

A Differential Scanning Calorimetric Study of the Interaction of Zinc Benzothiazole-2-Thiolate, Sulfur, Stearic Acid, and Zinc Stearate in the Absence and Presence of Polyisoprene

ADRIAAN S. LUYT

Department of Chemistry, Vista University (Soweto Campus), Private Bag X09, Bertsham, 2013, South Africa

SYNOPSIS

The interactions between mixtures of zinc benzothiazole-2-thiolate (ZMBT), sulfur, stearic acid, and zinc stearate were studied by DSC in the absence and presence of polyisoprene (IR). It was established that ZMBT reacts with stearic acid to form zinc stearate and 2-mercaptobenzothiazole (MBT). In the presence of stearate compounds, MBT is readily available from the start of vulcanization, whereas it becomes only slowly available in the absence of these compounds. The effectiveness of the vulcanization process increases for the systems IR/ZMBT/sulfur < IR/ZMBT/sulfur/stearic acid < IR/ZMBT/sulfur/zinc stearate. In view of the above results, interaction mechanisms are proposed for the different systems. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The investigation of zinc benzothiazole-2-thiolate (ZMBT) as a vulcanizing agent is normally restricted to structural studies and discussions on its role as a possible intermediate in the vulcanization process where 2-mercaptobenzothiazole (MBT) and 2,2'-dibenzothiazole (MBTS) are used as vulcanization accelerators.

Brydson,¹ in his discussion on the course of the vulcanization reaction, proposes that ZMBT is formed when MBT or MBTS reacts with Zn^{2+} in the presence of a fatty acid. ZMBT then reacts with sulfur to form perthiomercaptides that react with the rubber hydrocarbon to form rubber-bound intermediates. Luyt^{2,3} supported the idea, but added that ZMBT also forms in the absence of a fatty acid like stearic acid. Further support for this line of reasoning comes from Allen et al.⁴ to whom McCleverty referred in his study on the inorganic chemistry related to rubber vulcanization.⁵

McCleverty, however, stated that $[Zn(BTS)_2]_n$ is oligo- or polymeric and that it is unreactive toward

S_8 . He proposed that the structure of ZMBT contains $[Zn(BTS)_3(H_2O)]^-$, which is more reactive toward sulfur. He further stated that stearic acid, especially in the form of stearate, might form 1 : 1 adducts with ZMBT. Datta⁶ investigated the behavior of a related compound, zinc mercaptobenzimidazole (ZMB). He found that ZMB decomposes in the presence of H_2O_2 to form mercaptobenzimidazole (MB), zinc oxide, and water.

This paper reports on a DSC study of (i) a variety of dry mixtures of the different curatives and (ii) the influence of different curative combinations on the dynamic vulcanization of polyisoprene.

EXPERIMENTAL

ZMBT was prepared in our own laboratory by dissolving MBT in a sodium hydroxide solution, after which zinc sulfate solution was added. The ZMBT, which immediately precipitated, was filtrated and then purified by washing it in a Soxhlet apparatus with water, benzene, and acetone. All the other curatives were commercially available AR-grade materials. Experimental details were given in previous

Table I Grams of Ingredients in Compounds Investigated

Compound	IR	ZMBT	Sulfur	Stearic Acid	Zinc Stearate
1	20.6	2.55	1.76		
2	20.6	2.55	1.76	1.96	
3	20.6	2.55	1.76		4.35

papers.^{2,7} The amounts of ingredients mixed into the rubber are summarized in Table I.

calorimeter and interpreting the results through (ii) using a hot-stage microscope under similar conditions.

RESULTS AND DISCUSSION

A. Interactions between Dry Curatives

The mutual interactions of the curatives in different combinations of the dry substances were studied by (i) heating the dry mixture in a differential scanning

ZMBT/Sulfur/Zinc Oxide

In this combination, only the sulfur was observed to melt with two endotherms, indicating $S_\alpha \rightarrow S_\lambda$ and $S_\beta \rightarrow S_\lambda$ transitions (Fig. 1) in contrast to the ZMBT/sulfur combinations where all three of the well-known solid-state phase transitions of sulfur

