Influence of Zinc Oxide during Different Stages of Sulfur Vulcanization. Elucidated by Model Compound Studies

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ABSTRACT: The addition of zinc oxide (ZnO) as an activator for the sulfur vulcanization of rubbers enhances the vulcanization efficiency and vulcanizate properties and reduces the vulcanization time. The first part of this article deals with the reduction and optimization of the amount of ZnO. Two different rubbers, solution-styrene-butadiene rubber and ethylene–propylene–diene rubber, have been selected for this study. The results demonstrate that the curing and physical properties can be retained when the level of ZnO (Red Seal) is reduced to 1 or 2 phr, respectively. Of particular interest is nano-ZnO, characterized by a nanoscale particle distribution. The cure characteristics indicate that with nano-ZnO, a reduction of zinc by a factor of 10 can be obtained. In the second part, model compound vulcanization is introduced to investigate the effects of ZnO during the different stages of vulcanization. Experiments are described with two models, squalene and 2,3-dimethyl-2-butene, both with benzothiazolesulfenamide-accelerated vulcanization systems. The results demonstrate the influence of ZnO during the different stages of the vulcanization. With ZnO present, a marked decrease can be observed in the sulfur concentration during an early stage of vulcanization, along with a slight delay in the disappearance of the crosslink precursor. The crosslinked product distribution is influenced as well. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1388–1404, 2005

Key words: nanoparticles; rubber; vulcanization; zinc oxide

INTRODUCTION

Zinc oxide (ZnO) is added to rubber compounds to activate sulfur vulcanization and thereby reduce the vulcanization time. Besides its effect on the curing process, ZnO has many beneficial effects on the physical properties of rubber.[1] Furthermore, ZnO assists in the processing of uncured rubber.[2] For the protection of the environment and because of upcoming legislation regarding the use and application of ZnO and zinc-containing compounds, however, it is considered desirable to study the possibilities of reducing the ZnO content in rubber products.

The release of zinc into the environment from rubber occurs during the production, disposal, and recycling of rubber products (e.g., through leaching in landfill sites). It also occurs during service conditions (e.g., through the wear of tires or runoff from roofing foils). It is desirable to keep the ZnO content as low as possible to obtain not only a lower pollution impact but also an advantage from an economic point of view.

Another reason to search for ways of reducing the zinc content in rubber vulcanizates is associated with a problem related to mold fouling. Mold fouling causes a great number of problems and must be removed from the mold surface at regular intervals to obtain defect-free rubber articles. It has been reported that zinc sulfide (ZnS) dictates the process of mold fouling.[3] ZnS is considered to be a product of vulcanization reactions. In some rubbers such as natural rubber (NR) and ethylene–propylene–diene rubber (EPDM), there is evidence that a considerable amount of ZnO is consumed and transformed into ZnS.[3–5] Therefore, to reduce mold fouling, it is strongly desirable to reduce ZnO usage in rubber.

The physical and chemical properties of ZnO are largely determined by the manufacturing method. The ZnO used nowadays in rubber compounds is produced by either the direct American process or the indirect French process. The American process was developed by the treatment of oxidized ores or sulfide concentrates. In the French process, zinc metal is vaporized and then oxidized in a combustion zone. A third method of production involves the precipitation of zinc carbonate or hydroxide, which is then dried and calcined to remove water and carbon dioxide. This method, the so-called wet process, produces more fine particles of ZnO. More recently, a method was introduced by Nanophase Technologies Corp.,

which patented a physical vapor synthesis process for the production of nanoparticle-size ZnO.[6] These particles are nonporous and free of contamination. Most grades of ZnO contain more than 99% ZnO, and there can be more than 99.99% ZnO in the purest grades of ZnO from the French process.

ZnO is a dense material that tends to compact and disperse with difficulty. Therefore, it is distributed in the form of crystal particles in rubber mixes.[7] Nieuwenhuizen[8] in his thesis proposed a mechanism in which the ZnO surface functions both as a reactant and as a catalytic reaction template, activating and bringing together reactants. Molecules of accelerators, sulfur, and fatty acids diffuse through the rubber matrix and are adsorbed onto ZnO with the formation of intermediate complexes. An important parameter in this mechanism is a uniform dispersion of inorganic ZnO throughout the organic polymer matrix. For optimum dispersion, it is usually added early in the mixing stage, and some grades of ZnO are surface-modified, usually by the deposition of 0.2–0.4% stearic acid, propionic acid, or light oil, coatings of which facilitate mixing.

The efficiency of ZnO during vulcanization can be enhanced by the maximization of the contact between the ZnO particles and the accelerators in the rubber formulation. This contact is dependent on the size of the particles, their shape, and the specific surface area. The average particle size of conventional ZnO (Red Seal) is usually 0.3–1.0 μm, and its specific surface area is correspondingly 4–6 m^2/g. In so-called highly active ZnO, the mean particle size is reduced, and the specific area is increased; this results in easier and better dispersion and higher reactivity.[9] Active ZnO is commonly prepared with an average particle size of 0.1–0.4 μm and with a substantially higher Brunauer–Emmett–Teller specific surface of 30–50 m^2/g. The high surface area is due to the small particle size, as ZnO has little porosity. The higher activity of this active ZnO is probably due to the increased availability of Zn^{2+} ions at the surface in comparison with that of conventional particles.

One of the latest and probably most promising developments in this field is nano-ZnO.[10,11] It presents high activity because of its ultrasmall size and large surface area. Nano-ZnO has an average particle size of approximately 20–40 nm and a specific surface area of 15–45 m^2/g; depending on the preparation method, higher specific surface areas can be obtained, even up to 70–110 m^2/g.[6,12] The specific surface area of nano-ZnO is only slightly higher than that of active ZnO and does not correlate directly with the decrease in the average particle size, which can be due to several factors. The preparation conditions notoriously determine the final properties, such as the chemical activity and morphology, of nano-ZnO. Nanometer ZnO powders are commonly produced with a high-temperature furnace that pyro-lyzes the precursor powders. The particle size, however, is larger than that prepared by plasma pyrolysis technology, and the particles agglomerate easily; this might lead to a lower specific surface area. With the plasma pyrolysis technique, the agglomeration of the particles is significantly reduced. Furthermore, the apparent (bulk) density of ZnO (Red Seal) and active ZnO is about 0.4–0.6 g/cm^3, whereas for nano-ZnO, apparent density values of approximately 0.2 g/cm^3 have been reported. The lower apparent density implies a more voluminous material and thus a relatively lower specific surface area. In addition, the morphology of the ZnO powders varies considerably, from being predominantly nearly spherical for the conventional preparation methods to being elliptical or even needle-shaped for the more special nano-ZnO, and this influences the specific surface area.

It has been reported that the equivalent replacement of conventional ZnO (Red Seal) by nano-ZnO leads to an improvement in the properties of the rubber compound, especially the abrasion resistance, H-pullout force (a measure for rubber-cord adhesion), and tear strength.[10] This might be due to the fact that a higher specific surface area and, therefore, a greater amount of Zn are accessible in comparison with conventional ZnO. For this reason, nano-ZnO is believed to offer possibilities for greatly reducing the ZnO content in rubber compounds.

Effects of ZnO in accelerated sulfur vulcanization

The nature of sulfur vulcanization activation and acceleration has been the subject of many studies, and several theories on the role of ZnO have been postulated. The complexity of the vulcanization process has given rise to many uncertainties and contradictions in the literature about the influence of ZnO during the different stages of the process and its exact mechanisms. It is evident that to judiciously reduce ZnO levels in rubber compounding, additional insight into the mechanistic details should be obtained.

Accelerated sulfur vulcanization is generally accepted to take the course shown in Figure 1.[13,15,16] As a first step in the vulcanization process, accelerators and activators form an active accelerator complex (I), which subsequently interacts with sulfur to produce active sulfurating species (II). The actual composition depends on the accelerator system used. It has been suggested in many studies that Zn^{2+} ions play an important role in the formation of this active sulfurating agent. This reactive species reacts with allylic hydrogen atoms of rubber unsaturations to form a rubber-bound intermediate or preferentially designated as crosslink precursor (III). It is generally assumed that there is no major role for ZnO in the formation of crosslink precursors and that it first must be transformed into a zinc–accelerator complex to participate. Layer[17] suggested a mechanism for precursor forma-

accelerator + ZnO

Zinc-accelerator complex   (I)

S_8

Acc-S_x-Zn-S_x-Acc or polysulphidic accelerator   (II)

rubber

rubber-S_y-Acc   (III)

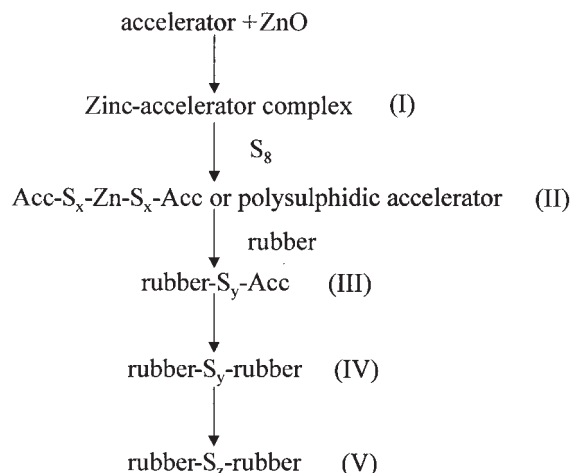rubber-S_y-rubber   (IV)

rubber-S_z-rubber   (V)

Figure 1   General scheme for sulfur vulcanization.[13,14]

tion via the interaction of an olefin, ZnO, and the polysulfidic accelerator tetramethylthiuram polysulfide (TMTP; Fig. 2).

