Thermochimica Acta, 207 (1992) 177–192
Elsevier Science Publishers B.V., Amsterdam

Thermal analysis of controlled-release elastomeric formulations.
Part 2. A DSC study of the effect of sodium lauryl sulphate loading on vulcanization

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(Received 20 December 1991)

Abstract

Controlled release of sodium lauryl sulphate (SLS) from monolithic elastomeric pellets represents one way of achieving long-term inhibition of bacterial oxidation of pyrite. The degree of cure of elastomeric formulations influences the rate of release of SLS. Vulcanization decreases the permeability of the elastomeric matrix and results in slower release of SLS. The effect of SLS loading on the vulcanization of natural rubber and synthetic *cis*-1,4-polyisoprene has been studied by DSC. Dynamic temperature scans show that the heat of reaction (ΔH), which is a measure of the area of the exothermic peak, decreases with increasing SLS content. The decrease in ΔH is not very significant at SLS levels up to 15%, but is clearly noticeable at levels of 25%. In the case of formulations which contain 35% SLS, no curing exotherms are observed. It is therefore concluded that rubber formulations which contain 35% or more SLS are unvulcanized. Analysis of curing exotherms by means of the Borchardt and Daniels DSC kinetics data analysis program gives inconclusive results. It is suggested that the complex chemistry of the accelerated sulphur vulcanization of olefinic rubbers makes it difficult to obtain reliable quantitative reaction kinetics information for this particular type of reaction.

INTRODUCTION

Acid mine drainage is produced from pyrite (FeS_2) by a combination of abiotic and microbial reactions when mining activities expose the pyrite to oxygen [1]. The acidophilic iron- and sulphur-oxidizer *Thiobacillus ferrooxidans* accelerates the acidification of coal waste by catalysing the oxidation of pyrite to ferric sulphate and sulphuric acid [2–4]. Sodium lauryl sulphate (SLS) has proved an effective inhibitor of acid mine drainage catalysed by *T. ferrooxidans* in coal waste dumps [5,6]. However, long-term inhibition of bacterial oxidation can only be achieved if a continuous supply of SLS is

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available [7]. The latter can be accomplished by incorporating the SLS into a polymeric matrix, from which it is released slowly by a diffusion-dissolution mechanism [8,9]. The development and laboratory evaluation of controlled-release devices of the monolithic elastomeric type, for attaining long-term inhibition of bacterial oxidation of pyrite, have been reported [10]. Thermoanalytical studies pertaining to the solubility limits of SLS in elastomers have been discussed in a previous paper [11].

Vulcanization of olefinic rubbers, which involves formation of crosslinks and introduction of combined-sulphur groups, decreases permeability markedly and results in slower release of SLS. The normal recipes used industrially for the vulcanization of olefinic rubbers include, in addition to sulphur, organic accelerators, zinc oxide and long-chain fatty acids, e.g. stearic acid. Organic accelerators alone increase the rate of sulphur combination and crosslinking, but provide only marginal improvement in crosslinking efficiency. The presence of both zinc oxide and a fatty acid is essential if an efficiently crosslinked network (i.e. a network with mainly monosulphidic bonds) is to be obtained. Network structures formed by accelerated sulphur vulcanization have a preponderence of alkenyl monosulphide and disulphide crosslinks and little or no cyclic monosulphide units [12].

