Various Ways to Reduce Zinc Oxide Levels in S-SBR Rubber Compounds

Geert Heideman,[1] Jacques W.M. Noordermeer,*[1] Rabin N. Datta,[1] Ben van Baarle[2]

Summary: Because of environmental concerns, the zinc content in rubber compounds has come under scrutiny. The research described in this article encompasses zinc-oxide, various zinc-complexes and alternative metal oxides as activators for sulphur vulcanisation. Regarding zinc complexes, it can be concluded that zinc-m-glycerolate is a good substitute for ZnO as activator for sulphur vulcanisation in s-SBR rubber, without detrimental effects on the cure characteristics. Of particular interest is also the positive effect of CaO and MgO in s-SBR, while BaO, Cu(II)O and BeO hardly show any activation. The present article also reports on the application of a novel activator for sulphur vulcanisation: ZnClay. Results with s-SBR rubber demonstrate, that this ZnClay can substitute conventional ZnO, retaining the curing and physical properties of the rubber products, while significantly reducing the environmental impact. A reduction of the zinc concentration with a factor 10 to 20 can be realised. Model Compound Vulcanisation studies are used to gain insight into the mechanism of this activator.

Keywords: activation; metal-oxides; sulphur-vulcanisation; zinc-complexes; zinc-oxide; Zn-clay

Introduction

Although zinc is generally considered one of the least harmful of the heavy metals, the Dutch Ministry of the Environment decided in 1985, based on a very large number of studies, to include zinc in a priority list of substances which were suspected to have negative environmental effects.[1] Zinc is defined as a heavy metal, although the statement that zinc is dangerous for the environment per se is not correct. Zinc is natural, recyclable and inherently part of our environment. It is the 17th most common element in the earth's crust and an essential element for man, animals and plants,[2] which is illustrated by the fact that for humans zinc deficiency can lead to adverse effects on growth, reproduction, cognition and immunity. Recently, the International Programme on Chemical Safety (IPCS) formed a Task Force on Zinc to establish Environmental Health Criteria for Zinc. Among its conclusions, the Task Force states: "Zinc is an essential element in the environment. The possibility exists for both a deficiency and excess of this metal. For this reason it is important that regulatory criteria for zinc, while protecting against toxicity, are not set so low as to drive zinc levels into the deficiency area".[3] Specifically soluble zinc compounds are classified as ecotoxic to aquatic organisms. Release of zinc into the environment from rubber occurs during production, during disposal and recycling of rubber products, for instance through leaching in land-fill sites. Also during service conditions, *e.g.* through wear of tires. It can be stated that it is desirable to keep the zinc oxide content in rubber compounds as low as possible, not only for environmental but also

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[1] University of Twente, Faculty of Science and Technology, Dept. of Rubber Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands
Fax: (+31) 53 4892151
E-mail: J.W.M.Noordermeer@utwente.nl
[2] TNO Industrial Technology, P.O. Box 6235, 5600 HE Eindhoven, The Netherlands

for economical reasons.[4] The increased attitude towards protecting the environment, gives rise to a demand for products that entail the least amount of environmental pollution impact.

The zinc ion is the central atom of the active complex in accelerated sulphur vulcanization.[5–8] In addition to its role as an activator for sulphur vulcanisation, there is also evidence that the inclusion of ZnO in a compound reduces heat-build-up and improves tire abrasion resistance. It has also been found that ZnO improves heat resistance of vulcanisates and their resistance to the action of dynamic loading.[9] Traditionally, typical recipes for sulphur 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 1 phr without serious detrimental effects on cure and physical properties.[1,8,10]

In view of the multiple action displayed by ZnO and zinc compounds, it is rather ambitious to eliminate ZnO completely. Where zinc oxide is commonly used in the vulcanisation recipe, not much is known about the accelerating properties of other metal oxides and zinc complexes and a comprehensive study was considered worthwhile. The sulphur vulcanisation of s-SBR rubber with several zinc compounds and alternative metal oxides as activators is described in this paper. The last part of this article is dedicated to the development of a novel activator, which contains only traces of zinc, but demonstrates an effectivity comparable to conventional systems. Besides the curing and physical properties, additional information about the reactions and mechanisms taking place in the rubber is desirable in order to understand the role and effectiveness of this activator for sulphur vulcanisation. Because of the insolubility of the rubber network, it is impossible to characterise the course of vulcanisation reactions in real rubber systems. Therefore, Model Compound Vulcanisation (MCV) with tetra-methyl-ethylene (TME) was selected to gain insight into the mechanism of this activator.

