Complexes of Tetramethylthiuram Disulfide with Zinc Dialkyldithiocarbamates and Their Role in the Sulfur Vulcanization of Natural Rubber

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Synopsis

Tetramethyl thiuram disulfide, which functions as an inhibitor of the zinc dialkyldithiocarbamate-accelerated sulfur vulcanization, has been investigated by Mooney scorch measurements at 120°C and continuous measurements in a Vuremo curometer at temperatures from 100 to 140°C. The inhibition effect is due to the formation of a complex with zinc dialkyldithiocarbamate. The stability of the complex was calculated using the Hückel method which includes charge self-consistency on the central atom. The calculations are in a good agreement with the experimental results which illustrate that tetramethylthiuram disulfide, unlike an actual prevulcanization inhibitor, plays a significant role in all the stages of vulcanization. It decreases the crosslinking rate and increases the ultimate extent of vulcanization and its activation energy.

INTRODUCTION

In the vulcanization process of rubbers by tetraalkylthiuram disulfide (TATD) in the presence of zinc oxide and in the absence of sulfur, TATD reacts with zinc oxide to give zinc dialkyldithiocarbamate (ZnDADC) in a two-third yield based on the amount of original TATD and perthio anions (alkyl)$_2$—N—C(:S)—SS$^-$.[1,2] In the next vulcanization step, the latter form thiuram polysulfides. Interchange between these polysulfides and ZnDADC would then yield the sulfur-donating complex which reacts with rubber to yield rubber-bound intermediate compounds and, finally, crosslinks.

The addition of a compound such as 2-mercaptobenzothiazole (MBT) (with which ZnDADC forms a complex rather than with TATD) causes the scorch delay. This finding[3] confirms the validity of the mechanism of the sulfur-free thiuram vulcanization proposed previously.[1,4]

If TATD forms a complex with ZnDADC, then in the case of the ZnDADC–sulfur vulcanization system, the addition of TATD must inhibit vulcanization. The experimental results presented herein support this proposition.
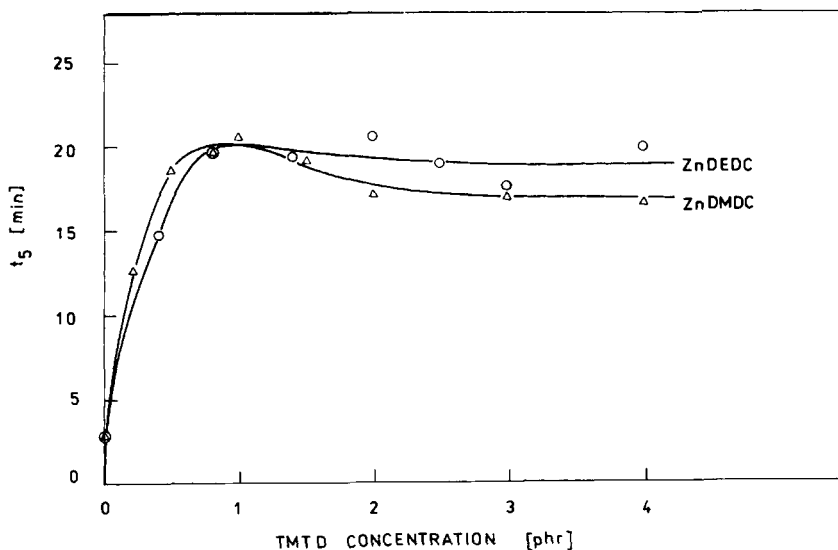
Fig. 1. Effect of tetramethylthiuram disulfide (TMTD) on Mooney scorch t_5 at 120°C. Mix formulation: natural rubber (pale crepe), 100 parts; ZnO, 5 phr; sulfur, 1 phr; zinc dimethyldithiocarbamate (ZnDMDC) or zinc diethyldithiocarbamate (ZnDECD), 2 phr; TMTD, variable.
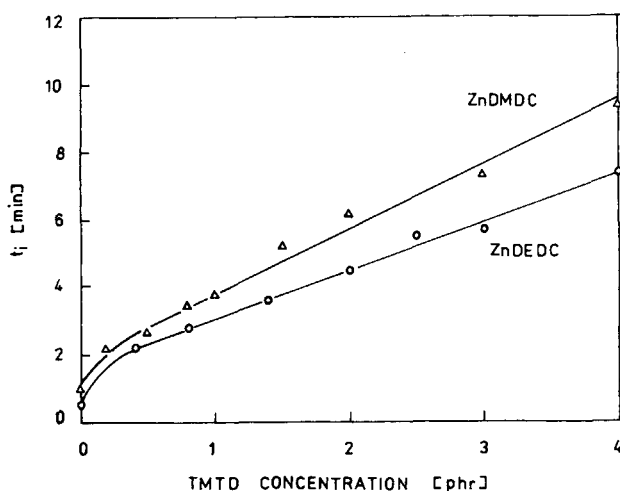

Fig. 2. Effect of TMTD on induction period t_i of vulcanization at 140°C. Mix formulation as in Fig. 1.

