

Effect of Temperature on the Course of Thiuram-Accelerated Sulfur Vulcanization

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Synopsis

Tetramethylthiuram disulfide-accelerated sulfur vulcanization of styrene-butadiene rubber has been investigated at temperatures from 100°C to 170°C over 0.5 to 600 min. Continuous measurements in a Vuremo curemeter were used to estimate the extent of crosslinking, which was plotted against cure time. Apart from the induction period (t_i), the kinetic graphs are satisfactory represented by a rate equation assuming three independent first-order reactions: fast crosslinking, degradation, and slow crosslinking. The rate equation contains seven kinetic parameters. Over the temperature range studied, there is no difference between the values of activation energy for t_i^{-1} , for fast crosslinking, and for degradation. The activation energy of slow crosslinking only is significantly greater. Due to the presence of Aerosil, the reciprocal values of the induction periods and the values of the ultimate extents of fast crosslinking are increased, and the values of the rate constants of degradation and slow crosslinking are decreased. Simultaneously, the activation energy of slow crosslinking is also significantly decreased. On the basis of these results, the proposed theory of tetramethylthiuram disulfide-accelerated sulfur vulcanization supposing that zinc dimethyldithiocarbamate is the actual accelerator in this type of curing system is discussed.

INTRODUCTION

In our recent publication,¹ we have presented experimental results which render possible an orientation in the field of sulfur vulcanization accelerated by tetramethylthiuram disulfide (TMTD) in the presence of zinc oxide. 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 the good agreement with findings of Scheele and Franck² that in TMTD-accelerated sulfur vulcanization systems the peak value of zinc dimethyldithiocarbamate (ZnDMDC) formation reaches an end value when the stocks contain 4 gram-atoms of sulfur per mole TMTD. These facts led us to suppose that ZnDMDC is the actual accelerator in TMTD-accelerated sulfur systems.

Support for this view derives from the experiments with model curing systems as well as from the study of the effect of Aerosil on the course of vulcanization.³ A highly dispersed silica gel, Aerosil functions not only as an active filler but also as a catalyst of the reaction of TMTD with zinc oxide leading to the formation of ZnDMDC.

The present work shows new features in thiuram-accelerated sulfur vulcanization which include a first-order "long time" crosslinking reaction. The cure curves have been characterized by seven kinetic parameters. The temperature dependence of these and the effect of Aerosil were examined.

EXPERIMENTAL

The mix formulation was Kralex 010.401 (a cold clear type of styrene-butadiene rubber sold by Kaučuk n.p. Kralupy nad Vltavou, Czechoslovakia), 100 parts; zinc oxide, 5 phr; sulfur, 2 phr; tetramethylthiuram disulfide, 4 phr; and Aerosil 200 (a flame-process silica gel sold by Degussa, Federal Republic of Germany), 0 and 20 phr.

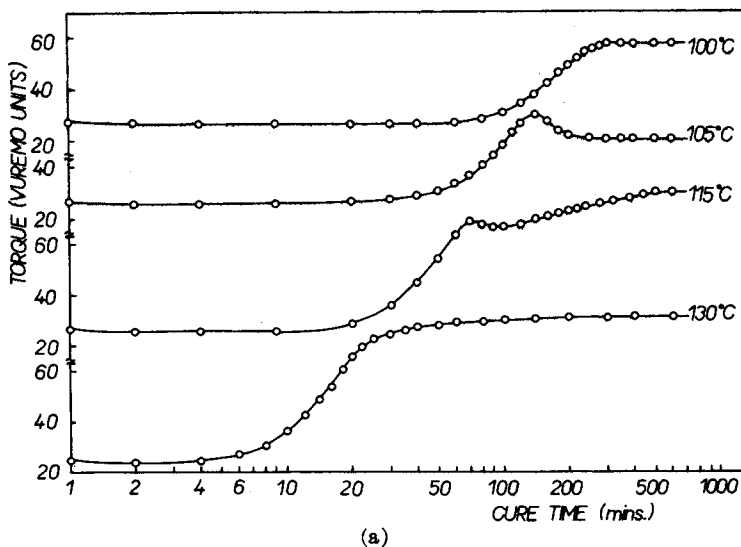
Mixing was on a laboratory mill with 400×130 mm rolls at 50°C . The rubber compounds were cured on a Vuremo curemeter. The apparatus and curemeter measurements have been completely described in our recent publication.⁴ The extent of vulcanization, M , was expressed in Vuremo units (torque) and plotted against time of cure. The ultimate extent of vulcanization reaction was calculated as a ($M_{\max} - M_{\min}$) value.

