

A Study of Curative Interactions in *cis*-1,4-Polyisoprene. X. The *cis*-1,4-Polyisoprene/Sulfur/Zinc Dimethyldithiocarbamate and *cis*-1,4-Polyisoprene/Sulfur/ Zinc Dimethyldithiocarbamate/ZnO Systems

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SYNOPSIS

Aspects of the mechanism of zinc dimethyldithiocarbamate (ZDMC)-accelerated sulfur vulcanization were discussed. The trends in the efficiency parameter E , confirmed that crosslinking is preceded by the formation of pendent groups RS_xSX [R = polyisoprenyl, X = $Me_2NC(S)$] in ZDMC-based systems. The index x in RS_xX was calculated as 5.82 in the *cis*-1,4-polyisoprene (IR)/sulfur/ZDMC/ZnO compound at the initial stages of curing, compared to 3.23 in the absence of ZnO. The high value of x supports the postulation that elemental sulfur and ZDMC react at the early stages of vulcanization, to form the active sulphurating agent $XS_xSZnSSX$. Crosslinks form by either a disproportionation reaction between two α -methyl or α -methylene pendent groups RS_xX , or a reaction between a pendent group RS_xX and the rubber chain—these routes are the same as that suggested for the IR/tetramethylthiuram disulfide (TMTD)/ZnO compound. The beneficial role of ZnO and zinc stearate is shown, as in the case of ZnO in the IR/TMTD/ZnO system, to be related to their ability to trap dimethyldithiocarbamic acid, which formed in the generation of pendent groups and crosslinks. ZnS is inactive in this regard. The formation of ZnS is characteristic of natural rubber/sulfur/ZDMC/ZnO systems, as opposed to IR/TMTD/ZnO mixtures where little ZnS forms.

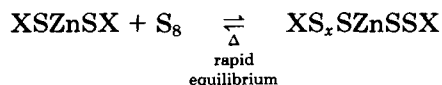
INTRODUCTION

A very intriguing debate in vulcanization chemistry concerns the mechanism of zinc dimethyldithiocarbamate (ZDMC)-accelerated sulfur vulcanization. ZDMC is only sparingly soluble in hydrocarbons but is rendered more soluble through coordination with nitrogen bases^{1,2} [either added as accelerator or present in raw natural rubber (NR)] or zinc carboxylates. Bateman et al.³ believed that the complexes [(XSS_xZnS_ySX) (L)] [L = nitrogen base or zinc carboxylate, X = $Me_2NC(S)$, x and $y \geq 1$], formed on the reaction of sulfur and ZDMC, were the active sulfurating agent in ZDMC-accelerated sulfur vulcanization systems. The presence of these zinc perthiomercaptides is, however, largely based


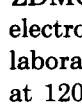
on circumstantial evidence. Kawaoka⁴ claimed the synthesis of a polysulfic homologue of ZDMC, viz., [$X(S)S(S)$]₂Zn, by fusion of sulfur with ZDMC at 140–150°C. Nuclear magnetic resonance investigations of Fackler et al.^{5,6} revealed that a chelate ring expansion occurred with the insertion of sulfur atoms into the complex zinc *p*-dithiocumate. The insertion of sulfur was limited to one atom. It was suggested that related zinc dithiolates such as ZDMC would activate sulfur in a similar manner. Further evidence for the formation of zinc perthiomercaptides, stemmed from the observed exchange between ZDMC and radioactive sulfur at 130°C in xylene. The rate of exchange was accelerated in the presence of a small amount of tetramethylthiuram disulfide (TMTD).⁷ On the other hand, Coleman et al.⁸ did not detect any changes due to new S—S bonds in the Raman spectrum of a sulfur/ZDMC (2.0/1.0 mole ratio) mixture after heating the sample at 125

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and 145°C. These results are consistent with those of Craig et al.,⁹ who observed no reaction between ZDMC and sulfur up to 150°C in the absence of a solvent. Nor was radioactive ZDMC found when a sulfur-35/ZDMC/palmitic acid mixture was heated for 60 min at 140°C,⁹ showing that sulfur did not exchange. Despite the contradictory experimental results that were presented with reference to the early formation of zinc perthiomercaptides, the authors believe that elemental sulfur and ZDMC do react as the first step in vulcanization.



An additional argument to substantiate this inference from the current study, will be given in the Results and Discussion section, second subsection.

