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THERMOANALYTICAL METHODS IN VULCANIZATE ANALYSIS. DIFFERENTIAL SCANNING CALORIMETRY. OBSERVATIONS ON THE VULCANIZATION PROCESS*

D. W. BRAZIER

Dunlop Research Centre,
Sheridan Park Research Community,
Mississauga, Ontario (Canada)

ABSTRACT

Differential scanning calorimetry was used to follow the unaccelerated and accelerated sulfur vulcanization process in natural rubber and polybutadiene compounds. It was established that in both hard and soft rubber vulcanization, the heat of vulcanization (ΔH_v) depends only on the sulfur concentration provided other ingredients (carbon black, zinc oxide, stearic acid) and the elastomer blend ratio remain constant. Organic accelerators alter the temperature dependence of the exotherm but have no effect on ΔH_v over a considerable concentration range.

The DSC exotherm was used to determine variations in sulfur/accelerator concentrations in production compounds. Analysis time is short—approx. 5 min—and a routine quality control method is suggested.

INTRODUCTION

The development of cure in resins and elastomers is generally monitored by following some physical property (e.g., viscosity, modulus, hardness) as a function of state of cure. Recently, considerable attention has been given to the use of isothermal and scanning calorimetry for determining cure in resins[1] but little attention has been paid[2] to elastomer curing or as more often termed—vulcanization. The purpose of this paper is to show how DSC can be used to monitor the cure characteristics of sulfur vulcanized elastomers and further, how DSC can be utilized as a rapid quantitative analytical method for determination of the concentration of cure ingredients. The objective was to determine curative concentrations on a time scale consistent with routine quality control.

For discussion, the DSC studies are divided into two parts. Results obtained for the unaccelerated sulfur vulcanization of natural rubber (hard rubber or ebonite vulcanization) are considered first and compared to literature results obtained by other thermal methods. The studies are then expanded to typical accelerated

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sulfur cures for elastomeric products and the analysis of production compounds considered.

EXPERIMENTAL

Materials and compounding

All materials used were of commercial grade as used in manufacture, and no special purification procedures were adopted. All laboratory stocks were prepared from natural rubber (No. 1 RSS) and polybutadiene (Taktene 1220). Two forms of sulfur were used, regular powdered sulfur and oiled Crystex (80% sulfur in oil). Commercial accelerators are identified in the text as follows: 2-benzothiazyl disulfide (MBTS), 2-mercaptobenzothiazole (MBT), (2-morpholinothio)benzothiazole (MOR).

Laboratory samples were compounded on either a 3×8 or 6×12 in. mill, following ASTM standard procedure D-15, *Compound and Sample Preparation for Physical Testing of Rubber Products*[3]. Because of the small sample size used in DSC, good dispersion is imperative so that the sample is representative of the total stock. All factory compounds studied were regular production Banbury mixes.

DSC

Throughout this work, a DUPONT 990 thermal analyzer with either a DSC base IA or II was used. All samples were run in standard hermetic sealed cups and a nitrogen atmosphere to prevent sulfur reaction with the silver components of the cell.

Some difficulty was experienced with sample preparation because of the nerve of the uncured rubber stocks which often prevented good sample–sample pan contact. Several procedures were evaluated (sample compressed between foil, addition of glass beads, etc.) however, the following procedure was adopted. After cooling, a cylinder was bored from the batch using a sharp 3 mm ID cork borer. Discs of the required size (10–20 mgs) were then razor cut and pressed into the sample cup. Duplicate runs were made with samples cut from various positions in the batch to ensure uniformity in mixing.

All areas were measured by planimetry and converted to heats using indium, tin and zinc as calibrants.

Hard rubber vulcanization

The thermochemistry of unaccelerated sulfur vulcanization of natural rubber has been extensively studied. As early as 1902, Weber[4] reported that spontaneous vulcanization of natural rubber with sulfur could not occur because of the low heat of reaction. Experimental methods used to determine the heat of vulcanization (hereafter ΔH_v) include derivation from heats of combustion of vulcanizates[5–7], calculation from temperature rises in compounds undergoing isothermal vulcanization[8–12], isothermal calorimetry[13–15] and DTA[16–19]. Agreement in reported values for ΔH_v is poor, as illustrated in Fig. 1 where several literature values have been recalculated to units of J g^{-1} vulcanizate.