Experimental

Rubber Compounds

A s-SBR masterbatch was prepared in an internal mixer (~50 kg) in order to obtain a homogeneous mixture and minimise the influence of mixing conditions. The composition of the s-SBR masterbatch is given in Table 1. The vulcanisation systems, including the various activators investigated, were added in a separate operation, on a two roll mill at 50 °C.

Model Compound Vulcanisation

The compositions of the MCV reaction mixtures are listed in Table 2. The reaction products were analysed with the aid of HPLC. Three different stages in the vulcanisation process were studied as a function of reaction time: curatives development, crosslink precursor formation, and the crosslinked products development. In this article only the crosslinked products development is reported.

Results and Discussion

Various Metal Oxides

There have been a number of investigations comparing different metal oxides as vulcanisation activators, mostly in combination with Tetra-Methyl-ThiuramDisulphide (TMTD) in NR, with rather variable results.[a.o.: 1,11–13] The effect of metal oxides was investigated in s-SBR rubber according to the recipes in Table 3, evaluating vulcanisation behaviour and physical properties.[14] A TBBS-accelerated vulcanisation system was used in the s-SBR compounds. Figure 1 shows the cure characteristics for the s-SBR compounds with oxides from the group IIa of the

Table 1.
Composition of the s-SBR masterbatch.

Masterbatch s-SBR	[phr]
s-SBR (Buna VSL 2525)	100
Carbon Black (N375 HAF)	50
Aromatic Oil (Enerflex 75)	5
Total	155

Table 2.
Composition of the reaction mixtures for Model Compound Vulcanisation.

	No activator		ZnO as activator		ZnClay as activator	
	Phr	Mmole	Phr	mmole	phr	Mmole
TME	100	5.941	100	5.941	100	5.941
TBBS[a)]	1.5	0.025	1.5	0.025	1.5	0.025
Sulphur	1.75	0.034	1.75	0.034	1.75	0.034
Activator	–	–	5	0.307	5	0.017[b)]
Stearic Acid	2	0.035	2	0.035	2	0.035

[a)] TBBS: N-tert-butylbenzothiazole-2-sulphenamide.
[b)] The value represents the actual Zn^{2+}-content of the ZnClay.

periodic table as activator, *viz.* MgO, CaO and BaO.

The scorch times for s-SBR compounds with MgO, CaO and BaO are comparable with the reference compound, and the rates of cure lower but mutually comparable. The extent of crosslinking (M_H-M_L) of the compounds is slightly lower for the BaO-containing compound, yet in contrast with ZnO at longer vulcanisation times no decrease or reversion is observed. It is evident that MgO as well as CaO lead to cure characteristics comparable with the ZnO reference compound and therefore can be considered as good activators for sulphur vulcanisation of s-SBR rubber.

Despite the extremely high toxicity of BeO by inhalation and ingestion, the efficiency of BeO as activator of sulphur cure was investigated in s-SBR compounds, mainly to study whether the Wurtzite crystal-structure of both oxides is the governing factor for the activity of ZnO. The cure characteristics of compounds with different levels of BeO as activator are given in Figure 2. In the presence of BeO the results do not differ very much from the vulcanisates without activator, indicating that BeO is not active as an activator in sulphur vulcanisation, neither seems the Wurtzite structure to be the governing factor for the activity of ZnO. Cu(II)O demonstrates hardly any activating influence in s-SBR compounds either. Substitution of ZnO (Red Seal) in s-SBR compounds by MgO or CaO seems to be possible without noticeable effects on the cure and physical properties, while the addition of Cu(II)O as activator leads to inferior cure characteristics. Though the results indicate a potential to reduce the need for ZnO, it does not constitute a very promising and realistic solution for the ZnO problem from an environmental point of view. These alternative metal oxides exert (un)foreseen environmental implications, even more problematic than the zinc-based systems.

Zinc Complexes

It is known that zinc cations from ZnO and/or zinc compounds react with organic accelerators, giving zinc-accelerator complexes, quoted to be one of the main steps in the

Table 3.
Composition of the s-SBR compounds (phr) with different metal oxides.