A structural analysis of the products that formed on heating the 2-methylpent-2-ene/sulfur/ZDMC/ZnO model compound formulation at 100°C,³ revealed important aspects with regard to the position of sulfur attachment to the trialkylethylene. In the initial cure stages, sulfidic crosslinks were formed predominantly by substitutive processes at the α -methyl or α -methylene carbon atoms in the alkene, to form mainly A₁- and B₁-type structures. (The notations refer to the point of sulfur attachment to the alkenyl group, A₁ =  and B₁ = ). A similar observation was made for the 2-methylpent-2-ene/TMTD/ZnO system heated at 140°C,³ wherein the initial sulfuration reaction proceeded via a disubstitutive process.

Attempts to relate the formation of ZnS with the chemistry of vulcanization revealed that the ZnS content was, in general, not a measure of the crosslink density, but could be connected in a qualitative fashion with the network degradation reactions.^{3,10,11}

The paper compares the ZDMC-accelerated sulfur vulcanization of *cis*-1,4-polyisoprene in the presence and absence of ZnO.

EXPERIMENTAL

The experimental details were given in previous papers.^{12,13} Samples were vulcanized in a DSC, and the network as well as extractables analyzed.

RESULTS AND DISCUSSION

DSC curing curves revealed pertinent differences between IR (100)/sulfur (9.46)/ZDMC (11.27)

(1.0/1.0 mole ratio) and the IR (100)/sulfur (9.46)/ZDMC (11.27)/ZnO (3.00) (1.0/1.0/1.0 mole ratio) vulcanization systems (Figs. 1 and 2).

A Mechanism for the Formation of Pendant Groups and the Initial Polysulfidic Crosslinks

Few previous studies have been concerned with the radical or polar nature of ZDMC-related vulcanization systems. Shelton and McDonel¹⁴ determined the effect free radical scavengers (such as benzoquinone) had on the rate of crosslinking in poly(butadiene *co*-styrene)/sulfur/ZDMC/ZnO systems, and suggested the mechanism to be predominantly polar. Similar conclusions were drawn by Wolfe,¹⁵ on studying the stereochemistry of the crosslinked products which were formed in the cyclohexene/sulfur/ZDMC and cyclohexene/sulfur/ZDMC/ZnO model compound formulations. The electron spin resonance (ESR) data, recorded in this laboratory for the IR/sulfur/ZDMC system heated at 120°C, is depicted in Figure 3(b). The signals due to copper(II) dimethyldithiocarbamate

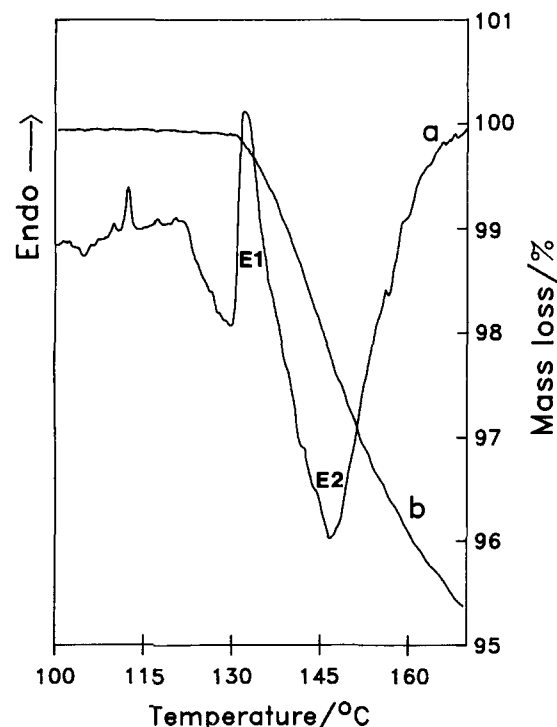


Figure 1 DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)/sulfur (9.46)/ZDMC (11.27) (1.0/1.0 mole ratio). The vulcanization quenched at 170°C appeared yellow/transparent, and had voids on swelling in benzene. M_i = 17.045 mg. (b) TGA spectrum.

