A DSC Study of Curative Interactions. I.
The Interaction of ZnO, Sulfur, and Stearic Acid

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SYNOPSIS

The interaction between combinations of sulfur, stearic acid, and ZnO were studied by differential scanning calorimetry in the absence of rubber. The only reaction observed was between ZnO and stearic acid. A small amount of zinc stearate formed as soon as the stearic acid melted, but the solid product blocked further reaction, which was only completed at 154°C. Water played a major role in the reaction, and in the presence of water, the reaction went to completion at lower temperatures. Sulfur, too, affected the temperature of the ZnO/stearic acid reaction. The preparation of zinc stearate by a number of routes was investigated.

INTRODUCTION

The theory of accelerated sulfur vulcanization suggests that the first step in the vulcanization process is the interaction between curatives, leading to the formation of an active sulfurating agent.[1] There have, however, been few studies of such interactions in the absence of rubber. Currell and Williams[2] reported fully on the phase transitions obtained in a differential scanning calorimetry (DSC) study of sulfur, whereas Kok[3] used DSC to investigate possible reactions between combinations of compounding ingredients in systems containing sulfur, stearic acid, ZnO, and accelerators N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and 2-mercaptobenzothiazole (MBT). He concluded that a CBS/stearic acid/ZnO reaction was energetically the most favorable. This would be in line with the theory of accelerated sulfur vulcanization that requires the formation of an active sulfurating agent as the first step in the reaction sequence. Failure to detect the melting of sulfur in a rescan of a sulfur/stearic acid mixture led him to conclude that there was also some interaction between sulfur and stearic acid.

As a prelude to a DSC study of the accelerated sulfur vulcanization of polyisoprene, a study was made of the interaction of the curatives in the absence of rubber. Irrespective of the accelerator employed, ZnO and stearic acid are generally used as activator and coactivator, respectively, and although it is commonly accepted that these react to form zinc stearate, the use of zinc stearate in place of ZnO and stearic acid does not produce the same activating effect.[4] This paper reports only on the thermograms obtained on heating sulfur, stearic acid, zinc stearate, and ZnO and on the interactions of combinations of these. These details are essential in interpreting thermograms of mixtures to which accelerators have been added. As will be shown, failure to correctly interpret the ZnO/stearic acid reaction, in particular, may lead to the misidentification of reactions occurring in the presence of accelerators. The interaction with the various accelerators will be reported on in subsequent papers.

EXPERIMENTAL

Materials: Sulfur (fumigation sulfur, chemical purity 99.5%) from AECI (South Africa); stearic acid (iodine value 8.0 Wijs) from Marine Oil Refiners (South Africa); zinc stearate (typical free fatty acid content 5%) from Cookson Chemicals (South Africa); ZnO (active grade, chemical purity 99.72%, particle size < 0.2 μm) from Zinc Process (South

Africa); and ZnS (chemical purity 99.99%) from Aldrich Chemical Co. (U.S.A.).

Components were pulverized with a pestle and mortar before mixing the powders in a polytop bottle by stirring with a spatula. Stearic acid was pulverized after freezing in liquid nitrogen. The stearic acid was then dried over P_2O_5 in a desicator for 24 h to remove atmospheric moisture that condensed onto the powder during the low-temperature grinding operation. Mixtures contained 1 mol equivalent of each component, except where otherwise stated. Samples (1.5–7 mg) were weighed on a microbalance, compressed to ensure good thermal contact, and enclosed in aluminum pans. The pans did not seal well enough to prevent the escape of volatiles during a run. Mixtures were heated in a Perkin–Elmer DSC-2 at a rate of 5 or 20°C/min as indicated on the thermograms. An empty pan served as reference sample. High-purity nitrogen, at a flow rate of 20 cm^3/min, was used as a purge gas. The temperature axis was calibrated with indium and potassium chromate, and the energy axis, with indium.

