Studies in Hard Rubber Reaction.   Part I. Heat of Hard Rubber Reaction

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INTRODUCTION

The formation of hard rubber is known to be accompanied by evolution of heat. In consequence of this and because of the poor conductivity of rubber the temperature inside the reacting mass may be so high as to spoil it. No mechanism could, however, be formulated regarding the evolution and dissipation of heat in hard rubber reaction, since the exact quantity of heat that is evolved is not known, in spite of a large amount of work done in this field.[1-9]

Evolution of exothermic heat in hard rubber reaction is mainly based on three determinations, viz., (1) heat of combustion,[4,6,7] (2) temperature rise that occurs during vulcanization,[3,5] (3) and calorimetry.[8,23] There are, however, large differences in values reported by the various investigators who employed them.

Differential thermal analysis (DTA) has been extensively used in the study of transitions and reactions of inorganic materials. Its application in the field of polymers is quite recent[10-13] and in the field of rubbers it has not been attempted thus far. The method can also give a reasonable estimate of heat of reaction by measurement of the area of the thermograph, when certain conditions are met. The present paper reports the results of such determinations in the case of rubber–sulfur mixtures of different compositions. Initiation temperatures are also obtained from the thermographs. Analysis of combined sulfur at different points of the thermograph lends useful information about the hard rubber reaction.

EXPERIMENTAL METHODS AND PROCEDURES

Apparatus

The apparatus, a modified version of Bourchardt's,[14] was fabricated in our laboratory for this purpose. It is suitable for working at up to 300° C.

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and consists of two Duralumin blocks A and B (Figure 1) and a brass block C. A contains the differential thermocouple, B serves as a sample holder, and C as furnace. The thermocouple is made of standard wire gauge 28 platinum, and platinum and 10% rhodium wires. The base and the complete housing of the apparatus are made of Sindanyo. B has three holes: the outer ones, S and S', are sample holders, and one (T) at the center accommodates the mercury thermometer for measuring the furnace temperature. By means of marks made on blocks A and B, the sample holders are centered with the thermocouple junctions TC & TC', and TC & TC' are fixed permanently in the holes in block A with araldite glass cement, the thermocouples being insulated from the metal block with porcelain beads. The lower reduced portion of A fits snugly, sliding within the upper cavity of B, and when the marks coincide the thermocouple ends enter the center of the sample holders. Furnace C is machined from brass rod on which the heating coil, consisting of 7½ ft. of standard wire gauge 26 nichrome wire, is wound to give a total resistance of 12 ohms. The thermocouple junctions are connected to a Leeds and Northrup Galvanometer Type 2430A through two 50-ohm variable resistors, controlling sensitivity and maintaining proper damping resistance. The leads from the heating coil pass through an outer insulating Sindanyo jacket and are connected to a Variac. The coil is insulated from the brass block by mica sheets.

The apparatus was calibrated by the known heat of reaction:

$$CuSO_4, 5H_2O \rightarrow CuSO_4 H_2O + 4H_2O(g) \ (\Delta H_{298}$$

$$= 54.3 \ kcal./mole)$$
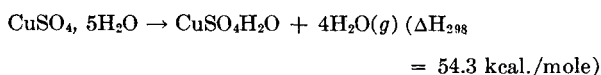
In these experiments a mixture of copper sulfate and dry alumina constituted the active material, and alumina was used as the inert material.

