

A Comparison of Tetraethylthiuram and Tetramethylthiuram Disulfide Vulcanization.

II. Reactions in Rubber

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ABSTRACT: The reactions of tetraethylthiuram disulfide (TETD) with polyisoprene were investigated under vulcanization conditions. Samples of polyisoprene compounded with various combinations of TETD, sulfur, and ZnO were heated in a differential scanning calorimeter to various degrees of vulcanization. The crosslink density of the compounds was determined by swelling, and the extractable residual curatives and reaction products were analyzed with high-performance liquid chromatography. TETD caused crosslinking to occur in the absence of added sulfur, as did tetramethylthiuram disulfide (TMTD), both sulfur donors. In the presence of sulfur, the formation of TETD polysulfides occurred immediately before the crosslinking reaction started. The TETD polysulfides were the initial crosslinking agents. The ready reaction between TETD and zinc oxide to form zinc diethylthiocarbamic acid resulted in considerably higher crosslink densities. This greater reactivity between TETD and zinc oxide, compared with that between TMTD and zinc oxide, did not lead to any noticeable differences in the vulcanizate. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1119–1127, 2002

Key words: vulcanization mechanism; polyisoprene; tetramethylthiuram disulfide; sulfur; zinc oxide; polysulfides; crosslinking

INTRODUCTION

The thiuram-accelerated sulfur vulcanization of rubber has been the subject of many studies, and there is general agreement in the literature regarding intermediates and byproducts of the vulcanization reaction, if not the reaction mechanism. The formation of accelerator polysulfides before the onset of crosslinking is well known, and these polysulfides are commonly regarded as the

active sulfuring agents in the vulcanization reaction. The formation of the polysulfidic accelerator species via a radical mechanism has been suggested by a number of authors,^{1,2} and these polysulfides react with the rubber chain to form the rubber-bound intermediate, the pendent group.

Moore and Watson³ heated a polyisoprene/tetramethylthiuram disulfide (TMTD) compound to 140°C and found that nitrogen and sulfur were combined in the network. Kruger and McGill⁴ investigated the TMTD- and zinc dimethyldithiocarbamate (ZDMC)-accelerated sulfur vulcanization of *cis*-1,4-polyisoprene (IR) and postulated that the TMTD polysulfides reacted with the polymer chain, resulting in the formation of polysulfidic pendent groups and dimethyldithiocarbamic acid (Hdmtc). Evidence for the formation of a

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rubber-bound accelerator intermediate has also come from model compound vulcanization studies. Porter,⁵ using 2-methylpent-2-ene/TMTD/ZnO/sulfur, showed that the concentration of the rubber-bound group R-SSC(S)NMe₂ was reduced to zero via heating with olefin and ZnO for 4 h at 140°C. Recent model compound studies with 2,3-dimethyl-2-butene (TME) have confirmed the formation of intermediate products (TME-S_n-dmtc).⁶⁻⁸ Versloot et al.⁸ obtained mainly intermediate products, that is, pendent groups, and small amounts of crosslinked products (TME-S_x-TME) in a TME/TMTD/sulfur mixture heated to 140°C. They proposed that the TMTD polysulfides were the active sulfurating agents, reacting with TME to produce pendent groups and Hdmtc. Hdmtc was, however, not thought to be involved in any further reactions leading to crosslinking, but instead it was proposed that it reacted further, producing dimethylammonium dimethyldithiocarbamate (dma · dmtc). Geysler and McGill⁶ regarded Hdmtc as a sufficiently stable intermediate at vulcanization temperatures to undergo an exchange reaction with thiuram-terminated pendent groups to produce hydrogen-terminated pendent groups (thiols) regenerating TMTD polysulfides.

A limited series of comparative studies on TME/tetraethylthiuram disulfide (TETD)/sulfur/ZnO and TME/TMTD/sulfur/ZnO systems by Versloot et al.⁹ revealed that TETD exhibited better accelerator properties (relative to TMTD) when viewed in terms of the shorter average sulfur bridge length (TME-S_x-TME). A further contributing factor to the enhanced vulcanization process was the production of zinc diethyldithiocarbamate (ZDEC) from TETD and ZnO, which, according to Versloot et al., exhibited greater catalytic activity than ZDMC toward crosslinking.

