N,N′-Pentamethylenethiuram Disulfide and *N,N′*-Pentamethylenethiuram Hexasulfide Accelerated Sulfur Vulcanization. IV. Vulcanization of Polyisoprene and 2,3-Dimethyl-2-butene in the Presence of ZnO

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ABSTRACT: Polyisoprene and model compound, 2,3-dimethyl-2-butene, were vulcanized with *N,N′*-dipentamethylenethiuram disulfide (CPTD), CPTD/sulfur and *N,N′*-dipentamethylenethiuram hexasulfide (CPTP6) in the presence of ZnO and zinc (bispentamethylenedithiocarbamate) (ZPD), and residual extractable curatives and reaction intermediates analyzed by HPLC at various stages of the reaction. CPTD and ZnO do not react at vulcanization temperatures and, as in zinc-free systems, the reaction is initiated by accelerator polysulfides that lead to the formation of thiuram terminated pendent groups. Pentamethylenedithiocarbamic acid, liberated in the process, is trapped by ZnO as ZPD. Crosslinking is more rapid than in the absence of ZnO. ZPD catalyzes the crosslinking of thiuram pendent groups, and high crosslink densities are achieved because the ZPD catalyzed crosslinking of thiuram crosslink pendent groups is more efficient than when thiuram pendent groups crosslink, mainly via a reaction with thiol pendent groups, as is suggested in the absence of zinc. When free sulfur is available in the system, ZPD acts as an accelerator in its own right. Thiuram pendent groups were not detected in ZPD/sulfur formulations with model compounds, but their formation or the formation of thiol pendent groups, either of which may form via sulfurated ZPD, cannot be excluded. ZPD promoted the rapid crosslinking of such pendent groups. Overall, the reaction mechanism with zinc-containing formulations is similar to those for the corresponding TMTD systems. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1112–1120, 2000

Key words: vulcanization; mechanism; polyisoprene *N,N′*-dipentamethylenethiuram sulfides; alkyldithiocarbamic acids; ZnO

INTRODUCTION

N,N′-dipentamethylenethiuram disulfide (CPTD) readily reacts with sulfur to form *N,N′*-dipentamethylenethiuram polysulfides (CPTP), the reaction being unaffected by the addition of ZnO.[1]

CPTD is thermally unstable and at vulcanization temperatures readily decomposes to *N,N′*-dipentamethylenethiourea (CPTU).[1,2] Piperidene, which catalyzes the degradation process, is generated by the decomposition of small amounts of pentamethylenedithiocarbamic acid (Hpmtc), formed in the slow dehydrogenation reaction between sulfenyl radicals and hydrogen in methylene groups on the undissociated disulfide.[2] In vulcanizates not containing ZnO, the same CPTD decomposition reaction applies, CPTU formation being unrelated to the crosslinking process per se.[3]

Some authors[4-6] report that tetramethylthiuram disulfide (TMTD) also decomposes at vulcanization temperatures, while others[7,8] report that it is thermally stable up to 190°C. Tetramethylthiourea (TMTU), released in TMTD accelerated sulfur vulcanization in the absence of ZnO, has been attributed to a side reaction involving the catalytic degradation of the accelerator polysulfides by dimethylamine, formed on the decomposition of dimethyldithiocarbamic acid (Hdmtc) that is liberated on pendent group formation by the reaction of tetramethylthiuram polysulfides (TMTP) with the polymer chain.[9] Its formation in vulcanizates has also been suggested to result as an integral part of the crosslinking process.[10] In TMTD formulations containing ZnO, TMTU is not detected as Hdmtc is trapped by ZnO.[6,9,11]
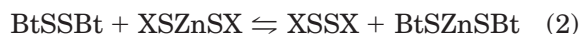
The role of active sulfurating agent in alkylthiuram disulfide accelerated sulfur vulcanization in the presence of ZnO has been attributed to both accelerator polysulfides and to zinc perthiomercaptides.[6,10,12–15] Neither CPTD[2] nor TMTD[7,16] react rapidly with ZnO at vulcanization temperatures, although when moisture is present, TMTD does rapidly form small amounts of zinc bis(dimethyldithiocarbamate) (ZDMC). In vulcanizates, zinc accelerator complexes form from the interaction of ZnO with alkyldithiocarbamic acids, released when accelerator polysulfides react with the polymer chain to form accelerator terminated pendent groups .[9,10,15]

$$RH + XS_xX \rightarrow RS_xX + HSX$$

$$2HSX + ZnO \rightarrow XSZnSX + H_2O \qquad (1)$$
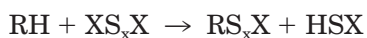
$$X = alkyldithiocarbamyl$$

