

A DSC Study of Curative Interactions. II. The Interaction of 2,2'-Dibenzothiazole with ZnO, Sulfur, and Stearic Acid

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SYNOPSIS

The interaction of combinations of sulfur, 2,2'-dibenzothiazole (MBTS), ZnO, and stearic acid were studied by differential scanning calorimetry. A MBTS/stearic acid interaction was indicated as evidenced by the effect the MBTS/stearic acid combination had on the melting of sulfur, the $S_{\alpha} \rightarrow S_{\beta}$ transition being suppressed in favor of a $S_{\alpha} \rightarrow S_{\lambda}$ transition. The dissolution/interaction of MBTS in molten sulfur was also delayed by the MBTS/stearic acid interaction, which, it is proposed, involved protonation of the N atom in MBTS by stearic acid. MBTS did not affect the formation of zinc stearate from ZnO and stearic acid, but when sulfur was added to the mixture, the ZnO/stearic acid reaction did not go to completion. No direct evidence for the formation of 2,2'-dibenzothiazole polysulphides was found, but the absence of the $S_{\lambda} \rightarrow S_{\mu}$ transition in sulfur/MBTS mixes was interpreted as indirect evidence of a reaction between these curatives. There was no evidence for the formation of a sulfur/MBTS/ZnO compound of the type generally attributed the role of an active sulfurating agent in accelerated sulfur vulcanization.

INTRODUCTION

2,2'-Dibenzothiazole (MBTS) is commonly used as an accelerator in sulfur vulcanization, but there have been few studies of its interaction with sulfur, stearic acid, and ZnO in the absence of rubber. Morita et al.¹ reported on differential thermal analysis experiments with various sulfur/sulfenamide blends. Coran² found infrared evidence for complex formation between MBTS and zinc stearate, but Milligan³ was unable to prepare benzene soluble complexes of MBTS and zinc carboxylates. Langenbeck and Rhiem^{4,5} investigated sulfur/MBTS interaction by determining the fusion temperature of various mixtures and obtained a temperature maximum at a composition corresponding to a compound with two sulfur atoms per MBTS molecule.

In a previous paper in this series⁶ (Part I), we reported on a differential scanning calorimetry (DSC) study of the interaction between sulfur, stearic acid, and ZnO. This paper reports on the

interaction of MBTS with the activator, coactivator, and sulfur in the temperature range of importance in vulcanization.

EXPERIMENTAL

2,2'-Dibenzothiazole was supplied by Karbochem. All curatives were industrial grade. Experimental details were given in the previous paper.⁶ In the legends to the figures, M_i refers to the mass before the DSC experiment, and M_f , to the mass after the rescan.

RESULTS AND DISCUSSION

MBTS

The off-white MBTS powder showed a sharp melting endotherm at 172.5°C when scanned to 190°C (Fig. 1). Melting ranges of 159–170°C (Ref. 7) and 170–175°C (Ref. 8) are found in the literature. On rescanning the sample, after it had been cooled rapidly to 50°C, a less intense, but broader melting peak occurred at 163°C. The mass reduction after the

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rescan was less than 0.3%, and the broader endotherm was ascribed to physical rather than to chemical changes in the sample.

MBTS/ZnO

No reaction peak was observed on heating an MBTS/ZnO mixture up to 200°C, and on rescanning a cooled sample, a broadish melting endotherm appeared. These spectra were virtually the same as those for pure MBTS (cf. Fig. 1).

MBTS/Stearic Acid

After the familiar stearic acid melting peak,⁶ a somewhat broad MBTS endotherm occurred at 158.5°C (Fig. 2). The endotherm initiated at 138°C, considerably lower than the temperature of 159°C at which the melting of pure MBTS initiated (cf. Fig. 1). The hot-stage microscope revealed that the endotherm coincided with the apparent dissolution of MBTS in stearic acid. Up to this temperature, solid particles of MBTS could be seen in the stearic acid melt, where small particles were seen to undergo Brownian movement. An exotherm above 170°C was

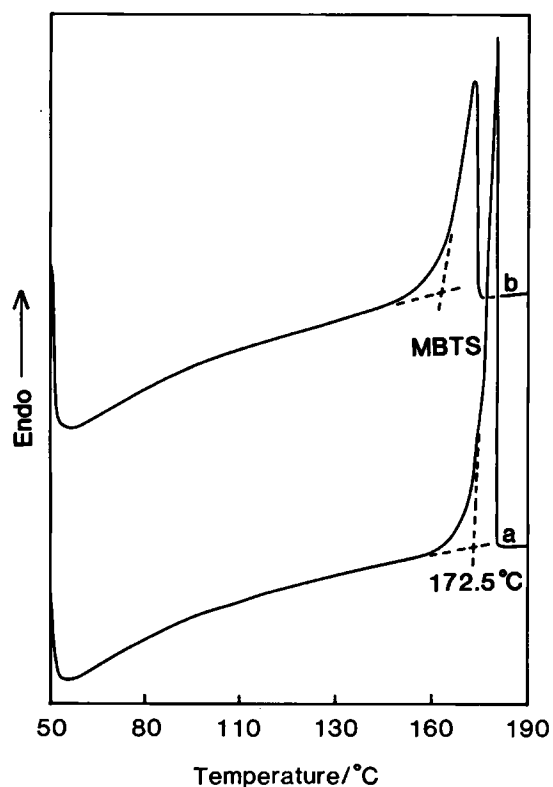


Figure 1 DSC thermograms of MBTS and a rescan after cooling to 50°C. $M_i = 1.700$ mg; $M_f = 1.695$ mg.