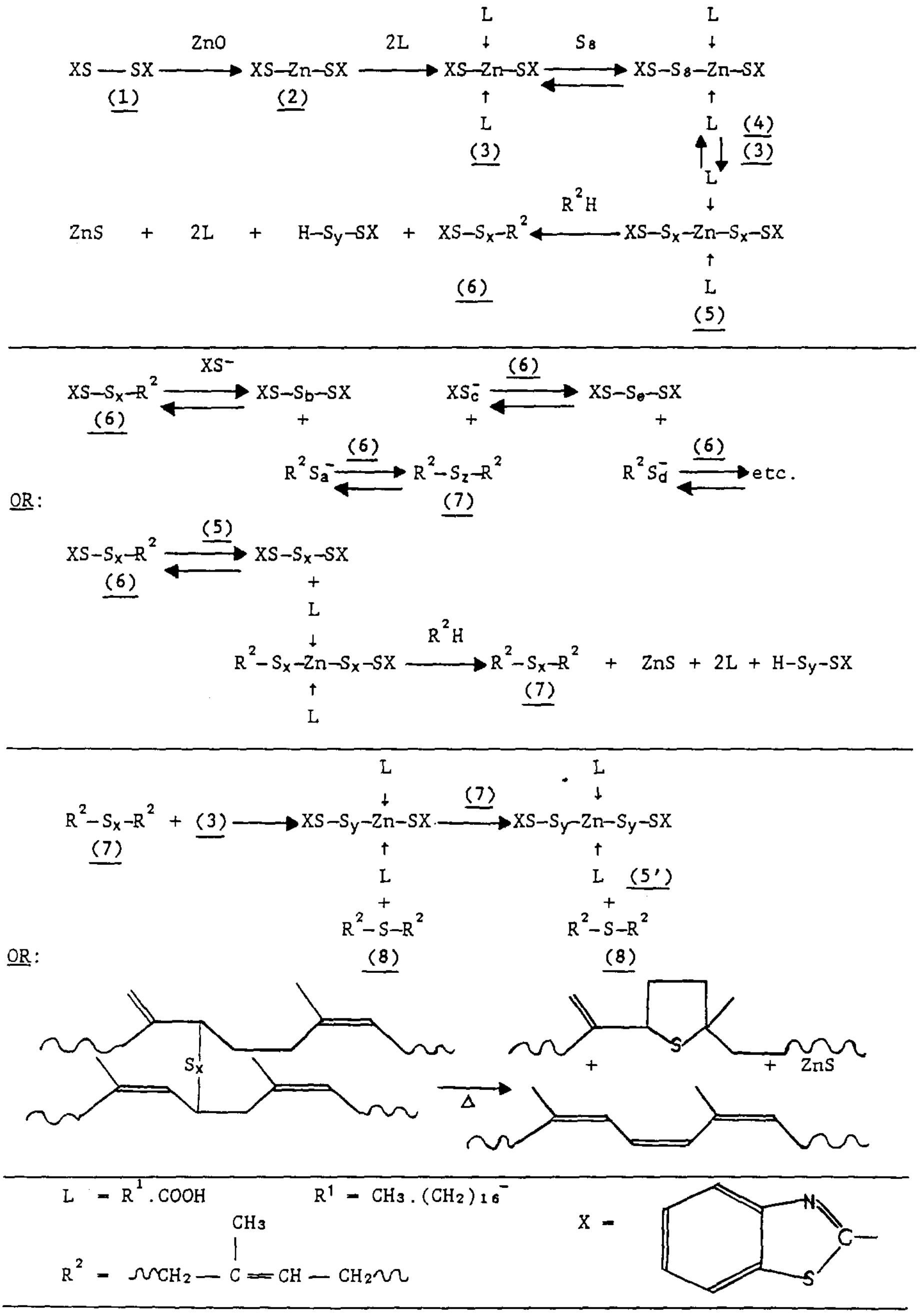
The chemistry of accelerated sulphur vulcanization is so complex that it is only within the last two decades that a coherent theoretical treatment has been possible. Even today, only the main stages are understood and there is still much to be learned about the effect of various additives. The initial step in vulcanization seems to be the reaction of sulphur with the zinc salt of the accelerator to give a zinc perthio-salt, XS_xZnS_xX, where X is a group derived from the accelerator. This salt reacts with the rubber hydrocarbon RH to give a rubber-bound intermediate (i):

$$XS_xZnS_xX + RH \rightarrow \underset{(i)}{XS_xR} + \underset{(ii)}{ZnS} + \underset{(iii)}{HS_{x-1}X}$$

and a perthio-accelerator group (iii) which, with further zinc oxide will form a zinc perthio-salt of lower sulphur content [13]. This may, nevertheless, again be an active sulphurating agent, forming intermediates $XS_{x-1}R$. In this way, each molecule of accelerator gives rise to a series of intermediates of various degrees of polysulphidity. The rubber-bound intermediate XS_xR then reacts with a molecule of rubber hydrocarbon RH to give a crosslink, and more accelerator is regenerated:

$$XS_xR + RH \rightarrow RS_{x-1}R + XSH$$

Even this is not the whole story, for, on further heating, the degree of polysulphidity of the crosslinks declines. This process is catalysed by XS_xZnS_xX, and can result in additional crosslinks. Reactions which may occur during the accelerated sulphur vulcanization of olefinic rubbers are summarized in Scheme 1.