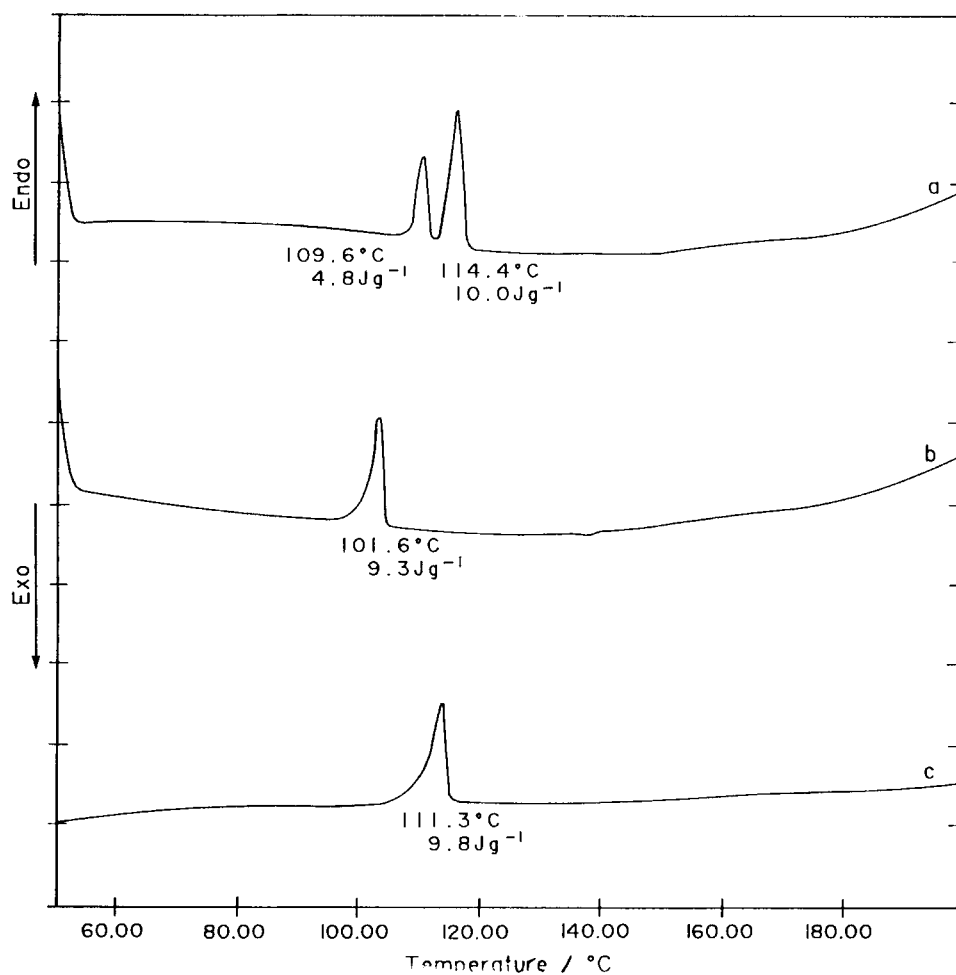


Figure 1 DSC curves for ZMBT/S/ZnO: (a) heating; (b) reheating; (c) reheating after cooling at 0°C for 15 h.

were observed. On the immediate reheating of the sample, a single peak appeared at a temperature corresponding to that of the $S_\alpha \rightarrow S_\beta$ transition of pure sulfur, while the peak appeared at a temperature corresponding to that of the $S_\beta \rightarrow S_\lambda$ transition when heated after being held at 0°C for 15 h. No interactions between sulfur and any of the zinc compounds were observed.

ZMBT/Stearic Acid

An endotherm was observed at about 50°C (Fig. 2), indicating stearic acid melt. A second endotherm was also observed at about 103°C , which corresponds to the melt temperature of zinc stearate. This indicates a reaction between ZMBT and stearic acid to form *inter alia* zinc stearate. On immediate reheating of the sample, a much larger endotherm was observed in the same temperature area, indicating a more complete formation of zinc stearate. The

DSC curve of the sample held at a low temperature shows a second peak at about 122°C that cannot be explained with the available information. Observations on the hot-stage microscope confirm the melting of stearic acid and subsequent reaction with ZMBT.

ZMBT/Sulfur/Stearic Acid

These DSC curves (Fig. 3) can be explained in a similar way as above, with the exception that (i) the Zn^{2+} /stearic acid reaction exotherm can clearly be observed together with (ii) the sulfur melt peak at about 115°C . On immediate reheating of the sample, only the zinc stearate melt endotherm was observed with an indication of an overlapping peak. This should be the case, because the sulfur melt peak on immediate reheating starts at almost the same temperature as does the zinc stearate melt peak. Heating of the sample held at a low temperature