Compound	1	2	3	4	5	6	7	8
Masterbatch s-SBR	155	155	155	155	155	155	155	155
Stearic Acid	2	2	2	2	2	2	2	2
ZnO	–	3	–	–	–	–	–	–
MgO	–	–	3	–	–	–	–	–
CaO	–	–	–	3	–	–	–	–
BaO	–	–	–	–	6	–	–	–
Cu(II)O	–	–	–	–	–	3	–	–
BeO	–	–	–	–	–	–	1	3
Accelerator (TBBS)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75

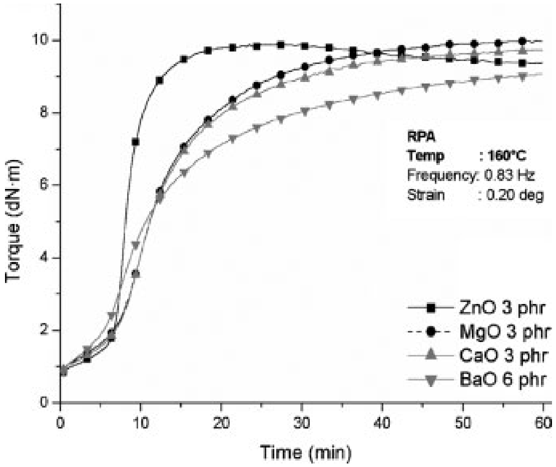

Figure 1.
Cure characteristics of s-SBR compounds with different metal oxides.

vulcanisation scheme.[5] It was therefore anticipated that via zinc complexes a better dispersion of zinc into the system is achieved and the zinc ions are free to form active accelerator complexes. The effect of the different zinc containing species was investigated in s-SBR rubber.[15] The compositions of the compounds are given in Table 4.

The 10 phr of zinc stearate corresponds with a molar amount of Zn^{2+}-ions comparable with approx. 1 phr of ZnO. Zinc stearate is very voluminous and from a mixing point of view it is rather troublesome to add larger amounts. The cure developments of the compounds with zinc stearate are combined in Figure 3, while in Figure 4 the results of swelling experiments are shown, as a measure for crosslink density.

The shape of the rheometer curve of a zinc stearate containing s-SBR compound differs significantly from the conventional ZnO activated compounds. Application of zinc stearate 10 phr results in a rather underdeveloped network, which is confirmed by the results of the swelling experiments. A

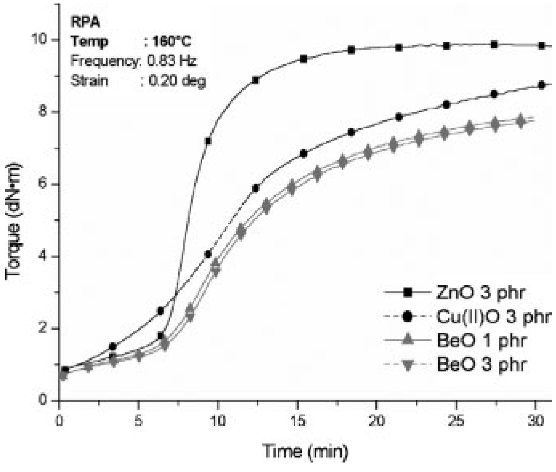

Figure 2.
BeO and Cu(II)O as cure activator in s-SBR compounds.

Table 4.
Composition of the s-SBR compounds (phr) with different zinc complexes.

Compound	S1	S2	S3	S4	S5	S6	S7	S8	S9
Masterbatch s-SBR	155	155	155	155	155	155	155	155	155
Stearic Acid	2	–	2	–	–	0.33	–	2	2
ZnO	0.5	3	3	–	–	0.5	–	–	–
Zinc stearate	–	–	–	10	20	6.11	–	–	–
Zinc-m-glycerolate[16]	–	–	–	–	–	–	6	–	–
Zinc-2-ethylhexanoate	–	–	–	–	–	–	–	4	–
Zinc borate	–	–	–	–	–	–	–	–	4.75
Accelerator (TBBS)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75

higher amount of zinc stearate affects the extent of cure as well as the crosslink density adversely. Addition of both ZnO and zinc stearate as activators is not advantageous: a lower extent of crosslinking as compared with only ZnO as activator, implying that there is no synergistic effect of ZnO and zinc stearate.