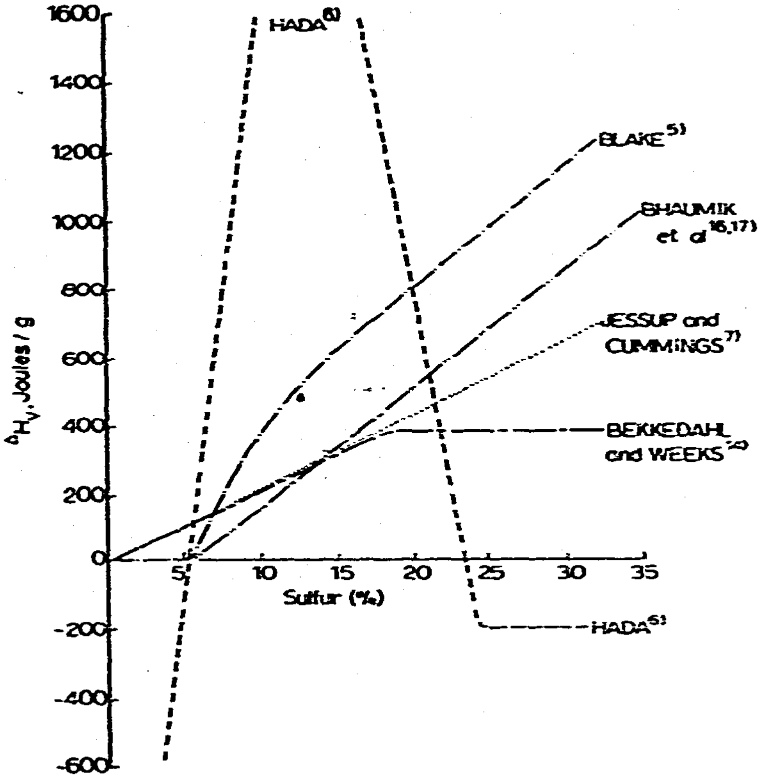

Fig. 1. Literature values for ΔH_v dependence on combined sulfur concentration. Values recalculated to J per g of vulcanizate for comparison.

Figure 2 illustrates a typical cure exotherm for natural rubber–sulfur as observed in the DSC. The derivative of the DSC curve is simultaneously recorded. Baseline shifts with the natural rubber–sulfur system present no problems, the observed difference before and after cure being consistent with specific heat changes on vulcanization. Although the specific heat of natural rubber increases with temperature (0.17%/°C[20]), sulfur vulcanizates decrease in specific heat as the combined sulfur content increases. At 90 °C, the combined sulfur dependence on vulcanizate specific heat in J g^{-1} °C^{-1} can be calculated from the relationship[14]

$$S_{90} = 2.156 - 0.478(X)$$

where X is the combined sulfur (sulfur atoms/isoprene unit). For the highest sulfur levels used here—X = 0.85—and assuming a similar dependence of specific heat at higher temperatures, a reduction of ~19% in specific heat as vulcanization proceeds can be anticipated. At a scan rate of 20 °C min^{-1} the vulcaniza-

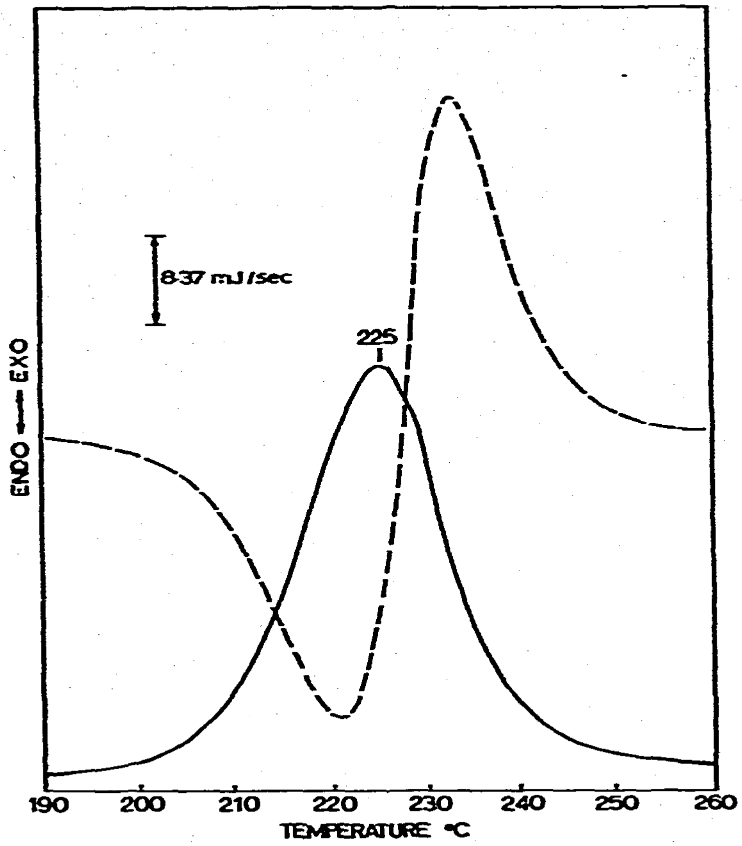

Fig. 2. DSC exotherm for natural rubber–sulfur (10 parts per hundred rubber). 20 °C min^{-1} scan rate.

tion exotherm is observed over a 70 °C range, which corresponds to approximately a 12% decrease in specific heat of the natural rubber. We conclude, therefore, that the observed baseline shifts are consistent with specific heat changes on vulcanization for the hard rubber system.

