A DSC Study of Curative Interactions. III. The Interaction of TMTM with ZnO, Sulfur, and Stearic Acid

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SYNOPSIS

The interaction among various combinations of sulfur, tetramethylthiuram monosulphide (TMTM), ZnO, and stearic acid were studied by differential scanning calorimetry in the absence of rubber. Sulfur and TMTM reacted to form tetramethylthiuram disulphide, and the ternary eutectic mixture melted at about 80°C. The absence of the $S_\lambda \rightarrow S_\mu$ transition in sulfur/TMTM mixes was related to a sulfur/TMTM interaction, wherein the eight-membered sulfur rings were opened at temperatures well below 170°C. The interaction of stearic acid with TMTM led to the decomposition of TMTM, but the reaction was largely suppressed when both ZnO and sulfur were present in the mixture. No evidence was found for the formation of a zinc-accelerator complex of the type normally attributed a role in the accelerated sulfur vulcanization.

INTRODUCTION

In previous papers in this series, we reported on a differential scanning calorimetry (DSC) study of the interactions among sulfur, stearic acid, and ZnO (Ref. 1, Part I) in the absence of rubber, and between these curatives and 2,2'-dibenzothiazole (MBTS) (Ref. 2, Part II). This paper reports on the interactions of tetramethylthiuram monosulphide (TMTM) with sulfur, stearic acid, and ZnO. There is evidence for the interaction of sulfur and TMTM to form tetramethylthiuram disulphide (TMTD)[3] and tetramethylthiuram polysulphides,[4] whereas TMTM is unreactive toward ZnO.[5,6] Interaction between other combinations of these curatives have not been reported on.

EXPERIMENTAL

TMTM was supplied by Bayer South Africa. Experimental details with respect to the DSC experiments have been given in the previous paper.[1] The onset or starting temperatures for the enthalpic

changes quoted in the text were determined by the intersection of the base line with a line drawn through the most steeply rising part of the peak. The initiation temperature refers to the temperature at which a deviation of the base line occurred in the formation of the peak.

Thin-layer chromatography (TLC) plates were prepared by applying Kieselgel 60 (Merck HF$_{254}$) in the form of a water-based slurry onto glass plates (20 × 20 cm^2), providing a layer of thickness of about 800 μm after drying. The residue from each DSC run was placed in 1.0 cm^3 of a CS$_2$/benzene (1/1 v/v) solvent mixture and mixed thoroughly. A 5.0 μL aliquot was carefully applied with a microsyringe onto the TLC plate. For elemental sulfur determination, the chromatogram was developed in n-pentane, after which the plate was dried. The top part of the plate was sprayed with a sodium azide/iodine detecting reagent.[7] Sulfur (R_f = 0.74) appeared as a white spot on a brown iodine background. The iodine was allowed to sublime and the plates redeveloped with a benzene/ethyl acetate/acetone (100/5/1 v/v/v) elutriant system,[8] in order to detect thiuram-related species. The plate was dried and investigated with UV light (λ = 254 nm), and often sublimed iodine was used to detect TMTM (R_f = 0.35), TMTD (R_f = 0.52), and ZDMC (R_f = 0.64). The current study revealed the sodium azide/iodine

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reagent to be very efficient in detecting TMTD, TMTM, and ZDMC as well. These species appeared as white spots on a brown background, and the spot sizes were substantially larger compared to the brown spots obtained on using sublimed iodine as detecting agent.

In the legends to the figures, Mi refers to the mass before the DSC experiment, and Mf, to the mass after the rescan.

RESULTS AND DISCUSSION

TMTM

It is well known that the yellow compound TMTM is an accelerator for sulfur vulcanization, but not a vulcanizing agent. Craig et al.[6] noted that its decomposition at 140°C, in the presence of natural rubber, was negligible, and Coleman et al.,[9] that homolysis at 125°C was extremely slow. These reports are consistent with the thermogram for TMTM (Fig. 1) that showed a melting peak at 106.0°C, in good agreement with literature values of 103–114°C.[10,11] On rescanning a sample stored at −30°C for 24 h, an almost identical thermogram was obtained.