The cure characteristics and swelling data of the compounds with the other zinc complexes are given in Figures 5 and 6, respectively. From the curing properties it can be seen that zinc-2-ethylhexanoate leads to an increase in scorch time and a slightly lower extent of crosslinking as compared to ZnO. With zinc-m-glycerolate present as activator the opposite effect is observed: a considerably higher crosslink density compared to the reference compound, but with a shorter scorch delay. Zinc borate demonstrates curing characteristics grossly comparable with the reference compound. An explanation for the differences in scorch time can be found in the differences in the strength of the coordination bonds in the zinc complexes. Another explanation can be deduced from the general statement that increasing the pH leads to activation of the vulcanisation. Krebs postulated that the accelerating properties of amines are related to their base strength.[17] The alkaline character of zinc-m-glycerolate can be the reason for the acceleration of sulphur vulcanisation of rubber in an analogous way as in the cases of currently used basic accelerators. The greater basicity of glycerolate in comparison with that of stearate and hexanoate is in good accordance with the higher

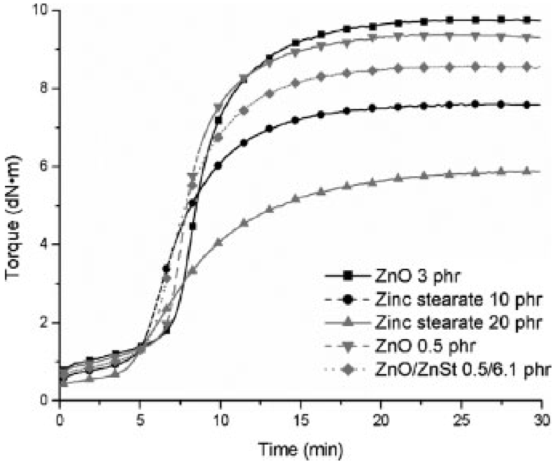

Figure 3.
Cure characteristics of s-SBR compounds with zinc stearate.

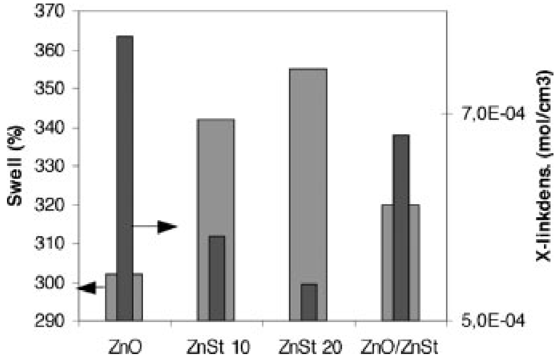

Figure 4.
Swelling and crosslink density of s-SBR compounds with zinc stearate.

vulcanisation rate found for zinc-m-glycerolate and zinc-2-ethylhexanoate. Overall, it can be concluded that particularly zinc-m- glycerolate is a good substitute for ZnO as activator for sulphur vulcanisation in s-SBR rubber, without detrimental effects on the cure properties. Although not further investigated in the present study, it is anticipated that a reduction of ZnO in s-SBR compounds can be achieved by designing proper zinc-containing complexes.

A Novel Activator for Sulphur Vulcanisation

In order to increase the activity of ZnO and thereby reduce the necessary amount, an option was to raise the availability of Zn^{2+}-ions at the surface of the crystals. The accessibility of Zn^{2+}-ions could be increased by loading a carrier with Zn^{2+} - ions, like done in the field of catalysis. A cheap mineral was chosen as carrier to provide the bulk material, loaded with Zn^{2+}-ions on the surface, to provide the activator function. It was assumed that the increased availability of the Zn^{2+}-ions could lead to a considerable reduction of zinc concentrations in rubber compounds and corresponding costs. The objective was to judge whether this novel activator could substitute conventional ZnO, retaining the curing and physical properties of the rubber products, and thereby significantly reducing the environmental impact. For these experiments a clay loaded with Zn^{2+}-ions was prepared and mixed to evaluate its

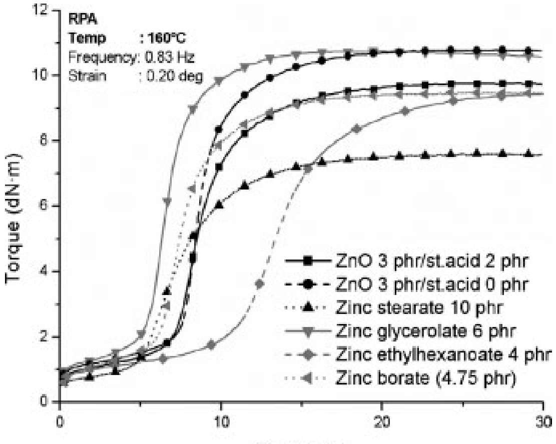

Figure 5.
Cure characteristics of s-SBR compounds with different zinc complexes.