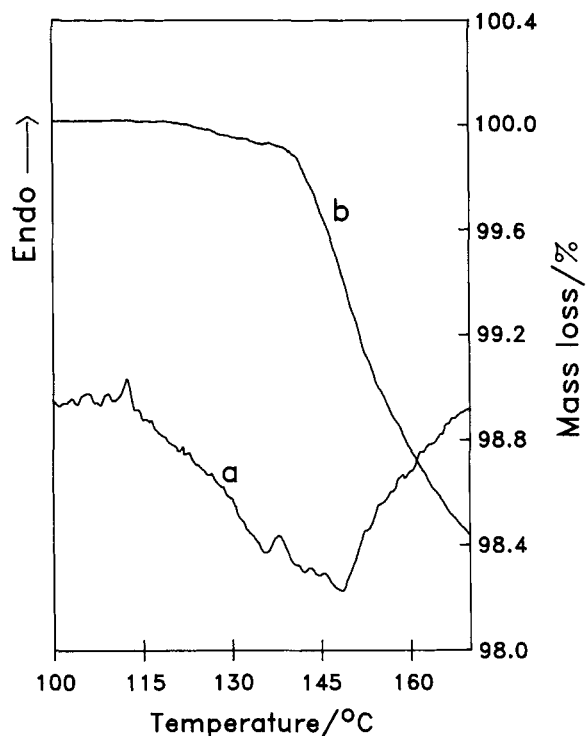
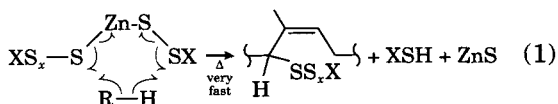


Figure 2 DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)/sulfur (9.46)/ZDMC (11.27)/ZnO (3.00) (1.0/1.0/1.0 mole ratio). The sample quenched at 170°C appeared yellow-white/transparent on swelling in benzene. $M_i = 17.932$ mg. (b) TGA spectrum.

(CuDMC)⁸ appeared very strong. Although no exact assignment of the peaks E3 were made, their relative positions compared favorably with the g values of 2.02 and 2.006, which were assigned⁸ to the thiuram persulphenyl and cyclic carbon radicals of the type $\text{Me}_2\text{N}-\dot{\text{C}}-\text{S}_x$, respectively. We therefore conclude that the participation of thiuram sulfenyl and thiuram persulphenyl radicals cannot be totally ignored in ZDMC-related vulcanization systems.

Since the initial sulphuration proceeded via a disubstitutive process in the 2-methylpent-2-ene/sulfur/ZDMC/ZnO system at 100°C,³ we inferred that pendent groups could form by reaction (1). The formation of the crosslink precursors RS_xSX ($\text{R} = \text{polyisoprenyl}$, $x \geq 1$) would, as before in the IR/TMTD/ZnO system,¹⁶ proceed via an irreversible concerted reaction without the formation of a true alkenyl radical intermediate.



The authors regard the formation of ZnS as characteristic of the ZDMC-accelerated sulfur vulcanization systems. Moore and Trego¹⁷ measured the formation of ZnS as the curing proceeded in the NR/sulfur/ZDMC/ZnO and IR/TMTD/ZnO compounds. The parameter F is defined as the number of sulfide ions per chemical crosslink formed.¹⁸ The F values, calculated from literature data,¹⁷ for the inefficient NR/sulfur/ZDMC/ZnO curing system, revealed $F = 3.5$ after only 0.25 h cure at 100°C (Table I). This phenomenon can be rationalized in terms of reaction (1), if the formation of pendent groups were a much faster process than the generation of crosslinks. F then decreased to 2.5 after 2.0 h, mainly because the chemical crosslink density increased substantially—the ZnS content increased by 88% in this time interval. Reversion was apparent after 20 h, and F increased slightly to 2.8. Calculations for the efficient IR/TMTD/ZnO system showed that the yield of ZnS became appreciable after only ~ 1 h cure time, and the maximum F value of 0.7 was reached at longer cure time. The fact that ZnS was formed rapidly (and in high yield) in NR/sulfur/ZDMC/ZnO cures, but slowly (and in low quantity) in IR/TMTD/ZnO vulcanizates (Table I), supports the contention that the *in situ*

