Effect of Thiourea on Thiuram-Accelerated Sulfur Vulcanization and Its Significance for Vulcanization Mechanism

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Synopsis

Tetramethylthiuram disulfide-accelerated sulfur vulcanization of natural rubber has been investigated at temperatures from 100°C to 140°C. Continuous measurements in a Vuremo curemeter were used to estimate the extent of crosslinking, which was plotted against cure time. The linearized forms of the cure curves clearly show that at lower cure temperatures, the course of vulcanization differs significantly from the first-order rate law. These digressions were removed by the addition of thiourea, which simultaneously speeds up the course of vulcanization and diminishes its activation energy on the one hand but, on the other hand, diminishes the ultimate extent of crosslinking. On the basis of the above results, the mechanism of thiuram-accelerated sulfur vulcanization, in which ionic and radical reactions take place, is discussed.

INTRODUCTION

Although the mechanism of accelerated sulfur vulcanization has been extensively studied over the past two decades, it is still not clear whether the process involves radical intermediates, ions, or a combination of both.

Researchers such as Craig,[1] Dogadkin,[2,3] Bevilacqua,[4] Scheele,[5] Blokh,[6] Tsurugi and Fukuda,[7] and their respective co-workers[8–10] have advanced free-radical mechanisms, whereas others such as Shelton with McDonel[11] and Coran[12] have proposed a mechanism involving both free-radical and ionic species.

Bateman et al.,[13] Porter,[14] and Allen and co-workers[15] have suggested a polar mechanism for accelerated sulfur vulcanization as an extension of their work on unaccelerated sulfur vulcanization.[13,14]

In discussing the mechanism of accelerated sulfur vulcanization, it is immediately apparent that it is difficult to generalize. There are many unanswered questions, and reasons have been published recently by Manik and Banerjee[16,17] as well as by Coleman et al.[18,19] to believe that both free-radical and ionic reactions are taking place simultaneously, with one or the other predominating at different stages of the overall vulcanization process depending on the vulcanizing system.

THEORY

The investigations[20–22] we have made into the kinetics of thiuram-accelerated sulfur vulcanization were aimed at explaining the mechanism and providing quantitative information for practical considerations, so as to make possible an evaluation of the chemical processes involved in vulcanization. Such being the

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goals, it was only natural that we studied first of all the kinetics of vulcanization reactions occurring in the absence of any additives that are not absolutely necessary.

The results of our kinetic study[20] of tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization at 145°C give the impression that crosslinking is a first-order reaction. At lower cure temperatures, however, the course of the vulcanization differs significantly from the first-order rate law.[23]

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 dimethyl dithiocarbamate (ZnDMDC)-accelerated sulfur vulcanization. These results are in accordance with our recent theory[20] 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.

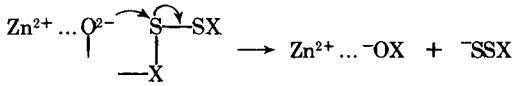
Support for this view derives from the temperature dependences of vulcanization reactions.[21,23] The activation energies of TMTD-accelerated sulfur vulcanizations in the absence (130 kJ/mole) and in the presence of Aerosil (99 kJ/mole) correspond exactly to the values calculated from the rate constants of the thiuram decrease in TMTD-accelerated sulfur vulcanization[8] (126 kJ/mole) and from the rate constants of crosslinking in the zinc dithiocarbamate-accelerated sulfur vulcanization (96 kJ/mole), respectively.[24,25]

The digressions of the course of TMTD-accelerated sulfur vulcanization from the first-order rate law have been removed also by the addition of stearic acid,[26] which reacts with zinc oxide to give zinc stearate. The latter is significantly more soluble in a rubber mix, and that is why it is more accessible to the reaction with TMTD producing ZnDMDC. Therefore, stearic acid diminishes the activation energy of thiuram-accelerated sulfur vulcanization.