The zinc accelerator complexes fulfill two roles in vulcanization. They accelerate crosslinking by catalyzing the reaction of thiuram pendent groups,[10,17,18] and act as accelerators in their own right.[6,11,13,17,19,20] ZnS forms in ZDMC vulcanizates,[13,21] and McGill and Shelver[17] suggest that ZDMC is converted to ZnS when it acts as an accelerator, but that it is not consumed when it catalyses the crosslinking of thiuram precursors. In IR/ZDMC/sulfur vulcanizates the ZDMC concentration decreased,[20] while in closed-model compound systems, where the escape of Hdmtc is prevented, a lesser decease was observed and was attributed to the reaction of Hdmtc with ZnS.[11]

The importance of sulfur-rich zinc(II) complexes in vulcanization has been emphasized by numerous authors,[6,13] and recently, evidence for sulfur-rich zinc(II) complexes has been demonstrated in theoretical Density Functional calculations and mass spectroscopic analysis of ZDMC/sulfur.[22] Ready exchange reactions between zinc accelerator complexes and accelerator disulfides in the presence of sulfur have been reported ,[23] while analogous exchange reactions involving accelerator polysulfides have been suggested as a route to the transient formation of sulfurated zinc complexes in benzothiazole systems.[24,25]

$$BtSSBt + XSZnSX \leftrightharpoons XSSX + BtSZnSBt \quad (2)$$

$$BtSZnSBt + BtS_xH \rightarrow BtSZnS_xBt + BtSH \quad (3a)$$

$$XSZnSX + XS_xX \rightarrow XSZnS_xX + XSSX \quad (3b)$$

where Bt = benzothiazole and X

$$= alkyldithiocarbamyl$$

Sulfur-rich ZDMC, formed after an exchange reaction between TMTP3 and ZDMC, was proposed to account for the catalytic activity of ZDMC in the crosslinking of a disulfidic pendent group (TME-S_2X) on model compound 2,3-dimethyl-2-butene (TME).[18] The ZDMC-accelerated reaction is widely thought to occur via thiuram-terminated polysulfidic pendent groups, similar to those found on vulcanization in the absence of ZnO,[6,13] although thiuram pendent groups have not been detected in model compound studies.[6,11,26] Geyser and McGill[11] proposed that polysulfidic thiuram pendent groups did form, but crosslinked immediately in the presence of ZDMC that catalyzed their crosslinking. It has also been suggested that sulfurated ZDMC may insert sulfur into the allylic C—H bond, and although thiol pendent groups were not detected in model compound vulcanizates, it was demonstrated that ZDMC catalyzes the crosslinking of thiol groups.[27]

This article compares CPTD and *N,N′*-dipentamethylenethiuram hexasulfide (CPTP6) accelerated sulfur vulcanization in the presence of ZnO with the vulcanization process that applies when ZnO is absent,[3] and with TMTD-accelerated sulfur vulcanization in the presence of ZnO, using polyisoprene (IR) and the 2,3-dimethyl-2-butene (TME) model compound.

Table I   Acronyms Used

Acronym	Name
CPTD	N,N′-dipentamethylenethiuram disulfide
CPTM	N,N′-dipentamethylenethiuram monosulfide
CPTP	N,N′-dipentamethylenethiuram polysulfide
CPTP6	N,N′-dipentamethylenethiuram hexasulfide
CPTU	N,N′-dipentamethylenethiourea
Hdmtc	Dimethyldithiocarbamic acid
Hpmtc	Pentamethylenedithiocarbamic acid
IR	Polyisoprene
TME	2,3-dimethyl-2-butene
TMTD	Tetramethylthiuram disulfide
TMTP	Tetramethylthiuram polysulfide
TMTU	Tetramethylthiourea
X in equations	alkyldithiocarbamyl
ZDMC	Zinc bis(dimethyldithiocarbamate)
ZPD	Zinc bis(pentamethylenedithiocarbamate)

EXPERIMENTAL

Materials and experimental procedures were described in earlier articles in this series.[1,3] Compounds, prepared on a Barbender Plasticorder, were vulcanized in a DSC at a programmed heating rate or isothermally in a press at 150°C and TME mixtures were vulcanized in evacuated sealed tubes at 150°C. Residual curatives, extractable reaction intermediates, and products were analyzed by HPLC.[1,8,28]

Formulations are indicated in the text as parts per 100 rubber. In the figures and tables the concentrations of reactants, intermediates, and products are expressed in terms of the concentration of reactants. Table I lists acronyms.