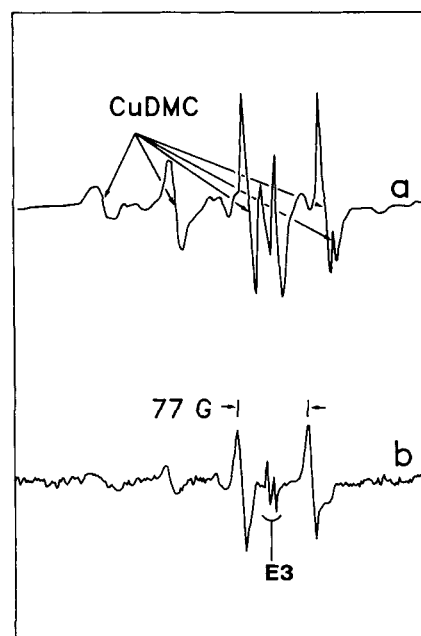


Figure 3 ESR spectra of curative combinations in the absence or presence of rubber. (a) Sulfur/TMTD (2.0/1.0 mole ratio) mixture heated at 145°C for 120 min, and then quenched with the spectrum recorded at -56°C.⁸ (b) IR (100)/sulfur (9.46)/ZDMC (11.27) formulation heated at 120°C, and spectrum recorded after ~ 5 min.

Table I The Changes in the Chemical Crosslink Density and F Value as the Cure Proceeded in the NR/sulfur/ZDMC/ZnO and IR/TMTD/ZnO Compounds¹⁷

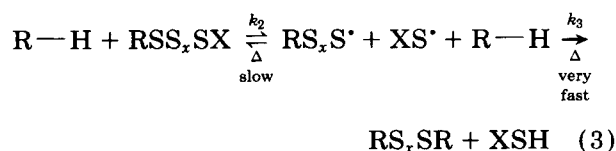
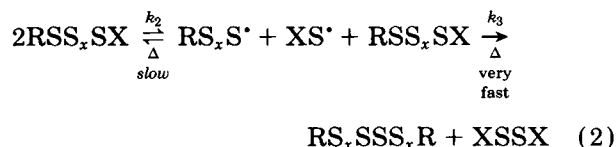
Compound (Curing Temp)	Cure Time (h)	$\frac{1}{2}M_{c,chem} \times 10^5$ (mol g ⁻¹ rubber network)	Sulfide ions ²⁻ per $\frac{1}{2}M_{c,chem}$ (F)
NR (100) sulfur (2.0)	0.25	1.50 ^a	3.5
ZDMC (2.0) ZnO (2.0)	2.0	4.03	2.5
(100°C)	20.0	3.12	2.8
IR (100) TMTD (4.0)	0.25	1.19 ^b	0
ZnO (4.0)	1.0	1.56	0.4
(140°C)	10.0	2.84	0.7

^a Obtained from stress/strain measurements.

^b Obtained from swelling measurements in *n*-decane.

formation of zinc perthiomercaptides was not the first step in TMTD-based vulcanization recipes.¹⁹

As in the IR/TMTD/ZnO system,¹⁶ the formation of the initial polysulfidic crosslinks would proceed via reactions (2) and/or (3) and would be rate determining.



The Nature of the Initial Pendent Groups and Crosslinks

Analysis on the IR/sulfur/ZDMC system (Table II) revealed that it was possible to account for 84.1 mol % ZDMC at the position 129.8°C along the DSC thermogram. The calculation incorporated the mass loss, which was related to the decomposition products of dimethyldithiocarbamic acid (DMDCA). DMDCA would form via reaction (1) in the early cure stages. The rest of the ZDMC molecules unaccounted for were most probably transformed to network-bound dimethyldithiocarbamyl radicals via

reaction (1). The steep decrease in E from 23.0 Sc atoms/crosslink at 129.8°C to 13.0 Sc atoms/crosslink at 132.4°C [Fig. 4(a)], led to the conclusion that most of the bound sulfur was initially combined in pendent groups. Similar remarks could be made for the IR/sulfur/ZDMC/ZnO mix (Table II), and provide evidence for the existence of pendent groups in these curing systems.