The onset temperatures for the enthalpic changes quoted in this paper were determined by the intersection of the base line with a line drawn through the most steeply rising part of the peak. 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

Sulfur

The thermogram of sulfur showed four endothermic peaks [Fig. 1(a)]. Following Currell and Williams,[2] the first peak at 107.0°C was attributed to the $S_\alpha \rightarrow S_\beta$ solid–solid transition. S_β is the more stable form of sulfur above 96°C,[5] but the transition is slow and the temperature at which it is observed depends on the heating rate. For example, Currell and Williams[2] reported a transition temperature of 100°C at a heating rate of 4°C/min; Miller,[6] of 111°C at 10°C/min; and Kok,[3] of 113°C at 20°C/min. Currell and Williams[2] found that nuclei of S_β were necessary for the solid–solid transition and that a single crystal of sulfur did not transform to S_β, but melted at 112°C. The small peak at 112.8°C [Fig. 1(a)] was thus attributed to a small fraction of the orthorhombic sulfur melting without undergoing the solid–solid transition. The intense peak at 119.0°C was ascribed to the fusion of S_β to form S_λ (119 [Ref. 2] and 125°C [Ref. 3]). S_λ refers to liquid
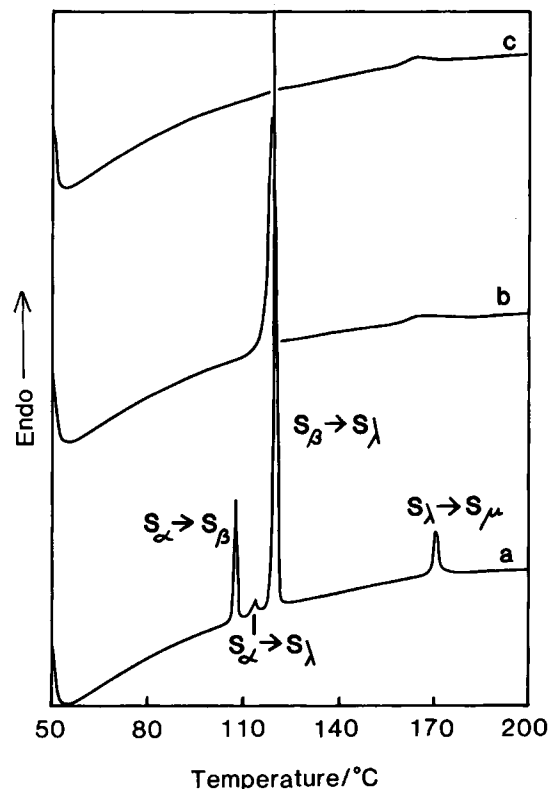

Figure 1 DSC thermograms of (a) orthorhombic sulfur heated at 5°C/min, (b) rescanned after 15 h at −30°C, and (c) rescanned directly after cooling to room temperature. Mi = 1.659 mg.

sulfur that consists mainly of S_8 molecules. It is thermodynamically possible for polymeric sulfur, S_ω, to form above at 159°,[2] and the small endotherm at 169°C was ascribed to the formation of S_μ, an equilibrium mixture of S_8 and S_ω. When the sample was cooled and rescanned directly, only the $S_\lambda \rightarrow S_\mu$ transition was observed [Fig. 1(c)], whereas on storing the sample at −30°C for 15 h, the $S_\beta \rightarrow S_\lambda$ transition also appeared in a rescan [Fig. 1(b)]. Samples were not stored for long enough for the S_β form to revert to the more stable orthorhombic S_α.

Stearic Acid

Stearic acid showed a large characteristic melting endotherm at 56.4°C (67–69 [Ref. 7] and 72.1°C [Ref. 8]); it crystallized rapidly when cooled to room temperature, and melting was once again observed on reheating (Fig. 2).

ZnO and ZnS

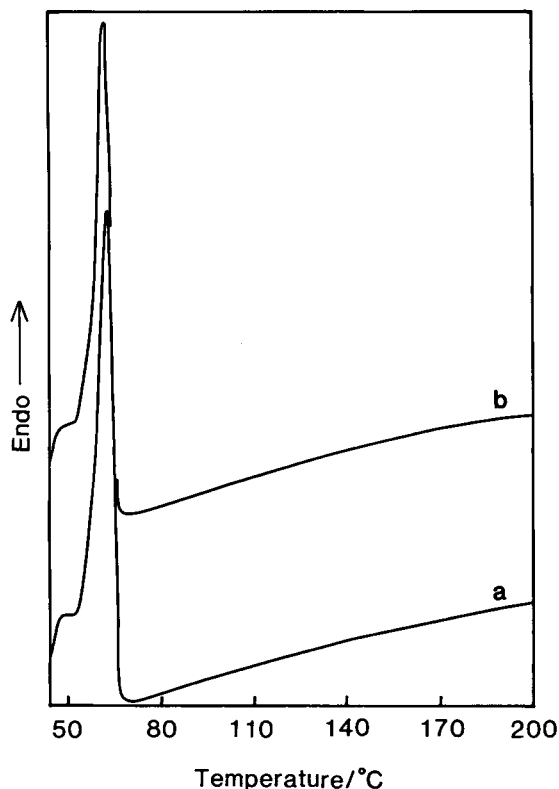DSC scans of ZnO and ZnS (a product of vulcanization reactions) gave straight lines when scanned up to 200°C.

