Effect of Zinc Oxide Concentration on the Course of Thiuram-Accelerated Sulfur Vulcanization

VRATISLAV DUCHÁČEK, *Department of Polymers, Institute of Chemical Technology, 166 28 Praha 6, Czechoslovakia*

Synopsis

Tetramethylthiuram disulfide-accelerated sulfur vulcanization of natural rubber has been investigated. Continuous measurements in a Vuremo curemeter at 145°C were used to estimate the effects of zinc oxide concentration on the induction periods, on the first-order rate constants, and on the ultimate extents of crosslinking, on the extents of degradation reaction (reversion), and on the extents of relaxation of vulcanizates at the cure temperature. The concentration of zinc oxide has practically no influence on the rate of thiuram-accelerated sulfur cure. The values of the ultimate extents of crosslinking increase with increasing the zinc oxide content in the rubber compound up to a certain limit corresponding to the theoretical amount of zinc oxide, which is necessary for the formation of zinc dimethyldithiocarbamate from tetramethylthiuram disulfide and zinc oxide during the vulcanization reaction. From the point of view of the reversion, however, this limit value of zinc oxide concentration is not sufficient. The relaxation measurements provide the same results. On the basis of these, for thiuram-accelerated sulfur vulcanizations, the optimum zinc oxide content in the rubber mix of 2.5 phr has been calculated. This value is in very good agreement with the optimum value of zinc oxide concentration found for both sulfenamides and thiazoles-accelerated sulfur cures.

INTRODUCTION

In a series of investigations, we have dealt[1-5] with the sulfur vulcanization of natural and styrene–butadiene rubbers accelerated with tetramethylthiuram disulfide (TMTD) in the presence of the excess of zinc oxide. The main features previously established are as follows:

The cure rates increase with increasing TMTD concentration, the sulfur content being kept constant, up to a TMTD:S weight ratio of 2:1. Beyond this value, the cure rates again decrease. This TMTD:S ratio corresponds to 3.8 gram-atoms of sulfur per mole TMTD, and it is in good agreement with findings of Scheele and Franck[6] that in TMTD-accelerated sulfur vulcanization systems the peak value of zinc dimethyldithiocarbamate (ZnDMDC) formation reaches an endvalue when the stocks contain 4 gram-atoms of sulfur per mole TMTD. These facts lead us to suppose that ZnDMDC is the acutal accelerator in TMTD-accelerated sulfur systems.

Support for this view derives from our experiments with model curing systems as well as from our studies of the effects of a flame-process silica (Aerosil),[1,2] of stearic acid,[3] and of the cure temperature[5] on the thiuram-accelerated sulfur vulcanization.

TABLE I
Mix Formulation of the Rubber Compounds[a]

Natural rubber (pale crepe)	Zinc oxide	TMTD	Sulfur
100	from 0 to 5	4.0	0.5
100	from 0 to 5	4.0	1.0
100	from 0 to 5	4.0	1.5
100	from 0 to 5	4.0	2.0
100	from 0 to 5	3.0	1.0
100	from 0 to 5	2.0	1.0
100	from 0 to 5	1.0	1.0

[a] In parts by weight.

The present work is the sixth contribution in this field. It is concerned with the influence of the zinc oxide concentration on the course of TMTD-accelerated sulfur vulcanization of natural rubber.

