Long-Time Sulfenamide-Accelerated Sulfur Vulcanization of Natural Rubber / Chlorobutyl Rubber Compounds

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Synopsis

Sulfenamide-accelerated sulfur vulcanization of natural rubber/chlorobutyl rubber compounds has been investigated at temperatures from 155 to 175°C over 0.1 to 400 min. Continuous measurements in a Cone Rheometer were used to estimate the extent of crosslinking, which was plotted against cure time. On the basis of a kinetic analysis, two first-order vulcanization reactions, crosslinking and degradation, have been evaluated. Over the temperature range studied, there is no significant difference between the values of activation energy for these reactions. The rate of the degradation is slower by a factor of 20 than the rate of crosslinking. The degradation reaction can be limited by increasing the "efficiency" of the vulcanizing system.

INTRODUCTION

The majority of articles devoted to the kinetics and mechanism of vulcanization of rubbers deal with the accelerated vulcanization of elastomers by elemental sulfur or by sulfur donors. Only a few articles deal with long-time vulcanization reactions,[1-3] for such studies consume a lot of experimental time.

Russell and co-workers[1] have investigated thiazole-accelerated sulfur vulcanization of natural rubber, Ducháček sulfur-free thiuram vulcanization of natural and butadiene rubbers[2] and thiuram-accelerated sulfur vulcanization of styrene–butadiene rubber[3]. In all these studies, the kinetic analysis of long-time cure curves leads to the proposal of three independent first-order reactions: fast crosslinking, degradation, and slow crosslinking. From the practical point of view, fast crosslinking and degradation are of prime importance.

Natural rubber/chlorobutyl rubber blends are widely used in the rubber industry, namely, in tire manufacturing, e.g., for tubeless tire innerliners, tire sidewalls, or tire curing members. In these cases, as well as in the general manufacture of thick-walled rubber products, overcuring may be a serious problem. That is why our present work deals with a kinetic study of vulcanization of natural rubber/chlorobutyl rubber compounds by a sulfenamide-accelerated sulfur vulcanizing system. The previous works on long-time vulcanization[1-3] investigated effects of temperature and accelerator concentration on the course of the vulcanization process. We have also studied the effect of the accelerator/elemental sulfur concentration ratio, but only for short-time cures.[4] In order to preserve the continuity of these studies,[2-4] and simulta-

neously in order to study the possibility of limiting the degradation reactions, the influence of vulcanizing system "efficiency," i.e., of the accelerator/sulfur concentration ratio, on protracted vulcanization has also been investigated.

EXPERIMENTAL

Materials

Natural Rubber. SMR 20 is exported by Malayan Rubber Fund Board.

Chlorobutyl Rubber. Exxon Chlorobutyl 1066 Rubber is sold by Exxon Chemical Co.

Carbon Black. Nigros G (N 660 carbon black) is sold by Urxovy závody n.p. Valašské Meziříčí, Czechoslovakia.

Plasticizer. Triumf oil is sold by Paramo n.p. Pardubice, Czechoslovakia.

Stearic Acid. Stearin is sold by STZ n.p. Ústí nad Labem, Czechoslovakia.

Phenyl-2-Naphthylamine. Fenyl-beta-naftylamin is sold by Spolek pro chemickou a hutní výrobu n.p. Ústí nad Labem, Czechoslovakia.

Zinc Oxide. Silver Seal zinc oxide is sold by Farby a laky n.p. Košeca, Czechoslovakia.

N-Cyclohexyl-2-Benzothiazylsulphenamide. Sulfenax CB is sold by CHZJD n.p. Bratislava, Czechoslovakia.

Compounding

The mix formulations are given in Table I. Rubbers with all additives excluding accelerator and sulfur were mixed in an internal mixer. Accelerator and sulfur were added on a laboratory mill with 400×150 mm rolls at $50°C$. Mooney viscosity of rubber compounds was 20 $ML(1 + 4)$ at $100°C$.

Curemeter Measurements

The rubber compounds were cured at temperatures 155, 165, and $175°C$ in a Monsanto Cone Rheometer. The oscillation angle was $1°$, and the oscillation

TABLE I
Mix Formulations of the Rubber Compounds[a]

(A/S)[b]	0.5	1	2	3	12
Natural rubber	55	55	55	55	55
Chlorobutyl rubber	45	45	45	45	45
Carbon black	50	50	50	50	50
Rosin	6	6	6	6	6
Plasticizer	3	3	3	3	3
Stearic acid	1.2	1.2	1.2	1.2	1.2
Phenyl-2-naphtylamine	1.0	1.0	1.0	1.0	1.0
Zinc oxide	3.5	3.5	3.5	3.5	3.5
Sulfur	2.35	1.75	1.30	1.00	0.50
N-cyclohexyl-2-benzo- thiazylsulphenamide	1.30	1.75	2.35	3.00	6.00

[a] In parts by weight.
[b] Accelerator concentration (A)/sulfur concentration (S) ratio.

rate 100 min^{-1}. The extent of crosslinking (torque), M, was expressed in Nm and plotted against time of cure, t. Thus the cure curves (Fig. 1) were obtained. The ultimate extent of vulcanization reactions was calculated as a $(M_{max}-M_{min})$ value.