A heating rate of 5°/min. was used in all the experiments, and galvanometer sensitivity was
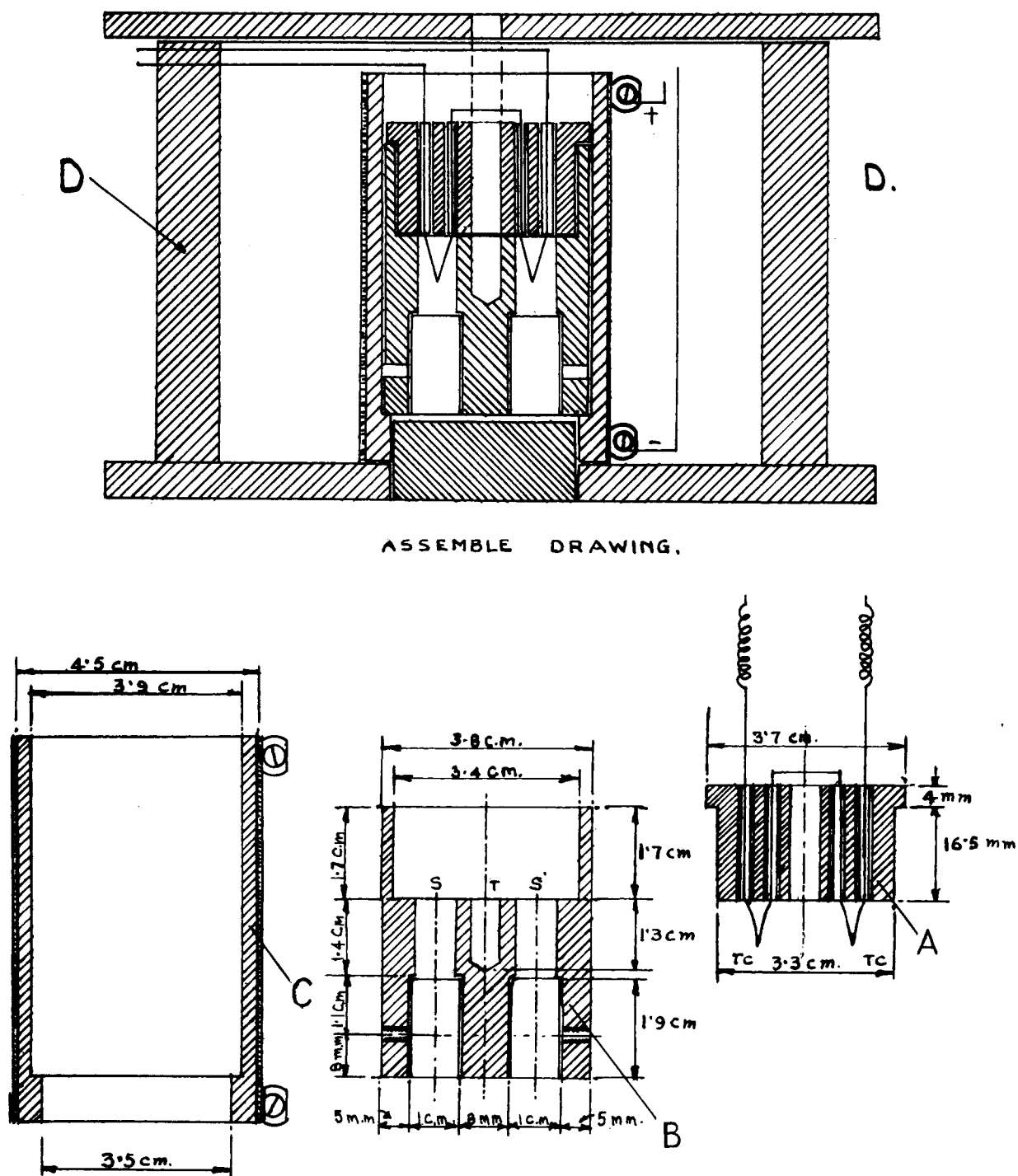
Fig. 1. Diagram of the DTA apparatus: (A) thermocouple head; (B) sample holder; (C) oven; (D) assemble drawing.

adjusted to accommodate all readings. It was, however, observed that the heating rate could be varied from 2.5 to 10°/min. without any effect on the measured heat evolution, provided the thermocouple was also calibrated at the same heating rate.

Procedure

The active materials in our work on hard rubber reaction consisted of rubber–sulfur compounds of known compositions (See Table I). These com-

TABLE I
Composition of Different Rubber–Sulfur Compounds

Compound no.	Pale crêpe, g.	Sulfur, g.	S on rubber pale crepe, %	S on rubber hydrocarbon, actual RH by difference	Free S after init. cure of 1 hr. at 153°C., %
115	92.6	7.4	8.0	8.7	5.9
114	90.9	9.1	10.0	10.9	7.1
113	86.9	13.1	15.0	16.3	10.1
112	83.3	16.7	20.0	21.7	14.1
111	80.0	20.0	25.0	26.1	16.5
107	75.0	25.0	33.3	36.2	18.7
109	70.0	30.0	43.0	46.7	23.3
106	68.0	32.0	47.0	51.1	27.5
110	65.0	35.0	54.0	58.7	28.6

TABLE II
Data Calculated from Thermographs

Compound no.	Free S on mix, %	Combined S by difference (calcd.), %	Init. temp., °C.	Mix, cal./g.	Rubber, cal./g.	Furnace temp. at peak point of thermograph, °C.
115	5.9	1.5	178	5	6	196
114	7.1	2.0	170	45	49	198
113	10.1	2.9	163	90	103	197
112	14.1	2.6	162	120	144	195
111	16.5	3.5	154	172	215	194
107	18.7	6.3	155	217	289	195
109	23.3	6.7	158	255	364	193
106	27.5	4.5	163	220	323	193
110	28.6	6.4	161	213	327	193

