Study of Curative Interactions in *Cis*-1,4-Polyisoprene (IR). VII. The *Cis*-1,4-Polyisoprene–Tetramethylthiuram Disulfide–ZnO System

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SYNOPSIS

A detailed account of the mechanism of crosslinking in the *cis*-1,4-polyisoprene (IR)–tetramethylthiuram disulfide (TMTD)–ZnO system is given. Many experimental observations were harmonized in terms of a radical mechanism, rather than an ionic mechanism. Electron spin resonance (ESR) spectra on the IR–TMTD–ZnO system, recorded at 120°C, *inter alia* revealed resonance lines in the vicinity of $g = 2.02$. These were related to the rapid formation of thiuram persulphenyl radicals $XS_x^{\bullet}$, on the homolytic splitting of tetramethylthiuram polysulfides. The Moore–Trego efficiency E dropped from 11.5 (at 140.0°C) to 3.5 (at 146.9°C), indicating that a substantial part of the sulfur atoms was initially to be associated with pendent groups. The formation of these pendent groups could be viewed as an irreversible, concerted reaction without the formation of a true alkenyl radical intermediate. Crosslinks would form by either a disproportionation reaction between two α-methylic or α-methylenic pendent groups RS_xX or a reaction between a pendent groups RS_xX (R = polyisoprenyl, $x \geq 2$, $X = Me_2NC(S)$) and the unsaturated polymer chain. The latter crosslink formation reactions were regarded as rate determining in the vulcanization sequence. A mechanism is proposed that does not require the participation of ZnO in the formation of the active sulfurating agent.

INTRODUCTION

The mechanism of the efficient vulcanization systems natural rubber (NR) or synthetic *cis*-1,4-polyisoprene (IR)-tetramethylthiuram disulfide (TMTD)-ZnO has received considerable attention.

There is evidence for the existence of network-bound accelerator residues, also referred to as pendent groups, believed to originate from the reaction of the active sulfurating agent with the unsaturated rubber chain. (i) Moore et al.[1] and Scheele et al.[2,3] showed that TMTD reacted at a rate 2–4 times greater than that by which zinc dimethyldithiocarbamate (ZDMC) was formed in NR or IR–TMTD–ZnO compounds. Hence, ZDMC must have been formed from a compound containing XS groups [$X = Me_2NC(S)$] other than TMTD. (ii) Analysis of NR or IR–TMTD–ZnO compounds[1,4] revealed that higher proportions of nitrogen and sulfur were combined with the rubber at the early cure stages than at longer cure times. These proportions decreased at a rate commensurate with the formation of ZDMC and crosslinks.[1] The formation of ZDMC and crosslinks had the same reaction rate.[1,3,4] (iii) Furthermore, model compound studies on the 2-methylpent-2-ene–TMTD–ZnO mixture heated at 140°C[5] revealed that pendent groups such as R′SSX (R′ mainly A_1 and B_1, the notation is explained further on) were precursors to crosslinks, but not species such as RSX, RX, or $RSC(O)NMe_2$. Rubber-bound intermediates such as RS_xSX (R = polyisoprenyl, $x \geq 1$) are regarded as the immediate precursors to crosslinks in thiuram-related vulcanization systems.

Interestingly, it has been established that the crosslinks in NR–TMTD–ZnO compounds are almost entirely sulfidic at optimum cure, there being about 15% C—C bonds.[6] This conclusion was confirmed in studies using model compounds.[7] In ad-

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dition, a structural analysis of the products that formed on heating the 2-methylpent-2-ene–TMTD–ZnO model compound formulation at 140°C, revealed important aspects with regard to the position of sulfur attachment at the trialkylethylene. In the initial cure stages, sulfidic crosslinks were formed predominantly by substitutive processes at the α-methylenic or α-methylic carbon atoms in the alkene, leading mainly to A_1- and B_1-type structures. This was in contrast to products formed on heating 2-methylpent-2-ene–sulfur mixtures in which crosslinks resulted mainly from substitutive-additive and di-additive reactions.[8]