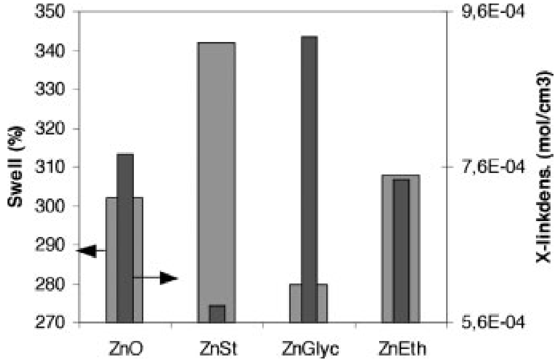

Figure 6.
Swelling and crosslink density of s-SBR compounds with zinc complexes.

effectiveness as activator for sulphur vulcanization.[18,19] The s-SBR compound compositions are shown in Table 5.

The activity of the unmodified clay material was also tested, as it contains small traces of zinc as well: compound S2. Its cure characteristic is shown in Figure 7. Compared to the compound with 3 phr ZnO a much lower cure rate is observed, more or less comparable with non-activated vulcanisation. The slightly earlier increase in torque might be due to a reinforcing effect of the clay.

Figure 7 represents the cure behaviour of s-SBR compounds with ZnClay as activator. Addition of the newly developed ZnClay as activator leads to much better results. As can be seen from this figure, about 5 phr of ZnClay is sufficient to reach a cure rate and delta torque comparable to the conventional system of phr ZnO. The results of swelling experiments with ZnClay are presented in Figure 8. A slightly higher swelling percentage corresponding to a lower crosslink density was found for the compounds with ZnClay, which is in accordance with the rheometer torque measurements.

The tensile properties of the compounds with ZnClay, S3 and S4 in Table 6, are grossly comparable with the standard compound S1. The higher values for the compression set and elongation at break are an indication of a slight under-vulcanisation of the test specimens. Overall, the cure and physical properties of the s-SBR compounds with the newly developed activator are grossly comparable with the ones obtained with the standard amount of 3 phr ZnO. The zinc content of ZnClay is around 5 wt %. It can be easily calculated that the zinc concentrations in the applied quantities of 5 and 2.5 phr ZnClay correspond with ~0.3 and ~0.15 phr ZnO, respectively. Thus a significant reduction of the zinc concentration with a factor of 10 to 20 can be realised, retaining the curing and physical properties of the rubber products as far as examined.

Table 5.
Composition of the s-SBR compounds (phr) with various activators.

Compound	S1	S2	S3	S4
Masterbatch s-SBR	155	155	155	155
Stearic Acid	2	2	2	2
ZnO (Red Seal)	3	–	–	–
Pure Clay (Montmorillonite)	–	5	–	–
ZnClay	–	–	2.5	5
Accelerator (TBBS)	1.5	1.5	1.5	1.5
Sulphur	1.75	1.75	1.75	1.75

Model Compound Vulcanisation

In this study TME was used as a model compound.[20] The reaction products are mainly of the type: TME-S_x-TME. Although TME is not directly comparable to a specific rubber, it was used because it has only one type of allylic position: the 4 methyl-groups, and therefore the reaction products have hardly any isomers. The crosslinked products can be separated by

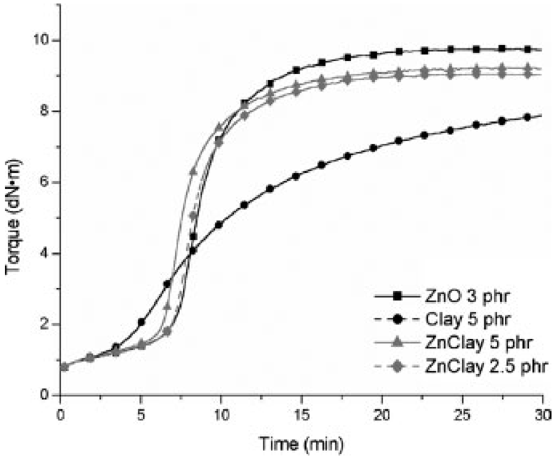

Figure 7.
Cure characteristics of mixes with ZnClay in s-SBR.

