

A Study of Curative Interactions in *cis*-1,4-Polyisoprene. IX. The Role of ZnO in Thiuram-Based Vulcanization 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

During the vulcanization of *cis*-1,4-polyisoprene (IR) with thiuram-related curing systems, dimethyldithiocarbamic acid (DMDCA) is formed as a byproduct, in the formation of either pendent groups or crosslinks. DMDCA is unstable, and decomposes instantly to Me_2NH and CS_2 in the absence of ZnO. The facile reaction of Me_2NH and thiuram-related molecules such as tetramethylthiuram polysulfides, tetramethylthiuram disulfide (TMTD), tetramethylthiuram monosulfide and pendent groups caused (i) increased induction periods, (ii) lower maximum crosslink densities, and (iii) the excessive formation of tetramethylthiourea (TMTU). A most important function of ZnO was to trap the DMDCA via the formation of zinc dimethyldithiocarbamate and water, thereby preventing the detrimental reactions above. The IR/TMTD/ZnO and IR/sulfur/TMTD/ZnO systems were therefore characterized by (i) shorter induction periods, (ii) higher maximum crosslink densities, and (iii) the absence of TMTU.

INTRODUCTION

It is well-known that ZnO is desirable for the development of good physical properties in thiuram-related vulcanization systems.^{1,2} The exact *modus operandi* remains debatable, but the most widely held opinion is that tetramethylthiuram disulfide (TMTD) and ZnO react to form the zinc perthiomercaptide XS_xSZnSX [$\text{X} = \text{Me}_2\text{NC}(\text{S}), x \geq 1$] prior to crosslinking.³⁻⁵ However, it was shown in a previous paper,⁶ that TMTD and ZnO were extremely reluctant to react at vulcanization temperatures, which argued against the formation of a zinc perthiomercaptide XS_xSZnSX as the first step in thiuram-related vulcanization systems.

Kinetic studies by Duchacek^{7,8} revealed that the vulcanization rate and crosslink density increased when the amount of ZnO was increased from 0 to 1.5 phr in a natural rubber (NR)(100)/TMTD(3.0)/ZnO(variable) compound, but remained unchanged with higher ZnO loadings. Moore et al.⁹ found that the relative extents (or rates) of pendent group and crosslink formation were substantially reduced when ZnO was omitted from a synthetic

cis-1,4-polyisoprene (IR)(100)/TMTD(4.0)/ZnO(4.0) compound vulcanized at 140°C. The crosslink density of the IR/TMTD/ZnO mixture was already 2.18×10^{-5} mol cm^{-3} rubber after 15 min, and that of the IR/TMTD sample negligible. A strong smell of Me_2NH was reported in the absence of ZnO. The unvulcanized material of the IR/TMTD mixture was extracted, and about 4.5 mol % of the original TMTD was found to have combined in pendent groups. The extracted adduct was reheated in the presence of ZnO, and a low crosslink density of 0.29×10^{-5} mol cm^{-3} resulted after 7.75 h. An elemental analysis of the extracted crosslinked material showed a reduction of 38% and 55% in the combined nitrogen and sulfur, respectively, and ZDMC was measured in the extract. It was concluded that the actual precursor to crosslinking, RS_xSX ($\text{R} = \text{polyisoprenyl}, x \geq 1$), was not formed by the simple interaction of IR and TMTD.

In contrast Parks et al.¹⁰ found that a substantial amount of benzothiazolyl groups became bound to the rubber chains on heating a natural rubber (NR)(100)/sulphur(0.5)/*N*-(*t*-butyl)-2-benzothiazolyl sulfenamide (BBS)(5.0) compound at 140°C. The extracted adduct was reheated in the presence of zinc oleate (3 phr) for 30 min, on which additional crosslinks resulted. It was concluded that

these pendent groups were converted into crosslinks, but unfortunately no quantitative data were presented. However, ZnO increased the relative rate of pendent group formation in the NR(100)/sulfur(0.5)/BBS(5.0)/ZnO(5.0)/stearic acid(3.0) system (and consequently the rate of vulcanization) considerably.

This paper examines the role of ZnO in TMTD-accelerated systems.