It is rather unlikely that three molecules at the same time engage in one transition state, but the reaction may take place on the surface of ZnO crystals.[8] Geyser and McGill[18] indeed observed an acceleration of precursor formation in the presence of ZnO when tetramethylthiuram disulfide (TMTD), sulfur, and a model olefin were heated. It might take place via a weakening of the S—S bond in the polysulfidic accelerator, because of coordination to the ZnO surface.

Polysulfidic crosslinks (IV) are formed through the reaction of these intermediates with another intermediate moiety or through the reaction with polymer chains. Various mechanisms have been proposed for the conversion of crosslink precursors into crosslinks. Basically, these reactions are catalyzed by zinc–accelerator complexes, although they can also occur in the absence of ZnO, albeit at significantly lower reaction rates. The initial crosslinks may eventually desulfurate to form shorter crosslinks (V) or degrade to cyclic sulfides. It has also been reported that in this stage of the vulcanization process zinc ions play a role.[19] The shortening of the polysulfidic crosslinks and isoallylic transformation reactions are catalyzed by a zinc–ac-

celerator complex, such as zinc/2-mercaptobenzothiazole (MBT). From this discussion, it is clear that the role of ZnO in sulfur vulcanization is still a subject of controversy. To nail down all the hypotheses, we applied model compound vulcanization (MCV).

MCV

MCV is widely used to gain mechanistic insight into rubber vulcanization because of its alleged good agreement with real rubber systems and the possibility of using conventional analytical techniques. It remains a very useful method because, despite recent developments in the field of analytical techniques, rubbers are difficult to analyze with standard analytical and spectroscopic techniques. The model compound should be as much as possible a representative for the reactive unit of the polymer. In particular, its chemical behavior should be similar to the behavior of the reactive unit of the polymer. Other factors, such as the presence of additional functional groups, the position and configuration of the double bond, and the occurrence of double bonds present in the model should be considered as well. An elementary disadvantage of these low-molecular-weight compounds is the high concentration of end groups. The reactivity of these end groups is considerably different from that of the methylene (—CH_2—) and methine (—CH—) groups, which constitute the majority of the reactive groups in a polymer. Other differences not to be neglected are the solubility of the chemicals in rubbers and model systems and the loss of volatiles from rubbers and open or closed model experiments.

Furthermore, the choice of a certain model compound should be determined by the purpose of the experiments. Squalene is the most used of the polyfunctional compounds as a model for NR because of its similarity to the real rubber structure. Polyfunctional models display a reactivity more similar to that of rubbers because of the presence of more than one double bond and relatively fewer end groups. These models are very well suited for investigating the fate of reactants. An investigation of crosslinks and main-chain modifications, however, is very difficult and
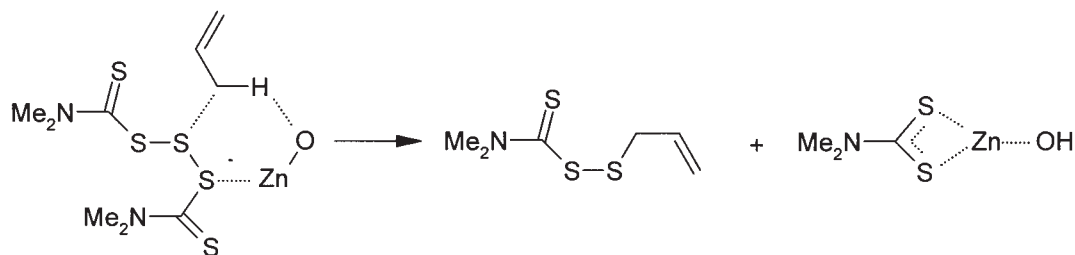
Figure 2   Precursor formation via the interaction of an olefin, ZnO, and TMTP as suggested by Layer.[17]

TABLE I
Types of ZnO Investigated

Type	Specific surface area (m^2/g)	Average particle size (μm)	Supplier
ZnO (Red Seal)	3–5	0.3–1.0	Grillo GmbH
ZnO (pure grade)	4–6	0.3–1.0	Merck B.V.
Active ZnO	30–50	0.1–0.4	Silox Société Anonyme
Nano ZnO	15–45	0.02–0.04	Degussa AG

requires elaborate separation and analytical procedures. Therefore, despite its simplicity, the monofunctional model 2,3-dimethyl-2-butene (TME) is a good choice for investigating crosslinks and product distribution. The model contains only one type of allylic position, and after vulcanization, hardly any isomerization products are obtained. High-temperature techniques, such as gas chromatography, should be avoided for analysis because of their profound effect on polysulfidic organic compounds. The conditions cause isomerization and degradation of disulfidic and polysulfidic products and possibly even of monosulfides. High-performance liquid chromatography (HPLC) separation at room temperature in combination with UV detection has been applied successfully in MCV as an analysis technique.[20]

The first part of this article describes the possibilities of optimizing ZnO by reducing the amount of ZnO and by incorporating the zinc in a more chemically active form. The effects of different amounts of standard ZnO (Red Seal), special ZnO's, and one of the latest developments in this particular area, nano-ZnO, on the cure and physical properties of solution-styrene-butadiene rubber (s-SBR) and EPDM rubber compounds have been investigated.

In the second part, the influence of ZnO as an activator on the different stages of the vulcanization process is explored. This section is divided into three parts: first, the influence of ZnO in an *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS) accelerated vulcanization system with squalene as a model olefin is studied; second, a more detailed study is described about the influence of ZnO in an *N-tert*-butylbenzothiazole-2-sulfenamide (TBBS) accelerated sulfur vulcanization with TME as a model compound, comprising an analysis of the reaction products as a function of time as well; and third, the results are compared with the real rubber results described previously to find explanations for the effects of ZnO, based on the insights obtained with the mechanistic studies.

EXPERIMENTAL

Materials

A solution butadiene–styrene rubber (Buna VSL 2525-0M) was obtained from Bayer GmbH (Germany).

Buna VSL 2525-0M contains 25 wt % 1,2-vinyl-butadiene and 25 wt % styrene; it has a Mooney viscosity [ML (1+4) at 100°C] of 54. Ethylidene norbornene (ENB) containing EPDM rubber (Keltan 4802), was obtained from DSM Elastomers B.V. (Vsittard, The Netherlands). Keltan 4802 contains 52 wt % ethylene units and 4.3 wt % ENB; it has a relatively narrow molecular weight distribution and a typical Mooney viscosity [ML (1+4) at 125°C] of 77. As a filler, carbon black (N-375 HAF, N-550 FEF, and N-762 SRF, Cabot B.V.) were used. An aromatic oil (Enerflex 75) was obtained from BP Oil Europe, paraffinic oil (Sunpar 2280) was obtained from Sun Petroleum Products Co., and stearic acid was obtained from J.T. Baker. Sulfur (J.T. Baker), TBBS (Santocure, Flexsys B.V.), MBT (Perkacit, Flexsys B.V.), and TMTD (Perkacit, Flexsys B.V.) were commercial grades and were used as such. The various types of ZnO's are given in Table I. The materials used in the model compound experiments are listed in Table II.

Rubber mixing

s-SBR and EPDM master batches were prepared in an internal mixer (~50 kg) to obtain homogeneous mixtures and to minimize the influence of mixing conditions. The vulcanization systems including the various ZnO's investigated were added in a separate operation on a two-roll mill at 50°C. The compounds were sheeted off at a thickness of approximately 2 mm, which was convenient for the subsequent preparation of test specimens. The compositions of the s-SBR and EPDM compounds with different levels of ZnO (Red

TABLE II
Materials Used for MCV

Material	Source
Squalene	Merck B.V.
TME	Aldrich
CBS	Flexsys B.V.
TBBS	Flexsys B.V.
Sulfur	Merck B.V.
ZnO	Merck B.V.
Stearic acid	Merck B.V.

TABLE III
Compositions of the s-SBR Compounds (phr) with Different Levels of ZnO (Red Seal)

	S1	S2	S3	S4	S5	S6	S7	S8	S9
s-SBR (Buna VSL 2525)	100	100	100	100	100	100	100	100	100
Carbon black (N375 HAF)	50	50	50	50	50	50	50	50	50
Aromatic oil (Enerflex 75)	5	5	5	5	5	5	5	5	5
Stearic acid	—	2	2	2	2	2	2	2	2
ZnO (Red Seal)	—	—	0.3	0.5	1	2	3	4	5
Accelerator (TBBS)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75

Seal) are given in Tables III and IV, respectively. The compounds with nano-ZnO are described in Table V.

Curing

The cure characteristics of the different compounds were measured at 160°C with an RPA2000 rubber process analyzer (Alpha Technologies, Swindon, UK), a type of moving-die rheometer. The optimal vulcanization time (t_{90}) and scorch time (t_{02}) of the compounds were determined. The compounds were cured in a Wickert (Landau, Germany) WLP 1600/5*4/3 laboratory press at 160°C and 100 bar according to t_{90} for the specific compounds.

Characterization

Tensile tests were carried out on dumbbell-shaped specimens (type 2) according to ISO 37. Young's modulus was determined from the initial slope of the stress–strain curve (0.1–0.25% strain) at a crosshead speed of 50 mm/min. The aging of the test specimens was carried out in a ventilated oven in the presence of air at 100°C for 3 days according to ISO 188. The tear strength was measured with trouser-shaped specimens according to ISO 34. Compression set tests were performed at 23 and 100°C for 72 h according to DIN 53517. The hardness of the samples was measured with a Zwick Shore A hardness meter according to DIN 53505. The fatigue to failure of the s-SBR compounds was measured with a Monsanto fatigue tester.

