Comparison of Tetraethyl- and Tetramethylthiuram Disulfide Vulcanization. I. Reactions in the Absence of Rubber

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ABSTRACT: The reactions of tetraethylthiuram di- and monosulfide (TETD and TETM, respectively) were investigated in the absence of rubber and compared with those reported previously for tetramethylthiuram compounds. The reactions of TETM, TETD, and zinc diethyldithiocarbamic acid with zinc oxide and sulfur were investigated by differential scanning calorimetry, and the reaction products analyzed by high performance liquid chromatography. TETM was shown to be more stable at vulcanization temperatures (±150°C), but also less reactive with sulfur than tetramethylthiuram disulfide (TMTD). The reactions of TETD are very similar to those of TMTD, the TETD reacting slower than the TMTD to form analogous products. In the presence of zinc oxide, the formation of the zinc compound of TETD, zinc diethyldithiocarbamic acid, occurred readily. TMTD does not react readily with zinc oxide. The reaction of TETD with sulfur lead to the formation of polysulfidic accelerator species, although the concentrations formed in the absence of rubber were considerably less than that formed by the corresponding TMTD system. These differences in reactivity would affect the vulcanization reactions that take place in the rubber. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2292–2299, 2001

Key words: vulcanization mechanism; tetraethylthiuram disulfide; sulfur; zinc oxide; polysulfides

INTRODUCTION

The effect of thiuram-derivative accelerators on sulfur vulcanization has been studied by many groups. Monosulfides such as tetramethylthiuram monosulfide (TMTM), disulfides such as tetramethylthiuram disulfide (TMTD), and tetraethylthiuram disulfide (TETD), and polysulfides such as dipentamethylenethiuram tetrasulfide, have been frequently used in industry. However, in recent years, an increased emphasis on safety has resulted in the increased use of those that do not form carcinogenic nitrosamines. TMTD has had to be replaced by noncarcinogenic nitrosamine-forming accelerators such as TETD. These di- and polysulfidic accelerators can vulcanize rubber in the absence of added sulfur, but are usually used with sulfur and zinc oxide.

Thiuram accelerators undergo several reactions before their reaction with the rubber chain. The thermal decomposition reactions of TMTD have been shown to result in the formation of TMTM, tetramethylthiourea (TMTU), CS_2, and sulfur.[1] The formation of polysulfides has also been shown to occur from the breakdown of TMTD. Electron paramagnetic resonance investi-

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gations by Blokh[2] indicated that TMTD dissociated into radicals when heated to 220°C. It was proposed that the TMTD could decompose homolytically or heterolytically to form radicals that, on recombination, would form polysulfides. Raman and electron spin resonance spectra[3] of TMTD heated to 145°C and held at that temperature for 2 h showed the formation of TMTU, tetramethylthiuram polysulfides (TMTP,) and sulfur. After 60 min, TMTD was nearly undetectable and by 120 min, the only products found were TMTU, TMTP, CS_2, and sulfur.

Geyser and McGill[4] proposed that the formation of TMTM and TMTP involved TMTD [XSSX, where X = $(CH_3)_2NC(S)$] homolysis forming $XS^\bullet$, followed by sulfur exchange between TMTD and $XS^\bullet$ leading to TMTM (XSX) formation. The high TMTD/$XS^\bullet$ ratio would lead to further sulfur extraction by persulfenyl radicals. TMTP formation occurred once the persulfenyl radical concentration was sufficiently large. In a mixture of TMTD and sulfur heated to 145°C, Coleman et al.[3] showed the formation of TMTP that reached a maximum concentration between 2 and 15 min. The final products, after 120 min, were CS_2, TMTU, and sulfur. Kruger and McGill[5] reported the formation of TMTP and a small amount of TMTM (5 mol %) in a sample of TMTD/sulfur heated in the differential scanning calorimeter (DSC) to 145.7°C and held isothermally for 5 min. Geyser and McGill[4] found that in the presence of sulfur, TMTP formation became more pronounced and less TMTM formed. Extraction of sulfur atoms from cyclic sulfur was thought to be favored over extraction from TMTD, because of the low TMTM concentrations.

