A DSC Study of Curative Interactions. IV. The Interaction of Tetramethylthiuram Disulfide with ZnO, Sulfur, and Stearic Acid

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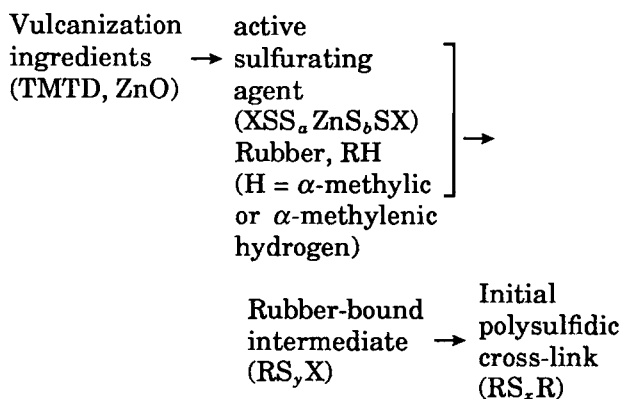
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SYNOPSIS

The interaction of combinations of sulfur, tetramethylthiuram disulfide (TMTD), ZnO, and stearic acid were investigated by differential scanning calorimetry in the absence of rubber. TMTD decomposed partially to tetramethylthiuram monosulphide on liquefaction. Sulfur and TMTD reacted at vulcanization temperatures, and although the exact composition of all the products was not established, several features involving DSC and HPLC analysis were interpreted in terms of the formation of tetramethylthiuram polysulfides (TMTP). TMTD decomposed much faster to volatile products such as Me_2NH, CS_2, and CS when heated in the presence of stearic acid. Contrary to literature reports on the facile reaction of TMTD and ZnO to yield zinc perthiomercaptides (or zinc dimethyldithiocarbamate), the TMTD/ZnO reaction was found to be extremely sluggish under a variety of conditions. In the presence of sulfur, too, the TMTD/ZnO reaction was of negligible importance. It was inferred that several reactions occurred concurrently on heating a TMTD/stearic acid/ZnO system. These reactions were not observed for the sulfur/TMTD/stearic acid/ZnO mixture per se, but, instead, the stearic acid/ZnO reaction was very prominent. The formation of zinc stearate occurred at temperatures as low as 77°C in the quadruple system. TMTD and zinc stearate were virtually unreactive at vulcanization temperatures. None of the reactions involving ZnO could be attributed to the formation of a zinc perthiomercaptide, generally accepted to be a precursor in thiuram vulcanization.

INTRODUCTION

There has been considerable debate concerning the mechanism of thiuram-accelerated sulfur vulcanization of natural rubber (NR). The most widely accepted mechanism for accelerated sulfur vulcanization, introduced in the 1960s, follows from work of which much was done at the British Natural Rubber Producer's Association. The mechanism for the formation of the initial polysulfidic cross-links on vulcanizing a NR/tetramethylthiuram disulphide (TMTD)/ZnO compound can be summarized as[1]

Vulcanization ingredients (TMTD, ZnO) → active sulfurating agent (XSS_aZnS_bSX) Rubber, RH (H = α-methylic or α-methylenic hydrogen) →

Rubber-bound intermediate (RS_yX) → Initial polysulfidic cross-link (RS_xR)

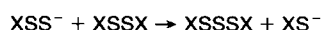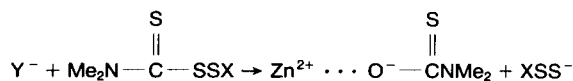where R = polyisoprenyl and X = dimethyldithiocarbamyl radical.

Zinc perthiomercaptides XSS_aZnS_bSX have been postulated to form *in situ* prior to cross-linking in NR/TMTD/ZnO vulcanization via the mechanism outlined in Scheme 1. Tetramethylthiuram polysulfides (TMTP) would result from the nucleophilic attack of a basic oxyanion Y^- (e.g., $Zn^{2+} \cdots O^{2-}$) on the harder thiocarbonyl carbon of TMTD, displacing a perthionanion. The latter would subsequently attack the softer disulfide sulfur of TMTD to give tetramethylthiuram trisulfide (TMTT). Further attack by Y^- on the TMTT would yield polysulfides of a higher sulfur rank x in an analogous manner. Interchange between the thiuram polysulfides and zinc dimethyldithiocarbamate dimethylthiocarbamate (or eventually zinc dimethyldithiocarbamate [ZDMC]) would then yield the sulfurating agent XSS_aZnS_bSX, in which a and b are small.[2-4] (See Scheme 1).

The electronic character of the active sulfurating agent XSS_aZnS_bSX was regarded[3] as extremely important, since it allowed a convenient explanation for the position of sulfur attachment to the isoprene unit.

In the case of the NR/sulfur/TMTD/stearic acid/ZnO system, too, ZDMC was believed to form *in situ* as the first step in vulcanization. The mechanism of ZDMC formation was thought to involve the reaction of ZnO, fatty acid, and accelerator,[1] but details of the intrinsic steps of such a reaction were not given. ZDMC then reacted with sulfur to form the active sulfurating agent XSS_aZnS_bSX:

$$XSSX \xrightarrow[\text{RCOOH}^*]{\text{ZnO}} XSZnSX \overset{S_8}{\rightleftharpoons} XSS_aZnS_bSX$$
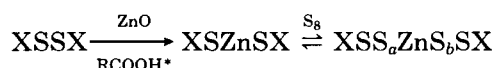
*R = $CH_3(CH_2)_{16}$. This paper reports on the interaction of combinations of TMTD, ZnO, stearic acid, and sulfur in the absence of rubber.

$$Y^- + Me_2N-\overset{\overset{S}{\|}}{C}-SSX \rightarrow Zn^{2+} \cdots O^- -\overset{\overset{S}{\|}}{C}NMe_2 + XSS^-$$

$$XSS^- + XSSX \rightarrow XSSSX + XS^-$$

$$Zn^{2+} \cdots O^- -\overset{\overset{S}{\|}}{C}NMe_2 + XS^- \rightarrow XSZnOX$$

$$2XZnOX + XSS_xSX \rightleftharpoons XSS_aZnS_bSX + XOZnOX + XS_iX$$

Scheme 1. A possible route toward the formation of zinc perthiomercaptides ZSS_aZnS_bSX via the TMTD/ZnO reaction.[2-4]

EXPERIMENTAL

General

TMTD was supplied by Orchem South Africa. Experimental procedures with respect to DSC and TLC investigations were given in previous papers in this series (Ref. 5, Part I, and Ref. 6, Part II). Except where otherwise indicated, curatives were mixed in 1.0 : 1.0 mol ratios.

The mass loss experiments were conducted with a DuPont 951 thermogravimetric analyzer (TGA), which was connected to a DuPont 9000 thermal analyzer. High-purity nitrogen, at a flow rate of 20 cm^3/min, was used as a purge gas. The temperature calibration of the TGA was confirmed to be synchronized with that of the DSC, by means of the dehydration pattern of copper sulfate pentahydrate. The procedure that was followed for the high-performance liquid chromatography (HPLC) determinations will be described in Paper V in this series.