RESULTS

IR(100)/CPTD(11.82)/ZnO(3.00)

In a DSC scan of IR/CPTD/ZnO at 5°C/min the melting of CPTD was the only thermal event observed, the enthalpy chances associated with the limited crosslinking reaction being too small to detect. Crosslinking occurred earlier than in the absence of ZnO (150 vs.170°C) and the crosslink density was much higher (2.65×10^{-5} mol/mL rubber at 170°C vs. 0.86×10^{-5} mol/mL at 180°C).[3] As noted earlier,[1] quantitative analyses of zinc bis(pentamethylenedithiocarbamate)(ZPD) and of accelerator sulfides, when present in a single system, are unreliable due to their interaction during the work-up of solutions for HPLC analysis. Nevertheless, the data in Table II are valid in so far as they point to zinc bis(pentamethylenedithiocarbamate) (ZPD) formation prior to crosslinking, a decrease in CPTD as vulcanization progresses, and the absence of CPTU formation. The negligible mass loss is consistent with CPTU not forming. Similar conclusions can be drawn from the isothermal vulcanization at 140°C (Fig. 1). The presence of ZnO leads to the formation of ZPD and the acceleration of crosslinking, the reaction initiating after 5 min (Fig. 1), compared to 18 min in the absence of ZnO.[3] A higher crosslink density develops in the presence of ZnO (2.7×10^{-5} mol/mL rubber at 21 min cf. 1.5×10^{-5} mol/mL at 27 min).[3]

IR(100)/CPTP6(16.57)/ZnO(3.00)

A DSC scan of IR/CPTP6/ZnO at 5°C/min revealed the melting endotherm of CPTP6 com-

Table II   Mass Loss, Crosslink Density, and HPLC Analysis of Reaction Products Extracted from IR(100)/CPTD(11.82)/ZnO(3.00) Heated at 5°C/min

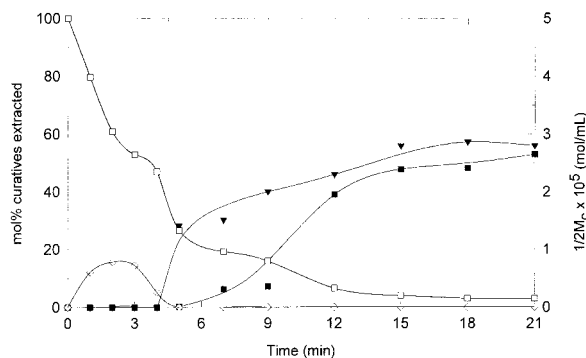| Temp (°C)	Mass Loss (%)	CPTM (mol %)	CPTD (mol %)	CPTP (mol %)	ZPD (mol %)	$1/2\ M_c$ (mol/mL $\times 10^5$)
110	0.10	0	100	0	3	0
130	0.09	6	73	2	12	0
137	0.08	9	58	2	17	0
143	0.11	11	42	0	24	0
150	0.17	24	12	0	41	0.92
157	0.18	18	5	0	51	1.61
163	0.17	14	2	0	58	2.30
170	0.28	9	2	0	62	2.65

Figure 1 Crosslink density and HPLC analysis of some reaction products extracted from IR(100)/CPTD(11.82)/ZnO(3.00) vulcanized at 140°C. (□ CPTD; ◇ CPTP; ▼ ZPD; ■ 1/2Mc).

Table III   Mass Loss, Crosslink Density, and HPLC Analysis of Sulfur Extracted from IR(100)/CPTP6(16.57)/ZnO(3.00) Heated at 5°C/min

Temp (°C)	Mass Loss (%)	Sulfur (mol %)	$1/2\ M_c$ (mol/mL $\times 10^5$)
135	0.04	27	0.01
139	0.08	29	0.28
144	0.30	25	4.90
150	0.37	21	7.43
155	0.88	2	11.70
160	1.03	0	12.20
170	1.87	0	8.79
180	1.77	0	6.27

mencing at 129°C (Fig. 2) and a large exotherm, coincident with the onset of crosslinking (Table III). The sharp endothermic event, overlapping the crosslinking exotherm, was similar to that observed in IR/TMTD/sulfur/ZnO systems.[15] Zinc accelerators have limited solubility in rubber and, in TMTD systems, an analogous endotherm was attributed to the crystallization in IR of the high concentrations of ZDMC produced in the reaction between Hdmtc and ZnO.[15] A similar explanation would apply here. HPLC analysis revealed the presence of large amounts ($>$40 mol %) of ZPD at 135°C and above. Above its melting point, CPTP6 rapidly disproportionates[1] into CPTP of different sulfur rank (CPTP1 to CPTP14) with the release of some sulfur. At 135°C, 27 mol % sulfur was detected, and this was completely consumed in crosslinking reactions by 155°C. No CPTU was found. Again, crosslinking occurred earlier in the presence compared to in the absence of ZnO (135°C cf. 150°C) and higher crosslink densities
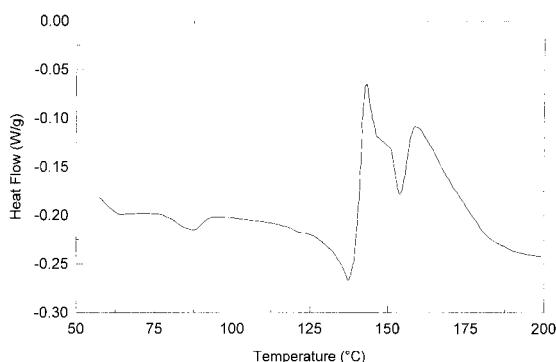
were achieved (12.20×10^{-5} mol/mL rubber at 160°C cf. 4.36×10^{-5} mol/mL at 163°C).[3]