Scheme 1

During the preparation of controlled-release rubber–SLS devices, it was found that samples which contained high loadings of SLS were insufficiently vulcanized, as suggested by their poor physical integrity. An increase in the vulcanization temperature during subsequent sample preparations did not improve the degree of cure of formulations which contained high loadings of SLS. This suggested that high SLS loadings had had a detrimental effect on vulcanization. It was, therefore, of interest to investigate analytical techniques which could provide some indication of the level at which the SLS started to interfere with the vulcanization reaction. The study reported here focuses on the use of the DSC method.

EXPERIMENTAL

Materials

Natural rubber (grade SMR 20), synthetic *cis*-1,4-polyisoprene (grade IR-80) and elastomer additives, namely, carbon black N220, zinc oxide, stearic acid, *N*-cyclohexyl-2-benzothiazole sulphenamide (ORAC CS), tetramethylthiuram disulphide (TMTD) and styrenated phenol antioxidant (OROX SP), were supplied by Karbochem. Sodium lauryl sulphate (TEXAPON K12) and sublimed sulphur were purchased from Henkel South Africa (Pty) Ltd. and BDH Laboratory Reagents, respectively.

Preparation of rubber–SLS formulations

Two types of masterbatch formulation were prepared, namely, natural rubber and synthetic polyisoprene, hereafter referred to as NR and IR respectively. Gum-stock rubber was softened by mechanical working on a two-roll rubber mill. Once it was in the softened state, vulcanization additives, carbon black and antioxidant were incorporated by further processing on the two-roll mill. The compositions of the masterbatch formulations are given in Table 1. Rubber–SLS formulations were prepared by blending masterbatch formulations with SLS, using a Model PLE 651 Brabender Plasti-Corder (Brabender, Germany) and an adjustable-speed Brabender two-roll mill. Since an accelerated sulphur vulcanization system was used, sulphur (2 parts per hundred parts of rubber (phr)) was also added to masterbatch formulations at that stage of the mixing process. After addition of SLS and sulphur, blending was continued for about 20 min to ensure homogeneous dispersion of SLS in the rubber matrices.

Vulcanization studies

In order to study the curing kinetics of masterbatch formulations, a mass of sulphur equivalent to 2 phr was blended with 400 g of each formulation. The curing rates of these formulations were determined by using a Monsanto 100 rheometer. This instrument is used to measure the increase in

TABLE 1

Compositions of rubber masterbatch formulations

Component	Formulation	
	A	B
Natural rubber (SMR 20) (parts)	100	
Synthetic *cis*-1,4-polyisoprene (IR-80) (parts)		100
Carbon black N220 (phr) [a]	9	9
Zinc oxide (phr)	5	5
Stearic acid (phr)	1	1
ORAC CS [b] (phr)	1.5	1.5
TMTD [c] (phr)	0.5	0.5
OROX SP [d] (phr)	2	2

[a] Parts per hundred parts of rubber.

[b] *N*-Cyclohexyl-2-benzothiazole sulphenamide (accelerator).

[c] Tetramethylthiuram disulphide (accelerator).

[d] Styrenated phenol (antioxidant).

the modulus of the elastomer, caused by the introduction of crosslinks, as a function of time. The rheographs obtained were used to calculate the time required to achieve a maximum degree of cure. Optimum time and temperature conditions for vulcanization were selected for subsequent sample preparations.

The effect of SLS loading on the vulcanization of elastomers was investigated by differential scanning calorimetry (DSC), using a Du Pont 9900 computer/thermal analyser and its Model 910 differential scanning calorimetry module. Indium metal was used as calibration standard. DSC scans were done on unvulcanized NR and IR formulations which contained from 0 to 35% SLS (referring to percentage of total mass). In all analyses, the sample mass was 17.1 mg and the heating rate was 10°C min^{-1}. Attempts were also made to analyse curing exotherms by means of the Borchardt and Daniels DSC kinetics data analysis program (Du Pont).

