction versus relative decrease of network chain density for EPDM sulfur vulcanizates devulcanized with amounts of DPDS ranging from $0–3 \times 10^{-4}$ mol/cm^3: (a) ENB-EPDM, (b) HD-EPDM, and (c) DCPD-EPDM.

diene monomers, as presented in Figures 2, 3, 5, and 6 show that the type of third monomer built into EPDM has a strong influence on whether crosslink scission or main-chain scission takes place during devulcanization. These results will be discussed in terms of the structure of the rubber network, crosslinked with either peroxide or sulfur.

Peroxide vulcanizates

Our results show that the third monomer determines whether random scission or crosslink scission is favored during devulcanization of peroxide vulcanizates, or even additional crosslinking occurs (DCPD-EPDM). Crosslink scission must be the result of the reaction of crosslinks located at the site of the residual double bond of the third monomer,[10,29] obtained with peroxide vulcanization.

During devulcanization of peroxide-vulcanized ENB-EPDM random scission seems to dominate. After crosslinking via the addition type reaction, the whole ENB moiety can be considered as an integral part of the crosslink. As a consequence, random scission is relatively more preferred, because scission of
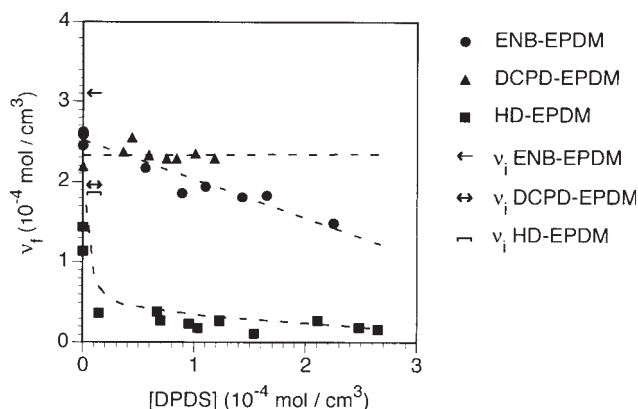

Figure 7 Network chain densities for EPDM sulfur vulcanizates devulcanized at 200°C versus concentration of DPDS.
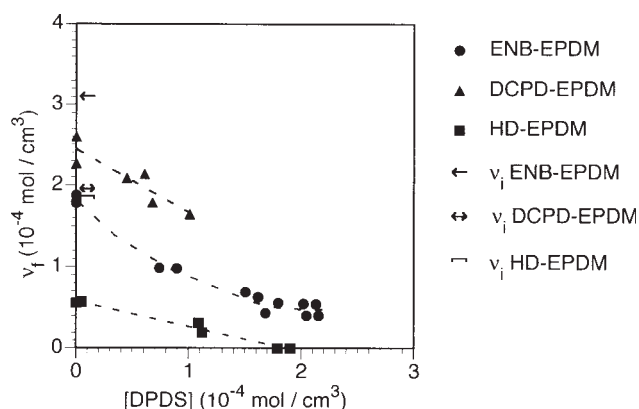

Figure 8 Network chain densities versus concentration of DPDS for EPDM sulfur vulcanizates devulcanized at 265°C.
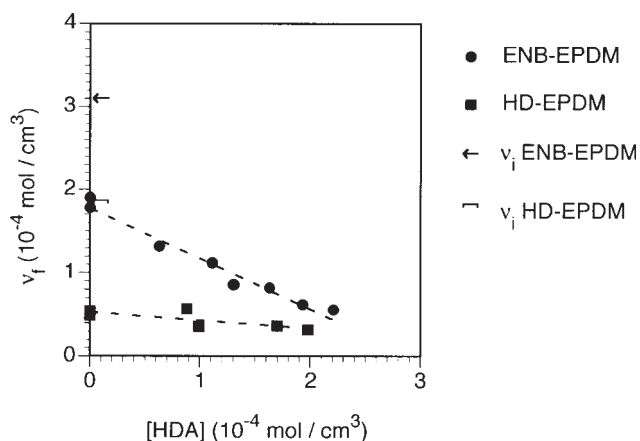
Figure 9 Network chain densities versus concentration of HDA for HD-EPDM and ENB-EPDM sulfur vulcanizates devulcanized at 265°C.