Model compound studies have also been undertaken to explain the effect of ZnO on the accelerated sulfur vulcanization of rubber. Geysler and McGill¹⁰ obtained no evidence for the existence of zinc perthiomercaptides in TME/TMTD/sulfur/ZnO systems, which supposedly formed before crosslinking in zinc-containing vulcanizates.¹¹ They did, however, show that the onset of pendent group formation was earlier and concluded that ZnO may facilitate the interaction between the TMTD polysulfides and the olefin by weakening the S—S bond in the polysulfide molecule. Hdmtc that formed with pendent group formation would react with ZnO to form ZDMC.

Moore and Watson³ reheated undercured polyisoprene (freed from all extra-network material except ZnO and small amounts of ZnS) in a vacuum at 140°C and found that relatively large amounts of N and S were combined with the rubber at short cure times. These were reduced with extended cure, accompanied by an increase in the crosslink density. In the presence of ZnO, the combined N and S were removed as ZDMC.

In a study of the reactions of TME-S_xX in the presence of sulfur, Nieuwenhuizen et al.¹² concluded that crosslinking by the disproportionation of pendent groups was possible but that pendent group chain reactions were slow. Thus, neither pendent group chain nor pendent group/pendent group reactions appeared to contribute significantly to crosslink formation. Shelver et al.¹³ showed that when Hdmtc was removed from a compound during vulcanization, the crosslinking of thiuram pendent groups was slow, indicating that Hdmtc played an active role in crosslinking. They suggested that Hdmtc reacted with sulfur to form a polysulfidic species that could react with the rubber chain to form a thiol-terminated pendent group and that crosslinking proceeded via the reaction of thiols and thiuram-terminated pendent groups only when the TMTD concentration became low.

Scheele and Lorenz¹⁴ concluded from studies of TMTD, TETD, and tetrapropylthiuram disulfide (TPTD) that all three thiuram accelerators reacted with rubber in a similar way but that the rates differed because of steric effects.

Although TMTD-accelerated sulfur vulcanization has been extensively studied in the past, there is still some debate concerning the mechanism. Curative interactions in the absence of rubber are discussed in another article;¹⁵ this article examines the TETD vulcanization of polyisoprene and compares it to what is known about TMTD-accelerated vulcanization.

EXPERIMENTAL

The materials used in this study were the following: polyisoprene (IR80; Karbochem, Newcastle, South Africa), TETD (Fluka, Buchs, Switzerland), ZDEC (Orchem, Sasolburg, South Africa), sulfur (AECI, Modderfontein, South Africa), zinc oxide (Zinc Process, Johannesburg, South Africa), Hdmtc, and sodium salt trihydrate (Na · detc; Aldrich, Steinheim, Germany). Other compounds were synthesized as detailed later.

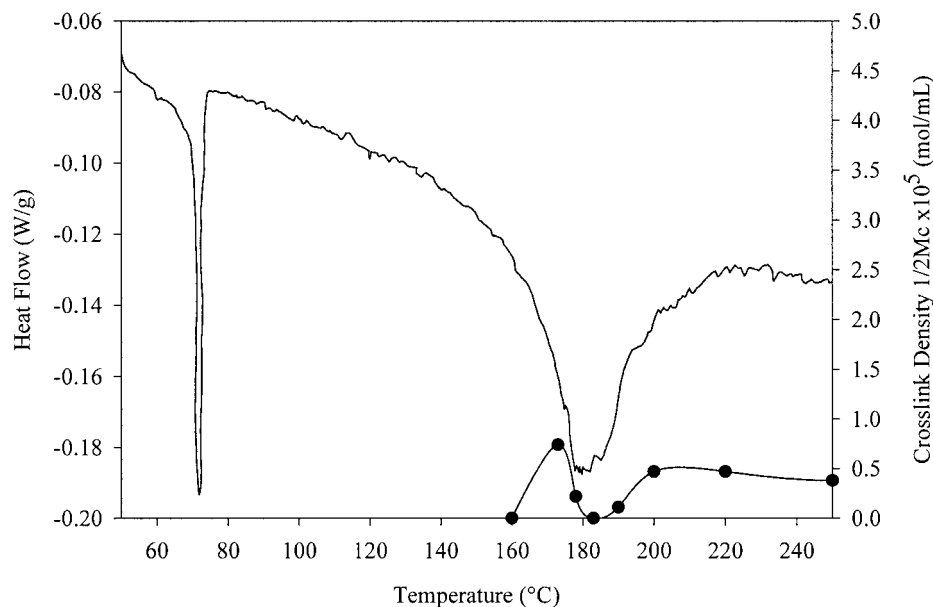


Figure 1 DSC heating curve of an IR (100)/TETD (10.94) compound heated at 2.5°C/min to 250°C and its crosslink density ($1/2M_c \times 10^5$).