The TMTD/ZnO Reaction in *n*-Butyl Ether

Various attempts, discussed under TMTD/ZnO in the Results section, were made to prepare ZDMC from TMTD and ZnO. One such attempt in *n*-butyl ether will be described in detail to illustrate the procedure that was followed for other similar attempts.

n-Butyl ether was dried over molecular sieves (3 Å, Merck) and distilled just prior to use. TMTD (0.1443 g, 0.600 mmol) and ZnO (0.0488 g, 0.600 mmol) were added to *n*-butyl ether (6.0 mL) in a 10 mL round-bottom flask equipped with a reflux condenser and thermometer. The mixture was heated in an oil bath at an average rate of $\sim$ 4.5°C/min and was agitated continuously. At $\sim$ 60°C, white crystals formed on the side walls of the flask (just above the meniscus), and at $\sim$ 90°C, a yellow color started to develop. Except for the precipitate on the side walls of the flask, all the TMTD had liquified at $\sim$ 122°C. The mixture refluxed at 138°C, whereupon the TMTD crystals above the meniscus were washed into the solution. The heat source and magnitude stirrer were removed after 3 h, and a white sediment settled immediately.

The resultant compounds were isolated with column chromatography and characterized by CHN analysis. Kieselgel S (63–100 μm, Riedel-de Haën) served as the stationary phase, and a benzene/ethyl acetate/acetone (100/5/1 v/v/v) system, as the mobile phase. Sulfur eluted first and then ZDMC (0.0279 g, 15.2 mol %). ANAL: Calcd $C_6H_{12}N_2S_4Zn$: C, 23.57; H, 3.96; N, 9.16. Found: C, 23.62; H, 3.98;

N, 8.96. The third fraction collected was TMTD (0.0723 g, 50.1 mol %). ANAL: Calcd for $C_6H_{12}N_2S_4$: C, 29.98; H, 5.03; N, 11.65. Found: C, 29.47; H, 4.79; N, 11.88. The yellow band was due to TMTM (0.0250 g, 20.0 mol %). ANAL: Calcd for $C_6H_{12}N_2S_3$: C, 34.59; H, 5.81; N, 13.45. Found: C, 34.86; H, 5.74; N, 13.81. It was possible to account for 85.3 mol % of the initial TMTD.

RESULTS AND DISCUSSION

TMTD

Apart from being an accelerator in the sulfur vulcanization of polyisoprenes, TMTD itself functions as an efficient cross-linker in the presence of ZnO.[3,7] As early as 1930, von Braun[8] reported that TMTD decomposed above 150°C with the formation of tetramethylthiourea (TMTU):

$$TMTD \underset{\Delta}{\rightarrow} TMTU + CS_2 + \frac{1}{8} S_8$$

Bedford,[9] Dogadkin,[10] Craig,[11] Blokh,[12] and their respective co-workers have suggested tetramethylthiuram monosulfide (TMTM) as an intermediate compound in the thermal breakdown of TMTD, to ultimately yield TMTU, CS_2, and sulfur:

$$TMTD \underset{\Delta}{\rightarrow} TMTM + S \underset{\Delta}{\rightarrow} TMTU + CS_2 + S$$
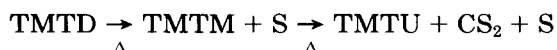
The more recent Raman spectroscopic studies[13] of TMTD heated for various times at 145°C revealed TMTD (973, 849, 558, 392 cm^{-1}) as the major compound after 30 min, with lesser amounts of TMTU (628, 492 cm^{-1}), CS_2 ($\sim$ 648 cm^{-1}), and tetramethylthiuram polysulfides (TMTP) (562, 515, 461 cm^{-1}). It was pointed out that TMTM (998, 575 cm^{-1}) had not been detected.

On heating the off-white TMTD used in this study, a sharp melting peak appeared at 138.9°C (literature values: 142–156°C [Ref. 14]; 146–148°C [Ref. 15]). However, since TMTD decomposes on melting, care must be taken not to view this endotherm as purely due to fusion [Fig. 1(a)]. The sample was cooled to $-30°C$ and stored for 24 h, whereupon the straw-colored residue solidified. A fresh TMTD sample, scanned at 5°C/min to 155°C, was analyzed with TLC. TMTD was the major component, and TMTM as well as a trace of sulfur were the only other constituents detected. By the analogy to arguments presented previously,[6] it was deduced
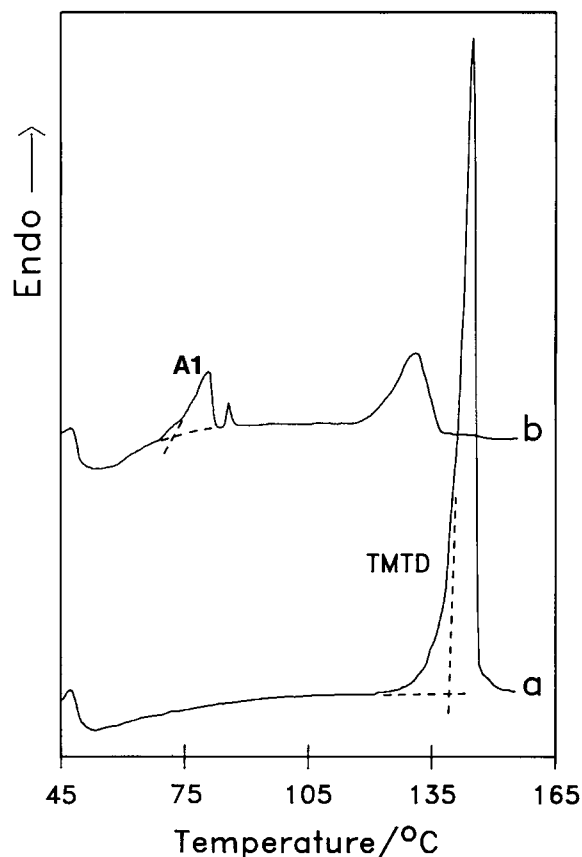

Figure 1 DSC spectra, scan rate 5°C/min. (a) TMTD; (b) rescan after 24 h at $-30°C$. Mi = 2.234 mg.