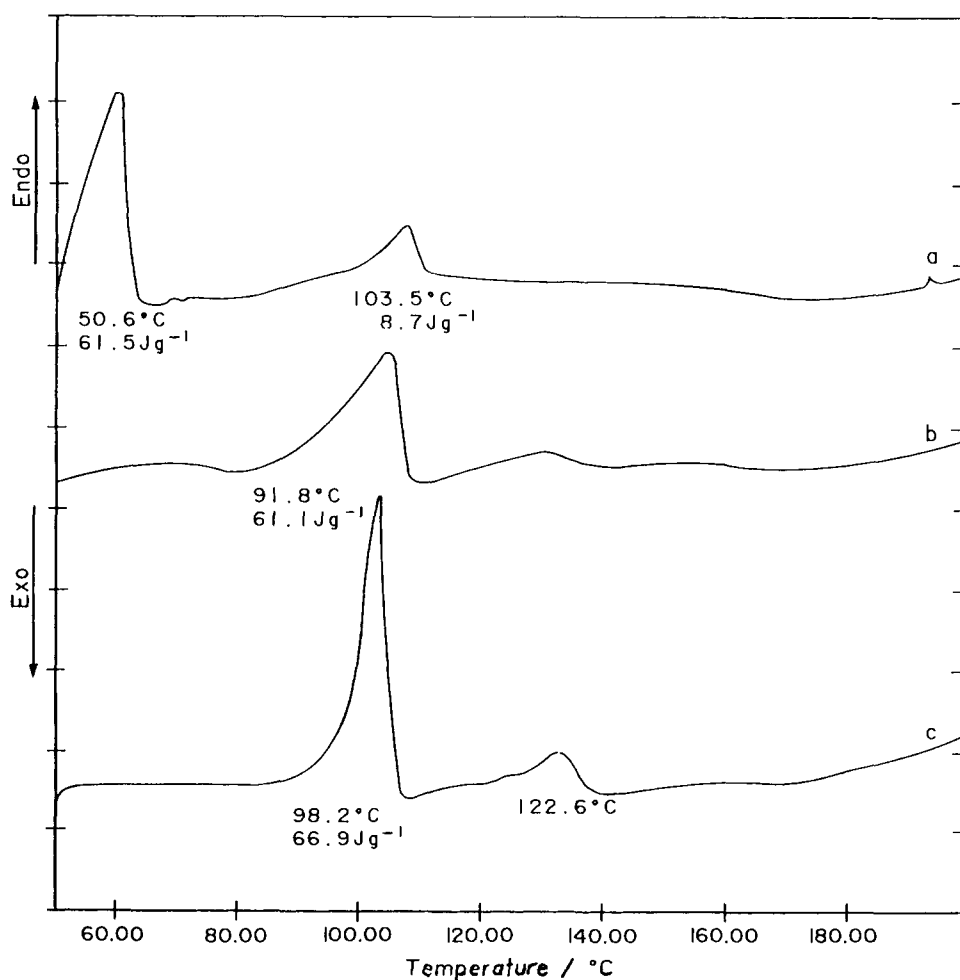


Figure 2 DSC curves for ZMBT/stearic acid: (a) heating; (b) reheating; (c) reheating after cooling at 0°C for 15 h.