Numerous authors have reported on the interaction of TMTD and ZnO to form zinc dimethyldithiocarbamate (ZDMC).[3,6–8] Kruger and McGill[5] obtained very little or no reaction with ZnO, and the presence of ZDMC in rubber was attributed to it being a byproduct of the crosslinking reaction in rubber. Craig et al.[6] heated radiosulfur labeled TMTD with ZnO and produced randomly radioactive ZDMC and radioactive sulfur in high yield. Jarrijon[9] obtained a 60 mol % conversion of TMTD to ZDMC when TMTD (three parts) was heated with ZnO (two parts) for 2 h at 147°C, in the absence of a solvent. He showed that a current of H_2S also promoted considerable formation of ZDMC. Geyser and McGill[10] showed that the variation in ZDMC, found by various authors, was associated with water adsorbed onto the ZnO surface. Some $XS^\bullet$ radicals from TMTD homolysis were adsorbed onto the ZnO surface where they reacted with the water molecules leading to an Hdmtc (dimethyldithiocarbamic acid) type adsorbent, which on reaction with ZnO produced ZDMC.

This report compares the results from a study of tetraethylthiuram monosulfide (TETM) and TETD reactions in the absence of rubber, with those from previous workers that were performed on TMTM and TMTD.

EXPERIMENTAL

The materials used in this study were as follows: tetraethylthiuram disulfide (TETD) (Fluka, Switzerland), zinc diethyldithiocarbamate (ZDEC) (Orchem, South Africa), sulfur (AECI, South Africa), zinc oxide (Zinc Process, South Africa), diethyldithiocarbamic acid, sodium salt trihydrate (Na.detc) (Aldrich). Other compounds were synthesized as detailed below.

Decomposition reactions and reactions between curatives were conducted in a TA Instruments DSC 10 module, connected to a TA 2000 Thermal Analyzer. High purity nitrogen, at a flow rate of 65 mL/min, was used as a purge gas. Heating rates were kept at 2.5°C/min to facilitate direct comparison between previous work on TMTD and also with the rubber systems. Mass loss determinations were conducted using a TA Instruments TGA 2050 Thermogravimetric Analyzer connected to a TA 2000 Thermal Analyzer. High purity nitrogen, at a flow rate of 100 mL/min was used as a purge gas. The heating rate was 2.5°C/min. A Waters high performance liquid chromatography (HPLC) system comprising a Waters 510 pump and a Waters 484 Tunable UV Absorbance Detector was used. The column was a μ-Bondapak C18 reverse phase column, and the eluent was methanol/water (85:15 v/v ratio) at a flow rate of 1 mL/min.

Samples of curatives and blends of curatives were heated in the DSC and then dissolved in approximately 5 mL of dichloromethane, followed by dilution in methanol. ZDEC was converted into its cobalt analogue by adding $CoCl_2$ to the ZDEC solution before HPLC analysis.[11]

Synthesis of Compounds

Tetraethylthiuram polysulfides (TETD polysulfides) were prepared by the method outlined by Levi.[12] Sulfur monochloride (1.3 mL) and sodium diethyldithiocarbamate (Na.detc) (2.5 g) were reacted at room temperature in sodium-dried ether for 30 min. An equilibrium series of polysulfides was produced; individual polysulfides in the mixture were identified on the basis of their HPLC retention times. Diethyldithiocarbamic acid (Hdetc) was synthesized by adding HCl (~0.8*M*) to Na.detc salt while immersed in an ice bath. A precipitate of TETD was formed, and Hdetc was recovered from the filtrate. Nuclear magnetic resonance (NMR) analysis confirmed the identification of the Hdetc. TETM preparation was based on a method by Klopping and van der Kerk.[13] Water was added in excess to dissolve the Na.detc salt (0.7 g) in an ice bath; solid KCN (7 g) was added in large excess. A saturated ammonium persulfate solution (8.0 g) was then added dropwise with cooling and stirring. A viscous dark brown liquid (TETM) was formed. Sulfur analysis by the method of Haslam and Willis[14] and NMR analysis confirmed the identification as TETM.