EXPERIMENTAL

Compounding

The mix formulation is given in Table I. Mixing was by masterbatch technique on a laboratory mill with 400 × 130 mm rolls at 50°C. Mooney viscosity of natural rubber compounds was 10 °ML(1 + 4) at 100°C. This, according to Wolstenholme,[7] is equivalent to a number-average molecular weight of 1.2×10^5.
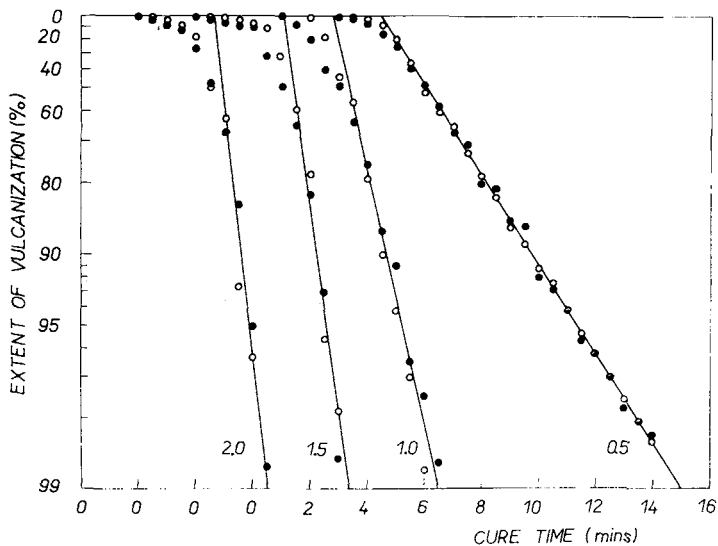

Fig. 1. Increase of extent of TMTD-accelerated sulfur vulcanization according to first order in natural rubber at 145°C. Mix formulation: natural rubber (pale crepe), 100; TMTD, 4; zinc oxide, 0 (O) and 5 (●); sulfur, variable. Numbers on the lines are concentrations of sulfur in phr.

Curemeter Measurements

The rubber compounds were cured at 145°C on a VUREMO curemeter, an instrument used to measure VUlcanization, RElaxation, and MOdulus. The apparatus and curemeter measurements have been completely described in our recent publication.[8]

The extent of vulcanization at any time t (modulus), M, was expressed in VUREMO units (torque) and plotted against time of cure, τ. Thus, the cure curves were obtained. The ultimate extent of vulcanization reaction was calculated as a $(M_{max} - M_{min})$ value. The cure curves have been analyzed by treating them as first-order reactions, following an induction period t_i:

$$M = (M_{max} - M_{min})(1 - e^{-kt}) + M_{min}$$

where k is the first-order rate constant and $t = (\tau - t_i)$. The evidence for the proposed reaction order $n = 1$ is given in Figures 1 and 2, where the logarithm of the relative extent of vulcanization, $(M_{max} - M)/(M_{max} - M_{min})$, is plotted against cure time.

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 curemeter.[8]

The extent of degradation reaction (reversion) was measured after 60 min of cure, and its value was expressed in per cent of the ultimate extent of vulcanization.

The extent of relaxation was measured in the first experimental point of the cure curve corresponding to the maximum modulus (extent of vulcanization) after 10 sec of relaxation. Its value was also expressed in per cent.
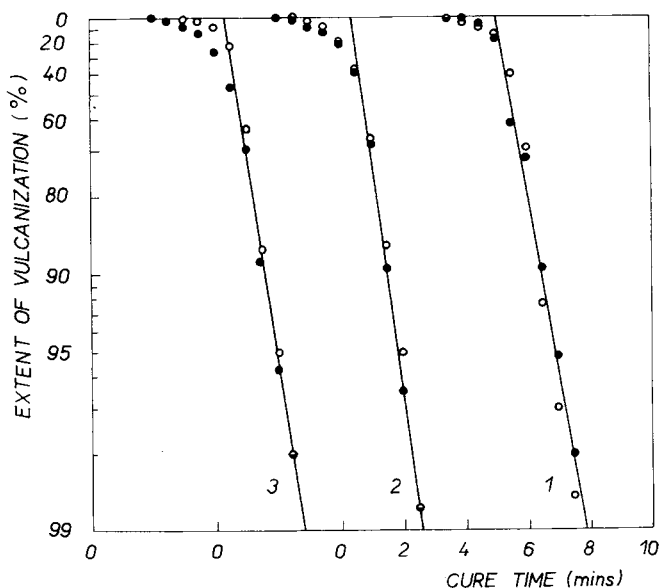

Fig. 2. Increase of extent of TMTD-accelerated sulfur vulcanization according to first order in natural rubber at 145°C. Mix formulation: natural rubber (pale crepe), 100; sulfur, 1; zinc oxide, 0 (O) and 5 (●); TMTD, variable. Numbers on the lines are concentrations of TMTD in phr.