a bond in the ENB-ring does not lead to crosslink scission. Some crosslink scission (up to 25%) was observed when peroxide vulcanizates of ENB-EPDM were exposed to ozone, an agent that selectively cleaves the double bond.[10]

HD-EPDM peroxide vulcanizates devulcanize by crosslink scission. Crosslink scission has also been observed in peroxide vulcanizates of HD-EPDM when exposed to ozone, as for ENB-EPDM, with 30% of the crosslinks reacting.[10] This is surprising because HD is hardly reactive during peroxide cure. It seems that the aliphatic main chain of HD-EPDM vulcanizates is more stable during devulcanization than the aliphatic crosslinks involving the HD unit.

Upon heating in the presence of alkanes, DPDS reacts with alkane decomposition products, as was demonstrated by the formation of alkylphenylsulfides and phenylthiol.[30] So, when random scission occurs, DPDS supposedly acts as a radical scavenger. Crosslink scission of peroxide-cured HD-EPDM depends on the DPDS concentration, with DPDS preventing recombination of radicals to crosslinks again.

Devulcanization of peroxide-cured EPDM in the presence of DPDS enhances devulcanization at 265°C for both types of EPDM, but at 200°C it only does so for HD-EPDM. A possible explanation is that at 200°C some crosslinking is taking place for ENB-EPDM, as a result of sulfur liberated from the DPDS under the conditions used as seen by the formation of diphenylmonosulfide.[30]
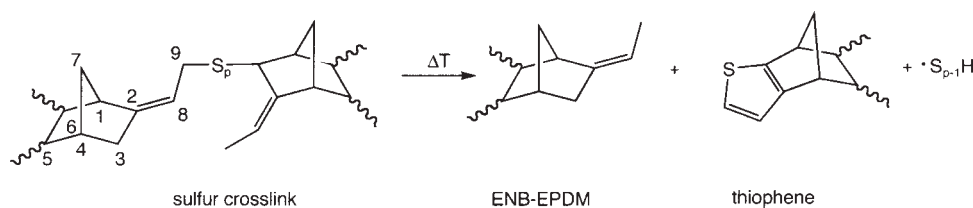
Sulfur vulcanizates

In EPDM sulfur vulcanizates not only the crosslink density, but also the distribution of the length of the sulfur-crosslink sulfur ranks varies with the termonomer built into the polymer. HD-EPDM sulfur vul-

canizates contain primarily polysulfidic crosslinks, whereas DCPD-EPDM tends to mono- and disulfidic crosslinks. Lyalin also found that sulfur vulcanizates of HD-EPDM had a much larger amount of polysulfidic crosslinks, compared to ENB- and DCPD terpolymers.[16] Deuri and Bhowmick found that the amount of polysulfidic crosslinks was the highest in ENB-EPDM and lower in DCPD and HD-EPDM.[31] In yet another study by Baranwal, both t_{90} and the monosulfidic crosslink density was highest in HD-EPDM and lower in ENB and DCPD-EPDM, while the overall crosslink density was comparable.[15] In summary, depending on the diene and vulcanization conditions employed, quite large differences in crosslink sulfur ranks can be obtained. It is practically impossible to obtain comparable crosslink densities and similar crosslink sulfur rank distributions for all three EPDMs by varying the curative package and vulcanization conditions. Rather, the sulfur vulcanizates and their corresponding sulfur ranks were considered representative for the respective EPDM types. On the one hand, it is well known that the dissociation energy of polysulfidic crosslinks is much lower than for disulfidic and monosulfidic crosslinks. On the other hand, it should be noted that sulfide interchange reactions and desulfurization will result in fast conversion of the original sulfur crosslinks at the high temperatures of devulcanization. Probably, the sulfur rank of the original vulcanizates is not relevant during devulcanization.

