

Kinetics of Thiuram-Accelerated Sulfur Vulcanization

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Synopsis

On the basis of continuous measurements in a Vuremo curemeter at 145°C, kinetics of tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization of natural rubber has been investigated. It was found that 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 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 actual accelerator in TMTD-accelerated sulfur systems. Support for this view derives from our experiments with model curing systems as well as from the generally known practical experience that dithiocarbamates are faster accelerators than thiuram disulfides. For the reasons described above and for the finding that the dependences of the ultimate extent of vulcanization (network chain density) on the concentration of TMTD in the absence and in the presence of elemental sulfur are analogous, the mechanism of thiuram-accelerated sulfur vulcanization is very probably similar to that of sulfur-free thiuram vulcanization.

INTRODUCTION

In a series of investigations, we have dealt¹⁻⁷ with the vulcanization of natural rubber and some synthetic rubbers by thiuram disulfides in the presence of zinc oxide and in the absence of elemental sulfur. This we have called "sulfur-free thiuram vulcanization."

It is our understanding that it is highly important in practical applications to have quantitative knowledge of the crosslinking phenomenon itself, as well as the rates of the individual reaction steps that are to be used for calculations of any kind. Therefore, we have scrutinized particularly the kinetics of vulcanization¹⁻⁵ but have hoped that, at the same time, the collected data would contribute toward the elucidation of the reaction mechanism.^{6,7}

It is advisable to distinguish sulfur-free thiuram vulcanization from sulfur vulcanization accelerated by thiuram compounds. In this paper, we present experimental results which render possible an orientation in the field of sulfur vulcanization accelerated by tetramethylthiuram disulfide (TMTD) in the presence of zinc oxide.

EXPERIMENTAL

Compounding

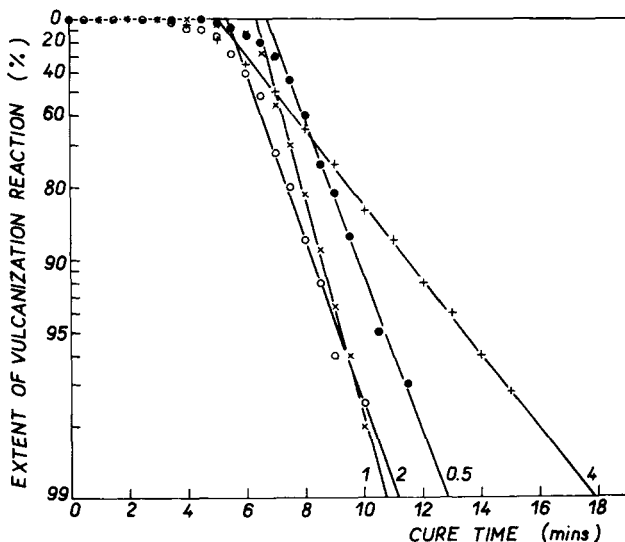
The mix formulation was natural rubber (pale crepe), 100 parts; zinc oxide, 5 phr; sulfur, tetramethylthiuram disulfide, and zinc dimethyldithiocarbamate, variable.

Mixing was by master batch technique on a laboratory mill with 400×130 mm rolls at 50°C . Mooney viscosity of rubber compounds was 10° ML (1 + 4) at 100°C . This, according to Wolstenholme,⁸ is equivalent to a number-average molecular weight of 1.2×10^5 .

Measurement of Induction Periods and Rate Constants of Vulcanization

The rubber compounds were cured at 145°C on a Vuremo curemeter, Type AC-01 (exported by Metrimpex, Budapest, Hungary). The apparatus and curemeter measurements have been fully described in another publication.⁵

The extent of vulcanization was expressed in Vuremo units (torque) and plotted against time of cure. Thus, the cure curves were obtained. The induction period t_i and the rate constant k of the vulcanization were calculated in accordance with the method of Scheele⁹ proposing the first-order reaction from the linearized cure curves, where the logarithm of the extent of vulcanization is plotted against cure time (see Fig. 1).