Sulfur/TMTM

Raman spectroscopy[4] revealed that TMTD was formed from a sulfur/TMTM (1.0/1.0 mol ratio) mixture at 125°C. After an induction period of 5 min, rapid conversion to TMTD occurred, and after 15 min, only TMTD and sulfur were detected. The formation of tetramethylthiuram polysulphides (TMTP), as intermediate products, were also established. Craig et al.[3] synthesized TMTD in 70% yield by heating a sulfur/TMTM (2.0 g atom/1.0 mol) mixture at 120°C for 30 min under nitrogen, whereas Scheele and Bielstein[12] regarded the sulfur/ TMTM reaction, which would yield TMTD in a natural rubber compound, as an important step prior to cross-link formation. As was the case in a natural rubber/TMTD/ZnO system, a natural rubber/sulfur/TMTM/ZnO compound yielded 66% zinc dimethyldithiocarbamate (ZDMC). However, no TMTD was detected at any stage of the reaction.

DSC spectra of sulfur/TMTM mixes, scanned up to 180°C, showed the melting of TMTM, followed by the melting of orthorhombic sulfur [Figs. 2(a) and 3(a)]. The melting of TMTM occurred at 97.3°C in the equimolar mixture, i.e., about 9°C lower than that of pure TMTM, which may be indicative of an interaction with sulfur. On cooling to
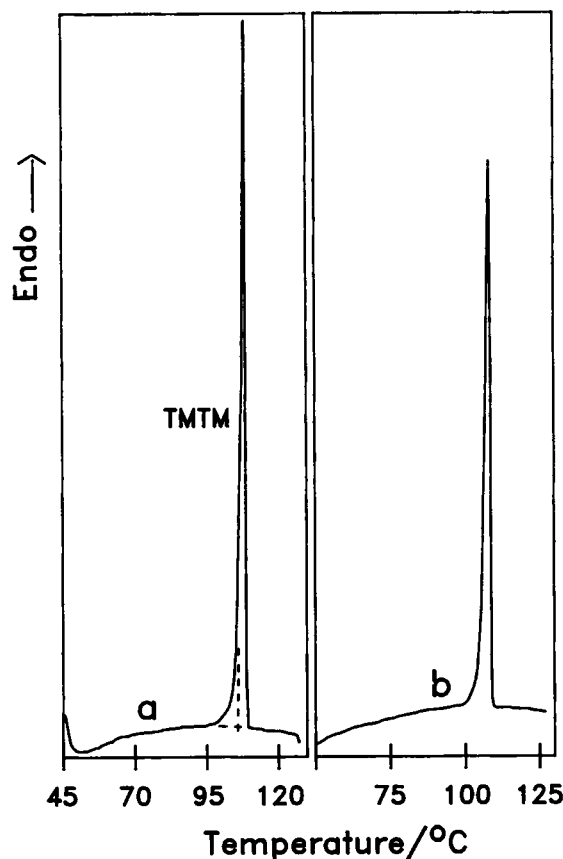

Figure 1 DSC spectra. Scan rate 5°C/min. (a) TMTM; (b) rescan after 24 h at −30°C. Mi = 1.511 mg; Mf = 1.507 mg.

room temperature, the sample proved to be a viscous yellow product that largely solidified on being stored at −30°C for 24 h. The rescan revealed a sharpish melting peak A1 below 80°C [Fig. 2(b)]. The sulfur/ TMTM (1.0/3.0 mol ratio) mixture, heated at 20°C/min, showed a similar endotherm below 80°C, together with a second broad endotherm in the temperature region where TMTM melted [Fig. 3(b)]. A TMTM-rich blend, heated to only 117°C and subsequently stored at −30°C for 24 h, showed a small endotherm at 67°C, as well as a large TMTM peak in the rescan [Fig. 3(c)]. Clearly, the sulfur/ TMTM interaction, leading to the low-temperature endotherm A1, occurred even below 117°C.