TABLE III
Data Calculated from Thermographs of 68/32 Rubber/Sulfur Compound

Time of precure at 153°C., hr.	Free S, %	Combined S by difference, %	Init. temp., °C.	Mix, cal./g.	Furnace temp. at peak point of thermograph, °C.
1	27.5	4.5	160	220	190
1½	24.8	7.2	140	168	188
2	22.0	10.0	138	157	188
3	17.6	14.4	130	132	188
3½	13.5	18.5	130	117	188
4	7.2	24.8	150	63	188
4½	6.2	25.8	155	36	187
6	5.8	26.2	135	3	186
8	1.9	30.1	—	—	—
10	1.5	30.5	—	—	—

pounds were prepared in a laboratory mixing mill of size 16 x 9-in. and were vulcanized in a press 12 x 12-in. for 1 hr. at 153°C. in a 6 x 6 x $^3/_{64}$-in. former. These partially vulcanized compounds were subsequently ground by passing three or four times through a tight nip of the same mill. Preliminary observations indicated that the heat of reaction was independent of the size of granules and hence no

sieving was necessary. In all the experiments with rubber–sulfur compounds, ebonite dust extracted with acetone, to remove free sulfur, was used as the reference material, so that the thermal characteristics of the reference and active material were similar. Recorded results are reproducible within ±5%.

The initiation temperature was measured at the

point of break of the thermograph from the base line.

The quantity of heat evolved was obtained by measuring the area under the thermograph on the basis of calibration of the heat per unit area, with the use of copper sulfate under identical conditions; the values were multiplied by 1.5, which is the ratio of the approximate specific heat of ebonite (0.33) or rubber–sulfur mixture to that of alumina (0.22) in the temperature range studied.*
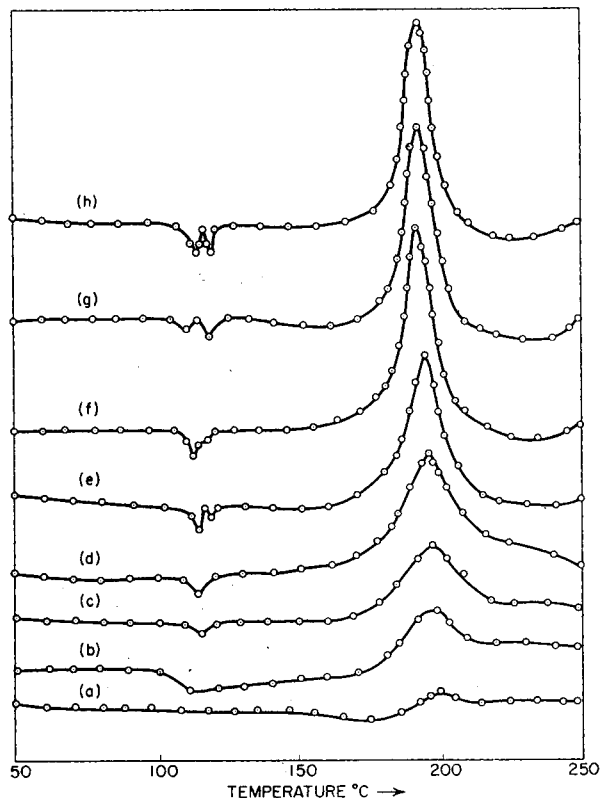

Fig. 3. Effect of sulfur concentration on heat evolution.

Fig. 2. Differential thermographs of samples containing increasing quantities of total sulfur (%); sample weight in grams: (a) 7.4%, 0.1704 g.; (b) 9.1%, 0.1518 g.; (c) 16.7%, 0.1514 g.; (d) 20.0%, 0.1519 g.; (e) 25.0%, 0.1517 g.; (f) 30.0%, 0.1450 g.; (g) 32.0%, 0.1475 g.; (h) 35.0%, 0.1412 g.

Results

Table II gives the data calculated from the thermographs of Figures 2a–h, and Figure 3 shows the plot of quantity of heat evolved against percentage of total sulfur initially present in the samp'e.

In the next set of experiments, a 68/32 rubber–

*In our earlier communication[16] this correction for the different specific heats of alumina and ebonite was not made.
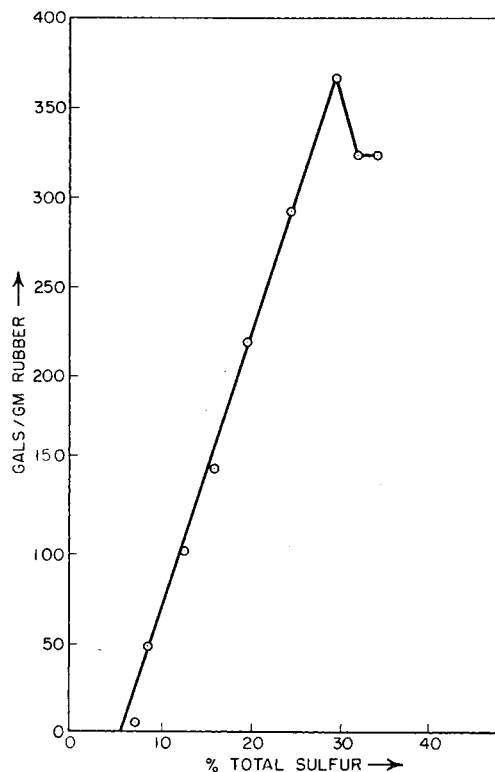
sulfur compound (No. 106), $6 \times 6 \times {}^{3}/_{64}$ in., was cured at 152°C. for different periods and the resulting compounds of gradually increasing vulcanization coefficients were used as active materials. The thermographs are shown in Figure 4 (a–h). Table III gives various data calculated from them.