The heat buildup was determined with a Goodrich flexometer (load = 11 kg, stroke = 0.445 cm, starting temperature = 100°C, running time = 2 h) according to ASTM D 623.

The swelling measurements were performed to obtain information about the crosslink density. The unextracted filled s-SBR samples were swollen until a constant weight in toluene at room temperature. The EPDM samples were swollen in decahydronaphthalene at room temperature as well. The crosslink density was calculated according to the Flory–Rehner equation[21,22] Although this equation as such is only valid for nonfilled systems, the data obtained with these measurements do give an indication of the relative crosslink densities. The Flory–Huggins parameter (χ) for s-SBR/toluene networks was taken from the literature (0.21).[23] For swollen EPDM–decahydronaphthalene networks, the χ parameter was calculated as $\chi = 0.121 + 0.278v_2$, as reported by Dikland,[24] where v_2 is the polymer network volume fraction at equilibrium swelling.

MCV

The MCV experiments were carried out in a glass ampule. The reaction mixture was weighed into this ampule. To minimize the influence of oxygen in the reactions, the ampule was fluxed with nitrogen and sealed off. The reaction was performed in a preheated thermostatic oil bath at 140°C for a fixed time. A magnetic stirrer was added to the mixture to provide

TABLE IV
Compositions of the EPDM Compounds (phr) with Different Levels of ZnO (Red Seal)

	E1	E2	E3	E4	E5	E6	E7
EPDM (Keltan 4802)	100	100	100	100	100	100	100
Carbon black (N550 FEF)	70	70	70	70	70	70	70
Carbon black (N762 SRF)	40	40	40	40	40	40	40
Paraffinic oil (Sunpar 2280)	70	70	70	70	70	70	70
Stearic acid	—	1	1	1	1	1	1
ZnO (Red Seal)	—	—	1	2	3	5	10
Accelerator (TMTD)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Second accelerator (MBT)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

TABLE V
Compositions of the s-SBR Compounds (phr) with Different Levels of Nano-ZnO

	S2	S7	S10	S11	S12	S13
s-SBR (Buna VSL 2525)	100	100	100	100	100	100
Carbon black (N375 HAF)	50	50	50	50	50	50
Aromatic oil (Enerflex 75)	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
ZnO (Red Seal)	—	3	—	—	—	—
Nano-ZnO	—	—	0.05	0.1	0.2	0.3
Accelerator (TBBS)	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75

adequate stirring during the reaction. After a definite period of time, the reaction was arrested by the ampule being taken out of the oil bath and immersed in liquid nitrogen. After cooling, the ampule was covered with aluminum foil to avoid a UV influence and was stored in a refrigerator. The compositions of the model compound samples are listed in Table VI. The experiments were divided into two parts: experiments with squalene as a model compound and CBS as an accelerator and experiments with TME as a model compound and TBBS as an accelerator.

The squalene model systems were vulcanized with CBS as an accelerator for comparison with the results obtained by Borros and Agullo.[25] For the TME system, TBBS was chosen in slightly different amounts, which were comparable to those of real rubber systems, particularly s-SBR. To examine the influence of ZnO during the many stages of vulcanization, samples with and without ZnO were prepared.

Analysis of the reaction products

A small portion of the filtered sample (ca. 0.03 g) was weighed and dissolved in 2.5 mL of acetonitrile, which contained an internal standard: dibutyldisulfide. The response factors for all the initial components in reference to the internal standard were measured with HPLC at a wavelength of 254 nm. The internal standard was added after the vulcanization as an extra component for quantitative analysis. Before injection in HPLC, the sample was filtered twice over a 45-μm porous filter. About 20 μL of this diluted sample was injected onto the HPLC column for analysis according to the conditions described in Table VII. The areas of the different peaks in the chromatogram were determined and converted into concentrations via the measured response factors for the many components. Reaction conversions as a function of the reaction time were calculated by the division of the initial concentration of the component by the starting concentration and are expressed as percentages.

Synthesis of the (mono)sulfidic crosslink

One of the reaction products, a monosulfidic crosslink, was synthesized to determine the exact retention time and response factor in the chromatograms. The monosulfidic crosslink of TME was synthesized by a three-step synthesis. The first step was to synthesize 1-bromo-2,3-dimethyl-2-butene (TME-Br) (Fig. 3) via the 1,4 addition of HBr to 2,3-dimethyl-1,3-butadiene. HBr was obtained by a HBr generator: tetralin was dried with magnesium sulfate and anhydrous calcium sulfate for several hours. The filtered tetralin was distilled under reduced pressure. Bromine was added dropwise to the tetralin to generate HBr. HBr was added to the redistilled 2,3-dimethyl-1,3-butadiene under a dry nitrogen flow for 6 h. The exothermic reaction was cooled in an ice bath. The product was purified by distillation and analyzed by ^{1}H-NMR.

^{1}H-NMR (CDCl$_3$, δ): 1.70 (s, 3H), 1.77 (s, 6H), 4.07 (s, 2H).

The second stage was the synthesis of 2,3-dimethyl-2-butene-1-thiol (TME-sH). In a nitrogen atmosphere, 26.47 g of TME–Br and 15.77 g of thiourea were dissolved in ethanol in a three-necked flask with a con-

TABLE VI
Model Compound Systems

	Squalene				TME		
	Mass (g)	(phr)	(mmol)		Mass (g)	(phr)	(mmol)
Squalene	0.5000	100	1.217	TME	0.5000	100	5.941
CBS	0.0060	1.2	0.023	TBBS	0.0075	1.5	0.025
S$_8$	0.0100	2	0.039	S$_8$	0.0088	1.75	0.034
ZnO	0.0250	5	0.307	ZnO	0.0250	5	0.307
Stearic acid	0.0100	2	0.035	Stearic acid	0.0100	2	0.035

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

denser and an oil lock on top. The solution was refluxed for 3 days. A rotavapor apparatus was used to evaporate the solvent. A white solid remained, which was dissolved in ultrasonically degassed and distilled water together with 8.28 g of NaOH. After 1 h of refluxing, the product was extracted with methylene chloride (three times with 50 mL). The methylene chloride was removed by rotavapor distillation. The product was distilled *in vacuo*. The structure of TME–SH is given in Figure 4.

^{1}H-NMR: (CDCl$_3$, δ): 1.40 (t, 1H), 1.66 (s, 3H), 1.72 (s, 3H), 1.80 (s, 3H), 3.18 (d, 2H).

The final step was the synthesis of the monosulfidic crosslink (Fig. 5). In a three-necked flask with a condenser and an oil lock, 0.4 g of solid sodium and 50 mL of isopropyl ether were heated to 70°C. In 10 min, 2 g of TME–SH dissolved in 50 mL of diisopropyl ether was added dropwise. The solution was stirred for 2 h until all the sodium had reacted. After the dropwise addition of 2.8 g of TME–Br, the solution was refluxed for 24 h. A white suspension was obtained. The crystals were filtered out, and the diisopropyl ether was evaporated under reduced pressure. A further purification was accomplished by vacuum distillation. The desired product was obtained as a colorless oil in a quantitative yield. The product was analyzed by ^{1}H-NMR.

^{1}H-NMR (CDCl$_3$, δ): 1.73 (s, 3H), 1.75 (s, 3H), 1.80 (s, 3H), 3.20 (s, 2H).

Although small impurities were detected, the major part was the desired product.

RESULTS

As mentioned before, the zinc ion is the central atom of the active complex in accelerated sulfur vulcanization. In addition to its role as an activator for sulfur
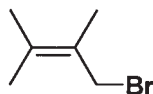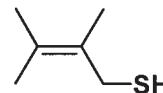
Figure 4   Structural formula of TME–SH.

vulcanization, there is also evidence that the inclusion of ZnO in a compound reduces heat buildup and improves tire abrasion resistance. Moreover, ZnO improves the heat resistance of vulcanizates and their resistance to the action of dynamic loading. Traditionally, typical recipes for the sulfur curing of SBR rubbers contain 5 phr ZnO. Over the years, lower levels have been used, and according to several researchers, it seems that ZnO levels can be reduced to a minimum of about 2 phr without serious detrimental effects on properties.[26,27] A small reduction in the modulus can be compensated by a slight increase in the levels of the accelerators. In contrast to s-SBR, higher levels of ZnO are normally used for EPDM.

ZnO optimization in s-SBR compounds

The s-SBR master batch according to Table III was investigated over a range of ZnO (Red Seal) levels, with the vulcanization behavior and physical properties evaluated. Vulcanization experiments without any ZnO as an activator were performed to separate the activity of the acceleration system itself and the activator. Figure 6 shows the cure characteristics for the s-SBR compounds, with the ZnO amount varied between 0 and 3 phr. The same cure rate and increase in torque were observed for compounds with 0.3–3 phr ZnO. The complete absence of ZnO led to a decrease in the cure rate and, therefore, much longer cure times. For the compounds with very low ZnO levels, in particular 0.3 phr ZnO, a slight decrease in the torque or reversion was observed at longer vulcanization times.

The results of swelling experiments with different levels of ZnO (Red Seal) are presented in Figure 7. A higher swelling percentage, corresponding to a lower crosslink density, was found for the compound without ZnO, and this agreed with the torque measurements.