(a)

Fig. 1. (continued)

Measurement of Network Chain Density

The ultimate extent of the vulcanization reaction was expressed as the network chain density ν , in moles/cm³. The time schedule for mixing, curing, swelling, and deswelling was standardized as far as possible.⁵

The swollen and deswollen weights were used to calculate the volume fraction of rubber, v_r , in the network swollen to equilibrium. For calculation of the network chain density, the Flory-Rehner equation¹⁰ was used, with the effective value of the natural rubber-toluene interaction parameter of 0.39 published by Meissner and Janáček.¹¹

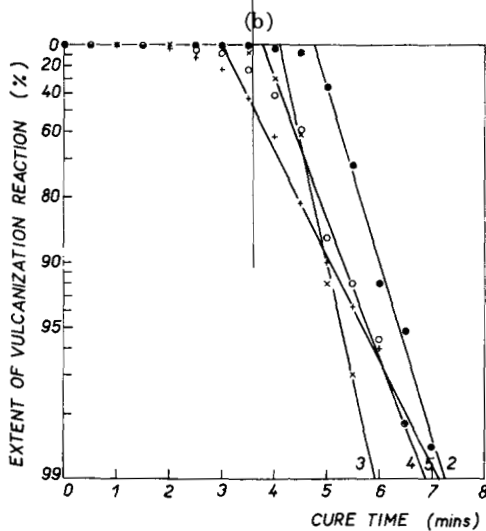
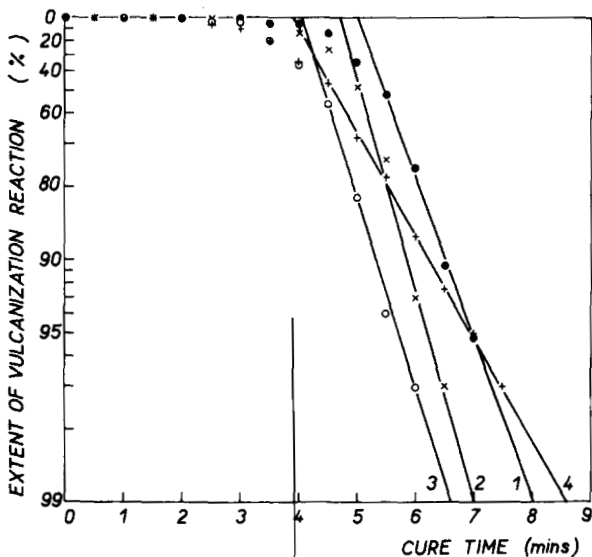
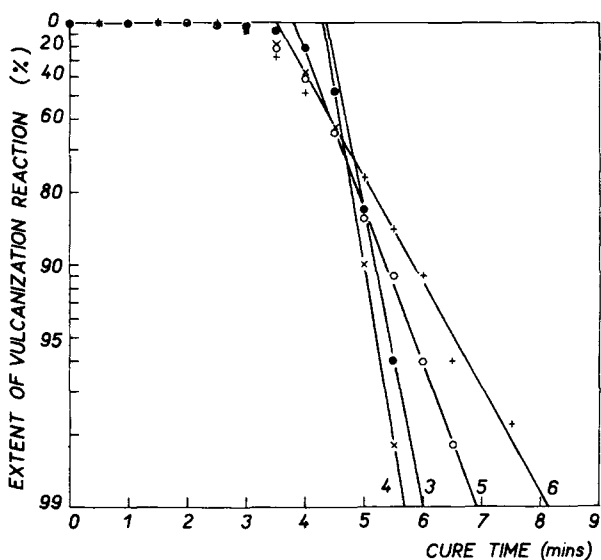


Fig. 1. (continued)



(d)

Fig. 1. Increase of extent of vulcanization at 145°C as first-order reactions in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (TMTD). Mix formulation: pale crepe, 100; zinc oxide, 5; TMTD, variable; sulfur, (a) 0.5; (b) 1.0; (c) 1.5; (d) 2.0. Numbers on lines are the concentrations of TMTD in phr.

RESULTS AND DISCUSSION

It is well known that sulfur cures accelerated by thiuram disulfides are faster than sulfur-free thiuram vulcanization. However, it might be asked whether the rate of cure can be increased at will and whether it is increased at all if, what would seem quite obvious, the concentration of the thiuram disulfide as accelerator is increased in the stock while the sulfur concentration is kept constant. This question is answered by a kinetic interpretation of the results.

In Figure 1, we plotted the extent of crosslinking as of first order. The maximum values of the extent of vulcanization for the individual TMTD:S ratios were taken as 100. It can be seen in this manner that the conversions fall on straight lines, thus satisfying the first-order rate law for all TMTD and sulfur concentrations.

