

Efficiency of Metal Activators of Accelerated Sulfur Vulcanization

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SYNOPSIS

The effects of copper, mercury, nickel, zinc, cadmium, indium, magnesium, and calcium stearates on the course of *N*-cyclohexyl-2-benzthiazylsulphenamide-accelerated sulfur vulcanization of natural rubber have been investigated on the basis of curemeter measurements at 145°C. The differences in the efficiencies of these metal activators of accelerated sulfur vulcanization have been discussed from the points of view of the electron configurations of the metals and their affinities to sulfur. We attempted to determine why zinc oxide is generally accepted as the best metal vulcanization activator. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The early process of rubber vulcanization discovered over 150 years ago involved heating natural rubber with sulfur alone¹ or with sulfur and lead oxide.² In the 1910s, it was found that addition of organic accelerators not only significantly increased the rate of vulcanization but also improved the quality of vulcanized rubber.³

During the 1920s, it was discovered that addition of zinc oxide and fatty acid, particularly stearic acid, substantially activated the vulcanization process and also improved the properties of the product. During the 1950s, a free radical mechanism of accelerated sulfur vulcanization was described and into the 1960s an ionic mechanism developed. At the present time, there is a feeling that vulcanization, being a complicated process involving reactions in hetero- and homogeneous phases, may be a mixture of ionic and radical pathways.^{4,5}

At the same time, it is clear that the role of zinc oxide in the activation of accelerated sulfur vulcanization has not been satisfactorily explained. It is known that zinc cations from zinc oxide and/or zinc stearate react with organic accelerators, giving zinc-accelerator complexes. These coordination compounds, and cadmium analogs, have been charac-

terized spectroscopically and crystallographically.⁴ But, why zinc oxide is generally known as the best activator of accelerated sulfur vulcanization is not clear enough. Our recent study⁶ on the stability of metal, particularly zinc and cadmium, complex compounds can be seen as a preliminary answer to this question.

The aim of the present work is to prove if the efficiency of metal activators is in accord with the stability of corresponding metal complex (coordination) compounds. For this reason, the influence of different metal stearates on the course of sulfenamide-accelerated sulfur vulcanization of natural rubber (NR) has been studied.

EXPERIMENTAL

Materials

The NR, pale crepe, is from the Malayan Rubber Fund Board. The stearic acid, stearin, is from STZ (Ustí n/L, Czechoslovakia). The sulfur (powder) is oil-treated (lubricated), with an elementary sulfur content of 93.7% (Lachema, Nový Bohumín, Czechoslovakia). *N*-Cyclohexyl-2-benzthiazylsulphenamide (CBS), Sulfenax CB, is from Istrochem (Bratislava, Czechoslovakia). Zinc stearate is from Chemische Werke Buna (Germany). Cadmium stearate, magnesium stearate, and calcium stearate are from STZ. Copper, mercury, nickel, and indium stearates were prepared in our laboratory.

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Preparation of Stearates

Stearic acid was neutralized with an equimolar amount of potassium hydroxide in boiling water. Thus, originally insoluble stearic acid was transformed into soluble potassium stearate.

Copper, mercury, nickel, and indium stearates were then precipitated from potassium stearate solution with salt solutions of respective metals. Stearate precipitates were washed thoroughly with water and then air dried at room temperature.

Compounding

The mix formulation in weight parts was: NR, 100; sulfur, 2; CBS, 1; metal stearate, variable.

Metal stearates were dosed in "mol parts," equimolarly to 0.5, 1.5, 3.0, 4.5, 6.0, and 8.0 phr zinc stearate.

NR with additives were mixed in a laboratory internal mixer, chamber volume 50 cm³, at temperatures between 50–60°C. Individual additives were added to NR in the following order: metal stearate and CBS during the first minute of mixing and sulfur after the next 4 min. The total mixing time was 7 min.

Two-millimeter thick sheets were prepared from the mixtures on an electrically heated two-roll mill, cylinder dimensions 100 × 200 mm, at 50°C.