EXPERIMENTAL

The experimental details were given in previous papers.^{11,12} Samples were vulcanized in a DSC, and the network as well as extractables analyzed. TLC and HPLC played a major role in the latter analysis.

RESULTS AND DISCUSSION

On vulcanization in the DSC, there was a definite distinction with respect to the formation of crosslinks and extractable compounds between the IR/TMTD or IR/sulfur/TMTD system on the one hand (Table I), and the IR/TMTD/ZnO or IR/sulfur/TMTD/ZnO mixture on the other (Table II). For example, the maximum crosslink density of the IR/TMTD vulcanizate was only 3.07×10^{-5} mol cm⁻³ at 159.1°C, while that of the IR/TMTD/ZnO compound increased progressively to 8.30×10^{-5} mol cm⁻³ at 190.0°C. The crosslink density of the IR/sulfur/TMTD system started to build up

at 143.2°C (0.41×10^{-5} mol cm⁻³), but was already higher at 131.9°C (1.46×10^{-5} mol cm⁻³) in the IR/sulfur/TMTD/ZnO compound. High concentrations of tetramethylthiourea (TMTU) (but no tetramethylthiuram monosulfide (TMTM)) were measured for the IR/TMTD or IR/sulfur/TMTD mixtures, and in contrast no TMTU (but TMTM) was detected in the IR/TMTD/ZnO or IR/sulfur/TMTD/ZnO compounds.

It was remarkable that the concentration of TMTU was already 31.9 mol % at 159.1°C for the IR/TMTD compound (Table I), and 34.6 mol % at 143.2°C for the IR/sulfur/TMTD system. Since no TMTU was found on heating either a TMTD sample, or a sulfur/TMTD (1.0/1.0 mole ratio) mixture isothermally⁶ for 5 min at 145.7°C, it was clear that the TMTU had not originated directly from thermal decomposition under these vulcanization conditions. Furthermore, a ratio of 3.5 TMTU molecules/crosslink was calculated for the IR/TMTD system quenched at 159.1°C, and 28.3 TMTU molecules/crosslink for the IR/sulfur/TMTD system quenched at 143.2°C. This implied that the IR molecules were involved in the formation of TMTU, but prior to crosslinking. These observations will now be harmonized.

The thiuram accelerator TMTD decomposes via a different route in the presence of compounds with an active hydrogen atom, due to the formation of the dimethyldithiocarbamic acid (DMDCA). For example, Dogadkin et al.¹ showed convincingly that TMTD interacted easily with geraniol, isopropylbenzene, and NR at about 140°C, in that DMDCA formed by means of the abstraction of an active hy-

Table I Analysis of the Compounds Shown, at Various Temperatures Along the DSC Curing Curve

Compound (Parts Per Hundred)	Temp. (°C)	Compounds Extracted (mol % of Initial Reagent, by HPLC or Detected by TLC)				Mass Loss (%)	Degree of Crosslinking (mol cm ⁻³ Rubber Network × 10 ⁵)			Polysulfides (%)
		S ₈	TMTD	TMTM	TMTU		1/2M _c	1/2M _c ^a	1/2M _c ^b	
IR (100) TMTD (8.6)	150.2					0.19	0.00			
	154.8					0.47	0.06			
	159.1	0.0	4.9	0.0	31.9	1.45	3.07	1.62		47.2
	190.0	0	^c	0		7.03	0.91			
IR (100) Sulfur (9.46) TMTD (8.86)	135.4					0.13	0.00			
	143.2	94.3	27.1	0.0	34.6	0.62	0.41		0.02	95.7
	151.0	69.2	9.8	0.0	60.1	3.90	4.97		1.42	71.5
	164.1	9.1	11.4	0.0	67.1	6.53	6.31		2.23	64.5
	190.3	0.0	4.3	0.0	57.7	8.05	3.24		1.95	39.9

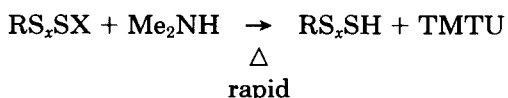
^a Crosslink density after 2 h propane-2-thiol/piperidine treatment.

