

NOTES

Application of Differential Thermal Analysis in Hard Rubber Reactions

The method of differential thermal analysis (DTA) has been applied in quite a large number of fields in recent years for studying the processes which a substance undergoes on heating.¹ The differential thermograph is commonly used to determine if a reaction or transition occurs and the temperature at which it takes place. It can also be applied for an approximate measure of the heat of reaction by determining the area under the curve in the DTA thermograph.

The method of DTA thus provides us with a suitable tool for determining (1) the initiation temperature of the exothermic hard rubber reactions, (2) the approximate heat of hard rubber reactions, (3) the effect of accelerators and other compounding ingredients on (1) and (2), and other related information. Systematic investigations have therefore been undertaken in this laboratory to elucidate the above points by using a modified version of Bourchardt's DTA apparatus,² designed and fabricated in our laboratory. The use of DTA in ebonite reactions has not been made until now, and the methods adopted earlier for obtaining the above information are based on either uncertain reaction conditions or assumptions, and contradictory values have been reported in the literature.³⁻⁹

Figure 1 represents the nature of the curves obtained by us by using as active material a rubber-sulfur (68:32) compound precured to different extent in a press at 153°C., ground, and sieved below 100 mesh. A sample of fully cured ebonite, ground sieved to the same size, and acetone-extracted, was used as the reference material. It may be seen that as the time of precure is increased the peak temperature and also the area under the curve decreases. This is presumably due to the fact that as the time of precure is increased, more and more of the rubber and sulfur remain in a combined form and only the residual active sites in the rubber and sulfur (which are still free) are available for reaction in the DTA.

Two endothermic changes are also observed at 100 and 115°C. which are due to the enantiomorphous change of α - to β -sulfur, and its subsequent melting. Besides these transitions and the main exothermic hard rubber reaction there is also an endothermic change at the end of the reaction beginning at about 200°C., accompanied by evolution of H₂S. This may be due to a dehydrogenation reaction of ebonite by sulfur at high temperature. This conclusion is further confirmed by our results in Figures 2A and 2B which show endothermic change of sulfur only at the temperature ranges mentioned above, when S-alumina and alumina are taken as active and reference material, respectively, but exhibits another large endothermic change at about 160°C. when sulfur-ebonite and ebonite dust itself are taken as active and reference material, respectively.

The results of our experiments show that for a 68:32 rubber-sulfur compound, precured for 1 hr. at 153°C. in a press

so as to contain 4.46% combined sulfur initially, the exothermic reaction starts at about 183°C. and this temperature decreases as the precured compound contains more and more combined sulfur. The heat of reaction obtained from

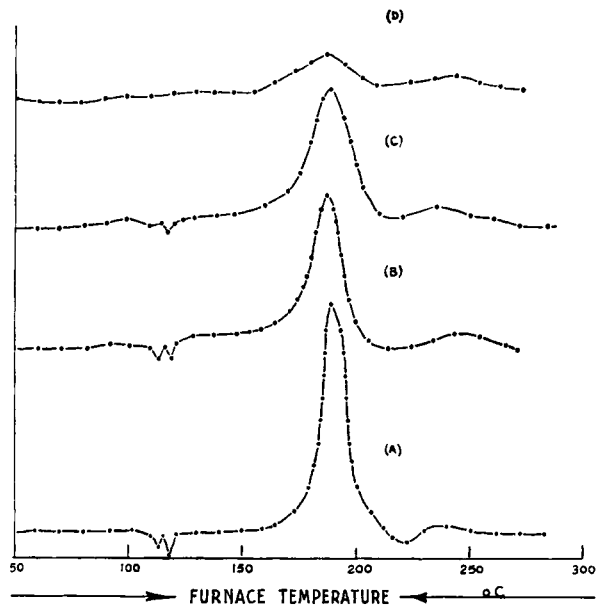


Fig. 1. Effect of combined sulfur on heat of reaction of 68/32 rubber-sulfur compound: (A) precure: 1 hr. at 153°C. active material: 0.1898 g.; (B) precure: 2 hr. at 153°C., sample: 0.2629 g.; (C) precure: 3 hr. at 153°C. active material: 0.2502 g.; (D) precure: 4 hr. at 153°C. active material: 0.2646 g.