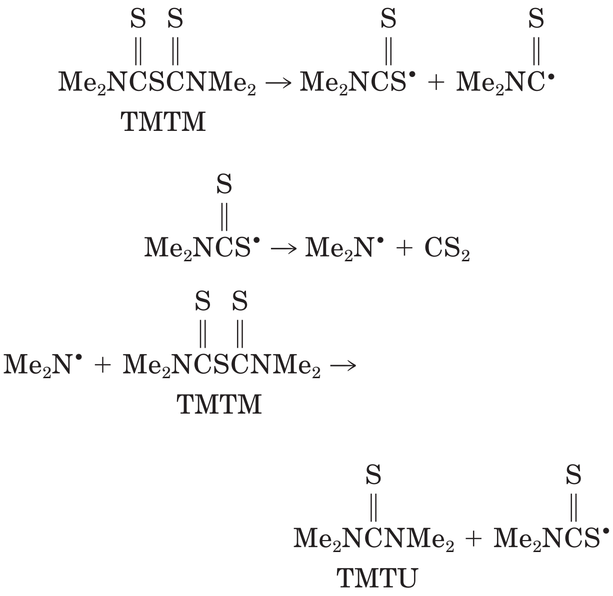
Tetraethylthiourea (TETU) was prepared by heating TETD in a sealed glass tube for 30 min at 190°C. Thin layer chromatography was used to separate the TETU. Sulfur analysis by the method of Haslam and Willis[14] and NMR analysis confirmed the identification as TETU.

RESULTS AND DISCUSSION

Reactions of TETM and TMTM

TETM is a brownish-yellow viscous liquid (bp 225–240°C)[15] which remained unreactive up to temperatures of 200°C. HPLC analysis yielded a single TETM peak and trace amounts of disulfide (TETD) and trisulfide (<1 mol %). Only a slight decomposition of TETM to TETU (3 mol %) occurred above 220°C. The mass loss at temperatures above 170°C can be attributed to TETM evaporation rather than TETM decomposition to TETU. Similarly, HPLC analysis of TETM held isothermally at 150°C showed no TETM decomposition, and the gradual mass loss could be ascribed to TETM evaporation.

Geyser and McGill[4] reported that TMTM decomposed to form TMTU and CS_2 when heated to 220°C, as was found by Coleman et al.[3] when TMTM was held at 145°C for 2 h. It was proposed that the mechanism involved the heterolytic cleavage of TMTM into thiuram sulfenyl and thiocarbonyl radicals. Thiuram sulfenyl radicals could lose CS_2, forming a dimethylamino radical that could attack undissociated TMTM forming TMTU and a thiuram sulfenyl radical.[3]



$$\underset{\text{TMTM}}{\mathrm{Me_2N\overset{\overset{S}{\|}}{C}S\overset{\overset{S}{\|}}{C}NMe_2}} \rightarrow \mathrm{Me_2N\overset{\overset{S}{\|}}{C}S^{\bullet}} + \mathrm{Me_2N\overset{\overset{S}{\|}}{C}{}^{\bullet}}$$

$$\mathrm{Me_2N\overset{\overset{S}{\|}}{C}S^{\bullet}} \rightarrow \mathrm{Me_2N^{\bullet}} + \mathrm{CS_2}$$

$$\mathrm{Me_2N^{\bullet}} + \underset{\text{TMTM}}{\mathrm{Me_2N\overset{\overset{S}{\|}}{C}S\overset{\overset{S}{\|}}{C}NMe_2}} \rightarrow \underset{\text{TMTU}}{\mathrm{Me_2N\overset{\overset{S}{\|}}{C}NMe_2}} + \mathrm{Me_2N\overset{\overset{S}{\|}}{C}S^{\bullet}}$$

A DSC curve of a TETM/sulfur (1.0:1.0 mol ratio) sample heated at 2.5°C/min to 200°C showed the characteristic sulfur melt endotherms at 105°C (Fig. 1). An endotherm starting in the region of 140°C was accompanied by a mass loss that increased progressively with temperature. HPLC analysis of the reaction products formed at different temperatures revealed TETD to be the

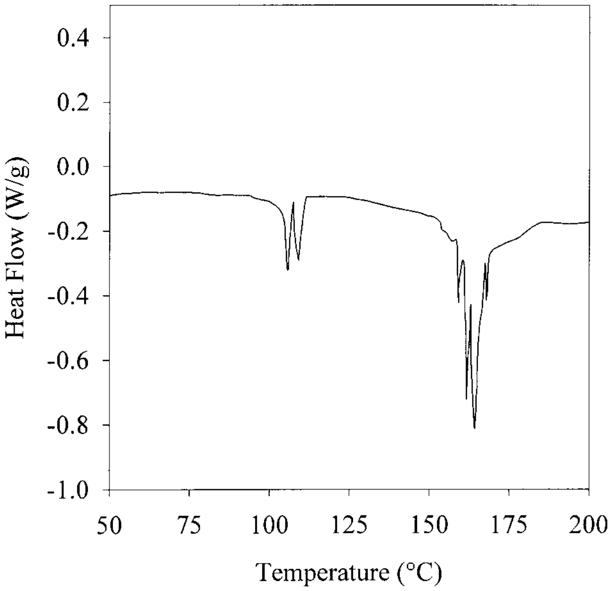


Figure 1 DSC curve of a TETM/sulfur mixture heated at 2.5°C/min.