To identify the products produced on heating the sulfur/TMTM (1.0/3.0 mol ratio) mixture, a sample was scanned to 180°C at 5°C/min and the residue analyzed by TLC. In comparing the spot sizes with those obtained with standard samples, it was estimated that a substantial amount of the original sulfur was present in the residue. There appeared
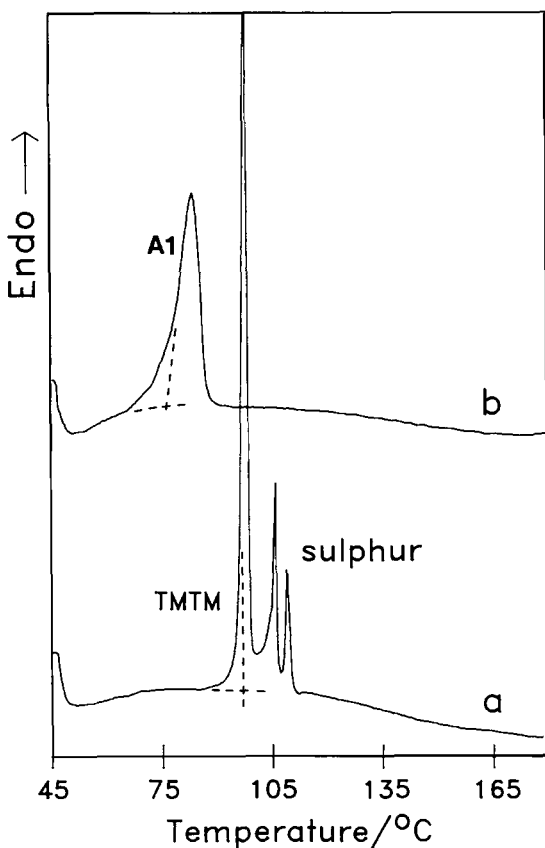
Figure 2   DSC spectra. Scan rate 5°C/min. (a) Sulfur/ TMTM (1.0/1.0 mol ratio); (b) rescan after 2 h at ambient temperature followed by 24 h at −30°C. Mi = 2.514 mg; Mf = 2.384 mg.

to be more TMTD than TMTM in the residue. The presence of TMTD agreed with the finding of Craig et al.[3] and Coleman et al.[4] who reported that TMTD was produced on heating a sulfur/TMTM mixture.

These results suggested an equilibrium reaction of the type

$$\text{TMTM} + \text{S} \underset{\Delta}{\rightleftharpoons} \text{TMTD}$$
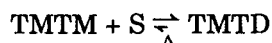
Long-chain TMTP molecules were suggested by Coleman et al.[4] as intermediates in the formation of TMTD. No evidence for TMTP was found in the TLC analysis, but these species were most probably unstable in solution (see future publication). Note that efforts to synthesize and isolate tetramethyl-thiuram trisulphide have failed previously.[5,13] Yet it is known that tetramethylthiuram tetrasulphide (melting point 98°C) was sufficiently stable to be recrystallized from solution,[13] while Wolfe[14] claimed the synthesis and isolation of tetramethylthiuram

hexasulphide by heating sulfur and TMTD for 5 h at 95°C in benzene.