Isothermal Raman spectroscopic studies[9] on the TMTD–ZnO (1.0/5.0 mol ratio) system in the absence of rubber, revealed that TMTD was still the major compound after 15 min at 125°C. Low-intensity bands at 515 and 461 cm^{-1} were indicative of the formation of tetramethylthiuram polysulfides (TMTP), and a small Raman line at 675 cm^{-1} was tentatively assigned to zinc dimethylmonothiocarbamate. 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. Electron spin resonance (ESR) studies on the TMTD–ZnO (1.0/5.0 mol ratio) system heated at 125°C revealed *inter alia* that singlets appeared at $g = 2.02$ and $g = 2.006$. These resonance lines were assigned to a thiuram persulphenyl radical $XS_xS^\bullet$ and a cyclic radical of the type $Me_2NC^\bullet S_x$ ($x \geq 3$), respectively. These results enabled Coleman et al.[9] to postulate a free radical mechanism for the formation of pendent groups in IR–TMTD vulcanization systems. A mixed ionic and free radical mechanism was, however, suggested in the presence of ZnO (Scheme 1). Since addition of ZnO to rubber–TMTD vulcanization systems increased the vulcanization rate, it was suggested that a rapid ionic reaction between TMTD and ZnO occurred initially (analogous to the mechanism in Scheme 1 of Ref. 10) to form TMTP, the existence of which was confirmed by Raman studies. These polysulfides would be susceptible to thermal homolytic cleavage at temperatures below that of the disulfide, to yield thiuram persulphenyl radicals which would, in turn, react reversibly with the elastomer to form a polyisoprenyl radical. The equilibrium would be displaced toward the formation of $R^\bullet$ in the presence of ZnO. The hydrocarbon radical then combined with a thiuram persulphenyl radical or TMTP, yielding the rubber-bound intermediate RS_xSX ($x \geq 1$).

$$XSSX \xrightarrow[\text{radical}]{\text{free}} XS^\bullet + XS_x^\bullet$$

or

$$XSSX + ZnO \xrightarrow{\text{ionic}} XS_xSX \rightarrow XS^\bullet + XS_x^\bullet$$

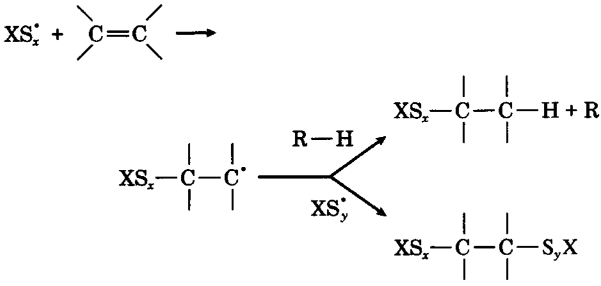
$$XS_x^\bullet(XS^\bullet) + R{-}H \rightleftharpoons R^\bullet + XS_xH(XSH) \xrightarrow{ZnO} R^\bullet + XSZnSX$$

$$R^\bullet + XS_xX \rightarrow RS_yX + XS_{x-y}^\bullet$$

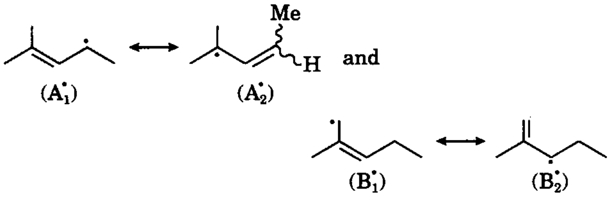
$$R^\bullet + XS_x^\bullet(XS^\bullet) \rightarrow RS_xX(RSX)$$

Scheme 1 Suggested routes for the formation of pendent groups in the IR–TMTD system (free radical) and in the IR–TMTD–ZnO compound (mixed ionic and free radical).[9]

The mechanism may, however, not be favored for the following reasons. (i) Bateman et al.[8] pointed out that persulphenyl radicals, if formed, would be expected to combine in an additive fashion to a double bond of the elastomer chain, in competition with substitutive sulfuration. This is contrary to the known di-substitutive sulfuration pattern for the efficient 2-methylpent-2-ene–TMTD–ZnO vulcanization mixture.



(ii) A reversible free radical mechanism would lead to the formation of mesomeric alkenyl radicals (such as $A_1^\bullet$ and $A_2^\bullet$), and therefore substantial amounts of the A_2- and B_2-type products would be expected. The almost complete retention of the alkenyl structure of 2-methylpent-2-ene in the initial products of the 2-methylpent-2-ene–TMTD–ZnO vulcanization argues against the intermediate formation of mesomeric alkenyl radicals.[8]



(iii) The addition of ZnO to rubber–TMTD vulcanization systems increases the vulcanization rate. It was therefore assumed that a rapid ionic reaction between TMTD and ZnO occurred initially to yield TMTP. However, the Raman spectra[9] revealed that TMTP was rapidly formed in the sulfur–TMTD (2.0/1.0 mol ratio) mix heated at 145°C, and TMTP was likewise rapidly formed in the sulfur–TMTD–ZnO (2.0/1.0/5.0 mol ratio) system heated at 125°C. Similar remarks can be made for the TMTD and TMTD–ZnO samples, but one may question whether this is convincing evidence for the involvement of ZnO in enhancing the formation of TMTP.