RESULTS AND DISCUSSION

Monsanto rheographs

The rheographs of NR and IR masterbatch formulations (i.e. formulations containing no SLS) are shown in Fig. 1. Information about the curing rates of these formulations is summarized in Table 2. Vulcanization results in an increase in the modulus of the elastomer. In practice, the increase in the torque is measured as a function of time (Fig. 1). The torque values (given in lbf in) are considered to be a direct measure of the modulus. Table 2 shows that at 150°C, the time required to achieve a degree of cure of 90%, $t_c(90)$, was 4.5 min for NR formulations and 7.0 min for IR

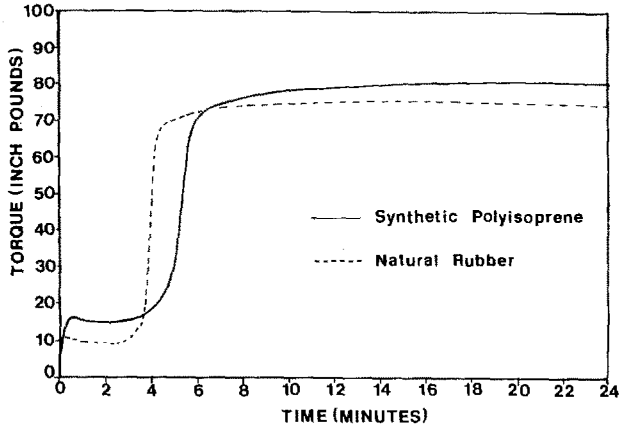


Fig. 1. Monsanto rheographs of NR and IR masterbatch formulations.

formulations, while $t_c(98)$ was 7.2 min and 13.6 min for NR and IR respectively.

The rheographs showed that a maximum degree of cure should be obtained if masterbatch formulations are vulcanized at 150°C for 24 min. However, during the preparation of controlled-release rubber-SLS pellets, the poor physical integrity of pellets which contained 45 and 55% SLS suggested that such pellets were insufficiently vulcanized. Higher curing temperatures and increased curing times did not improve the quality of these samples. Because the release rate of SLS from rubber pellets depends on the degree of cure of the rubber formulations, it was important to obtain more information about the effect of SLS loading on vulcanization.

Single dynamic temperature scans

The objectives of the DSC study were to determine a pattern which would illustrate how the SLS loading influenced the vulcanization of

TABLE 2

Information obtained from Monsanto rheographs of rubber masterbatch formulations

	Masterbatch formulation	
	NR	IR
Vulcanization temp. (°C)	150	150
Highest modulus, M_H (lbf in)	75	81
Lowest modulus, M_L (lbf in)	9	14.5
Difference between M_H and M_L, ΔM (lbf in)	66	66.5
$t_c(2)$ (min)	3.1	3.2
$t_c(50)$ (min)	3.9	5.3
$t_c(90)$ (min)	4.5	7.0
$t_c(98)$ (min)	7.2	13.6

TABLE 3

Information obtained from non-isothermal DSC scans of NR–SLS formulations

SLS content (%)	Heat of reaction, ΔH (J g^{-1})	Onset temperature (°C)	Peak temperature (°C)
0	7.3	139.4	147.6
2	8.9	140.9	148.7
4	9.4	141.7	149.1
5	9.7	141.8	149.2
6	9.6	141.8	149.4
8	9.5	141.6	149.2
10	9.4	141.3	149.0
11	9.3	141.0	148.9
12	9.1	140.9	148.7
13	8.9	140.7	148.4
14	8.6	140.4	148.0
15	8.0	140.2	147.6
25	0.9	137.7	143.8
35	[a]	[a]	[a]

[a] No curing exotherm observed.

rubber formulations and also to determine at which level of SLS content the inhibition of the vulcanization process became significant. The information obtained from single dynamic temperature scans of NR–SLS and IR–SLS formulations is summarized in Tables 3 and 4 respectively. A typical curing exotherm is shown in Fig. 2. Figure 3 shows the curing

TABLE 4

Information obtained from non-isothermal DSC scans of IR–SLS formulations

SLS content (%)	Heat of reaction, ΔH (J g^{-1})	Onset temperature (°C)	Peak temperature (°C)
0	7.5	150.4	154.8
2	7.7	151.4	155.9
3	7.7	152.3	157.1
4	7.8	153.1	157.8
6	7.4	153.0	157.6
8	6.8	152.6	157.2
10	6.3	151.3	156.5
11	5.9	150.6	155.8
12	5.6	150.2	155.1
13	5.4	149.5	154.6
14	5.0	148.9	154.3
15	4.6	148.6	154.1
25	1.6	147.2	151.6
35	[a]	[a]	[a]

[a] No curing exotherm observed.

