# Study of Curative Interactions in *cis*-1,4-Polyisoprene. XI. Network Maturing Reactions in the *cis*-1,4-Polyisoprene–Sulfur–Zinc Dimethyldithiocarbamate and *cis*-1,4-Polyisoprene–Sulfur–Zinc Dimethyldithiocarbamate–ZnO Systems

F. W. H. KRUGER and W. J. MCGILL*

Polymer Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000, South Africa

## SYNOPSIS

The network maturing reactions of the inefficient *cis*-1,4-polyisoprene (IR)–sulfur–zinc dimethyldithiocarbamate (ZDMC) and IR–sulfur–ZDMC–ZnO vulcanization systems were discussed. The Moore–Trego efficiency $E$ was exceptionally high and increased, for example, from 13.0 at 132.4°C to 49.9 at 170.0°C in the IR–sulfur–ZDMC mixture. Calculations showed that $\sim$ 60% of the elemental sulfur was combined in the network in the form of cyclic sulfides and/or vicinal crosslinks at 148.2°C. The inefficient use of sulfur at the initial cure stages may be attributed to the insolubility of ZDMC in rubber. The increase in $E$ at the later stages of vulcanization was attributed to a decrease in the total number of polysulfidic crosslinks, as the number of mono- and/or disulfidic crosslinks remained constant. The destruction of polysulfidic crosslinks was enhanced in the absence of ZnO, due to the catastrophic attack of thiophilic species such as $Me_2NH$. The $Me_2NH$ resulted from the rapid decomposition of dimethyldithiocarbamic acid, which formed as a by-product in the initial crosslink reactions. No evidence was found for the participation of ZDMC in crosslink desulfuration. ZDMC is not a vulcanizing agent.

## INTRODUCTION

The network maturing reactions of synthetic *cis*-1,4-polyisoprene (IR)–sulfur–ZDMC–ZnO systems are concerned with the fate of the initial polysulfidic crosslinks on further heating.

Morrison et al.[1,2] identified the competition between desulfuration and decomposition reactions, of di- and polysulfidic crosslinks $RS_xR$ (R = polyisoprenyl, $x \geq 2$) in particular, as a major factor in determining the final vulcanizate network. Effective desulfuration would eventually result in thermally stable monosulfidic crosslinks, while the decomposition of sulfidic crosslinks would yield conjugated species, cyclic sulfides, and ZnS.

Porter[3] studied the interactions of methylpentenyl di- or trisulfide-2-methylpent-2-ene–ZnO mixtures at 140°C and found that the complex [(XSZnSX) (L)] [L = pyridine, X = $Me_2NC(S)$] had catalyzed the crosslink-shortening process of these sulfides. There was an increase in the number of crosslinked species with the reactants $A_1SSSA_1$, $B_1SSSB_1$, and $B_1SSB_1$, but a decrease in the case of $A_1SSA_1$. Interestingly, some insertion of additional sulfur atoms into the original disulfides $A_1SSA_1$ and $B_1SSB_1$ was also observed. (The notations refer to the position of sulfur attachment to the alkenyl moiety, $A_1 = $ ⟨structure⟩ and $B_1 = $ ⟨structure⟩ ). Considerable amounts of ZnS were always formed. It was postulated that the soluble ZDMC complex [(XSZnSX) (L)] (L = pyridine, zinc carboxylate) would behave similarly in real vulcanization systems, favoring the desulfuration of the initial polysulfidic crosslinks over their destruction. This would result in a heat-resistant network with a high degree of

crosslinking, which is typical of an efficient vulcanization (EV) system.