Curemeter Measurements

The rubber compounds were cured at 145°C in a VUREMO curemeter, an instrument used to measure VULcanization, RELaxation, and MODulus. The apparatus and curemeter measurements have been completely described in our recent publication.⁷

The oscillation angle was 1° and the oscillation rate 2 min⁻¹. The extent of crosslinking (modulus in torsion), M , was expressed in kPa and plotted against time of cure. Thus, the cure curves were obtained. A three-parameter exponential function was used for the description of cure curves, i.e.,

$$M - M_{\min} = (M_{\max} - M_{\min}) \cdot (1 - e^{-k(t-t_i)})$$

where M_{\min} and M_{\max} are the minimum and maximum modulus values (kPa) of the vulcanizing mixture, respectively, M is a modulus value at any time t (min), k is the first-order rate constant of the crosslinking reaction (min⁻¹), and t_i is the induction period (min).

RESULTS AND DISCUSSION

Table I shows that copper stearate does not influence hardly (decreases slightly) the extent of crosslinking, but by increasing its concentration it decreases significantly the rate of sulphenamide-accelerated sulfur vulcanization of natural rubber. This finding can be explained on the basis of the known fact that metal atoms with nonfull orbits form the most stable complex compounds⁸ that cannot function as sulfurating reagents. Copper has atoms with a nonfull orbit. And, so has nickel. 3*d*-orbits of its atoms have one more vacancy than 4*s*-orbits of copper atoms. Nevertheless, by increasing nickel stearate concentration in the rubber mix the extent of its crosslinking is increased, too. On the other hand, mercury stearate is only slightly more effective than copper stearate; even mercury cation has full *d*-orbit (Hg²⁺/Xe/4*f*¹⁴5*d*¹⁰) and could form then a less strong coordination bond with a sulfur atom having nonfull *p*-orbit (S/Ne/3*s*²3*p*⁴) than nickel cation and hence could be a more effective activator.

The explanation for these inconsistencies can be based upon the observation of a vulcanizate color, which is black in the presence of practically ineffective copper and mercury stearates. Cu²⁺ and Hg²⁺ cations have namely great affinity to sulfur, about which very small solubility product values of their sulfides (Table II) give evidence. In connection with the indubitable sulfide formation, it can be asked if coordination compounds containing Cu²⁺ and Hg²⁺ cations and accelerator ligands are formed at all. An Ni²⁺-containing complex is formed undoubtedly and is more stable than a Zn²⁺-containing one as nickel stearate is a less effective vulcanization activator than zinc stearate. This follows unambiguously from the comparison of kinetic parameters of vulcanization shown in Table I. Nickel sulfide solubility product value is also by many orders greater than those of copper and mercury sulfides and even by one order greater than that of zinc sulfide.

Cadmium and indium cations have structures of the first possible coordination spheres analogous to that of zinc cation: Cd²⁺/Kr/4*d*¹⁰, In³⁺/Kr/4*d*¹⁰, Zn²⁺/Ar/3*d*¹⁰. Their full *d*-orbits could lead to coordination bonds of less strength than in the case of nickel. For this reason, stearates derived from these metals could be more effective activators of sulfur vulcanization than nickel stearate. This is, however, true in the case of zinc stearate and in that of maybe slightly more effective cadmium stearate; even the value of solubility product of cadmium sulfide is by four orders lower than that of zinc sulfide (Table II).

Table I Effect of Metal Stearates on the Vulcanization of NR Cured with Sulfur (2 phr) in the Presence of CBS (1 phr) at 145°C

Stearate	Concentration (mol parts)	t_i (min)	t_{90} (min)	k (min ⁻¹)	$M_{\max} - M_{\min}$ (kPa)
—	—	4.0	6.0	1.2	55
Copper	1.5	5.0	13.0	0.29	50
	4.5	6.0	19.0	0.175	50
	6.0	6.5	22.0	0.148	50
Mercury	1.5	4.5	9.0	0.54	50
	4.5	7.0	12.0	0.46	55
	6.0	7.5	14.5	0.33	65
Nickel	0.5	4.0	6.0	1.2	50
	1.5	3.5	7.0	0.66	70
	3.0	3.5	9.5	0.38	90
	4.5	4.0	13.5	0.24	110
	6.0	4.0	16.5	0.184	125
	8.0	3.5	20.0	0.139	135
Zinc	0.5	5.0	7.0	1.2	60
	1.5	3.0	5.5	0.92	110
	3.0	6.5	10.0	0.66	140
	4.5	6.5	10.5	0.58	145
	6.0	7.5	13.0	0.42	150
	8.0	8.0	15.5	0.31	165
Cadmium	0.5	3.5	4.5	2.3	75
	1.5	2.5	5.5	0.76	100
	3.0	3.0	5.5	0.92	120
	4.5	3.0	8.5	0.42	145
	6.0	3.0	13.5	0.22	165
	8.0	3.0	20.0	0.135	190
Indium	0.5	3.5	6.0	0.92	60
	1.5	4.5	8.0	0.66	100
	3.0	4.5	9.5	0.46	115
	4.5	4.5	9.5	0.46	125
	6.0	7.5	13.0	0.42	125
Magnesium	1.5	3.0	4.5	1.5	55
	4.5	3.5	5.5	1.1	50
	6.0	3.5	5.5	1.1	50
Calcium	1.5	3.5	4.5	2.3	55
	4.5	3.5	4.5	2.3	50
	6.0	3.5	4.5	2.3	50