In Fig. 3, the values of ΔH_v are shown as a function of combined sulfur content. In this work, we have made the assumption that by the end of the exotherm, the combined sulfur is equivalent to the added sulfur and that no free sulfur remains in the compound. This was found to be the case in the DTA work of Bhaumik et al.[16], who analyzed their somewhat larger samples for free sulfur as a function of distance along the exotherm. Further evidence that all sulfur has been utilized is found in the observation that on rescanning, no further exotherm is observed. Included in Fig. 3 for comparison are the isothermal results of Bekkedahl and Weeks[14].

A linear dependence of ΔH_v on the sulfur concentration is apparent from Fig. 3. However, the plot does not pass through the origin. This could be accounted for by experimental error but may also indicate a contribution to the observed exotherm from processes other than vulcanization. Sulfur is the only ad-

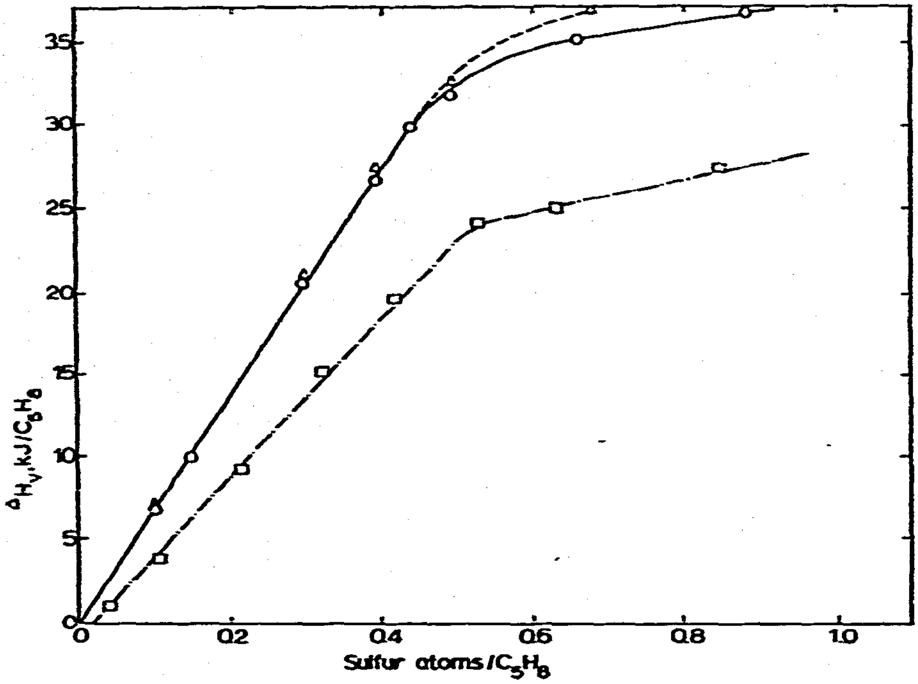

Fig. 3. Heat of vulcanization dependence on sulfur concentration in unaccelerated natural rubber vulcanization. □, Present results 20 °C min^{-1}; ○, isothermal calorimetry 25 °C[14]; △, isothermal calorimetry 155 °C[14].

ditive in the hard rubber reaction. Elemental sulfur (rubber grade) shows three endothermic events when scanned in the DSC at 20 °C min^{-1}. These transitions and their enthalpies are 111 °C rhombic–monoclinic transition (10.6 J per g of S), 123 °C melting monoclinic sulfur (42.6 J g^{-1}), and 182 °C λ–π liquid–liquid transition (12.2 J g^{-1}). We assume in all our work that sulfur is in the liquid state at vulcanization temperatures. The small enthalpy of the λ–π transition has a negligible effect on the exothermic ΔH_v peak.

The cause of the break in the curve at about 0.45 sulfur/C_5H_8 (18 % sulfur) is not clear. The glass transition of natural rubber with 18 % combined sulfur is 25 °C[21]. However, this is not considered the cause because similar breaks are observed in isothermal vulcanization at 155 °C and the present work at 160–220 °C. The most likely explanation appears to be that a change in the mechanism occurs at this sulfur level. A similar break is observed at all scan rates used in this work (2–50 °C min^{-1}). In an earlier publication[2] we reported ΔH_v as dependent upon scan rate. However, recent work with the cell base II has given results in which ΔH_v is virtually independent of scan rate from 2 to 20 °C min^{-1} and then falls off at higher scan rates.

It is not intended to discuss in any detail the complex chemistry of the sulfur vulcanization process. For our purpose we can consider sulfur vulcanization to be a series of simultaneous and consecutive reactions leading to a variety of sulfidic structures (cyclic sulfide, polysulfides, disulfides, etc.). Figure 4 illustrates the typical structure of a natural rubber–sulfur vulcanization[22]. The observed ΔH is the sum of the heat of formation of types of sulfidic structures. Further, it is known that such structures mature with time and temperature and since relatively high temperature are used in DSC studies, ΔH_v probably contains a contribution from maturation processes. Vulcanization is thus very complex compared to resin cures where stoichiometric reactions between known reactive centres occur.