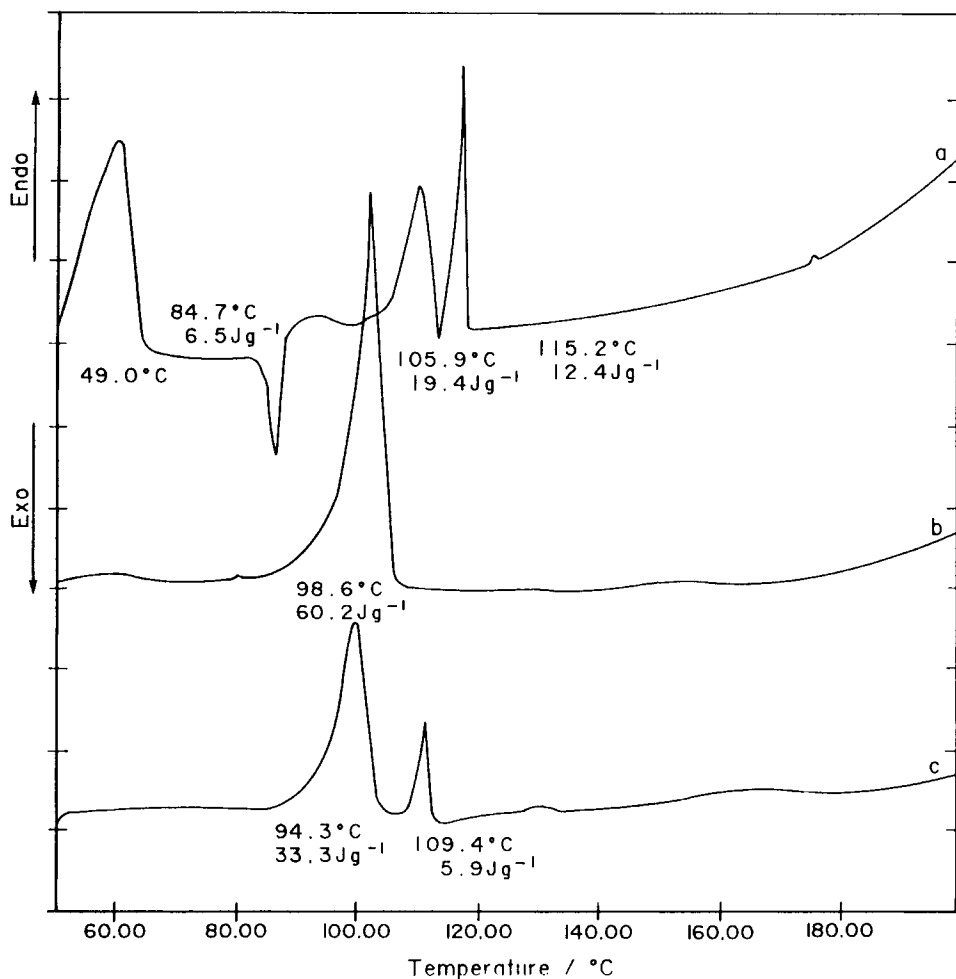


Figure 3 DSC curves for ZMBT/S/stearic acid: (a) heating; (b) reheating; (c) reheating after cooling at 0°C for 15 h.

clearly shows the respective zinc stearate and sulfur melt peaks. Because of a series of thermal events, it was not possible to clearly confirm the DSC results through hot-stage microscopy.

ZMBT/Stearic Acid/Zinc Oxide

This DSC curve (Fig. 4) looks similar to those of the previous two cases, with the exception that a much stronger interaction exotherm was observed with the zinc stearate melt peak visibly larger. It appears that Zn^{2+} is more readily available when ZnO is also present. A strange observation, which cannot be explained at this stage, is the total absence of any peak on immediate reheating of the sample. The normal zinc stearate melt peak does, however, appear on reheating of the sample held at a low temperature.

ZMBT/Sulfur/Stearic Acid/Zinc Oxide

Nothing new can be added to the explanation of these curves (Fig. 5) than was already mentioned in the previous explanations. It seems as if the only reaction occurring is that between Zn^{2+} (from both ZMBT and ZnO, but more readily from ZnO) and stearic acid to form zinc stearate.

ZMBT/Sulfur/Zinc Stearate

All three curves (Fig. 6) clearly show overlapping endotherms for the melting of sulfur and zinc stearate (as explained before). No reaction was observed, although the smaller peak areas on the reheat curves may indicate reaction with ZMBT, resulting in the melting of smaller amounts of sulfur and zinc stearate.

