

Effect of Aerosil on the Course of Thiuram Accelerated Sulfur Vulcanization

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Synopsis

Tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization of natural rubber has been investigated at temperatures from 100°C to 145°C. Continuous measurements in a Vuremo curemeter were used to estimate the extent of crosslinking, which was plotted against cure time. The cure curves as well as their linearized forms (dependences of the logarithm of the extent of vulcanization on the cure time) clearly show that at lower cure temperatures the course of the vulcanization differs significantly from the first-order rate law. These digressions have been removed by the addition of a highly dispersed silica gel, Aerosil, which simultaneously speeds up the course of the vulcanization up to the value corresponding to the rate of zinc dimethyldithiocarbamate (ZnDMDC)-accelerated sulfur vulcanization. These results are in accordance with our recent theory supposing that ZnDMDC is the actual accelerator in TMTD-accelerated sulfur systems. In the presence of Aerosil, the formation of ZnDMDC from TMTD is catalyzed via dispersed silica gel. Support for this view derives from the temperature dependences of vulcanization reactions. The activation energies of TMTD-accelerated sulfur vulcanizations in the absence (31 kcal/mole) and in the presence of Aerosil (23.5 kcal/mole) correspond exactly to the values calculated from the rate constants of the thiuram decrease in TMTD-accelerated vulcanization (30 kcal/mole) and from the rate constants of crosslinking in the dithiocarbamate-accelerated sulfur vulcanization (23 kcal/mole), respectively.

INTRODUCTION

The investigations¹ we have made concerning the kinetics of the thiuram-accelerated sulfur vulcanization were aimed at explaining the mechanism and providing quantitative information for practical considerations, so as to evaluate the chemical processes involved in vulcanization. Such being the goals, it was only natural that we study first of all the kinetics of vulcanization reactions occurring in the absence of all additives which are not absolutely necessary.

Our work had progressed to the point where we could also begin to consider vulcanizations in the presence of fillers important for practical vulcanizates. We began this series with an investigation of the kinetics of such vulcanizations in the presence of a highly dispersed silica gel, Aerosil, for it functions not only as an active filler but, according to Scheele and co-

workers,² in thiuram cures also as a catalyst of the reaction leading to the formation of dithiocarbamates from thiuram disulfides.

Numerous publications have appeared concerning both the experimental and theoretical aspects of the interaction between filler surface and polymer, and it would be impossible to comment here even on the better contributions. Besides, it is not imperative that they be discussed at this point, since the present work is concerned with what we consider to be the more neglected features, namely, the influence of the filler on the course of the vulcanization.

EXPERIMENTAL

In order to preserve the continuity of our quantitative studies of thiuram-accelerated sulfur vulcanization,¹ we continued to use natural rubber (pale crepe).

The mix formulation was pale crepe, 100 parts; zinc oxide, 5 phr; sulfur, 2 phr; tetramethylthiuram disulfide, zinc dimethyldithiocarbamate, and Degussa Aerosil 200 (silica gel), variable.

Mixing, measurement of the course of the vulcanization in a Vuremo curemeter, as well as calculations of the rate constants of vulcanization and activation energies have been described in our recent publications.^{1,3}

RESULTS AND DISCUSSION

The results of our kinetic study¹ of the thiuram-accelerated sulfur vulcanization at 145°C give the impression that crosslinking is a first-order reaction. However, Figure 1 shows that at lower cure temperature (e.g., 125°C), the course of the vulcanization differs significantly from the first-order rate law. Figure 2 shows these features better. In this figure, we plotted the extent of crosslinking as of first order. The maximum values of crosslinking have been taken as 100. It can be seen in this manner that

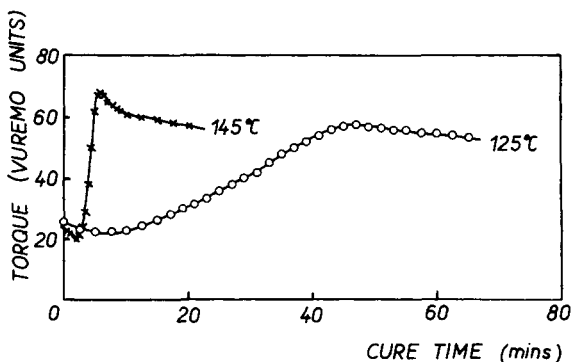


Fig. 1. Effect of cure temperature on shape of cure curve in sulfur vulcanization of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation: natural rubber (pale crepe), 100; zinc oxide, 5; sulfur, 2; TMD, 4 (phr).