Calculations analogous to those that were presented in detail before²⁰ showed that the number of sulfur atoms per pendent group was unexpectedly large in the ZDMC-based compounds (Table III). On the assumption that tetrasulfidic and disulfidic crosslinks prevailed as the initial crosslinks in the IR/sulfur/ZDMC system at 129.8°C, it was calculated that pendent groups of the type RS_xX ($x = 3.23$) were formed. The pendent groups were even longer in the presence of ZnO, where groups RS_xX ($x = 5.82$) were present at 124.5°C along the cure curve, on the assumption that pentasulfidic and disulfidic crosslinks prevailed. The average value of the indice $x = 2.24$ at 140.0°C in the IR/TMTD/ZnO system.¹⁶ These findings thus constitute an important difference between the IR/TMTD/ZnO and IR/sulfur/ZDMC/ZnO vulcanizates in that the initial polysulfidic crosslinks were presumably much longer in the latter system, due to the unusually high sulfur rank of the pendent groups. It could therefore imply that the value of the indice x in the postulated active sulfurating agent $XS_xSZnSSX$, was exceedingly high and supports the reaction of elemental sulfur and ZDMC⁴⁻⁷ as the first step in ZDMC-accelerated sulfur vulcanization.

The Role of ZnO in ZDMC-Based Cures

Comparing crosslink density measurements on the IR/sulfur/ZDMC and IR/sulfur/ZDMC/ZnO systems (Table II), it was clear that ZnO had accelerated vulcanization. The crosslink density of 1.26×10^{-5} mol cm⁻³ rubber at 129.8°C in the IR/sulfur/ZDMC system was lower than that of 2.01×10^{-5} mol cm⁻³ rubber at 124.5°C in the IR/sulfur/ZDMC/ZnO compound. The maximum crosslink density of 16.53×10^{-5} mol cm⁻³ rubber (at 148.2°C) in the IR/sulfur/ZDMC/ZnO system was appreciably higher than the maximum crosslink density of 11.88×10^{-5} mol cm⁻³ rubber (at 146.9°C) in the IR/sulfur/ZDMC vulcanizate. Both compounds suffered considerable reversion at higher temperatures. (DMDCA) would form via reactions (1) and (3) above and the advantageous effects of ZnO in ZDMC-based cures could again be attributed to the removal of DMDCA from the vulcanizates, in the

Table II Analysis of the Compounds Shown, at Various Stages of Vulcanization

Compounds (parts per hundred)	Temp (°C)	Compounds Extracted (mol % of initial reagent) or TLC Observation					Mass Loss (%)	Degree of crosslinking (mol cm ⁻³ rubber network × 10 ⁶)			Polysulfides (%)
		S ₈	TMTD	TMTM	TMTU	ZDMC		$\frac{1}{2}M_c$	$\frac{1}{2}M_c$	$\frac{1}{2}M_c^d$	
IR (100), sulfur (9.46), ZDMC (11.27) [Fig. 1(a)]	129.8 132.4 146.9 170.0	82.2 79.1 4.2 0.0	0.0 0.0 0.0 0.0	0.0 0.0 0.0 0.0	0.0 0.0 0.0 0.0	83.3 78.8 43.7 44.2	0.06 0.17 2.22 4.70	1.26 4.30 11.88 5.37 11.69 ^e	0.03 0.45 3.45 3.53	97.7 89.7 71.0 34.4	
IR (100), sulfur (9.46), ZDMC (11.27), zinc stearate (23.31) [Fig. 2(a)]	124.5 148.2 170.0	83.4 0.0 0				0.03 0.55 1.56	2.01 16.53 9.44 19.50 ^e	0.09 4.87	95.7 70.6		
IR (100), sulfur (9.46), ZDMC (11.27), ZnS (3.59) [Fig. 5(b)]	170.0	0	✓ ^a	0	0	2.66	9.13				
IR (100), sulfur (9.46), ZDMC (11.27), ZnS (3.59) [Fig. 5(b)]	170.0	0	✓ ^a	0	0	4.83	11.15 13.48 ^e				

^a Symbol ✓ = compound barely detected with TLC.

^b Symbol √ = compound easy to detect with TLC.

^c Crosslink density after 2 h propane-2-thiol/piperidine treatment.

^d Crosslink density after 4 h propane-2-thiol/piperidine treatment.

^e Maximum ν value after vulcanizing compound in a Rheometer.