EXPERIMENTAL

Compounding

The mix formulation was natural rubber (pale crepe), 100 parts; zinc oxide, 5 phr; sulfur, 1 phr; zinc dimethyldithiocarbamate or zinc diethyldithiocarbamate, 2 phr; tetramethylthiuram disulfide, variable.

Mixing was by master batch technique on a laboratory mill with 400 × 130 mm rolls at 50°C. Mooney viscosities of the rubber compounds were 10 ML(1 + 4)
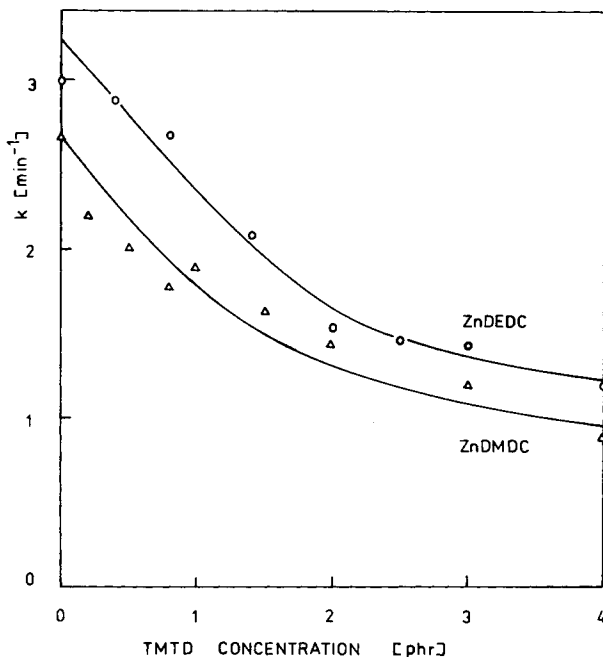
Fig. 3. Effect of TMTD on rate constant k of vulcanization at 140°C. Mix formulation as in Fig. 1.

at 100°C. This, according to Wolstenholme,[5] is equivalent to a number-average molecular weight of 1.2×10^5.

Measurement of Kinetic Parameters of Vulcanization

The rubber compounds were cured at 100, 120, and 140°C on a Vuremo curometer Type AC-01 (Metrimpex, Budapest, Hungary). The apparatus and curometer measurements have been fully described before.[4]

The extent of vulcanization at any time, M (modulus), was expressed in Vuremo units (torque) and plotted against time of cure. Thus, cure curves were obtained. The ultimate extent of vulcanization was calculated as $M_{max} - M_{min}$ value. The induction period t_i and the rate constant k of the vulcanization were calculated in accordance with the method of Scheele[6] proposing a first-order reaction from the linearized cure curves, where the logarithm of the extent of vulcanization is plotted against the cure time (Fig. 4).

Some lag time is involved in heating the specimen of a rubber compound to the impressed temperature. Therefore, the elapsed cure times were corrected in accord with the correction curve for the Vuremo curometer.[4]