Interestingly, the rescan spectrum of the sulfur/ TMTM (1.0/1.0 mol ratio) mixture showed neither the melting of TMTD nor of elemental sulfur. This was ascribed to the formation of an eutectic mixture of sulfur, TMTM, and TMTD that melted below 80°C [Fig. 2(b)], since a sulfur/TMTM/TMTD (1.0/0.7/0.3 mol ratio) mixture showed a single endotherm at 81.3°C on heating at 1°C/min (Fig. 4). The composition of the latter "eutectic" mixture was based on the TLC analysis of the sulfur/TMTM (1.0/3.0 mol ratio) mixture after heating to 180°C. In the rescan spectra of sulfur/TMTM mixtures containing 3 mol of TMTM, a TMTM or TMTD melting peak was observed in addition to the eutectic melting peak [Fig. 3(b) and (c)]. Notice that the eutectic peak appeared only in the rescan, i.e., after the formation of TMTD.
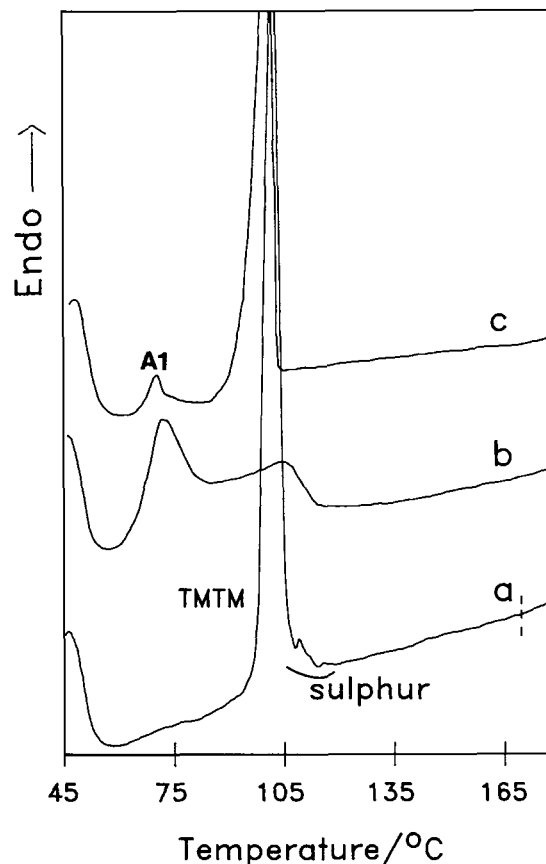

Figure 3   DSC spectra. Scan rate 20°C/min. (a) Sulfur/ TMTM (1.0/3.0 mol ratio); (b) rescan (see text for details). Mi = 2.196 mg. (c) Rescan after a sulfur/TMTM (1.0/3.0 mol ratio) mixture was heated to 117°C, cooled, and stored at −30°C for 24 h.
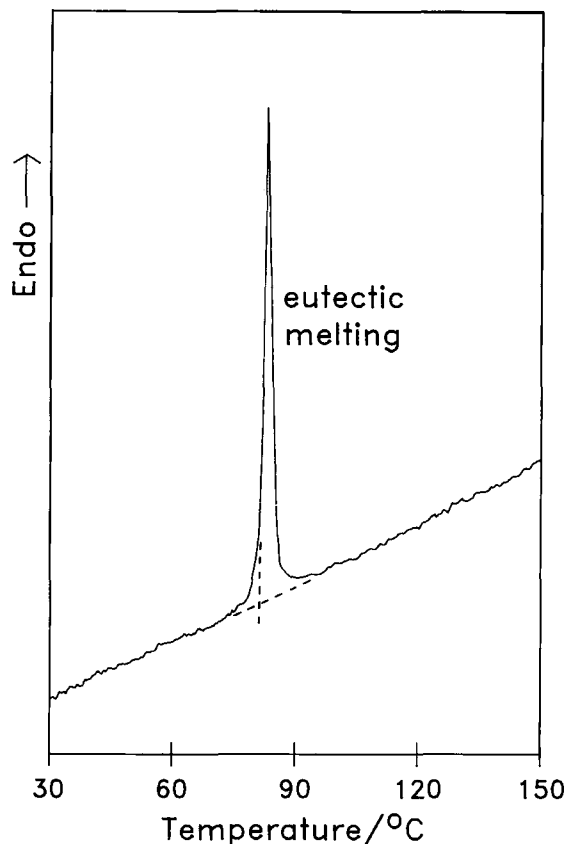
Figure 4 DSC spectrum. Scan rate 1°C/min. Sulfur/TMTD/TMTM (1.0/0.7/0.3 mol ratio). $Mi = 3.572$ mg.