A natural rubber (NR) (100)–sulfur (2.0)–ZDMC (2.0)–ZnO (2.0) mixture, cured at 100°C, revealed a marked increase in the Moore–Trego crosslink efficiency $E$ as the cure proceeded. The $E$ value increased from 7.2 after 0.25 h to 18.2 after 20.0 h. The same remark held for the parameter $E'$ (the $E$ value after treating the vulcanizate with triphenylphosphine), in that it increased from 1.2 after 0.25 h to 13.7 after 20.0 h. Treating the NR–sulfur–ZDMC–ZnO vulcanizate with sodium di-$n$-butyl phosphite after 20 h cure time revealed that $\sim$ 79% of the crosslinks was still di- or polysulfidic in nature. The latter observation may also be perceived from the difference between the $E$ and $E'$ values, in that the average number of sulfur atoms per crosslink decreased progressively from 6.0 at 0.25 h to 4.5 at 20.0 h. These values, calculated for the number of sulfur atoms per crosslink, should serve as a guide only on the grounds of limitations outlined earlier.[4] The progressive increase in the $E$ and $E'$ values was explained[5] in terms of an increasing degree of main-chain modification, through the incorporation of sulfurated groups such as cyclic monosulfides and possibly some pendent groups $RSS_xX$ ($R$ = polyisoprenyl, $x \geq 0$). These changes in the network structure of the inefficient vulcanization system NR–sulfur–ZDMC–ZnO were in strong contrast to those of the EV system NR or IR–TMTD–ZnO, wherein the $E$ and $E'$ values decreased toward extended cure times.[6] Modulus reversion is typical of ZDMC-accelerated sulfur vulcanization of NR.[7]

The previous publication[8] dealt with the formation of polysulfidic crosslinks in ZDMC-accelerated sulfur vulcanization of IR. This work discusses the network maturing reactions based on experimental data given in that publication.

## RESULTS AND DISCUSSION

### On the Inefficient Use of Sulfur in ZDMC-based Vulcanization Systems

At the position 148.2°C along the differential scanning calorimetry (DSC) cure curve[8] of the IR (100)–sulfur (9.46)–ZDMC (11.27)–ZnO (3.00) system, the mass loss was only 0.55%, thus allowing calculation of the number of sulfur atoms per pendent group. The calculation, outlined in an earlier paper,[4] was based on the assumption that pentasulfidic and disulfidic crosslinks prevailed. A meaningless figure of 28.0 sulfur atoms per pendent group was, however, obtained (Table I). Furthermore, if it were assumed that each pendent group moiety SX was associated with the more realistic value of 5.0 sulfur atoms, then (5.0 sulfur atoms) ($7.4 \times 10^{-5}$ mole pendent groups/cm$^3$ rubber) = $37.0 \times 10^{-5}$ mole sulfur atoms/cm$^3$ rubber were to be associated with pendent groups. Adding the number of sulfur atoms bound as crosslinks would imply that ($37.0 + 68.1$) $\times 10^{-5}$ mol = $105.1 \times 10^{-5}$ mol sulfur atoms/cm$^3$ rubber, originally added as elemental sulfur, were to be associated with crosslinks and pendent groups. Since all of the elemental sulfur had reacted at 148.2°C (Table 2 of Ref. 8), it meant that ($268.0 - 105.1$)/2.68 $\cong$ 60% of the initial elemental sulfur was combined with the network in the form of, for example, cyclic sulfides and/or vicinal crosslinks. This illuminative result would imply that the utilization of elemental sulfur to form crosslinks was extraordinary inefficient right from the start in the IR–sulfur–ZDMC–ZnO system. It is known that ZDMC is only sparingly soluble in many solvents,[9] and the isoprene rubbers are no exception.[3,10] The inefficient use of sulfur in ZDMC-accelerated vulcanization systems may be related to the insolubility of ZDMC (es-

---

Table I   Calculation of the Number of Sulfur Atoms per Pendent Group at 148.2°C, in the DSC Scan of the IR–Sulfur–ZDMC–ZnO Vulcanization Compound from Table II of Ref. 8

| Quantity Calculated | mol/cm$^3$ Rubber Network |
|---|---|
| Crosslink density | $16.53 \times 10^{-5}$ |
| Number of pendent groups | $7.4 \times 10^{-5}$ |
| Network-bound sulfur atoms[a] | $268.0 \times 10^{-5}$ |
| Sulfur atoms in crosslinks[b] | $68.1 \times 10^{-5}$ |
| Sulfur atoms in pendent groups[c] | $199.9 \times 10^{-5}$ |
| Sulfur atoms per pendent group | $28.0?$[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 indice $x$ in $RS_xX$.

pecially at the high concentrations of ZDMC used in the current study).