TABLE II

Average Values of Induction Periods t_i and of
First-Order Rate Constants k in Vulcanizations of Natural Rubber
at 145°C in the Presence of Different Amounts of Zinc Oxide (from 0 to 5 phr)

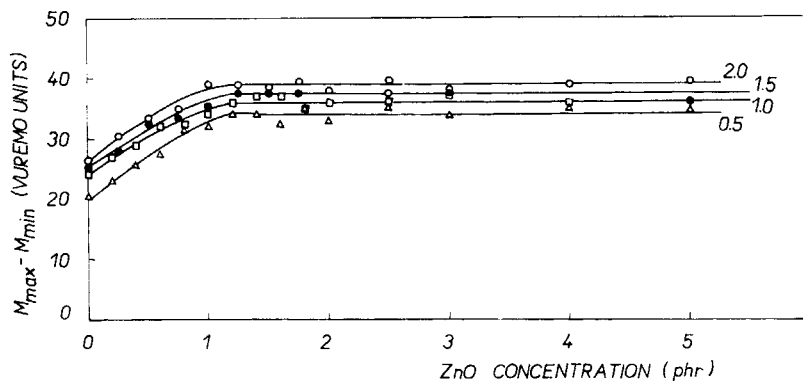| TMTD content, phr	Sulfur content, phr	t_i, min	k, min^{-1}
4.0	0.5	3.5 ± 0.5	0.451 ± 0.03
4.0	1.0	3.8 ± 0.5	1.36 ± 0.1
4.0	1.5	4.0 ± 0.3	1.72 ± 0.3
4.0	2.0	3.7 ± 0.4	2.79 ± 0.3
3.0	1.0	3.6 ± 0.4	1.82 ± 0.3
2.0	1.0	3.6 ± 0.4	2.08 ± 0.3
1.0	1.0	4.0 ± 0.4	1.59 ± 0.2

Fig. 3. Effect of sulfur content in rubber mix on the dependence of the ultimate extent of vulcanization, $(M_{max} - M_{min})$, at 145°C on zinc oxide concentration. Mix formulation: natural rubber (pale crepe), 100; TMTD, 4; sulfur, variable; zinc oxide, variable. Numbers on the curves are concentrations of sulfur in phr.
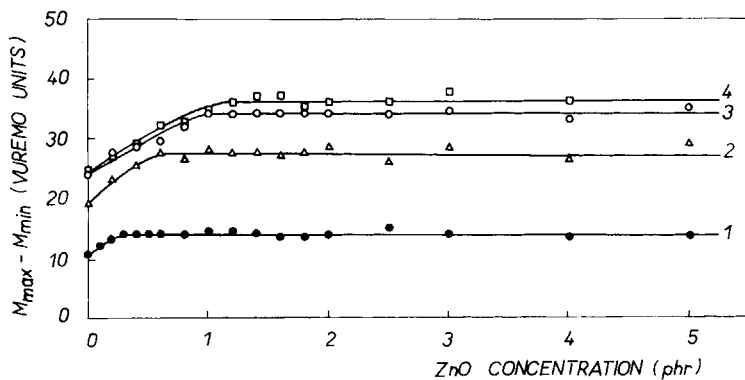

Fig. 4. Effect of TMTD content in rubber mix on the dependence of the ultimate extent of vulcanization, $(M_{max} - M_{min})$, at 145°C on zinc oxide concentration. Mix formulation: natural rubber (pale crepe), 100; sulfur, 1; TMTD, variable; zinc oxide, variable. Numbers on the curves are concentrations of TMTD in phr.