that peak A1 at 72°C [Fig. 1(b)] stemmed from a ternary eutectic. The peaks at higher temperatures probably originated from TMTM and TMTD. The mass loss of a TMTD sample, heated at 5°C/min in a TGA, was 0.3 and 4.4% at 155 and 180°C, respectively. (In the legends to the figures, M_i refers to the mass before the DSC experiment, and Mf, to the mass after the rescan.) The volatilization of TMTD and its decomposition products thus occurred relatively slowly at these temperatures:

$$TMTD \underset{\substack{\Delta \\ slow}}{\rightarrow\rightarrow} 2Me_2N^{\boldsymbol{\cdot}} + CS_2 + CS + S$$
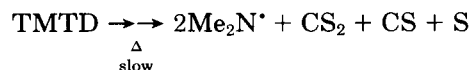
To study curative interactions prior to vulcanization, a TMTD sample was scanned at 20°C/min to 145.7°C and held isothermally for 5 min. This approach, in which relatively short times were allowed for interactions to occur, is more realistic in terms of vulcanization reactions. The product was analyzed quantitatively with HPLC, and TMTD (45.1 mol %) as well as TMTM (43.6 mol %) were

found. No TMTU was present. A TGA analysis showed a mass loss of 0.77%, which was equivalent to 0.8 mol % of the TMTD molecules present in the original sample. The fact that 10.5 mol % of the initial TMTD could not be accounted for in the experiment will receive attention below. The rapid formation of such a high percentage of TMTM was illuminative with respect to the literature cited above. It was therefore concluded that the formation of TMTM was an important immediate reaction in the decomposition of TMTD. The mol ratio of TMTD and TMTM that was found in the HPLC analysis could point to an equilibrium reaction (1), occurring rapidly prior to vulcanization (the latter aspect will be elaborated on in a later publication):

$$2TMTM + \tfrac{1}{4}S_8 \underset{\Delta}{\rightleftharpoons} 2TMTD \underset{\Delta}{\rightleftharpoons}$$

$$TMTM + TMTP \quad (1)$$
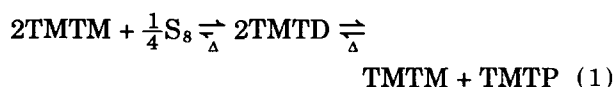
Sulfur/TMTD

Evidence that sulfur and TMTD reacted at vulcanization temperatures has been assessed with several analytical techniques.[13,16,17] It was evident that the liquefaction exotherm of TMTD, expected at 147.0°C, had not occurred on heating a sulfur/TMTD mixture at 20°C/min to 155°C (Fig. 2). The hot-stage microscope revealed that the dissolution of TMTD in sulfur coincided with the large endotherm A2 at 126.8°C. The partly concealed endotherm A3 was not identified, but could have been related to a chemical reaction between sulfur and TMTD.

Thermal events of the sulfur/TMTD mixture scanned at 20°C/min became less well resolved when heated at 5°C/min (cf. Figs. 2 and 3). The endothermic events of the sulfur/TMTD mixture then initiated at 95.1°C, which was well below the initiation temperature of a pure $S_\alpha \rightarrow S_\beta$ transition at 107.0°C.[5] The lower initiation temperature may be indicative of some interaction or mutual solubilization. The yellow molten sample was cooled and kept at −30°C for 72 h. The broadish peak in the rescan spectrum was related to a ternary eutectic (cf. Ref. 6). A TLC analysis on the sulfur/TMTD mixture, scanned at 5°C/min to 155°C, revealed elemental sulfur as the major component in the residue. TMTD and TMTM were also present, and a comparison of the spot sizes revealed that TMTD was in excess. A few unidentified products of higher polarity than TMTM were also detected, albeit very little.

In a quantitative experiment, a sulfur/TMTD sample was scanned at 20°C/min to 145.7°C, where
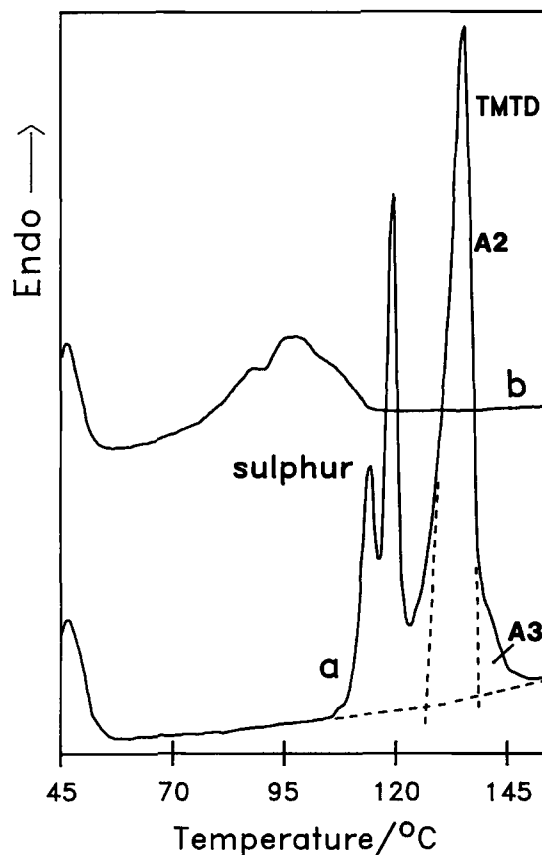

Figure 2 DSC spectra, scan rate 20°C/min. (a) Sulfur/TMTD (1.0/1.0 mol ratio); (b) rescan after 24 h at room temperature followed by 6 days at −30°C. Mi = 3.727 mg; Mf = 3.712 mg.

it was held isothermally for 5 min. The HPLC analysis revealed that elemental sulfur (100.4 mol %), TMTD (70.8%), and TMTM (5.0%) were present in the sample. No TMTU was found. A mass loss of 0.65% was measured with TGA, which was equivalent to 1.3 mol % TMTD molecules in the original sample. Therefore, only 77% mol % of the initial TMTD could be accounted for. The Raman spectroscopic studies of Coleman et al.[13] on the sulfur/TMTD (2.0/1.0 mol ratio) system at 145°C showed that a substantial amount of TMTP formed after 5 min, as was evident from a strong signal at 515 cm⁻¹. The fact that the initial elemental sulfur could be quantitatively accounted for after a similar experiment conducted in this laboratory was informative since it implied that any TMTP formed in the sulfur/TMTD interaction was unstable in solution. It was thus possible that part of the TMTP formed in the sulfur/TMTD reaction (or on the decomposition of TMTD, vide supra) had actually decomposed via a depolymerization reaction during the workup
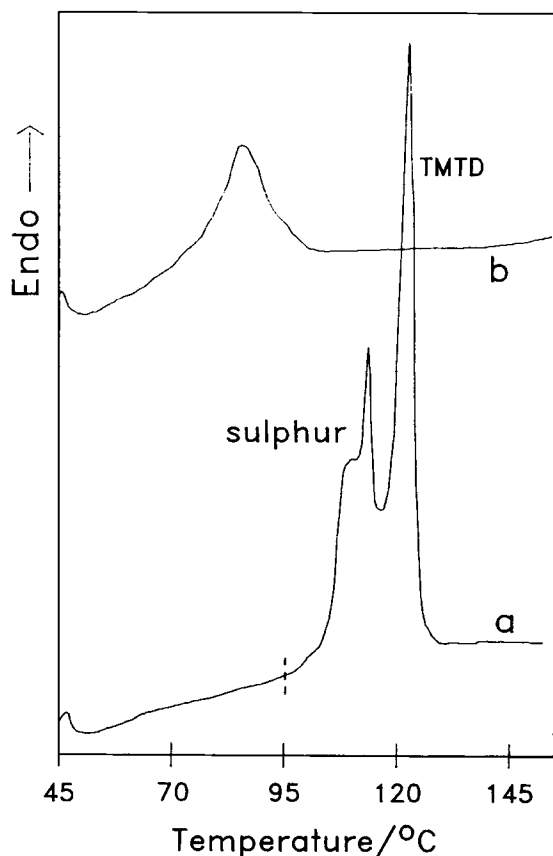
Figure 3 DSC spectra, scan rate 5°C/min (a) Sulfur/ TMTD (1.0/1.0 mol ratio); (b) rescan after 72 h at −30°C. Mi = 4.497 mg; Mf = 4.435 mg.