Vulcanization reactions were conducted in a TA Instruments DSC 10 module (New Castle, DE) 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 a direct comparison between previous work on TMTD and studies in the absence of rubber.¹⁵ Mass-loss determinations were conducted with 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 consisting of a Waters 510 pump and a Waters 484 tunable UV absorbance detector was used (Waters, Milford, MA). The column was a μ -Bondapak C18 reverse-phase column (Waters, Milford, MA), and the eluent was methanol/water (85/15 v/v) at a flow rate of 1 mL/min.

Compounds were mixed in a Brabender plasticorder (Duisberg, Germany). A refrigerated mixing head was used to ensure that the temperature did not exceed 45°C, thus preventing any premature reaction before heating for differential scanning calorimetry (DSC). Compounded rubber samples were encapsulated in DSC pans and heated to the desired temperature or degree of vulcanization. The samples were removed, the reaction was quenched by cooling in liquid nitro-

gen, and the rubber sample was placed in benzene to extract the residual curatives and reaction products. Uncrosslinked samples were dissolved, evaporated, and extracted with isopropyl alcohol. The crosslinked samples that did not dissolve were extracted for 24 h more in benzene. The benzene extracts were combined and used for HPLC analysis, whereas the swollen rubber samples were used to determine the crosslink density ($1/2M_c$; mol of crosslink/mL of rubber). The rubber extracts, either isopropyl alcohol or benzene extracts, were evaporated and analyzed by HPLC. ZDEC was converted into its cobalt analogue by the addition of CoCl_2 to the ZDEC solution before HPLC analysis.¹¹ The experimental techniques are described in another article.

The syntheses of the various compounds and intermediates used are described in another article.

RESULTS AND DISCUSSION

IR/TETD and IR/TMTD Vulcanization

The DSC curve of an IR (100 phr)/TETD (10.94 phr) compound shows the TETD melt endotherm at 70.7°C (Fig. 1). The broad endotherm starting at 150°C may be associated with the mass loss encountered in this region. In the IR (100)/TMTD (8.86) system, a mass loss of 7.03% was recorded, although the associated endotherm was smaller.¹⁶

Table I Curatives and Reaction Products Extracted from an IR (100)/TETD (10.94) Compound Heated to Various Temperatures

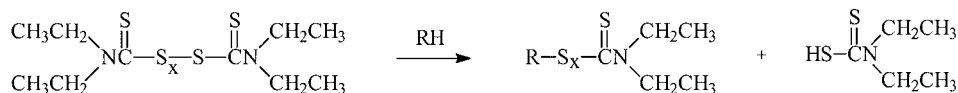
| Temperature (°C) | Mass Loss (%) | $1/2M_c$ ($\times 10^5$ mol/mL) | Extractable Curatives (mol %) | | | | |
|---------------------|------------------|-------------------------------------|-------------------------------|------|------|--------|------------|
| | | | TETD | TETM | TETU | Sulfur | dea · dmtc |
| 69 | 0.01 | — | 97 | 0 | 0 | 0 | 0 |
| 113 | 0.01 | — | 99 | 0 | 0 | 0 | 0 |
| 130 | 0.06 | — | 101 | 1 | 0 | 0 | 0 |
| 150 | 0.30 | — | 68 | 4 | 0 | 0 | 0 |
| 160 | 0.56 | — | 51 | 5 | 0 | 1 | 0 |
| 173 | 1.55 | 0.74 | 27 | 7 | 0 | 0 | 0 |
| 178 | 0.42 | 0.22 | 24 | 1 | 1 | 2 | 1 |
| 183 | 3.83 | — | 10 | 2 | 1 | 0 | 0 |
| 190 | 4.60 | 0.11 | 5 | 2 | 1 | 0 | 0 |
| 200 | 7.20 | 0.47 | 3 | 2 | 4 | 1 | 0 |
| 220 | 8.07 | 0.47 | 0 | 0 | 4 | 2 | 0 |
| 250 | 9.55 | 0.38 | 0 | 0 | 2 | 1 | 0 |