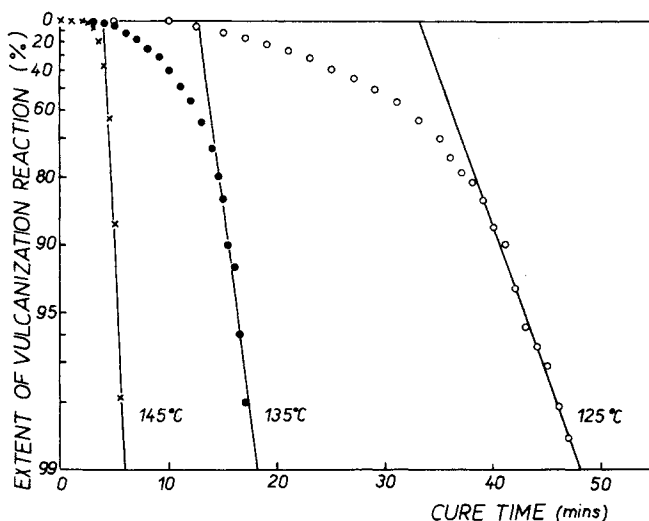


Fig. 2. Increase of extent of vulcanization at 145°C, 135°C, and 125°C as first-order reaction in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation as in Fig. 1.

at 145°C the conversions fall on a straight line, thus satisfying the first-order rate law; but at 135°C and 125°C, the experimental points lie on the straight lines from 70% and 80% conversion only, respectively.

The digressions of the course of the vulcanization from first-order law, which can be seen at lower cure temperatures, are in accordance with our proposed theory¹ supposing that zinc dimethyldithiocarbamate (ZnDMDC) arising during the vulcanization reaction from tetramethylthiuram disulfide (TMTD) and zinc oxide is the actual accelerator in TMTD-accelerated sulfur systems. Provided that our theory is correct, the compounds speeding up the formation of ZnDMDC from TMTD would not only speed up the course of the vulcanization, but simultaneously they would also remove the deviation from first-order rate law.

Support for this view derives from the effect of Aerosil on the course of the vulcanization shown in Figure 3. According to Scheele and co-workers,² when Aerosil is introduced in the sulfur-free thiuram rubber mix, the rate constants for thiuram disappearance and dithiocarbamate formation are greater than in the absence of Aerosil, for it takes place in a heterogenous catalysis of the conversion of TMTD on ZnDMDC via dispersed silica gel.

The catalysis of a chemical reaction is usually accompanied by a diminution in the energy of activation. In Table I shows the rate constants of vulcanization in the absence and in the presence of Aerosil in the cure temperature range from 100°C to 145°C. A logarithmic plot of the rate constants of vulcanization versus reciprocal absolute temperature gives, however, straight lines (Fig. 4), demonstrating the phenomenal rise in rate constants and allowing calculation, from the slopes, of the activation energies.

TABLE I
First-Order Rate Constants of Vulcanization k
and Activation Energies E in the Cure of Natural Rubber^a

Cure temperature, °C	$x = 0$	$x = 2.5$	$x = 5$	$x = 10$	$x = 20$	$x = 30$
	k, min^{-1}					
100	—	—	0.072	0.085	0.100	0.085
105	0.035	0.068	0.096	0.154	0.177	0.209
110	0.079	0.121	0.164	0.256	0.270	0.252
115	0.121	0.207	0.247	0.331	0.371	0.371
120	0.211	0.250	0.343	0.523	0.622	0.548
125	0.315	0.365	0.418	0.719	0.920	0.822
130	0.479	0.476	0.885	1.09	1.21	1.24
135	0.958	0.719	1.10	1.44	2.10	1.92
140	1.04	1.10	1.64	2.09	2.56	2.88
145	3.07	1.32	2.00	3.05	—	—
	$E, \text{kcal/mole}$					
	31.1	21.7	24.0	22.2	24.7	24.7
	average 23.5					

With 2.0 phr sulfur accelerated by 4.0 phr TMTD in the presence of 5 phr zinc oxide and x phr Aerosil.