High Performance Liquid Chromatography and detected at a wavelength of 254 nm.

Although no unambiguous identification of the reaction products was possible, an indication of the amount of conversion could be obtained from a correlation between the breakdown of crosslink-precursors and the formation of reaction products. The crosslink-precursors are intermediate stages in the MCV, being reactants of one TME-molecule with an accelerator moiety. These intermediates are not further shown in the present context. The reaction products then originate from the reaction of such an intermediate with another TME-molecule, or from the reaction between two intermediates. It is evident that the peaks appearing in the chromatogram, when the signals of the crosslink-precursors are decreasing, are to be interpreted as crosslinked products. Three new peaks were observed in the chromatograms at retention times of 10, 12, and 17 minutes, corresponding to various sulphur chain lengths, or otherwise called sulphur-ranks, in the reaction products formed. The differences in trends between the three different sulphur-ranks can then be compared.

The peak areas of the crosslinked products for the samples without activator, and with ZnO resp. with ZnClay present as activators, are plotted versus reaction time in Figures 9, 10 and 11. Longer retention time corresponds to a more non-polar molecule, *e.g.* a higher sulphur rank. Hann reported a linear correlation between sulphur rank and the logarithm of the retention time, the retention time being longer

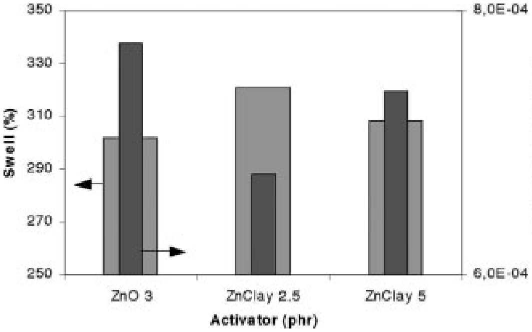

Figure 8.
Swell and crosslink density of s-SBR compounds with ZnClay.

Table 6.
Properties of s-SBR compounds with ZnClay.

Compound	S1	S3	S4
Hardness (Sh A)	67	65	68
M_{25} (MPa)	1.2	1.1	1.1
M_{50} (MPa)	1.8	1.6	1.7
M_{100} (MPa)	3.4	2.7	3.0
M_{300} (MPa)	17.7	13.0	13.1
Tensile strength (MPa)	21.3	21.9	21.8
Elongation at Break (%)	345	440	444
Tear strength (N/mm)	37	36	38
Compression Set 72 h/23 °C (%)	6	10	10

with higher sulphur-rank.[21] Therefore, the three peaks can be interpreted as reaction products with different sulphur chain lengths, with the peak at 17 minutes corresponding to the highest sulphur-rank. An important aspect of the vulcanisation process is crosslink-shortening. The initially formed polysulphidic bridges tend to reduce their sulphur chain-length by releasing sulphur and forming shorter crosslinks, from poly- to tri-, di-, and monosulphidic crosslinks. Figure 9, representing the results of the sample without activator, illustrates this phenomenon. The fast increase after approximately 30 minutes reaction time of the products corresponding to 12- and 17-minutes retention time, is immediately followed by a gradual decrease of both these products. The product corresponding to the 10-minutes retention time subsequently increases, clearly indicating the increase of short crosslinks at the expense of larger ones. With ZnO added as activator, the rate of product formation as well as the amount of reaction products turns out to be lower and the distribution of the products slightly different, as shown in Figure 10. In both systems, however, the reaction product with the retention time of 10 minutes increases, whereas the others level off or even decrease. The developments of the crosslinked products of the samples with ZnClay as activator are depicted in Figure 11. The amount of reaction products formed in these samples is considerably higher than without any activator or with ZnO present, and the products are formed at shorter reaction times. Concerning the distribution of the crosslinked products, no significant differences between ZnClay and the two other systems are observed.