Reversion has been extensively studied for polydiene rubbers, especially NR.[32–34] For reversion of sulfur-vulcanized NR, a variety of saturated cyclic sulfides[35] has been demonstrated in combination with conjugated dienes and trienes.[36] Solid-state ^{13}C NMR of ^{13}C-labeled ENB-EPDM, which was sulfur vulcanized for prolonged times (120 min at 150°C or for 30 min. at 180°C) has shown that decrosslinking occurs and a cyclic thiophene species (Scheme 3) is formed.[37] This suggests that the scission of the C—S bond of one alkenylsulfide unit of the sulfur crosslink occurs and that a new C—S bond is formed at the other allylic position of the second alkenylsulfide unit.

Baranwal et al.[15] found that during oxidative aging at 177°C, the majority of the sulfur crosslinks are converted into monosulfidic or carbon–carbon crosslinks in HD-EPDM and ENB-EPDM vulcanizates, while the overall crosslink density is hardly decreased.[15] In a study by Deuri et al., desulfuration of polysulfidic crosslinks in ENB-, DCPD-, and HD-EPDM vulcanizates took place during aging under nitrogen atmosphere.[31] Lyalin found that vulcanizates of HD-EPDM showed reversion during aging for 2 h at 183°C, while vulcanizates of ENB- and DCPD-EDPM did not.[16] Baranwal et al. found that after aging in air at 288°C for 2 h, both ENB- and

Scheme 3 Devulcanization of sulfur-vulcanized ENB-EPDM.

HD-EPDM showed a large decrease in crosslink density, while the crosslink density of DCPD-EPDM increased,[15] even though HD-EPDM had the highest density of monosulfidic crosslinks to start with in their case. At 288°C, all the crosslinks that remained in ENB-, DCPD-, and HD-EPDM vulcanizates were monosulfidic or carbon–carbon of nature. In ENB-EPDM, some monosulfidic and carbon–carbon crosslinks are formed during devulcanization, as published in our earlier paper on this subject.[4]

Figure 5 shows that ENB-EPDM sulfur vulcanizates react mainly by crosslink scission. The reaction scheme presented in Scheme 3 explains the high reactivity of sulfur-vulcanized ENB-EPDM for devulcanization by crosslink scission. In case the sulfur crosslink is attached at the allylic C9 position of ENB, the S-atom is folded more or less toward the other allylic position at C3 because of the steric conformation of the inflexible, bicyclic norbornane moiety. The same goes for folding of the S-bridge to the C9 position if it is attached at the C3exo position.

HD-EPDM sulfur vulcanizates appear to devulcanize by a combination of crosslink and random scission. This is quite remarkable, because peroxide vulcanizates of HD-EPDM devulcanize by crosslink scission only and the thermal stability of sulfur crosslinks is lower than that of carbon–carbon bonds in the main chain. Therefore, it is not likely that random scissions contribute to the higher fraction of S_f, for these devulcanizates. For sulfur-vulcanized HD-EPDM, crosslink scission by folding into a ring structure, like for ENB-EPDM, is less straightforward, because the butenyl side chain attached to the EPM main chain will prefer trans C—C configurations, and the allylic positions will not be folded toward each other. Instead of assuming that HD-EPDM sulfur vulcanizates devulcanize by a combination of crosslink and random scission, it is more reasonable to assume that main-chain scission in the neighborhood of the crosslink sites takes place. In fact, this corresponds to "directed scission" as defined by Horikx.[24] In natural rubber, disappearance of polysulfidic crosslinks is often accompanied by migration of the double bond and the formation of conjugated structures.[36] In HD-EPDM, sulfur vulcanizates the majority of the crosslinks is of the polysulfidic type (Table II). During devulcanization, desulfuration of the polysulfidic crosslinks may be accompanied by migration of the double bond toward the polymer backbone. This results in the activation of the hydrogen in the β-position in the backbone for H-abstraction, which eventually may lead to scission of the main chain. In the ENB-EPDM, the double bond cannot migrate toward the main chain.