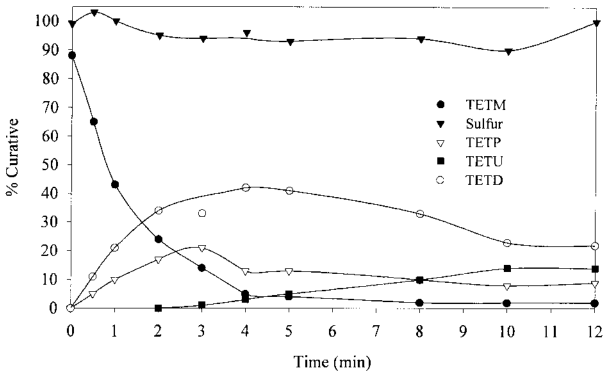


Figure 2 Analysis of curatives and reaction products from a TETM/sulfur mixture heated isothermally at 150°C.

major product (43 mol % at 140°C). Tri- (5 mol % at 140°C) and tetrasulfides (7 mol % at 140°C), followed by some higher sulfur content (5–7) polysulfides (0–3 mol % at 140°C), were also produced. At temperatures above 140°C, the decrease in total tetraethylthiuram polysulfides (TETP) and TETD concentrations was accompanied by an increase in TETU production and CS_2 evolution. The mass losses occurring were attributed partly to some TETM and TETU evaporation, as well as CS_2 production. Isothermal heating of a TETM/sulfur mix (1.0:1.0 mol ratio) showed TETD to be the major product (Fig. 2). A maximum concentration of 43 mol % TETD was obtained after 4 min. Lesser amounts of tri- (7 mol % after 3 min) and tetrasulfides (9 mol % after 3 min), and traces of penta-, hexa-, and heptasulfides (0–3 mol % after 3 min), were observed on HPLC analysis. The decline in total TETP concentration, after 3 min, was accompanied by the formation of TETU. It can therefore be concluded that with longer reaction times, TETP will undergo desulfurization as well as CS_2 evolution.

When TMTM and sulfur are heated together at 125°C, a 5-min induction period precedes the formation of TMTD and TMTP[3]; this was also observed by Geyser and McGill.[4] Kruger and McGill[16] proposed that an equilibrium reaction was established between TMTM and TMTD.

$$XSX + S_8 \rightleftharpoons XSSX \text{ where } X = (CH_3)_2NC(S){-}$$

The TMTM/sulfur reaction occurred more readily than the corresponding TETM/sulfur reaction. More TMTD was produced (53 mol % after 4 min) in the TMTM/sulfur (1.0:0.25 mol ratio) mix at 130°C, than TETD obtained (43 mol % after 4 min) in the TETM/sulfur (1.0:1.0 mol ratio) system at 150°C. Geyser and McGill[4] showed the total TMTP concentration to be stable after 5 min at 130°C. Because no increases in the elemental sulfur concentration were observed after 5 min, it can be concluded that no desulfurization of TMTP had occurred.

Reactions of TETD and TMTD

The DSC curve (Fig. 3) showed the melting endotherm of TETD at 71°C (69–71°C[17]). No further thermal events were observed until the higher temperature regions where a broad endotherm, starting at 170°C, occurred. HPLC analysis of the products formed when TETD samples were heated to different temperatures revealed TETM (28 mol % at 170°C) to be the major product of the TETD reaction. TETP reached a maximum of 14 mol % at 170°C. The tri- (7 mol %) and tetrasulfides (5 mol %) were the most prominent, with traces of penta- and hexasulfides (<1 mol %) detected at 170°C. There was a notable decrease in the concentrations of TETM and TETP at temperatures above 170°C. Degradation of TETP and the remaining TETD was accompanied by the forma-