The stoichiometry below was observed[5] on heating the crosslink precursor EtSSX ($Et = CH_2CH_3$) with 2-methylpent-2-ene (R'H) and ZnO at 140°C.

$$1.78\mathrm{EtSSX} \xrightarrow[\mathrm{ZnO}\atop\Delta]{\mathrm{R'H}} 0.55\mathrm{EtS_{2.5}Et} + 0.45\mathrm{R'S_{1.4}Et} + 0.72\mathrm{ZDMC}$$

Crosslinked sulfides are thus believed to form by two routes of approximately equal importance: one involving two molecules of the precursor and the other involving one molecule of the precursor and one molecule of the rubber.

This study reports on the vulcanization of an IR–TMTD–ZnO system in a DSC, based on analysis of the vulcanizates at various stages along the curing curve. It allows aspects of the vulcanization mechanism to be clarified.

EXPERIMENTAL

Experimental details were given in previous studies[11,12] of this publication series. Samples were vulcanized in a DSC, and the network as well as the extractables analyzed. Thin-layer chromatography (TLC) and high-pressure liquid chromatography (HPLC) played a major role in the latter analysis.

RESULTS AND DISCUSSION

The IR–TMTD–ZnO Curing Curve

The DSC curve of the IR (100)–TMTD (8.86)–ZnO (3.00) (1.0/1.0 mol ratio) system showed that TMTD liquified at 133.2°C, i.e., 9.5°C earlier than in the IR–TMTD system (Fig. 1). A similar phenomenon was observed in the absence of IR[10] and may provide an additional reason for the fact that ZnO, in general, advances TMTD-based cures.[1,13] In contrast with the IR–TMTD vulcanization thermogram,[14] wherein endothermic events overlapped with the melting of TMTD, exothermic events dominated in the IR–TMTD–ZnO curing curve just after the TMTD had melted. This was *inter alia* due to the relatively small quantities of gases that were evolved on heating the IR–TMTD–ZnO compound (Table I). Craig[15] mentioned that CO_2, COS, CS_2, H_2, and Me_2NH were detected with a mass spectrometer on analyzing the gases from a NR–TMTD–ZnO vulcanizate.

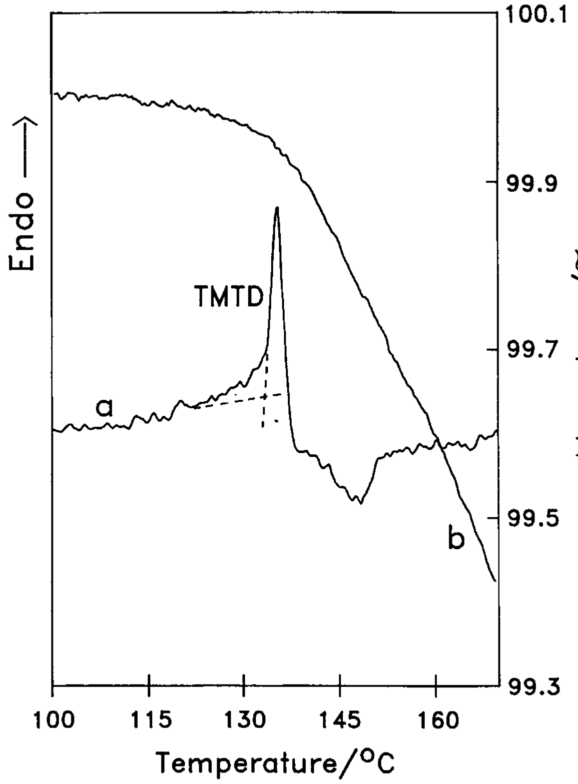


Figure 1 DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)–TMTD (8.86)–ZnO (3.00) (1.0/1.0 mol ratio). The vulcanizate quenched at 170°C appeared white/slightly transparent on swelling in benzene. M_i = 20.228 mg. (b) TGA spectrum.

In order to dilute the TMTD–ZnO (1.0/1.0 mol ratio) mixture discussed in a previous paper,[10] a poly(ethylene-co-propylene) (EPM) (100)–TMTD (8.86)–ZnO (3.00) compound was prepared. EPM is a completely saturated elastomer and therefore does not lend itself to crosslinking by the more conventional techniques used with the diene rubbers.[16] After melting of TMTD at 141.5°C, a straight baseline was observed on scanning the EPM–TMTD–ZnO mixture to 190°C (Fig. 2). The EPM–TMTD–ZnO thermogram was thus totally different from the IR–TMTD–ZnO curing curve (cf. Figs. 1 and 2), implying that the EPM was inert toward the thiuram persulphenyl radicals that formed from TMTD at elevated temperatures.[9] Furthermore, the TLC

Table I Analysis of the Compounds Shown at Various Stages of Vulcanization[a]

