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Effect of High-Abrasion Furnace Carbon Black on the Course of Thiuram-Accelerated Sulfur Vulcanization

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Synopsis

The effect of high-abrasion furnace (HAF) carbon black on the course of the 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. Results now available show (1) HAF carbon black does not alter the mechanism of the thiuram-accelerated sulfur cure; it also has no qualitative effect on the kinetics of the vulcanization reactions involved. (2) Quantitatively speaking, essential differences take place. The rate constants of vulcanization rise considerably when HAF carbon black is used; there is a dependence on the HAF carbon black content of the rubber compound. Yet the activation energies of vulcanizations are practically the same as in carbon black-free mixture, amounting to about 31 kcal/mole. (3) Measurements of the course of vulcanizations prove the reinforcing effect of HAF carbon black.

INTRODUCTION

The answer to the question as to the origin of the activity displayed by so-called "active" fillers capable of enhancing the physical properties of vulcanizates has aroused lively interest and activity also in the field of vulcanization. That is why our kinetic study[1] of the thiuram-accelerated sulfur vulcanization had progressed to the point where we could consider vulcanization in the presence of fillers important for practical vulcanizates. We began this series with an investigation[2] relating to the effect of a flame process silica, Aerosil, for it functions not only as an active filler but also as a catalyst of the conversion of thiuram disulfide on the actual accelerator in this vulcanizing system—zinc dithiocarbamate.

The present work is the second contribution in this field. It is concerned with the influence of high-abrasion furnace (HAF) carbon black on the course of tetramethylthiuram disulfide-accelerated sulfur vulcanization of natural rubber.

EXPERIMENTAL

The mix formulation was natural rubber, ribbed smoked sheets (RSS 2 sold by Malayan Rubber Fund Board), 100 parts; zinc oxide, 5 phr; sulfur, 2 phr; tetramethylthiuram disulfide, 4 phr; and Continex HAF carbon black (sold by Continental Carbon Company), variable.

Mixing was by masterbatch technique. Natural rubber with carbon black were mixed in an internal mixer, zinc oxide, sulfur, and tetramethylthiuram disulfide being added on a laboratory mill with 400 × 130 mm rolls at 50°C. Considerable care was needed to ensure uniform dispersion of the solid materials in the rubber for nonuniform dispersion is a major source of error in this type of kinetic study.

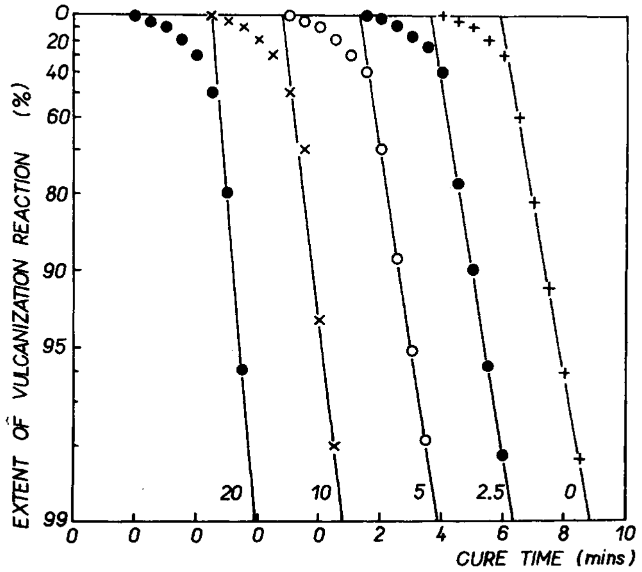
The rubber compounds were cured on a Vuremo curemeter. The apparatus and curemeter measurements have been completely described in our recent publication.[3] The extent of vulcanization, M, was expressed in Vuremo units (torque) and plotted against time of cure. The ultimate extent of vulcanization reaction was calculated as $M_{\max} - M_{\min}$ value.

RESULTS AND DISCUSSION

In our kinetic study[2] concerning the influence of Aerosil on the thiuram-accelerated sulfur vulcanization, it was established that at lower cure temperatures the course of vulcanization differs significantly from the first-order rate law. These digressions diminish with increasing the concentration of Aerosil which simultaneously speeds up the vulcanization.