TABLE III
Comparison of Limit Values of Zinc Oxide Concentration Corresponding to Maximum
Extents of Vulcanization with Theoretical Amounts of Zinc Oxide Necessary for
Formation of ZnDMDC from TMTD in TMTD-Accelerated Sulfur Cures
of Natural Rubber

TMTD, content, phr	Sulfur content, phr	Number of gram-atoms of sulfur per mole TMTD	Conversion of TMTD on ZnDMDC according to Scheele and Franck,[6] %	Theoretical amount of zinc oxide, phr	Experimental limit value of zinc oxide concentration, phr
4.0	0.5	0.94	84	1.14	1.2
4.0	1.0	1.87	89	1.18	1.2
4.0	1.5	2.81	93	1.25	1.25
4.0	2.0	3.75	92	1.24	1.25
3.0	1.0	2.50	91	0.92	1.0
2.0	1.0	3.75	92	0.62	0.6
1.0	1.0	7.50	93	0.32	0.3

RESULTS AND DISCUSSION

In order to gain a general view of the conditions existing in the sulfur cure accelerated with TMTD, we investigated the effect of zinc oxide concentration on the course of the vulcanization (a) at constant TMTD content (4 phr) with increasing amounts of sulfur (from 0.5 to 2.0 phr) and (b) at constant sulfur content (1.0 phr) with increasing amounts of TMTD (from 1.0 to 4.0 phr).

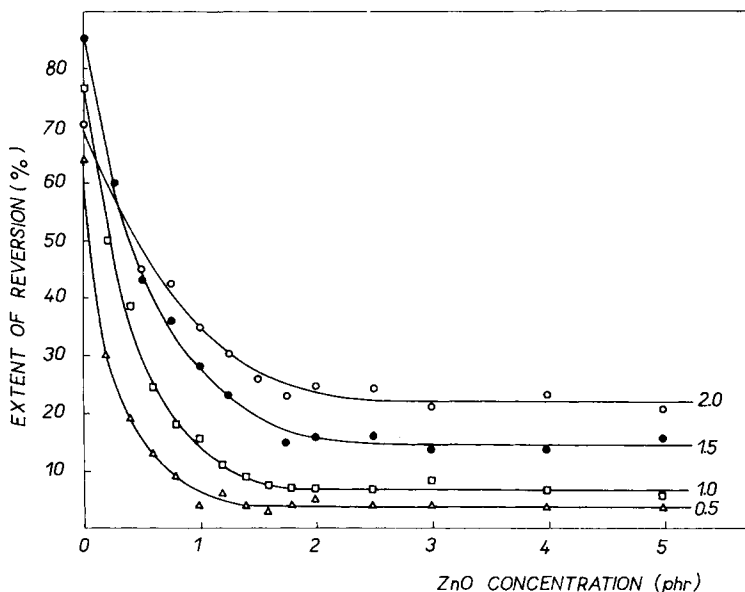Figures 1 and 2 show that the concentration of zinc oxide in the compound

Fig. 5. Effect of sulfur content in rubber mix on the dependence of the extent of reversion at 145°C on zinc oxide concentration. Mix formulation as in Fig. 3. Numbers on the curves are concentrations of sulfur in phr.