Figure 5 shows the graph of per cent combined sulfur versus amount of heat evolved.

Finally, experiments were conducted so as to arrest the reaction of the 68/32, 70/30, and 83/17 rubber solidus sulfur compounds at 125, 145, 160, 175, 190, and 210°C., and the resultant samples were analyzed for free sulfur.[15] For this purpose the heating was stopped at these temperatures during the course of the usual DTA experiments, and samples were immediately cooled by placing the sample holder in a refrigerator. Free-sulfur contents of these samples are given in Table IV and are plotted against temperature in Figure 6.

DISCUSSION

Typical differential thermographs obtained as in Figure 4 (a–h) have been reported earlier by the authors.[16] Two endothermic reactions starting at about 95 and 110°C. correspond to the temperatures of the enantiomorphous change of α to β

TABLE IV
Distribution of Free and Combined Sulfur at Different
Points of the Thermographs

	Rubber/sulfur	Free S	Combined S, (calcd.)
At 125°C.			
	83/17	14.0	2.7
	70/30	25.3	4.7
	68/32[a]	27.4	4.6
	68/32[b]	19.0	13.0
At 146°C.			
	83/17	14.0	2.7
	70/30	25.4	4.6
	68/32[a]	26.4	5.6
	68/32[b]	19.3	12.7
At 160°C.			
	83/17	12.8	3.9
	70/30	24.7	5.3
	68/32[a]	21.6	10.4
	68/32[b]	16.5	15.5
At 175°C.			
	83/17	11.1	5.6
	70/30	20.3	9.7
	68/32[a]	16.7	15.3
	68/32[b]	10.7	21.3
At 190°C.			
	83/17	0.7	16.0
	70/30	1.1	28.9
	68/32[a]	0.8	31.2
	68/32[b]	0.3	31.7
At 210°C.			
	83/17	0.2	16.5
	70/30	0.5	29.5
	68/32[a]	0.3	31.7
	68/32[b]	0.2	31.8

[a] Initial combined sulfur, 4.5%.

[b] Initial combined sulfur, 10.0%.

sulfur and its melting (Fig. 7). The endothermic change following the exothermic hard-rubber reaction is due to dehydrogenation, as will be discussed later.

Heat of Hard-Rubber Reaction

A number of authors have determined the heat of hard-rubber reaction[4,6-9] and obtained values differing widely from each other. For instance, the value reported by Blake,[4] who used the heat of combustion method, is 300 cals./g., which differs markedly from the 75 cals./g. given by McPherson & Bekkedahl,[8] who used isothermal calorimetry. Both these methods are liable to unaccountable errors. In Blake's method, the heat of the hard-rubber reaction is a difference between two large amounts of heat of combustion and is only a small percentage of either. In McPherson and Bekkedahl's method no account is taken of the endother-
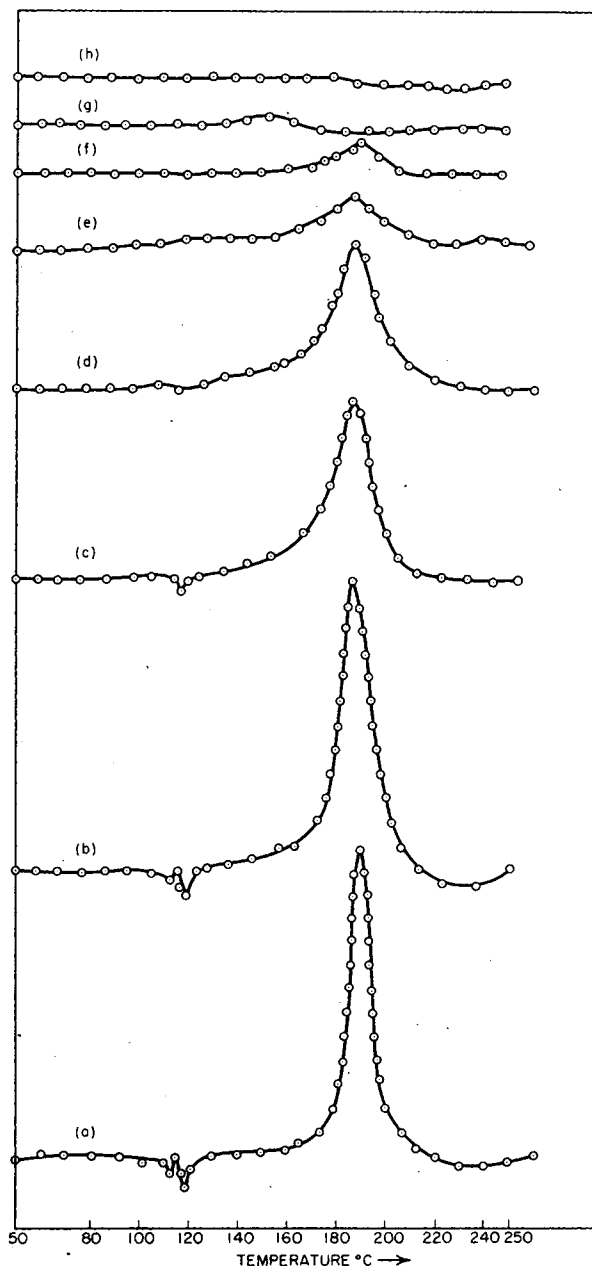