Calculation of the Stability of TATD–ZnDADC Complexes

The stability of the proposed complexes was calculated using the Hückel method including charge self-consistency on the central atom.[7-9] According to Mulliken,[10] the charges on the atoms and the allocations of the electrons in the bonds were investigated on the basis of atomic orbit coefficient calculations
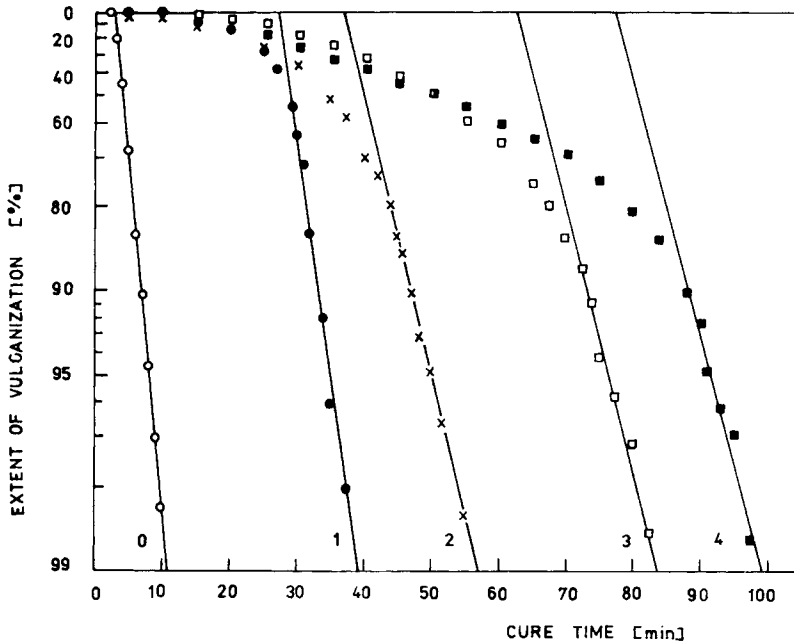
Fig. 4. Effect of TMTD on increase of extent of vulcanization at 120°C as first-order reaction. Mix formulation as in Fig. 1. Numbers on lines are concentrations of TMTD in phr.
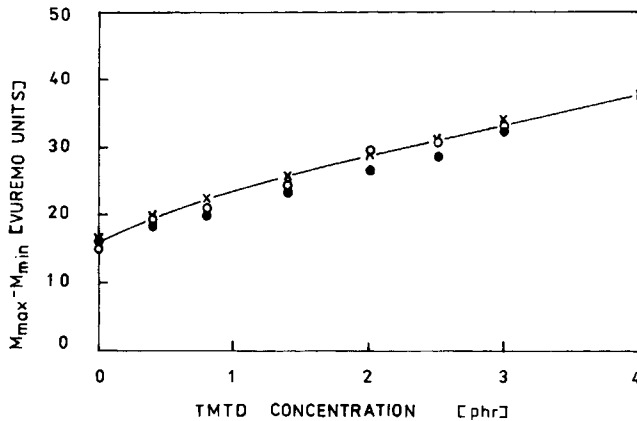

Fig. 5. Effect of TMTD on ultimate extent ($M_{max} - M_{min}$) of vulcanization. Mix formulation as in Fig. 1: (×) 190°C; (○) 120°C; (●) 100°C.

for the full molecular orbits. For these calculations, a BESM-6 computer (working rate of about a million operations per second and storage of 32,768 ten-order numbers) was used. The method and the working program used have been described before.[11]

RESULTS AND DISCUSSION

The effect of increasing concentration of tetramethylthiuram disulfide (TMTD) on Mooney scorch of a natural rubber compound with 1 phr sulfur accelerated by 2 phr zinc dimethyldithiocarbamate (ZnDMDC) or zinc diethyldi-
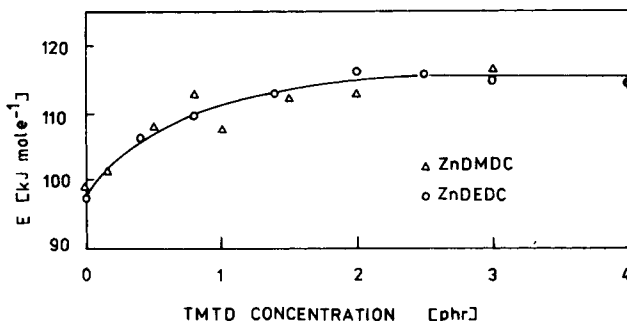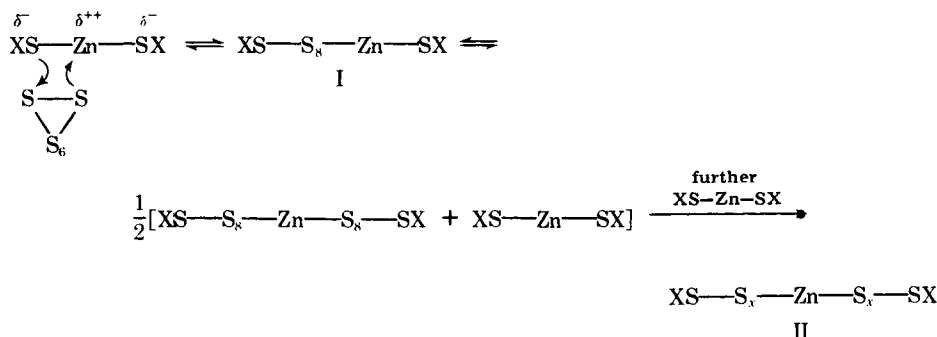
Fig. 6. Effect of TMTD on activation energy of vulcanization E. Mix formulation as in Fig. 1: (△) ZnDMDC; (○) ZnDEDC.