The variation in the $E$ values at different points along the DSC cure curve with the IR–sulfur–ZDMC and IR–sulfur–ZDMC–ZnO compounds is depicted in Table II. It was evident that sulfur utilization became less efficient during the later stages of cure, which tied in with the corresponding observations of Moore et al.[5] on the NR–sulfur–ZDMC–ZnO system. A possible reason for the increase in $E$, from 16.2 at 148.2°C to 28.4 at 170.0°C in the IR–sulfur–ZDMC–ZnO system, may be the spontaneous decomposition of the polysulfidic crosslinks as the cure proceeded. Polysulfidic crosslinks decompose above 130°C[11] (130–150°C)[2] and monosulfidic crosslinks above 150–170°C[11] (or 170°C).[1]

The poor sulfur utilization was even more pronounced in the IR–sulfur–ZDMC system where the Sc atoms–crosslink ratio increased from 21.6 at 146.9°C to 49.9 at 170.0°C. The increase in $E$ was mainly due to the intense decrease in the crosslink density value between 146.9 and 170.0°C (Table II). The enhanced decomposition of polysulfidic crosslinks in the absence of ZnO could be related to the formation of species such as $Me_2NH$ and $H_2S$. In the absence of a chemical trap, such as ZnO, $Me_2NH$ would be released on the decomposition of dimethyldithiocarbamic acid (DMDCA), which was formed during crosslinking.[8] Calculations using the thermogravimetric analysis (TGA) and high-pressure liquid chromatography (HPLC) data[8] to account for the original ZDMC concentration revealed that the volatiles of the IR–sulfur–ZDMC system could not only be due to $Me_2NH$ and $CS_2$ since the mass loss was too high at 170°C. An explanation may be that $H_2S$ was formed in a substantial quantity, but the exact route whereby it was generated remained speculative. The detrimental effect of $Me_2NH$ and

$H_2S$ on the decomposition of polysulfidic crosslinks will be rationalized below.

It is well-known that amines accelerate sulfur vulcanization,[12–14] and Krebs[13] postulated that this activation of sulfur was due to the heterolytic fission of the $S_8$ ring. Mayer[15] cited references to substantiate that elemental sulfur, as well as polysulfides, were attacked and easily split by nucleophilic reagents such as $HS^-$, $S^{2-}$, and amines. In addition, Bartlett et al.[16,17] found that the heterolysis of $S$—$S$ bonds by diethylamine was considerably enhanced in the presence of $H_2S$ and $SO_2$ (which formed the highly thiophilic reagents $HS^-$ and $HSO_3^-$ in the presence of the amine). Since $Me_2NH$ and most probably $H_2S$ were produced on vulcanizing the IR–sulfur–ZDMC compound, $HS^-$ could easily have formed from the reaction between the Brōwnsted–Lowry acid and base. The reaction between especially polysulfidic crosslinks in the vulcanizate network and $HS^-$ would cause severe destruction of the crosslinks, in particular at vulcanization temperatures. The addition of sufficient ZnO to react with DMDCA formed in the ZDMC-accelerated compounds is therefore imperative, since these reversion reactions would be inhibited.

Furthermore, accelerated sulfur vulcanization recipes generally contain nitrogen bases (either added as accelerator or present in raw NR, and industrial sulfur is usually contaminated with minor amounts of $H_2S$, $H_2SO_3$, $H_2SO_4$, etc.[7,16–18] The preceding arguments may be relevant to explain the importance of stearic acid, customarily added as a co-activator to vulcanization compounds in industry. Being a weak acid, stearic acid could neutralize species such as amines, $HS^-$, $HSO_3^-$, etc., thereby inhibiting the demolition of pendent groups and sulfidic crosslinks by these thiophilic reagents. As a rule, fatty acids increase the crosslinking yield of

**Table II   Change in the Crosslink Density, Moore–Trego Parameter $E$, Polysulfidic and Mono- and/or Disulfidic Crosslinks as the Cure Proceeded in the Vulcanization System Shown**

| Compound (parts per hundred) | Temp. (°C) | Crosslink Density per mol/cm³ Rubber Network × 10⁵ | Crosslink Efficiency ($E$) | Polysulfidic Crosslinks per mol/cm³ Rubber Network × 10⁵ | Mono- and/or Disulfidic Crosslinks per mol/cm³ Rubber Network × 10⁵ |
|---|---|---|---|---|---|
| IR (100) | 129.8 | 1.26 | 23.0 | 1.23 | 0.03 |
| sulfur (9.46) | 132.4 | 4.30 | 12.0 | 3.86 | 0.44 |
| ZDMC (11.27) | 146.9 | 11.88 | 21.6 | 8.44 | 3.44 |
| | 170.0 | 5.37 | 49.9 | 1.85 | 3.52 |
| IR (100) | 124.5 | 2.01 | 22.1 | 1.92 | 0.09 |
| sulfur (9.46) | 148.2 | 16.53 | 16.2 | 11.67 | 4.87 |
| ZDMC (11.27) ZnO (3.00) | 170.0 | 9.44 | 28.4 | | |

sulfur-based vulcanizates at the expense of non-crosslinking species, i.e., decrease the $E$ value.[19]