Fig. 4. Differential thermographs of 68:32 rubber/sulfur sample containing decreasing quantities of free sulfur (%); sample weight in grams: (a) 27.5%, 0.1898 g.; (b) 22.0%, 0.2437 g.; (c) 17.6%, 0.2988 g.; (d) 13.5%, 0.2903 g.; (e) 7.2%, 0.2646 g.; (f) 6.2%, 0.2759 g.; (g) 5.8%, 0.2800 g.; (h) 1.9%, 0.2789 g.

mic dehydrogenation which occurs at high temperatures with high sulfur compounds. The average value obtained by us, viz., 220 cals./g. of 68/32 stock, appears to be a reasonable value within the limits of experimental error (±15%) of the DTA method employed in the present study.
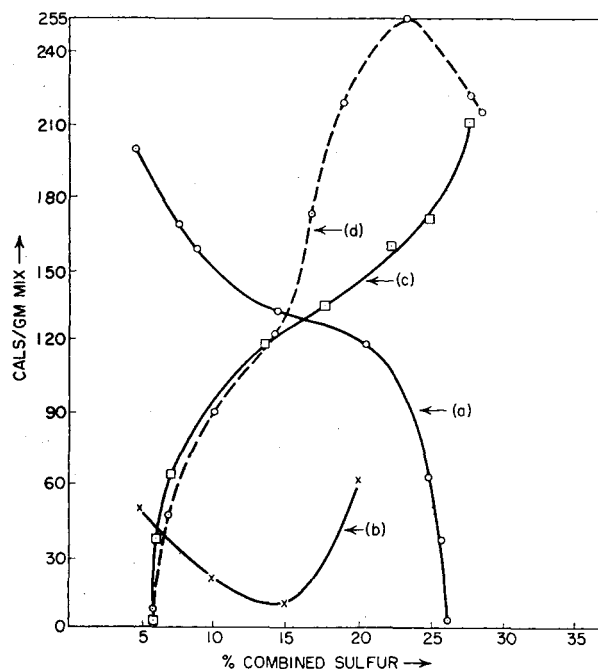
Fig. 5. Effect of free/combined sulfur of different samples on heat evolution: (a) effect of combined sulfur of 68:32 rubber/sulfur sample on heat evolution; (b) differential plot of heat evolution with combined sulfur; (c) effect of free sulfur of type B samples on heat evolution; (d) effect of free sulfur of type A samples on heat evolution.
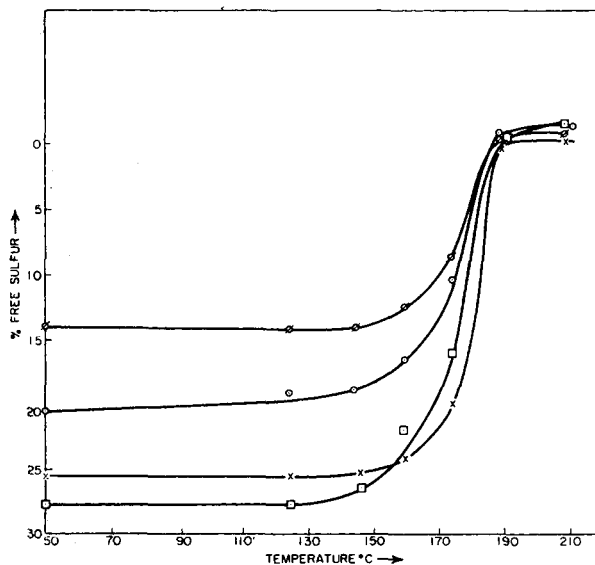