procedure for the HPLC analysis—the very stable sulfur octet ring and other products would then result. This would explain the experimental observation that the yield of thiuram species was always less than 100 mol %, after heating TMTD, sulfur/ TMTD, and TMTD/ZnO mixtures to ~ 146°C. Furthermore, a large amount of the current knowledge on sulfur vulcanization stems from studies with low molecular mass model compounds,[1-3] and this approach to simulate vulcanization reactions should be viewed with caution if the stability of the intermediate species is dependent on the inherent physical properties of the reaction medium.

Another point of interest in connection with the RPHPLC analysis described in the preceding paragraph was the particularly high concentration of TMTD (70.8 mol %) relative to TMTM (5.0%). This was in strong contrast to the corresponding yields of TMTD (45.1 mol %) and TMTM (43.6%) found, after treating TMTD under similar conditions (*vide supra*). These results suggest that equilibria of the type shown below were involved in the

immediate reactions between sulfur and TMTD. The formation of TMTM was inhibited in the presence of sulfur, which forced the equilibrium toward sulfides with a higher sulfur rank:

$$\mathrm{TMTM} + \tfrac{1}{8}\mathrm{S_8} \underset{\Delta}{\rightleftharpoons} \mathrm{TMTD} + \mathrm{S_8} \underset{\Delta}{\rightleftharpoons} \mathrm{TMTP} \quad (2)$$

Furthermore, the $S_\lambda \rightarrow S_\mu$ transition of elemental sulfur was absent on scanning a sulfur/TMTD mixture at 5°C/min to 180°C. An endotherm, which was associated with the formation of gases, initiated at 162.0°C. These phenomena pointed to an early reaction between sulfur and TMTD, and based on the Raman spectroscopic studies of Coleman et al.,[13] the product could have been TMTP. The formation of the relatively unstable TMTP molecules prior to vulcanization would be in harmony with the accelerating property of TMTD in sulfur vulcanization.

TMTD/Stearic Acid

A TMTD/stearic acid mixture scanned to 180°C revealed the melting of stearic acid at 57.6°C, followed by the liquefaction of TMTD at 143.6°C. The broadish endotherm with a crest temperature at 168°C was connected with the evaporation of gases (Fig. 4). The sample was cooled to −30°C, and the rescan spectrum after 72 h showed a melting endotherm at 43.7°C, corresponding well in shape and size to that of the melting of stearic acid in the original scan. The TGA thermogram of the TMTD/ stearic acid mixture displayed a mass loss commencing at 146.6°C, i.e., concurrently with the liquefaction of TMTD, and the maximum rate of evaporation (8.2%/min) occurred at 167°C [Fig. 4(c)]. The gases had a sulfurous odor. The mass loss was 7.6 and 41.1% at 155 and 180°C, respectively, which was much higher than the values of 0.3 and 4.4% recorded for pure TMTD. Assuming these gases were solely generated from TMTD, then ~ 90 mol % of the theoretical TMTD had decomposed at 180°C in the presence of stearic acid. Arguments presented earlier[6] to explain the instability of TMTM in the presence of stearic acid will also hold in the present situation.

TMTD/ZnO

The generally accepted mechanism of NR/TMTD/ ZnO vulcanization rests on the *in situ* formation of zinc perthiomercaptides via Scheme 1. Bateman et al.[3] relied on literature evidence in support of $XSS_a ZnS_b SX$ formation.
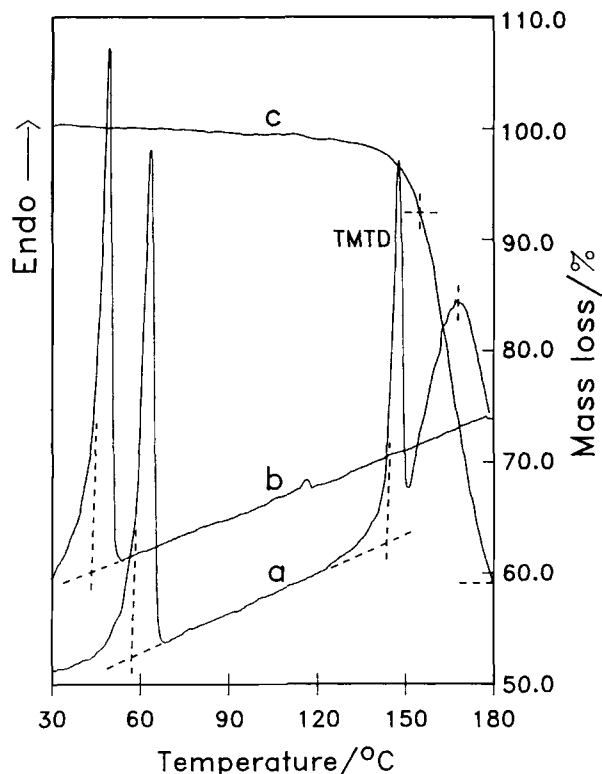
Figure 4 DSC spectra, scan rate 5°C/min: (a) TMTD/stearic acid (1.0/1.0 mol ratio); (b) rescan after 72 h at −30°C. Mi = 4.409 mg. TGA spectrum, scan rate 5°C/min; (c) TMTD/stearic acid (1.0/1.0 mol ratio).

Kawaoka[18] found that a TMTD/ZnO mixture, heated at 147°C, gave a vigorously exothermic reaction. The reaction products consisted largely of zinc dimethyldithiocarbamate dimethylthiocarbamate and sulfur, but little ZDMC was formed. In another report, Kawaoka[19] studied the action of H_2S on the TMTD/ZnO reaction. Although ZDMC was the major product, other considerations[20] led to the conclusion that H_2S did not play an important role in the diene rubber/TMTD/ZnO cure. It is well known that ZDMC forms in NR/TMTD/ZnO vulcanization systems,[11,21,22] and therefore any reference to these reports does not establish that ZDMC formed prior to cross-linking.