The physical properties of the compounds with 0 and 1–5 phr ZnO are presented in Table VIII. A lower value for the elongation at break and a higher compression set at 100°C for the compound without ZnO were found. This could be attributed to the lower crosslink density, as already observed with the swell-
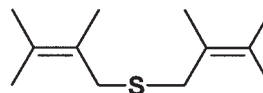

Figure 3   Structural formula of 1-bromo-2,3-dimethyl-2-butene.

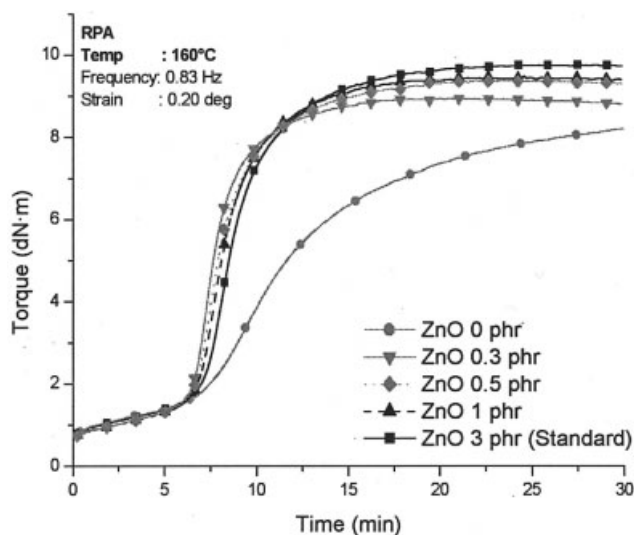**Figure 5**   Structural formula of the monosulfidic crosslink.

Figure 6 Cure characteristics of s-SBR compounds with different levels of ZnO (Red Seal).

ing and torque measurements. The influence of ZnO on the heat buildup, as suggested in the literature, could not experimentally be corroborated. No major differences were observed between the compounds with 1–5 phr ZnO. Concerning the abrasion resistance, no substantial increase with an increasing ZnO level was detected either. As shown in Table VIII, the fatigue-to-failure properties decreased at higher ZnO levels. This might be to some extent related to an increased modulus.

In summary, the data revealed that a reduction to 1 phr ZnO in s-SBR compounds seemed to be possible without major effects on the cure and physical properties.

ZnO optimization in EPDM compounds

EPDM was also investigated over a range of ZnO (Red Seal) levels, with the vulcanization behavior and physical properties evaluated according to the recipes in Table IV. Figure 8 shows that the cure characteristics for EPDM with 3–10 phr ZnO (Red Seal) were comparable. The state of cure: difference between maximum and minimum torque in RPA 2000 (M_H–M_L) of the compound with 1 phr ZnO was lower, and the cure curves displayed a slight decrease or reversion. The swelling percentages and crosslink densities of the EPDM compounds are depicted in Figure 9. As already expected from the rheograms, a considerably higher swelling percentage was measured for the compound without ZnO, and a slightly higher swelling percentage was measured for the compound with 1 phr ZnO in comparison with the percentages of the compounds with 3–10 phr.

The mechanical properties of the cured compounds with different ZnO levels are listed in Table IX. When ZnO was omitted, the crosslink density was considerably lower, and this resulted in notoriously inferior mechanical properties. The inclusion of only 1 phr ZnO in the compound recipe led to a significantly higher crosslink density. The crosslink density of the standard 5 phr ZnO compound, however, was still distinctly higher, as deduced from the values of the elongation at break and compression set.

Overall, a reduction to 2 phr ZnO (Red Seal) in the EPDM compounds seems to be possible without noticeable effects on the cure and physical properties. Depending on the exact requirements for a specific compound, a further reduction might still be possible.

Other ZnO's

When pure ZnO (99.5%; Merck) was used as an activator in s-SBR and EPDM compounds instead of ZnO (Red Seal), no major differences were observed in the cure and physical properties, as illustrated in Figures 10 and 11.

Another parameter that is reported to affect the activity of ZnO is the specific surface area. The substitution of 3 phr ZnO (Red Seal) by 3 phr active ZnO led in both rubbers to a slight, virtually insignificant increase in the change in torque, as shown in Figures 10 and 11. Also, no major differences in the physical properties were observed.

To study the effects of dispersion in greater detail, we performed experiments with nano-ZnO (Table V). The cure characteristics of s-SBR compounds with different levels of nano-ZnO are presented in Table X.

The cure characteristics indicate that with nano-ZnO as an activator, a pronounced reduction of the ZnO content can be achieved. It seems to be possible
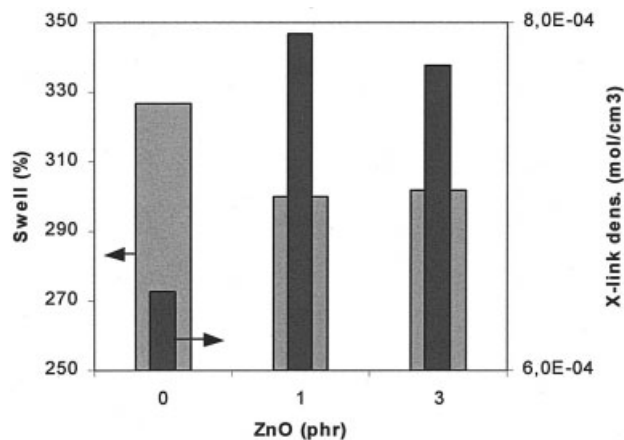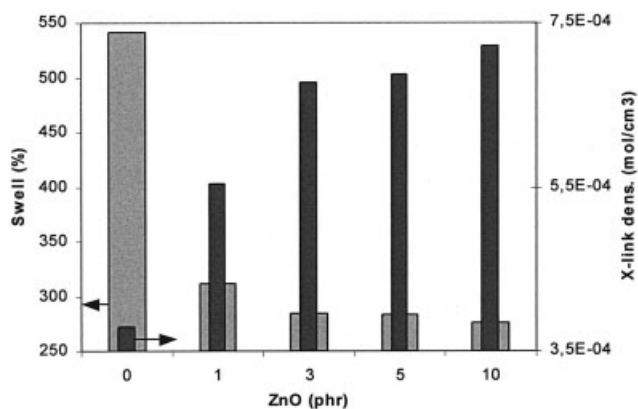

Figure 7 Swell and crosslink density of s-SBR compounds with different levels of ZnO (Red Seal).

TABLE VIII
Properties of s-SBR Compounds with Different ZnO (Red Seal) Levels

	S1	S2	S5	S6	S7	S8	S9
Hardness (Shore A)	65	64	64	65	65	65	65
M_{25} (MPa) (Modulus 25%)	1.1	1.1	1.1	1.1	1.1	1.1	1.1
M_{50} (MPa) (Modulus 50%)	1.7	1.6	1.6	1.6	1.6	1.6	1.5
M_{100} (MPa) (Modulus 100%)	2.9	2.6	2.7	2.7	2.8	2.8	2.6
M_{300} (MPa) (Modulus 300%)	14.4	12.8	12.9	13.3	14.5	13.6	12.7
Tensile strength (MPa)	16.1	15.6	22.2	20.6	24	23.6	23.1
Elongation at break (%)	320	335	431	397	432	429	458
Tear strength (N/mm)	35.9	37	36.4	34.7	34	32.8	36.2
Compression Set at 72 h and 23°C (%)	6	9	8	8	10	8	8
Compression Set at 72 h and 100°C (%)	62	63	55	52	55	52	63
After 72-h and 100°C aging							
M_{25} (MPa) (Modulus 25%)	1.4	1.4	1.6	1.7	1.7	1.7	1.6
M_{50} (MPa) (Modulus 50%)	2.2	2	2.7	2.7	2.8	2.7	2.7
M_{100} (MPa) (Modulus 100%)	4.2	4	5.7	5.9	5.8	5.8	5.7
M_{300} (MPa) (Modulus 300%)	—	—	—	—	—	—	—
Tensile strength (MPa)	14.2	13.2	17.6	16.7	18.5	18.7	18.8
Elongation at break (%)	216	220	213	190	215	210	213
Abrasion resistance (mm³)	96	75	97	96	97	102	95
Fatigue to failure (kc)	29	34	50	49	53	42	34
Goodrich Heat Build-up							
Permanent set (%)	9.9	11.2	12.4	11.8	11.8	11.2	12.1
Holder temperature (°C)	131.6	131.3	136.2	135.2	136.1	135.4	138
Needle temperature (°C)	155.6	156.5	165.5	161.9	165.5	163.8	164.7

to reduce the quantity of ZnO to 0.2–0.3 phr without detrimental effects on the curing properties.

Considerations on ZnO levels needed for proper vulcanization

This part describes the possibilities of reducing and optimizing the amount of ZnO in two different rubbers, s-SBR and EPDM. We found that it was possible to

reduce the quantity of 3–5 phr ZnO traditionally used in rubber formulations and still obtain acceptable properties. The cure characteristics and physical properties (tensile strength, elongation at break, Young's modulus, compression set, and hardness) of s-SBR compounds with ZnO (Red Seal) as an activator did not improve significantly anymore with levels higher than a minimum of 1 phr. Apparently, the effect of ZnO (Red Seal) in the TMTD/MBT-accelerated vulcanization system in EPDM was more conspicuous than that in the TBBS-accelerated system in s-SBR. Although in s-SBR the cure and mechanical properties of compounds without ZnO
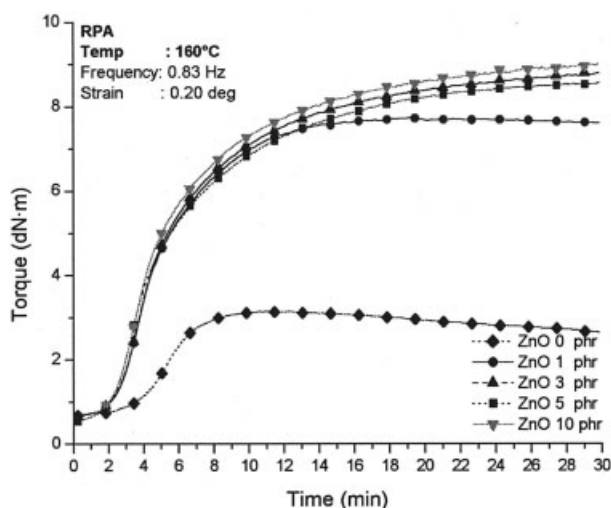
Figure 8 Cure characteristics of EPDM compounds with different levels of ZnO (Red Seal).