An analysis of the curatives and products formed when the compounded rubber was heated for DSC at 2.5°C/min to preselected temperatures or degrees of vulcanization is shown in Table I. The amount of extractable TETD decreased rapidly above 130°C and was essentially depleted by the peak of the endotherm. This was accompanied by the production of a small amount of TETM (reaching 7% at 173°C). Small amounts of tetraethylthiourea (TETU) were also detected at higher temperatures.

Crosslink formation started at 173°C and did not reach very high values; all samples were lightly crosslinked gels. At this stage of the reaction, only 34% of the accelerator was extractable; this, together with the small mass losses, points to a large proportion of the accelerator being bound to the rubber chain as pendent groups. The low crosslink densities, despite the formation of

large numbers of pendent groups, were possibly due to the formation of mainly monosulfidic pendent groups that were more stable and did not react to form crosslinks.^{5,8} The monosulfidic pendent groups were formed as a result of the low polysulfide concentrations.

Although no TETD polysulfides were extractable from the rubber, their formation at these temperatures has been shown.¹⁵ The polysulfide accelerator species are considered to be very reactive, and the low concentrations formed in the IR/TETD system would not be extractable. The reaction of the TMTD polysulfidic accelerator with the chain has been shown to occur with the resultant formation of a pendent group and Hdmtc.¹⁷ It is suggested that the reaction of TETD polysulfides with the rubber chain also leads to the formation of pendent groups and diethylthiocarbamic acid (Hdetc) as follows:



RH = RUBBER HYDROCARBON

x = 1, 2, 3,

No Hdetc was extractable from the IR/TETD systems. Kruger and McGill¹⁸ proposed that Hdmtc formed in TMTD systems was unstable at vulcanization temperatures, decomposing to dimethyl-

amine and CS₂. It was concluded that Hdetc either decomposed as soon as it was produced or was a reactive intermediate that underwent further reaction in the crosslinking process. The high yields of

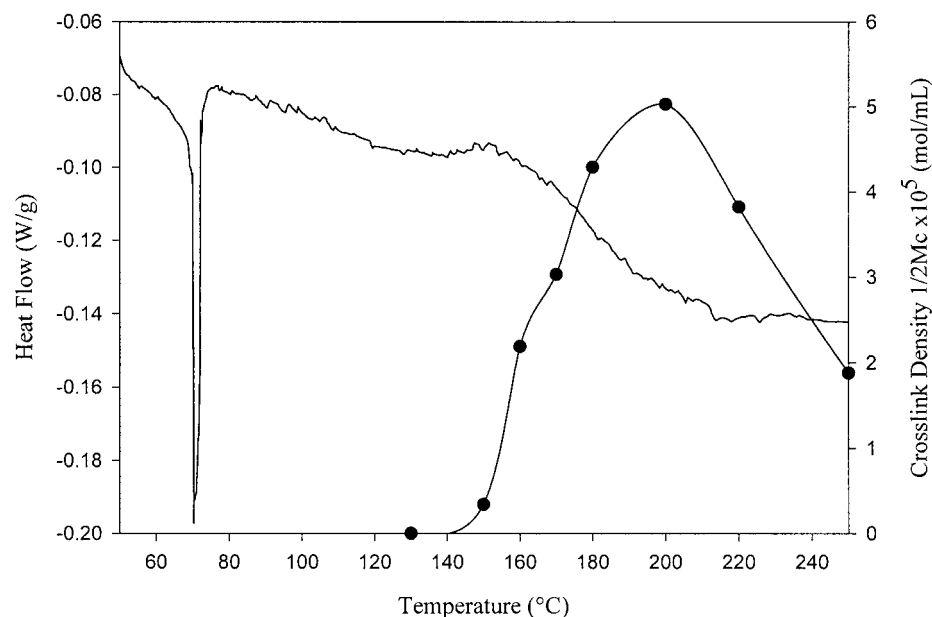


Figure 2 DSC heating curve of an IR (100)/TETD (10.94)/ZnO (3.00) compound heated at 2.5°C/min to 250°C and its crosslink density ($1/2M_c \times 10^5$).

tetramethylthiourea (TMTU) obtained in an IR/TMTD cure were attributed to dimethylamine attack on TMTD-, tetramethylthiuram monosulfide (TMTM-), and thiuram-terminated pendent groups. Kruger and McGill, therefore, attributed the low crosslink densities to pendent group destruction and to the inefficiency of TMTD as a sulfur donor.