Furthermore, it was noteworthy that the $S_\lambda \rightarrow S_\mu$ transition, which was expected at about 170°C,[1] did not appear in the DSC spectrum of the sulfur/TMTM (1.0/1.0 mol ratio) mixture [Fig. 2(a)]. The absence of the transition could be related to a sulfur/TMTM interaction wherein the eight-membered sulfur rings were opened at temperatures well below 170°C. Based on the Raman spectroscopic results of Coleman et al.,[4] the product could have been TMTP. Since the rate-determining step in sulfur vulcanization has previously been proposed to be the opening of the S_8 ring,[15] an early reaction between sulfur and TMTM would be in line with the accelerating property of TMTM in sulfur vulcanization.

On heating a sulfur/TMTM (1.0/3.0 mol ratio) mixture to higher temperatures at 20°C/min, an endotherm, associated with a decomposition reaction and the evolution of gases, initiated around 170°C. A progressive mass loss from 2.1% at 180°C to 40.0% at 230°C occurred. The evaporation endotherm became poorly defined above 210°C.

TMTM/Stearic Acid

A TMTM/stearic acid mixture was scanned to 180°C [Fig. 5(a)]. After the familiar stearic acid and TMTM melting peaks at 57.9 and 102.6°C, respectively, an endotherm initiated at 144°C. The latter peak was indicative of a TMTM/stearic acid interaction and originated from the evolution of volatiles. A mass reduction of 35.6% was calculated after the rescan, which was slightly less than the 43.2% loss expected if all of the TMTM had been evolved. A sharp sulfurous smell was evident on opening the DSC pan. The brown residue was not analyzed further.

Ferington and Tobolsky[16] demonstrated that TMTM was an efficient initiator for the polymerization of methyl methacrylate at 70°C, which was regarded as conclusive evidence that TMTM dissociated into free radicals. We concluded that TMTM was unstable in the presence of stearic acid due to it being able to abstract a proton from the
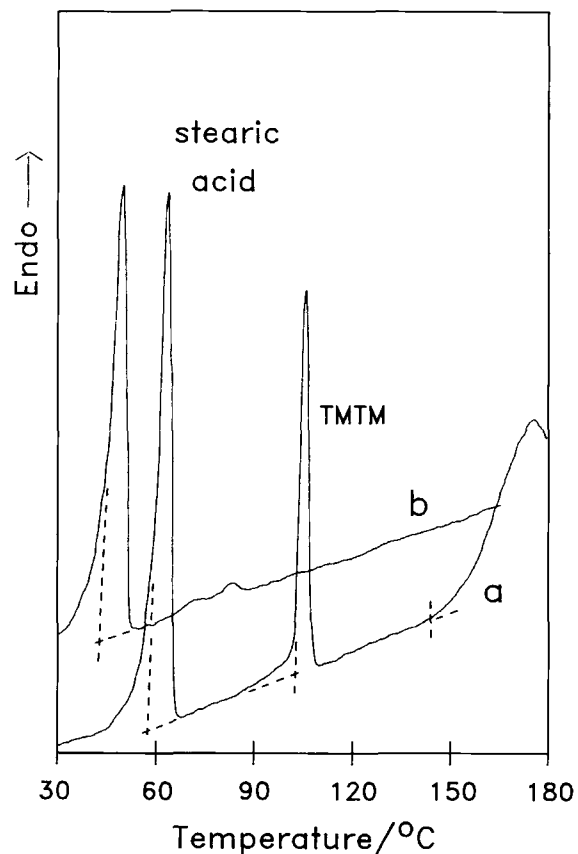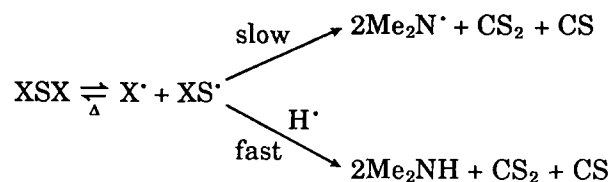

Figure 5 DSC spectra. Scan rate 5°C/min. (a) TMTM/stearic acid (1.0/1.0 mol ratio); (b) rescan after 15 days at −30°C. $Mi = 3.611$ mg; $Mf = 2.326$ mg.