Figure 2   DSC thermograms of (a) stearic acid heated at 20°C/min and (b) rescanned after 5 h at room temperature. Mi = 1.602 mg.

Stearic Acid/ZnO Mixtures

Reaction Endotherms

The DSC thermogram of a mixture of stearic acid and ZnO (Fig. 3) showed three thermal events: Stearic acid melted at 53.4°C, while a much smaller endotherm was observed at 111.0°C (see below). At 154.0°C, a predominantly endothermic event initiated, which was associated with the stearic acid/ZnO reaction to form zinc stearate and water. The average of four thermograms showed zinc stearate forming at a temperature of 154.6°C (standard deviation 1.19%). The rescan spectrum, after cooling to 45°C, showed a strong zinc stearate melting endotherm at 114.5°C. There was no evidence for the melting of free stearic acid, indicating that the reaction had gone to completion. A mass loss of 2.42% was found on weighing the sample before and after the reaction. If it is assumed that water was the only volatile product given off in the reaction, the mass loss also implied that the initial stearic acid had reacted quantatively with ZnO : 8.26 μmole of stearic acid and 4.13 μmol of ZnO gave 4.05 μmol of water, which was very close to the theoretical stoichiometry.

The small endotherm at 111.0°C in Figure 3 (scan rate 5°C/min) was attributed to the melting of a small amount of zinc stearate that had formed at temperatures well below 154°C, the temperature at which the bulk of the stearic acid/ZnO reaction occurred. Although the onset temperature of 113.0°C was very reproducible at a scan rate of 20°C/min, the enthalpy of fusion for a series of samples ranged from 7.6 to 16.5 J/g mix. The 113.0°C peak was also observed when a gold pan was used to perform the experiment, which ruled out the possibility that the oxide layer on the aluminum pan's surface had interferred with the stearic acid/ZnO reaction. (Examples of Al_2O_3 participation in organic reactions involving, for example, alcohol and amide functionalities, are available in the literature.[9]) An attempt to increase the size of the peak by scanning a sample to 125°C at 20°C/min, followed by cooling of the mixture to 37°C and reheating to 125°C, was unsuccessful. Even when the heating and cooling cycle was repeated five times, no growth in peak size was achieved. Holding the sample isothermally at 100°C for 30 min, too, did not have any effect on the peak
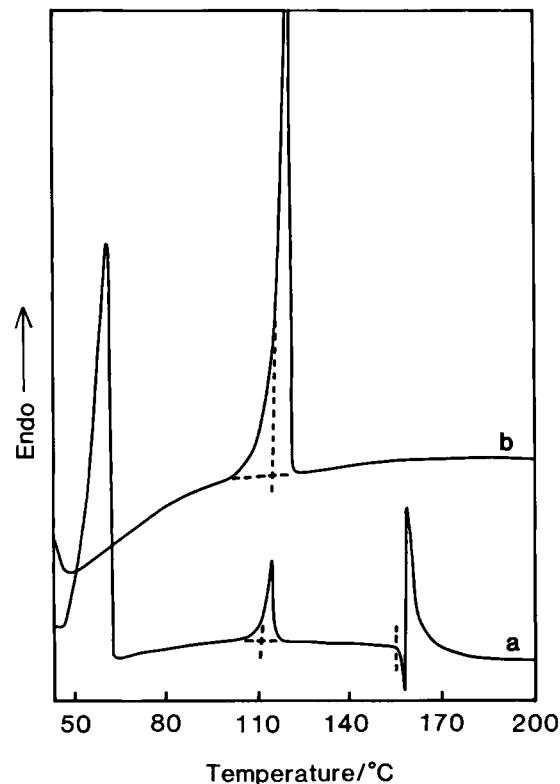