of natural rubber has practically no influence on the rate of TMTD-accelerated sulfur cure. In Table II are assembled the average values of the induction periods and these of the rate constants of the vulcanization reaction when cure takes place in the absence and in the presence of different amounts of zinc oxide in the range of its content in the rubber mix from 0 to 5 phr. The values of these kinetic parameters are in a good accordance with our experimental results published recently.[1]
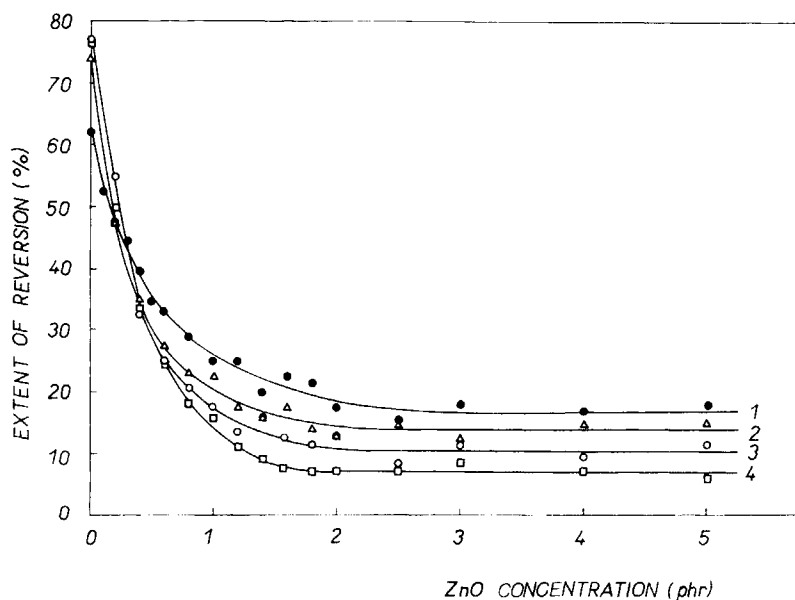

Fig. 6. Effect of TMTD content in rubber mix on the dependence of the extent of reversion at 145°C on zinc oxide concentration. Mix formulations as in Fig. 4. Numbers on the curves are concentrations of TMTD in phr.
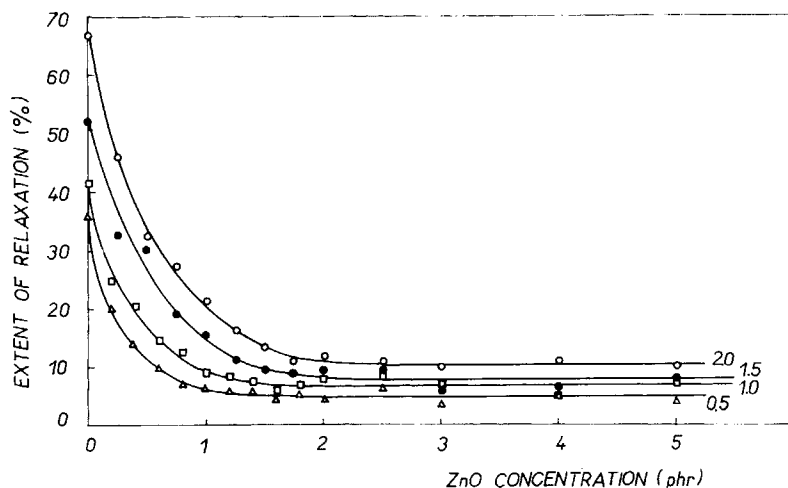

Fig. 7. Effect of sulfur content in rubber mix on the dependence of the extent of relaxation at 145°C on zinc oxide concentration. Mix formulation as in Fig. 3. Numbers on the curves are concentrations of sulfur in phr.

Essential changes appear, however, in the values of the ultimate extents of vulcanization. As it is shown in Figures 3 and 4, these are increased with increasing the zinc oxide concentration up to a certain limit. Table III shows that the limit value of the zinc oxide content in the rubber compound corresponds exactly to the theoretical amount of zinc oxide which is necessary for the formation of ZnDMDC from TMTD according to the findings of Scheele and Franck.[6]

On the basis of these results, one is inclined to believe that the optimum concentration of zinc oxide is directly proportional to the TMTD content and that at the constant concentration of TMTD it is practically independent on the amount of sulfur in the rubber stock.