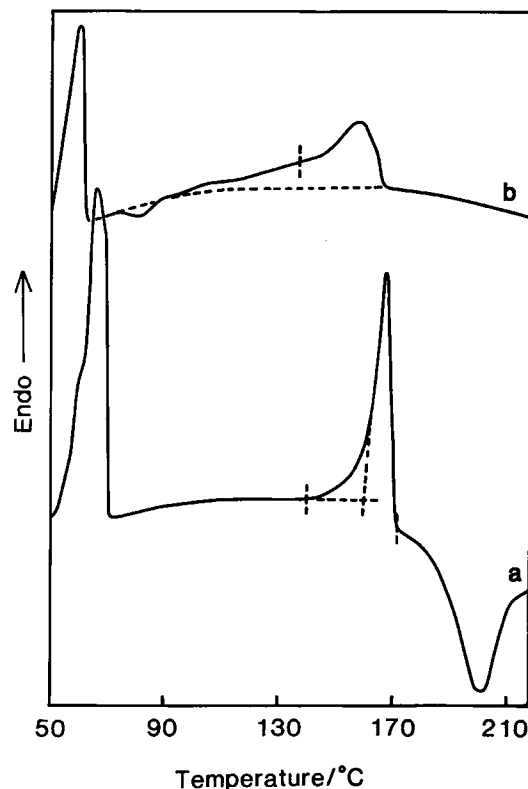


Figure 2 DSC thermograms of (a) MBTS/stearic acid (1.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after 72 h at -30°C. $M_i = 5.186$ mg; $M_f = 5.077$ mg.

attributed to an MBTS–stearic acid interaction, the exact nature of which was unknown. The sample was cooled, and after 72 h at -30°C, a rescan spectrum revealed a drastically reduced stearic acid melting peak. A broad endotherm followed and may, *inter alia*, have been associated with the dissolution of residual MBTS in the region above 135°C. No exotherm was observed above 170°C, but it is not known why the MBTS/stearic acid reaction did not go to completion. This high-temperature reaction, which led to a dark brown product, was not investigated further as it occurred well above normal vulcanization temperatures.

Sulfur/MBTS

Sulfur/MBTS blends, with mol ratios of 1.0/3.0, 1.0/1.0, and 3.0/1.0 were studied. In all cases, the melting of sulfur was observed, followed by an endotherm, the size of which increased as the amount of MBTS in the blend increased (Figs. 3–5). Heating of the samples on the hot-stage microscope revealed that the endotherm, following on the melting of sulfur, could be attributed to the apparent dissolution

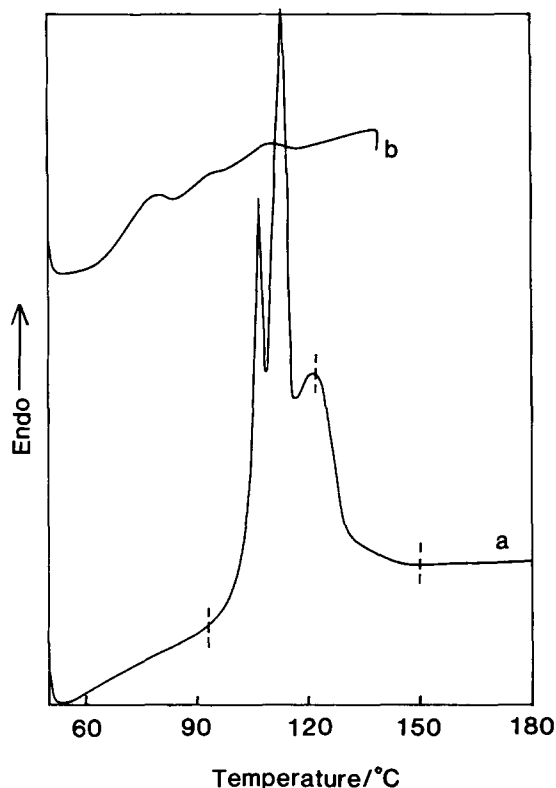


Figure 3 DSC thermograms of (a) sulfur/MBTS (3.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after 69 h at -30°C. $M_i = 7.633$ mg; $M_f = 7.622$ mg.

of MBTS in molten sulfur. Most importantly, the S_λ to S_μ transition⁶ was not present in the thermogram. This indicated that sulfur had undergone a reaction and was no longer present as sulfur-8 rings that could form polymeric sulfur.