Wolfe[27] has used the dependence of the stereochemistry on the polar or nonpolar nature of the reaction of sulfur in the presence of accelerators based on derivatives of dithiocarbamic acid to determine between free radical and ionic mechanism. He concludes that ZnDMDC-accelerated sulfur vulcanization proceeds via an ionic mechanism, while TMTD-accelerated sulfur vulcanization proceeds via a free-radical reaction. In the presence of zinc oxide, TMTD will form ZnDMDC as the vulcanization proceeds, causing mixed-ionic and free-radical reactions.[18,19]

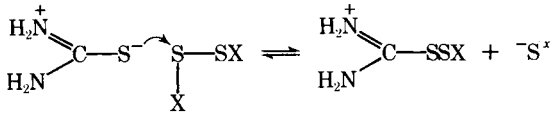
The experimental results discussed above,[20–23,26] in accord with the views of Scheele,[5,8] give the impression that the thiuram-accelerated sulfur vulcanization as well as sulfur-free thiuram vulcanization[28,29] are based on a reaction of thiuram disulfide with zinc oxide, in which rubbers are involved by crosslinking.

On the basis of our investigations on the TMTD–zinc oxide vulcanizing system,[28,29] we support the mechanism of the initial steps of vulcanization as shown in reaction scheme (1) and explain the acceleration effect of added thiourea by postulating a thioanion disulfide interchange, reaction (2), to give a further source of XSS^-, reaction (3), in accord with the theory of Bateman and coworkers:[13]



(1)

where X represents $(CH_3)_2N—\overset{\overset{\displaystyle S}{\|}}{C}—$,



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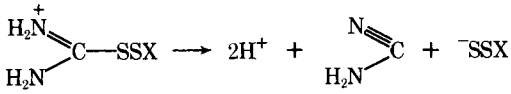


(3)

Thiourea also acts as a radical scavenger,[30] and we suggest[28,29] that the conversion of the rubber-bound intermediate into crosslinks is by free-radical process in accord with the theories of Scheele[5] and Bevilacqua.[4] This would explain the retardation effects of thiourea in the later stages of vulcanization.

Therefore, we present in this paper the effect of thiourea on the course of TMTD-accelerated sulfur vulcanization.

EXPERIMENTAL

In order to preserve the continuity of our quantitative studies of thiuram-accelerated sulfur vulcanization,[20,22,23,26] 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, 4 phr; thiourea, variable.

Mixing, measurements of the progress of the vulcanization in a Vuremo curemeter, as well as calculations of the kinetic parameters of the vulcanization (induction period, rate constant, and ultimate extent) and activation energy of vulcanization have been completely described in our recent publications.[20,22,26,29] Mooney viscosity of natural rubber compounds was 10° ML(1 + 4) at 100°C. This, according to Wolstenholme,[31] is equivalent to a number-average molecular weight of 1.2×10^5.

RESULTS AND DISCUSSION

In Figure 1, the extent of crosslinking at 110°C is plotted as of first order. The maximum values of crosslinking have been taken as 100. It can be seen in this manner that, in the presence of 4 phr thiourea, the conversions fall on a straight line, thus satisfying the first-order rate law; but in the presence of 1.0 phr, 0.2 phr, and 0.0 phr thiourea, the experimental points lie on straight lines from 50%, 70%, and 85% conversion only, respectively.

Increasing the concentration of thiourea in the rubber mix simultaneously increases the slopes of linearized cure curves for thiourea and not only diminishes the digressions of the crosslinking from the first-order rate law, but also speeds up the vulcanization process. Tables I, II, III, and IV show these features. The following kinetic parameters are shown: $t_{10\%}$ (the time necessary for a 10% increase in the ultimate extent of vulcanization; characterizes the scorch time of rubber mix at cure temperature); t_i (the induction period of vulcanization); $t_i - t_{10\%}$ (the parameter characterizing quantitatively the deviation of vulcanization course from the first-order rate law); and k (the first-order rate constant of