Figure 3   DSC thermograms of (a) stearic acid/ZnO (1.0/1.0 mol ratio) heated at 5°C/min and (b) rescanned directly after cooling to room temperature. Mi = 3.022 mg, Mf = 2.949 mg.

size. When a sample, held isothermally at 125°C for 30 min was cooled to 75°C and rescanned to 215°C (20°C/min), zinc stearate formed at about 183°C. This was confirmed by the fact that the rescan spectrum now displayed a large zinc stearate melting peak at 113°C.

However, when a stearic acid/ZnO mixture (2.0/ 1.0 mol ratio) was scanned at 20°C/min to 125°C, cooled to ambient temperature, and the sample remixed using a stainless-steel spatula, the peak at 113.0°C did increase in size on rescanning. The procedure was repeated with the same sample, and as the zinc stearate peak increased after each remixing operation, so did the stearic acid peak decrease (Fig. 4). This showed that, as soon as stearic acid melted, it reacted at the surface of the ZnO particles, but that the resultant zinc stearate formed an impenetrable coating on the ZnO surface. This blocked further reaction at the lower temperature. By crushing the agglomerate during remixing, fresh ZnO was exposed and some further reaction could ensue. This reaction occurred below 65°C.

The Effect of Water on the Formation of Zinc Stearate

A dramatic change in the stearic acid/ZnO thermogram was obtained when water was added to the mixture (Fig. 5). Just after the stearic acid had melted, a large exotherm was observed, followed by an endotherm. Note that the stearic acid/ZnO reaction peak, previously observed at 165°C, was now absent. The zinc stearate melting peak at 115°C in the rescan spectrum led to the assignment of peak C3 in the original spectrum to the melting of zinc stearate.

It was postulated that the peak C2 was due to the evaporation of water. The postulate was verified by scanning a stearic acid/ZnO/water mixture up to the point marked I in Figure 5, when the sample was rapidly removed from the DSC and allowed to cool. It showed a mass loss of 4.0% compared to that of the original sample, while on subjecting the sample to vacuum, a further mass loss of 2.7% occurred and peak C2 did not appear in the rescan. The addition of more water to the stearic acid/ZnO mixture increased peak C2 at the expense of C1, indicating a partial overlap of these peaks. Peak C1 was attributed to the enthalpy of the stearic acid/ZnO reaction, coupled with the latent heat of crystallization of zinc stearate, since this reaction occurred at temperatures well below that at which zinc stearate melted. As with the low temperature reaction, the
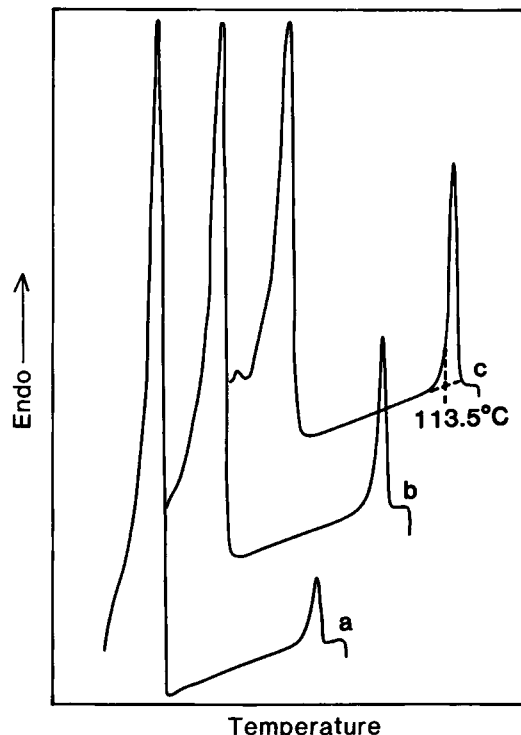

Figure 4 DSC thermograms of (a) stearic acid/ZnO (2.0/1.0 mol ratio) heated at 20°C/min, and (b, c) rescanned after stirring with a spatula at room temperature after each heating cycle. The sample mass reduced from (a) 2.851 mg to (b) 2.594 mg to (c) 2.167 mg on heating.

shape of the stearic acid/ZnO reaction exotherm above 150°C was also affected by overlap with the endotherm because of the evaporation of water formed in the reaction.