On cooling the MBTS-rich blend (1.0/3.0 sulfur/MBTS mol ratio) at 5°C/min from 160°C, crystallization of MBTS from the sulfur/MBTS melt could be observed as an exotherm at 114°C [Fig. 4(b)]. Reheating the sample led to the reappearance of peak C1 [Fig. 4(c)]. A sample, cooled from 160°C and stored at -30°C for 69 h, showed an endotherm with an enthalpic value comparable to that of the original peak in the temperature region of C1. This underlined the fact that peak C1 in the original thermogram did not represent the MBTS-sulfur interaction, but merely reflected the enthalpy of dissolution of MBTS in sulfur.

The high viscosity that developed in the melt retarded crystallization on cooling. On reheating a sample that had been cooled rapidly from 160°C, the C1 endotherm was preceded by an exotherm with a trough at 76°C [Fig. 4(d)]. The exotherm was attributed to crystallization MBTS from the sulfur/

MBTS solution, crystallization of which was prevented by rapid cooling to a temperature where molecular mobility was severely restricted. The rescan thermogram of mixes with a high sulfur content (Fig. 3) was featureless, due to the reluctance of the mixture to crystallize. Neither a sulfur nor an MBTS dissolution endotherm was observed.

The literature suggests a sulfur/MBTS reaction to yield 2,2'-dibenzothiazole polysulfides (MBTP). Ultraviolet spectrophotometric studies on NR/sulfur/MBTS and NR/sulfur/MBTS/zinc stearate vulcanization systems revealed that MBTP was formed in the cure delay period prior to vulcanization.^{9,10} Since the maximum concentration of these polysulfides coincided with the onset of cross-linking, this component was considered as a likely precursor to cross-linking. An average of five sulfur atoms per molecule of MBTS was estimated with polarography in the NR/sulfur/MBTS/zinc stearate compound.¹⁰ Langenbeck and Rhiem^{4,5} investigated the sulfur/MBTS interaction by setting up a fusion point vs. composition curve and, on the basis of their

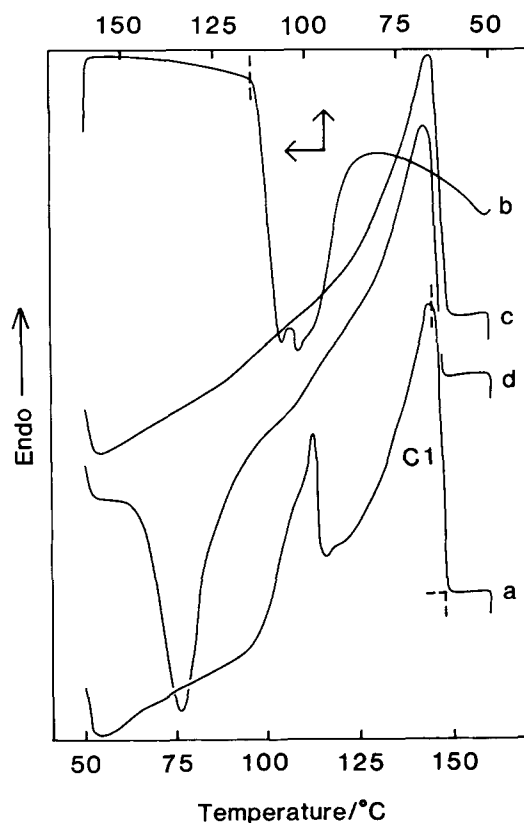


Figure 4 DSC thermograms of (a) sulfur/MBTS (1.0/3.0 mol ratio) heated at 5°C/min; (b) sample (a) cooled at 5°C/min; (c) a rescan of (b); and (d) a rescan of a sample cooled rapidly from 160 to 50°C. $M_i = 5.786$ mg.

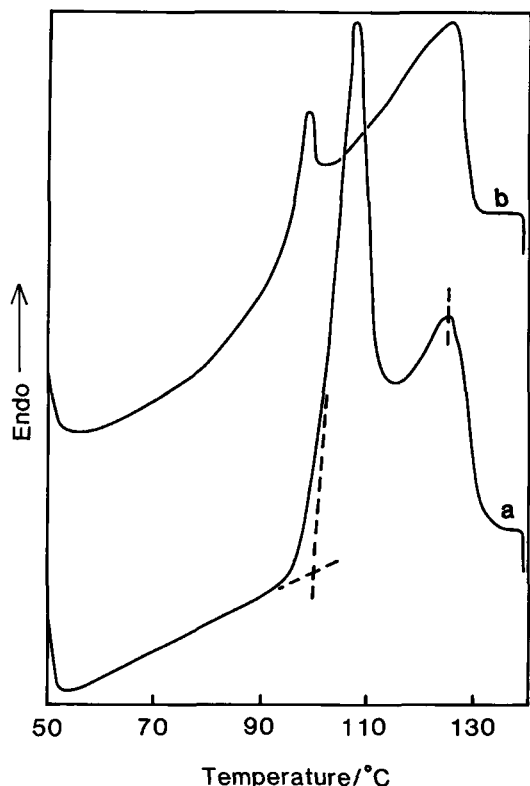


Figure 5 DSC thermograms of (a) sulfur/MBTS (1.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after 69 h at -30°C. $M_i = 4.884$ mg; $M_f = 4.876$ mg.

phase diagram, suggested the formation of MBTP. This approach, hampered in part because samples with a sulfur content of 25–55% by mass did not recrystallize properly, revealed a definite maximum at 16% sulfur. The peak therefore corresponded to an addition compound in which two sulfur atoms combined with MBTS. As noted above, the absence of the $S_\lambda \rightarrow S_\mu$ transition may indicate that sulfur had interacted with MBTS, possibly to form MBTP.