IR/TETD/ZnO and IR/TMTD/ZnO Vulcanization

The DSC curve of an IR (100)/TETD (10.94)/ZnO (3) compound showed the TETD melting endo-

therm at 70.5°C (Fig. 2). A small exothermic event starting in the region of 120°C was attributed to crosslinking reactions, as measurable crosslink densities were obtained from 150°C. The total mass loss of 3.06% at 250°C was considerably lower than the corresponding IR/TETD system heated to the same temperature (9.55%).

An analysis of the material extractable from the IR/TETD/ZnO system revealed a steady decrease in the TETD concentration with increasing temperature (Table II). More TETD was ex-

Table II Curatives and Reaction Products Extracted from an IR (100)/TETD (10.94)/ZnO (3.00) Compound Heated to Various Temperatures

| Temperature (°C) | Mass Loss (%) | $1/2M_c$ ($\times 10^5$ mol/mL) | Extractable Curatives (mol %) | | |
|------------------|---------------|----------------------------------|-------------------------------|------|------|
| | | | TETD | TETM | ZDEC |
| 69 | 0.02 | — | 89 | 0 | 0 |
| 71 | 0.02 | — | 95 | 0 | 0 |
| 114 | 0.02 | — | 88 | 1 | 1 |
| 130 | 0.01 | — | 73 | 2 | 2 |
| 150 | 0.13 | 0.34 | 29 | 4 | 19 |
| 160 | 0.21 | 2.19 | 18 | 5 | 6 |
| 170 | 0.23 | 3.03 | 14 | 5 | 6 |
| 180 | 0.38 | 4.29 | 10 | 2 | 7 |
| 200 | 1.06 | 5.03 | 10 | 1 | 9 |
| 220 | 2.14 | 3.82 | 6 | 0 | 7 |
| 250 | 3.06 | 1.88 | 7 | 0 | 8 |

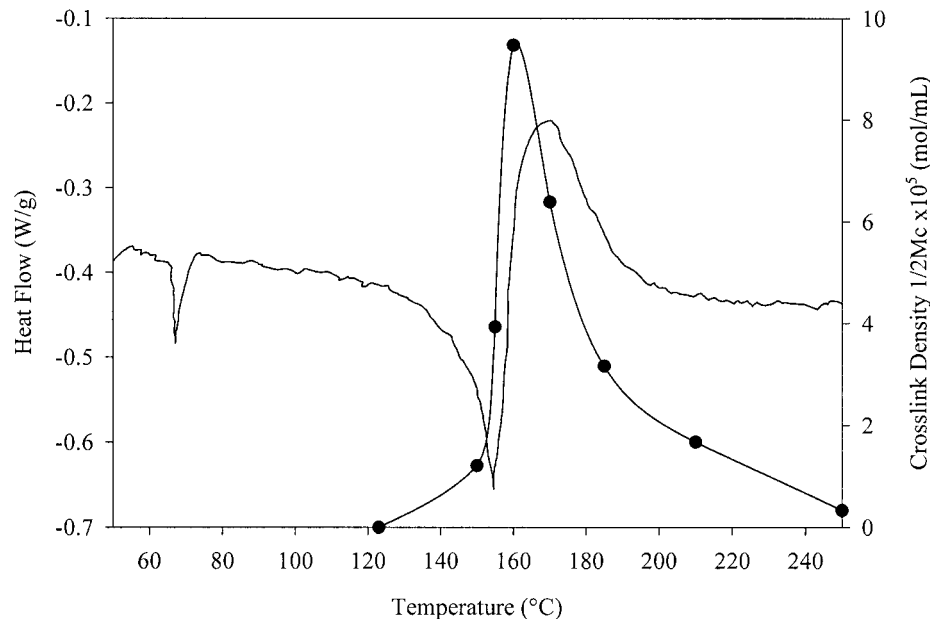


Figure 3 DSC heating curve of an IR (100)/TETD (10.94)/sulfur (9.46) compound heated at 2.5°C/min to 250°C and its crosslink density ($1/2M_c \times 10^5$).