thiocarbamate (ZnDEDC) is shown in Figure 1. The maximum inhibition of vulcanization by TMTD was found at the molar ratio TMTD:ZnDADC = 1:2. This finding leads us to assume the formation of a complex of TMTD with ZnDADC, which functions as a prevulcanization inhibitor of ZnDADC-accelerated sulfur vulcanization.

In the absence of TMTD, ZnDADC reacts with sulfur to give the complex I, which, in a series of equilibrium reactions, forms the active sulfurating agent II^{12}:

$$\overset{\delta^-}{XS}-\overset{\delta^{++}}{Zn}-\overset{\delta^-}{SX} \rightleftharpoons XS-S_x-Zn-SX \rightleftharpoons$$

I

$$\frac{1}{2}[XS-S_x-Zn-S_x-SX + XS-Zn-SX] \xrightarrow{\text{further} \atop XS-Zn-SX}$$

$$XS-S_x-Zn-S_x-SX$$

II

where X represents $(alkyl)_2N-C(:S)-$. The active sulfurating agent II then reacts with rubber to yield a rubber-bound intermediate compound which then reacts further with the rubber macromolecules to yield crosslinks.

In the presence of TMTD, ZnDADC forms a complex with the latter rather than with the sulfur. That is why no crosslinking appears until the amount of original TMTD is consumed. There is no direct evidence for the existence of a TMTD–ZnDADC complex based on experimental methods. On the basis of molecular orbit calculations, the following model structure of the TMTD–ZnDADC complex has been investigated:
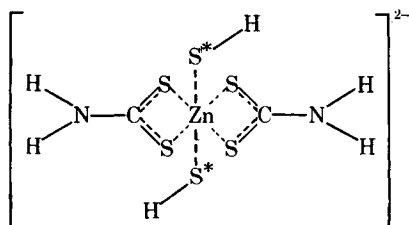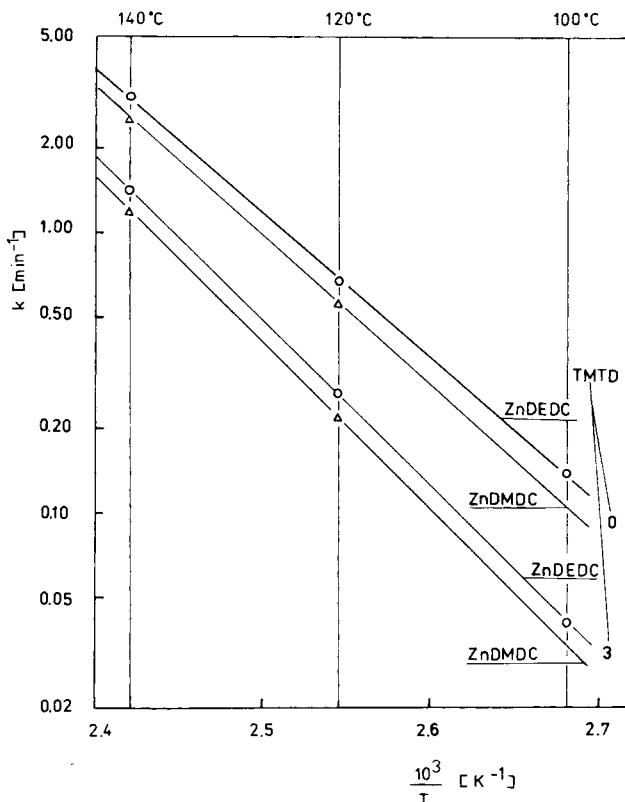
Fig. 7. Effect of TMTD on temperature dependence of rate constants of vulcanization k. Mix formulation as in Fig. 1. Numbers on lines are concentrations of TMTD in phr.

Analogous structures containing the atoms of magnesium or cadmium rather than the zinc atom have also been calculated.