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

^c Barely detected with TLC.

mation of the active sulfurating agent tetramethylthiuram polysulfide XSS_xX ($x \geq 2$), which would strongly affect the vulcanizate properties.

Moreover, Me_2NH formed in IR/TMTD and IR/sulfur/TMTD vulcanizates would be prone to react with the thiocarbonyl carbon of the dimethyldithiocarbamyl moiety of the pendent groups to form TMTU and a thiol. Since the crosslink precursors such as RS_xSX ($x \geq 1$) were thereby demolished, the actual crosslink reaction via pendent groups was largely prevented in the above-mentioned compounds.



The thiol would behave like sulfur in unaccelerated sulfur vulcanization, forming a more inefficient network due to the formation of, for example, cyclic sulfides. The large DSC exotherm that was observed for the IR(100)/sulfur(9.46)/TMTD(8.86) vulcanization,²² could therefore partially be attributed to an unaccelerated sulfur vulcanization peak.

The high mass loss (7.03%) in the IR/TMTD system, compared to the low mass loss (0.67%) of the IR/TMTD/ZnO compound at 190.0°C (cf. Tables I and II), underlined the effectiveness of ZnO in functioning as a chemical trap for DMDCA. With the formation of ZDMC, the vulcanizate would be deprived of DMDCA (and hence Me_2NH), and therefore no TMTU was formed in the IR/TMTD/ZnO vulcanizate. Dogadkin et al.²³ reported that TMTU was not found in NR or IR/TMTD/ZnO vulcanizates, and Craig et al.^{16,24} measured a low concentration of TMTU in vulcanized NR/TMTD/ZnO systems. Moore et al.⁹ found TMTU only in a fully cured IR/TMTD/ZnO compound (unreacted TMTD would have interfered if their analysis procedure was applied at the earlier stages of vulcanization). However, Porter³ found exceedingly high concentrations of TMTU early in the 2-methylpent-2-ene/TMTD/ZnO model compound vulcanization. Substantial amounts of CS_2 were measured as well, implying that part of the DMDCA which was formed had decomposed to Me_2NH and CS_2 . The TMTU could have originated via the detrimental reaction of Me_2NH and TMTD, or possibly Me_2NH and pendent groups. Dogadkin et al.¹ also found that part of the DMDCA formed in the isopropylbenzene/TMTD/ZnO vulcanization mixture had degraded to Me_2NH and CS_2 (rather than reacting with ZnO), and ascribed it to poor dispersion of ZnO in the solution. It is evident that care should be taken in

extrapolating from observations in model compound studies, to events in the real vulcanizate.

The explanations that were presented in the preceding paragraphs, are illuminating with respect to the mechanistic aspects of TMTD-based vulcanization systems. Moore et al.⁹ found that the relative extents (or rates) of pendent group and crosslink formation were substantially reduced when ZnO was omitted from an IR(100)/TMTD(4.0)/ZnO(4.0) compound, vulcanized for 15 min at 140°C. The crosslink density results of the IR/TMTD or IR/sulfur/TMTD system (Table I), and the IR/TMTD/ZnO or IR/sulfur/TMTD/ZnO compound (Table II) were more informative. They revealed *inter alia* that the induction period had decreased in the presence of ZnO, and that the extent of crosslink formation was considerably enhanced. These fundamental differences between TMTD-based vulcanizates with or without ZnO can now readily be explained. In the absence of ZnO, Me_2NH would rapidly be released on the decomposition of DMDCA at vulcanization temperatures. The destructive attack of Me_2NH on accelerator molecules and pendent groups will adversely effect the rate and extent of pendent group formation, which will increase the induction period and suppress the generation of crosslinks. (It was inferred from the current results that Me_2NH would be prone to react with pendent groups RS_xX , but this was not explicitly proven). DMDCA (and hence Me_2NH) will, on the other hand, be removed from the vulcanizate in the presence of ZnO, through the formation of ZDMC. The detrimental reactions of Me_2NH would be inhibited, which would lead to higher crosslink densities and consequently better physical properties of the end product.