carboxylic acid. For example, the thiuram sulphenyl radical XS˙ would form dimethyldithiocarbamic acid [$Me_2NC(S)SH$], which is known to be unstable[6,17]:

$$XSX \underset{\Delta}{\rightleftharpoons} X˙ + XS˙ \nearrow^{slow} 2Me_2N˙ + CS_2 + CS$$

$$\searrow_{fast}^{H˙} 2Me_2NH + CS_2 + CS$$

The rescan spectrum of a sample stored at $-30°C$ showed a melting endotherm with a shape typical of that of stearic acid, but at the lower temperature of $43.2°C$ [Fig. 5(b)]. The enthalpy change associated with the peak was close to that of the stearic acid melting endotherm in the original sample. It is believed that thiuram sulfenyl radicals had reacted with stearic acid by attacking the hydrogen atoms of the alkyl chain, rather than the proton on the carboxylic acid group. Previous researchers have, for example, found that the light-promoted chlorination of carboxylic acids occurred preferentially at the α or β carbons of the alkyl chain.[18] Note that if carboxylic radicals were formed via the thiuram sulfenyl radical/stearic acid reaction, these radicals were expected to decarboxylate readily.[19]

TMTM/ZnO

The thermogram of a TMTM/ZnO mixture scanned to $187°C$ showed only the characteristically sharp melting peak of TMTM. There was no indication of interaction with ZnO, and the rescan spectrum was identical to the original. The mass loss after the rescan was negligible. Craig et al.[5,6] also found no interaction between TMTM and ZnO at curing temperatures.

Sulfur/TMTM/Stearic Acid

The thermogram of a sulfur/TMTM/stearic acid mixture (Fig. 6) showed stearic acid melting at $58.1°C$ and TMTM melting at $95.7°C$, followed by the melting of sulfur. The $10°C$ decrease in the TMTM melting point may again be regarded as evidence of a sulfur/TMTM interaction. The endotherm above $150°C$ was associated with the thiuram/stearic acid reaction leading to the evolution of gases. A strong sulfurous smell was evident on opening the DSC. The shape of the endotherm obtained below $60°C$ in the rescan of a sample stored
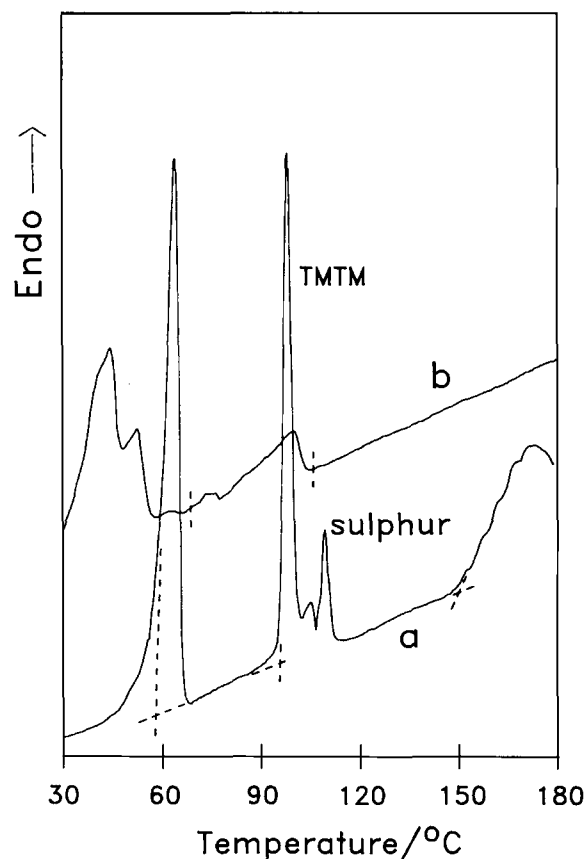

Figure 6   DSC spectra. Scan rate $5°C$/min. (a) Sulfur/TMTM/stearic acid (1.0/1.0/1.0 mol ratio); (b) rescan after 48 h at $-30°C$. $Mi = 5.354$ mg; $Mf = 4.152$ mg.

at $-30°C$ for 48 h was typical of that sometimes found with stearic acid and may be related to the thermal history of the fatty acid prior to DSC analysis. The reduced melting point may again be indicative of a stearic acid derivative, e.g., dehydrogenated stearic acid. Endotherms between 69 and $106°C$ probably originated from the eutectic mixture and free sulfur. The mass loss during the heating process was 22.5%, lower than the 27.8% expected if all of the TMTM had decomposed.