## The Participation of ZDMC in Crosslink Desulfuration Reactions

The preceding evidence on the inefficient use of sulfur in NR or IR–sulfur–ZDMC–ZnO systems was in contrast to the model compound studies of Porter[3] that crosslink shortening was catalyzed by the complex [(XSZnSX) (L)] (L = pyridine) in methylpentenyl di- or polysulfide-2-methylpent-2-ene-ZnO mixtures at 140°C. If ZDMC were able to desulfurate crosslinks and form additional crosslinks simultaneously, the increase in the Moore–Trego efficiency parameter at the advanced stages of cure was not to be expected. Furthermore, Porter[3,20] remarked that ZDMC itself was sparingly soluble in rubber but was rendered more soluble through coordination with nitrogen bases (either added as accelerator or present in raw NR) or zinc carboxylates. However, the authors could find no evidence in the literature for the existence of ZDMC–zinc carboxylate complexes. In contrast to Porter,[3,20] Moore's study[5] of the NR (unextracted)–sulfur–ZDMC–ZnO compound showed an increase in $E$ with cure time, and ∼ 79% crosslinks were still di- or polysulfidic in nature after 20 h at 100°C. The type of NR used for these experiments was RSS1,[21] which typically has a nitrogen content of 0.37%.[22]

The contention that ZDMC did not play a major role in network maturing reactions of ZDMC-containing vulcanizates may also be substantiated by comparing the relative importance of desulfuration versus decomposition of polysulfidic crosslinks in the IR–sulfur–ZDMC system (Table II). It was clear that while the polysulfidic crosslinks degraded preferentially toward the later stages of curing (from $8.44 \times 10^{-5}$ mol/cm$^3$ rubber at 146.9°C to $1.85 \times 10^{-5}$ mol/cm$^3$ rubber at 170°C), the concentration of the mono- and/or disulphidic crosslinks remained constant at ∼ $3.48 \times 10^{-5}$ mol/cm$^3$ rubber in this temperature range. The polysulfidic crosslinks of the IR–sulfur–ZDMC system were thus prone to decompose rather than to be desulfurated by ZDMC.

ZDMC is not a vulcanizing agent, i.e., it cannot vulcanize unsaturated elastomers in the absence of sulfur. The DSC showed a straight line on heating an IR (100)–ZDMC (11.27) mixture at 2.5°C min to 190°C. No crosslinks were formed since the sample dissolved easily in benzene. With reference to the analytical data on the IR (100)–sulfur (9.46)–ZDMC (11.27) compound (Table 2 of Ref. 8), it was conspicuous that the ZDMC concentration had

remained constant at ∼ 44 mol % between 146.9 and 170.0°C. This immediately demonstrated the uninvolvement of ZDMC in the crosslink desulfuration reactions of the IR–sulfur–ZDMC system, since the concentration of ZDMC would have decreased if it were interacting with the network-bound sulfur to form new monosulfidic crosslinks.

Evidence was presented earlier[8] that ZDMC-accelerated sulfur vulcanization was characterized by the formation and subsequent decomposition of $XSS_xZnS_ySX$ ($x, y \geq 1$), with the concomitant formation of ZnS. Porter[3] also showed that if the ZDMC complex [(XSZnSX) (L)] (L = pyridine) were involved in the desulfuration of sulfides in methylpentenyl di- and trisulfide-2-methylpent-2-ene-ZnO mixtures, then substantial amounts of ZnS were formed concurrently. In contrast the research of Moore et al.[5] on the NR (100)–sulfur (2.0)–ZDMC (2.0)–ZnO (2.0) system revealed that the yield of ZnS was exceptionally high after 2 h cure (i.e., 32.2 mol %, calculated on the total zinc), but *decreased* slightly to 28.1 mol % after 20 h cure, which we suggest argues against the participation of ZDMC in the desulfuration of the initial polysulfidic crosslinks.