Sulfur/MBTS/Stearic Acid

DSC curves of the sulfur/MBTS/stearic acid mixtures displayed melting endotherms of stearic acid and orthorhombic sulfur. The hot-stage microscope revealed that sulfur and stearic acid were immiscible, but dissolution of MBTS in sulfur coincided with the endotherm seen just after the $S_\beta \rightarrow S_\lambda$ transition in Figure 6.

In all three mixtures described below, dissolution of MBTS in the sulfur melt was affected by the presence of stearic acid; e.g., in the sulfur/MBTS/stearic acid (1.0/3.0/1.0 mol ratio) mixture (Fig.

7), the sulfur/MBTS dissolution/interaction commenced at 129°C, about 32°C higher than in the absence of stearic acid (cf. Fig. 4). If the delayed dissolution involved an interaction of MBTS with sulfur, this may be ascribed to a change in the nucleophilicity of MBTS resulting from an interaction with stearic acid.

In considering the molecular orbital diagram of the aromatic benzothiazole group, the N atom has a lone pair of electrons situated orthogonal to the molecular pi-electrons. The lone pair would allow the benzothiazole group not only to function as a base, but also to possess a certain degree of nucleophilic character. In the presence of stearic acid, however, the MBTS molecule could be protonated at the N position, rendering it less active toward sulfur. This reaction would be limited to the liquid stearic acid/solid MBTS interface.

A DSC trace of the sulfur/MBTS/stearic acid (3.0/1.0/1.0 mol ratio) mixture revealed the typical orthorhombic sulfur transitions (Fig. 6), viz. a small peak ascribed to $S_\alpha \rightarrow S_\beta$, a minor $S_\alpha \rightarrow S_\lambda$ transi-

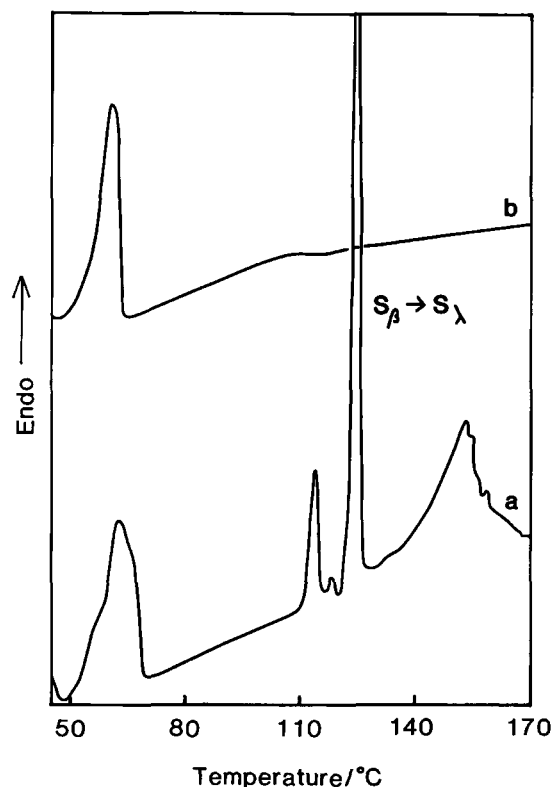


Figure 6 DSC thermograms of (a) sulfur/MBTS/stearic acid (3.0/1.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after 18 h at -30°C. $M_i = 5.003$ mg; $M_f = 4.991$ mg.

tion, and a large $S_\beta \rightarrow S_\lambda$ endotherm. On decreasing the sulfur in the mixture to 1 mol, allotropic sulfur transitions were observed at 112.0 and 116.5°C (Fig. 8). Based on their relative positions, these endotherms were associated with the $S_\alpha \rightarrow S_\lambda$ and $S_\beta \rightarrow S_\lambda$ transitions, respectively. Notice that the $S_\alpha \rightarrow S_\lambda$ peak was much greater than was the $S_\beta \rightarrow S_\lambda$ endotherm. With 3 mol of MBTS in the mixture, the $S_\beta \rightarrow S_\lambda$ peak virtually disappeared and only the $S_\alpha \rightarrow S_\lambda$ transition was prominent (Fig. 7). Identification of the sulfur transition as $S_\alpha \rightarrow S_\lambda$ was confirmed by the enthalpy change of 75 J/g associated with the endotherm. This figure was much higher than was the enthalpy change of only 15 J/g calculated for the $S_\alpha \rightarrow S_\beta$ transition in pure sulfur.⁶ The $S_\beta \rightarrow S_\lambda$ transition is associated with an enthalpy change of 53.5 J/g,⁶ but as the orthorhombic form is the stable allotrope at room temperature, such a transition has to be preceded by a $S_\alpha \rightarrow S_\beta$ change or a $S_\beta \rightarrow S_\lambda$ transition,⁶ which was not observed in Figure 7.