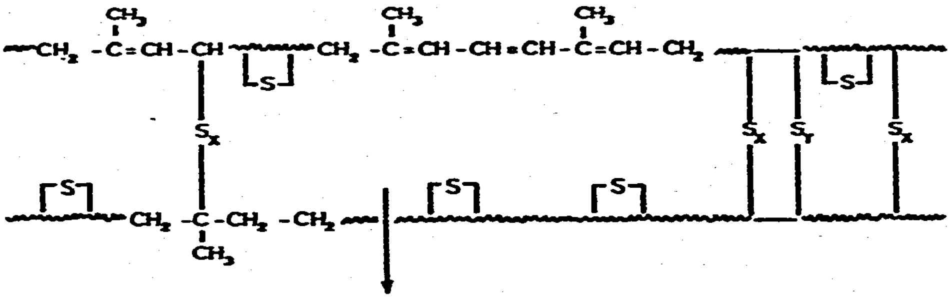

Fig. 4. Typical structure of sulfidic products in unaccelerated natural rubber vulcanization[22].

Kinetic analysis of the dynamic DSC exotherms is thus expected to give little useful information. Typical results obtained using the approach of Crane et al.[23] are shown in Fig. 5 for a natural rubber compound with 10 parts per hundred sulfur. Significant departure from linearity is apparent at the beginning and end of vulcanization. From the linear sections we estimate an overall activation energy of ~250 kJ mol^{-1} and an order of reaction of ~1.5.

Accelerated sulfur vulcanization

Commercial elastomeric products are generally vulcanized with 1–2% by weight sulfur in the presence of an organic accelerator. From the hard rubber results, ΔH_v at these sulfur levels will be in the range 5–20 J per g of vulcanizate. Table 1 contains formulations of typical tire compounds which will be analyzed for sulfur and accelerator in the last section. These compounds, based on natural rubber–polybutadiene blends, contain carbon black, stearic acid, zinc oxide and other ingredients as well as the sulfur–thiazole accelerator cure system. Before ΔH_v can be used for the quantitative determination of sulfur content, the effect of each additive on ΔH_v must be determined.

(a) Effect of accelerators. Organic accelerators are used in vulcanization for two main reasons—they increase the rate of sulfur combination and increase the efficiency of sulfur utilization. The accelerator is used in conjunction with stearic acid and zinc oxide, and the latter play an important role in the overall vulcanization mechanism through the formation of a complex. The mechanism is com-

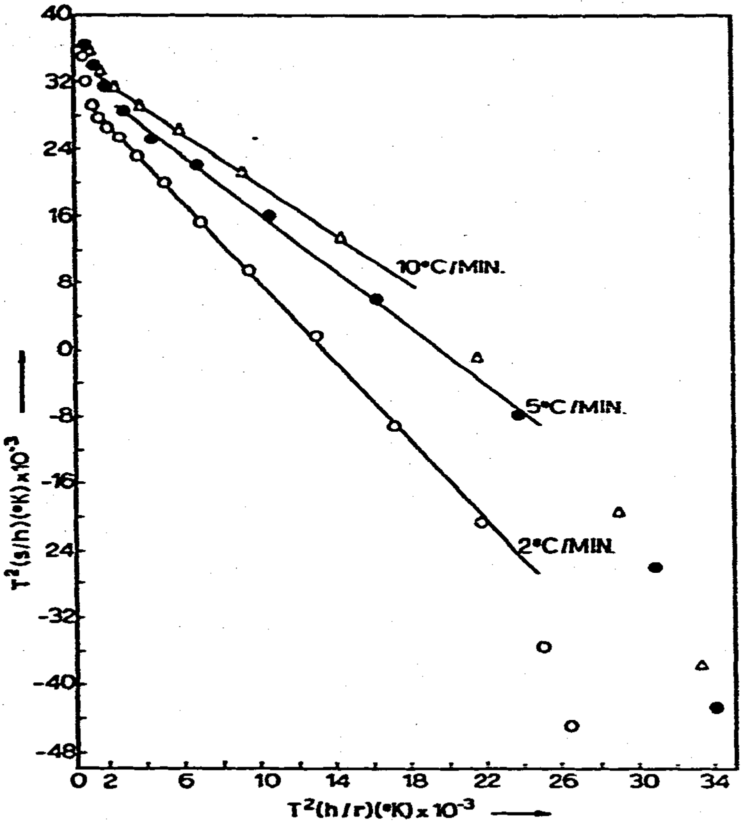

Fig. 5. Kinetics of unaccelerated vulcanization of natural rubber–sulfur (10 parts per hundred rubber). Treatment[23] given in Appendix.