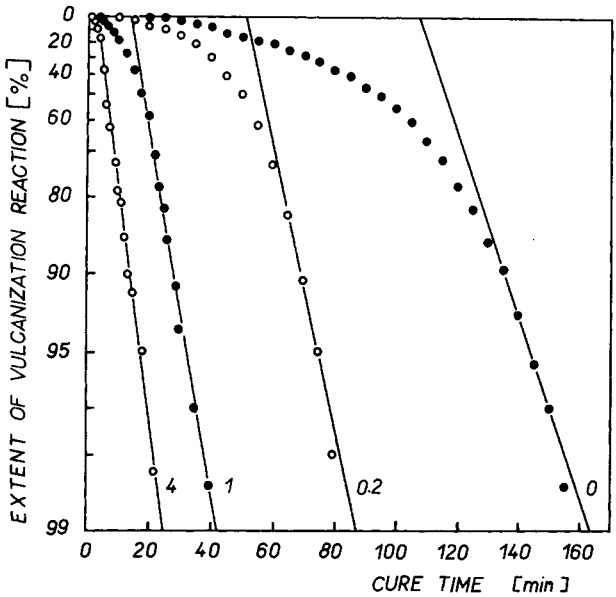


Fig. 1. Increase of extent of vulcanization at 110°C as first-order reaction in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation: natural rubber (pale crepe), 100; zinc oxide, 5; sulfur, 2; TMTD, 4; thiourea, variable. Numbers on curves are thiourea concentrations in phr.

vulcanization), in the absence or presence of thiourea in the cure temperature range from 100° to 140°C.

The kinetic analysis of the plots shown in Figure 1 would be consistent with the kinetic treatment of Coran.[32] The deviations from the first-order behavior are explained by Coran's k_1, k_2, and k_4/k_3 relationships based on the following model scheme of accelerated sulfur vulcanization:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} B^* \xrightarrow{k_3} \alpha V_u$$

$$A + B^* \xrightarrow{K_4} \beta B$$

TABLE I
Scorch Times $t_{10\%}$ in the Cure of Natural Rubber[a]

Cure temperature, °C	$t_{10\%}$, min					
	$x = 0$	$x = 0.2$	$x = 0.5$	$x = 1.0$	$x = 2.0$	$x = 4.0$
100	99	56	37	26.0	17.5	7.5
105	55	33	20.0	16.0	9.0	3.5
110	48	24.0	13.0	7.0	3.5	2.0
115	26.5	14.0	7.6	3.6	2.0	1.4
120	14.5	9.5	5.5	3.0	2.5	1.0
125	10.2	5.7	3.3	2.0	1.2	0.8
130	7.0	3.4	2.6	1.3	0.9	0.6
135	5.0	3.0	1.9	1.1	0.7	0.5
140	3.3	1.9	1.1	0.8	0.5	0.3

[a] With 2.0 phr sulfur accelerated by 4.0 phr tetramethylthiuram disulfide in the presence of 5 phr zinc oxide and x phr thiourea.

TABLE II
Induction Periods of Vulcanization t_i in the Cure of Natural Rubber[a]

Cure temperature, °C	t_i, min					
	$x = 0$	$x = 0.2$	$x = 0.5$	$x = 1.0$	$x = 2.0$	$x = 4.0$
100	339	157	113	51.5	22.0	7.5
105	167	80	47	32.0	13.5	3.5
110	107	50	29.5	13.2	5.0	2.0
115	63	28.5	17.0	6.7	2.9	1.4
120	34.5	20.3	12.0	4.4	2.5	1.0
125	20.3	11.0	6.8	3.0	1.3	0.8
130	12.6	7.3	4.8	2.3	1.1	0.6
135	8.5	5.6	3.0	2.0	0.8	0.5
140	5.0	3.2	2.0	1.3	0.6	0.3

[a] With 2.0 phr sulfur accelerated by 4.0 phr tetramethylthiuram disulfide in the presence of 5 phr zinc oxide and x phr thiourea.