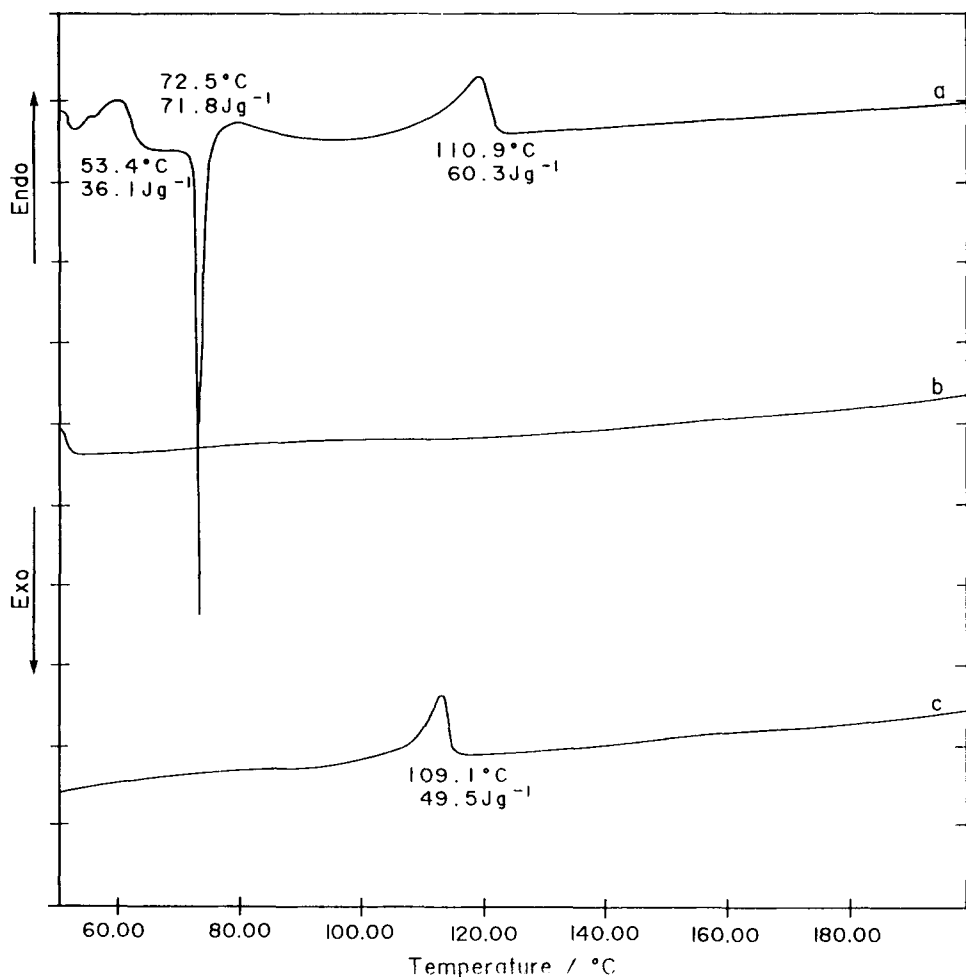


Figure 4 DSC curves for ZMBT/stearic acid/ZnO: (a) heating; (b) reheating; (c) re-heating after cooling at 0°C for 15 h.

To summarize, one can establish with relative certainty that ZMBT reacts with molten stearic acid to form zinc stearate, which, during vulcanization, makes Zn^{2+} more available.² It also seems as if sulfur reacts with the MBT that becomes available when ZMBT lets off Zn^{2+} during reaction with stearic acid.

B. Interactions in the Presence of Polyisoprene

Figure 7 shows the dynamic vulcanization of polyisoprene in the presence of ZMBT/sulfur, ZMBT/sulfur/stearic acid, and ZMBT/sulfur/zinc stearate, respectively. It appears that the rate of vulcanization is not influenced remarkably by the presence of either stearic acid or zinc stearate. The onset of vulcanization is, however, at a lower temperature in the presence of the stearate compounds. It is also

conspicuous that the vulcanization reaction is considerably less energetic in the presence of these compounds. With stearic acid present, a weak zinc stearate melting peak is observed before the onset of vulcanization. This is to be expected in view of the reaction between ZMBT and stearic acid as explained in the previous section.

The DSC cure curve of polyisoprene in the presence of ZMBT/sulfur corresponds well to the curve obtained for polyisoprene in the presence of MBT/sulfur/ ZnO ,² but there is no comparison between curves (b) and (c) in this figure and those with stearate compounds in the presence of MBT and MBTS, respectively.^{2,3}

Analysis of IR/ZMBT/sulfur samples after heating to 160°C (which is just before the onset of vulcanization) shows that no vulcanization occurred. In comparison, both the samples that contained