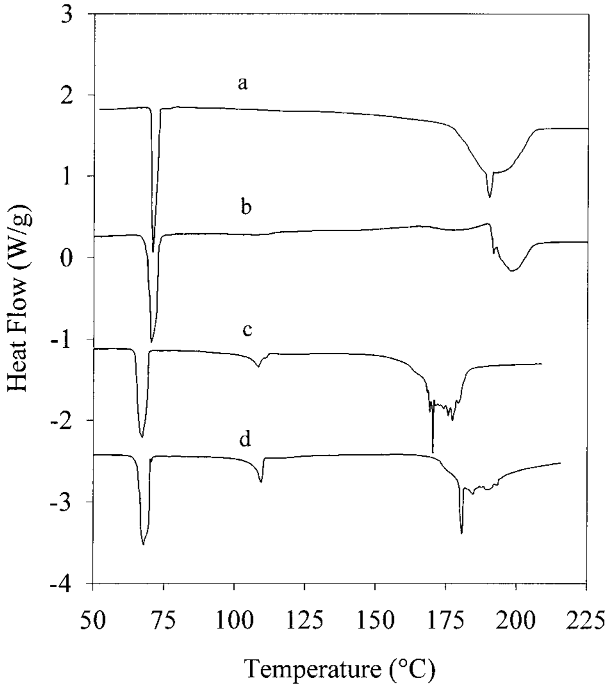


Figure 3 DSC curves of curatives heated at 2.5°C/min. (a) TETD, (b) TETD/ZnO, (c) TETD/sulfur, and (d) TETD/sulfur/ZnO.

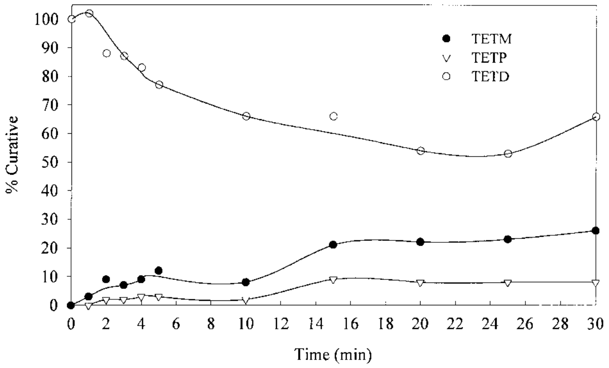


Figure 4 Analysis of curatives and reaction products of TETD heated isothermally at 150°C.

tion of decomposition products TETU, CS_2, and sulfur. The mass loss increased to 51% at 194°C and was mainly attributed to evaporation of TETM, TETU, and CS_2. IR spectroscopic analysis of the volatiles collected from the TETD decomposition at 200°C confirmed the presence of CS_2. Small traces of cyclic sulfur were also detected by HPLC (0.4 mol % at 194°C). Heating TETD at 195°C for 90 min resulted in nearly all the sample decomposing and evaporating, with only TETU being observed on HPLC analysis of the residue.

Kruger and McGill[5] found that TMTD melted at 138.9°C when heated at 5°C/min in the DSC. Thin-layer chromatography analysis of the sample revealed TMTD to be the major component, with TMTM and traces of sulfur also detected. When a sample was heated to 145.7°C and held isothermally for 5 min, both TMTD (45.1 mol %) and TMTM (43.6 mol %) were found.[5] No TMTU was detected. A study by Geyser and McGill[4] found that TMTD formed TMTM (32 mol %) and TMTP (±13 mol %) when it was heated to 150°C and held isothermally for 5 min; 46 mol % TMTD remained. When heated to higher temperatures, TMTD and TMTP decomposed to form TMTU, sulfur, and CS_2.

Isothermal studies of TETD at 150°C (Fig. 4) showed equilibrium conditions to be reached after 20 min, with TETD stabilizing at 56 mol % and TETM at 23 mol %. Small traces of tri- and tetrasulfides (3–5 mol %) were also detected, but no traces of sulfur were found. No TETU was detected and a low mass loss of 0.92% after 30 min indicated that no CS_2 was evolved.

Geyser and McGill[4] showed TMTD to react much faster under similar conditions with equilibrium being reached after 2 min: TMTD (46 mol %), TMTM (32 mol %), tri- and tetrasulfides (5–10 mol %), penta- and hexasulfides (<2 mol %). Small traces of sulfur (<2 mol %) were present after 3 min. Similar to TETD, no thiourea (TMTU) was detected and a low mass loss (0.22%) was recorded. They suggested that homolysis of the TMTD, followed by sulfur exchange reactions between $XS^\bullet$ and TMTD, resulted in the rapid formation of TMTM.

$$\mathrm{XSSX} \rightarrow 2\,\mathrm{XS}^\bullet$$

$$\mathrm{XS}^\bullet + \mathrm{XSSX} \rightarrow \mathrm{XSX} + \mathrm{XSS}^\bullet$$

$$\mathrm{XSS}^\bullet + \mathrm{XSSX} \rightarrow \mathrm{XSX} + \mathrm{XSSS}^\bullet$$

$$\text{Where } \mathrm{X} = (\mathrm{CH_3})_2\mathrm{NC(S)}\text{—}$$

Radical recombination reactions would lead to the formation of TMTP.