Compound (parts per hundred)	Temp. (°C)	Compounds Extracted/mol % of Initial Reagent, or TLC Observation					Mass loss (%)	Degree of Crosslinking/ Mole mL Rubber Network × 10^5			Polysulfides (%)
		S_8	TMTD	TMTM	TMTU	ZDMC		1/2Mc	1/2Mc[b]	1/2Mc[c]	
IR (100)	140.0		15.2	48.9	0.0	19.2	0.11	1.42	0.67	0.56	52.8
TMTD (8.86)											
ZnO (3.00)	146.9	0.0	9.7	33.1	0.0	34.5	0.22	3.16	3.23		26.3
[Fig. 1(a)]											
	169.9		3.2	14.2	0.0	52.7	0.59	5.27	5.10		3.2
	190.0	0	⍻	0		✓	0.67	8.30			
EPM (100)	190.0	⍻	✓	✓		⍻	0.28	?[d]			
TMTD (8.86)											
ZnO (3.00)											
(Fig. 2)											

[a] Symbols: ⍻ = compound barely detected with TLC; ✓ = compound easy to detect with TLC.

[b] Crosslink density after 2 h propane-2-thiol–piperidine treatment.

[c] Crosslink density after 4 h propane-2-thiol–piperidine treatment.

[d] Neither a control sample of pure EMP, scanned at 2.5°C/min to 190°C, nor this sample dissolved in benzene. The sample was assumed not to have crosslinked.

analysis revealed that a negligible amount of ZDMC originated under these conditions (Table I), but that TMTD and tetramethylthiuram monosulphide (TMTM) were the major constituents of the sample. Similar results were obtained on treating the TMTD–ZnO (1.0/1.0 mol ratio) mixture under a variety of conditions[10] and underlined the finding that TMTD and ZnO were per se very unreactive.

Evidence for the Active Sulfurating Agent TMTP

Contradictory evidence exists in the literature with respect to the composition of extra-network material of alkene–TMTD–ZnO systems, vulcanized at ~ 140°C. For example, Craig et al.[17,18] isolated fair yields of TMTM from NR–TMTD–ZnO compounds and found that the amount of TMTM decreased on extended cure times. Scheele et al.[19] explicitly pointed out that no TMTM was found in NR–TMTD–ZnO cures, and Moore et al.[1] could not detect TMTM in fully cured IR–TMTD–ZnO vulcanizates. The HPLC analysis of the IR–TMTD–ZnO system under discussion revealed that TMTD had reacted very fast to yield a large percentage of TMTM in the initial stages of curing (Table I). Calculations revealed that 11.5 TMTM molecules/crosslink were present at 140.0°C, implying that TMTM was rapidly formed prior to crosslinking. A characteristic feature of the TMTD or TMTD–ZnO samples, heated in the absence of IR, was the rapid formation of TMTM on the liquefaction of TMTD.[10] The extensive formation of TMTM prior to crosslinking in the IR–TMTD–ZnO mixture could therefore be connected to the spontaneous decomposition of TMTD at elevated temperatures.

The Raman spectroscopic experiments on the thermal decomposition of TMTD or TMTD–ZnO samples[9] revealed that TMTP molecules were formed as early products. It was inferred from HPLC measurements, which revealed TMTD (45.1 mol %) and TMTM (43.6 mol %) to be present after heating TMTD for 5 min at 145.7°C, that an equilibrium of the kind in reaction (1) was established at the very early stages of vulcanization.[10]

$$\text{2TMTM} + \tfrac{1}{4}\text{S}_8 \underset{\Delta}{\rightleftharpoons} \text{2TMTD} \underset{\Delta}{\rightleftharpoons} \text{TMTM} + \text{TMTP} \qquad (1)$$

The equilibrium should be forced to the right-hand side in the IR medium, due to the removal of TMTP in the formation of pendent groups. This would offer an explanation for the high concentration of TMTM (48.9 mol %) compared to the low concentration of TMTD (15.2%) at 140.0°C on heating the IR (100)–TMTD (8.86)–ZnO (3.00) mixture (Table I).

ESR studies on TMTD-containing systems in the absence of rubber provided evidence that sulfidic free radicals were involved in the formation of the rubber-bound intermediate compound.[9] Interestingly, ESR analysis prior to 1973[4,20] failed to produce convincing evidence for the presence of radicals,