On the other hand, Craig et al.[17,23-25] expressed conflicting opinions with regard to the TMTD/ZnO reaction in the 1950s, but it seemed that TMTD and ZnO showed little tendency to react in the absence of rubber. Isothermal Raman spectroscopic studies on the TMTD/ZnO (1.0/5.0 mol ratio) system at 125°C revealed that TMTD was still the major compound after 15 min. Low-intensity bands at 515 and 461 cm^{-1} were indicative of the formation of

TMTP, and a small Raman line at 675 cm^{-1} was tentatively assigned to zinc dimethylmonothiocarbamate. Furthermore, the spectrum after 30 min resulted mainly from TMTD (973, 849, 558, 392, 360, 170 cm^{-1}), and the more intense signals at 515 and 461 cm^{-1} would imply that the amount of TMTP had increased. The fingerprint frequencies of ZDMC (1 387, 962, 568 cm^{-1}) and sulfur (470, 216, 152 cm^{-1}) were very weak after 30 min, but became prominent after 240 min. Coleman et al.[13] also remarked that TMTM, CS_2, and TMTU were not detected. However, there was a small peak at 998 cm^{-1} that is characteristic of TMTM, but Coleman et al. made no reference to this peak.

The thermogram of a TMTD/ZnO system scanned at 20°C/min up to 155°C is depicted in Figure 5. The temperature was lowered to 147°C and the sample held isothermally for 30 min. Despite
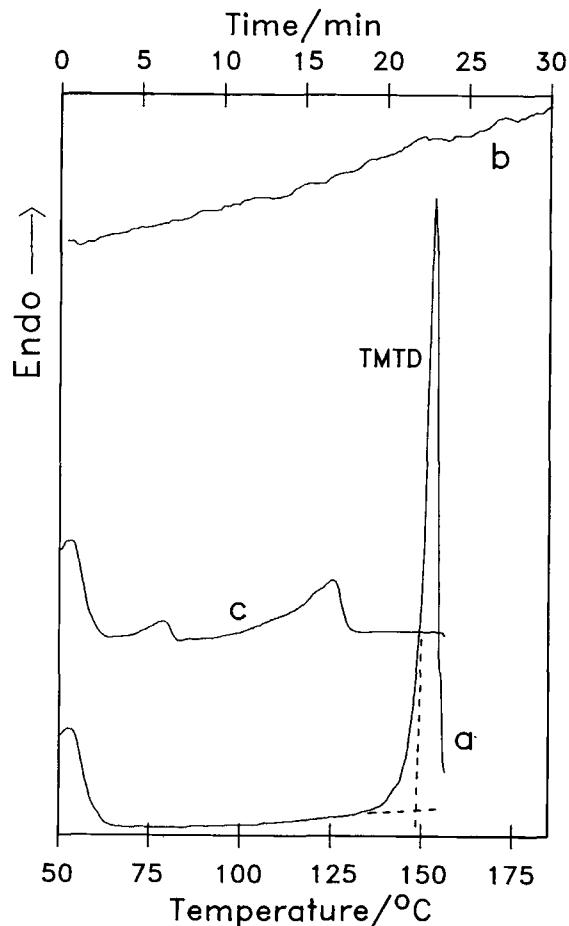

Figure 5 DSC spectra. (a) TMTD/ZnO (1.0/1.0 mol ratio) sample scanned at 20°C/min to 155°C; (b) isothermal scan at 147°C for 30 min; (c) rescan after 72 h at −30°C. Mi = 2.020 mg; Mf = 1.894 mg.

a very sensitive DSC setting of 0.42 mJ/s, no noteworthy thermal events were observed. This conflicts with the report of Kawaoka[18] that TMTD and ZnO reacted vigorously and exothermically at 147°C to yield zinc dimethyldithiocarbamate dimethylthiocarbamate as the major product. A TLC analysis on a TMTD/ZnO sample, conducted after the isothermal experiment, disclosed that TMTM, TMTD, and a little sulfur were the only products. TMTD was in excess, and no ZDMC was detected with sublimed iodine as indicator. The rather broad endotherms in the rescan thermogram were reminiscent of the rescan spectrum obtained after heating TMTD to 155°C (cf. Fig. 1). The total mass loss was 6.2% after the rescan experiment.

Exactly the same results were found on substituting the active grade ZnO (particle size less than 0.2 μm) used in the experiments above, with Red seal ZnO (particle size 0.8 μm).

A HPLC analysis performed on a TMTD/ZnO sample, heated at 20°C/min and kept at 147°C for 30 min, revealed that TMTD (51.1 mol %) and TMTM (24.9%) were present. A small amount of ZDMC (2.1 mol %) was measured as cobalt (III) dimethyldithiocarbamate (CoDMC), implying that virtually none of the TMTD and ZnO had reacted to form ZDMC. No correction was made for the interference of TMTD or TMTM in the zinc/cobalt exchange reaction (see Paper V in this series). A mass reduction of 1.24% was equivalent to 1.7 mol % TMTD, which meant that 79.8% of the initial TMTD could be accounted for. The latter observation has been dealt with before.

In a further experiment, TMTD liquefied at 135.8°C on scanning a TMTD/ZnO mixture at 5°C/min to 270°C. A complex series of thermal events were noted above $\sim$ 170°C and sulfurous odor was evident at these higher temperatures. The mass reduction of 79.2% after the DSC scan implied that virtually all the initial TMTD had evaporated. The gray-light brown product was analyzed with HPLC, but no TMTD, TMTM, and ZDMC was found.

The *in situ* formation of ZDMC as the first step in thiuram-accelerated sulfur vulcanization of NR has all along been an extremely important facet of the mechanism.[2-4] Research by Moore and Watson[22] on the synthetic cis-1,4-polyisoprene (IR) (100)/ TMTD (4.0)/ZnO (4.0) compound vulcanized at 140°C showed the ZDMC yield to increase from 19.3 mol % (after 15 min) to 31.6% (after 30 min) to 52.2% (after 120 min). These quantities were much larger than was the low yield of ZDMC, found on heating a TMTD/ZnO mixture in the DSC for 30

min at 147°C. Since TMTD was in a molten state at 147°C, it was reasonable to assume that the ZnO particles were sufficiently wetted for a reaction to proceed. However, it could have been that the TMTD reacted superficially with ZnO to yield ZDMC, which formed an impermeable coating around the ZnO particles. ZDMC melts at $\sim$ 250°C.[14,15] A physical incrustation around a ZnO particle would inhibit the diffusion of reagents to and from the reaction zone, thereby preventing further chemical reactions. This phenomenon was indeed observed for the stearic acid/ZnO reaction, in the formation of zinc stearate.[5] The TMTD/ZnO reaction may proceed better in an inert solvent medium, especially if the compounds other than ZnO could dissolve to some extent. Such an approach was intended to simulate the postulated TMTD/ZnO reaction in the presence of IR or NR.

A TLC analysis, performed after refluxing a 0.1M solution of TMTD and ZnO at 121 or 150°C in n-decane/benzene for 3 h, showed large amounts of TMTD and TMTM, but ZDMC formed in low quantity (less than 10 mol % of the initial TMTD).

A 0.1M solution of TMTD and ZnO (1.0/1.0 mol ratio) was refluxed at 138°C in n-butyl ether for 3 h. The products were isolated with conventional chromatography, and ZDMC (15.2 mol %), TMTD (50.1%), and TMTM (20.0%) were found. It was possible to account for 85.3 mol % of the initial TMTD.