tracted than TMTD for the corresponding IR/TMTD/ZnO system¹⁸ (29 mol % TETD at 150°C vs 15.2 mol % TMTD at 140°C); however, TETD was consumed faster in the presence of ZnO. This was due to the reaction of TETD and ZnO.¹⁵

The earlier onset of crosslinking relative to the IR/TETD system was evident from the measurable crosslink densities at 150°C (0.34×10^{-5} mol/mL). The higher crosslink density at 200°C (5.03×10^{-5} mol/mL) compared with that of the IR/TETD system at the same temperature (0.47×10^{-5} mol/mL) highlights the important role of ZnO in the crosslinking reaction.

An analysis of the curatives and products extractable from an IR/TMTD/ZnO compound revealed a large percentage of TMTM in the initial stages of the cure (48.9 mol % at 140°C).¹⁹ Kruger and McGill⁴ suggested that the drop in TMTM concentrations at higher temperatures was due to the action of TMTM with polysulfidic crosslinks, extracting the sulfur to yield shorter crosslinks and TMTD. The Hdmtc produced from further pendent group formation would react with ZnO, producing ZDMC, which could also desulfurate crosslinks. A maximum crosslink density of 8.30×10^{-5} mol/mL was reported at 190°C.⁴ Studies by Moore and Watson³ confirmed the findings by Scheele and Lorenz¹⁴ that the rate of ZDMC formation paralleled the rate of crosslinking in IR/TMTD/ZnO and NR/TMTD/ZnO vulcanization.

This implies that ZDMC is formed as a direct result of crosslink formation rather than as a precursor for crosslinks.

Versloot et al.⁸ showed that crosslink formation due to the reaction between the pendent groups (R-S_x-dmtc) and model compound (TME) only occurred in the presence of ZDMC. Crosslinking due to pendent group disproportionation and ZDEC-catalyzed crosslinking should, therefore, lead to the production of more crosslinks than in the IR/TETD system.

IR/TETD/Sulfur and IR/TMTD/Sulfur Vulcanization

In the presence of added sulfur, the DSC curve changes considerably (Fig. 3). An IR (100)/TETD (10.94)/sulfur (9.46) compound heated at 2.5°C/min showed a TETD melting endotherm at 67.8°C. The endotherm starting at 125°C was accompanied by a detectable mass loss, indicating the escape of volatile reaction products.

HPLC analysis of the extractable curatives and reaction products revealed a rapid decrease in the concentrations of TETD and sulfur (Table III). At 155°C, only 12 mol % TETD and 41 mol % sulfur were extractable. The corresponding increase in the concentrations of TETD polysulfides (19 mol % at 123°C) can be ascribed to an interaction between sulfur and TETD.¹⁵ Very little TETM was formed in this system. The TETD polysul-

Table III Curatives and Reaction Products Extracted from an IR (100)/TETD (10.94)/Sulfur (9.46) Compound Heated to Various Temperatures

| Temperature (°C) | Mass Loss (%) | $1/2M_c$ ($\times 10^5$ mol/mL) | Extractable Curatives (mol %) | | | |
|---------------------|------------------|-------------------------------------|-------------------------------|------|----------------------|--------|
| | | | TETD | TETM | TETD Polysulfides | Sulfur |
| 25 | 0.00 | — | 105 | 0 | 0 | 93 |
| 63 | 0.00 | — | 77 | 0 | 1 | 61 |
| 123 | 0.04 | — | 66 | 0 | 19 | 79 |
| 150 | 1.06 | 1.21 | 25 | 1 | 15 | 53 |
| 155 | 2.82 | 3.93 | 12 | 1 | 7 | 41 |
| 160 | 6.28 | 9.47 | 3 | 0 | 2 | 27 |
| 170 | 8.40 | 6.39 | 0 | 0 | 0 | 20 |
| 185 | 9.00 | 3.16 | 0 | 0 | 0 | 1 |
| 210 | 9.38 | 1.67 | 0 | 0 | 0 | 0 |
| 250 | 9.78 | 0.33 | 0 | 0 | 0 | 0 |