Figure 9 Swell and crosslink density of EPDM compounds with different levels of ZnO (Red Seal).

TABLE IX
Properties of EPDM Compounds with Different ZnO (Red Seal) Levels

	E1	E2	E3	E4	E5	E6	E7
Hardness (Shore A)	43	43	59	61	63	63	62
M_{25} (MPa) (Modulus 25%)	0.6	0.6	0.9	0.95	1	1	1
M_{50} (MPa) (Modulus 50%)	0.7	0.7	1.3	1.48	1.6	1.6	1.6
M_{100} (MPa) (Modulus 100%)	0.9	0.9	2.4	2.82	3.1	3.2	3.1
M_{300} (MPa) (Modulus 300%)	1.8	2	7.4	8.79	9.4	9.7	9.4
Tensile strength (MPa)	2.5	3.1	13.7	13	13	13	12.6
Elongation at break (%)	655	661	563	450	413	406	407
Tear strength (N/mm)	17.4	24.1	40.6	36	34.5	36.5	34.3
Compression Set at 72 h and 23°C (%)	23	23	5	6	5	5	6
Compression Set at 72 h and 100°C (%)	99	94	81	68	65	61	66
After 72-h and 100°C aging							
M_{25} (MPa) (Modulus 25%)	0.9	0.8	1.2	1.2	1.3	1.4	1.3
M_{50} (MPa) (Modulus 50%)	1.2	1	2.2	2.2	2.3	2.3	2.3
M_{100} (MPa) (Modulus 100%)	2.1	1.5	4.6	4.7	5.1	5.0	4.8
M_{300} (MPa) (Modulus 300%)	6.1	4.3	12.5	—	—	—	—
Tensile strength (MPa)	13.3	9.3	12.3	12.4	12.1	12.4	12.6
Elongation at break (%)	742	—	281	260	243	248	268

or very low levels were somewhat inferior, in EPDM these properties were seriously affected. As a result, the EPDM compounds required higher amounts of ZnO (Red Seal), that is, 2 phr at least, to obtain properties comparable to those of standard compounds containing 3–5 phr ZnO. In general, the previously described results have demonstrated the possibility of reducing and optimizing the amount of ZnO (Red Seal), yet at the same time they show that no general conclusions can be drawn and that every application requires its own specific optimization.

A parameter of paramount importance in the activation of sulfur vulcanization is the accessibility of Zn. Although the more active, higher specific surface ZnO did not result in a significant improvement, experiments with nano-ZnO have proved that it is possible to reduce the quantity of ZnO by a factor of 10 and yet retain the curing properties of the rubber products. Nano-ZnO represents a new route for reducing ZnO levels in rubber compounds. The main disadvantage of nano-ZnO is its high price in comparison with that of conventional ZnO, mainly because of the current small-scale production.

MCV

A detailed investigation of the function of ZnO during the many stages of vulcanization was carried out with the polyfunctional model squalene and the monofunctional model TME. The experiments with squalene
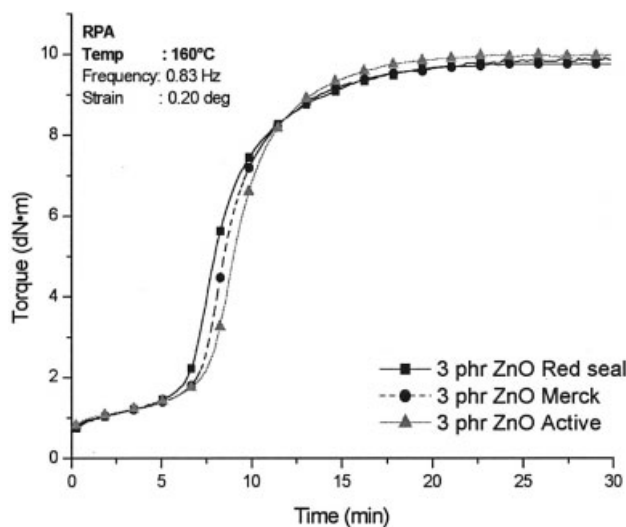
Figure 10 Comparative curing behavior of s-SBR compounds containing ZnO, pure ZnO, and active ZnO.
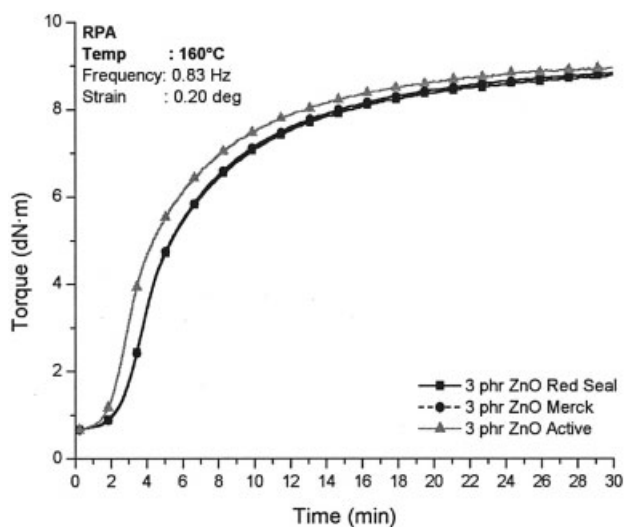
Figure 11 Comparative curing behavior of EPDM compounds containing ZnO, pure ZnO, and active ZnO.

TABLE X
Cure Characteristics of s-SBR Compounds with Different Nano-ZnO Levels

Parameter	Nano-zinc				ZnO (Red Seal)	
	S10	S11	S12	S13	S2	S7
Phr	0.05	0.10	0.20	0.30	0	3
M_H–M_L (dN m)	8.76	8.76	9.08	9.07	8.43	9.08
t_{02} (min)	4.48	4.44	4.21	4.44	4.48	4.48
t_{90} (min)	18.07	12.45	10.24	11.09	22.05	11.53

were used to compare the results with the literature; Borros and coworkers[25,28] performed a similar study with squalene on the effect of the activator during the scorch and curing times. In an analogous manner, in this study the changes in the composition of the model compound samples as a function of time were studied. The development of the initial ingredients and the formation of MBT were characterized and quantified by HPLC–UV. To obtain more information about other stages of the vulcanization, the monofunctional model TME was used. With this model compound, besides the development of the initial ingredients and the formation of MBT, the crosslinked products and the crosslink precursors could be characterized by HPLC at a wavelength of 254 nm.

Reactions in squalene

Squalene was reacted for 5–60 min in the presence of sulfur and CBS, with and without ZnO, according to the recipes given in Table VI. Stearic acid, used to solubilize the zinc into the rubber system, was added as well, and it might set zinc ions free to form complexes with accelerators. The vulcanization reaction was carried out at 140°C, a representative temperature for NR vulcanization, as chosen for the majority of MCV studies.[29–32] At higher vulcanization tempera-

tures, such as 160°C, which is selected as a vulcanization temperature for many rubbers, the reactions proceed much more quickly, particularly in model compound systems. To follow the development of the reactions more gradually, a lower reaction temperature was preferred.

The reactions were carried out for a definite time period, and the reaction products were analyzed with HPLC. The weight percentages for every component could be calculated via the internal standard. On the basis of the data for the various reaction times, the concentration development of the many components as a function of the reaction time could be plotted.

Figure 12 shows the CBS concentration in the samples with ZnO (designated as ZnO) and without ZnO (designated as none) as a function of the reaction time, as analyzed with HPLC–UV. Another material to be considered in the model system is elemental sulfur. The fate of elemental sulfur as a function of the reaction time is depicted in Figure 13.