Fig. 6. Disappearance of free sulfur of various samples at different points of thermographs: (□) 68:32 rubber/sulfur, free sulfur 27.5%; (○) 68:32 rubber/sulfur, free sulfur 20.6%; (φ) 83:17 rubber/sulfur, free sulfur 14.1%; (×) 70:30 rubber/sulfur, free sulfur 25.5%.
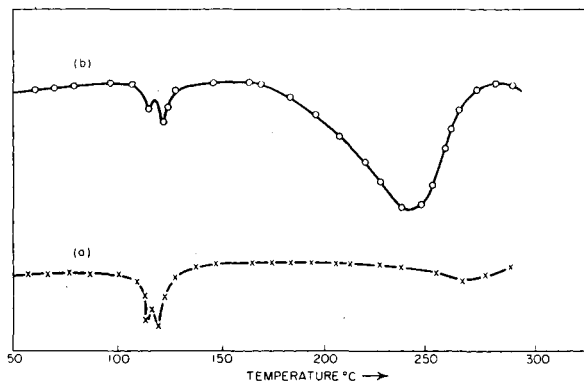

Fig. 7. Differential thermographs of sulfur in (a) alumina and (b) ebonite dust: (a) active material weight 0.2028 g., reference material alumina; (b) active material weight 0.1016 g., reference material ebonite dust.

It will be seen from Figure 3 that heats of reaction per gram of rubber increase with percentage of total sulfur. The linear fit is observed up to 30% sulfur (on mix), beyond which heat evolution decreases. The decrease of quantity of heat evolved beyond 30% is obviously caused by the endothermic dehydrogenation reaction, which becomes prominent at high temperature and with high sulfur content (see below). The linear relationship obtained by the authors differs from the observation of McPherson and Bekkedahl who obtained a change of slope indicating no further evolution of heat after 19% sulfur.

Heat of Reaction with Variation of Combined Sulfur of the 68/32 Stock

The samples formed by heating a 68/32 stock for different periods at 153°C. contain a progressively decreasing ratio of free sulfur to total sulfur, whereas in the other type, mentioned above, the ratio increases. As expected, heat of reaction decreases with increase of combined sulfur in the preheated compound as less sulfur and reactive sites in rubber are available for further reaction in the DTA apparatus. This is evident in Figure 4 (a–h) and also in Figure 5 (a) which shows heat evolution at different combined sulfur levels of the 68/32 stock.

Figure 5 (a) shows some interesting features. It is seen that with increasing combination of sulfur the heat of reaction first decreases at a rapid rate, then less rapidly, and finally very rapidly. The sharp fall in the beginning cannot be accounted for as due to increased combination of sulfur alone, because the difference in values of exothermic heat that might have evolved are much less than would have been expected from Figure 3 and Table II;

this means that some other reaction or reactions which absorbed heat are taking place simultaneously. It may be noted that this stage more or less coincides with what is technically known as "rotten rubber stage" in which severe deterioration of physical properties takes place and oxidative degradation reactions occur more easily. So it may be assumed that energies required for the breaking and rearrangement of linkages are absorbed and contributed to a decrease in heat liberation. In addition, the evolution of heat while preheating at 153°C. will be greater as the combined sulfur increases, because the initiation of exothermic reaction takes place at lower temperatures. In the middle portion (12–20% combined sulfur), the rate of decrease of heat evolution is slow, possibly because the breaking and rearrangement mentioned above are almost complete but not yet over. Evaluation of physical properties lends support to this assumption.[22] After about 20% combined sulfur the decrease is very rapid. An evaluation of combined sulfur (Table IV, Fig. 6) of the various stocks used for the thermographs in Figure 2 (a–h) shows that at the point where the slope begins to be steep (intersection of two slopes), the combined sulfur reaches 0.5 g.-atoms of sulfur per isoprene unit. The reaction is vigorous after this point. So, if the preheated compound already contains combined sulfur beyond this point, much heat must have been evolved during the preheating and the heat evolution in the DTA will, therefore, be correspondingly less. This explains the steep fall of the curve in Figure 5 (a) after about 20% sulfur.

It may be seen in Figure 5 (b) that a differential plot of heat evolution (stock 106) with combined sulfur shows a minimum at 15% combined sulfur. This supports the above observation that reactivity increases as the combined sulfur reaches 0.5 g.-atom of sulfur per isoprene unit. Some physical properties also show a break as the combined sulfur reaches 16%. To name a few: tensile strength, dielectric strength, power factor, and oxygen absorption. Whether this is just a coincidence cannot, however, be told until much more is known about the rubber-sulfur reaction in general and the hard-rubber reaction in particular.

At about 16% sulfur, it may be assumed that a sulfur atom is linked to every alternate isoprene molecule, leaving a double bond adjacent to a sulfur linkage. Other evidences[24] suggest that these double bonds increase in reactivity owing to the adjacent sulfur linkage; this may explain the greater reactivity above 16%.