As in the case with the sulfur/stearic acid/ZnO mixture,⁶ we attribute the absence of S_β formation

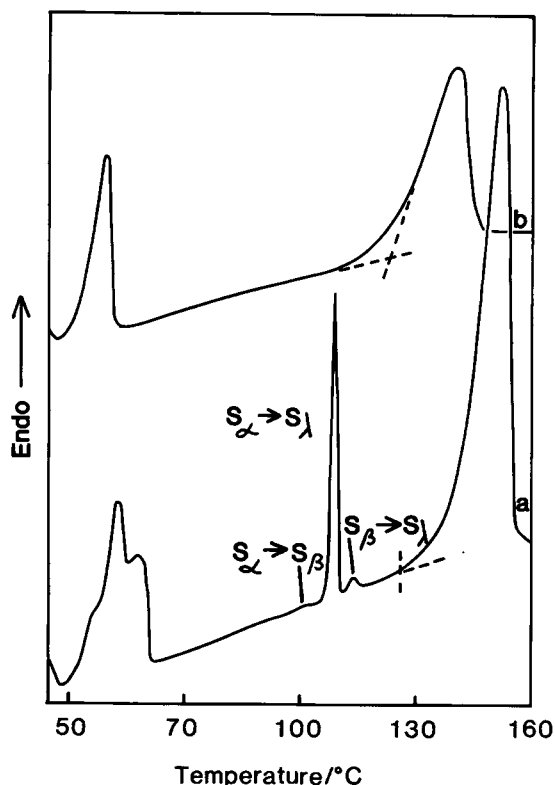


Figure 7 DSC thermograms of (a) sulfur/MBTS/stearic acid (1.0/3.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after cooling to room temperature. $M_i = 4.970$ mg; $M_f = 4.967$ mg.

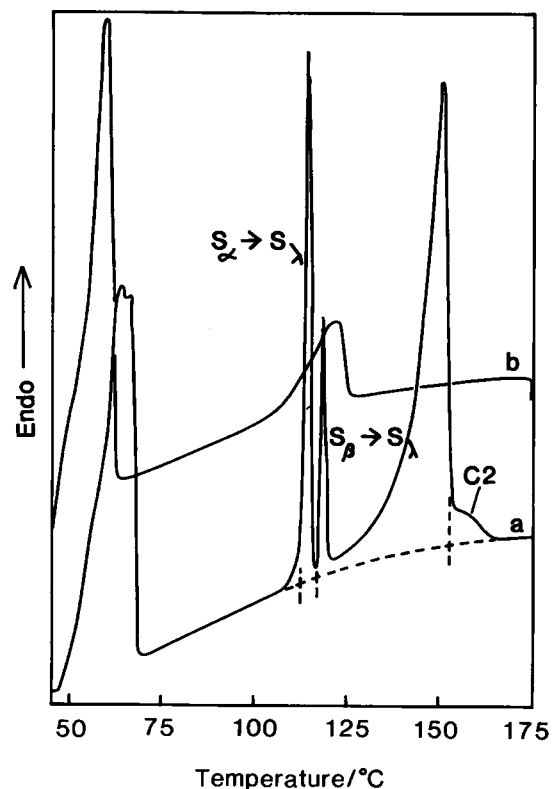


Figure 8 DSC thermograms of (a) sulfur/MBTS/stearic acid (1.0/1.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after cooling to room temperature. $M_i = 8.102$ mg; $M_f = 8.069$ mg.

to a reaction product (here an MBTS/stearic acid product) encapsulating the sulfur particles, isolating them from one another, and preventing nucleation of the S_β phase by traces of S_β present as an impurity in the orthorhombic sulfur phase.

On rescanning, a strong stearic acid melting peak was followed by a broadish sulfur/MBTS interaction peak (Figs. 7 and 8). Some rescan spectra also revealed cold crystallization of MBTS, manifested as an exotherm just after the stearic acid had melted. Only in the sulfur/MBTS/stearic acid (3.0/1.0/1.0 mol ratio) mixture (Fig. 6) was no sulfur/MBTS peak found in the rescan. The mixture, stored at -30°C for 18 h, showed a stearic acid melting peak, but virtually no other thermal events were recorded in the rescan (Fig. 6). This was consistent with the rescan spectra in the absence of stearic acid where the sulfur-rich mixture, too, did not yield a sulfur/MBTS peak (cf. Fig. 3).