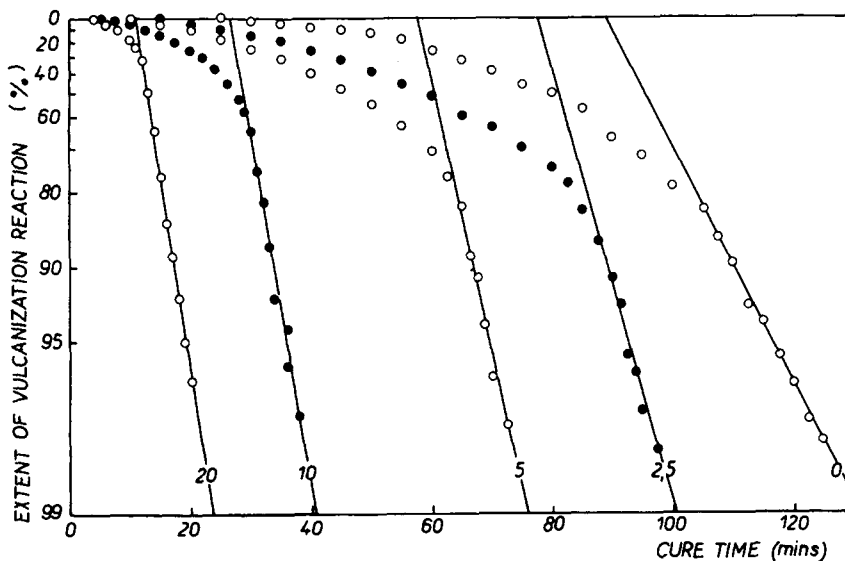


Fig. 3. Effect of Aerosil on increase of extent of vulcanization at 115°C as first-order reaction in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation: natural rubber (pale crepe), 100; zinc oxide, 5; sulfur, 2; TMTD, 4; Aerosil, variable. Numbers on the lines are concentrations of Aerosil in phr.

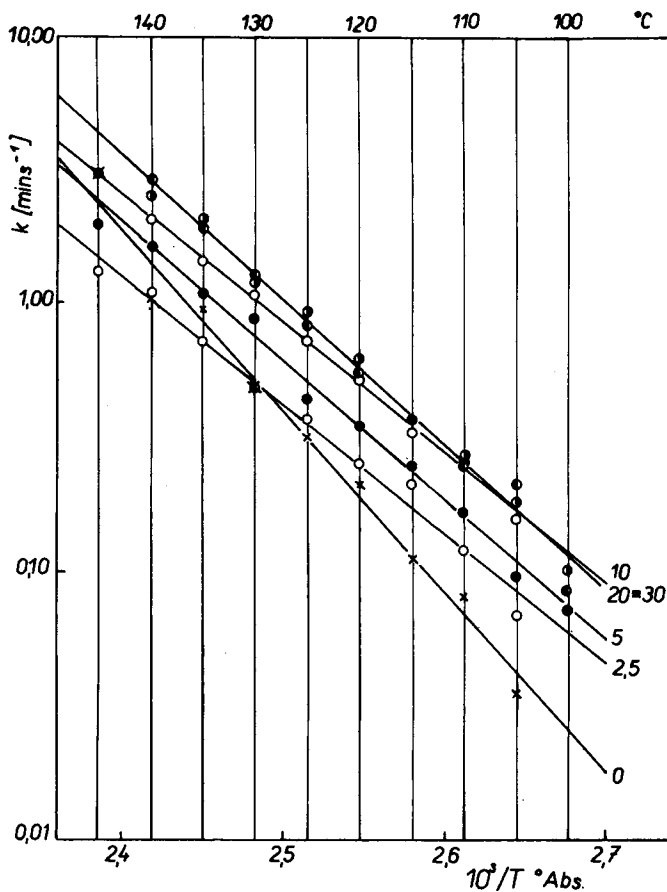


Fig. 4. Effect of Aerosil on temperature dependence of rate constants of vulcanization k in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation as in Fig. 3. Numbers on lines are concentrations of Aerosil in phr.