It is common practice in industry to use ZnO in excess with respect to the accelerator added, in order to optimize the vulcanizate properties. A solution of TMTD and ZnO (1.00/29.55 mol ratio) was refluxed for 3 h in n-decane/benzene at 150°C—the concentration was 0.1M with respect to TMTD. The products were isolated, and ZDMC (16.7 mol %), TMTD (45.8%), and TMTM (12.5%) were present. It was possible to account for 75.0 mol % of the initial TMTD. The low yield of ZDMC was also not in line with the observations of Scheele et al.,[21] that the ZDMC yield of an NR (100)/TMTD (2.6)/ZnO (5.4) (1.00/6.15 mol ratio) compound was already 24.1 mol % after 90 min at 110°C and 23.1 mol % after 40 min at 120°C. The maximum yield of ZDMC was always 66 mol % in Scheele's studies. The large difference in the rate of ZDMC formation in the absence or presence of NR must be ascribed to a different reaction mechanism whereby ZDMC was formed. The above results conflict with the mechanism that requires the formation of zinc perthiomercaptides prior to vulcanization. This point will receive more attention in a later publication.

Sulfur/TMTD/Stearic Acid

The thermogram of the sulfur/TMTD/stearic acid mix scanned at 5°C/min showed stearic acid melting at 57.3°C (Fig. 6). The endothermic event at 104.4°C could have been associated with a sulfur/TMTD interaction, a mutual solubilization, and/or the $S_\alpha \rightarrow S_\beta$ transition. The peak at 108.5°C was probably due to a $S_\alpha \rightarrow S_\lambda$ transition, followed by a large $S_\beta \rightarrow S_\lambda$ phase change at 113.3°C. The dissolution endotherm of TMTD overlapped with the sulfur melting and had a crest temperature at 129.1°C. The mass reduction of 18.4% at 180°C implied that the endotherm initiating at 136.9°C was due to the evaporation of gases, arising from the thiuram sulfenyl radical/stearic acid reaction.[6] About 40 mol % of the initial TMTD was still present at 180°C. A sulfurous odor was evident on opening the DSC, and the brownish residue was rather hard. The sample was rescanned after 6 days at −30°C. The melting endotherm between 30 and
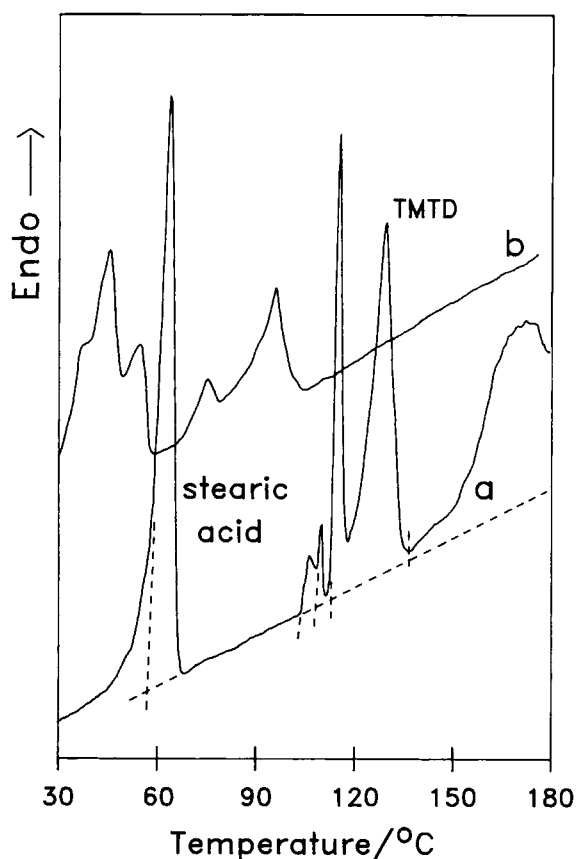

Figure 6 DSC spectra, scan rate 5°C/min. (a) Sulfur/TMTD/stearic acid (1.0/1.0/1.0 mol ratio); (b) rescan after 6 days at −30°C. Mi = 6.356 mg; Mf = 4.740 mg.
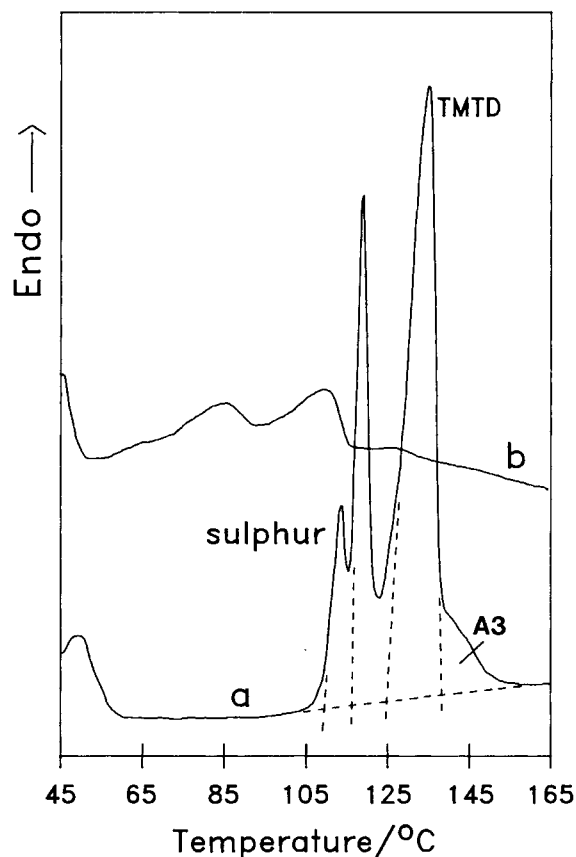

Figure 7 DSC spectra, scan rate 20°C/min. (a) Sulfur/TMTD/ZnO (1.0/1.0/1.0 mol ratio); (b) rescan after 2 weeks at −30°C and then 48 h at room temperature . Mi = 4.882 mg.

60°C has been dealt with previously[6] and could have originated from dehydrogenated stearic acid.

Sulfur/TMTD/ZnO

The DSC analysis on the sulfur/TMTD/ZnO mix gave information in conflict with research published previously. Kawaoka[26] reported that a sulfur/TMTD/ZnO mixture reacted at vulcanization temperatures with the formation of 14 products. The reaction started at ~ 110°C and, at 140°C, proceeded rapidly. The main products were ZDMC, zinc dimethyldithiocarbamate dimethylthiocarbamate, sulfur, and $ZnSO_3$, while COS was identified among the gaseous products. However, when a sulfur/TMTD/ZnO mixture was scanned at 20°C/min to 165°C, the endotherms at 109.0 and 116.1°C were undoubtedly due to the melting of sulfur (rather than a reaction, Fig. 7). The $S_\beta \rightarrow S_\lambda$ transition overlapped with the TMTD dissolution at 125°C,

which was, in turn, well below the liquefaction of pure TMTD at 147.0°C. A concealed endotherm A3, also noted in previous experiments (cf. Fig. 2), could have originated from an interaction between sulfur and TMTD. The sample was cooled, and a mass reduction of 1.0% was measured. The viscous product was stored for 2 weeks at −30°C, but did not solidify. A sulfur seed was added to initiate crystallization, whereupon the sample solidified after 48 h at room temperature. The residue was a beige-yellow solid, and the rescan showed two broadish isotherms below 118°C.