TABLE III
Deviation Parameters of the Course of Vulcanization from the First-Order Rate Law ($t_i - t_{10\%}$) in the Cure of Natural Rubber[a]

Cure temperature, °C	$(t_i - t_{10\%})$, min					
	$x = 0$	$x = 0.2$	$x = 0.5$	$x = 1.0$	$x = 2.0$	$x = 4.0$
100	240	101	66	25.5	4.5	0.0
105	112	47	27.0	16.0	4.5	0.0
110	64	26.0	16.5	6.2	1.5	0.0
115	36.5	14.5	9.4	3.1	0.9	0.0
120	20.0	10.8	6.5	1.4	0.0	0.0
125	10.1	5.3	3.5	1.0	0.1	0.0
130	5.6	3.9	2.2	1.0	0.2	0.0
135	3.5	2.6	1.1	0.9	0.1	0.0
140	1.7	1.3	0.9	0.5	0.1	0.0

[a] With 2.0 phr sulfur accelerated by 4.0 phr tetramethylthiuram disulfide in the presence of 5 phr zinc oxide and x phr thiourea.

TABLE IV
First-Order Rate Constants of Vulcanization k in the Cure of Natural Rubber[a]

Cure temperature, °C	k, min^{-1}					
	$x = 0$	$x = 0.2$	$x = 0.5$	$x = 1.0$	$x = 2.0$	$x = 4.0$
100	0.029	0.050	0.057	0.065	0.073	0.101
105	0.040	0.066	0.087	0.100	0.138	0.160
110	0.079	0.118	0.159	0.169	0.159	0.297
115	0.121	0.139	0.173	0.319	0.334	0.365
120	0.211	0.300	0.324	0.365	0.434	0.529
125	0.315	0.422	0.535	0.565	0.598	1.00
130	0.511	0.605	0.622	0.693	1.01	1.07
135	0.845	0.850	1.07	1.03	1.81	2.05
140	1.35	1.44	1.59	1.92	2.82	3.29

[a] With 2.0 phr sulfur accelerated by 4.0 phr tetramethylthiuram disulfide in the presence of 5 phr zinc oxide and x phr thiourea.

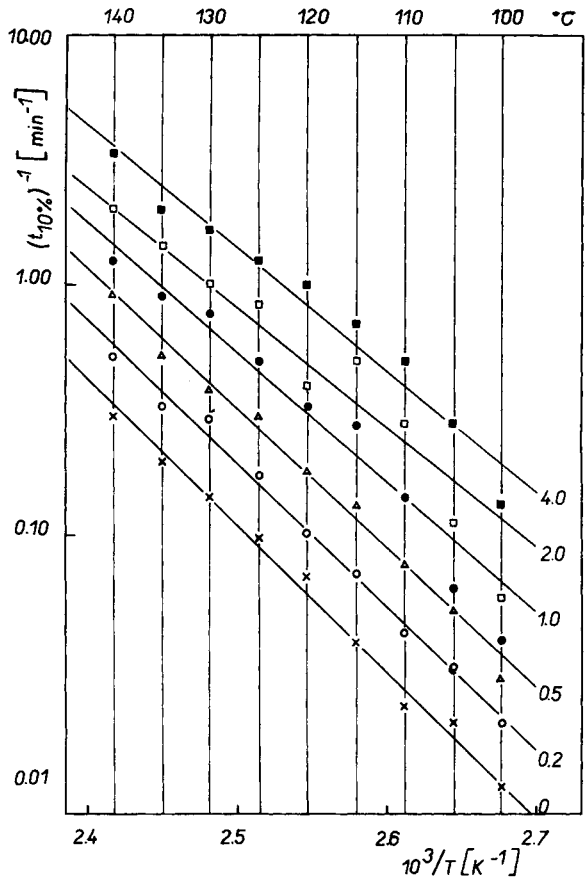


Fig. 2. Effect of thiourea on temperature dependence of reciprocal scorch times $(t_{10\%})^{-1}$ in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation as in Fig. 1. Numbers on curves are thiourea concentrations in phr.

where A is the accelerator and/or its reaction products, B is a precursor to crosslinks, B^* is an activated form of B, V_u is a crosslink, and α and β adjust stoichiometry.

An interesting observation from the Coran's work was that crosslink formation appeared to occur in a first-order fashion only after the nearly complete disappearance of the accelerator A. In our case, A is represented by TMTD, the parameter $t_i - t_{10\%}$ corresponds to Coran's k_1 and k_4/k_3 relationships, and our first-order rate constant k equals Coran's constant k_2.