RESULTS AND DISCUSSION

Influence of Accelerator / Sulfur Concentration Ratio on Shape of Cure Curves

Figure 1 shows that the shapes of the cure curves of natural rubber/chlorobutyl rubber blends depend significantly on the accelerator/sulfur concentration ratio. In order to draw conclusions from these, it is highly important to determine quantitatively the rates of the individual reaction steps.

In order to preserve the continuity of our quantitative studies of long-time rubber vulcanization,[2,3] we have analyzed the cure curves by the same method used first by Russell and co-workers.[1]

Kinetic Analysis

The cure curves have been analyzed by treating them as the sum of two independent first-order reactions:

$$\text{Crosslinking: } x = X(1 - e^{-kX^t})$$

$$\text{Degradation: } d = D(1 - e^{-kD^t})$$

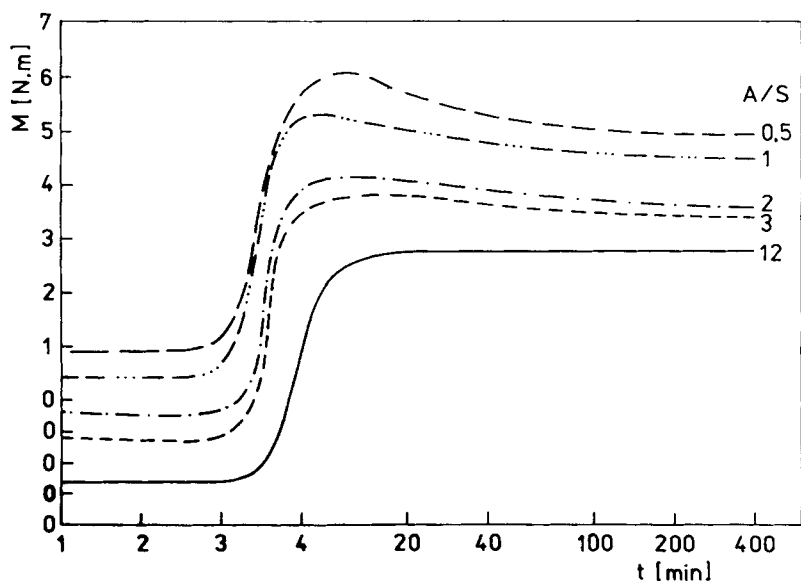where the contributions to the extent of crosslinking at any time t are given

Fig. 1.   Influence of accelerator concentration/sulfur concentration ratio (A/S) on vulcanization course of natural rubber/chlorobutyl rubber compounds at 155°C. Mix formulations are given in Table I.
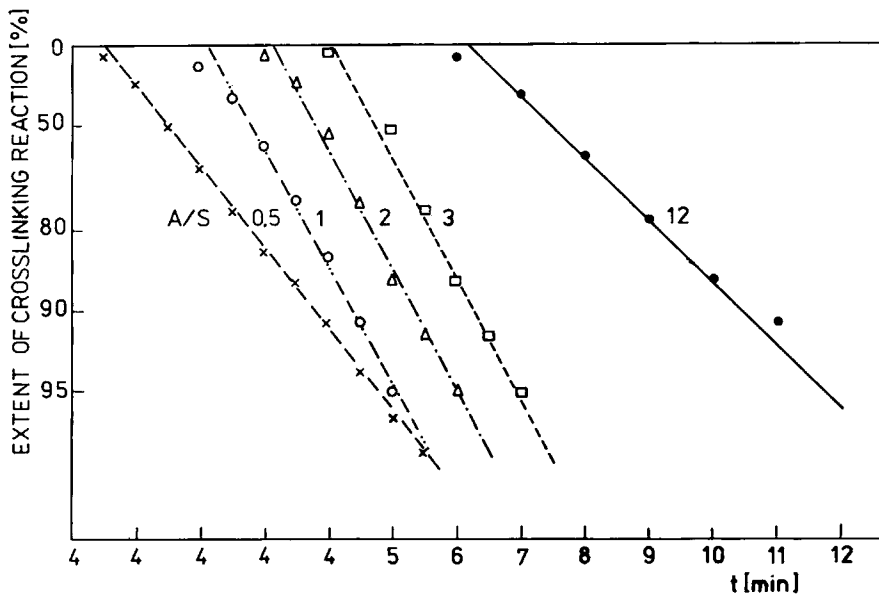
Fig. 2.   Influence of accelerator concentration/sulfur concentration ratio (A/S) on increase of extent of crosslinking reaction according to first order in vulcanization of natural rubber/chlorobutyl rubber compounds at 155°C. Mix formulations are given in Table I.

by x and d; k_x and k_d are the respective rate constants; and X and D are the ultimate extents of the vulcanization reactions.