On isothermal heating of IR/CPTP6/ZnO at 140°C, the concentration of CPTP decreased rapidly, and large amounts of ZPD formed (Fig. 3). Crosslinking occurred after 3 min compared to 7 min in the absence of ZnO, and the crosslink density of 12.0×10^{-5} mol/mL rubber after 9 min was higher than the value of 5.5×10^{-5} mol/mL obtained after 16 min without ZnO.[3]

IR(100)/CPTD(11.82)/sulfur(9.46)/ZnO(3.00)

A DSC scan of IR/CPTD/sulfur/ZnO at 5°C/min revealed an endotherm attributed to the phase transitions of sulfur and a broad crosslinking exotherm above at 146°C (Fig. 4). As in the IR/CPTP6/ZnO system (Fig. 2), and by analogy to Kruger and McGill,[15] the overlapping endotherm can be ascribed to the precipitation of ZPD in the

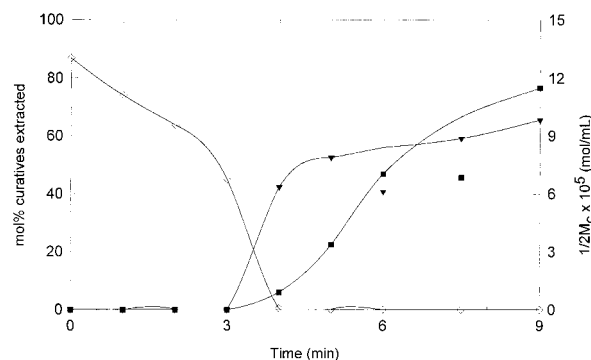**Figure 2** DSC scan of IR(100)/CPTP6(16.57)/ZnO(3.00) at 5°C/min.

Figure 3 Crosslink density and HPLC analysis of some reaction products extracted from IR(100)/CPTP6(16.57)/ZnO(3.00) heated at 140°C. (◇ CPTP; ▼ ZPD; ■ 1/2Mc).
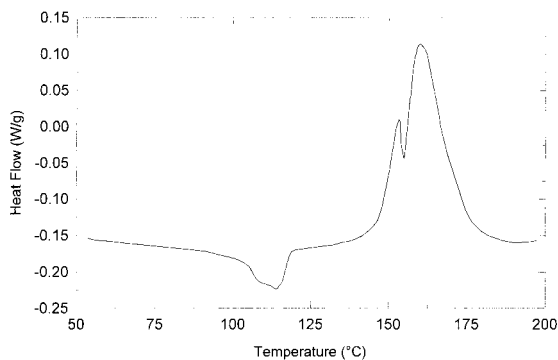
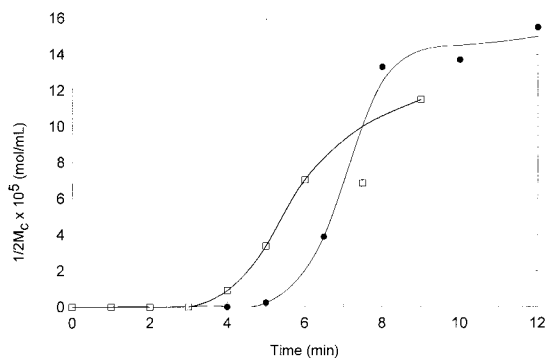**Figure 4** DSC scan of IR(100)/CPTD(11.82)/sulfur(9.46)/ZnO(3.00) heated at 5°C/min.

Figure 5 Crosslink density for (●) IR(100)/CPTD(11.82)/sulfur(9.46)/ZnO(3.00) and (□) IR(100)/CPTP6(16.57)/ZnO(3.00) heated at 140°C.

rubber. In the absence of ZnO, an endotherm was observed immediately prior to the crosslinking exotherm due to the evolution of H_2S, formed in an exchange between thiol crosslink precrusors and Hpmtc.[3] In ZnO containing formulations, Hpmtc will be trapped by ZnO, preventing the exchange reaction, and consequently, no H_2S evolution endotherm was observed in Figure 4.

Table IV shows crosslink density as a function of temperature. HPLC confirmed the formation of substantial amounts of ZPD (>40 mol %) by 120°C, well prior to crosslinking. On comparison with the system in the absence of ZnO it is seen that crosslinking initiated above 142°C, compared to 147°C, and the maximum crosslink density was 14.0×10^{-5} mol/mL rubber at 157°C compared to 3.5×10^{-5} mol/mL at 163°C.[3]

Isothermal vulcanization of IR/CPTD/sulfur/ZnO at 140°C exhibited a marginally longer scorch period than the IR/CPTP6/ZnO system, but the crosslink density attained by the IR/CPTD/sulfur/ZnO was higher (Fig. 5).