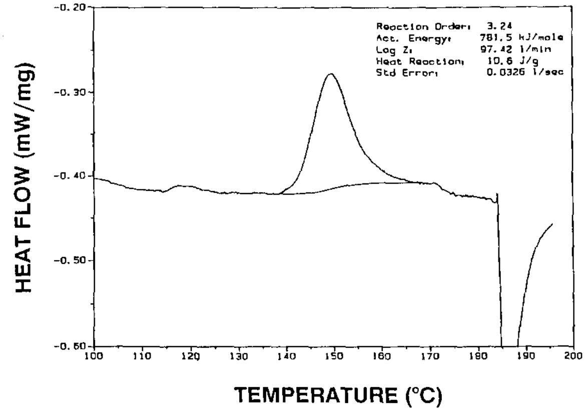


Fig. 2. Typical curing exotherm.

exotherms for NR formulations which contained 0%, 5%, 13% and 15% SLS, and Fig. 4 gives the curing exotherms for IR formulations which contained 0%, 11% and 15% SLS. These figures, as well as Tables 3 and 4, show that the area of the exothermic peak (as given by the ΔH values), the onset temperature, and the peak temperature were influenced by the SLS content of the formulation.

Figures 5–7 illustrate the effect of the SLS content on the curing of NR formulations. The heat of reaction (ΔH) is a measure of the area of the exothermic peak and is therefore an indication of the extent to which curing occurred. Figure 5 shows that ΔH increased with an increase in the SLS content until an SLS level of 5% was reached. Above this 5% level, ΔH started to decrease and at an SLS level of 25% the peak area

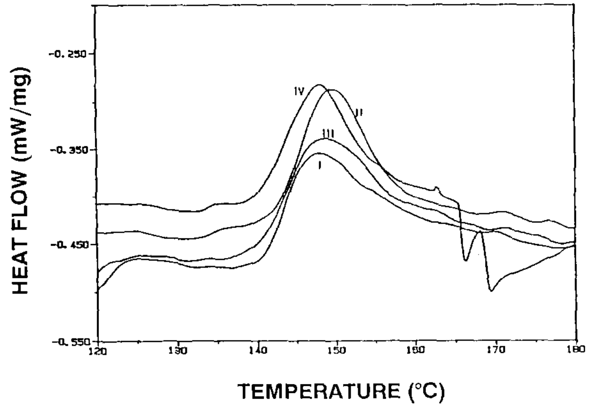


Fig. 3. Curing exotherms of NR formulations which contained 0% SLS (curve I), 5% SLS (curve II), 13% SLS (curve III) and 15% SLS (curve IV).

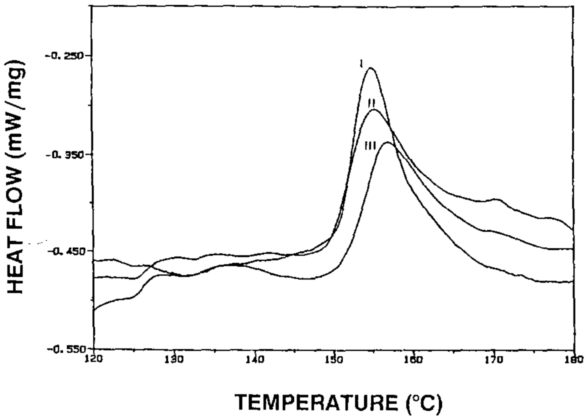


Fig. 4. Curing exotherms of IR formulations which contained 0% SLS (curve I), 11% SLS (curve II) and 15% SLS (curve III).

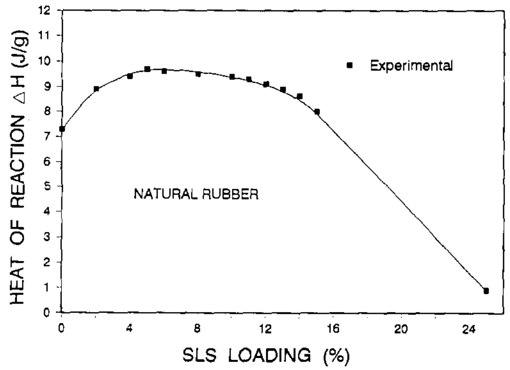


Fig. 5. Effect of SLS loading on heat of reaction: NR formulations.