RESULTS AND DISCUSSION

Influence of Temperature on Shape of Cure Curve

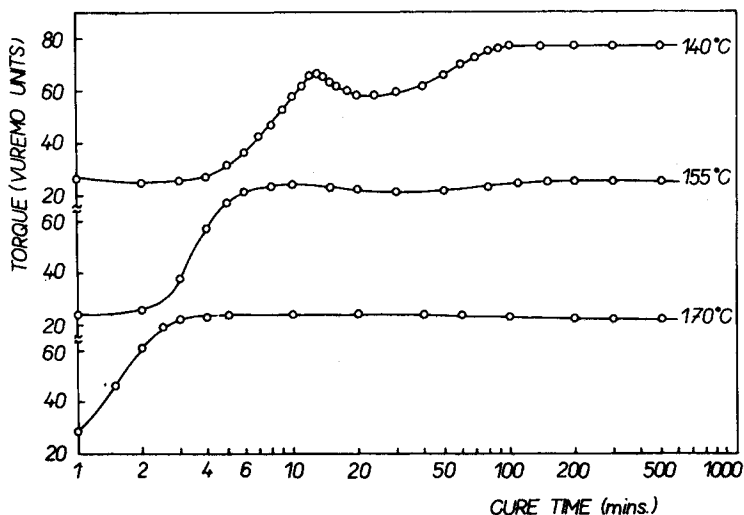
Figure 1 shows that the shape of the cure curves of thiuram-accelerated sulfur systems depends significantly on the cure temperature. For the elucidation of this finding as well as of the crosslinking phenomenon itself, it is highly important to have quantitative knowledge of the rates of the individual reaction steps.

The shape of cure curves obtained at some temperatures resembles that which we have obtained⁴ for the sulfur-free thiuram vulcanization. Therefore, we have analyzed the cure curves by the same method used first by Russell and co-workers.⁵



(a)

Fig. 1 (continued)



(b)

Fig. 1. Influence of cure temperature on the vulcanization of SBR: (a) at 100°C to 130°C; (b) at 140°C to 170°C. Mix formulation: Kralex 010.401, 100 phr; ZnO, 5 phr; TMTD, 4 phr; sulfur, 2 phr.

Kinetic Analysis

The cure curves have been analyzed by treating them as the sum of three independent first-order reactions, following an induction period t_i :

Fast crosslinking

$$x = X(1 - e^{-k_i t})$$

Degradation

$$\delta = \Delta(1 - e^{-k_\delta t})$$

Slow crosslinking

$$f = F(1 - e^{-k_f t})$$

where the contributions to the extent of crosslinking at any time t are given by x , δ , and f ; k_i , k_δ , and k_f are the respective rate constants; and X , Δ , and F are the ultimate extents of the vulcanization reactions.

The seven kinetic parameters (t_i , k_i , X , k_δ , Δ , k_f , and F) were determined by graphic fitting of master curves to the data. This method is detailed in a publication of Redding and Smith.⁵ The evidence for the proposed reaction order $n = 1$ is given in Figure 2, where the logarithm of the extent of the vulcanization reactions is plotted against cure time. Figure 3 shows a typical result. In this graph, the full line represents the sum of the three constituent curves fitted to the experimental points shown, and this is described by the expression

$$E = X(1 - e^{-k_i t}) + \Delta(1 - e^{-k_\delta t}) + F(1 - e^{-k_f t})$$

where E is the extent of crosslinking at time t , and $t = (\text{cure time} - t_i)$.