TME/CPTP6/ZnO (34.0 : 1.0 : 2.0 mol ratio)

TME/CPTP6/ZnO was vulcanized at 140°C in sealed glass reaction tubes completely immersed in an oil bath. A decrease in the concentration of CPTP and an increase in ZPD was evident (Fig. 6). ZPD and pendent groups formed concurrently (cf. Fig. 6 and 7). In the absence of ZnO the formation of pendent groups occurred considerably slower, with the formation of all precursors, but especially those of sulfur rank 3 and 4, increasing more rapidly after 5 min.[3] The two stage formation of crosslink precursors is less evident on addition of ZnO to the system, although an increased rate of formation of precursors of higher sulfur rank can be seen after 4.5 min. Crosslinked products were detected at 6 min (Fig. 8), compared to 8 min in the absence of ZnO, and on further heating a decrease in the concentration of crosslinked model compounds of higher sulfur rank (tetra-, penta-, and hexasulfidic) was found at the expense of an increase in the concentra-
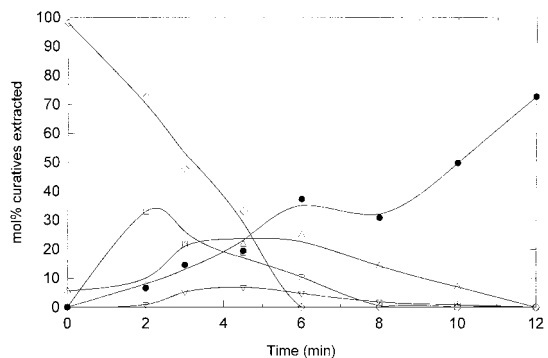
Table IV   Mass Loss, Crosslink Density and HPLC Analysis of Sulfur Extracted from IR(100)/CPTD(11.82)/sulfur(9.46)/ZnO(3.00) Heated at 5°C/min

Temp (°C)	Mass Loss (%)	Sulfur (mol %)	$1/2\ M_c$ (mol/mL $\times 10^5$)
25	0.00	85	0
120	0.11	71	0
137	0.16	61	0
143	0.31	71	0.02
150	3.18	70	4.60
157	4.79	17	14.01
163	0.00	1	12.60
175	0.00	0	7.77

Figure 6 HPLC analysis of reaction products found in TME/CPTP6/ZnO (34.0 : 1.0 : 1.0 mol ratio) heated at 140°C. (▽ CPTM; □ CPTD; ◇ CPTP; △ sulfur; ● ZPD).
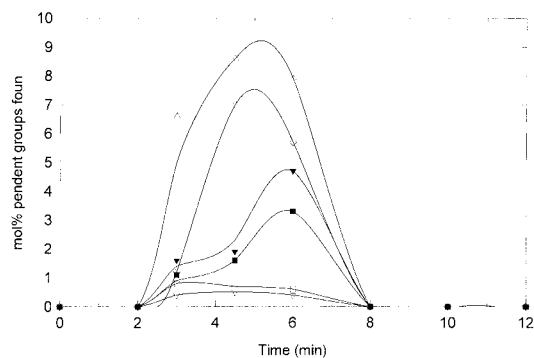
Figure 7 HPLC analysis of pendent groups found in TME/CPTP6/ZnO (34.0 : 1.0 : 1.0 mol ratio) heated at 140°C. ($\triangledown$ R-S$_1$-X; $\square$ R-S$_2$-X; $\triangle$ R-S$_3$-X; $\diamond$ R-S$_4$-X; $\blacktriangledown$ R-S$_5$-X; $\blacksquare$ R-S$_6$-X).

Figure 9 Crosslink density and HPLC analysis of extracted reaction products found in IR(100)/ZPD(12.80)/sulfur(9.46) heated at 140°C. ($\triangle$ Sulfur; $\blacktriangledown$ ZPD; $\blacksquare$ 1/2Mc).

tions of mono- and disulfidic crosslinked model compound.

IR(100)/ZPD(12.80)/sulfur(9.46)

On heating IR/ZPD/sulfur at 140°C a rapid increase in crosslink density was measured and was accompanied by the consumption of all the sulfur and part of the ZPD (Fig. 9).