The kinetic parameters were determined by graphical 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 Figures
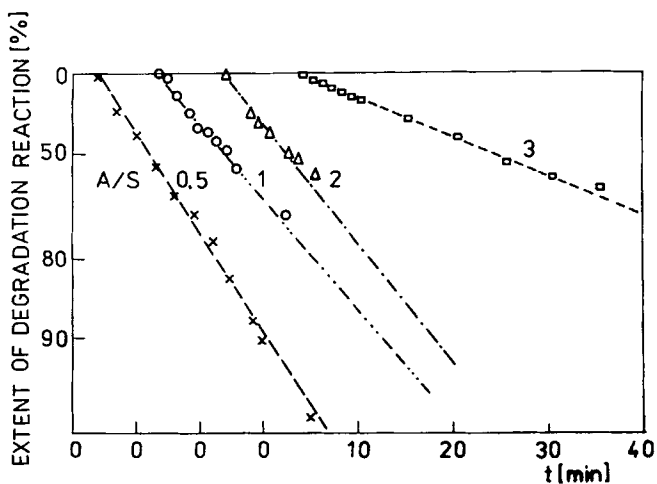

Fig. 3.   Influence of accelerator concentration/sulfur concentration ratio (A/S) on increase of extent of degradation reaction according to first order in vulcanization of natural rubber/chlorobutyl rubber compounds at 155°C. Mix formulations are given in Table I.

TABLE II

Concentration and Temperature Dependences of Kinetic Parameters
of Vulcanization of Natural Rubber/Chlorobutyl Rubber Compounds[a]

$T(°C)$	A/S[b]	0.5	1	2	3	12
155	k_x (min^{-1})	0.74	1.02	1.05	1.04	0.54
	k_d (min^{-1})	0.034	0.027	0.015	0.010	—
	X (N m)	5.2	4.9	4.5	4.5	4.4
	D (N m)	0.8	0.7	0.6	0.4	0.0
165	k_x (min^{-1})	1.38	2.52	3.18	2.79	1.08
	k_d (min^{-1})	0.071	0.057	0.030	0.026	—
	X (N m)	5.1	5.0	4.8	4.5	4.1
	D (N m)	0.9	0.8	0.6	0.6	0.3
175	k_x (min^{-1})	3.02	4.10	4.72	4.39	1.84
	k_d (min^{-1})	0.135	0.100	0.053	0.035	—
	X (N m)	5.0	4.9	4.6	4.4	4.3
	D (N m)	1.2	1.0	0.8	0.7	0.4
	E_x (kJ mol^{-1})	103	102	102	104	100
	E_d (kJ mol^{-1})	106	105	105	100	—

[a] Mix formulations are given in Table I.
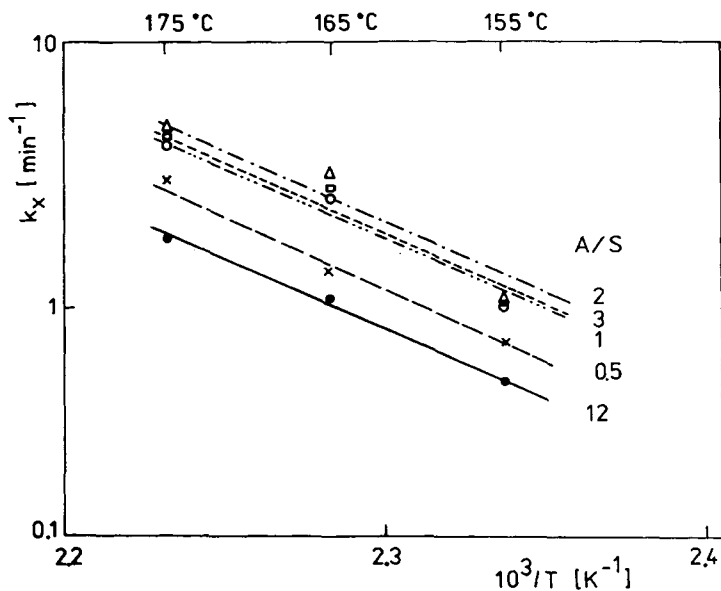[b] Accelerator concentration (A)/sulfur concentration (S) ratio.