## CONCLUSIONS

The network maturing reactions of ZDMC-based vulcanization systems appeared to be dominated by the catastrophic destruction of polysulfidic crosslinks rather than their desulfuration. No experimental evidence was found that ZDMC could enhance the desulfuration of polysulfidic crosslinks in ZDMC-accelerated systems.

The maximum crosslink density was substantially larger in the IR–sulfur–ZDMC–ZnO system ($16.53 \times 10^{-5}$ mol/cm$^3$ rubber), compared to the IR–sulfur–ZDMC compound ($11.88 \times 10^{-5}$ mol/cm$^3$ rubber). Likewise, the efficiency parameter was much higher for the IR–sulfur–ZDMC mixture at the advanced cure stages ($E$ = 49.9 at 170.0°C) than for the IR–sulfur–ZDMC–ZnO compound ($E$ = 28.4 at 170.0°C). These phenomena inter alia resulted from the rapid decomposition of DMDCA, which originated in the crosslinking process[8] to form Me$_2$NH and CS$_2$ in the absence of ZnO. Calculations also pointed to the formation of substantial quantities of a foreign product, possibly H$_2$S, on curing the IR–sulfur–ZDMC system. The reactions between the polysulfidic crosslinks, especially, and the highly thiophilic reagents such as Me$_2$NH and HS$^-$, were suggested as an explanation for the excessive de-

struction of the IR–sulfur–ZDMC network at vulcanization temperatures.

## REFERENCES

1. N. J. Morrison and M. Porter, *Rubber Chem. Technol.,* **57,** 63 (1984).
2. N. J. Morrison and M. Porter, *Plast. Rubber Process. Appl.,* **3,** 295 (1983).
3. M. Porter, in *The Chemistry of Sulphides,* A. V. Tobolsky, Ed. Interscience Publishers, New York, 1968, p. 165.
4. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **44,** 587 (1992).
5. C. G. Moore and B. R. Trego, *J. Appl. Polymer Sci.,* **8,** 1957 (1964).
6. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **45,** 573 (1992).
7. L. Bateman, C. G. Moore, M. Porter, and B. Saville, in *The Chemistry and Physics of Rubber-like Substances,* L. Bateman, Ed., Maclaren, London, 1963, Chap. 15.
8. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **45,** 755 (1992).
9. R. O. Babbit, Ed., *The Vanderbilt Rubber Handbook,* R. T. Vanderbilt Company, Norwalk, CT, 1978.
10. J. A. Brydson, *Rubber Chemistry,* Applied Science Publishers, London, 1978, Chap. 8.
11. M. L. Bhaumik, D. Banerjee, and A. K. Sircar, *J. Appl. Polym. Sci.,* **9,** 1367 (1965).
12. W. A. Pryor, *Mechanisms of Sulphur Reactions,* McGraw-Hill, New York, 1962, Chap. 5.
13. H. Krebs, *Rubber Chem. Technol.,* **30,** 962 (1957).
14. M. M. Coleman, J. R. Shelton, and J. L. Koenig, *Ind. Eng. Chem. Prod. Res. Develop.,* **13,** 154 (1974).
15. R. Mayer, in *Organic Chemistry of Sulphur,* S. Oae, Ed., Plenum Press, New York, 1977, Chap. 2, p. 45.
16. P. D. Bartlett, E. F. Fox, and R. E. Davis, *J. Am. Chem. Soc.,* **83,** 103 (1961).
17. P. D. Bartlett, A. K. Colter, R. E. Davis, and W. R. Roderick, *J. Am. Chem. Soc.,* **83,** 109 (1961).
18. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry, a Comprehensive Text,* Wiley, New York, 1980, p. 508.
19. B. Saville and A. A. Watson, *Rubber Chem. Technol.,* **40,** 100 (1967).
20. M. Porter, in *Organic Chemistry of Sulphur,* S. Oae, Ed., Plenum Press, New York, 1977, Chap. 3.
21. C. G. Moore, L. Mullins, and P. McL. Swift, *J. Appl. Polym. Sci.,* **5,** 293 (1961).
22. G. Martin, in *The Applied Science of Rubber,* W. J. S. Naunton, Ed., Edward Arnold Publishers, London, 1961, Chap. 2.