

A Comparison of the Tetramethylthiuram Disulphide Accelerated Sulfur Vulcanization of Polybutadiene and Polyisoprene

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SYNOPSIS

A detailed study of the vulcanization of polybutadiene with various combinations of sulphur, tetramethylthiuram disulphide, ZnO, stearic acid, and zinc dimethyldithiocarbamate is reported. Vulcanization was conducted by heating samples at 2.5°C/min in a differential scanning calorimeter. The reaction was stopped at various points along the vulcanization exotherm, the soluble reaction products and residual curatives were extracted and analyzed, and the crosslink density and percentage polysulphidic crosslinks were determined. The overall reaction mechanism was found to be similar to that for polyisoprene, but the reaction, once initiated, was faster than in polyisoprene, the crosslink density was higher, and the percentage polysulphidic crosslinks was lower. These differences are discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

There are numerous differences between the vulcanization of natural rubber and polybutadiene (BR); much of the information on these differences has been gleaned from studies on model compounds. For example, Wolfe¹ investigated the effect of sulfur, zinc dimethyldithiocarbamate (ZDMC), tetramethylthiuram monosulphide (TMTM), and tetramethylthiuram disulfide (TMTD) on *cis,cis*-1,5-cyclo-octadiene. BR undergoes significant *cis-trans* isomerization during vulcanization² and shows a reduced response to zinc compounds, being able to achieve substantial degrees of crosslinking with *N*-cyclohexyl-2-benzothiazole sulfenamide in the absence of zinc.³ The results for BR vulcanizates are not fully supported by the results obtained with model compounds and Skinner⁴ proposed that the combination of the accelerator with the network prevented desulfuration to monosulphides in BR and allowed vicinal crosslinking to proceed.

In a detailed study of the reactions occurring in TMTD accelerated sulfur vulcanization of polyiso-

prene (IR), Kruger and McGill⁵⁻¹² suggested certain modifications to the existing^{13,14} vulcanization theories. This article reports on a DSC study of TMTD accelerated sulfur vulcanization of BR and compares the reactions occurring in BR with those reported for IR.

EXPERIMENTAL

The polybutadiene used was Afdene Buna CB11 with a *cis*-1,4 content of 96%. Vulcanization of all compounds was done by heating in the DSC at 2.5°C/min and the network, as well as extractables, were analyzed at various points along the thermogram. Curatives were added in 1.00/1.00 mol ratios, the formulations used being given in mass units in the legends to the Figures. Full experimental details were given earlier.¹⁵

RESULTS

BR/Sulfur/ZnO

Following the melting and dissolution of sulphur in BR at 112°C, the DSC thermogram (Fig. 1) showed

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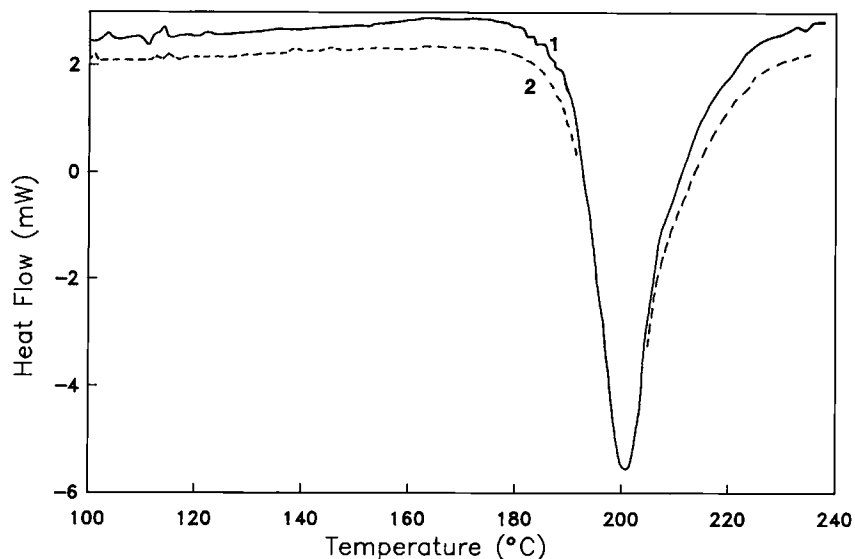


Figure 1 DSC spectra: (1) BR (100)/sulfur (9.46) and (2) BR (100)/sulfur (9.46)/ZnO (3.00), $\Delta H = 18$ J/g rubber.

a single large vulcanization exotherm, initiating at 185°C , some 10°C later than in the case of IR.⁵ However, the reaction was faster once initiated, as indicated by the more steeply rising exotherm, and the reaction in both polymers was completed at 230°C . As in the case of IR, neither the thermogram nor the crosslink density were affected by the inclusion of ZnO in the compound (Table I).

BR/Sulfur/TMTD

Coleman et al.¹⁶ presented Raman spectroscopic evidence for the formation of tetramethylthiuram polysulfides (TMTP), following the interaction of sulfur with TMTD, and Kruger and McGill suggested that the endotherm observed at 127°C in a sulfur/TMTD mixture,¹⁷ and at 128°C in an IR compound,⁵ was associated with the formation of TMTP. In BR, the melting of sulfur and the sulfur/TMTD interaction were not observed as separate events (Fig. 2). At high temperatures, sulfur and TMTD are more soluble in BR than in IR¹⁸ and this could explain the lower temperature of their dissolution and possibly the presence of a single melting/interaction endotherm at the lower temperature of 108°C .