In the presence of stearic acid, a shoulder was seen after the MBTS/sulfur interaction peak and may be attributed to the $S_\lambda \rightarrow S_\mu$ transition.⁶ In a

spectrum, scanned at 20°C/min, the latter transition appeared as a well-resolved peak at 165°C. The $S_\lambda \rightarrow S_\mu$ transition was not observed in the absence of stearic acid (Fig. 3). This transition indicated that the reactivity of MBTS toward sulfur had been reduced, and the residual free sulfur could now form polymeric sulfur. It was proposed above that protonation of MBTS by stearic acid impeded the formation of MBTP, and this interpretation is in line with the fact that organic acids, such as salicylic and palmitic acids, delay vulcanization, especially when MBTS is used as accelerator.^{11,12}

Sulfur/MBTS/ZnO

No thermal events, other than those mentioned for the sulfur/MBTS system, were observed for the sulfur/MBTS/ZnO combination.

MBTS/Stearic Acid/ZnO

It was possible to identify all thermal events for the MBTS/stearic acid/ZnO mixture scanned up to 190°C (Fig. 9). The endotherm at 108°C was ascribed to the melting of a small amount of zinc stearate, formed concurrently with the fusion of stearic acid. The shape of the peak at 150°C was characteristic of the stearic acid/ZnO reaction.⁶ Four analyses showed that this reaction occurred at an average temperature of 154.5°C (standard deviation 2.0%), in excellent agreement with the reaction temperature for the pure stearic acid/ZnO mixture.⁶

In a recent DSC study of CBS/stearic acid/ZnO (1.00/1.55/27.00 mol ratio) and MBT/stearic acid/ZnO mixtures, Kok¹³ interpreted thermal events, initiating at about 137°C, as evidence for the formation on the active sulfurating complex, generally accepted as the first step in accelerated sulfur vulcanization.¹⁴ However, we found the same kind of reaction profile for the MBTS/stearic acid/ZnO combination, and it is possible that the formation of zinc stearate was mistakenly identified by Kok as an accelerator/stearic acid/ZnO reaction. On heating stearic acid and ZnO (1.55/27.00 mol ratio), Kok¹³ found the base line to drift strongly in the endothermic direction in the region where we observed the stearic acid/ZnO reaction,⁶ but failed to observe the enthalpic changes associated with the formation of zinc stearate. Yet he did observe a very strong signal for the melting of zinc stearate in a rescanning.

The addition of ZnO to MBTS/stearic acid mixtures did not influence the reactions occurring at

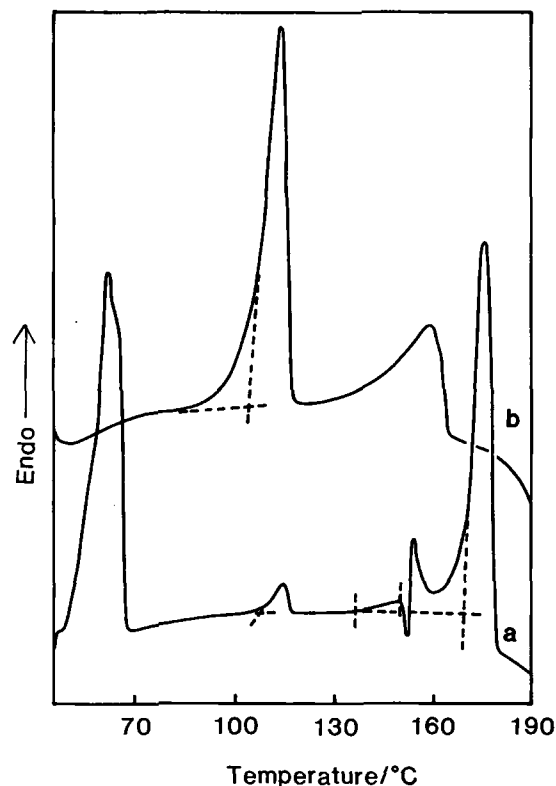


Figure 9 DSC thermograms of (a) MBTS/stearic acid/ZnO (1.0/1.0/1.0 mol ratio) heated at 5°C/min and (b) a rescanning after cooling to 45°C. $M_i = 6.473$ mg; $M_f = 6.363$ mg.

lower temperatures. Melting of MBTS initiated at 137°C in MBTS/stearic acid/ZnO mixtures (Fig. 9) and at 138°C in the absence of ZnO (cf. Fig. 2). On rescanning the latter system, a strong zinc stearate melting peak was seen at 105°C, followed by a broad endotherm attributed to the melting of MBTS. A mass loss of 1.7% was found after the rescanning, slightly in excess of the 1.3% expected for the evaporation of the water formed in the stearic acid/ZnO reaction.

Coran¹⁵ heated an MBT/stearic acid/ZnO (2.0/1.0/2.0 mol ratio) mixture at about 130°C, and since 1.5 mol of water was the only product lost, the empirical formula of the reaction product was calculated as $[\text{ZnMBT}]_2 [\text{zinc stearate}] \cdot \text{ZnO}$. The molecular mass was determined from osmotic pressure measurements as 1482, and a complex product structure was suggested. The product melted sharply at 108–109.5°C, which was reminiscent of the characteristically sharp melting endotherms for zinc stearate obtained throughout the present work. However, as we have reported,⁶ the melting point

of zinc stearate depended strongly on the method of preparation as well as on impurities—zinc stearate formed in the presence of 1 mol equivalent of MBTS fused at 105°C (Fig. 9). The possibility that the MBT/stearic acid/ZnO reaction product melting at 108–109.5°C was zinc stearate cannot be overlooked.