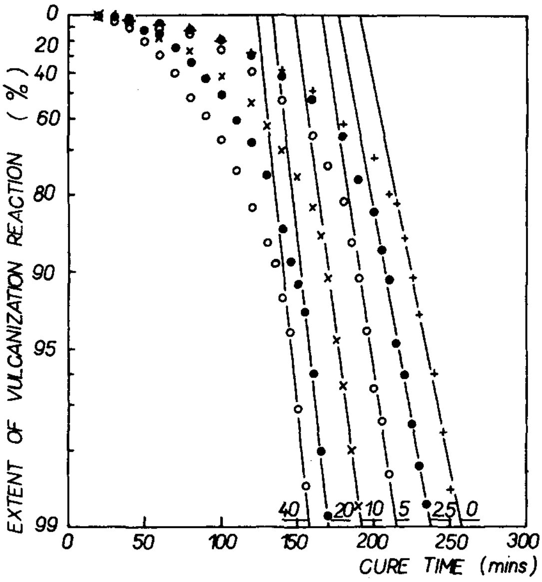
In Figure 1 we plotted the extent of tetramethylthiuram disulfide-accelerated sulfur vulcanization of natural rubber in the absence and in the presence of HAF carbon black as of first order. The maximum values of crosslinking have been taken as 100. It can be seen in this manner that at 140°C, the conversions fall on straight lines, thus satisfying the first-order rate law (Fig. 1a); but at 105°C, the experimental points lie on the straight lines from about 80% to 90% of conversion only (Fig. 1b).

In contrast with the effect of Aerosil, HAF carbon black does not diminish the digressions of the course of vulcanization from the first-order law



(a)

Fig. 1 (*continued*)



(b)

Fig. 1. Effect of HAF carbon black on the increase of the extent of vulcanization as first-order reaction in the sulfur cure of natural rubber accelerated by tetramethylthiuram disulfide (TMTD) at (a) 140°C and (b) 105°C. Mix formulation: natural rubber (RSS 2), 100; zinc oxide, 5; TMTD, 4; sulfur, 2; HAF carbon black, variable. Numbers on the lines are the concentrations of HAF carbon black in phr.

which can be seen at higher conversions but it has rather an opposite effect. It seems that by increasing the concentration of HAF carbon black, the digressions are slightly increased.

According to our recently proposed theory of thiuram-accelerated sulfur vulcanization,[1,2] these digressions indicate that the rate-controlling step is the initial reaction of tetramethylthiuram disulfide with zinc oxide leading to the formation of zinc dimethyldithiocarbamate which functions as the actual accelerator, its reaction with sulfur forming the activated complex, and not the subsequent reaction of the activated complex with rubber hydrocarbon.

Our reason for discussing Figure 1 so thoroughly was to make clear that the vulcanization reactions involved in thiuram-accelerated sulfur cures, even in the presence of HAF carbon black, remained accurately mensurable and were not fundamentally affected by the presence of carbon black. One is hence forced to conclude that the kinetics of thiuram-accelerated sulfur vulcanization remain practically the same, qualitatively speaking, whether carbon black is present or not.

Essential changes appear, however, from a quantitative standpoint. In Table I are assembled the rate constants of vulcanization when cure takes place in the absence or in the presence of different amounts of HAF carbon black in the range of cure temperatures from 100°C to 140°C. In our opinion, the figures in the table disclose an important fact: the presence of HAF carbon black induces a rise in the rate constants of vulcanization. When 40 phr of carbon black has been introduced, the rate constants

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

Cure temperature, °C	$x = 0$	$x = 2.5$	$x = 5$	$x = 10$	$x = 20$	$x = 40$
Rate Constant of Vulcanization k, min^{-1}						
100	—	—	0.046	0.054	0.077	0.089
105	0.070	0.076	0.096	0.106	0.122	0.144
110	0.102	0.121	0.144	0.159	0.235	0.300
115	0.230	0.218	0.288	0.320	0.407	0.512
120	0.307	0.329	0.405	0.450	0.584	0.698
125	0.511	0.575	0.698	0.730	0.795	1.00
130	0.885	0.900	1.00	1.00	2.09	1.53
135	1.54	1.33	2.15	1.84	2.10	3.10
140	1.84	1.92	2.30	2.56	—	—
Activation Energy E, kcal/mole						
	30.5	30.5	30.1	30.1	31.0	30.6

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

of vulcanization are greater by a factor of 2 than in the absence of carbon black. There is, besides, a dependence of the rate constants of vulcanization on the amount of HAF carbon black put into the mixture. Thus, one is inclined to believe that what takes place is a heterogeneous catalysis of the reaction of tetramethylthiuram disulfide with zinc oxide via dispersed carbon black, as in the case of Aerosil.[2]

But the catalysis of a chemical reaction is usually accompanied by a diminution in the energy of activation. This has been found in our recent study of the effect of Aerosil on the course of thiuram-accelerated sulfur vulcanization.[2] A logarithmic plotting of the rate constants of vulcanization in the absence and in the presence of HAF carbon black against the reciprocal absolute temperature gives straight, parallel lines in Figure 2, bringing into evidence the phenomenal rise in the rate constants and allowing the calculation of the activation energies, amounting to some 31 kcal/mole. Consequently, there can be no mention of a lowering of the activation energy through the use of HAF carbon black.