TABLE I

COMPOUND FORMULATIONS—TYPICAL TIRE COMPONENTS IN PARTS PER HUNDRED RUBBER

Compound	*A*	*B*	*C*
Natural rubber	80	80	60
Polybutadiene	20	20	40
Carbon black	50[a]	50[a]	55[b]
Stearic acid	3	1.8	2.5
Zinc oxide	3	3	3
Antioxidant	3	—	2.25
Oil/plasticizer	17	11.5	16
Bonding agent	—	2.7	—
Sulfur	2.2[c]	2.2[c]	1.5
Accelerator (MOR)	1.2	1.2	1.0
Inhibitor	—	—	0.3

[a] N326 (HAF-LS) carbon black. [b] N339 carbon black. [c] Added as 2.75 phr oiled Crystex (80% sulfur in oil).

plex and is reviewed in several texts[22-24]. From our point of view, the major effect on vulcanization, apart from an increased rate, is the change in distribution of various sulfidic products (Fig. 4) brought about by the presence of accelerator. The actual distribution is dependent upon the type of accelerator and the sulfur–accelerator ratio.

Table 2 summarizes the characteristics of DSC exotherms obtained with several thiazole accelerators in a natural rubber–carbon black compound. The three temperatures T_0, T_p and T_c are the onset temperature, the peak temperature and the return to base temperature, respectively. Table 2 also contains data obtained by varying sulfur and accelerator in Compound A, Table 1. These data provide a calibration plot to be used in later analysis. Also included in Table 2 are rheometer data at 150 °C on the same compounds. The rheometer is extensively used to assess cure characteristics.

TABLE 2

EFFECT OF THIAZOLE ACCELERATORS ON DSC VULCANIZATION CHARACTERISTICS

Formulation: natural rubber 100, HAF-LS 50, zinc oxide 5, stearic acid 3, sulfur 2, accelerator 1.2

Accelerator	T_0 (°C)	T_p (°C)	T_c (°C)	ΔH_v (J g^{-1})
None	192	222	245	9.4
MBTS	168	201	238	6.6
MBT	168	201	240	7.4
MOR	164	193	218	7.2

Formulation: Compound A Table 1

Sulfur variation—MOR constant 1.2 phr

Sulfur, phr	1.20	1.68	2.24	2.80	3.36
ΔH_v (J g^{-1})	5.02	7.45	11.25	13.43	18.36
T_p (°C)	207	207	207.5	207.5	207
Rheometer, 150 °C:					
t_s(2), min.[a]	6.5	6.0	5.5	5.5	5.0
t_c (90%), min[b]	11.5	11.0	11.5	11.5	11.0
ΔM in lb.[c]	28	41	40	43	57

MOR variation—sulfur constant 2.24 phr

MOR, phr	0.4	0.8	1.2	1.6	2.0
ΔH_v (J g^{-1})	10.75	10.88	11.25	10.88	11.25
T_p (°C)	221	210	207	205	203
Rheometer, 150 °C:					
t_s (2), min[a]	5	6	6	6	5
t_c (90%), min[b]	17	13	12	10	9
ΔM in lb.[c]	34	39	42	44	43

[a] Time to 2 in.lb. rise after minimum viscosity. [b] Time for 90% of ΔM to be developed. [c] ΔM difference in initial and final viscosity.

The addition of thiazole accelerators generally reduces ΔH_v compared to the unaccelerated compound. However, the minimum addition (0.4 phr in this work) results in the reduction and further addition has no effect on ΔH_v. At a scan rate of $20\,^{\circ}\mathrm{C\,min^{-1}}$ the cure exotherm is observed at lower temperatures in the presence of accelerator. However, the total temperature range over which vulcanization is observed remains the same as the unaccelerated compound or is increased.

The observation that ΔH_v is unaffected by the concentration of accelerator above a certain minimum means that ΔH_v can be used for sulfur determination. An estimation of the accelerator level comes from the observed T_p value. T_p depends upon accelerator concentration in a non-linear manner. For MOR (see Table 2) at the 1–2 phr level, the rate of reduction in T_p is 10 °C/phr MOR. Reproducibility in T_p is $\pm 0.5\,^{\circ}\mathrm{C}$ allowing a ± 0.1 phr variation in MOR to be determined. MBTS at the same level yields a T_p dependence of 6 °C/phr MBTS.

(b) Effect of stearic acid/zinc oxide. Table 3 contains data on the effect of stearic acid and zinc oxide on the DSC exotherm of an unaccelerated natural rubber–carbon black compound.

TABLE 3

EFFECT OF STEARIC ACID AND ZINC OXIDE ON NATURAL RUBBER VULCANIZATION EXOTHERM

Formulation: phr natural rubber 100; sulfur 2; HAF-LS carbon black 50.