Conclusions

In sulphur vulcanisation of s-SBR compounds, CaO and MgO are suitable alternatives to ZnO as activators, albeit with a slightly lower cure rate and state of cure.

Particularly zinc-m-glycerolate is also a good substitute for ZnO as activator, without detrimental effects on the cure characteristics. The differences in activity of the

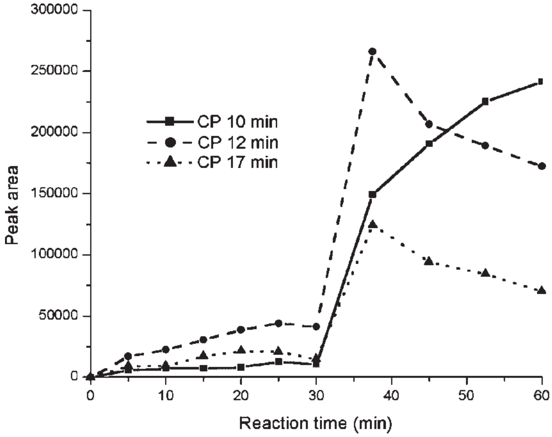

Figure 9.
Crosslinked products (CP) concentration of a sample without activator.

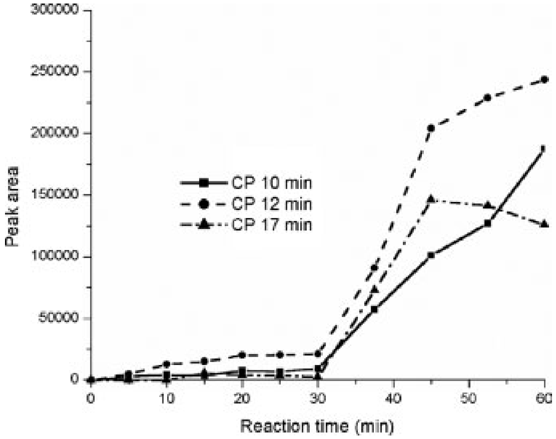

Figure 10.
Crosslinked products (CP) concentration of a sample with ZnO.

other zinc-complexes tested can be related to the strength of the coordination bonds in these zinc-complexes. Furthermore, their activity can be affected by sterical hindrances caused by the substituents, and the basicity of the ligands. The higher activity of zinc-m-glycerolate compared to zinc-stearate is in agreement with the concept that the accelerating properties of activators and accelerates are a function of their basicity.

Experiments with ZnClay have shown that with only 5 phr of ZnClay the cure and physical properties of s-SBR compounds are grossly comparable with the ones obtained with a standard amount of 3 phr ZnO. The zinc concentrations in the applied quantities of 5 and 2.5 phr ZnClay correspond to ~0.3 and ~0.15 phr ZnO, respectively. Thus, a significant reduction of the zinc concentration with a factor 10 to 20 is possible, without significantly jeopardising the curing and physical properties of the rubber products.

By means of MCV additional information about the reactions and chemical mechanisms in real rubber vulcanisates can be obtained, though it is sometimes difficult to reach clear conclusions because of the great many reactions and products

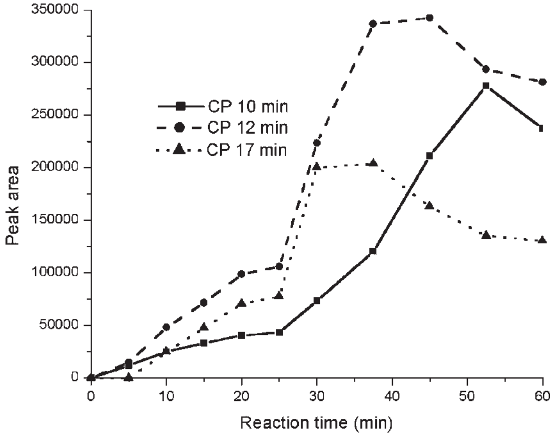

Figure 11.
Crosslinked products (CP) concentration of a sample with ZnClay.

involved in the sulphur chemistry. A somewhat faster formation of reaction products or 'crosslinking' is observed. The latter is also observed to some extent in the s-SBR compounds, demonstrated by the slightly shorter scorch time. Based on the results it can be concluded that systems with Zn^{2+}-ions provided on a support represent a new route to reduce zinc-levels, and therefore to minimise its environmental impact.

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