fides would react with the rubber chain to form pendent groups and Hdetc. No Hdetc was extractable in this system. Kruger and McGill¹⁸ suggested that Hdmtc, formed in TMTD vulcanization, is unstable, decomposing to dimethylamine and CS₂. Delépine²⁰ showed that TMTD and dimethylamine react to form TMTU and dma · dmtc as major products. In a model compound study, Geysler and McGill⁶ showed Hdmtc to be relatively stable at vulcanization temperatures, as reflected by the absence of TMTU and dma · dmtc. The initial mass loss from both the TETD and TMTD systems can, therefore, be attributed to the loss of Hdetc and Hdmtc, respectively. This would occur either as the acid itself or, after decomposition, as an amine and CS₂.

Both Kruger and McGill¹⁶ and Geysler and McGill¹⁰ reported the formation of relatively large amounts of TMTU on crosslinking in IR/TMTD/sulfur and TME/TMTD/sulfur systems. Little TETU was detected in the TETD systems. The formation of TETU as a product of the crosslinking reaction has, however, been questioned by Kruger and McGill.²¹

Above 160°C, reversion reactions dominated over crosslinking reactions, as seen from the drop in the crosslink density from 9.47×10^{-5} mol/mL at 160°C to 3.16×10^{-5} mol/mL at 185°C.

IR/TETD/Sulfur/ZnO and IR/TMTD/Sulfur/ZnO Vulcanization

The vulcanization reaction in the IR/TETD/sulfur/ZnO compound is evident in the DSC curve as a peak initiating at about 125°C, as indicated by

the rapid increase in crosslinking (Fig. 4). The mass losses recorded would suggest that some products of the crosslinking process are lost from the system, possibly dimethylamine and CS₂. The evaporation of these volatile products could account for the endotherm superimposed on the crosslinking exotherm.

HPLC analysis of the curatives and reaction products at various points along the cure curve revealed a faster decrease in the TETD and sulfur concentrations at vulcanization temperatures with respect to the IR/TETD/sulfur system (Table IV). Very similar product spectra were obtained for both systems, that is, with and without ZnO. At temperatures greater than 120°C, TETD and its polysulfides were consumed faster in the presence of ZnO. This could be attributed to a reaction between TETD and sulfur to form polysulfides that would react with the rubber chain, as well as a reaction between TETD and ZnO to form ZDEC. The formation of pendent groups led to the formation of Hdetc, which could also react with ZnO to form ZDEC.

The rapid increase in the crosslink density from 135°C (4.28×10^{-5} mol/mL) to 145°C (23.3×10^{-5} mol/mL) indicated a much more efficient vulcanization system in the presence of ZnO.

The heating of an IR (100)/TMTD (8.86)/sulfur (9.46)/ZnO (3) compound by Kruger and McGill²¹ showed the dissolution of sulfur and TMTD in the rubber. A sharp exotherm occurring above 130°C was ascribed to the crosslinking reaction. The rapid increase in the crosslink density was analogous to that observed in the TETD system. The