Zinc oxide	*Stearic acid*	ΔH_v *(J per g of vulcanizate)*	T_o (°C)	T_p (°C)
5	0	8.62	194	221.5
5	3	6.44	194	221.5
5	5	6.44	194	221.5
0	3	7.78	198	226.0
1	3	5.73	196	222.5
3	3	5.85	196	222.0
8	3	9.71	195	220.0

The addition of a low level of stearic acid reduces ΔH_v but further addition has no effect. T_o and T_p are unaffected by stearic acid. Addition of ZnO also reduces ΔH_v but further addition after ~3 phr, then increases ΔH_v. Most commercial compounds have 3–5 phr ZnO and ΔH_v increases by approx. 0.5 J per g of vulcanizate over this range. Since this could be of the same order of magnitude change produced in ΔH_v by 0.08 phr sulfur, it is necessary to determine ZnO levels in all compounds. A rapid method for determining ZnO based on derivative thermogravimetric analysis (DTG)[25] as suggested by Maurer[26] was developed and will be described in the succeeding paper.

T_p also exhibits a small dependence on ZnO concentration indicating the role of ZnO as a mild accelerator. The magnitude of T_p reduction is small (0.25 °C/phr ZnO in the 3–5 phr range) and can be neglected compared to the effect of accelerators on T_p. In compounds containing thiazole accelerators, no dependence of T_p on ZnO concentration was observed experimentally.

(c) Effect of carbon black. The addition of carbon black to a compound results in the reduction of ΔH_v. In this work, only the effect of HAF–LS carbon black was investigated. Figure 6 illustrates ΔH_v as a function of carbon black loading in an MBTS accelerated natural rubber compound. ΔH_v reduced rapidly as black is added and reaches a plateau at about 60 phr carbon black when expressed in terms of J per g of vulcanizate. The alternate plot with ΔH_v in units of J/C_5H_8 shows about a 50% reduction in ΔH_v at the 50 phr carbon black level. Similar results were obtained by Bruce et al.[27] who found a 30% reduction in ΔH_v when Micronex carbon black was added at 50 phr to a sulfenamide accelerated system. Recent work in the laboratory has shown the reduction to be dependent both on the accelerator and type of carbon black used.

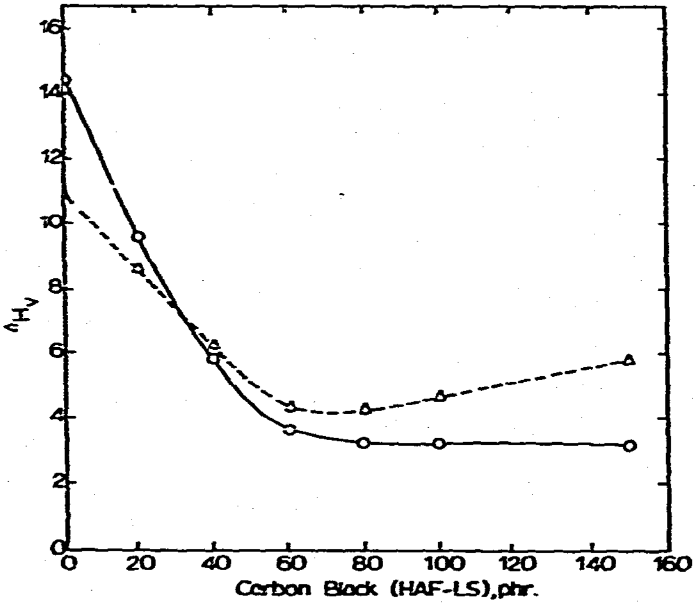

Fig. 6. Dependence of heat vulcanization on carbon black level. Formulation: NR 100, ZnO 5, stearic acid 3, sulfur 2, MBTS 0.5. O, in J per g of vulcanizate; Δ, in 10^{-2} J/C_5H_8.

Most commercial formulations contain at least 50 phr carbon black and the plateau in ΔH_v is approached. For the MOR accelerated compounds in Table 1, we found that at the levels of carbon black used ΔH_v was falling at a rate of ~0.05 J/phr carbon black. Clearly batch to batch analysis of carbon black concentration is required as in the case of zinc oxide.

(d) Variation in blend ratio. A limited study of the variation of ΔH_v with natural rubber/polybutadiene blend ratio was undertaken and the results are given in Table 4. The exothermicity of polybutadiene is more than twice that of natural rubber. For the blends of interest to us, i.e., 80:20 and 60:40 natural rubber:polybutadiene, a significant error in the ratio is necessary to affect ΔH_v. Nevertheless, large variations can occur and the blend ratio was always checked using the DTG technique[25].

TABLE 4

EFFECT OF NR:BR RATIO ON ΔH_v

Formulation: NR and BR as shown; HAF-LS 50, zinc oxide 5, stearic acid 3; sulfur 1.5, MOR 1.0

Ratio NR:BR	*100:0*	*80:20*	*60:40*	*0:100*
ΔH_v (J g^{-1})	5.8	6.2	7.1	13.1
T_p (°C)	196	202	204	218
Rheometer 150 °C:				
t_s (2) min	4.8	5.8	6.5	7.5
t_c (90%) min	10.0	11.5	12.0	22.0
ΔM in. lb.	42	43	44	44

Analysis of production compounds

Our objective has been to determine whether DSC offers a rapid approach to the assessment of the cure characteristics and curative levels of production mixes. DSC scans were run on 20 consecutive mixes of the compounds shown in Table 1 and typical scans are shown in Fig. 7.