Initiation of Exothermic Reaction

It may be seen in Table II and Figure 2 that the exothermic reaction is first observed at about 7% total sulfur, since no heat evolution in the compound containing about 5% sulfur and only a small heat evolution (5 cal./g. of mix) at 7.4% sulfur is observed. An extrapolation of the straight line in Figure 3, however, shows that heat evolution starts at about 5% sulfur. It is possible that the present method is not sufficiently accurate to measure a small amount of heat evolved at such a low sulfur combination and so no heat evolution was observed before 7% sulfur was combined. This level of combined sulfur corresponding to initiation of exothermic reaction falls within the range, 4.0–8.0, stated by other workers.[3,5,20,21]

Temperature of Initiation of Exothermic Reaction

It is noted in Table II and Figure 2 that the temperature at the initiation of exothermic reaction decreases as the sulfur composition of the stock increases from 8 to about 20%, and then remains more or less constant. This again points to the greater reactivity of the stock as the composition approaches 0.5 g.-atom of sulfur per C_5H_8·unit.

In the case of the 68/32 stock (Table III, Figure 4) the initiation temperature reaches a minimum at 130°C. as more and more sulfur is combined at the precuring stage, and then increases. This occurrence of a minimum lends support to the fact that the reactivity increases as the composition approaches 16% sulfur by weight. The increase of initiation temperature at the later stage may be explained as due to the nonavailability of reaction sites as the combined sulfur reaches the saturation point.

The steep increase of combined sulfur (decrease of free sulfur) in Figure 6 shows that, depending on the composition and period of preheating of the stock, the reaction becomes explosive after a certain temperature is reached.

Dehydrogenation Reaction

It has been mentioned earlier in this paper that at the end of the exothermic hard-rubber reaction an endothermic change, due to dehydrogenation reaction, is observed. This conclusion is borne out very well in Figure 7 which depicts the DTA thermograph of ebonite versus ebonite plus sulfur. The effects of the dehydrogenation reaction on the two types of samples used in the present investigation, A (Table II) and B (Table III) are shown

in Figure 5 (c) and (d) respectively, where free sulfur is plotted against heat evolution. Type A samples contain an increasing quantity of both free sulfur and total sulfur whereas type B samples contain a fixed quantity (32%) of total sulfur but a decreasing quantity of free sulfur. As the dehydrogenation process increases with proportion of sulfur, in type A the endothermic process will be observed only with high sulfur stocks, starting with sample No. 111 where the total sulfur (20%) is just above the critical value (18%). In type B, whose total sulfur is 32%, the endothermic process will ultimately be observed in all the samples and the extent of the endothermic process will always be higher until the identical sample (106) is reached. For this and other reasons type B samples are expected to have lower heat evolution at equal amounts of free sulfur. This expectation is borne out in Figure 5 (c) and (d).

Figure 5 (c) and (d) also shows that heat evolution occurs in two well-defined steps indicating two types of sulfur combination. Instead of a monotonous increase the curves become somewhat convex towards the free sulfur axis, suggesting that the first stage of reaction is nearing completion. Before the curve flattens out it shows an upward trend, the slope of which is larger than the initial one.· The curve of type A samples becomes convex once again, ultimately sloping downward after a maximum. The curve of type B samples is, on the other hand, concave toward the free sulfur axis, somewhat like the curve of activated adsorption.

Figure 7 shows that the endothermic dehydrogenation reaction starts at about 170°C., i.e., about the same temperature at which the exothermic reaction starts. From this we can draw either of the following two inferences: (1) that the exothermic reaction is the sum total of two opposing reactions, e.g., exothermic hard-rubber reaction and endothermic dehydrogenation reaction, and (2) that the dehydrogenation reaction starts after the sulfur combining by the exothermic reaction is complete—that is, only when excess sulfur is present in the ebonite (Figure 7 corresponds to ebonite and sulfur as active mass)—and as such does not have much effect on the measured heat of the exothermic reaction. In order to arrive at a conclusion regarding this we estimated the total sulfur of the 68/32 (106) stock, heated to various temperatures in the DTA. The results show about 29% sulfur at 160°C., which goes down to about 26% at 210°C. This shows that dehydrogenation and the exothermic reaction proceed simultaneously.

However, it does not substantially affect our determination of the heat of hard-rubber reaction: a similar loss of total sulfur was observed in the reference sample (ebonite), which means that the endothermic reactions virtually cancel one another in high sulfur mixes. If the stock contains sulfur lower than 18%, where the dehydrogenation reaction is negligible, the results are expected to be vitiated. The linear fit in Figure 3 shows that this does not occur to a great extent. A difference in the thermal characteristics of the reference and active mass is, however, observed in Figure 2 (a–h) in that the base line moves higher after the reaction; this may be attributed to the dehydrogenation in the reference sample. It may be mentioned that the temperature inside the reacting mass must be much higher than that indicated by the thermometer, and that a higher temperature aids the dehydrogenation reaction.