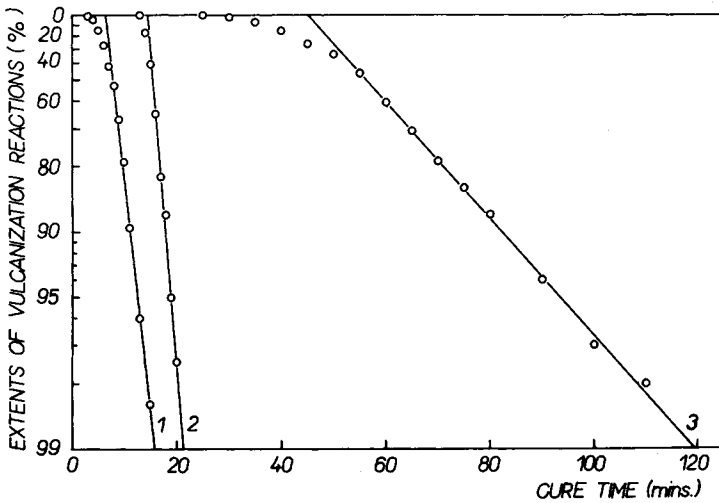


Fig. 2. Increase of extent of vulcanization reactions according to first order in SBR at 140°C: (1) fast crosslinking; (2) degradation, (3) slow crosslinking. Mix formulation as in Fig. 1.

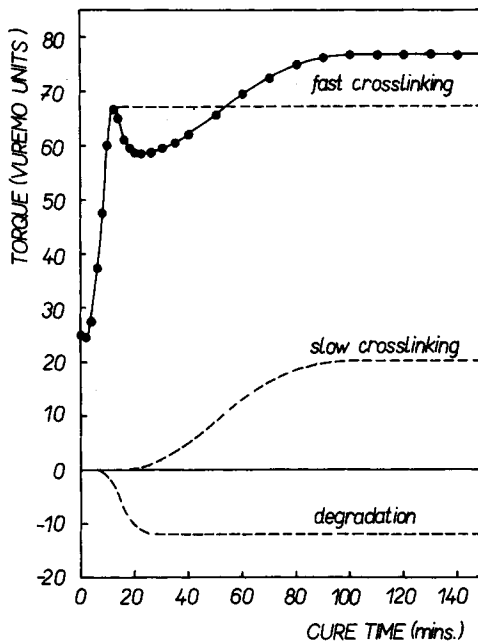


Fig. 3. Kinetic analysis of experimental data of vulcanization of SBR at 140°C: (—) calculated curve fitted to data; (----) estimated contributions from individual reactions. Mix formulation as in Fig. 1.

Temperature Dependence of Kinetic Parameters and the Effect of Aerosil

Tables I and II give the values for the seven parameters for TMTD-accelerated sulfur vulcanization of styrene-butadiene rubber (SBR) at curing temperatures in the range from 100° to 170°C in the absence and in the presence of 20 phr of Aerosil, respectively. Due to the presence of Aerosil, the reciprocal values of the induction periods and the values of the ultimate extents of fast crosslinking are increased. This is in accordance with our recent results and views.³ Simul-

taneously, the values of the rate constants of degradation and slow crosslinking are decreased.

Arrhenius plots of $\log(t_i^{-1})$, $\log k_i$, $\log k_\delta$, and $\log k_f$ versus reciprocal absolute temperature are given in Figures 4 and 5. Activation energies calculated from