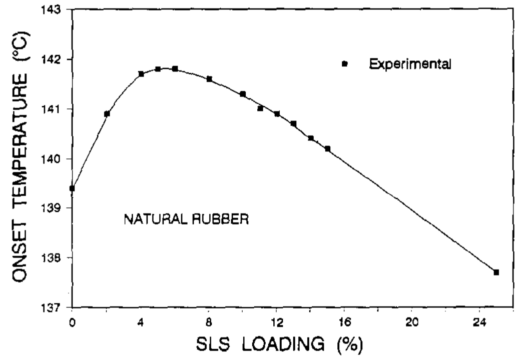


Fig. 6. Effect of SLS loading on onset temperature: NR formulations.

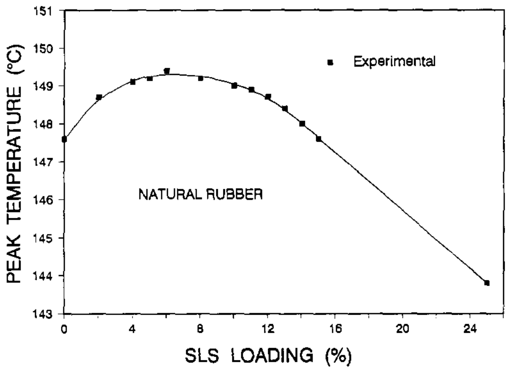


Fig. 7. Effect of SLS loading on peak temperature: NR formulations.

decreased considerably. It is therefore suggested that at levels of up to 5% the SLS actually played a positive role in the curing process, possibly because of its lubrication effect, which may result in better dispersion of the vulcanization additives. At levels of 6–15% SLS, the peak areas decreased slightly. This was probably because the SLS which existed as a separate phase in some way interacted with the sulphur or other vulcanization additives and thereby inhibited the curing reaction to a certain extent. At SLS levels of 25% and more, the SLS interfered seriously with the curing reaction, since most of the SLS was present as a dispersed phase.

When the onset and peak temperatures were plotted against the SLS loading, as in Figs. 6 and 7 respectively, the same trend was observed. Initially, both the onset and the peak temperature increased until an SLS level of 6% was reached. At SLS levels above 6%, the onset temperature, as well as the peak temperature, decreased slightly. At SLS levels of 25% and more, both the onset and the peak temperature dropped markedly. The reasons for these temperature shifts are not clear at this stage.

Figure 8 shows the effect of the SLS loading on the curing of IR. At SLS levels up to 4%, which was close to the solubility limit of SLS in IR [11], the SLS loading had little effect on the area of the exotherm, as shown by the ΔH values. Above the 4% SLS level, the ΔH values decreased markedly. The decrease in ΔH was particularly significant in the case of IR formulations which contained 25% SLS.

From this investigation, it is evident that if rubber–SLS formulations with different SLS contents are vulcanized at the same temperature for the same period of time, the degree of curing of such formulations will vary as a function of the SLS content. This effect was not very significant at SLS levels up to 15%, but was clearly noticeable at levels of 25%. For NR and IR formulations which contained 35% SLS, no curing exotherms were observed. It was therefore apparent that rubber formulations which contained 35% or more SLS could be regarded essentially as unvulcanized. It

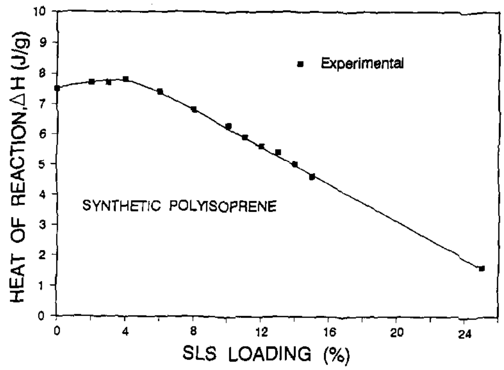


Fig. 8. Effect of SLS loading on heat of reaction: IR formulations.

was not possible to quantify the effect of SLS loading by using the DSC technique, but it was nevertheless possible to provide an indication of the presence or absence of vulcanization.