When the 68/32 mix was vulcanized in a platen press at 153°C. for 6 hr. a much smaller loss of sulfur (about 4% less) was obtained. This may be due to the lower vulcanization temperature than in the DTA and also to the smaller temperature rise in the mass of the sample because of better heat exchange with metal platens.

The end product after the DTA experiment thus differs a little from that obtained by press curing. However, the present method will give an approximate measure of the heat liberation at different compositions and will also be useful in the study of the influence of various additives on the exothermic reaction. The latter aspect of the work is well under progress and will be reported on later.

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Synopsis

A method for the determination of heat of hard-rubber reaction by the application of differential thermal analysis is reported. The heat of reaction was determined with stocks containing different rubber/sulfur ratios and also with a 68/32 stock, preheated to contain different amounts of combined sulfur. Heat evolution is observed first with samples containing about 7% sulfur and therefrom the amount of heat evolved shows a nearly linear increase up to 30% sulfur. With increasing combined sulfur in the 68/32 stock, the quantity of exothermic heat gradually diminishes; so also does the temperature of initiation, i.e., the temperature at which heat evolution appears to begin. Initiation of exothermic reaction appears to be a function of composition and temperature of the mass. An increase in the rate of reaction was observed when the composition reached 0.5 g.-atom of sulfur per isoprene unit. An endothermic dehydrogenation reaction is observed at the end of the hard-rubber reaction. This, however, does not affect the determination of exothermic heat, because there is similar dehydrogenation taking place in the reference material (ebonite) which almost balances this heat loss. The final product has a lower sulfur content due to loss of sulfur as hydrogen sulfide.

Résumé

On décrit une méthode pour déterminer la chaleur de réaction du caoutchouc dur par l'application de DTA. La chaleur à réaction a été déterminée avec des échantillons contenant différents rapports soufre-caoutchouc et aussi avec un échantillon 68/32 préchauffé, contenant différentes quantités de soufre combiné. Le dégagement de chaleur est observé d'abord avec un échantillon contenant environ 7% de soufre et on constate ensuite que la quantité de chaleur dégagée augmente presque linéairement jusqu'à une teneur en soufre de 30%. Avec l'augmentation du soufre combiné dans l'échantillon 68/32, la quantité de chaleur exothermique diminue graduellement, ainsi que la température d'initiation, c.à.d. la température à laquelle le dégagement de chaleur semble commencer. L'initiation de la réaction exothermique semble être une fonction de la composition et de la température de la masse. On observe une augmentation de la vitesse de réaction lorsque le teneur en soufre atteint 0.5 atome-gramme par unité isoprénique. On observe une réaction de déshydrogénation endothermique à la fin de la réaction de vulcanisation du caoutchouc dur. Ceci, dependant, n'affecte pas la détermination de la chaleur exothermique parce qu'une réaction semblable de déshydrogénation a lieu dans le matériel de référence (ébonite) qui compense à peu près cette perte de chaleur. Le produit final, a une teneur en soufre plus faible par suite de la perte de soufre sous forme d'hydrogène sulfuré.

Zusammenfassung

Eine Methode zur Bestimmung der Reaktionswärme der Hargummibildung durch DTA wird beschrieben. Die Reaktionswärme wurde an Proben bestimmt, die ein verschiedenes Kautschuk/Schwefel-Verhältnis besassen, und auch an einer 68/32-Probe, deren Gehalt an gebundenem Schwefel durch Hitzevorbehandlung variiert wurde. Die erste Wärmeentwicklung wird bei einer Probe mit ungefähr 7% Schwefel beobachtet; die entwickelte Wärmemenge steigt von hier nahezu linear bis zu einem Schwefelgehalt von 30%. Mit steigender Bindung des Schwefels in der 68/32-Probe nimmt die exotherme Wärmemenge graduell ab; ebenso nimmt die Starttemperatur ab, das ist die Temperatur, bei der die Wärmeentwicklung beginnt. Der Start der exothermen Reaktion scheint eine Funktion der Zusammensetzung und Temperatur der Masse zu sein. Erreicht die Zusammensetzung einen Wert von 0,5 Grammatomen Schwefel pro Isopreneinheit, so wird ein Ansteigen der Reaktionsgeschwindigkeit beobachtet. Am Ende der Hartgummibildung wird eine endotherme Dehydrierungsreaktion beobachtet. Dadurch wird aber die Bestimmung der exothermen Wärme nicht beeinträchtigt, weil beim Bezugsmaterial (Ebonit) eine ähnliche Dehydrierung stattfindet, die diesen Wärmeverlust weitgehand ausgleicht. Das Endprodukt besitzt einen geringeren Schwefelgehalt, da Schwefel als Schwefelwasserstoff verlorengeht.