In a subsequent experiment, a sulfur/TMTD/ZnO mixture was scanned at 20°C/min to 140°C, where it was held isothermally for 30 min. No thermal events were observed at a DSC sensitivity of 0.42 mJ/s, in strong contrast to the assertion that the sulfur/TMTD/ZnO reaction proceeded rapidly at 140°C to form ZDMC, sulfur, etc.[26] A mass reduction of only 0.5% was evidence that hardly any gaseous products had formed under these experimental conditions. A TLC examination, using sublimed iodine as detecting reagent, showed that elemental sufur, TMTD, and TMTM were the major constituents in the sample. TMTD was in excess relative to TMTM. A spot of negligible size appeared at the same R_f value as that of an authentic ZDMC standard, indicating that virtually no ZDMC had formed.

The Raman spectroscopic studies of Colemen et al.[13] tied in with the DSC findings. A sulfur/TMTD/ZnO (2.0/1.0/5.0 mol ratio) mixture was heated at 125°C, and the spectra were recorded after various times. Strong TMTP Raman signals (515, 461 cm^{-1}) were already evident after 2 min, but a substantial amount of TMTD (849, 558, 360 cm^{-1}) was also present. The concentration of TMTP reached a maximum between 5 and 15 min, while that of elemental sulfur was at a minimum—the same remark applied in connection with the sulfur/TMTD (2.0/1.0 mol ratio) system. These results were in harmony with the fact that the peak enthalpies, profiles, and positions involved on heating a sulfur/TMTD mixture at 20°C/min to 155°C remained constant with the addition of ZnO (cf. Figs. 2 and 7). Of major importance was the fact that although the Raman bands of TMTD, sulfur, and TMTP dominated the spectrum recorded after 30 min no ZDMC signals were discernible. The concentration of sulfur increased between 15 and 120 min, and the Raman lines of ZDMC (1 387, 962, 568 cm^{-1}) as well as sulfur (470, 216, 152 cm^{-1}) appeared strong after 240 min. Throughout the experiments, neither CS$_2$

($\sim$ 648 cm^{-1}) nor TMTU (662, 628, 492 cm^{-1}) was detected. It is therefore concluded that the sulfur/TMTD/ZnO reaction was very sluggish toward the formation of ZDMC.

TMTD/Stearic Acid/ZnO

The thermogram of a TMTD/stearic acid/ZnO mixture scanned at 5°C/min (Fig. 8) showed stearic acid melting at 58.3°C and a small zinc stearate fusion endotherm at 109.4°C.[5] A TMTD liquefaction endotherm at 133.4°C occurred somewhat lower than that of pure TMTD at 138.9°C (cf. Fig. 1). Complex thermal events followed directly on the TMTD liquefaction peak, and it was inferred that several products were formed at that stage. The involvement of ZnO in the TMTD/stearic acid/ZnO reaction was *inter alia* linked with the formation of zinc stearate, which formed at $\sim$ 155°C in the absence of TMTD.[5] The sample was cooled and stored at −30°C for 6 days, and the resultant brownish past was rescanned. A melting peak at 34.3°C had the same shape as the melting of stearic acid in the original scan, but was less intense. It was ascribed to a stearic acid derivative (cf. Ref. 6). The peak with a crest temperature at 111.6°C was assigned to the fusion of zinc stearate, based on its relative position and shape (cf. Ref. 5). It was clear that the stearic acid/ZnO reaction did not proceed quantitatively.

A TGA curve of the mixture revealed that a mass loss started concurrently with the liquefaction of TMTD at 132.0°C. The mass loss was 13.6 and 31.9% at 155 and 180°C, respectively, implying that roughly 75 mol % of the theoretical TMTD had evaporated at 180°C.

Arguments have been presented for the formation of dimethyldithiocarbamic acid (DMDCA) on heating TMTD (or TMTM) and stearic acid.[6] DMDCA is unstable[27,28] and would decompose to Me$_2$NH and CS$_2$ at vulcanization temperatures. In the presence of ZnO, however, DMDCA and ZnO would react to form ZDMC. Bedford and Gray[29] described the reactions of dimethylammonium dimethyldithiocarbamate [Me$_2$NC(S)SNH$_2$Me$_2$] and ZnO to form ZDMC, Me$_2$NH, and H$_2$O as violent. When Bedford and Gray[29] added ZnO to a XSNH$_2$Me$_2$/CS$_2$ mixture, ZDMC and H$_2$O formed as the only products:

$$2XSH + ZnO \rightarrow ZDMC + H_2O$$

Thus, whereas the endothermic peak above 150°C in the TMTD/stearic acid thermogram (Fig. 4) was

mainly due to the evaporation of gases such as Me_2NH and CS_2, the endotherm above 150°C in the TMTD/stearic acid/ZnO thermogram (Fig. 8) was ascribed to multiple events. The latter comprised the TMTD/stearic acid and stearic acid/ZnO reactions and most probably the DMDCA/ZnO reaction to yield ZDMC. In forming ZDMC, the evaporation of gases such as CS_2 and Me_2NH would be minimized, which would reduce this endothermal contribution to the total enthalpy (cf. Figs. 4 and 8). Note that the DTGA curves showed a higher maximum mass loss rate (8.2%/min at 166.6°C) for the TMTD/stearic acid mixture heated at 5°C/min compared to that of the TMTD/stearic acid/ZnO system (4.9%/min at 154.0°C).

Sulfur/TMTD/Stearic Acid/ZnO

Melting of stearic acid commenced at 52.7°C when a sulfur/TMTD/stearic acid/ZnO mixture was scanned at 5°C/min (Fig. 9). The peak at 110.0°C