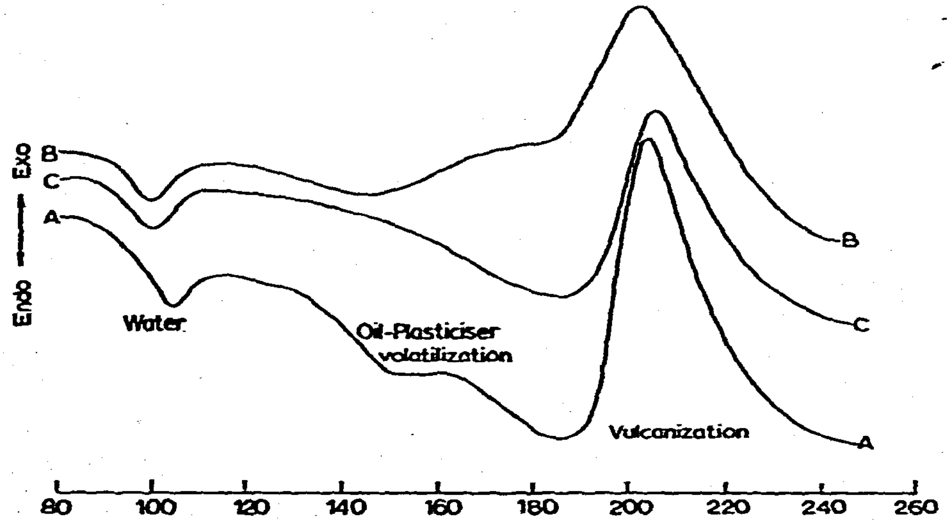

Fig. 7. Typical DSC scans of production compounds A, B, and C, Table 1.

Three distinct events are apparent in the scans. The first centred at ~102°C corresponds to the loss of water from the compound. The endotherm appears quite large because of the high heat of volatilization of water (2.26 kJ g^{-1}) and the peak corresponds to less than 1 percent water in all cases. Immediately after mixing, laboratory compounds did not show this water endotherm, although it did appear in aged laboratory compounds. The endothermic events between 100 and 160 °C are believed to be related to additives other than the cure system, e.g., volatilization of oils, plasticizers, and antidegradants. These events are not present in simple accelerated sulfur compounds of natural rubber. The third event is the actual vulcanization exotherm.

Establishing the baseline for the compounds containing oil and plasticizer presents a problem. Acetone extraction of the compound would remove sulfur as well as the oil. Further, any pretreatment of the sample results in increased experimental time. The procedure adopted has been to determine T_o and T_c for a control compound and use the intercept of these values with the scan to construct the baseline. For Compound C for example, T_o was 186 °C and T_c 248 °C. Our interest is only in the vulcanization exotherm and the sample was scanned from 150 to 250 °C at 20 °C min^{-1} for a test time of 5 min. Using several DSC cells and one cell base, cool down time was eliminated.

Results obtained on consecutive mixes of compounds B and C—Table 1 are summarized in Table 5. The results are expressed as the percentage of batches within the stated limits of the nominal sulfur and accelerator loading. Results have been corrected for any variation in ingredients which affect ΔH_v. Using the DTG method, a maximum variation for Compound B of ±4 phr in NR with 75% of the samples falling within ±1.5 phr; the BR variation was ±2 phr. For Compound C, the values were ±2 phr for both NR and BR. A variation of ±2 phr in carbon black content was found for the B series, except for one batch which was high in carbon black by 10 phr because of a low NR content. Throughout the C series, carbon black levels were within ±2 phr. Oil content varied by ±0.5 wt.% throughout both series of compounds.

TABLE 5

SULFUR LEVEL VARIATION CALCULATED FROM ΔH_v. PRODUCTION COMPOUNDS

Compound	*Sulfur content calculated from* ΔH_v	*% Batches within limits*	T_p *(°C)*
B (Table 1)	2.20±0.05	42	198–203
(nominal	±0.08	85	(All ±0.15 of
2.2 phr)	±0.15	100	nominal)
C (Table 1)	1.50±0.05	40	209–211
(nominal	±0.10	60	
1.5 phr)	±0.15	85	
	±0.30	100	

Cure development was also monitored at 150 °C using the rheometer and a good correlation found between both rheometer cure rate and level of cure and the sulfur–accelerator levels calculated from the DSC exotherm.