TME/ZPD/sulfur (34.0 : 1.0 : 1.0 mol ratio)

On isothermal heating of TME/ZPD/sulfur at 140°C in sealed glass reaction tubes completely immersed in an oil bath, the concentration of ZPD and sulfur decreased steadily over a 15-min period. No thiuram pendent groups were detected, but the amount of crosslinked model compound increased rapidly after a short induction period (Fig. 10). A large amount of insoluble yellow crys-
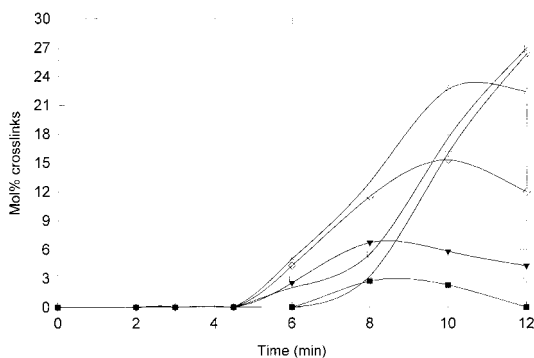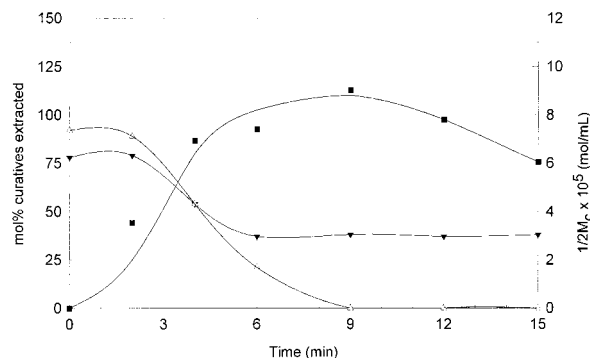
talline product was formed during crosslinking, but attempts to isolate this compound from ZnS were impossible, as both compounds were insoluble in organic solvents.

IR(100)/CPTD(11.82)/ZPD(12.80)

The addition ot ZPD to an IR/CPTD compound led to crosslinking commencing after 4 min compared to 18 min in the absence of ZPD, and the crosslink density increased to a maximum of 3.53×10^{-5} mol/mL rubber at 15 min compared to 1.6×10^{-5} mol/mL (Fig. 11).

IR(100)/CPTP6(16.57)/ZPD(12.80)

In IR/CPTP6 compounds, too, the addition of ZPD accelerated the onset of crosslinking and this occurred immediately on heating (Fig. 12). In the absence of ZPD,[3] crosslinking only initiated from
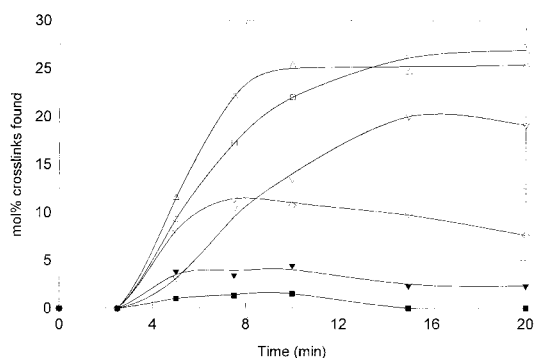

Figure 8 HPLC analysis of crosslinked model compound found in TME/CPTP6/ZnO (34.0 : 1.0 : 1.0 mol ratio) heated at 140°C. ($\triangledown$ R-S$_1$-R; $\square$ R-S$_2$-R; $\triangle$ R-S$_3$-R; $\diamond$ R-S$_4$-R; $\blacktriangledown$ R-S$_5$-R; $\blacksquare$ R-S$_6$-R).

Figure 10 HPLC analysis of crosslink products found in TME/ZPD/sulfur heated at 140°C. ($\triangledown$ R-S$_1$-R; $\square$ R-S$_2$-R; $\triangle$ R-S$_3$-R; $\diamond$ R-S$_4$-R; $\blacktriangledown$ R-S$_5$-R; $\blacksquare$ R-S$_6$-R).
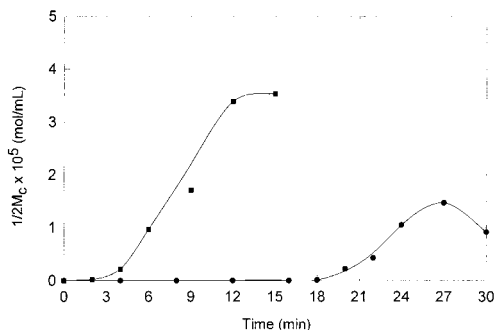
Figure 11 Crosslink density of (●) IR(100)/CPTD(11.82) and (■) IR(100)/ZPD(12.80)/CPTD(11.82) heated at 140°C.

8 min, and the crosslink density of 5.5×10^{-5} mol/mL rubber was lower.

DISCUSSION

Effect of ZnO on the Crosslinking Process

Addition of ZnO to CPTD (Fig. 1), CPTP6 (Fig. 2), and CPTD/sulfur (Fig. 5) systems resulted in a decrease in the onset temperature of crosslinking, or scorch time in isothermal cures, and to increased crosslink densities (cf. ref. 3). Addition of ZnO to TME/CPTP6 (Figs. 6–8) likewise resulted in a shorter induction period, an increase in the total amount of pendent groups, and higher concentrations of crosslinked model compound.