On the one hand, the value of the activation energy of the vulcanization in the absence of Aerosil (31 kcal/mole) is in very good accordance with that for the thiuram decrease (30 kcal/mole) published for the TMTD-accelerated sulfur cure of natural rubber by Scheele and Franck.⁴ On the other hand, the average value of the activation energy of vulcanization in the presence of Aerosil (23.5 kcal/mole) is practically identical with the activation energy published for the dithiocarbamate-accelerated sulfur vulcanization (23.0 kcal/mole) by Gordon.^{5,6}

All these results endorse our proposition¹ that ZnDMDC is the actual accelerator in TMTD-accelerated sulfur cures. The next support for this view derives from the measurements of the rate constants of vulcanization of the model rubber compounds which contain merely 10% original TMTD and ZnDMDC at a concentration of 90 mole-% based on the amount of TMTD originally present. Table II shows the result. The rate con-

TABLE II
First-Order Rate Constants of Vulcanization k
and Activation Energies E in the Cure of Natural Rubber^a

Cure temperature, °C	$x = 0$	$x = 20$
	k, min^{-1}	
100	0.105	0.109
105	0.144	0.159
110	0.286	0.307
115	0.460	0.390
120	0.536	0.575
125	0.766	0.793
130	1.00	1.10
135	1.92	1.77
140	2.50	2.60
145	3.29	3.68
	$E, \text{kcal/mole}$	
	23.1	23.1

^a With 2.0 phr sulfur accelerated by 0.4 phr TMTD and 4.6 phr ZnDMDC in the presence of 5 phr Zinc oxide and x phr Aerosil.

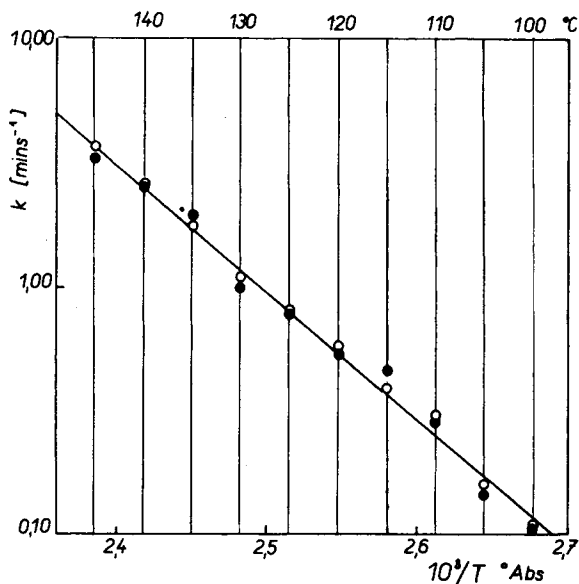


Fig. 5. Temperature dependence of rate constants of vulcanization k in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide and zinc dimethyldithiocarbamate in the absence (●) and presence (○) of 20 phr Aerosil. Mix formulation: natural rubber (pale crepe), 100; zinc oxide, 5; sulfur, 2; TMTD, 0.4; ZnDMDC, 4.6; Aerosil, 0 and 20 (phr).

stants of first-order vulcanization reaction of the model compounds are almost independent of Aerosil content in the rubber mix and are practically the same as those of TMTD-accelerated compounds in the presence of 20 or 30 phr of Aerosil (Table I).

From the temperature dependence of the rate constant of vulcanization of the model compounds in the absence and in the presence of 20 phr of Aerosil (Fig. 5), activation energies of 23.1 kcal/mole are calculated. This value corresponds exactly to the average value of activation energy for TMTD-accelerated sulfur vulcanization in the presence of Aerosil (23.5 kcal/mole, see Table I).

The experimental results described above do not fully explain the role of the reactive components at the Aerosil-rubber interface, but they are in accordance with the mechanism of the thiuram-accelerated sulfur vulcanization proposed in our recent study.¹ According to this, the first step in thiuram vulcanization leading to the sulfurating complexes, rubber-bound intermediate compound, and finally to the crosslinks is a nucleophilic attack of a basic oxyanion, which Bateman and co-workers⁷ have called Y^- , on the electrophilic thiocarbon atom of TMTD. The oxyanion Y^- can be derived, e.g., from zinc oxide ($Zn^{++} \dots O^{--}$) or from a zinc salt of fatty acids ($RCO_2Zn^+ \dots -OH$). In this manner, also a polar silica surface could function and thus accelerate the vulcanization process.

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