CONCLUSIONS

We have shown that the vulcanization characteristics of elastomers can be rapidly determined using DSC. Although vulcanization is chemically a very complex process, the DSC exotherm provides quantitative information on the curative compositions. The observation of a DSC exotherm is characteristic of all sulfur curable elastomers. The effects of other ingredients in the formulation of the exotherm have been determined and it is hoped that this approach will provide further information on the actual reactions occurring during vulcanization. Kinetic analysis of accelerated sulfur systems is expected to be simpler than the unaccelerated system, however, considerably more work is needed before useful kinetic data are available. In the meantime, the DSC thermogram provides an alternate method for rapid quality control analysis of elastomer mixes for the rubber industry.

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APPENDIX

Several analytical methods for determining kinetic constants from the dynamic vulcanization exotherm were attempted; however, the method of Crane et al.[23] is currently being used. The basic expression developed is

$$\left[\frac{\mathrm{d}^2 Hp/\mathrm{d}T^2}{\mathrm{d}Hp/\mathrm{d}T}\right] T^2 = \left(\frac{E}{R}\right) - \frac{nT^2}{(1-x)\Delta Hp}\left(\frac{\mathrm{d}Hp}{\mathrm{d}T}\right) \tag{1}$$

where ΔHp is the total heat of vulcanization and x is the fraction of vulcanization at temperature T. The first and second derivatives of Hp with respect to time are read directly from the DSC and DSC curve (Fig. 2) and the values with respect to temperature calculated through the scan rate relation. A computer was then used to calculate the terms of eqn (1), which is plotted in the form

$$T^2\left(\frac{S}{h}\right) = \left(\frac{E}{R}\right) - nT^2\left(\frac{h}{r}\right)$$

where h and S are the first and second derivatives of Hp, respectively, and r is $(1-x)\Delta Hp$. Typical results are shown in Fig. 5.

REFERENCES

1 S. Sourour and M. R. Kamal, *Thermochim. Acta*, 14 (1976) 41 and numerous references cited therein.
2 D. W. Brazier and G. H. Nickel, *Rubber Chem. Technol.*, 48 (1975) 26.
3 *Annual Book of ASTM Standards*, Part 28, *Rubber, Carbon Black, Gaskets*, American Society for Testing and Materials, Philadelphia, 1972.
4 C. O. Weber, *The Chemistry of India Rubber*, Griffin & Co., London 1902.
5 J. T. Blake, *Ind. Eng. Chem.*, 22 (1930) 737.
6 K. Hada, K. Fukaya and T. Nakajima, *J. Rubber Soc. Japan*, 2 (1931) 389.
7 R. S. Jessup and A. D. Cummings, *J. Res. Nat. Bur. Stand.*, 13 (1934) 357.
8 E. Seidl, *Gummi-Ztg.*, 25 (1911) 710.
9 Y. Toyabe, *J. Rubber Soc. Japan.*, 2 (1931) 389.
10 S. Oberto, *Rubber Chem. Technol.*, 10 (1937) 725.
11 D. L. Bruce, R. Lyle and J. T. Blake, *Ind. Eng. Chem.*, 36 (1944) 37; *Rubber Chem. Technol.*, 17 (1944) 404.
12 A. A. Perks, *J. Soc. Chem. Ind. London*, 45 (1926) 145T.
13 A. T. McPherson and N. Bekkedahl, *J. Res. Nat. Bur. Stand.*, 14 (1935) 601.
14 N. Bekkedahl and J. J. Weeks, *J. Res. Nat. Bur. Stand.*, 73A (1969) 221.
15 V. L. Hock and G. Schroter, *Kolloid-Z.*, 152 (1957) 98.
16 M. L. Bhaumik, D. Banerjee and A. K. Sircar, *J. Appl. Polym. Sci.*, 6 (1962) 674.
17 M. L. Bhaumik, D. Banerjee and A. K. Sircar, *J. Appl. Polym. Sci.*, 9 (1965) 1367.
18 M. L. Bhaumik, D. Banerjee and A. K. Sircar, *J. Appl. Polym. Sci.*, 9 (1965) 1731.
19 M. L. Bhaumik, D. Banerjee and A. K. Sircar, *J. Appl. Polym. Sci.*, 9 (1965) 2285.
20 L. A. Wood and N. Bekkedahl, *J. Polym. Sci., Part B*, 5 (1967) 169.
21 G. M. Martin and L. Mandelkern, *J. Res. Nat. Bur. Stand.*, 62 (1959) 141.
22 L. Bateman, C. G. Moore, M. Porter and B. Saville, in L. Bateman (Ed.), *The Chemistry and Physics of Rubber Like Substances*, MacLaren & Sons, London, 1963, Ch. 15.
23 L. W. Crane, P. J. Dynes and D. H. Kaelble, *J. Polym. Sci. Polym. Lett.*, 11 (1973) 533.
24 W. Hofman, *Vulcanization and Vulcanizing Agents*, MacLaren & Sons, London, 1967.
25 D. W. Brazier and G. H. Nickel, *Rubber Chem. Technol.*, 48 (1975) 661.
26 J. J. Maurer, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 14 (1973) 518.
27 D. L. Bruce, R. Lyle and J. T. Balke, *Rubber Chem. Technol.*, 17 (1944) 404.