The transition from the actual structure to the model was enforced by the limited working rate. We propose that the chosen model transmits the basic peculiarities of the complex formation with sufficient accuracy since the first coordination shell is calculated exactly and the influence of the farther shells on the central atom is not significant (it quenches sufficiently through two or three atoms).

The allocations of the electrons in the ρ bonds corresponding to the first coordination shell are as follows:

$$\rho(ZnS) = 0.06 \qquad\qquad \rho(ZnS^*) = 0.20$$
$$\rho(MgS) = -0.03 \qquad\qquad \rho(MgS^*) = 0.00$$
$$\rho(CdS) = 0.30 \qquad\qquad \rho(CdS^*) = 0.15$$

These results show that the zinc-containing complex is sufficiently stable; however, the Zn–S bonds are unstable. The complex compound with magnesium cannot exist. Since the Cd–S bond is very strong, the complex with cadmium cannot be an effective accelerator and/or a vulcanization agent.

The induction periods of vulcanization are increased simultaneously while increasing the Mooney scorch times by the addition of TMTD. The concentration dependences of the induction periods (Fig. 2) and rate constants of vulcanization (Fig. 3) do not show a maximum. The values of induction periods

increase and the rate constants decrease when the content of TMTD in the rubber mix is increased.

Differences between the courses of the concentration dependences of Mooney scorch times and those of the induction periods of vulcanization are in agreement with the effect of TMTD on the sulfur vulcanization of natural rubber.[13,14]

At concentrations of TMTD exceeding the molar ratio TMTD:ZnDADC = 1:2, TMTD functions not only as a prevulcanization inhibitor but also as an accelerator of sulfur vulcanization of natural rubber. Therefore, when increasing the concentration of TMTD in the rubber compound, the course of crosslinking approaches the course of sulfur cure accelerated by TMTD. The characteristic digressions pertain from the first-order rate law at lower extents of vulcanization.[13,14] These digressions (Fig. 4) explain why the dependences of the induction periods of vulcanization on the concentration of TMTD are not analogous to the concentration dependences of the scorch times.

The experimental results are supported by the concentration dependences of the extent of vulcanization as well as by the temperature dependences of the rate of vulcanization.

The ultimate extent of vulcanization expressed as a $M_{max} - M_{min}$ value increases throughout the range of TMTD concentrations used when the content of TMTD in the rubber mix is increased (Fig. 5).

The activation energies of vulcanization (Fig. 6), calculated from the temperature dependences of the rate constants of vulcanization (Fig. 7) increase with increasing concentration of TMTD in accordance with the finding[13,14] that the activation energy of TMTD-accelerated sulfur vulcanization is greater than that of ZnDADC-accelerated sulfur vulcanization.

The experimental results show that TMTD, unlike prevulcanization inhibitors, plays a significant role in all the stages of the ZnDADC-accelerated sulfur vulcanization of natural rubber.

References

1. L. Bateman, C. G. Moore, M. Porter, and B. Saville, in *Chemistry and Physics of Rubber-Like Substances*, L. Bateman, Ed., Wiley, New York, 1963, pp. 522–551.
2. B. A. Dogadkin, *Chemistry of Elastomers*, Khimiia, Moscow, 1972, p. 392.
3. V. Ducháček, *J. Appl. Polym. Sci.*, **16**, 3245 (1972); *Rubber Chem. Technol.*, **46**, 504 (1973).
4. V. Ducháček, *Angew. Makromol. Chem.*, **23**, 21, (1972).
5. W. E. Wolstenholme, *Rubber Chem. Technol.*, **38**, 777 (1965).
6. W. Scheele, *Rubber Chem. Technol.*, **34**, 1306 (1961).
7. R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
8. C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*, Benjamin, New York, 1964.
9. I. B. Bersuker, *Structure and Properties of Coordination Compounds*, Khimiia, Leningrad, 1971.
10. R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
11. A. B. Bolotin, R. Sh. Frenkel, A. O. Litinskii, and V. Ducháček, *Liet. Fiz. Rink.*, **16**, 671 (1976).
12. C. G. Moore, *Proceedings of the N.R.P.R.A. Jubilee Conference, Cambridge, 1964*, Maclaren, London, 1965, p. 189.
13. V. Ducháček and V. Brajko, *J. Appl. Polym. Sci.*, **18**, 2797 (1974).
14. V. Ducháček, *J. Appl. Polym. Sci.*, **22**, 227 (1978).