Figure 12 shows that the breakdown of the accelerator starts at shorter reaction times in the presence of ZnO. Therefore, ZnO activates the breakdown of CBS in squalene. After 1 h, almost all the accelerator had been consumed in both systems. Concerning the sulfur concentration, a very fast decay was observed in the first 5–10 min for both systems. Presumably, the
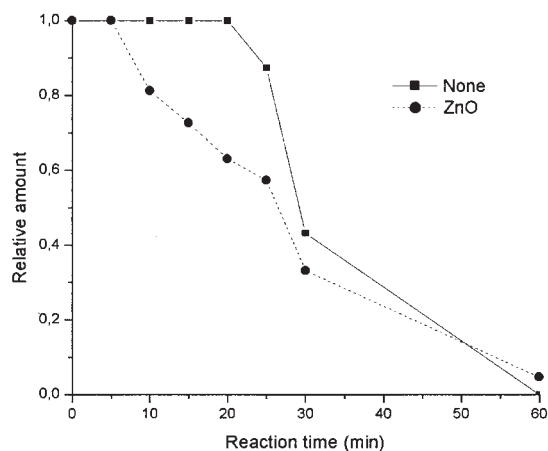
Figure 12 Breakdown of CBS in squalene as a function of the reaction time with and without ZnO as an activator.
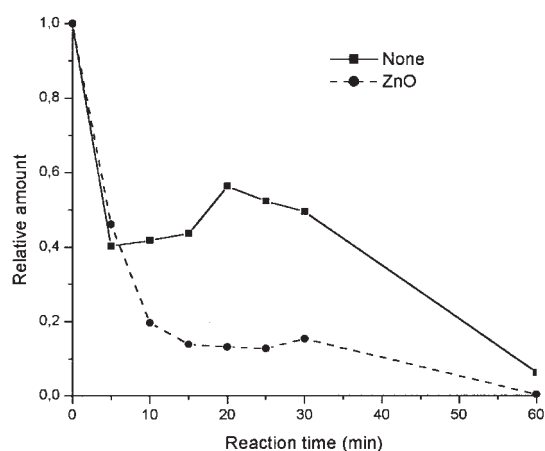
Figure 13 Sulfur concentration in squalene as a function of the reaction time with and without ZnO as an activator.
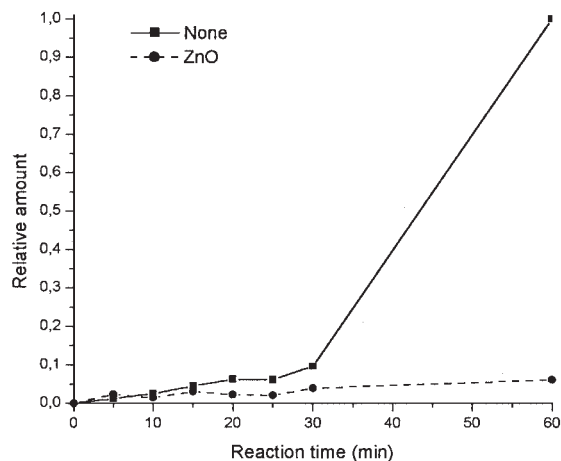
Figure 14 MBT concentration in squalene as a function of the reaction time with and without ZnO as an activator.

Figure 15 Breakdown of TBBS in TME as a function of the reaction time with and without ZnO as an activator.

sulfur was incorporated into the accelerator during the first 10 min to form polysulfidic species. In the presence of ZnO, however, much more sulfur was consumed in this initial stage of the reaction.

MBT was formed during the course of the reaction as a decomposition product of the accelerator or as a side product from the transformation of a crosslink precursor into a crosslink. The formation of MBT is shown in Figure 14. When ZnO was present in the reaction mixture, the MBT concentration remained at a low level, contrary to the case in which no ZnO was added: MBT tended to accumulate at longer reaction times. A possible explanation could be the formation of a complex between the zinc ions and MBT (ZnMBT). Although it has been proven by others that mercaptobenzothiazole-sulfide (MBTS) is also formed very rapidly during the earlier stages of the vulcanization, it reacts readily and remains at a negligible level.[33,34] This explains the fact that hardly any MBTS was detected in our experiments.

Unfortunately, it was very difficult to analyze the crosslinked products of the squalene samples with this HPLC–UV setup. Other techniques, such as gel permeation chromatography, are suitable for studying the crosslinking of high-molecular-weight squalene.[35] The resulting chromatograms, however, are not unequivocal and are rather difficult to interpret. As mentioned earlier, in TME model systems, the crosslinked products and the crosslink precursors can be properly characterized. Therefore, we decided to study the crosslinking reaction in detail in TME model systems, rather than in squalene.

Reactions in TME

Although TME is less similar to rubbers, its simplicity (i.e., monofunctionality and one type of allylic position) offers great advantages for the study of the vul-

canization reaction intermediates and products. With this model compound, three different stages in the vulcanization process were studied as a function of time: the kinetics of the curative formation and disappearance, the formation and disappearance of the crosslink precursor, and the formation of the crosslinked products.
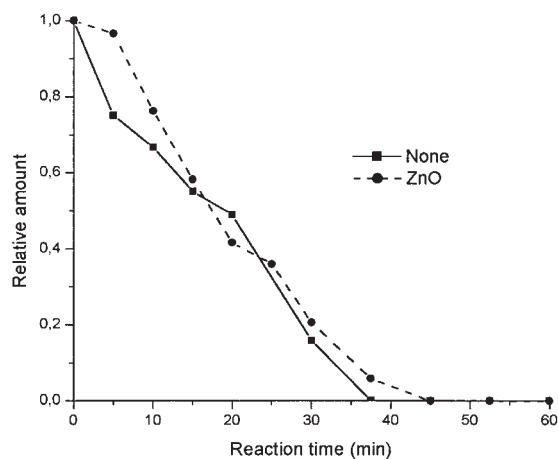
The initial ingredients could be identified and characterized in the chromatogram. For instance, TBBS eluted at a retention time of 4.2 min, the internal standard eluted at 6.3 min, and sulfur eluted at 14 min. Figures 15 and 16 show a reduction in the amounts of some of the initial vulcanization ingredients (TBBS and sulfur, respectively) for samples with and without ZnO. Figure 15 shows that ZnO hardly has any influence on the decomposition and breakdown of TBBS. In the TME samples, a very fast decay of sulfur in the first 5 min was observed, comparable to the results obtained in squalene. The amount of sulfur remained
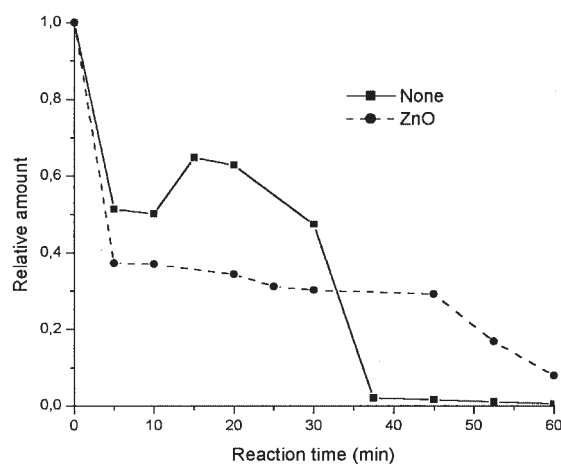

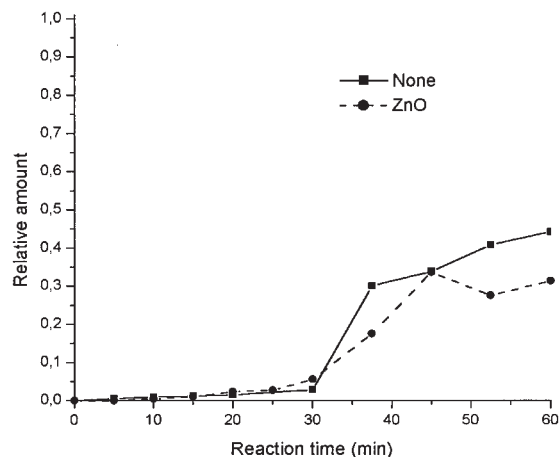**Figure 16** Sulfur concentration in TME as a function of the reaction time with and without ZnO as an activator.

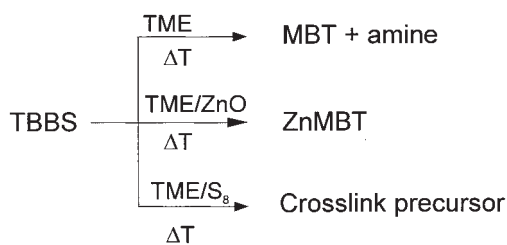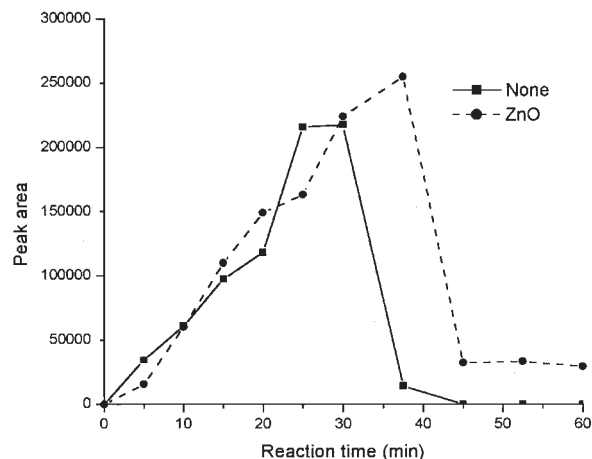**Figure 17** MBT concentration in TME as a function of the reaction time with and without ZnO as an activator.

Figure 19 Crosslink precursor (TME-S_x-MBT) concentration as a function of the reaction time with and without ZnO as an activator.

higher for the sample without ZnO than for the sample with ZnO, at least up to about 35 min. Then, sulfur started to decrease very quickly until almost all the sulfur was consumed.

The development of MBT with the reaction time is plotted in Figure 17. For both systems, with and without ZnO, the formation of MBT started around 30 min. A relative amount of 1 corresponds to the complete conversion of TBBS into MBT. After 40 min of reaction, almost all TBBS had reacted (Fig. 15), whereas the relative amounts of MBT formed were only in the range of 0.2–0.4. This was a strong indication that TBBS was also converted into other reaction products or intermediates. Possible reaction products that may be formed from TBBS are summarized in Figure 18.