In DCPD–EPDM, the allylic methylene carbon is part of a strained ring. For sulfur-vulcanized DCPD-EPDM devulcanization towards the cyclic sulfide cannot occur and migration of the double bond towards the main chain as for HD-EPDM is not possible either. This explains the low susceptability of DCPD-EPDM for devulcanization. Furthermore, the DCPD residue has a tendency toward formation of new carbon–carbon crosslinks, as indicated by the increase of the crosslink density for peroxide-cured DCPD-EPDM during aging, as demonstrated by Landi and Easterbrook.[28] The increase was higher, the higher the DCPD content of the EPDM. This explains the increasing crosslink density of DCPD-EPDM during thermal devulcanization.

Our results show that the effectivity of DPDS in aiding the devulcanization of sulfur vulcanizates depends on the relative decrease in crosslink density that is already obtained in the case of purely thermal devulcanization. DPDS is only active when thermal devulcanization already results in crosslink or main-chain scission. The addition of DPDS does not change the way in which devulcanization takes place—by crosslink scission, random scission, or "directed scission" in the neighborhood of the crosslinks. For DCPD-EPDM, the addition of DPDS is therefore not effective. At 265°C, DPDS does cause some scission in DCPD-EPDM, even though crosslinking also proceeds. For ENB-EPDM, there is a concentration-dependent effect and for HD-EPDM there is a significant decrease in crosslink density with DPDS added. During devulcanization of ENB-EPDM, sulfur vulcanizates in the presence of DPDS, reaction products of DPDS with alkane decomposition products have been observed,[4] which shows DPDS reacts with broken chains preventing chain recombination. In the same way, it probably scavenges broken crosslinks.

Whereas HD-EPDM sulfur vulcanizates can be fully devulcanized in the presence of DPDS, they hardly respond to the addition of HDA. In contrast, ENB-EPDM sulfur vulcanizates provide the same response to equimolar levels of DPDS and of HDA.

So, the mode of action of HDA on sulfur vulcanizates is different from that of DPDS. Disulfides react by radical mechanisms[30,38,39] involving chain scission. Amines react by a nucleophilic mechanism at lower temperature[40]; at higher temperatures radical mechanisms involving hydrogen abstraction from the amines can also play a role.[41,42] This also results in large differences in devulcanization of natural rubber vulcanizates and latex articles.[43]

CONCLUSIONS

The behavior of EPDM vulcanizates during devulcanization strongly depends on the diene type built into the polymer. The diene monomer determines the efficiency, the occurrence of further crosslinking and also the mechanism via which devulcanization occurs: random scission, crosslink scission, or chain scission in the neighborhood of the crosslink sites: ''directed scission.'' The addition of devulcanization chemicals is only effective when thermal devulcanization does already occur, that is, they aid in obtaining higher devulcanization yields which is the case for ENB- and HD-EPDM.

Peroxide-cured ENB-EPDM devulcanizes mainly by random scission, whereas sulfur vulcanizates of ENB-EPDM devulcanize mostly by crosslink scission. However, devulcanization is far from complete. Both DPDS and HDA aid in the devulcanization.

HD-EPDM sulfur vulcanizates show substantial thermal devulcanization already in the absence of devulcanization aids probably via ''directed scission.'' DPDS is effective as devulcanization aid, while HDA apparently is not. HD-peroxide vulcanizates, however, devulcanize by crosslink scission. With sufficient DPDS, HD-EPDM peroxide vulcanizates can be devulcanized virtually without any chain scission, and therefore the highest molecular weight fragments are obtained compared to the other vulcanizate systems, which is advantageous for future renewed use.

Devulcanization of DCPD-EDPM peroxide and sulfur vulcanizates is practically impossible. The residual DCPD unsaturation causes further crosslinking during devulcanization. Only by extensive random scission, at temperatures close to the decomposition temperature of EPDM, devulcanization of DCPD-EPDM vulcanizates may be achieved.

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