Logarithmic plots of the reciprocal scorch times $(t_{10\%})^{-1}$, of the reciprocal induction periods $(t_i)^{-1}$, and of the first-order rate constants of vulcanization k versus reciprocal absolute temperature give straight lines (Figs. 2, 3, and 4, respectively), demonstrating the phenomenal rise in these kinetic parameters and allowing calculation, from the slopes, of the activation energies (Table V).

In the absence of thiourea, the activation energies calculated from the reciprocal induction periods (128 kJ/mole) and from the rate constants of vulcanization (129 kJ/mole) are in very good accordance with the activation energy for thiuram decrease (126 kJ/mole) published for TMTD-accelerated sulfur cure

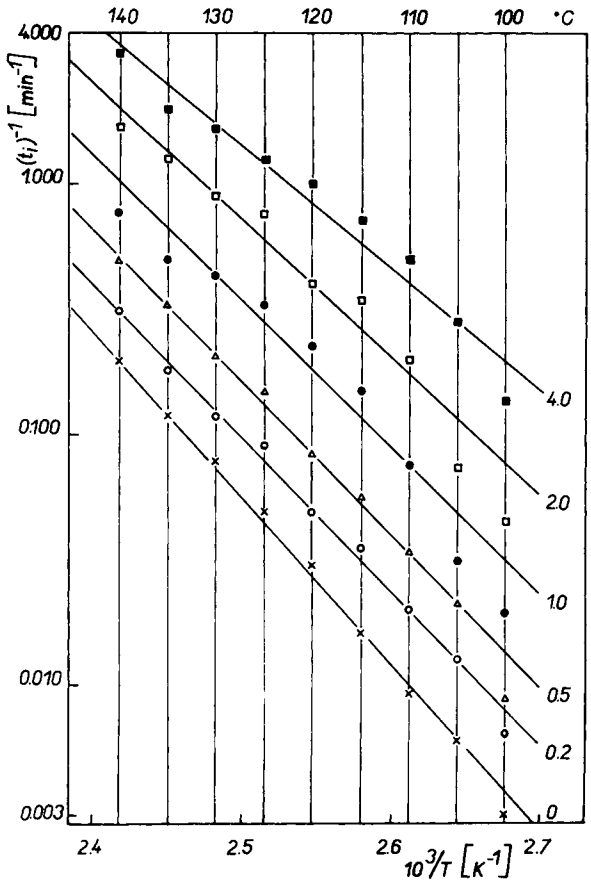


Fig. 3. Effect of thiourea on temperature dependence of reciprocal induction periods of vulcanization $(t_i)^{-1}$ in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation as in Fig. 1. Numbers on curves are thiourea concentrations in phr.

of natural rubber by Scheele and Franck.[8] When the concentration of thiourea is increased, the values of activation energy calculated from both these kinetic parameters decrease; in the case of calculations from $(t_i)^{-1}$ as well as from $(t_{10\%})^{-1}$, the values decrease to 93 kJ/mole, corresponding to the activation energy published for dithiocarbamate-accelerated sulfur vulcanization (96 kJ/mole) by Gordon.[24,25]

All these results endorse our proposition that ZnDMDC is the actual accelerator in TMTD-accelerated sulfur cures, and simultaneously they render possible an explanation of the acceleration effect of thiourea on the course of TMTD-accelerated sulfur vulcanization.

In accordance with the views of Moore[32] and Bateman et al.,[13] thiourea will engage in a thioanion–disulfide interchange reaction (2) to give a supply of the intermediate compound, which would lose a proton to a suitable base and thence decompose rapidly to a perthioanion XSS^-, reaction (3).