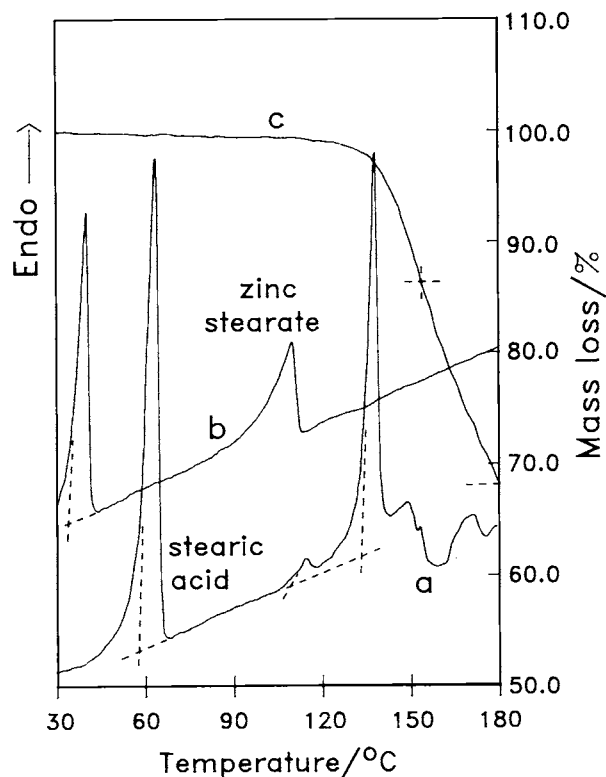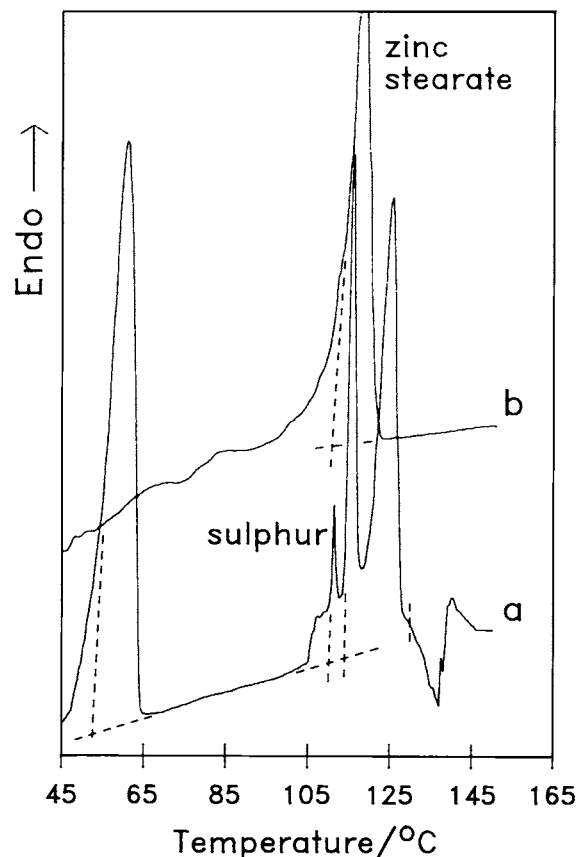**Figure 9** DSC spectra, scan rate 5°C/min. (a) Sulfur/TMTD/stearic acid/ZnO (1.0/1.0/1.0/1.0 mol ratio); (b) rescan after 24 h at −30°C. Mi = 7.000 mg; Mf = 6.732 mg.

Figure 8 DSC spectra, scan rate 5°C/min: (a) TMTD/stearic acid/ZnO (1.0/1.0/1.0 mol ratio); (b) rescan after 6 days at −30°C. Mi = 4.938 mg. TGA spectrum, scan rate 5°C/min; (c) TMTD/stearic acid/ZnO (1.0/1.0/1.0 mol ratio).

was due to a $S_\alpha \rightarrow S_\lambda$ transition, followed by a large $S_\beta \rightarrow S_\lambda$ phase change at 113.8°C. The usual small zinc stearate melting peak, resulting from a partial reaction of stearic acid and ZnO at low temperatures, was not observed per se (cf. Ref. 5), although it was almost probably concealed in the DSC spectrum between 104 and 114°C. The TMTD liquefaction endotherm had a crest temperature at 125.9°C. A reaction profile characteristic of the formation of zinc stearate commenced at ∼ 130°C (cf. Ref. 5). It was once again found that the stearic acid/ZnO reaction occurred at random temperatures in the presence of sulfur (cf. Ref. 5). Stearic acid/ZnO reaction temperatures as low as 77.4°C were recorded on heating a sulfur/TMTD/stearic acid/ZnO mixture at 2.5°C/min. The sample was cooled from 150°C and stored at −30°C for 24 h. Microscopic investigation revealed a whitish sample with brown decomposition areas. Low-intensity melting endotherms below 95°C in the rescan spectrum were associated with

thiuram species and sulfur, and a prominent melting peak for zinc stearate appeared at 110.8°C. A total mass loss of 3.8% was calculated, somewhat higher than the theoretical value of 2.1% expected due to the loss of H_2O from the stearic acid/ZnO reaction.

A sulfur/TMTD/stearic acid/ZnO system was, in addition, heated at 20°C/min up to 140°C, i.e., just after the TMTD liquefaction peak, and held isothermally for 30 min. The thermogram trace was very unstable for the first 6.5 min of the isothermal run, due to the formation of zinc stearate. The sample was cooled and kept at −30°C for 72 h. A large zinc stearate melting peak was evident in the rescan spectrum. The total mass reduction was 9.6%, implying that at least 7.5% of the volatiles had to be ascribed to species other than H_2O. It was therefore deduced that the TMTD/stearic acid reaction, which led to the decomposition of TMTD (cf. Figs. 4 and 6), could occur as a side reaction in the sulfur/TMTD/stearic acid/ZnO system. It probably resulted from the interaction of free stearic acid, which did not react with ZnO to yield zinc stearate, and TMTD or TMTP (*vide post*).

TMTD/Zinc Stearate

A TMTD/zinc stearate mixture was heated at 20°C/min to 140°C, where it was kept isothermally for 10 min. The zinc stearate melted at 112.9°C, and besides the melting of TMTD, no other events were noted during the isothermal run. The sample was cooled and kept at −30°C for 72 h and appeared light brown with darker decomposition areas. The large zinc stearate melting endotherm at 108.9°C was the only peak in the rescan spectrum. The total mass reduction of 1.9% implied that TMTD and zinc stearate, as such, were relatively unreactive under these conditions.

The results in the last two sections above argue against the formation of ZDMC as the very first step in NR/sulfur/TMTD/stearic acid/ZnO vulcanization systems, as postulated in the literature.[1]

CONCLUSIONS

DSC and HPLC experiments were interpreted in terms of the facile formation of TMTP on heating TMTD or sulfur/TMTD mixtures. The $S_\lambda \rightarrow S_\mu$ transition of elemental sulfur was, for example, absent on scanning a sulfur/TMTD mixture to 180°C, indicating that the eight-membered sulfur rings had reacted at lower temperatures. It appeared, in ad-

dition, that the stability of the intermediate species XSS_ySX was dependent on the inherent physical properties of the reaction medium. The reluctance of TMTD and ZnO to react at vulcanization temperatures was unexpected and argued against the formation of XSS_aZnS_bSX, postulated as the active sulfurating agent in IR or NR/TMTD/ZnO vulcanization systems. TMTD (or TMTP) decomposed much faster in the presence of stearic acid, and complex thermal events were observed after the melting of TMTD in the TMTD/stearic acid/ZnO mixture. These high-temperaure reactions were virtually absent on heating the sulfur/TMTD/stearic acid/ZnO mixture, but the stearic acid/ZnO reaction was prominent. The TMTD/zinc stearate mixture was reluctant to react when subjected to 140°C for 10 min. With reference to the mechanism of vulcanization, this implied that the thiuram/stearic acid reaction was of negligible importance in the sulfur/TMTD/stearic acid/ZnO system, once stearic acid had been removed through the formation of zinc stearate.

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