As indicated in Figure 18, MBT may form a complex with zinc ions to form ZnMBT. ZnMBT precipitates in the reaction mixture and is therefore difficult to analyze with HPLC. In the systems without ZnO, however, this complex cannot be formed. As indicated in the general scheme for sulfur vulcanization (Fig. 1), crosslink formation requires intermediate compounds, such as crosslink precursors, formed via accelerator scission before the formation of crosslinked products. These precursors consist of the mercapto part of the accelerator, bonded to the allylic position of the model molecule via a polysulfidic bridge (rubber-S_y-acc). New peaks appeared in the chro-

matograms at retention times of approximately 7, 10, 12, and 17 min. Although no direct identification of the crosslink precursor was possible, the peak that represented the crosslink precursor could be identified via TBBS and MBT graphs. If the relative amounts of TBBS and MBT were low, those groups could be attached to TME or formed into a complex with a zinc ion. The peak at 7 min clearly shows a maximum around a reaction time of 30 min. Furthermore, the peak at 7 min is the first peak appearing during the reaction. Therefore, it is logical to accept that the peak at 7 min represents the crosslink precursor. This agrees with the concept that the formation of crosslink precursors occurs before the formation of crosslinks. In Figure 19, the crosslink precursor development is plotted as a function of the reaction time. The peak areas in the HPLC chromatograms are plotted as a function of the reaction time. It was not possible to
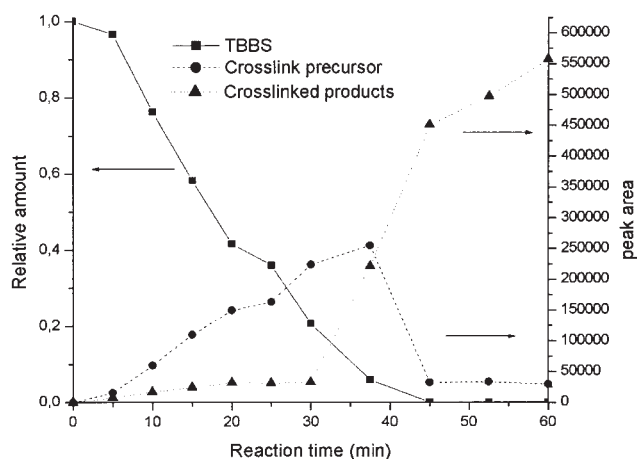

Figure 18 Reaction products of TBBS.

Figure 20 TBBS, crosslink precursor, and crosslinked product concentrations as a function of the reaction time with ZnO.
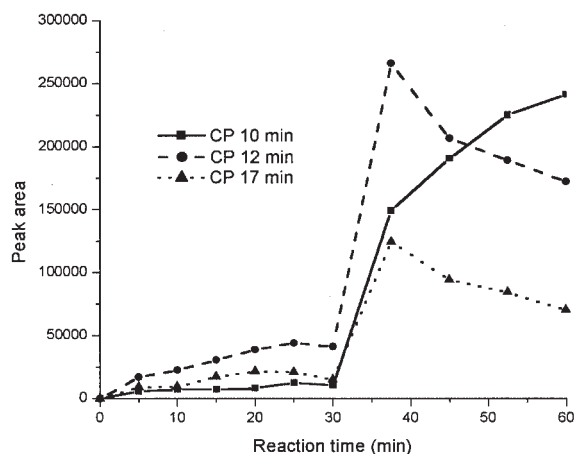
Figure 21 Crosslinked product development as a function of the reaction time without ZnO.

derive the relative amounts from these graphs because the exact response factors were not known.

Figure 19 shows no significant difference in the rate of crosslink precursor formation in the two systems, and this is in good agreement with the decomposition of TBBS as summarized in Figure 20. A maximum concentration of the crosslink precursor was observed around a reaction time of 30 min. In the samples with ZnO present, the breakdown of the crosslink precursor was delayed to some extent.

Contrary to the peak at 7 min, the peaks at 10, 12, and 17 min are most likely related to the crosslinked products. Versloot[36] demonstrated that two molecules of TME react with sulfur to form a sulfur-bridged structure. These crosslinked polysulfidic products are mainly formed without isomerization, but some isomerization might occur.[29]

The polarity of a compound in a common HPLC setup determines the retention time in the chromatographic column. The column used in the experiments was a reverse-phase column, for which the retention time was related to the nonpolar part of the molecules. A higher retention time corresponded to a more nonpolar molecule, such as a higher sulfur rank. Furthermore, Hann[37] reported a linear correlation between the sulfur rank and the logarithm of the retention time, with the retention time increasing with longer sulfur bridge length. On the basis of this relation, even with no direct identification of the reaction products, it may be concluded that if the three peaks can be interpreted as reaction products with different sulfur chain lengths, the peak at approximately 17 min corresponds to the longest sulfur bridge.

It is interesting to analyze the peaks of the reaction products in more detail. Figures 21 and 22 show the development of three of the reaction products in time measured with HPLC. Figure 21 corresponds to the case without ZnO, whereas in Figure 22, a system with

ZnO is shown. In these figures, the peak areas as obtained from the chromatograms are plotted as a function of time. The different (poly)sulfidic crosslinked products cannot be compared absolutely, whereas the response factors of these products were not all determined. Only the trends between the different systems can be compared.

The crosslinked product concentration increased rapidly around 30 min, the time by which the accelerator had almost completely dissociated, as shown in Figure 15; the concentration of the crosslink precursor started to decrease, as depicted in Figure 19. Both Figures 21 and 22 show that the reaction product with a retention time of approximately 12 min increased earlier and faster than the product with a retention time of 10 min. The onset of the actual vulcanization or crosslink formation was slightly delayed when ZnO was present. Furthermore, the distribution of the crosslinks was clearly influenced by ZnO. On the basis of the literature, crosslink shortening at longer reaction times was expected.

The identification of those peaks with liquid chromatography/mass spectrometry did not succeed in revealing the structure, mainly because of the complexity of the reaction mixture. Another approach to obtaining evidence about the exact nature of crosslinked products and their position in the chromatogram could be to coinject authentic crosslinked products in their pure form. The monosulfidic crosslink was prepared according to the procedure described in the Experimental section. An HPLC measurement was performed with this monosulfidic crosslinked product. The ingredients for the synthesis were injected separately to identify the peaks of the initial components in the chromatogram of the monosulfidic crosslink. The peak with a retention time of approximately 6 min represented the monosulfidic crosslink.

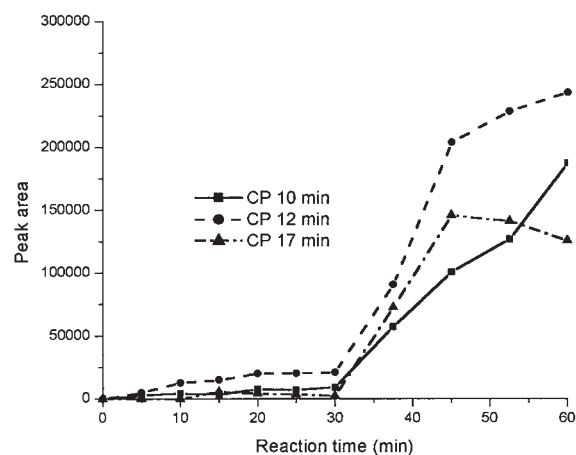The linear correlation between the sulfur rank and the logarithm of the retention time, as proposed by Hann,[37]

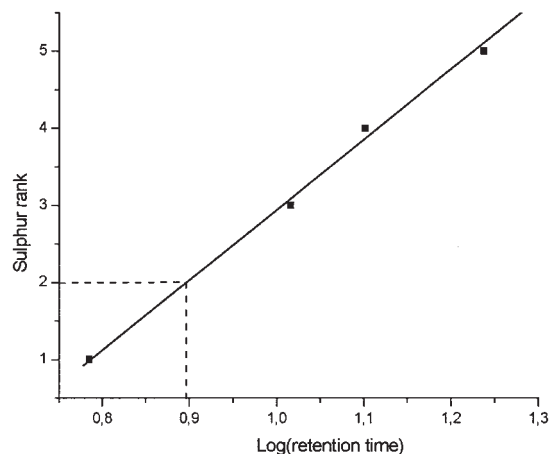**Figure 22** Crosslinked product development as a function of the reaction time with ZnO.

Figure 23 Sulfur rank versus the logarithm of the retention time.

is graphically represented in Figure 23 with the data of the unknown peaks and the synthesized monosulfidic crosslink. On the basis of this plot, it can be concluded that the peaks at 10, 12, and 17 min indeed correspond to S_3, S_4, and S_5 TME crosslinks. The disulfidic crosslink should then be located in the chromatogram at a logarithm of the retention time of approximately 0.89, corresponding to a retention time of 7.9 min. The monosulfidic and disulfidic crosslinks were not clearly observed in the reaction mixtures because of the low resolution in the chromatograms and the presence of interfering components. The monosulfidic and disulfidic crosslinks were generally assumed to be quite stable, although no direct indication about their stability could be obtained. The higher sulfur ranks, however, were found to be rather unstable (Figs. 21 and 22) and tended to decrease and perhaps even degrade again with increasing reaction times.

DISCUSSION

The results obtained so far apply to model compounds, that is, squalene and TME, and these findings may not necessarily be extrapolated to real rubbers such as EPDM and s-SBR. However, the general trend of the reactions is unlikely to be influenced by the particular allylic structures of the various rubbers involved.

As mentioned earlier, for the sulfur vulcanization of rubbers in the presence of accelerators, an activator such as ZnO is an essential ingredient. It enhances the vulcanization efficiency and vulcanizate properties and reduces the vulcanization time. The dispersion, particle size, and specific surface area, which are parameters of paramount importance for the activity of ZnO in rubber compounds as discussed in the previous section, are much less important in MCV. The diffusion of the vulcanization ingredients in these liquid model systems is much faster than that in real rubbers. In addition, stearic acid was added to the model systems because it has

shown an influence on the cure characteristics in a benzothiazole accelerator system used for s-SBR, as discussed in the previous section. Stearic acid may set zinc ions free to form complexes with accelerators. In MCV studies, stearic acid can also have an influence on the system via the pH.