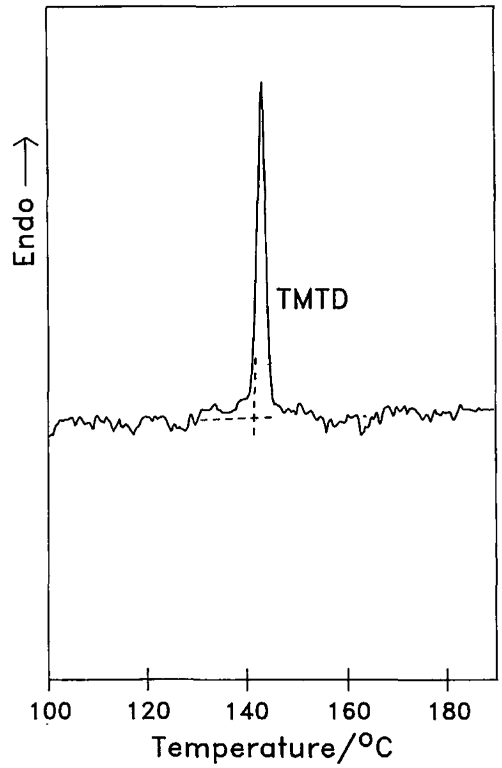


Figure 2 DSC spectrum. Scan rate 2.5°C/min. (a) EPM (100)-TMTD (8.86)-ZnO (3.00) (1.0/1.0 mol ratio). The sample appeared pinkish after the scan and whitish/opaque on swelling in benzene. M_i = 14.502 mg.

which were to be associated with vulcanization reactions in TMTD-related compounds. These experiments were plagued by the presences of minor amounts of copper, present as an impurity, which formed copper(II) dimethyldithiocarbamate (CuDMC) at vulcanization temperatures. CuDMC generates very strong ESR signals[21] [Fig. 3(a)] and may result in a misinterpretation of the spectra obtained for thiuram vulcanization systems. The ESR spectrum of the IR–TMTD–ZnO mixture, heated at 120°C, is shown in Figure 3(b). The signals due to CuDMC appeared very strong and a separation distance of ~ 77*g* for these peaks was calculated. Recently, Banerjee[22] applied ESR spectroscopy in an attempt to elucidate aspects on the mechanism of thiuram vulcanization. The spectra published were interpreted in terms of a sulfidic radical $RCH_2S_x^{\bullet}$. However, the separation distance between the peaks was ~ 75*g* and the signals resembled those characteristic for CuDMC. In addition, although no exact assignment of the peaks B_1 were made [Fig. 3(b)], their relative position compared favorable with the *g* values of 2.02 and 2.006, which were assigned[9] to the thiuram persulphenyl and cyclic carbon radicals of the type $Me_2N\text{–}C^{\bullet}S_x$, respectively. This would imply that the conclusions regarding the ESR results obtained on TMTD mixtures in the absence of rubber holds in the real vulcanizate.

Since TMTD was an efficient initiator for the polymerization of methyl methacrylate at 70°C, Ferrington et al.[23] concluded that TMTD dissociated into free radicals at vulcanization temperatures. The above-mentioned results led us to believe that the unstable TMTP species formed in reaction (1) rapidly established an equilibrium with thiuram persulphenyl and thiuram sulphenyl radicals.

$$XSS_xSX \underset{\substack{\text{rapid}\\ \text{equilibrium}}}{\xrightleftharpoons[\Delta]{}} XS_xS^{\bullet} + XS^{\bullet}$$

The Existence and Nature of the Pendent Groups

It was evident from the HPLC analysis that TMTD had reacted rapidly so that only 15.2 mol % was extracted at 140.0°C (Table I). Neglecting the sulfur atoms of the network-bound SX groups, another source of combined sulfur (Sc) in the network was related to the decomposition of TMTD to TMTM.

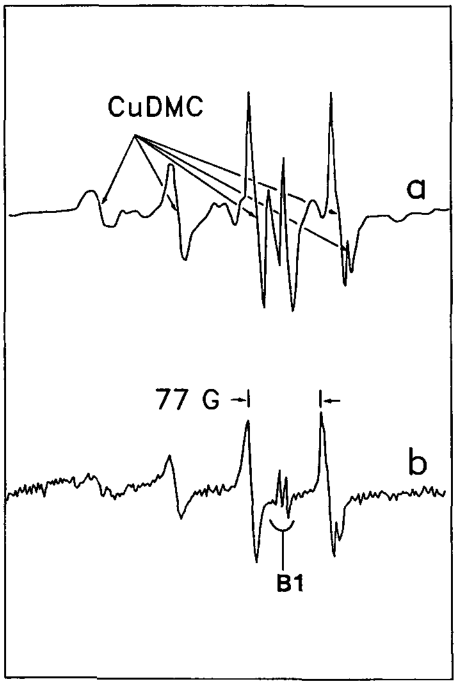


Figure 3 ESR spectra of curative combinations in the absence or presence of rubber. (a) Sulfur–TMTD (2.0/1.0 mol ratio) mixture heated at 145°C for 120 min, then quenched and spectrum recorded at −56°C.[9] (b) IR (100)–TMTD (8.86)-ZnO (3.00) formulation heated at 120°C, and spectrum recorded after ~ 5 min.

Since TMTM (48.9 mol %) was present at 140.0°C, the crosslink efficiency E was estimated as (0.489) (33.5×10^{-5} mol Sc atoms cm^{-3} rubber)/1.42×10^{-5} mol crosslinks cm^{-3} rubber = 11.5 Sc atoms/crosslink (cf. Ref. 14). The relatively sharp decrease in E from 11.5 (at 140.0°C) to 3.5 (at 146.9°C), shown in Figure 4, indicated that a substantial part of the Sc not in SX moieties was initially associated with pendent groups.