As noted above, zinc stearate encrusted the ZnO particles in the absence of water. Water promoted the low-temperature reaction, and it was not immediately clear why water, formed in the reaction, did not likewise facilitate continuation of the reaction between the dry reagents at low temperatures. It must be assumed that the small amount of water formed in the reaction was readily lost from the mixture.

The DSC thermogram of Kok[3] did not show clear evidence for a reaction between ZnO and stearic acid, though the base line drifted strongly in the endothermic direction above 170°C. On rescanning, an endotherm, attributed to the melting of zinc stearate, was, however, observed.

Characteristics of Zinc Stearate

The melting point of zinc stearate, prepared in the DSC by the above procedures, differed considerably
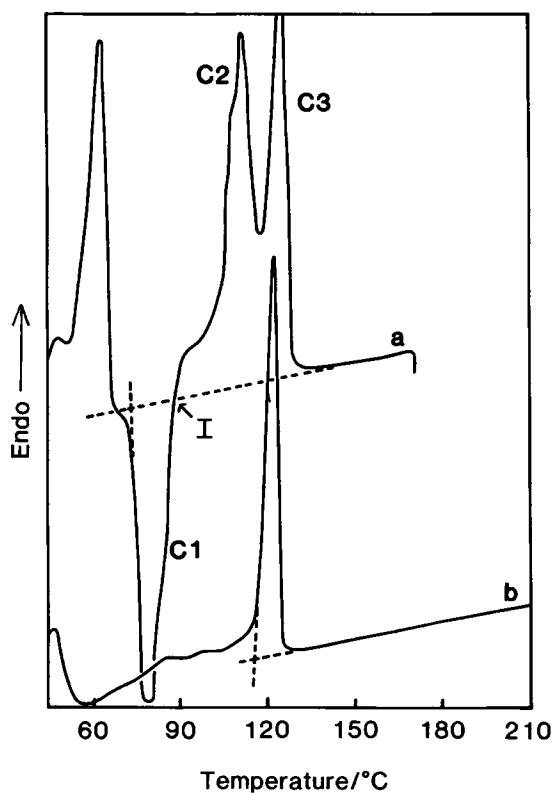
Figure 5 DSC thermograms of (a) stearic acid/ZnO/water (1.0/1.0/1.0 mol ratio) heated at 5°C/min and (b) rescanned directly after cooling to room temperature. Mi = 2.534 mg, Mf = 2.379 mg.

from values reported in the literature. A few experiments were conducted to clarify this aspect, and the results are summarized in Table I. With reference to the first three methods of zinc stearate preparation, it was evident that the mild solvent fusion process (method 1) gave a product with a relatively high melting enthalpy of 190 J/g zinc stearate. The melting temperature of 122.0°C compared favorably with the literature data depicted in Table I. Although the wet fusion process (method 2) yielded a product with a melting enthalpy of only 177 J/g zinc stearate, a CHN analysis confirmed that the stearic acid/ZnO reaction had gone to completion. This was in line with the DSC spectrum, which showed no free stearic acid melting peak. Zinc stearate produced by the high-temperature fusion process (method 3) revealed a much lower melting enthaply of 115 J/g. The same trend applied to the DSC methods of synthesis (methods 4 and 5) in that the zinc stearate melting enthalpy decreased with an increase in the temperature of preparation. There was an excellent correlation between the melting points of zinc stearate prepared by methods 2–5. Clearly, the melting point of zinc stearate, and especially the enthalpy of melting, depended strongly on the method of preparation. The higher-temperature methods of zinc stearate synthesis may, *inter alia*, result in dehydrogenation of the fatty acid chain to form conjugated unsaturations,[10] and the brown-colored products that were found under the more drastic conditions of preparation may be indicative thereof. Commercially zinc stearate is made by the wet fusion method, and, as expected, the thermal values of a commercial sample of zinc stearate, as used by the tire industry in South Africa, corresponds well with those of the wet fusion preparation (method 4).