From the point of view of the thermal stability of the vulcanizate network, however, the above discussed limit values of zinc oxide content in the rubber mix are not sufficient. The dependences of the extents of degradation reaction (reversion) on the concentration of zinc oxide at different levels of both TMTD and sulfur (Figs. 5 and 6) show clearly that the optimum value of zinc oxide content lies in the range of concentrations from 1.5 to 2.5 phr. There is a dependence on TMTD and sulfur contents in the rubber compound.

The relaxation measurements shown in Figures 7 and 8 provide the same results. The values of the extents of relaxation, which are in a correlation with the polysulfide crosslinks content in the vulcanizate network,[9,10] decrease with increasing the zinc oxide concentration analogically as these of the extents of degradation.

CONCLUSIONS

The experimental results presented above show that in the case of thiuram-accelerated sulfur vulcanization, the optimum zinc oxide content in the
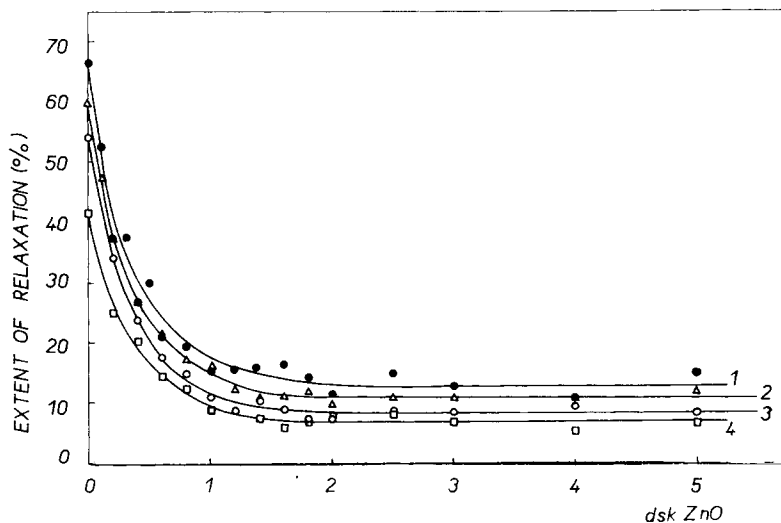

Fig. 8. Effect of TMTD content in rubber mix on the dependence of the extent of relaxation at 145°C on zinc oxide concentration. Mix formulation as in Fig. 4. Numbers on the curves are concentrations of TMTD in phr.

rubber mix corresponds generally to the value of 2.5 phr. This is in very good agreement with the optimum values of zinc oxide concentration found by Brajko[11] for both sulfenamides- and thiazole-accelerated sulfur cures.

References

1. V. Duchácek, *J. Appl. Polym. Sci.*, **18,** 125 (1974).
2. V. Duchácek and V. Brajko, *J. Appl. Polym. Sci.*, **18,** 2797 (1974).
3. V. Duchácek, Scientific Papers of Prague Institute of Chemical Technology, in press.
4. V. Duchácek, *J. Appl. Polym. Sci.*, **19,** 645 (1975).
5. V. Duchácek, *J. Appl. Polym. Sci.*, **19,** 1617 (1975).
6. W. Scheele and A. Franck, Kaut. *Gummi,* **11,** WT 51 (1958); *Rubber Chem. Technol.,* **32,** 139 (1959).
7. W. E. Wolstenholme, *Rubber Chem. Technol.,* **38,** 777 (1965).
8. V. Duchácek, *J. Appl. Polym. Sci.,* **15,** 2079 (1971); *Rubber Chem. Technol.,* **45,** 945 (1972).
9. A. Y. Coran, *Rubber Chem. Technol.,* **37,** 643 (1964).
10. V. Duchácek, *Chem. Prum.,* **22,** 178 (1972).
11. V. Brajko, Rubber Bulletin, Rubber and Plastics Research Institute (Gottwaldov, Czechoslovakia) Press, August 1970.