The TETD reactions are similar to those of TMTD; the difference appears to lie in the rate of reaction of the TETD. It is therefore proposed that TETD and TMTD would react via the same mechanism type, resulting in analogous products, but at different rates.

Reactions with Zinc Oxide

The DSC curve of TETD and ZnO showed no differences to that of the TETD heating curve [Fig. 3(a,b)]. Analysis of the products at different temperatures along the heating curve revealed a faster decrease for TETD in the presence of ZnO. Low concentrations of polysulfides were found, as was seen in the TETD system in the absence of sulfur. As the temperature increased, the concentrations of the TETD, TETM, and TETP dropped with a concomitant increase in ZDEC formation. The presence of ZnO appeared to promote the earlier decomposition of TETD which was accompanied by the formation of TETM and lesser amounts of TETP. At 140°C, HPLC analysis showed 55 mol % TETD, 20 mol % TETM, 6 mol % TETP, and 14 mol % ZDEC. In the absence of ZnO, 97 mol % TETD was still present at 140°C. The amount of ZDEC increased with further heating to 28% at 150°C, and 35% at 163°C.

Kruger and McGill[5,18] heated a dried TMTD/ZnO mixture (1.0:1.0 mol ratio) to 147°C and held it isothermally for 30 min. Very little ZDMC (2.1 mol %) was formed, and TMTD (51 mol %) and TMTM (24.9 mol %) were the only other products present. They attributed the low ZDMC yield to

TMTD reacting on the surface of the ZnO, coating the ZnO particles with ZDMC and thereby inhibiting further reaction. Geyser and McGill[10] found that an undried mixture of TMTD and ZnO (1.0:1.0 mol ratio) formed 21 mol % ZDMC when it was heated to 150°C and held isothermally for 15 min. The improved reaction was attributed to an autocatalytic reaction initiated by H_2O adsorbed on the surface of the ZnO.

In an analogous experiment with TETD, ZnO was dried and then reacted with TETD in a 1.0:1.0 mol ratio. HPLC analysis of the products formed once again showed high yields of ZDEC, 21% at 140°C, 31% at 150°C, and 39%at 160°C. When both the TETD and the ZnO were dried before reaction, HPLC analysis of the products also yielded a high concentration of ZDEC (21 mol % at 160°C). The effectiveness of ZnO as a trap for accelerator fragments, as suggested by Geyser and McGill,[10] can be seen by the decreased mass losses observed in TETD/ZnO mixes. In the presence of ZnO and H_2O, an Hdetc type adsorbent could be formed on the surface of the ZnO, which could react to form ZDEC. The ready formation of ZDEC, even in dried samples, is an important difference between TMTD and TETD. ZDMC (or ZDEC) has been suggested as the precursor to crosslink formation,[19,20] although Kruger and McGill[21] found that it formed as a byproduct of crosslinking and was not the initial crosslink precursor.

Reactions with Sulfur

The DSC curve of a TETD/sulfur (1.0:1.0 mol ratio) mixture [Fig. 3(c)], heated at 2.5°C/min, showed the TETD melt at 68°C. The endotherm starting at 103°C was associated with the melting and subsequent dissolution of sulfur with the TETD. Analysis of the reaction products at different temperatures along the DSC curve revealed that interaction between TETD and sulfur only occurred above 112°C. The concentration of TETD gradually decreased from 99 mol % at 97°C to 28 mol % at 150°C. TETP (3–8) were the major products and reached a maximum of 38 mol % at 150°C. The tri- (11 mol %) and tetrasulfides (18 mol %) were the major polysulfidic species with lesser amounts of the higher polysulfides (5–8) being produced. TETM formation (4 mol % at 150°C) was not significant in the presence of sulfur. The endotherm starting at 160°C was associated with a rapid mass loss and a decrease in the TETP concentration. TETP decomposed by releasing sulfur to form lower sulfur content polysulfides and TETD. At higher temperatures, TETD in turn decomposed to form TETU, CS_2, and sulfur.