We feel that the increase in the speed of thiuram-accelerated sulfur vulcanization brought about by HAF carbon black—a fact which became evident in the course of the present exploratory investigation—has both practical and theoretical significance.

According to Cotten and co-workers,[4] the curing characteristics of carbon black depend on oxygen-containing groups (such as carboxylic acids, phenols, or quinones) at its sulface. But the surface chemistry of carbon black is undoubtedly also an important factor in rubber reinforcement.[4]

The rise in the crosslinking rate has the same quantitative and qualitative kinetics as the increase in modulus values with the vulcanization time. One would thus have expected HAF carbon black, in thiuram-accelerated sulfur vulcanizations, to also bring about an important increase in the

TABLE II

Ultimate Extent of Vulcanization $M_{max} - M_{min}$ in the Vulcanization of Natural Rubber[a]

Cure temperature, °C	Extent of Vulcanization $M_{max} - M_{min}$, Vuremo units					
	$x = 0$	$x = 2.5$	$x = 5$	$x = 10$	$x = 20$	$x = 40$
100	—	—	39	43	50	67
105	37	38	40	44	51	69
110	38	40	42	46	54	70
115	39	39	42	46	55	71
120	39	41	43	47	56	72
125	40	43	47	49	57	73
130	43	45	46	50	59	75
135	44	47	48	52	61	81
140	45	47	49	54	63	82

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

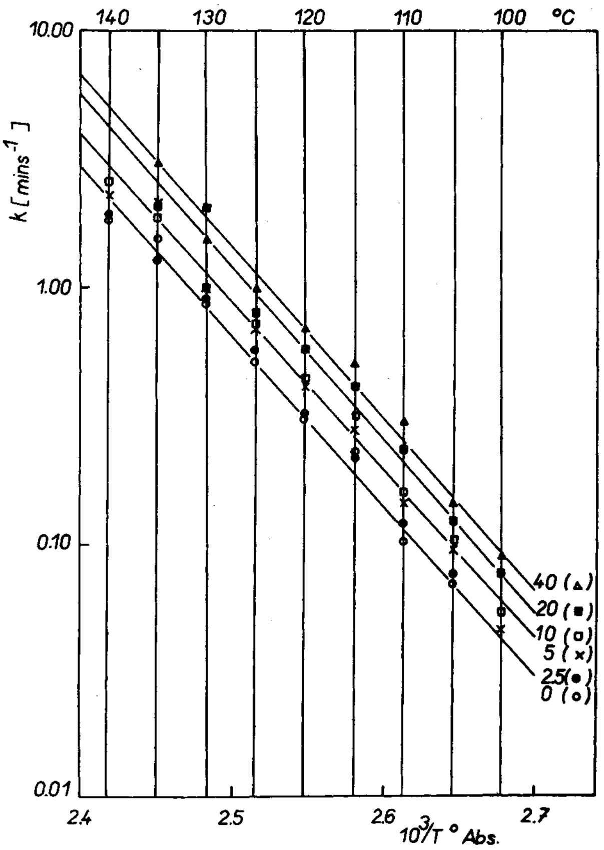


Fig. 2. Temperature dependence of the rate constants of vulcanization, k, in the sulfur cure of natural rubber accelerated by tetramethylthiuramdisulfide (TMTD) in the absence and presence of HAF carbon black. Mix formulation as in Fig. 1. Numbers on the lines are the concentration of HAF carbon black in phr.

modulus values with the vulcanization time. This might easily have been explained as a reinforcing effect of HAF carbon black.

In reality, curemeter measurements of $(M_{max} - M_{min})$ values (the ultimate extent of the vulcanization) as a function of the HAF carbon black concentration proved that a reinforcing effect which Meissner[5] would like to think of as a supplementary crosslinking takes place here. Table II compares the $(M_{max} - M_{min})$ values in the absence or in the presence of HAF carbon black. It will be seen that the values of $(M_{max} - M_{min})$ increase with increasing HAF carbon black concentration in accordance with the results and theories of Wolff,[6] Cotten,[7] and Dannenberg.[8] They do show also a slight dependence on temperature. This is in accordance with the theory of the rubber-like elasticity[9] (the modulus values increase with increasing temperature) and simultaneously proves that the crosslinking efficiency of the thiuram-accelerated sulfur vulcanization is not diminished but, on the contrary, increased with increasing cure temperature.

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