The rate of ZDMC formation was a much slower process than that at which TMTD disappeared in the IR (100)-TMTD (8.86)-ZnO (3.00) vulcanization (Table I). The 19.2 mol % ZDMC that was extracted at 140.0°C was considerably less than the 84.8 mol % TMTD that had reacted at that stage. These results thus reconfirmed the findings of Scheele et al.[2,3] and Moore et al.[1] that TMTD had reacted at a rate 2–4 times greater than that by which ZDMC was formed. The ZDMC must therefore, at least in part, be formed from some compound other than TMTD containing SX groups, such as pendent groups.

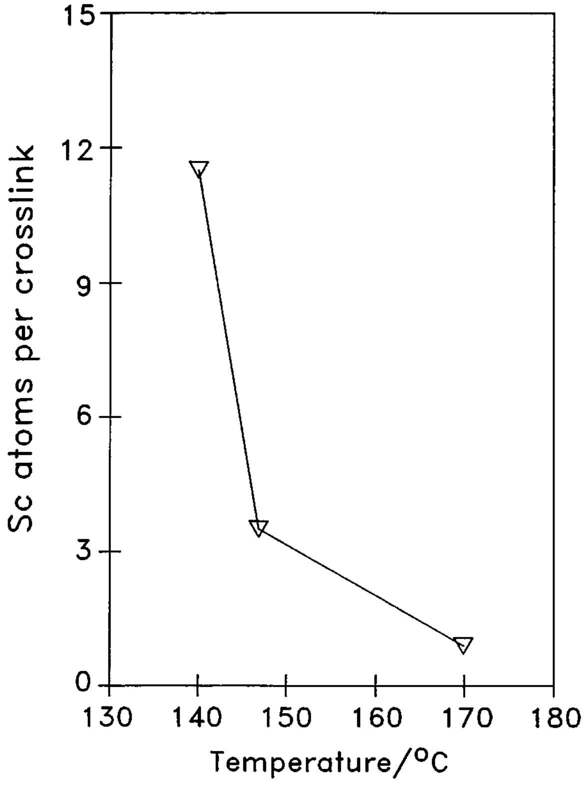


Figure 4 The variation of the Sc atoms/crosslink ratio as curing proceeded for the vulcanization system IR (100)-TMTD (8.86)-ZnO (3.00). The calculations did not take the sulfur atoms of the network-bound SX groups into account. The data points were connected merely to illustrate the general trends in E.

Table II Calculation of Number of Sulfur Atoms per Pendent Group at 140.0°C, in the DSC Scan of the IR–TMTD–ZnO Vulcanization Compound from Table I

Quantity Calculated	mole cm^{-3} rubber network
Crosslink density	1.42×10^{-5}
Number of pendent groups	10.3×10^{-5}
Network-bound sulfur atoms[a]	16.4×10^{-5}
Sulfur atoms in crosslinks[b]	3.6×10^{-5}
Sulfur atoms in pendent groups[c]	12.8×10^{-5}
Sulfur atoms per pendent group	2.24[d]

[a] Refers to sulfur other than in the SX moieties of pendent groups.
[b] Assume trisulfidic and disulfic crosslinks.
[c] Neglecting sulfur in the SX moieties of pendent groups.
[d] Refers to the index x in RS_xX (R = polyisoprenyl).

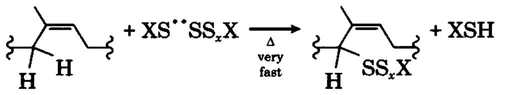
Calculations using the HPLC and thermogravimetric analysis (TGA) results in Table I revealed that it was possible to account for 84.6 mol % of the initial TMTD at 140.0°C in the thermogram. It was therefore inferred that the 15.4% TMTD unaccounted for was network bound, which meant that (0.154) (33.5×10^{-5} mol TMTD cm^{-3} rubber) (2) = 10.3×10^{-5} mol cm^{-3} pendent groups were present at that stage (Table II). The polysulfidic determination on the IR–TMTD–ZnO system (Table I) showed that 52.8% of the crosslinks were polysulfidic at 140.0°C. There were thus 1.42×10^{-5} mol crosslinks cm^{-3} rubber [(0.528)(3) + (0.472)(2)] = 3.6×10^{-5} mol cm^{-3} sulfur atoms combined in the network as sulfidic crosslinks, on the assumption that trisulfidic and disulfidic crosslinks prevailed (cf. Ref. 14). Since 48.9 g atom % sulfur had originated from the decomposition of TMTD to TMTM at that stage, approximately (0.489) (33.5×10^{-5}) − 3.6×10^{-5} = 12.8×10^{-5} mol cm^{-3} sulfur atoms were combined in pendent groups. Therefore $12.8 \times 10^{-5}/10.3 \times 10^{-5} + 1 = 2.24$ sulfur atoms were linked with each pendent group, implying that 24% of the pendent groups were trisulfidic and 76% disulfidic (Table II).