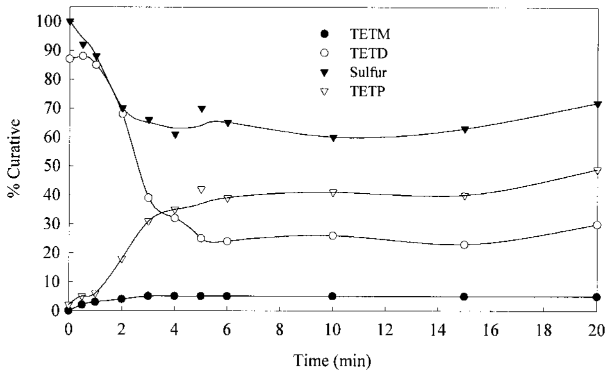


Figure 5 Analysis of curatives and reaction products of a TETD/sulfur mixture heated isothermally at 150°C.

Isothermal heating of TETD/sulfur (1.0:1.0 mol ratio) (Fig. 5) at 130°C, resulted in the formation of a similar product spectrum. The concentration of TETD decreased as it reacted with sulfur forming polysulfides, with equilibrium being reached after 6 min. At equilibrium, 26 mol % TETD, trisulfide (10 mol %), and tetrasulfides (18 mol %) were the most abundant species; higher sulfur ranked polysulfides were in smaller concentrations. The total TETP concentration stabilized at 42 mol %. TETM was formed in much lower concentrations (5 mol %), suggesting that radicals produced from the homolysis of TETD react preferentially with cyclic sulfur, abstracting sulfur to form TETP.

The reaction of TMTD and sulfur was studied at 130 and 150°C.[4] At 130°C, the reaction reached equilibrium conditions after 2 min, with approximately 60 mol % of the TMTD in the form of polysulfides and about 5 mol % TMTM. At 150°C, the reaction reached equilibrium slightly quicker, after 1 min, but the product spectrum was very similar. Geyser and McGill[4] suggested that the sulfur atoms add to the TMTD sequentially to form higher and higher polysulfides.

$$\mathrm{XSSX} \rightarrow 2\,\mathrm{XS}^{\bullet}$$

$$\mathrm{XS}^{\bullet} + \mathrm{S}_8 \rightarrow \mathrm{XS}_2^{\bullet} + \mathrm{S}_7$$

$$\mathrm{XS}_2^{\bullet} + \mathrm{S}_8 \rightarrow \mathrm{XS}_3^{\bullet} + \mathrm{S}_7$$

$$XS^{\bullet} + XS_2^{\bullet} \leftrightarrow XS_3X$$

$$XS_2^{\bullet} + XS_2^{\bullet} \leftrightarrow XS_4X$$

$$XS^{\bullet} + XS_3^{\bullet} \leftrightarrow XS_4X$$

This is in contrast with other authors who have suggested that the accelerator radical reacts with S_8 which produces high sulfur polysulfides which later desulfurate.[3,22,23]

The TETD/sulfur studies showed many similarities with the TMTD/sulfur system studied by Geyser and McGill.[4] In both cases, polysulfides were the major products with the TMTD accelerator exhibiting greater reactivity toward sulfur. The total polysulfidic species produced by TMTD were much higher than in the corresponding TETD system. In both systems, the monosulfide formation was negligible in the presence of added sulfur. Both thiuram systems showed very small mass losses, which indicated that no CS_2 or thiourea formation had occurred.

Reactions with Sulfur and Zinc Oxide

An undried TETD/sulfur/ZnO mix (1.0:1.0:1.0 mol ratio) heated at 2.5°C/min to 200°C revealed a DSC curve very similar to a TETD/sulfur mixture [Fig. 3(c,d)]. The effect of the added ZnO was seen from the later decomposition endotherm at 170°C, as compared with 150°C for the TETD/sulfur mix. HPLC analysis of the products at different temperatures along the DSC curve revealed a rapid TETD decomposition up to 150°C (18 mol % remaining), accompanied by a gradual decrease in the sulfur concentration (52 mol % at 150°C). The TETD and sulfur concentration decline was accompanied by a corresponding increase in the amount of polysulfides (total of 42 mol % at 130°C). TETM formation reached a maximum of 8 mol % at 120°C. The faster decomposition of TETD in the presence of ZnO led to the earlier production of TETP.