The formation of CPTP in CPTD, CPTD/sulfur, and CPTP6 in the presence of ZnO[1] and the detection of thiuram pendent groups in model compounds (Fig. 7) showed that the reaction initiated via the same mechanism as in the absence and presence of ZnO.[1] The favorable effect ZnO has on vulcanization is often attributed to the formation of zinc alkyldithiocarbamates.[6,13] However, as with TMTD,[7,17] CPTD and ZnO do not readily react at vulcanization temperatures,[1] and it is suggested that zinc dialkylthiocarbamates form in vulcanizates as a result of the interaction of ZnO with dithiocarbamic acids, released on thiuram pendent group formation .[9,10]

Comparison of Figure 7 with data in the absence of ZnO[3] shows that in model compounds the formation of thiuram pendent groups is more rapid, and this may be attributed to the higher concentration of CPTP in the system, ZnO trapping Hpmtc, preventing the attack of Hpmtc on CPTP as demonstrated for TMTD systems .[29]

This will account for the faster formation of pendent groups in the presence of ZnO.

$$XS_xX + HSX \rightleftharpoons XSX + XSSX + XS_yX + HS_zX$$

$$(4)$$
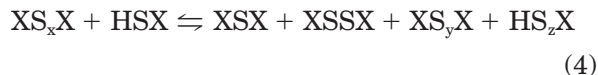
It has been shown[17,18] that, in zinc containing systems, crosslinking is catalyzed by the zinc accelerator complex. The rapid decrease in pendent groups and earlier onset of crosslinking in TME/CPTP6/ZnO (Figs. 7 and 8) compared to TME/CPTP6,[3] support the involvement of zinc perthiomercaptides in catalyzing crosslinking of thiuram pendent groups. Crosslinking in rubber likewise starts earlier in the presence of ZnO, but later than when ZPD is added directly (cf. Figs. 3 and 12).

When IR/TMTD/sulfur was heated, the reaction stopped prior to crosslinking, and residual curatives extracted, reheating on addition of zinc salts (zinc stearate, ZDMC, ZnO) led to more rapid and more extensive crosslinking.[17] The following series of experiments underlines the importance of zinc containing compounds in promoting the crosslinking of pendent groups. IR/CPTP6 was heated to a point prior to crosslinking, and residual curatives extracted. On reheating the sample that would contain mainly thiuram pendent groups,[17,29] limited crosslinking occurred slowly (Fig. 13). Addition of zinc stearate, ZPD, and ZnO to extracted samples prior to reheating increased the rate of crosslinking, as well as resulting in higher degrees of crosslinking (the presence of zinc stearate and ZPD promoting faster crosslinking than ZnO). Analysis of the extracts from samples heated with ZnO and zinc stearate revealed the presence of small amounts of ZPD (3–5 mol %) that would result from the
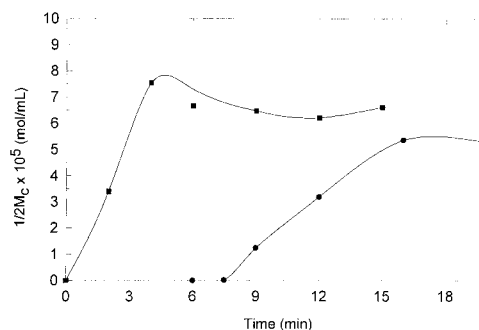

Figure 12 Crosslink density of (●) IR(100)/CPTP6(16.57) and (■) IR(100)/ZPD(12.80)/CPTP6(16.57) heated at 140°C.
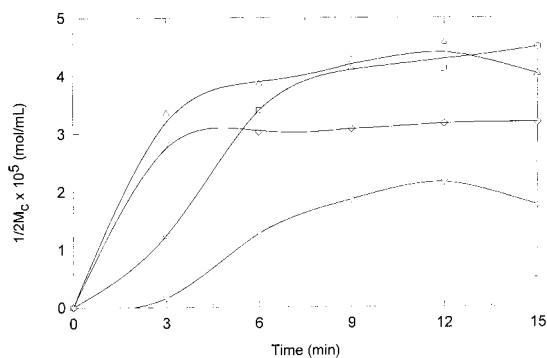
Figure 13 Crosslink density measured on reheating IR containing pendent groups formed on heating IR/CPTP6 at 140°C for 7.5 min. Residual curatives were extracted and zinc compounds added prior to reheating. ▽ IR(100); □ IR(100)/ZnO(6); ◇ IR(100)/ZPD(12.8); △ IR(100)/zinc stearate(23.9).

interaction between ZnO or zinc stearate and thiuram-terminated pendent groups during crosslinking.