TABLE I
Temperature Dependence of Kinetic Parameters of Vulcanization of SBR^a

Cure temp., °C	t_i , min	k_i , min ⁻¹	X, Vuremo units	k_δ , min ⁻¹	Δ , Vuremo units	k_f , min ⁻¹	F, Vuremo units
100	145	0.024	31	—	—	—	—
105	76	0.053	34	0.061	12	—	—
110	63	0.079	39	0.072	7	0.0043	8
115	48	0.107	44	0.115	3	0.0071	12
120	25	0.110	46	—	—	—	—
125	22	0.174	48	—	—	—	—
130	10	0.209	57	—	—	—	—
135	8.0	0.383	42	0.580	3	0.044	13
140	5.5	0.490	43	0.794	12	0.063	20
145	4.0	0.625	42	1.05	3	0.115	18
150	2.6	0.822	49	—	—	—	—
155	2.1	1.09	50	—	—	—	—
160	1.6	1.65	49	—	—	—	—
165	1.1	2.30	49	—	—	—	—
170	0.8	3.22	50	—	—	—	—

^a Sulfur, 2 phr; TMTD, 4 phr; ZnO, 5 phr.

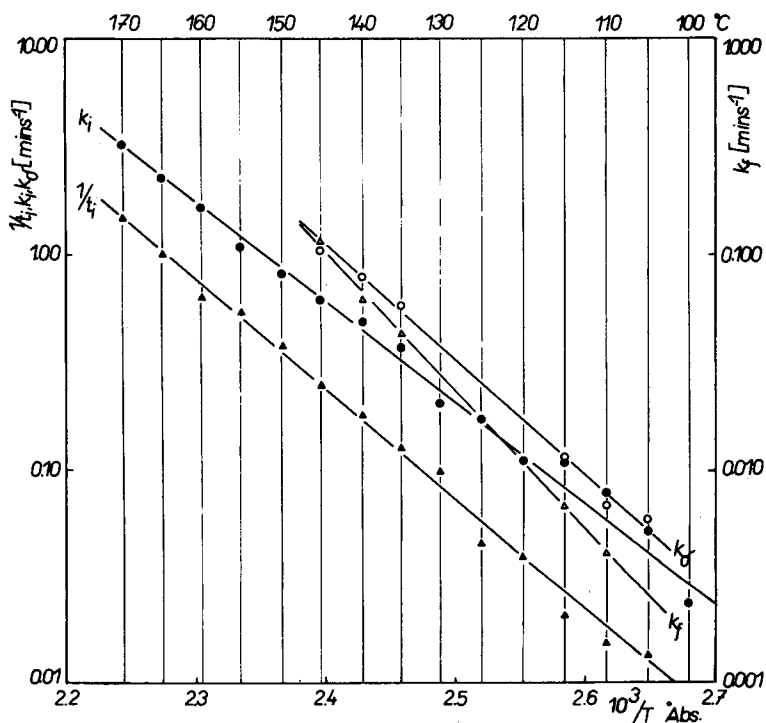


Fig. 4. Effect of temperature on kinetic parameters t_i^{-1} , k_i , k_δ , and k_f for vulcanization of SBR in the absence of Aerosil. Mix formulation as in Fig. 1.

TABLE II
Temperature Dependence of Kinetic Parameters of Vulcanization of SBR in the Presence of Aerosil^a

Cure temp., °C	t_i , min	k_i , min ⁻¹	X, Vuremo units	k_b , min ⁻¹	Δ , Vuremo units	k_f , min ⁻¹	F, Vuremo units
100	85	0.025	54	—	—	—	—
105	57	0.058	54	0.012	7	—	—
110	40	0.058	54	0.018	10	—	—
115	25	0.097	55	0.024	10	—	—
120	16	0.190	52	0.044	13	—	—
125	11.8	0.184	62	—	—	—	—
130	6.4	0.383	61	—	—	—	—
135	5.0	0.479	55	0.104	9	0.013	6
140	3.3	0.719	56	0.177	8	0.023	9
145	2.4	0.920	56	0.242	8	0.023	11
150	1.4	1.20	59	0.360	5	0.039	9
155	1.2	1.28	59	0.410	5	0.56	8
160	0.8	1.80	61	—	—	—	—
165	0.6	2.60	63	—	—	—	—
170	0.5	4.26	61	—	—	—	—

^a SBR: sulfur, 2 phr; TMTD, 4 phr; ZnO, 5 phr. Aerosil: 20 phr.