In contrast, ZnO was found to increase the induction period for the reaction between TMTD and sulfur, held isothermally at 130°C. The total amount of TMTP was higher in the presence of ZnO. Geyser and McGill[10] did not obtain appreciable ZDMC formation from the TMTD/sulfur/ZnO mixes, and attributed this to the displacement of water on the surface of the ZnO by the sulfur.

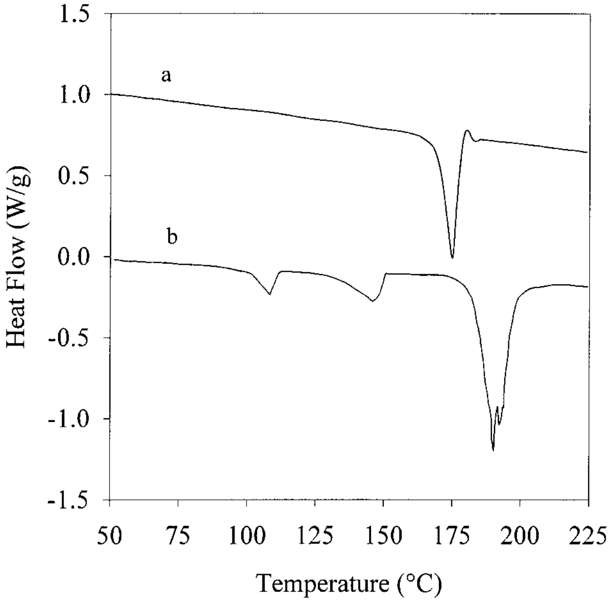


Figure 6 DSC curves of curatives heated at 2.5°C/min. (a) ZDEC, and (b) ZDEC/sulfur.

The effect of water was investigated by drying the ZnO for 24 h before mixing with TETD and sulfur. A dried mixture of TETD/sulfur/ZnO (1.0:1.0:1.0 mol ratio) produced a yield of 28 mol % ZDEC when heated to 160°C, compared with 27 mol % ZDEC for an undried TETD/sulfur/ZnO mix heated to the same temperature.

Reactions of ZDEC and ZDMC

The DSC curve of ZDEC heated at 2.5°C/min to 250°C showed the melt endotherm at 175.1°C [Fig. 6(a)]. Analysis of the products formed at different temperatures revealed only the presence of ZDEC.

This stability and lack of reaction was also shown for ZDMC. Kruger and McGill[5] heated ZDMC at 10°C/min and showed a double-component melting endotherm with peaks at 249.5 and 252.4°C. HPLC analysis revealed only the ZDMC (analyzed as CoDMC, cobalt(III) dimethyldithiocarbamate). A similar result was obtained by Geyser and McGill.[10]

A ZDEC/sulfur (1.0:1.0 mol ratio) mix heated at 2.5°C/min to 250°C showed the sulfur melt endotherm at 108.9°C, and an endotherm at 147.3°C that could be attributed to the dissolution of ZDEC into the molten sulfur [Fig. 6(b)]. HPLC analysis of samples heated to different temperatures revealed only ZDEC, analyzed as CoDEC (cobalt(III) diethyldithiocarbamate), and sulfur.

Although no products from the interaction of ZDEC and sulfur at vulcanization temperatures were observed, the ZDEC did undergo a rapid decomposition when heated above its melting point. By 200°C, all of the ZDEC had decomposed, accompanied by a 37.2% mass loss, and the formation of a small amount of TETU (12 mol %).

Geyser and McGill[10] heated ZDMC/sulfur (1.0: 1.0 mol ratio) mixtures to various temperatures under different conditions and found no interaction to occur at vulcanization temperatures. They did show that ZDMC decomposed rapidly in the presence of sulfur when heated above 230°C, with a mass loss of 54.1% at 280°C; this mass loss corresponded to all of the ZDMC present in the sample.

CONCLUSIONS

It has been shown that TMTD decomposes to form radicals and it is proposed that TETD also would decompose to form radicals at sufficiently high temperatures. The product spectra of TETD and its mixtures with other curatives were analogous to those of TMTD when performed under similar conditions. The difference seems to lie in the slower rate of reaction for TETD and sulfur as compared with TMTD and sulfur. It is therefore proposed that TETD and TMTD would react via the same mechanism, but at different rates. In the presence of ZnO, TETD reacted to a much larger extent than TMTD, resulting in the formation of ZDEC and the earlier formation of TETD polysulfides and TETM.

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