As the ZPD concentration in ZnO containing formulations builds up, it can act as an accelerator in its own right, in addition to catalyzing the crosslinking of thiuram pendent groups. As in systems in which ZPD was added to the compounds, it is not possible to determine its relative contribution as an accelerator or as a catalyst for the crosslinking of thiuram pendent groups. Heating ZPD with sulfur revealed a 8 mol % decrease in the concentration of sulfur at 150°C, while increasing the temperature to 180°C resulted in the reestablishment of the initial sulfur concentration, indirectly supporting the contention for the transient formation of sulfur-rich ZPD that can act as an accelerator.

Effect of ZPD on the Crosslinking Process

Generally accepted theories of vulcanization accelerated by zinc-accelerator complexes involve the formation of thiuram pendent groups similar to those applicable to vulcanization in the absence of zinc.[6,13] ZPD accelerated sulfur vulcanization of IR and TME occurred rapidly (Figs. 9 and 10). However, as with ZDMC-accelerated systems,[11,26] vulcanization of TME/sulfur/ZPD occurred without the detection of thiuram pendent groups, while the formation and rapid crosslinking of thiol pendent groups[27] cannot be excluded. An induction period prior to crosslink formation is clearly evident with TME (Fig. 10), which implies the formation of an intermediate. Because pen-

dent groups were not detected, the induction period cannot be attributed to a delay in their reacting further, and the induction period must be ascribed to the formation of sulfurated ZPD.

The addition of ZPD to compounds containing IR/CPTD (Fig. 11) and IR/CPTP6 (Fig. 12) led to the shortening or elimination of the induction period, faster crosslinking, and higher crosslink densities. The presence (in IR/CPTP6) or formation (in IR/CPTD) of CPTP will ensure the formation of thiuram pendent groups, and their more rapid crosslinking can be attributed to the catalytic effect of ZPD that facilitates the crosslinking process, as was shown in Fig. 13, and also demonstrated in ZDMC systems.[11,17,18] With CPTP6, where CPTP were present from the outset, no induction period is found (Fig. 12), while in CPTD compounds where CPTP had to form, the induction period is shortened from 18 to 3 min (Fig. 11).

In IR/CPTD/ZPD and IR/CPTP6/ZPD, a second crosslinking process, initiated by ZPD acting as an accelerator in its own right, will occur in parallel to the CPTP initiated reaction in which crosslinking of thiuram precursors is catalyzed by ZPD. This requires the presence of sulfur. Little free sulfur will be available in the IR/CPTD/ZPD system, and the role of ZPD in this system will essentially involve promotion of the crosslinking of thiuram pendent groups. An induction period still applies (Fig. 11) (as CPTP have to form), but is considerably shortened (3 vs. 18 min) due to ZPD promoting crosslinking. The crosslink density achieved is more than double that in the absence of ZPD, confirming the greater efficiency achievable in the presence of a catalyst that crosslinks thiuram pendent groups. It is not possible to quantify the role of ZPD as a catalyst vs. its role as accelerator, although as little free sulfur is available, its catalytic role will dominate in IR/CPTP6/ZPD systems.

Sulfur was released rapidly on heating IR/CPTP6[3] and IR/CPTP6/ZPD systems (Fig. 12) and, thus, was available for crosslinking reactions in which ZPD acts as an accelerator. The induction period was eliminated in the latter system, but this need not be attributed to the ZPD accelerated reaction, as it may equally be due to ZPD catalyzing the crosslinking of thiuram pendent groups that form rapidly, CPTP being present from the outset. The catalytic role of ZPD will ensure more rapid crosslinking and the attainment of a higher crosslink density (8.00 vs. 6.5 $\times 10^{-5}$ mol/mL) than in IR/CPTP6.[3]

CONCLUSIONS

CPTD does not react with ZnO at vulcanization temperatures, and the vulcanization process in ZnO containing formulations is initiated by the interaction of CPTP with the polymer chain to form thiuram pendent groups, as happens in the absence of ZnO. Hpmtc, liberated in the process, is trapped by ZnO. The formation of thiol pendent groups is prevented, and ZPD catalyses the crosslinking of thiuram pendent groups, ensuring more rapid crosslinking and the formation of a higher crosslink density than in the absence of zinc. In ZPD formulations the accelerator has two roles. When CPTD/sulfur or CPTP6 is present, thiuram-terminated pendent groups form and ZPD catalyzes their crosslinking. When free sulfur is available, ZPD additionally acts as an accelerator in its own right. Thiuram pendent groups were not detected in such model compound systems, but thiuram pendent groups will rapidly crosslink in the presence of ZPD, and their formation, via sulfurated ZPD, which would have a transient existence, cannot be excluded. Vulcanization reactions with CPTD accelerated systems are analogous to those for TMTD accelerated systems.

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