From Figure 1 it can, furthermore, be seen that the slopes of the curves increase with increasing TMTD concentration; in other words, the rates of crosslinking increase with increasing TMTD content. This process, however, is limited. Maximum values of the rate constants of vulcanization were found when the stocks contain 1, 2, 3, and 4 phr of TMTD per 0.5, 1.0, 1.5, and 2.0 phr of sulfur, respectively. With higher TMTD:S ratio, the values of the rate constants of vulcanization again decrease. Figure 2 shows these features better.

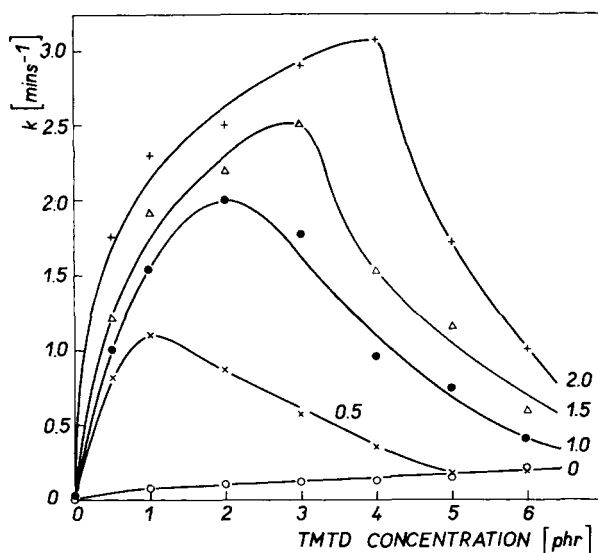


Fig. 2. Influence of TMTD concentration on rate constant of vulcanization, k , and the effect of sulfur (at 145°C). Mix formulation: pale crepe, 100; zinc oxide, 5; sulfur, variable; TMTD, variable. Numbers on curves are the concentrations of sulfur in phr.

It is quite evident that the acceleration of vulcanization is not dependent on the absolute amount of TMTD, but is determined rather by the TMTD:S ratio. Thus, it will be generally impossible to increase the cure rate by merely increasing the concentration of TMTD at a given sulfur concentration. If this is done, it is possible that just the opposite result is obtained; however, the cure rate increases if at a constant TMTD content the sulfur concentration is increased, and it reaches its peak value if 1 g sulfur is present per 2 g TMTD.

The optimum TMTD:S weight ratio 2:1 (i.e., 3.8 gram atoms of sulfur per mole TMTD) is in good accord with the findings of Scheele and Franck¹² that in thiuram-accelerated sulfur systems the peak value of zinc dithiocarbamate formation reaches an endvalue (of about 90 mole-% based on the amount of original thiuram disulfide) when the stocks contain 4 gram atoms of sulfur per mole thiuram disulfide. These facts lead us to assume that zinc dimethyldithiocarbamate (ZnDMDC) is the actual accelerator in TMTD accelerated sulfur systems.

Support for this view derives from the kinetic analysis of model rubber compounds which contain only 10% of original TMTD and ZnDMDC in the concentration, corresponding to 90 mole-% of the amount of TMTD originally present. Table I shows the results. The rate constants of the first-order vulcanization reaction of model compounds are practically the same as those of TMTD-accelerated compounds. The delay in the induction periods of the latter is attributable to the formation of ZnDMDC by the reaction of TMTD with zinc oxide. That is why the values of the

TABLE I
Kinetic Parameters of TMTD- and ZnDMDC-Accelerated Sulfur
Vulcanization of Natural Rubber at 145°C

Mix formulation, weight parts					Kinetic parameters	
Pale crepe	Zinc oxide	TMTD	Sulfur	ZnDMDC	t_i , min	k , min ⁻¹
100	5	1.0	0.5	—	5.4	1.10
100	5	0.1	0.5	1.15	2.3	1.27
100	5	2.0	1.0	—	3.7	2.00
100	5	0.2	1.0	2.30	2.4	2.09
100	5	3.0	1.5	—	3.1	2.50
100	5	0.3	1.5	3.45	2.4	2.55
100	5	4.0	2.0	—	3.3	3.07
100	5	0.4	2.0	4.60	2.3	3.29