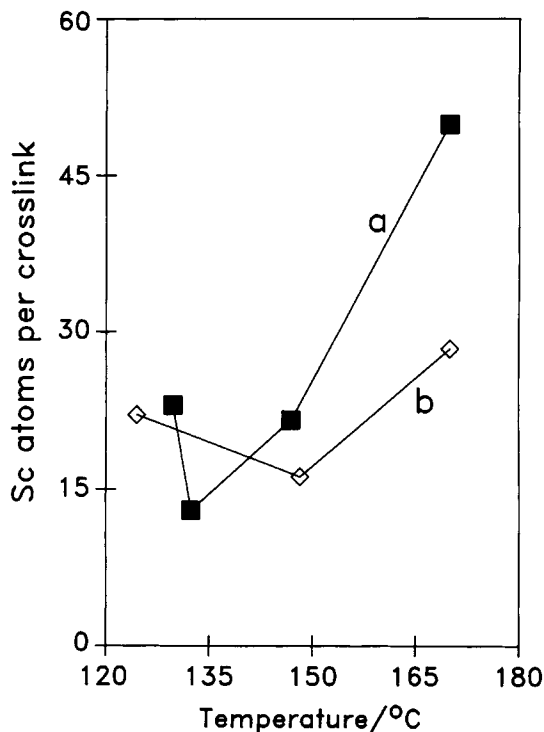


Figure 4 The variation of the Sc atoms/crosslink ratio as the cure proceeded for the vulcanization systems below. The calculations did not take the sulfur atoms of the network-bound SX groups into account. The data points were connected merely to illustrate the general trend in E. (a) IR (100)/sulfur (9.46)/ZDMC (11.27). (b) IR (100)/sulfur (9.46)/ZDMC (11.27)/ZnO (3.00).

formation of ZDMC.²¹ The effectiveness with which ZnO trapped the DMDCA in the ZDMC-containing systems will be demonstrated with reference to their curing curves.

A TGA analysis confirmed that the large endothermic peak E1, in the DSC curing curve of the IR/sulfur/ZDMC compound (Fig. 1), was due to the evaporation of gases. The DTGA curve showed that vulcanization had commenced simultaneously with the endotherm E1 at 130.6°C and that the maximum rate of evaporation (0.43%/min) occurred at 145.4°C. This was again significant, since the latter temperature coincided virtually with the trough temperature of the exotherm E2 at 146.9°C. The interaction of the curatives with the IR chain was thus highly exothermic, but the events were partially masked by the endothermic volatilization. The extractable sulfur was nearly exhausted at 146.9°C (Table II), and therefore the remaining part of the exotherm was due to network maturing reactions. Calculations using the TGA and HPLC data to account for ZDMC in the system revealed that the volatiles of the IR/sulfur/ZDMC system were not only due to Me₂NH and CS₂, since the mass loss was too high at 170°C.

The spectacular difference between the DSC curves of the IR/sulfur/ZDMC and IR/sulfur/ZDMC/ZnO compounds (Figs. 1 and 2) was attributed to the formation of ZDMC and H₂O in the DMDCA/ZnO reaction. The DTGA curve revealed that, in the presence of ZnO, the evaporation became appreciable only at 139.1°C. The maximum evaporation rate of 0.20% min⁻¹ at 148.4°C in the IR/sulfur/ZDMC/ZnO compound was considerably less than the 0.43% min⁻¹ in the IR/sulfur/ZDMC mixture. The mass loss of the IR/sulfur/ZDMC/ZnO system was only 1.56% at 170.0°C, much lower than the mass loss of 4.70% in the absence of ZnO (Table II).

Table III Calculation of the Number of Sulfur Atoms per Pendent Group at 129.8°C and 124.5°C in the DSC Scan of the IR/Sulfur/ZDMC and IR/Sulfur/ZDMC/ZnO Systems of Table II

System, Quantity Calculated	IR Sulfur ZDMC (mol cm ⁻³ rubber network)	IR Sulfur ZDMC ZnO
Crosslink density	1.26×10^{-5}	2.01×10^{-5}
Number of pendent groups	10.7×10^{-5}	7.2×10^{-5}
Network-bound sulfur atoms ^a	28.9×10^{-5}	44.5×10^{-5}
Sulfur atoms in crosslinks	5.0×10^{-5} ^b	9.8×10^{-5} ^c
Sulfur atoms in pendent groups ^d	23.9×10^{-5}	34.7×10^{-5}
Sulfur atoms per pendent group	3.23 ^e	5.82 ^e

^a Refers to sulfur other than in the SX moieties of pendent groups.

^b Assume tetrasulfidic and disulfidic crosslinks.

^c Assume pentasulfidic and disulfidic crosslinks.

^d Neglecting sulfur in the SX moieties of pendent groups.