It was noticeable that pendent groups of a higher sulfur rank than disulfidic have never been reported in model compound studies.[5] The authors suggest that polysulfidic pendent groups of the type RS_xSX (R = polyisoprenyl, $x \geq 2$), are formed *in situ* in the thiuram-based vulcanization of the isoprene rubbers, since polysulfidic crosslinks of the type RSS_xSR ($x \geq 1$) were formed throughout in the TMTD and ZDMC-based cures of this study (cf. Ref. 14 and future publications). The possibility that polysulfidic pendent groups such as $R'S_xSX$ (R' = 2-methylpent-2-enyl, $x \geq 2$) were too unstable to be isolated (or formed) in the thiuram-based vulcanization of model compounds is therefore not to be excluded. Similar remarks in connection with the stability of TMTP molecules were made in an earlier publication.[10]

Mechanism for the Formation of Pendent Groups

Coleman et al.[9] could not detect thiuram sulphenyl radicals $XS^{\bullet}$ in the ESR runs of TMTD mixtures at 145°C, but the reasonably stable thiuram persulphenyl radical species[24] were easily observed. Their mechanism therefore suggested that either the thiuram sulphenyl radical $XS^{\bullet}$ or the thiuram persulphenyl radical $XS_x^{\bullet}$ would abstract a hydrogen radical from the IR chain to generate a polyisoprenyl radical at vulcanization temperatures (Scheme 1). However, while monosulphenyl radicals are well established as abstractors of hydrogen atoms,[25,26] no evidence has yet been obtained that persulphenyl radicals could perform the same function. It may be that the thiuram radicals $XS^{\bullet}$ were too short-lived to be detected with the ESR technique at 145°C.

It is therefore postulated that pendent groups would be formed via the abstraction of hydrogen atoms from the IR chain by thiuram sulphenyl radicals. Neglecting other factors, the allylic hydrogen atoms of the IR chain would be the easiest to abstract since their bond energy is the lowest. Based on the standard bond dissociation energy values for the homolysis of a covalent bond, the sequence in order of decreasing reactivity for the ease of abstraction of hydrogen atoms should be: allylic > tertiary > secondary > primary > vinylic.[27] The remaining thiuram persulphenyl and isoprenyl radicals would in turn combine to form polysulfidic pendent groups, as shown in reaction (2):



(2)

Bateman et al.[8] was strongly opposed to a radical mechanism in NR–TMTD–ZnO compounds, wherein thiuram persulphenyl radicals would react with the polyisoprene chains to yield precursors to crosslinks. A major argument against a free radical mechanism was that the di-substitutive sulfuration pattern inherent in the efficient 2-methylpent-2-ene–TMTD–ZnO vulcanization mixture was not to be expected on the strength of objections mentioned earlier. However, the authors hold the opinion that a free radical mechanism involving thiuram persulphenyl radicals could be compatible with the di-substitutive sulfuration pattern, by virtue of the following argument. It is known that sulfur is an extremely fast and efficient radical trap.[28] The formation of a pendent group via route (2) could therefore be viewed as an irreversible, concerted reaction without the formation of a true alkenyl radical intermediate. The reaction between the allylic positions of the IR chain and the TMTP molecules would thereby be exceedingly fast, primarily due to the reactivity of the thiuram radicals, in order to form a pendent group bound to the α-methylic or α-methylenic positions of the IR chain.

The resultant dimethyldithiocarbamic acid (DMDCA) formed via reaction (2) [and reaction (4) below] reacted rapidly with the ZnO in the IR (100)–TMTD (8.86)–ZnO (3.00) mixture to form ZDMC. (We will expand on the latter assertion in a later paper). In fact, the formation of ZDMC surpassed the generation of crosslinks at 140.0°C, as the ratio of 4.5 ZDMC molecules/crosslink was calculated (Table I). Since TMTD and ZnO were very reluctant to react per se,[10] and the reaction of pendent groups to form crosslinks is the rate-determining step in the vulcanization sequence (cf. discussion in following section), we regard this calculation as further evidence in favor of reaction (2).

Formation of the Initial Polysulfidic Crosslinks

Reactions (3) and (4) below would be the most prominent in forming the initial polysulfidic crosslinks. A common factor in these routes is the homolytic splitting of S–S bonds in α-methylic or α-methylenic pendent groups to form thiuram persulphenyl and thiuram sulphenyl radicals. The authors believe that this step, in particular, is the rate-limiting reaction step in thiuram-accelerated sulfur vulcanization. Results in the literature,[1,4] and those reported in this series of papers, have provided indirect evidence that accelerator moieties do combine with the isoprene chain in the course of NR or IR–TMTD–ZnO vulcanization. The fact that pendent groups that are precursors to crosslinks were stable enough to be detected prior to crosslinking would imply that these groups react relatively slowly.