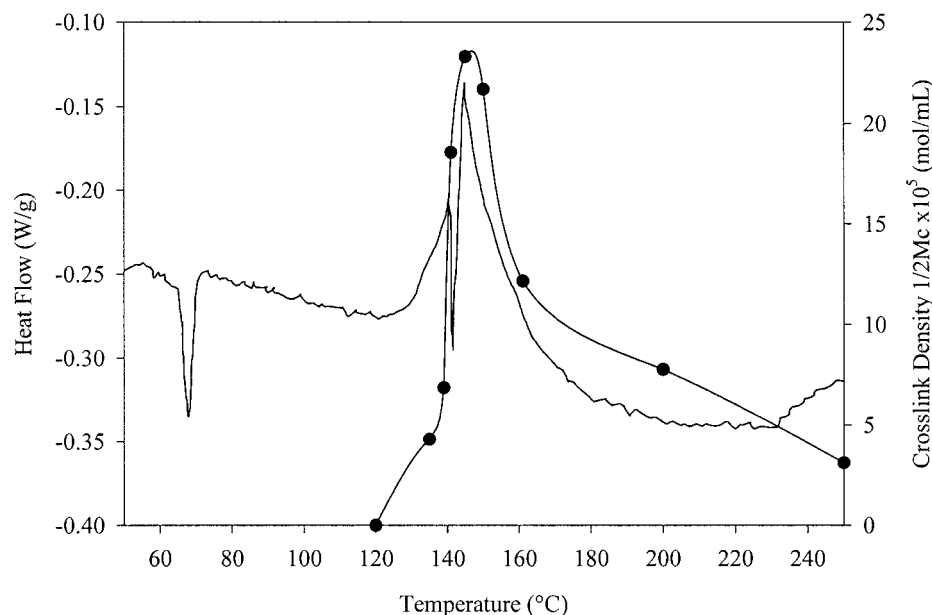


Figure 4 DSC heating curve of an IR (100)/TETD (10.94)/sulfur (9.46)/ZnO (3.00) compound heated at 2.5°C/min and its crosslink density ($1/2M_c \times 10^5$).

formation of significant amounts of ZDMC was also found. A careful examination of the DSC curves of the TETD- and TMTD-accelerated systems shows marked similarities; in both cases, an endothermic event is superimposed on the exotherm accompanying crosslinking. HPLC analysis of the extractable curatives revealed a rapid increase in the ZDMC concentration from 22.5 mol % at 131.9°C to 56.0 mol % at 136.9°C. The increase in the ZDMC concentration paralleled the dramatic increase in the crosslink density

from 1.46×10^{-5} mol/mL at 131.9°C to 11.51×10^{-5} mol/mL at 136.9°C. A maximum crosslink density of 23.77×10^{-5} mol/mL was obtained at 146.9°C.²¹

Kruger and McGill²¹ concluded that TMTD and sulfur reacted independently of ZnO, producing the active sulfurating agents, the TMTD polysulfides. These then reacted with the rubber chain to produce pendent groups and Hdmtc. ZDMC initially proceeded faster than the formation of crosslinks and was attributed to an

Table IV Curatives and Products Extracted from a IR (100)/TETD (10.94)/Sulfur (9.46)/ZnO (3.00) Compound Heated to Various Temperatures

| Temperature (°C) | Mass Loss (%) | $1/2M_c$ ($\times 10^5$ mol/mL) | Extractable Curatives (mol %) | | | | |
|------------------|---------------|----------------------------------|-------------------------------|------|-------------------|--------|------|
| | | | TETD | TETM | TETD Polysulfides | Sulfur | ZDEC |
| 67 | 0.00 | — | 85 | 0 | 7 | 84 | 0 |
| 120 | 0.04 | — | 67 | 1 | 17 | 90 | 3 |
| 135 | 0.14 | 4.28 | 29 | 2 | 6 | 71 | 30 |
| 139 | 0.36 | 6.85 | 12 | 5 | 4 | 64 | 6 |
| 141 | 0.45 | 18.56 | 10 | 2 | 1 | 18 | 7 |
| 145 | 1.92 | 23.30 | 11 | 1 | 1 | 2 | 15 |
| 150 | 2.81 | 21.68 | 2 | 2 | 1 | 0 | 4 |
| 161 | 3.53 | 12.15 | 9 | 0 | 0 | 0 | 7 |
| 200 | 7.33 | 7.76 | 3 | 0 | 0 | 1 | 8 |
| 250 | 9.32 | 3.11 | 0 | 0 | 0 | 0 | 0 |

Hdmtc-ZnO reaction. The reactions of TETD in the presence of ZnO have also been shown to be similar to those of TMTD, despite the ready reaction between TETD and ZnO.¹⁵

CONCLUSIONS

Reactions in the absence and presence of rubber showed that the TETD polysulfides were the initial active sulfurating agents. TETD was able to crosslink polyisoprene in the absence of added sulfur via the reaction of TETD polysulfides and the rubber chain to form pendent groups and Hdetc. In the presence of ZnO, Hdetc reacted with ZnO to form ZDEC. The presence of ZnO in the formulation dramatically increased the crosslink densities obtained. It can be concluded from the DSC cures, changes in the extractable curatives and reaction products, and crosslink densities obtained, that the mechanism of TETD vulcanization is very similar to that of TMTD vulcanization. The ready formation of ZDEC, as opposed to the limited reactivity of TMTD and ZnO, did not appear to affect the vulcanizate. TETD vulcanization was, however, shown to be slightly slower than TMTD vulcanization.

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