^e Refers to the index x in RS_xX (R = polyisoprenyl).

The analytical data on the IR/sulfur/ZDMC and IR/sulfur/ZDMC/ZnO systems (Table II) further revealed that the concentration of ZDMC decreased at a much slower rate in the presence of ZnO, since ZDMC was replenished through the DMDCA/ZnO reaction. For example, the ZDMC concentration was 81.3 mol % at 148.2°C in the presence of ZnO, but only 43.7% at 146.9°C in the absence thereof. All these results thus clearly show that ZnO had reacted vigorously with DMDCA at vulcanization temperatures. It should be borne in mind that this reaction enthalpy also contributed to the net enthalpy in the DSC curves.

The fact that ZDMC decomposed during the vulcanization process has been mentioned in the literature,^{3,15,22} but received little attention. The authors, however, regard it as extremely important, for it implied that the IR/TMTD/ZnO vulcanization mechanism, was different to that of the IR/sulfur/ZDMC compound. The former system vulcanized with the formation of ZDMC,^{16,23} while the latter compound vulcanized with the decomposition of ZDMC. This is regarded as further evidence contradicting the postulate³ that a zinc perthiomercaptide is formed as the first step in the TMTD-based vulcanization mixtures.¹⁹

The Effect of Zinc Stearate on ZDMC-Based Cures

It was found that zinc stearate could perform the same role as ZnO, in that the DMDCA formed in ZDMC-based cures reacted with zinc stearate. This was evident from the DSC curing curves, for the endotherm E1 in the thermogramme of the IR/sulfur/ZDMC compound (Fig. 1), became largely diminished on heating an IR (100)/sulfur (9.46)/ZDMC (11.27)/zinc stearate (23.31) (1.0/1.0/1.0 mole ratio) mixture [Fig. 5(a)]. The mass loss of the IR/sulfur/ZDMC system was 4.70% at 170.0°C, higher than the 2.66% loss measured in the presence of zinc stearate (Table II). The presence of ZDMC in the IR/sulfur/ZDMC/zinc stearate vulcanizate at 170°C was confirmed with TLC. Free stearic acid was in all probability also formed, since free lauric acid has been isolated from IR/TMTD/zinc laurate compounds.²⁴ Bedford and Grey²⁵ remarked that zinc soaps had reacted with dimethylamine dimethyldithiocarbamate in CS₂ to form ZDMC and free fatty acid.

Note that ZDMC and stearic acid reacted at vulcanization temperatures to yield zinc stearate as the major nonvolatile product. The ZDMC/stearic acid (1.0/2.0 mole ratio) DSC spectrum recorded at 20°C/min showed the melting of stearic acid and a

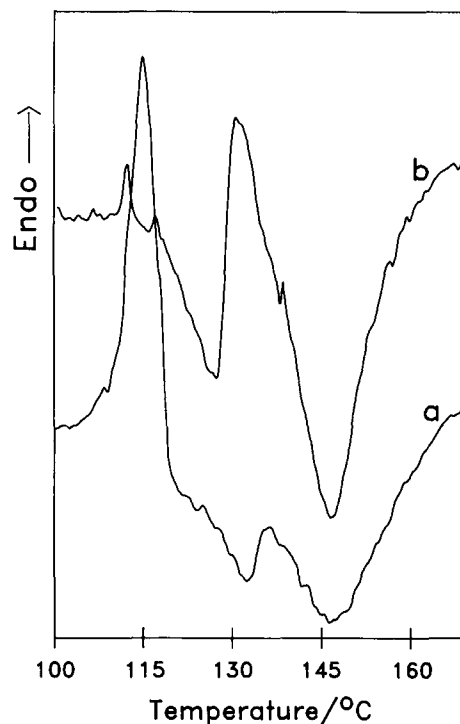


Figure 5 DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)/sulfur (9.46)/ZDMC (11.27)/zinc stearate (23.31) (1.0/1.0/1.0 mole ratio). $M_i = 17.093$ mg. (b) IR (100)/sulfur (9.46)/ZDMC (11.27)/ZnS (3.59) (1.0/1.0/1.0 mole ratio). $M_i = 17.152$ mg. The vulcanization in (a) appeared dark-yellow/transparent, and that in (b) white/opaque on swelling in benzene.