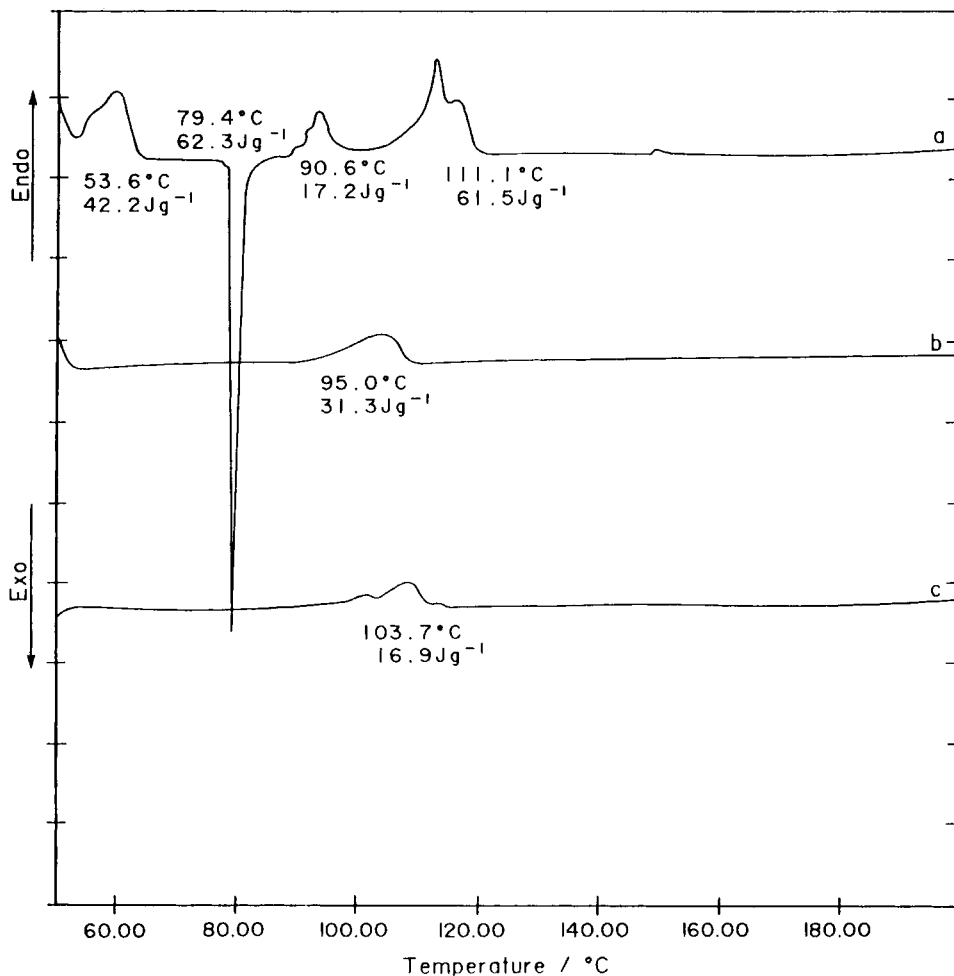


Figure 5 DSC curves for ZMBT/S/stearic acid/ZnO: (a) heating; (b) reheating; (c) reheating after cooling at 0°C for 15 h.

stearate compounds show signs of cross-linking (Table II) when heated to 155°C, which also is before the onset of the vulcanization peak (Fig. 7). The IR/ZMBT/sulfur system shows a very low polysulfidic cross-link density at 170°C, increasing rapidly up to 180°C, after which it decreases. The monosulfidic cross-link density increases steadily, with the total cross-link density relatively low, showing the expected reversion after 180°C. The IR/ZMBT/sulfur/stearic acid system shows a similar cross-link density trend, but the values are somewhat higher than in the absence of stearic acid. With zinc stearate present, the cross-link densities are significantly higher and, contrary to the other systems, the monosulfidic and polysulfidic cross-link densities maintained generally the same values.

In all three systems, the original concentrations of ZMBT and S₈ are, respectively, 27.6 and 30.3

mmol mL⁻¹. If all the ZMBT decomposes, the available MBT will be 55.2 mmol mL⁻¹. In all three systems, about one-third of the sulfur was consumed at the start of vulcanization (Table II)—in every case, the concentration of extractable sulfur decreases until it reaches a zero value at a temperature immediately after the peak maximum. The extractable MBTS remains at a constant low value, which may be attributed to experimental error. The extractable MBT in the case of the IR/ZMBT/sulfur system starts at a low value and increases steadily—the reason for this may be that the ZMBT does not decompose as readily in the absence of stearate. In both the other systems, the extractable MBT remains approximately constant at half the value expected should ZMBT fully decompose.