MBTS/Zinc Stearate

Coran² found infrared spectroscopic evidence of complex formation between MBTS and zinc stearate. An MBTS/zinc stearate (1.0/5.0 mol ratio) mixture was heated at about 135°C for 10 min and the solidified residue analyzed. By analogy to spectroscopic bands observed for an MBTS/zinc chloride mixture, it was deduced that chelate formation of MBTS and zinc stearate had occurred. Campbell and Wise¹⁰ related differences in the curing characteristics of the NR/sulfur/MBTS and NR/sulfur/MBTS/zinc stearate formulations to Zn^{2+} -MBT-stearate ion complexes, postulated to form during vulcanization.

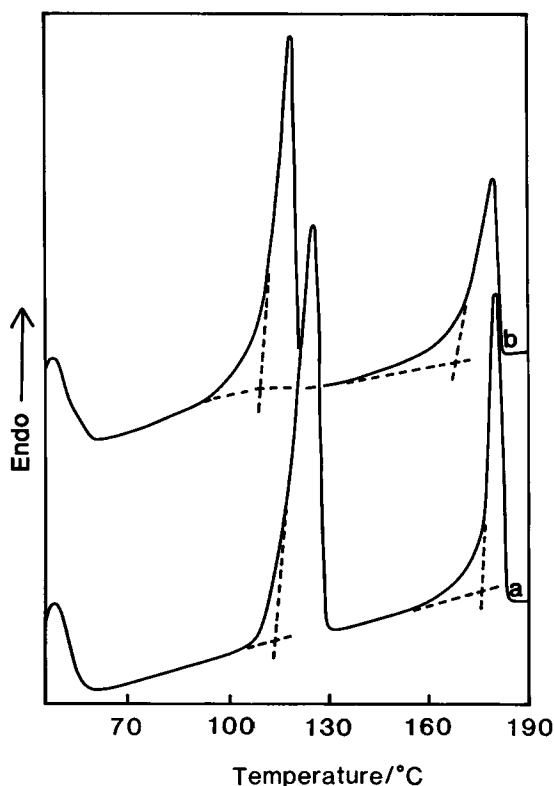


Figure 10 DSC thermograms of (a) MBTS/zinc stearate (1.0/1.0 mol ratio) heated at 20°C/min and (b) a rescan after 24 h at -30°C. $M_i = 2.889$ mg; $M_f = 2.879$ mg.

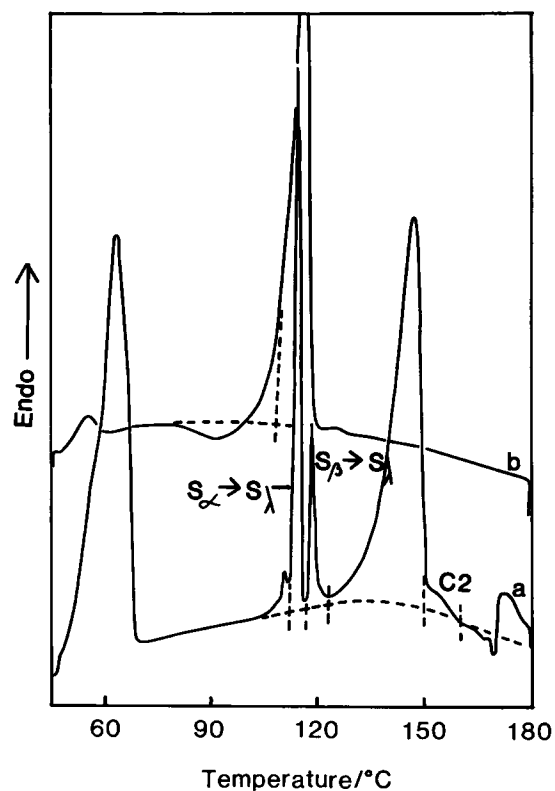


Figure 11 DSC thermograms of (a) sulfur/MBTS/stearic acid/ZnO (1.0/1.0/1.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after cooling to room temperature. $M_i = 9.025$ mg; $M_f = 8.935$ mg.

An MBTS/zinc stearate combination, scanned at 20°C/min up to 190°C, showed zinc stearate melting at 114°C and an MBTS melting endotherm at 176°C (Fig. 10). The sample was cooled and stored at -30°C for 24 h before rescanning. Zinc stearate melted at 110°C, and a MBTS melting endotherm, somewhat broader than in the original sample, followed at 168°C. In a subsequent experiment, an MBTS/zinc stearate mixture was heated at 20°C/min to 140°C and held isothermally for 10 min. Zinc stearate melted at 113°C, but no thermal events were observed during the isothermal part of the run, indicating that no MBTS/zinc stearate interaction occurred. The rescan spectrum, after storing of the sample at -30°C for 24 h, revealed zinc stearate melting at 114°C. The melting enthalpy was 84% of that of the original scan, and the mass reduction, only 0.25%. These findings suggested that MBTS and zinc stearate were unreactive at vulcanization temperatures. This contrasted with the work outlined above, but was in agreement with that of Milligan,³ who was unable to prepare benzene-soluble complexes of MBTS with zinc carboxylates.