Furthermore, it was conspicuous that Parks et al.¹⁰ managed to introduce a large proportion of benzothiazolyl moieties as pendent groups on vulcanizing a NR/sulfur/BBS mixture, but Moore et al.⁹ could find only a small quantity of dimethyldithiocarbamyl units as pendent groups on heating an IR/TMTD compound. These observations could be rationalized in terms of the increased stability of the aromatic benzothiazolyl group, as opposed to the electrophilic character of the dimethyldithiocarbamyl group. The benzothiazolyl groups would therefore be more stable in the presence of *t*-butylamine, than would the dimethyldithiocarbamyl group in the presence of Me_2NH .

Exactly the same mechanism of crosslink formation which was suggested for the IR/TMTD/ZnO vulcanization system,¹³ would apply in the IR/TMTD curing system, had the detrimental reactions

involving Me_2NH not occurred. Pendent groups of the type RS_xX ($x \geq 2$) were also formed, as was perceived by the large number of polysulphidic crosslinks (47.2 mol %) at 159.1°C.

CONCLUSION

The poor physical properties that are generally associated with thiuram-related vulcanization systems in the absence of ZnO, were traced back to the formation and subsequent decomposition of DMDCA. The Me_2NH generated on the decomposition of DMDCA, caused reactions detrimental to the vulcanization process, such as the demolishing of accelerator molecules and pendent groups. The presence of ZnO in thiuram-based vulcanization systems is thus imperative to specifically prevent these unwanted reactions, but is not a requirement for the formation of pendent groups of the type RS_xSX ($x \geq 2$).

We wish to thank the Foundation for Research and Development and Gentyre Industries for financial assistance.

REFERENCES

1. B. A. Dogadkin and V. A. Shershnev, *Rubber Chem. Technol.*, **33**, 401 (1960).
2. D. Craig, W. L. Davidson, and A. E. Juve, *J. Polym. Sci.*, **5**, 709 (1950).
3. M. Porter, in *Organic Chemistry of Sulphur*, S. Oae, Ed., Plenum Press, New York, 1977, Chap. 3.
4. 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.
5. C. G. Moore, B. Saville, and A. A. Watson, *J. Appl. Polym. Sci.*, **3**, 373 (1960).
6. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2669 (1991).
7. V. Duchacek, *Chem. Abstr.*, **72**, 101600n (1970).
8. V. Duchacek, *Chem. Abstr.*, **73**, 4696m (1970).
9. C. G. Moore and A. A. Watson, *J. Appl. Polym. Sci.*, **8**, 581 (1964).
10. C. R. Parks, D. K. Parker, and D. A. Chapman, *Rubber Chem. Technol.*, **45**, 467 (1972).
11. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **42**, 2661 (1991).
12. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **44**, 581 (1992).
13. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, **45**, 563 (1992).
14. W. A. Pryor, *Mechanisms of Sulphur Reactions*, McGraw-Hill, New York, 1962, Chap. 3.
15. C. Walling, *Free Radicals in Solution*, John Wiley and Sons, New York, 1957.
16. D. Craig, W. L. Davidson, and A. E. Juve, *J. Polym. Sci.*, **6**, 177 (1951).
17. F. W. Shaver, in *Encyclopedia of Chemical Technology*, 2nd ed., A. Standen, Exec. Ed., John Wiley and Sons, New York, 1968, p. 17.
18. B. A. Dogadkin and V. A. Shershnev, *Chem. Abstr.*, **52**, 10626c (1958).
19. B. A. Dogadkin, A. V. Dobromyslova, and V. A. Shershnev, *Chemical Abstracts*, **55**, 5006c (1961).
20. T. W. G. Solomons, *Organic Chemistry*, John Wiley and Sons, New York, 1980, Chap. 17.
21. M. Delépine, *Bull. Soc. Chim.*, **7**, 988 (1910).
22. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, Paper VI in the press.
23. B. A. Dogadkin and V. A. Shershnev, *Chem. Abstr.*, **53**, 20879 (1959).
24. D. Craig, W. L. Davidson, and A. E. Juve, *J. Polym. Sci.*, **6**, 7 (1951).

Received January 24, 1991

Accepted April 11, 1991