DSC kinetics data analysis method

Attempts were also made to obtain quantitative reaction kinetics information from single dynamic DSC scans of reaction exotherms by using the Borchardt and Daniels DSC kinetics data analysis program (hereafter referred to as BDK). The BDK method assumes that the reaction obeys the relationship

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)(1-\alpha)^n \qquad (1)$$

where α is the fractional conversion (dimensionless), $k(T)$ is the specific rate constant at temperature T (s^{-1}) and n is the reaction order (dimensionless). The method also assumes that the temperature dependence of the reaction rate follows the Arrhenius expression

$$\ln k(T) = \ln Z - \frac{E}{RT} \qquad (2)$$

where Z is the pre-exponential factor (s^{-1}), E is the activation energy (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

The DSC exotherm is used to measure the two basic parameters required to solve the above-mentioned equations, namely, (i) the reaction rate $\mathrm{d}\alpha/\mathrm{d}t$, obtained by dividing the peak height at temperature T by the total peak area, and (ii) the fraction unreacted $(1-\alpha)$, obtained by measuring the ratio of the partial area at temperature T to the total peak area, to obtain α, and then subtracting this value from unity.

The use of the DSC kinetics method for obtaining reaction kinetics information has been discussed by Kah et al. [14] and Provder et al. [15]. This method is based on the assumption that the rate of evolution of heat from a reaction is proportional to the rate of the chemical reaction, and therefore the total amount of heat evolved up to any stage of the reaction is proportional to the amount of reactants consumed up till then. If it is assumed that the reagents are present in stoichiometric proportions and that there is only one slow step in the reaction mechanism, the general nth order rate expression can be written in terms of concentration in logarithmic form as follows:

$$\ln k(T) = \ln\left\{\frac{1}{C_0}\left[\frac{\mathrm{d}C}{\mathrm{d}t}\right] \Big/ \left[\frac{C_0 - C}{C_0}\right]^n\right\} \tag{3}$$

where C_0 is the initial concentration, C is the amount reacted at time t, $\mathrm{d}C/\mathrm{d}t$ is the rate of disappearance of reactants, n is the order of the reaction and $k(T)$ is the temperature-dependent rate constant.

Rewriting eqn. (3) in terms of the observable variables obtained from the DSC scan gives the following equation:

$$\ln k(T) = \ln\left\{\frac{1}{\Delta H_0}\left[\frac{\mathrm{d}H(t, T)}{\mathrm{d}t}\right] \Big/ \left[\frac{\Delta H_0 - H(t, T)}{\Delta H_0}\right]^n\right\} \tag{4}$$

where ΔH_0 is the total heat of reaction, $H(t, T)$ is the amount of heat evolved up to time t and temperature T and $\mathrm{d}H(t, T)/\mathrm{d}t$ is the time- and temperature-dependent heat flow.

By substituting the Arrhenius expression into eqn. (4) and rearranging, the following equation is obtained:

$$\left\{\ln\frac{1}{\Delta H_0}\left[\frac{\mathrm{d}H(t, T)}{\mathrm{d}t}\right]\right\} = \ln Z - \frac{E}{RT} + n\left\{\ln\left[\frac{\Delta H_0 - H(t, T)}{\Delta H_0}\right]\right\} \tag{5}$$

which is of the form

$$P = a + bx + cy \tag{6}$$

The data are fitted to this expression by a multiple-regression technique. The DSC kinetics method therefore permits the calculation of the parameters E and Z in the Arrhenius expression (eqn. (2)), the heat of reaction ΔH and the order of the reaction n from a single DSC scan of a reaction exotherm.

BDK analyses

The information obtained from BDK analyses of the curing exotherms of NR–SLS and IR–SLS formulations is given in Tables 5 and 6 respectively.

TABLE 5

Information obtained from BDK analysis of curing exotherms: NR–SLS formulations

SLS content (%)	Heat of reaction, ΔH (J g^{-1})	Activation energy E (kJ mol^{-1})	log Z (min^{-1})	Reaction order n
0	9.3	710	88.9	3.0
2	10.9	715	89.3	3.2
4	10.8	756	94.3	3.2
5	10.9	797	99.4	3.6
6	11.4	729	90.9	3.2
8	10.7	798	99.5	3.8
10	11.4	689	86.0	3.5
11	11.8	849	106.0	4.6
12	11.2	751	93.8	4.0
13	11.7	703	87.8	4.1
14	10.9	872	109.0	5.0
15	10.0	950	118.9	5.4
25	[a]	[a]	[a]	[a]
35	[b]	[b]	[b]	[b]

[a] Curing exotherm unsuitable for analysis by BDK program.