The proposed reactions for the IR/ZMBT/sulfur system are

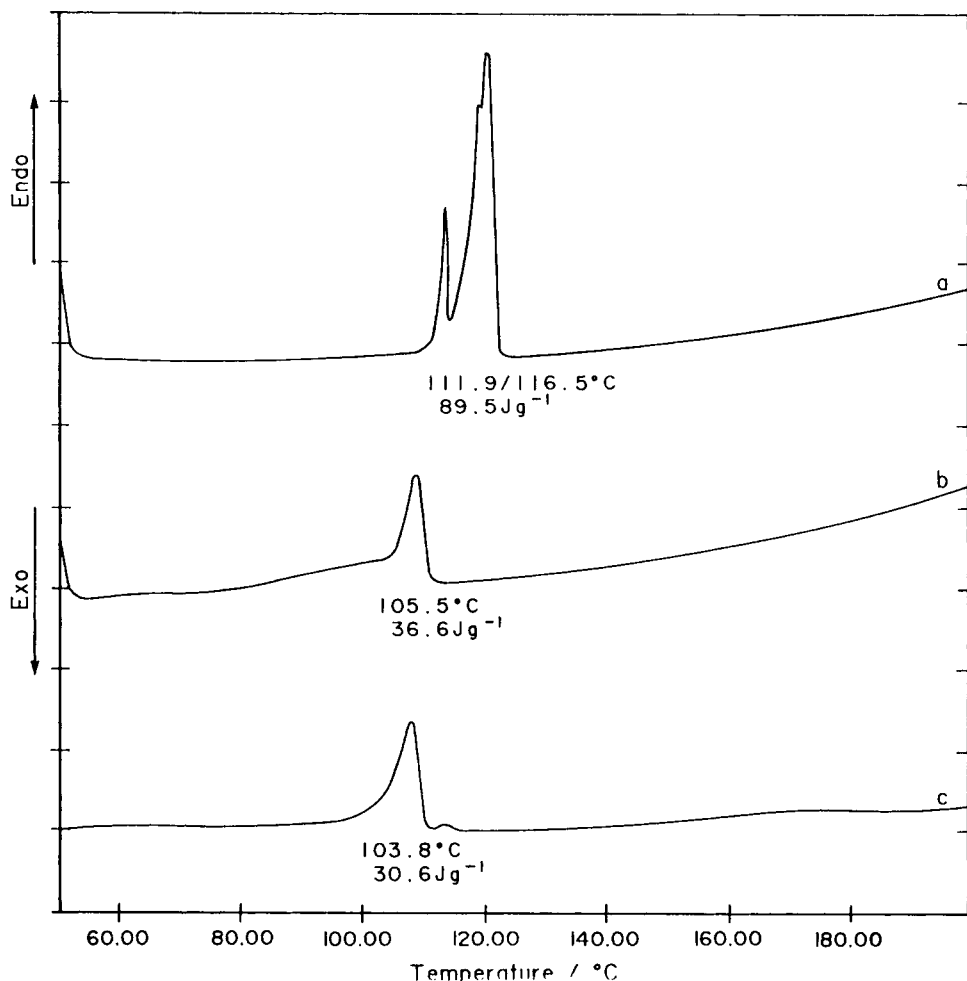
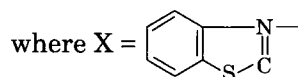
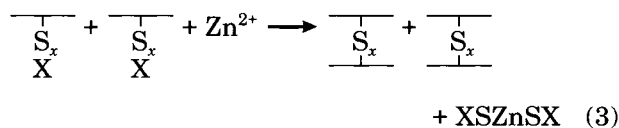
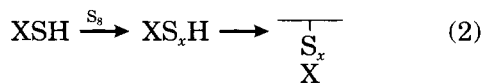
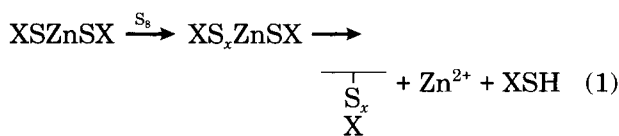
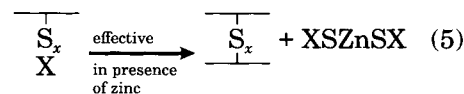
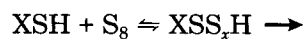
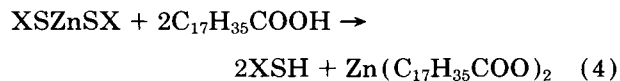


Figure 6 DSC curves for ZMBT/S/zinc stearate: (a) heating; (b) reheating; (c) reheating after cooling at 0°C for 15 h.



This mechanism explains the steady formation of extractable MBT.

According to Datta,⁶ ZMB decomposes in the presence of H₂O₂ to form MB. As described earlier, ZMBT undergoes a similar type of reaction in the presence of stearic acid to form MBT and zinc stearate. This explains the immediate availability of MBT as well as the observation of the zinc stearate melting peak before vulcanization. In the IR/ZMBT/sulfur/stearic acid system, the following reactions are proposed to play a role:



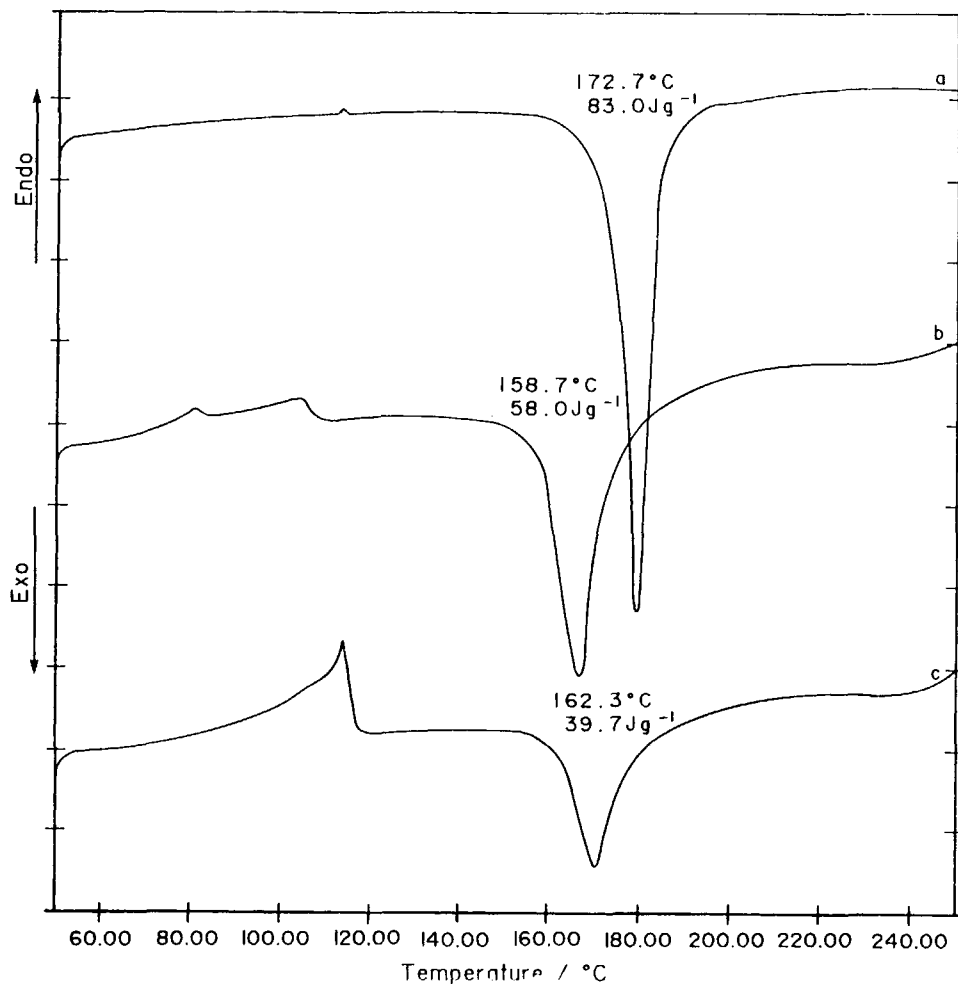
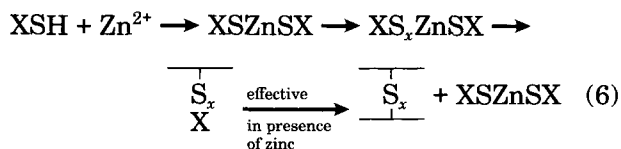


Figure 7 DSC cure curves for (a) IR/ZMBT/S (17.64 mg); (b) IR/ZMBT/S/stearic acid (17.40 mg), and (c) IR/ZMBT/S/zinc stearate (5.92 mg).

Table II Cross-link Densities and Amounts of Extractables during Vulcanization of (a) IR/ZMBT/S, (b) IR/MBTS/S/Stearic Acid, and (c) IR/MBTS/S/Zinc Stearate

Termination Temp (°C)		10 ³ Cross-Link Density (mmol mL ⁻¹)			10 ² Extractables (mmol mL ⁻¹)		
		Mono-S	Poly-S	Total	MBT	MBTS	S
155	(b)	5.85	28.0	33.9	31.4	0.42	18.6
	(c)	42.2	43.1	85.3	27.3	1.01	17.3
160	(a)	No vulcanization observed—sample dissolved in benzene					
165	(b)	17.3	56.2	73.5	37.1	0.71	5.93
	(c)	65.4	85.3	151	32.3	0.51	9.78
170	(a)	0.00	2.47	2.47	6.92	0.96	20.3
175	(b)	9.79	38.6	48.4	26.9	1.18	0.53
	(c)	60.0	85.7	146	26.4	1.39	2.89
180	(a)	11.6	52.6	64.2	16.0	0.81	3.62
185	(b)	10.9	20.1	31.0	25.1	1.11	0.00
	(c)	49.8	44.0	93.8	27.4	1.64	0.00
190	(a)	15.5	17.5	33.0	24.6	1.57	0.00



As described in earlier publications,^{2,3} the presence of Zn^{2+} makes the total vulcanization process more effective.

For the system IR/ZMBT/sulfur/zinc stearate, the cross-link densities obtained are much higher, which points to the process being more effective. The reason for this is the immediate availability of Zn^{2+} from zinc stearate, which catalyzes cross-link formation. In contrast to the IR/ZMBT/sulfur/stearic acid system, where Zn^{2+} only becomes available after reaction between ZMBT and stearic acid, the Zn^{2+} is in this case immediately available after zinc stearate melting. The primary reaction mechanism for this system therefore corresponds to the proposed mechanism for the IR/ZMBT/sulfur system (reactions 1, 2, and 3) except that the higher immediately available concentration of Zn^{2+} makes the process a lot more effective.

In conclusion, it may be stated that the availability of Zn^{2+} independent of what its source is is an all important factor in the optimization of the vulcanization process. Therefore, the exact role of

Zn^{2+} in the vulcanization of IR using MBT-related accelerators is presently under investigation.

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