(i) After the homolytic splitting of a pendent group RS_xSX ($x \geq 1$), these radicals could interact with another pendent group to form a polysulfidic crosslink and TMTD (or TMTP).

$$2\mathrm{RSS}_x\mathrm{SX} \underset{\substack{\Delta \\ \text{slow}}}{\overset{k_2}{\rightleftharpoons}} \mathrm{RS}_x\mathrm{S}^\bullet + \mathrm{XS}^\bullet$$

$$+\mathrm{RSS}_x\mathrm{SX} \underset{\substack{\Delta \\ \text{very} \\ \text{fast}}}{\overset{k_3}{\longrightarrow}} \mathrm{RS}_x\mathrm{SSS}_x\mathrm{R} + \mathrm{TMTD} \qquad (3)$$

Such a disproportionation reaction between two α-methylic or α-methylenic pendent groups would be in accord with the di-substitutive sulfuration pattern inherent in the efficient 2-methylpent-2-ene–TMTD–ZnO formulation. Crosslinking via reaction (3) may also account for the small quantities of TMTD that were always present in the TMTD-based cures investigated in this study (cf. Table I).

(ii) Another route to crosslink formation after the homolytic splitting of a pendent group $\mathrm{RS}_x\mathrm{SX}$ relies on arguments that have already been presented above. It would involve the abstraction of an allylic hydrogen atom from the IR chain by a thiuram sulphenyl radical, followed by the combination of the remaining thiuram persulphenyl and polyisoprenyl radicals.

$$\mathrm{R{-}H} + \mathrm{RSS}_x\mathrm{SX} \underset{\substack{\Delta \\ \text{slow}}}{\overset{k_2}{\rightleftharpoons}} \mathrm{RS}_x\mathrm{S}^\bullet + \mathrm{XS}^\bullet$$

$$+\,\mathrm{R{-}H} \underset{\substack{\Delta \\ \text{very} \\ \text{fast}}}{\overset{k_3}{\longrightarrow}} \mathrm{RS}_x\mathrm{SR} + \mathrm{XSH} \qquad (4)$$

The fact that the alkenyl structure of 2-methylpent-2-ene was almost retained in the 2-methylpent-2-ene–TMTD–ZnO model compound vulcanization[8] argues against the formation of mesomeric alkenyl radicals in reaction (4), implying that the substitution reaction was exceedingly fast. The combination of the thiuram persulphenyl and polyisoprenyl radicals can be viewed as an irreversible, concerted reaction without the formation of a true alkenyl radical intermediate. In addition, if these alkenyl radicals had a reasonable lifetime, a large number of carbon–carbon crosslinks would have been formed in the NR–TMTD–ZnO system. The number of carbon–carbon crosslinks was, however, negligible in such systems,[6,7] which means that the assumption was wrong. The DMDCA formed in reaction (4) would react with ZnO to form ZDMC, which would, in part, explain the literature[1,3,4] findings and those reported in this study (Table I), viz. that the increase in the ZDMC concentration paralleled the curing curve.

The crosslinks formation reactions proposed above would be in harmony with the model compound study involving the precursor EtSSX.[5]

Kinetic Considerations

All the mechanistic steps proposed hitherto for the IR–TMTD–ZnO vulcanization mechanism are reconcilable with the kinetic scheme that was suggested by Coran[29] for the delayed action accelerators. In particular, the present study confirmed the relative magnitudes of the rate constants in IR–TMTD–ZnO vulcanization, i.e., $k_3 \gg k_2$. The reaction step characterized by k_2 in reactions (3) and (4) was thus the rate-determining step for crosslink formation in TMTD-related vulcanization systems and would have the highest activation energy.

CONCLUSIONS

The mechanism presented for crosslinking in the IR–TMTD–ZnO system agrees in broad outline with mechanisms that have been proposed. There are, however, pertinent differences with reference to the intrinsic steps of the mechanisms suggested. For example, the proposed mechanism does not require participation by ZnO in the generation of the active sulfurating agent—Bateman et al.[8] as well as Coleman et al.[9] regarded this step as important in order to explain the well-known beneficial role of ZnO in TMTD-based cures.[4,30] The observation by Bateman et al.[8] that sulfidic crosslinks were formed predominantly by substitutive processes at the α-methylic or α-methylenic carbon atoms on heating a 2-methylpent-2-ene–TMTD–ZnO mixture were in line with the radical mechanism proposed in this study. The exact role of ZnO in TMTD-based vulcanization systems will be dealt with in a forthcoming paper.

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