The lower activation efficiency of indium stearate in comparison with those of zinc and cadmium stearates is probably connected with the higher oxidation number of indium (+3) in comparison with oxidation numbers of zinc and cadmium stearates (+2).

In the cases of metals of the magnesium group, the probability of a complex formation is small. That is why ionic rather than covalent character of bonds in compounds of these metals causes their inability to form complexes with ligands containing sulfur

and/or nitrogen.^{6,10} This fact excludes the possibility of a complex formation of the type of an active sulfurating vulcanization intermediate. The extent of vulcanization values shown in Table I proves this clearly. The basic character of magnesium and calcium stearates is the reason for the acceleration of sulfur vulcanization of rubber by an analogous way as in the cases of currently used basic accelerators. The greater basicity of calcium in comparison with that of magnesium¹¹ is in good accordance with

Table II Order Values of Solubility Products, K_s , of Selected Bivalent Metal Sulfides

	Sulfide				
	HgS	CuS	CdS	ZnS	NiS
K_s	10^{-52}	10^{-46}	10^{-29}	10^{-25}	10^{-24}

From ref. 9.

greater vulcanization rate constant values of rubber compounds containing calcium stearate.

With the metals that can form metal-accelerator complexes, the vulcanization rate constant values are lower and even decrease with increasing concentration of the metal stearates in rubber compounds. This finding cannot be elucidated without taking into account the effect of these metal stearates on the ultimate extent of crosslinking. By increasing these metal stearates' concentration, the ultimate extent of crosslinking values are significantly increased, too (about three times in comparison with those for compounds without metals or with metals that cannot form metal-accelerator complexes). Considering that a time dependence of the extent of crosslinking (cure curve) is of logarithmic (first-order) character, a significant increase in the ultimate extent of crosslinking must result in a more significant decrease in the first-order rate constant value at a constant actual rate of crosslinking reaction. Thus, decreases in the vulcanization rate constant with increasing concentrations of zinc, cadmium, and nickel stearates (Table I) are not probably done by the decreases in the actual rates of crosslinking reaction but rather by significant increases in the ultimate extents of crosslinking.

CONCLUSIONS

Irving and Williams¹² found the order Cu^{2+} , Ni^{2+} > Zn^{2+} > Mg^{2+} , Ca^{2+} for the stability of metal complexes irrespective of the nature of the coordinated ligand or the number of ligand molecules involved. A theoretical justification for this stability order follows from considerations of the reciprocal of the ionic radii and the second ionization potentials of the metals concerned.

On the basis of experimental results obtained, their discussion, and in accordance with Irving's and Williams' finding,¹⁰ the following order for the stability of metal complexes with accelerator ligands

can be presented: Cu^{2+} , Hg^{2+} > Ni^{2+} , Zn^{2+} , Cd^{2+} , In^{2+} > Mg^{2+} , Ca^{2+} .

The most stable copper and mercury complexes can form no active sulfurating vulcanization intermediate if coordination compounds containing copper and mercury cations and accelerator ligands are formed at all due to the great affinity of these metals to sulfur, leading to very small solubility product values of the respective metal sulfides.

Magnesium and calcium have only a slight tendency to form complexes. This fact eliminates the possibility of formation of an active sulfur-containing complex.

Nickel, zinc, cadmium, and indium have a definite ability to form complexes, but they form significantly less strong coordination bonds than, e.g., copper and mercury. This is why these metals, especially zinc and cadmium, form active sulfurating vulcanization intermediates.

While cadmium is generally accepted now as a healthily hazardous metal, zinc oxide is really the best metal activator of sulfur vulcanization, giving active zinc-accelerator complexes (vulcanization intermediate compounds).

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