In the case of sulfur-free thiuram vulcanization,[13,32] perthioanion XSS^- will rapidly effect the heterolysis of an S–S bond in another TMTD molecule to give trisulfide. Participation of this thiuram trisulfide in processes similar to reaction (1) will lead to the formation of higher polysulfides. Interchange between the

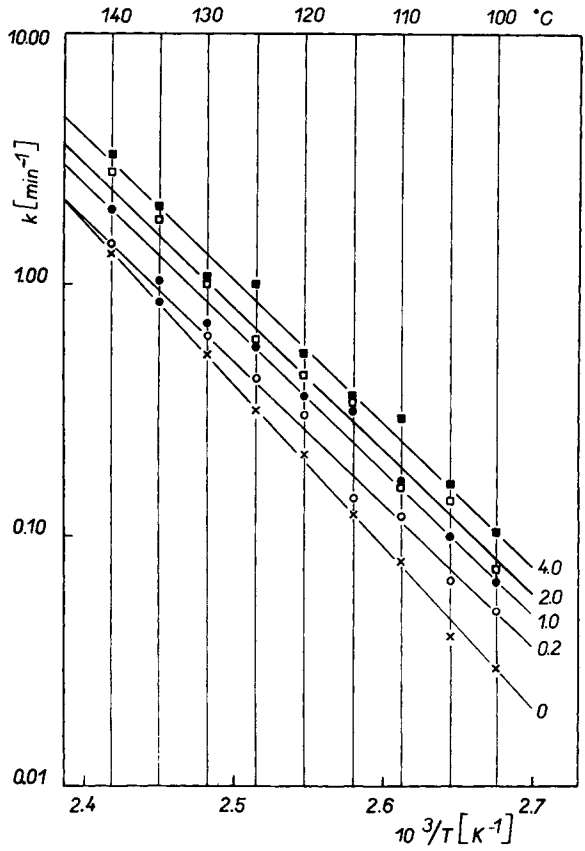


Fig. 4. Effect of thiourea on temperature dependence of first-order rate constants of vulcanization k in sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide. Mix formulation as in Fig. 1. Numbers on curves are thiourea concentrations in phr.

latter and ZnDMDC would then yield the actual sulfurating complexes,[13] which react with rubber macromolecules (RH) to give rubber-bound intermediate compound RS_nSX.

For maximum acceleration effect of thiourea on sulfur-free thiuram vulcanization found at a low TMTD concentration (1 phr),[29] it is probable that in this case, production of perthioanions XSS^- by reaction (1) is very small, and that

TABLE V
Activation Energies of Vulcanization E in the Cure of Natural Rubber[a]

Calculated from	T, kJ/mole					
	$x = 0$	$x = 0.2$	$x = 0.5$	$x = 1.0$	$x = 2.0$	$x = 4.0$
$(t_{10\%})^{-1}$	113	117	107	100	92	93
$(t_i)^{-1}$	128	117	116	112	105	93
k	129	109	108	110	109	111

[a] With 2.0 phr sulfur accelerated by 4.0 phr tetramethylthiuram disulfide in the presence of 5 phr zinc oxide and x phr thiourea.

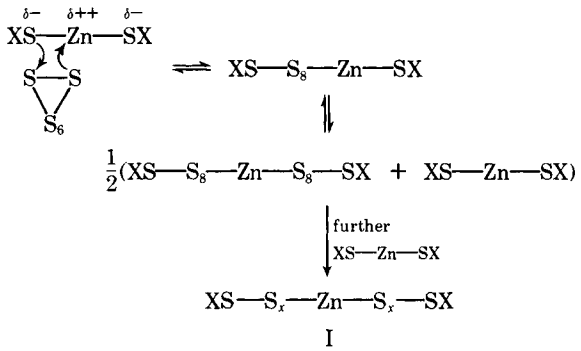
is why the effect of thiourea is the greatest. At high TMTD concentrations, the excess of anions XSS^- and XO^- produced by reaction (1) diminishes the rate of equilibrium reaction (2), and therefore the rate of formation of the sulfurating complexes is diminished too.

In our case of TMTD-accelerated sulfur vulcanization (i.e., at relatively high TMTD concentrations), however, XS^- anions produced by equilibrium reaction (2) would react in the presence of H^+ cations produced by reaction (3) with zinc oxide to give ZnDMDC:

$$2XS^- + Zn^{2+} \ldots O^{2-} + 2\,H^+ \rightarrow XSZnSX + H_2O \tag{4}$$

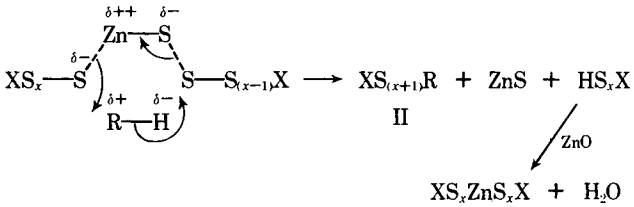
Thus, by the consumption of XS^- anions, the equilibrium of reaction (2) is advanced to the right and the formation of ZnDMDC by reaction (4) is accelerated.