Table I Thermal Characteristics of Zinc Stearate for Various Preparations (DSC Scan Rate 20°C/min)

	Preparation							
	1	2	3	4	5	6	7	8
ΔH/J g^{-1}	190	117	115	145	134	143	—	—
T_f/°C	122.0	114.8	114.5	114.8	114.0	114.5	130	120

ΔH expressed in terms of the maximum theoretical amount of zinc stearate that could form. *Preparation 1.* Stearic acid (1.7069 g, 6.0 mmol) and an aqueous slurry of ZnO (0.2482 g, 3.05 mmol) were refluxed in petroleum ether (30 mL, boiling point 100–120°C) for 5 min at 105°C. The white product was filtered and the fine soap particles dried under high vacuum at 60°C. *Preparation 2.* Stearic acid (4.4989 g, 15.82 mmol) and ZnO (0.6434 g, 7.91 mmol) were heated in a beaker under atmospheric conditions up to 80°C. Two drops of water were added to the molten mixture, and, within seconds, zinc stearate formed and solidified. The mixture was heated to 120°C (when the zinc stearate melted), stirred to ensure complete reaction, and cooled after 3 min. A CHN analysis was done on the hard whitish product: ANAL: Calcd for $C_{36}H_{70}O_4Zn$: C, 68.38; H, 11.16; N, 0.00; Found: C, 68.21; H, 10.96; N, 0.00. *Preparation 3.* Stearic acid (4.4989 g, 15.82 mmol) and ZnO (0.6434 g, 7.91 mmol) were mixed and heated in a beaker up to 175°C under atmospheric conditions. Waxy smelling volatiles were given off, and the product was cooled after 1 min. A hard brown product was formed. *Preparation 4.* A stearic acid/ZnO/water (1.0/1.0/0.5 mol ratio) mixture was scanned at 20°C/min in the DSC up to 170°C and was cooled to ambient temperature. The stearic acid/ZnO reaction occurred at about 73°C. *Preparation 5.* The stearic acid/ZnO (1.0/1.0 mol ratio) mixture was scanned as above up to 210°C, and the reaction initiated at 165°C. *Preparation 6.* Commercial as sample as used by the tire industry. *Preparation 7.* Ref. 7. *Preparation 8.* Ref. 8.

Stearic Acid/ZnS Mixtures

Unlike stearic acid/ZnO mixtures, stearic acid/ZnS mixtures did not interact at temperatures up to 250°C. This is important as ZnS is a product of accelerated sulfur vulcanization. In a later paper we will show that ZnO and zinc stearate behave similar during vulcanization, but that ZnS is virtually unreactive.

Sulfur/Stearic Acid/ZnO Mixtures

DSC spectra of the sulfur/stearic acid/ZnO mixture [Fig. 6(a)] were interpreted with reference to the previous spectra. After a prominent stearic acid melting peak, there was an endotherm with at least two overlapping component peaks. Based on the relative positions of the component peaks C4 and C5, the peak at 107.8°C was assigned to the $S_\alpha \rightarrow S_\beta$ transition (cf. Fig. 1 for sulfur), and the peak at 112.0°C, to the fusion of zinc stearate (cf. Fig. 3 for stearic acid/ZnO). In a number of spectra, the $S_\beta \rightarrow S_\lambda$ peak at 118.9°C appeared less intense than did the $S_\alpha \rightarrow S_\lambda$ transition [Fig. 6(b)], but their relative
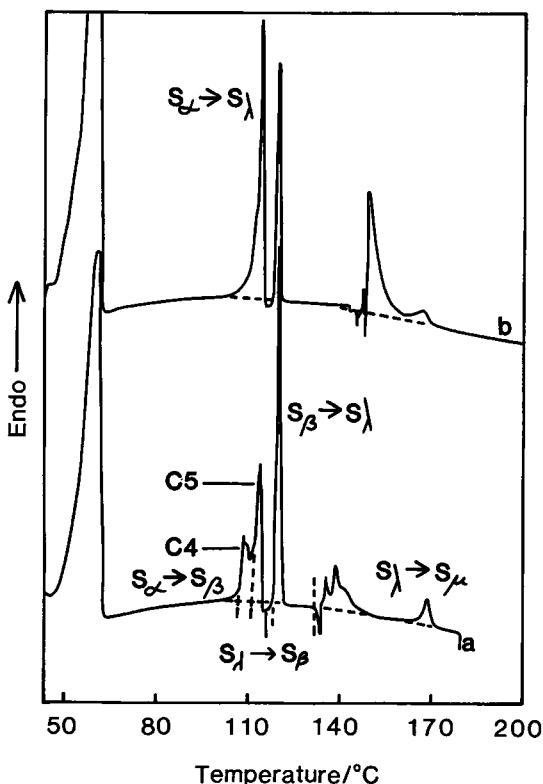