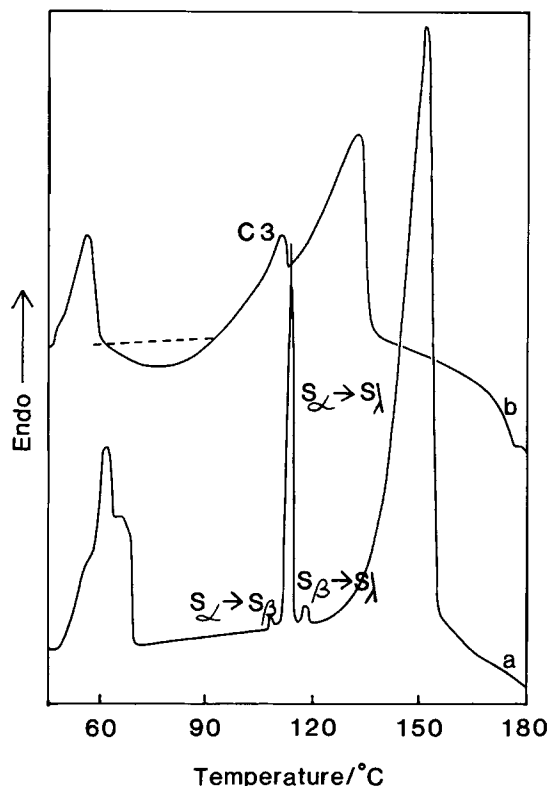


Figure 12 DSC thermograms of (a) sulfur/MBTS/stearic acid/ZnO (1.0/3.0/1.0/1.0 mol ratio) heated at 5°C/min and (b) a rescan after 24 h at -30°C. $M_i = 8.039$ mg; $M_f = 7.989$ mg.

He concluded that complex formation was not solely due to coordination of the benzothiazolyl nitrogen to the zinc atom of the carboxylate.

Sulfur/MBTS/Stearic Acid/ZnO

The sulfur/MBTS/stearic acid/ZnO mixture revealed the melting of stearic acid (Fig. 11), followed by an intense $S_\alpha \rightarrow S_\lambda$ endotherm at 111.8°C. The small endotherms just prior to the $S_\alpha \rightarrow S_\lambda$ transition were associated with the $S_\alpha \rightarrow S_\beta$ transition and/or the melting of a small amount of zinc stearate. The $S_\beta \rightarrow S_\lambda$ phase change was at 116.5°C. The dissolution of MBTS in sulfur, delayed by the presence of the stearic acid/MBTS interaction, initiated at about 123°C. A small $S_\lambda \rightarrow S_\mu$ endotherm C2 overlapped with the sulfur/MBTS interaction, and at 160°C, the characteristic ZnO/stearic acid reaction profile⁶ was seen. A rescan showed a small stearic melting peak below 65°C and a large zinc stearate melting peak at 107.6°C. As was the case with other mixtures having a sulfur/MBTS mol ratio of 1.0/

1.0, the MBTS/sulfur dissolution peak was not seen in the rescan.

A similar interpretation held for the DSC thermogram of the sulfur/MBTS/stearic acid/ZnO (1.0/3.0/1.0/1.0 mol ratio) system (Fig. 12), although the stearic acid/ZnO reaction was now incomplete. The small zinc stearate melting exotherm, expected at 108–111°C, as well as the high-temperature stearic acid/ZnO reaction profile were absent. The sample was cooled, stored at -30°C for 24 h, and rescanned. A substantial stearic acid melting peak remained, whereas the small zinc stearate melting endotherm C3 was further evidence that the stearic acid/ZnO reaction had not gone to completion. In mixes where the MBTS loading was higher, the stearic acid peak was bigger in the rescan (cf. Figs. 11 and 12). The characteristic skew shape of the endotherm accompanying the dissolution of MBTS in sulfur was evident, with a crest temperature of 132.1°C.

CONCLUSIONS

Most thermal events could be associated with physical changes such as the allotropic transitions and the melting of sulfur or the dissolution of MBTS in molten sulfur. Prominent thermal reactions observed were the formation of zinc stearate and an exothermic MBTS/stearic acid reaction that occurred well above normal vulcanization temperatures. Indirect evidence pointed to some interaction occurring between the latter curatives at lower temperatures. No reaction peaks attributable to the formation of 2,2'-dibenzothiazole polysulfide could be detected, though the $S_\lambda \rightarrow S_\mu$ transition, and the delay in the sulfur/MBTS interaction in the presence of stearic acid, pointed to MBTP formation. There was no evidence for the formation of a sulfur/MBTS/ZnO compound of the type thought to act as the active sulfurating agent in vulcanization.

We wish to thank the Foundation for Research and Development and Gentyre Industries for financial assistance.

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Received May 4, 1990

Accepted August 13, 1990