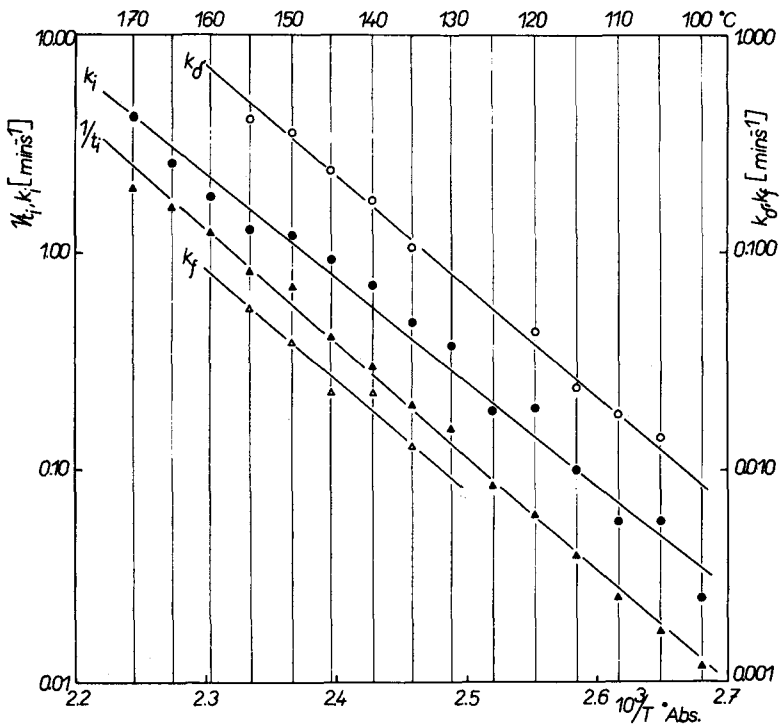


Fig. 5. Effect of temperature on kinetic parameters t_i^{-1} , k_i , k_b , and k_f for vulcanization of SBR in the presence of Aerosil. Mix formulation: Krallex 010.401, 100 phr; ZnO, 5 phr; TMTD, 4 phr; sulfur, 2 phr; Aerosil, 20 phr.

TABLE III
Activation Energies of Vulcanization of SBR^a

Calculated from	Activation energy, kcal/mole	
	0 phr Aerosil	20 phr Aerosil
(Induction period) ⁻¹	23.3	24.0
Rate constant for fast crosslinking	21.9	21.9
Rate constant for degradation	24.3	22.8
Rate constant for slow crosslinking	29.2	23.3

^a Sulfur, 2 phr; TMTD, 4 phr; ZnO, 5 phr.

these are given in Table III. Their values, calculated from the temperature dependence of $\log(t_i^{-1})$, $\log k_t$, and $\log k_d$, are practically independent of calculated parameters and of the presence of Aerosil (23 ± 1 kcal/mole).

Due to the presence of Aerosil, the value of the activation energy calculated from $\log k_f$ (29.2 kcal/mole), which corresponds to that published by Scheele and Franck² for thiuram decrease in thiuram-accelerated sulfur cure (30 kcal/mole), is decreased to the value of 23.3 kcal/mole, which is in a good agreement with the activation energy of dithiocarbamate-accelerated sulfur vulcanization (23.0 kcal/mole) published by Gordon.^{7,8}

CONCLUSIONS

These results confirm the validity of our theory^{1,3} of thiuram-accelerated sulfur vulcanization supposing that ZnDMDC arising from TMTD and zinc oxide is the actual accelerator in this type of curing system. The formation of ZnDMDC from TMTD during the curing process affects particularly the slow crosslinking reaction. Therefore, the activation energy of slow crosslinking is in very good accordance with the activation energy of TMTD decrease, and its value differs significantly from the activation energies of fast crosslinking and degradation. Simultaneously, these facts answer the question why the shape of the cure curves depends strongly on the temperature of cure.

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