Figure 6   (a) Mi = 4.478 mg and (b) Mi = 4.504 mg duplicate DSC thermograms of sulfur/stearic acid/ZnO (1.0/1.0/1.0 mol ratio) heated at 5°C/min.

heights varied greatly. Currell and Williams[2] showed that in highly pure single crystals, i.e., in the absence of S_β seed crystals, the $S_\alpha \rightarrow S_\beta$ solid–solid transition did not occur and instead S_α melted to give S_λ directly. It is suggested that the small amount of zinc stearate formed early in the reaction encrusted some sulfur particles, allowing those from which the S_β phase was absent to melt without the solid–solid phase transformation being seeded by neighboring grains.

Indeed, the transitions in mixes where zinc stearate was formed in the reaction were even more complex. Figure 6(a) showed a $S_\alpha \rightarrow S_\beta$ transition, followed by a $S_\alpha \rightarrow S_\lambda$ transition. There was a small, but definite, exotherm after the S_α had melted, and this was attributed to molten sulfur coming into contact with particles of the S_β phase, which nucleated its crystallization. The final large endotherm represented the melting of S_β.

The distinct $S_\lambda \rightarrow S_\mu$ transition at about 165°C [Fig. 6(a)] indicated that sulfur as such did not partake in the stearic acid/ZnO reaction, shown here at 133.0°C. Another interesting observation was that the stearic acid/ZnO reaction commenced at random temperatures between 89 and 144°C when a sulfur/stearic acid/ZnO mixture was scanned at 5°C/min. Unless very special precautions are taken, sulfur contains traces of impurities such as H_2S,[11-13] which may effect the stearic acid/ZnO reaction in the same way as does water.

Sulfur/Stearic Acid Mixture

The DSC thermogram of a sulfur/stearic acid mixture displayed the characteristics of stearic acid and sulfur transitions as the only thermal events. On rescanning, in a mixture cooled to 50°C for 5 min, the stearic acid melting peak had exactly the same enthalpy as that of the original sample, indicating that no interaction had occurred between sulfur and stearic acid. The sulfur melting endotherm was absent, though the $S_\lambda \rightarrow S_\mu$ peak appeared at 167°C. In a similar study, Kok[3] heated a sulfur/stearic acid (2.77/1.00 mol ratio) mixture at 20°C/min to 230°C and, since virtually no sulfur melting peak was observed on rescanning, concluded that some interaction had occurred between sulfur and stearic acid. As indicated earlier, sulfur is reluctant to crystallize on cooling samples heated to high temperatures and care must be taken in interpreting rescan spectra. We found that only in a sample stored at −30°C for 70 h did the sulfur melting peak also appear on rescanning.

Sulfur/ZnO Mixtures

Sulfur and ZnO are inert toward each other when scanned up to 200°C. The rescan spectrum of samples, stored at room temperature for 19 h, showed a single sharp melting peak at 104.0°C, attributed to the $S_\beta \rightarrow S_\lambda$ transition, together with the $S_\lambda \rightarrow S_\mu$ transition at 164°C. The former peak occurred at a much lower temperature than the 116.2°C of the original scan, but the melting enthalpy remained unchanged.

CONCLUSIONS

Immediately after it had melted, stearic acid reacted with ZnO to give zinc stearate, but as the product was formed below its melting point, it solidified and prevented further reaction. Zinc stearate also coated sulfur particles, many of which now melted directly, without undergoing the $S_\alpha \rightarrow S_\beta$ solid–solid transition. On cooling, the recrystallization of sulfur did not occur rapidly, especially in the presence of stearic acid, but it did not react with either ZnO or stearic acid. Rescan spectra can readily be misinterpreted if insufficient time is allowed for compounds to recrystallize.

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