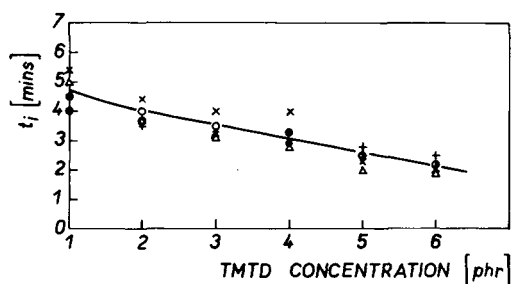


Fig. 3. Influence of TMTD concentration on induction period of vulcanization, t_i , in the absence and presence of sulfur (at 145°C). Mix formulation as in Fig. 2.

induction periods are independent of the sulfur concentration. This is shown in Figure 3.

This explanation of our experimental results is also in accordance with the generally known practical experience that dithiocarbamates are faster accelerators than thiuram disulfides.

Our speculation is in accord with the one of Bevilacqua¹³ based on stress-strain and chemical evaluations of natural rubber-TMTD-zinc oxide system that the rate of disappearance of TMTD is faster than the rate of appearance of ZnDMDC and of crosslinks, but the latter two are closely related. The second conclusion was previously reached by Scheele and co-workers⁹ based on estimation of crosslinks by swelling.

All the presented results, in accord with the views of Scheele,^{9,12} give the impression that the thiuram-accelerated sulfur vulcanization as well as sulfur-free thiuram vulcanization⁶ are based on a reaction of thiuram disulfide with zinc oxide, in which rubbers are involved by crosslinking. Figure 4 shows that the dependences of the ultimate extent of vulcanization (network chain density) on the concentration of TMTD in the absence and in the presence of different amounts of elemental sulfur (from 0.5 to 2.0 phr) are analogous.

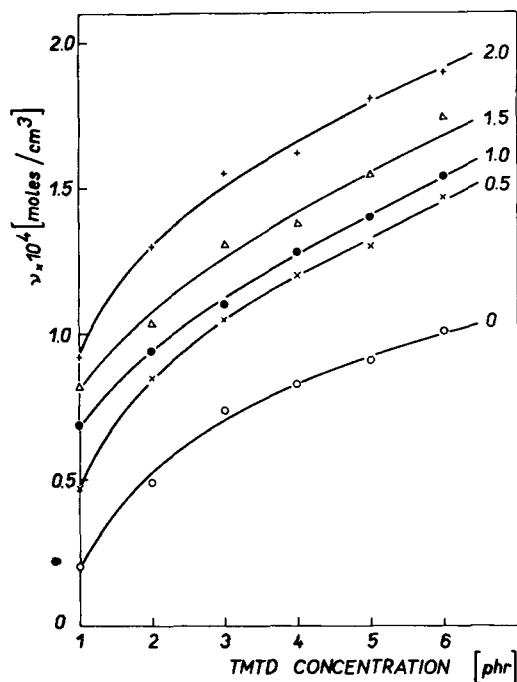


Fig. 4. Influence of TMTD concentration on ultimate extent of vulcanization, ν , and the effect of sulfur (at 145°C). Mix formulation as in Fig. 2. Numbers on curves are the concentrations of sulfur in phr.

CONCLUSIONS

Although the mechanism of accelerated sulfur vulcanization has been extensively studied, it is still not clear whether the process involves radical intermediates, ions, or a combination of both. Most workers have proposed a radical mechanism,^{9,14-17} whereas others^{18,19} have proposed a mechanism involving both free-radical and ionic intermediates. Bateman et al.^{20,21} have proposed an ionic mechanism. Recently, Manik and Banerjee^{22,23} have again proposed a mechanism involving both free-radical and ionic species.

For the reasons described above, the mechanism of thiuram-accelerated sulfur vulcanization is very probably similar to that of sulfur-free thiuram vulcanization.⁶ In the initial steps of the vulcanization (formation of ZnDMDC from TMTD and zinc oxide, and its reaction with elemental sulfur leading to the sulfurating complexes which react with rubber to give rubber-bound intermediate compound), mainly ionic reactions take place. In the next steps of the vulcanization (conversion of the sulfurated rubber-bound intermediate compound into the crosslinks), mainly radical reactions take place.

Dedicated to Professor Dr. Ivan Franta on the occasion of his 70th birthday.

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