slight exotherm that initiated at 108°C (Fig. 6). The exotherm transformed into an endotherm at 137°C. The sample was held isothermally for 30 min at 150°C, and some thermal events did occur since the recorder pen went off scale at a range setting of 0.1 mcal s⁻¹ (0.418 mJ s⁻¹). The off-white sample was rescanned after 90 min at room temperature and the melting of zinc stearate was very prominent. A mass reduction of 24.5% was calculated after the rescanning experiment, somewhat lower than the theoretical amount of 27.7% expected if Me₂NH and CS₂ had formed quantitatively. In conjunction with the remarks in the preceding paragraph, it is suggested that an equilibrium reaction of the kind shown below could exist in the vulcanization of IR/sulfur/ZDMC/zinc stearate mixtures. The equilibrium would of course be favored to the right-hand side of an open system, due to the evaporation of low molecular mass species. A literature search failed to yield information regarding the existence of ZDMC/zinc carboxylate complexes.

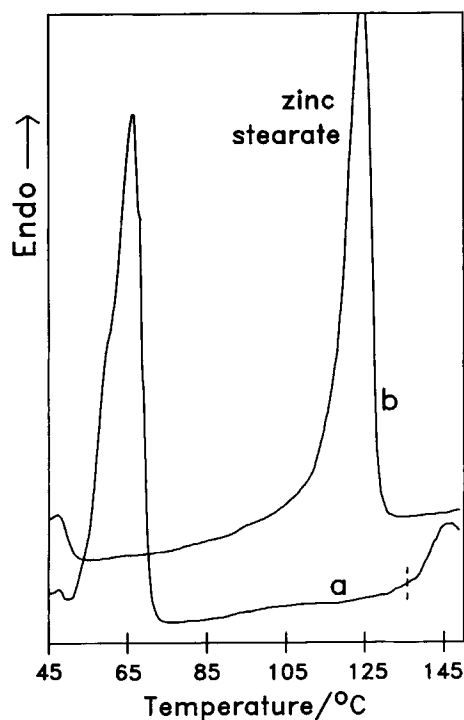
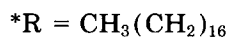
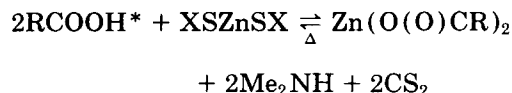


Figure 6 DSC spectra. (a) ZDMC/stearic acid (1.0/2.0 mole ratio) sample scanned at 20°C/min to 150°C; (b) rescan (see text for details). $M_i = 3.968$ mg, $M_f = 2.996$ mg.



The Effect of ZnS on ZDMC-Based Cures

Since the DSC curve of the IR (100)/sulfur (9.46)/ZDMC (11.27)/ZnS (3.59) (1.0/1.0/1.0 mole ratio) system duplicated that of the IR (100)/sulfur (9.46)/ZDMC (11.27) compound [cf. Figures 5 (b), 1], it was concluded that the ZnS/DMDCA reaction was negligible under these conditions. The mass losses of the two systems were also virtually the same at 170.0°C (Table II), giving additional support for the assertion above. Thus ZnS, formed from ZDMC during vulcanization, would be unreactive towards DMDCA.

The maximum crosslink densities of the vulcanization systems below were in the expected order: IR/sulfur/ZDMC/ZnO \gg IR/sulfur/ZDMC/ZnS \geq IR/sulfur/ZDMC (Table II). A Rheometer was used to cure the samples used for these determinations, since it had the distinct advantage of sealing the compounds at high pressure during vulcaniza-

tion. The formation of voids, which would influence the crosslink density values, was therefore eliminated.

CONCLUSIONS

Crosslinking in ZDMC-accelerated sulfur vulcanization systems, was found to proceed via the formation of pendent groups which subsequently reacted to yield crosslinks. Calculations revealed that pendent groups of the type RS_xX ($x = 3.23$) and RS_xX ($x = 5.82$) were formed in the initial cure stages of the IR/sulfur/ZDMC and IR/sulfur/ZDMC/ZnO compounds, respectively. It could therefore imply that the value of the indice x in the postulated active sulfurating agent XS_xSZnSSX was exceedingly high. The reaction of elemental sulfur and ZDMC as the first step in ZDMC-accelerated sulfur vulcanization systems was thus supported. ZnO and zinc stearate trapped DMDCA and led to higher crosslink densities, but ZnS was inactive.

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