According to Bateman, Moore, and co-workers,[13,33] in the next step of the vulcanization process the active sulfurating agent (I) is formed according to the reaction sequence



(5)

The active sulfurating agent I then reacts with the rubber hydrocarbon to give the rubber-bound intermediate compound II:



(6)

Table VI shows that on increasing the concentrations of thiourea in the rubber mix, the ultimate extent of vulcanization is diminished. This second action of thiourea on the thiuram-accelerated sulfur vulcanization is also similar to its effect on the sulfur-free thiuram vulcanization and cannot be explained by a polar mechanism of vulcanization.

Because thiourea is known not only as a secondary accelerator of thiuram vulcanization,[34,35] but also as a radical scavenger,[30] a probable route for the conversion of the rubber-bound intermediate compound II into the crosslinks is by the radical reactions (7) to (9), in accord with the theories of Scheele[5] and Bevilacqua:[4]

$$2XS_{(x+1)}R \rightarrow 2RS^{\cdot}_n + 2XS^{\cdot}_{(x+2-n)} \tag{7}$$

TABLE VI
Ultimate Extents of Vulcanization ($M_{max} - M_{min}$) in the Cure of Natural Rubber[a]

Cure temperature, °C	($M_{max} - M_{min}$), Vuremo units					
	$x = 0$	$x = 0.2$	$x = 0.5$	$x = 1.0$	$x = 2.0$	$x = 4.0$
100	36	35	34	33	31	29
105	37	36	34	32	31	29
110	37	37	35	33	31	30
115	38	37	35	33	31	30
120	39	38	36	33	32	30
125	42	39	38	36	34	32
130	43	42	40	39	36	33
135	44	44	42	40	37	34
140	45	44	43	42	39	37

[a] With 2.0 phr sulfur accelerated by 4.0 phr tetramethylthiuram disulfide in the presence of 5 phr zinc oxide and x phr thiourea.

$$2RS^{\cdot}_{n} \rightarrow RS_{2n}R \tag{8}$$

$$2XS^{\cdot}_{(x+2-n)} \rightarrow XS_{2(x+2-n)}X \tag{9}$$

This radical mechanism leads to the same formal stochiometry for crosslinking formation, reaction (10), which is described by Bateman and co-workers:[13]

$$2XS_{(x+1)}R \rightarrow RS_{2n}R + XS_{2(x+2-n)}X \tag{10}$$

Table VI also shows that the values of ($M_{max} - M_{min}$) increase with increase in cure temperature. This finding is in accordance with the theory of rubber-like elasticity[36] (the modulus values increase with increasing temperature), and it was already discussed in our previous publications.[26,37]

CONCLUSIONS

All the results discussed above confirm the validity of our proposition[20] that the mechanism of thiuram-accelerated sulfur vulcanization is very probably similar to that of sulfur-free thiuram vulcanization.[29]

In the initial steps of the vulcanization (formation of ZnDMDC from TMTD and zinc oxide and its reaction with elemental sulfur leading to the active sulfurating agent I, which reacts with rubber hydrocarbon to give rubber-bound intermediate compound II), characterized by the rate of crosslinking (i.e., by the kinetic parameters $t_{10\%}$, t_i, and k), mainly ionic reaction take place according to the theory of Bateman, Moore, and co-workers.[13,33]

In the next steps of the vulcanization (conversion of the rubber-bound intermediate compound II into the crosslinks), characterized by the ultimate extent of crosslinking (i.e., by the ($M_{max} - M_{min}$) kinetic parameter), mainly radical reactions take place according to the theories of Scheele[5] and Bevilacqua.[4]

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