Sulfur/TMTM/ZnO

An intense TMTM melting peak at $95.3°C$ and the transitions of sulfur were the only thermal events seen on heating a sulfur/TMTM/ZnO mixture to $170°C$. Note the $10°C$ decrease in the TMTM melting point. Attempts to completely solidify the viscous, sticky residue failed. Whitish particles, presumably of ZnO, could be seen under the microscope. A mass loss of 0.9% was recorded.

TMTM/Stearic Acid/ZnO

The small peak at 111°C, just after the melting of TMTM in Figure 7(a), was assigned to the melting of a small amount of zinc stearate, formed immediately after the stearic acid had melted.[1] The endotherm commencing at 125°C and growing more intense toward higher temperatures could be due to a TMTM/stearic acid interaction. Note that the profile characteristic of the stearic acid/ZnO reaction at about 155°C[1] was not observed in this spectrum. Microscopic examination of the heated sample after storage at −30°C for 48 h revealed it to be a brown paste with a whitish layer on top. The rescan spectrum [Fig. 7(b)] showed a melting endotherm below 45°C, ascribed to the stearic acid derivative, as discussed above. The fusion of zinc stearate at 107°C was also observed, indicating that some reaction had occurred despite the absence of the characteristic reaction profile in the first scan. From the size of the melting peak of the zinc stearate peak
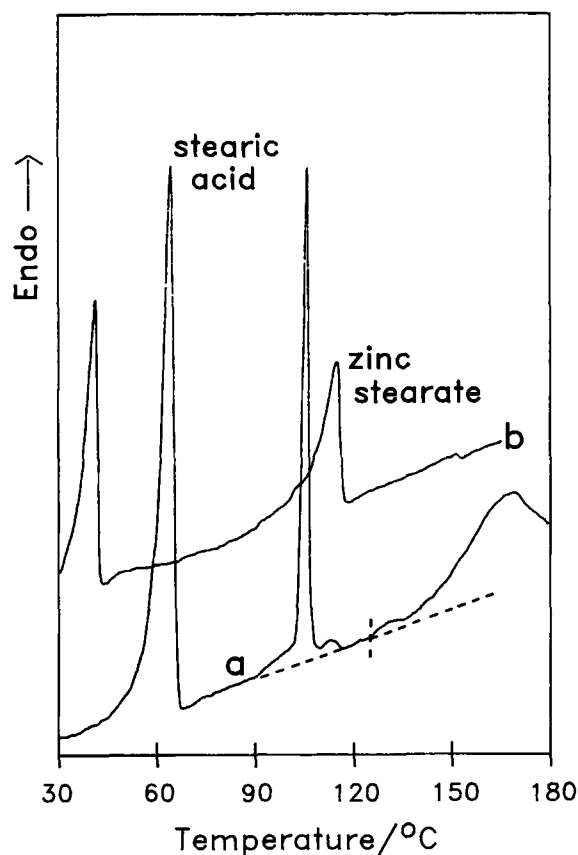