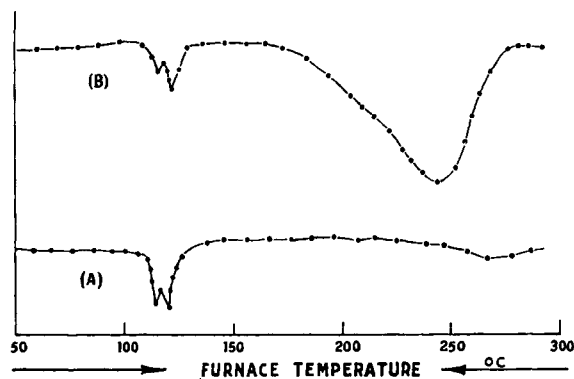


Fig. 2. (A) Active material: sulfur in Al₂O₃ (0.2028 g.), reference material: Al₂O₃; (B) active material: sulfur in ebonite dust (0.1016 g.), reference material: ebonite dust.

this compound is 147 cal./g. of the mix, the thermograph being calibrated from the known heat of reaction of dehydration of copper sulfate:



$$\Delta H_{298} = 54.3 \text{ Kcal./mole}$$

The DTA method thus promises to throw new light on the hard rubber reaction. Detailed results will be published later on.

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The Infrared Spectrum of Cyclized Natural Rubber and Its Retention of Solvents

Recently published infrared spectra¹ of cyclized rubber differ from those previously published,²⁻⁴ and it has been suggested that the strong band at $\sim 800 \text{ cm.}^{-1}$, which increases in intensity with increase in cyclization, is diagnostic for cyclization in rubber. Although it was recognized that this band was in the same region as the C—Cl stretching frequency, such an assignment was dismissed, since no direct chlorination of the polymer was involved in the cyclization process.

Working with rubbers cyclized in benzene by stannic chloride, we have shown that the band at $\sim 800 \text{ cm.}^{-1}$ does not arise from cyclized rubber but is in fact a C—Cl band of the solvent used to prepare the films from which the spectra were obtained.

A film cast from a dilute solution of carbon tetrachloride in benzene gave a spectrum with a doublet at 788 and 768 cm.^{-1} ; a dilute solution of carbon tetrachloride in carbon disulfide showed a doublet at 789 and 767 cm.^{-1} . The ratio of the intensities of the doublet in each case was the same.

Films cast from nonchlorinated solvents show weak bands characteristic of the solvent, these bands are absent when the spectrum is obtained by the potassium bromide disk method,

TABLE I
Solvent Retention of Films Less than 0.2 mm. Thick of a Cyclized Rubber Cast from Various Solvents at Atmospheric Pressure and Room Temperature and Pumped for 3 hr. at 25°C. and 100°C. at 0.5 mm. Hg

Solvent	Molecules solvent retained per 100 moles of C_5H_8 units in polymer	
	25°C.	100°C.
CCl_4^a	13.42	8.55
CHCl_3	9.77	1.64
CH_2Cl_2		0.1
CH_3CHCl_2	7.76	2.89
$\text{CH}_2\text{CICH}_2\text{Cl}$	9.75	5.54
$\text{CHCl}_2\text{CHCl}_2$	13.1	
$\text{CHCl}=\text{CHCl}$	4.31	4.1
$\text{CCl}_2=\text{CCl}_2$	3.8	6.17
CBr_4		2.05
CHBr_3	11.7	8.3
CH_2Br_2	10.5	7.3
C_6H_6	2.3	
CS_2	1.84	

* After 24 hr. at room temperature and atmospheric pressure, solvent retention for CCl_4 , 19.75; after 3 days at 20°C., and 10^{-4} mm. Hg, 17.75; after 5 hr. at 155°C. and 10^{-4} mm. Hg, 4.56.

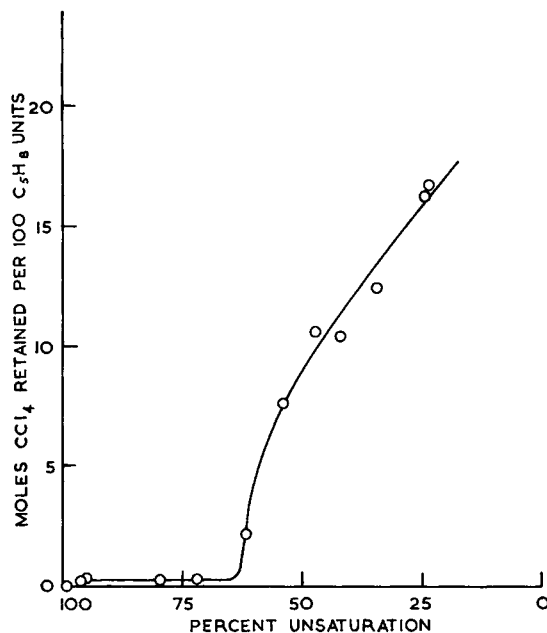


Fig. 1. Dependence of solvent retention by films of cyclized rubber on their unsaturation.

and in both cases no band is observed at $\sim 800 \text{ cm.}^{-1}$. A film cast from carbon disulfide has a band at 1515 cm.^{-1} , i.e., in the same position as a band characteristic of carbon disulfide.

Table I shows that the retention of solvent by cyclized rubber films is not confined to carbon tetrachloride, and furthermore that it is not due to attachment of solvent frag-