Fig. 4.   Influence of accelerator concentration/sulfur concentration ratio (A/S) on temperature dependence of rate of crosslinking reaction in vulcanization of natural rubber/chlorobutyl rubber compounds. Mix formulations are given in Table I.
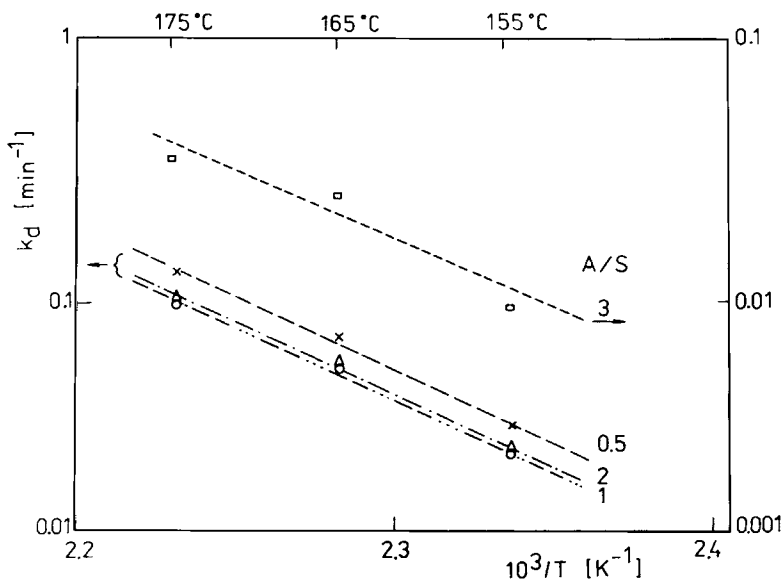
Fig. 5. Influence of accelerator concentration/sulfur concentration ratio (A/S) on temperature dependence of rate of degradation reaction in vulcanization of natural rubber/chlorobutyl rubber compounds. Mix formulations are given in Table I.

2 and 3, where the logarithms of the extents of crosslinking and degradation reactions respectively are plotted against cure time.

Table II shows some results. Keeping the accelerator/sulfur concentration value at a constant value (of 3), the extents of crosslinking change very little with the accelerator/sulfur concentration ratio (A/S). Increasing its value by a factor of 24 (mixture 12), the extent of crosslinking decreases only up to 85% of its original value (mixture 0.5). Over the the same range, the values of the first-order rate constants of degradation decrease significantly. The first-order rate constants of crosslinking reach a maximum at an A/S value about 2, at which same value the extent of degradation is decreased by up to 75% (mixture 2) of its original value (mixture 0.5). Further increase in the A/S value causes further suppression of the degradation reaction: At an A/S value of 12, the extent of the degradation reaction at 155°C is zero; at 165 and 175°C its values are equal to 30% of its original value.

Arrhenius plots of the logarithm of the first-order rate constants of crosslinking and degradation reactions versus reciprocal absolute temperature are given in Figures 4 and 5, respectively. Activation energies calculated from these are also given in Table II. Their values for both reactions, crosslinking as well as degradation, are practically the same, about 100 kJ mol^{-1}, and independent of A/S value. Experimental points for $A/S = 1$, 2, and 3 in Figure 4 could also lie on curves. From the theoretical point of view, however, there is no reason for curved courses of these Arrhenius plots.

CONCLUSIONS

Both crosslinking and degradation reactions taking place in the sulfenamide-accelerated vulcanization of natural rubber/chlorobutyl rubber can be

described by a first-order rate law. This is probably a general feature of accelerated sulfur vulcanization, since analogous findings have been described for thiazole-accelerated vulcanization of natural rubber[1] and thiuram-accelerated vulcanization of styrene-butadiene rubber.[3]

In our system, the original rate of the degradation (mixture 0.5) is by a factor of 20 lower than the rate of crosslinking. It is possible to eliminate the degradation at cure temperatures below about 150°C and to limit it significantly at higher temperatures by increasing the "efficiency" of a vulcanizing system, i.e., by increasing the sulfenamide accelerator concentration. This finding is of a great practical importance, namely for manufacturing of thick-walled rubber products. On the other hand, increasing the accelerator concentration the cost of a rubber mix increases too. Thus a compromise between the technological and economic points of view must be found.

References

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5. R. B. Redding and D. A. Smith, *J. IRI*, **4**, 198 (1970).