For MCV, the crosslinked reaction products, as evaluated with HPLC, can be added by the summation of all the peaks of the various sulfur chains, that is, the area of S_3 plus the area of S_4 and so forth. In Figure 24, the crosslink development obtained with the TME model compounds and the rheograms of s-SBR compounds for systems with and without ZnO are combined into one graph.

At first sight, the MCV results are not at all in agreement with the s-SBR compounds. After 60 min of MCV, the total peak area of the crosslinks in the sample with ZnO was still increasing and reached a higher final level than the sample without ZnO. This is in good agreement with the higher torque level observed in the s-SBR compound with ZnO present. The onset of vulcanization, in particular, was delayed in the model compounds. This can be explained by the lower vulcanization temperature, 140°C instead of 160°C, used for the MCV studies. The crosslink distribution might be influenced as well, as indicated by Berg et al.[20,38] He studied the influence of temperature on the crosslink distribution in ethylidene norbornane (ENBH) as a model molecule for EPDM at reaction temperatures of 120, 140, 160, and 180°C. They found that a higher temperature led to the formation of disulfidic bridges at the expense of higher sulfidic bridges.

An important characteristic of the vulcanization process is the scorch delay. In the literature, several reasons for scorch delay have been suggested: the thermal stability of the accelerator and, alternatively, exchange reactions between accelerator polysulfides and other reac-
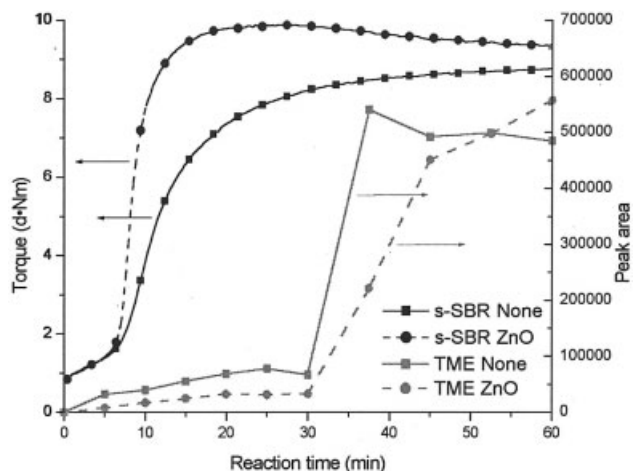

Figure 24 Cure torque of the s-SBR compounds and completely crosslinked products in MCV of TME as a function of the reaction time.
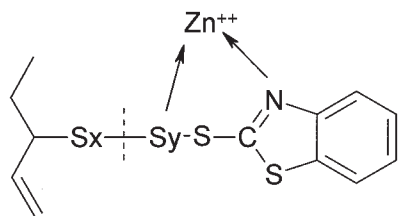
Figure 25 Interaction of zinc with the crosslink precursor.[40]

tion intermediates. The accelerator decomposes at the onset of the crosslink formation (Fig. 20), and this suggests that the cure delay is caused by a more rapid reaction of the intermediate compounds, such as crosslink precursors, with the vulcanizing agents rather than with the rubber hydrocarbons to yield crosslinks.

It has been reported that MBT has a catalytic effect on CBS decomposition.[39] Other authors have emphasized the role of ZnO in the decomposition of the accelerator. A third effect that has been mentioned in the literature is the influence of the presence of the model compound and the type of model molecule.[25] The decomposition rate of the accelerator can be followed quite accurately via the decrease in the accelerator content in the model compounds as a function of time. In squalene, CBS is broken down more quickly when ZnO is present. In TME, however, hardly any difference between the two systems was observed. Apparently, the role of ZnO in the decomposition of the accelerator is more pronounced in squalene, and this may be due to the influence of the type of model olefin or due to the fact that CBS was used instead of TBBS as with TME.

The sulfur insertion in the active sulfurating species is more difficult to evaluate because the zinc complexes are not detectable with the chosen method. However, the sulfur content at short reaction times can be compared; in that stage, not all the accelerator is consumed and complex formation is taking place for the system with ZnO. A smaller amount of sulfur for the ZnO system in comparison with the ZnO-free system can be considered an indication that sulfur is inserted into the complex or accelerator. In squalene and TME, the sulfur content at short reaction times was lower when ZnO was present in the samples.

Hardly any difference was noted between the precursor developments for the ZnO-free and the ZnO-containing systems. Apparently, ZnO does not accelerate the reactions that occur before the actual crosslinking in the TME model compound. The rate of decomposition of the crosslink precursor is not lower but occurs at longer reaction times. The delay in decomposition might be caused by the interaction of zinc with the precursor, as earlier proposed by Coran[40] (Fig. 25).

For the TME model compounds, the reaction products could also be monitored. It seemed that the actual

crosslinking proceeded somewhat more slowly if ZnO was present. From the results for the ZnO-free and the ZnO systems, it can be concluded that ZnO favors the formation of crosslinks with a higher sulfur rank. The samples without ZnO produced a relatively large amount of shorter crosslinks. This seems to be in contrast to several studies that led to the conclusion that crosslinks contain fewer sulfur atoms when ZnO is used.

Although the many steps in the vulcanization reactions could be studied in detail by MCV, the results are not at all in agreement with the s-SBR rubber compounds. The effect of temperature has been mentioned already as an explanation for the difference in the cure delay. Another fundamental difference between the model and the rubber, which plays an important role in this complex interplay of reactions, is the number of end groups. The end groups have a —CH_3—configuration, and in a macromolecular molecule, —CH_2 forms the major reactive group. The position and configuration of the double bond are also important aspects. In the previous section, s-SBR was used as the main polymer, for which the polybutadiene moiety was 25% of the vinyl configuration. A model that represents the vinyl configuration very well is 3-methyl-1-pentene. Versloot[36] already showed that 3-methyl-1-pentene is more reactive toward elemental sulfur than TME. The higher reactivity of the vinyl configuration present in s-SBR can also partly explain the observed delay in cure in the TME model experiments.

The experimental studies reported in this section have provided mechanistic insight into ZnO-activated vulcanization, albeit without complete conclusive evidence. However, the effects of ZnO during the different stages of vulcanization have been identified, and an experimental base has been laid for further investigations and the development of activators.

CONCLUSIONS

It can be concluded from the experiments described in this article that for the sulfur vulcanization of rubbers in the presence of accelerators, an activator such as ZnO is an essential ingredient. It enhances the vulcanization efficiency and vulcanizate properties and reduces the vulcanization time. The cure characteristics and physical properties (tensile strength, elongation at break, Young's modulus, compression set, and hardness) of compounds with conventional ZnO (Red Seal) do not change significantly with levels of 1 phr or more in s-SBR and 2 phr or more in EPDM. So, it is possible to reduce the quantity of ZnO used traditionally in rubber formulations (3–5 phr).

The dispersion, particle size, and specific surface area are parameters of paramount importance for the activity of ZnO. Active ZnO, with a somewhat larger specific surface area than conventional ZnO (Red Seal), apparently has a negligible influence on the cure

characteristics and physical properties. Nano-zinc, on the other hand, as a newcomer, represents a new dimension for the activation of sulfur curing. In comparison with conventional ZnO, only one-tenth of the amount of nano-ZnO is necessary to achieve the same cure characteristics. This might be associated with the ultrasmall average particle size and the high specific area of nano-ZnO.

The overall conclusion is that, to achieve a pronounced reduction of zinc levels in rubbers, small particles and a high surface area are predominant parameters. Better accessibility of the zinc ions is most likely the key factor for achieving a higher chemical activity.

As may be inferred from the previous discussion, MCV, traditionally invoked as a technique for elucidating reaction mechanisms in real rubbers, does not always provide clear evidence. Many intermediates and products are formed with sulfur chemistry. The separation and subsequent analysis of all products formed is an extensive task and virtually impossible. Because of this complexity, it is hardly possible to analyze the reaction steps under general conditions applicable for all types of rubbers and vulcanization systems. Therefore, the current conclusions can only be applied to sulfur vulcanization with the benzothiazolesulfenamide accelerator type.

The many reaction steps could be studied in detail via MCV studies with squalene and TME as model compounds. In the squalene/CBS system, the different effects were more pronounced than in TME/TBBS. The rapid reduction of the sulfur concentration in the first 5–10 min was assumed to be caused by incorporation in the active sulfurating species. In the presence of ZnO, much more sulfur was consumed during this initial stage of the reaction. The MBT concentration remained at a low level when ZnO was present in the reaction mixture, and this was caused by the formation of a complex between the zinc ions and MBT (ZnMBT). Although no conclusive evidence was obtained about the model-bound crosslink precursor, it can be stated that ZnO caused a slight delay in the disappearance of the crosslink precursor. The onset of the crosslinking reactions only started when the accelerator was almost completely dissociated and the concentration of the crosslink precursor started to decrease. At long reaction times, especially in the absence of ZnO, the sulfur bridges were shortened because of the reversion reactions.

In contrast to the squalene experiments, in the TME experiments ZnO hardly had any influence on the many reaction rate constants. The role of ZnO, usually described as a catalyst for the vulcanization, in particular for the decomposition of the accelerator, apparently depends on the type of accelerator and the type of model olefin. Overall, the results have proved again the stunning versatility by which zinc or zinc compounds influence the different stages of the vulcanization process.

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