[b] No curing exotherm observed.

For NR formulations which contained different loadings of SLS, the heat of reaction (ΔH) increased with increasing SLS content until a level of 13% SLS was reached. Thereafter ΔH started to decrease. Other trends

TABLE 6

Information obtained from BDK analysis of curing exotherms: IR–SLS formulations

SLS content (%)	Heat of reaction, ΔH (J g^{-1})	Activation energy E (kJ mol^{-1})	log Z (min^{-1})	Reaction order n
0	9.6	1241	152.4	3.4
2	9.7	1217	149.0	2.9
3	9.8	1120	137.5	3.3
4	9.7	1230	150.3	2.7
6	9.6	1097	133.8	2.8
8	7.5	1180	145.1	3.3
10	7.3	1036	127.9	3.2
11	7.2	1017	124.7	3.3
12	7.0	1004	123.2	2.8
13	6.7	843	103.0	2.8
14	6.6	730	89.9	2.9
15	6.0	981	120.2	2.6
25	2.2	1346	166.6	4.0
35	[a]	[a]	[a]	[a]

[a] No curing exotherm observed.

which could be observed were that the activation energy, log Z and reaction order increased with increasing SLS content.

IR-SLS formulations exhibited different trends, as shown in Table 6. For these formulations, the ΔH values decreased significantly above the 6% SLS level, while the values of E, log Z and n decreased with increasing SLS content until a level of 15% was reached. In the case of IR formulations which contained 25% SLS, ΔH decreased markedly, while the values of E, log Z and n were all higher than those obtained for an IR formulation which contained no SLS.

The preliminary results obtained from BDK analyses of curing exotherms are considered to be inconclusive. Tables 5 and 6 show that the values of E, log Z and n were scattered. The fact that the two types of rubber formulations exhibited different trends with regard to the values of E and log Z also raises questions about the reliability of these particular sets of data. In addition, it was noticed that the values of ΔH obtained by BDK analysis were higher than those obtained from dynamic temperature scans. It is clear that considerably more experimental work and careful consideration of data will be required before any conclusions can be reached from the kinetics data analysis study.

It is of course possible that the inability of the BDK method to provide reliable reaction kinetics information could be attributed to the complexity of the accelerated sulphur vulcanization reaction. Scheme I shows that a variety of reactions occur during accelerated sulphur vulcanization of olefinic rubbers. It is clear that the assumptions that reagents are present in stoichiometric proportions and that there is only one slow step in the reaction mechanism are not valid for this particular type of reaction.

In future work, a systematic approach will be followed, whereby the effects of single additives are first determined before the combined effects of two or more additives are evaluated. Such an approach could possibly provide more useful data. It is also important to conduct a thorough analysis of the curing exotherms of NR and IR formulations which contain no SLS before any attempts are made to analyse curing exotherms of formulations which contain different loadings of SLS. Investigations regarding the use of the BDK method to obtain reaction kinetics information for the accelerated sulphur vulcanization reaction are continued and the results will be reported in a forthcoming article.

CONCLUSIONS

This study showed that dynamic DSC scans can indicate the presence or absence of vulcanization. Single dynamic temperature scans of NR-SLS and IR-SLS formulations showed qualitatively that the degree of cure of such formulations varied as a function of the SLS content. The area of the exothermic peak, as given by the ΔH values, decreased with increasing

SLS content. The effect of SLS loading was not very significant at SLS levels up to 15%, but was clearly noticeable at levels of 25%. In the case of formulations which contained 35% SLS, no curing exotherms were observed. It can therefore be concluded that rubber formulations which contained 35% or more SLS were unvulcanized.

Attempts to obtain quantitative reaction kinetics information by using the Borchardt and Daniels DSC kinetics data analysis program gave inconclusive results. This was possibly because the complexity of the accelerated sulphur vulcanization reaction made the assumptions that reagents are present in stoichiometric proportions and that there is only one slow step in the reaction mechanism invalid.

ACKNOWLEDGEMENT

The financial support of this work by the Water Research Commission of South Africa is gratefully acknowledged.

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