Figure 7 DSC spectra. Scan rate 5°C/min. (a) TMTM/stearic acid/ZnO (1.0/1.0/1.0 mol ratio); (b) rescan after 48 h at −30°C. Mi = 4.272 mg; Mf = 3.096 mg.
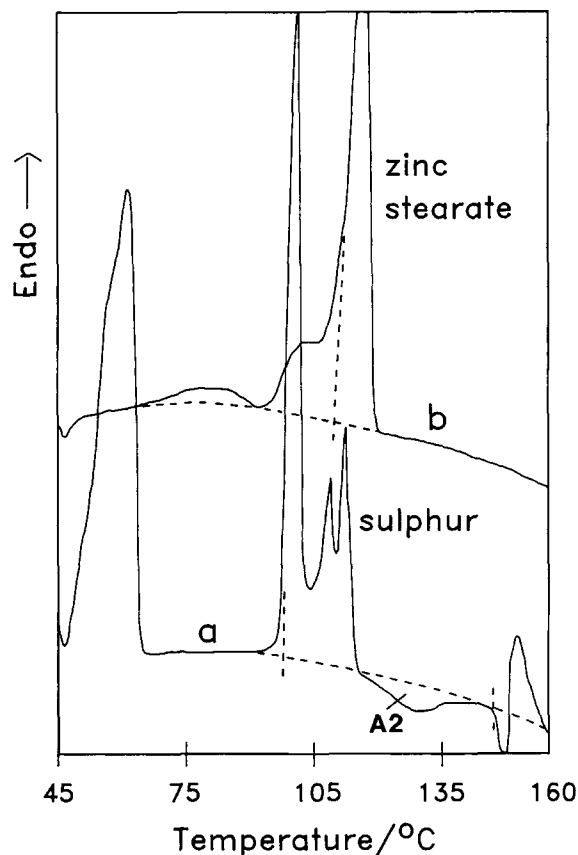

Figure 8 DSC spectra. Scan rate 5°C/min. (a) Sulfur/ TMTM/stearic acid/ZnO (1.0/1.0/1.0/1.0 mol ratio); (b) rescan after 3 h at room temperature. Mi = 7.530 mg; Mf = 7.208 mg.

and the presence of an acid derivative peak below 45°C, it was evident that the stearic acid/ZnO reaction had not proceeded quantitatively. The reason was not evident. A mass loss of 27.5% was calculated after the rescan, less than the theoretical amount of 36.3 mass % TMTM started with.

Sulfur/TMTM/Stearic Acid/ZnO

Following the melting of stearic acid, TMTM melted some 8°C lower than did pure TMTM (Fig. 8). The $S_\alpha \rightarrow S_\lambda$ and $S_\beta \rightarrow S_\lambda$ allotropic transitions of elemental sulfur were easily recognized (the early formation of a small amount of zinc stearate again reduced the $S_\alpha \rightarrow S_\beta$ transition[1]). The profile at 147°C was characteristic of the formation of zinc stearate, but duplicate experiments revealed that the reaction occurred randomly at temperatures between 87 and 147°C. A similar result was obtained earlier for sulfur/stearic acid/ZnO mixtures.[1] The dotted base

line was estimated from the rescan spectrum, and endotherm A2 was not identified. The rescan spectrum of a sample, stored at room temperature for 3 h, revealed a prominent melting peak for zinc stearate at 109.9°C. The poorly defined endothermic events at lower temperatures were probably due to the melting of thiuram species and sulfur. The mass reduction was only 4.3% after the rescan experiment. No acid melting peak was observed, and assuming that the stearic acid/ZnO reaction had gone to completion, the evaporation of water would have given a mass loss of 2.2%. Thus, a mass loss of only 2.1% needed to be accounted for and would indicate the decomposition and evaporation of very little of the thiuram species, implying that the extent of the TMTM/stearic acid reaction was limited.

CONCLUSIONS

Three reactions involving TMTM were identified. A sulfur/accelerator reaction was connected to an equilibrium among sulfur, TMTM, and TMTD. There is strong evidence from Raman spectroscopy[4] for the formation of TMTP on heating sulfur and TMTM. The absence of a $S_\lambda \rightarrow S_\mu$ transition at about 170°C on heating sulfur/TMTM mixtures could, in addition, point to an early reaction between these compounds. A high-temperature reaction occurred between TMTM and stearic acid, both in the presence and absence of sulfur, leading to a large mass loss in each case. In the quaternary system sulfur/TMTM/stearic acid/ZnO, very little TMTM (or TMTP)/stearic acid interaction occurred, as evidenced by the small mass loss. This was also evident from the slope of the thermogram at higher temperatures (cf. Figs. 6 and 8).

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