In BR, there was a considerably longer delay before the onset of crosslinking than in IR and the exotherm, associated with crosslinking and network maturing reactions, was not completed until 220°C had been reached. Kruger and McGill⁶ suggested that interaction of TMTP and rubber would lead to

the formation of polysulfidic pendent groups, which are precursors to crosslink formation.



where $\text{XS}— = (\text{CH}_3)_2\text{NC}(\text{S})—$

Decomposition of dimethyldithiocarbamic acid (DMDCA), liberated in the process, would yield dimethylamine and CS_2 , which are highly volatile and would be lost from the system. TGA curves for BR showed a mass loss commencing around 130°C (Fig. 2). However, no distinct endotherm, indicative of the rapid evolution of volatiles, was observed and the exotherm was much broader than in the case of IR. Reversion occurred before the peak in the DSC exotherm and the bulk of the exotherm appeared to be associated with reactions that led to little change in crosslink density. This is misleading, as the early part of the exotherm overlapped with an endotherm corresponding to the evaporation of volatiles, as reflected by the TGA and also shown by Kruger and McGill⁵ for IR. It is noteworthy that at 160°C , that is, soon after the onset of the vulcanization exotherm, the crosslink density was already high and reached a maximum value at 175°C (Table I). This corresponded to the slight plateau in the DSC curve and approximated the temperature at which the evolution of volatiles had been completed. In line with the increase in crosslink density, the percentage of polysulfidic linkages increased in going from 160° to 175°C and then decreased. The percentage in-

Table I Analysis of Compounds at Various Stages of Vulcanization

Compound (Parts per 100 BR)	Temperature (°C)	Degree of Crosslinking (mol/mL, Rubber Network $\times 10^4$)	Polysulphides (%)
S (9.46)	230	1.20	
S (9.46) ZnO (3.00)	230	1.25	
S (9.46)	160	1.47	45.5
TMTD (8.87)	175	2.14	48.9
	190	1.86	40.4
	210	1.48	13.3
S (9.46)	160	1.66	46.6
TMTD (8.87)	175	1.81	40.2
Stearic acid (10.53)	190	1.57	30.8
	210	1.37	8.7
TMTD (8.87)	155	0.03	
	175	0.56	
	210	0.78	
TMTD (8.87)	143	0.95	
ZnO (3.00)	155	1.17	
	175	1.25	
S (9.46)	125	1.34	51.5
TMTD (8.87)	132	2.90	52.3
ZnO (3.00)	134	2.99	48.2
	160	2.91	9.4
S (9.46)	125	—	—
TMTD (8.87)	132	2.10	46.7
ZnO (3.00)	134	2.66	40.8
Stearic acid (10.53)	160	2.87	11.5
S (9.46)	138	1.57	45.1
ZDMC (11.27)	140	2.17	33.5
	142	2.20	32.4
	160	2.03	2.5
S (9.46)	128	1.20	53.4
ZDMC (11.27)	133	1.91	38.8
Stearic acid (10.53)	137	2.14	34.5
	160	1.97	1.7
S (9.46)	134	1.43	
ZDMC (11.27)	138	1.62	
ZnO (3.00)	160	1.56	

crease in the polysulfidic content was much less than the increase in crosslink density and the percentage of polysulfidic linkages fell to a low value of only 13% at 210°C. In contrast, the percentage of polysulfidic linkages in IR decreased progressively as the

reaction proceeded, the percentage of polysulfidic linkages being much higher (95–40%) at all stages of the vulcanization reaction.⁵

TLC analysis at 178° and 210°C showed that no TMTD, TMTM, or free sulfur were present at these

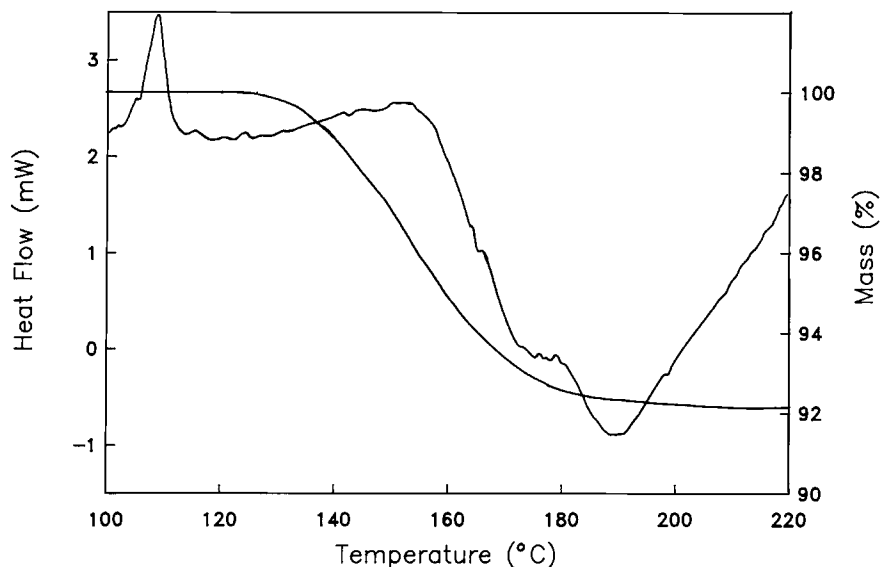


Figure 2 DSC spectrum and TGA curve for BR (100)/sulfur (9.46)/TMTD (8.87), $\Delta H = 30 \text{ J/g}$ rubber.

points in the reaction. The finding that reversion reactions dominated as soon as no free sulfur was present concurred with the findings of Kruger and McGill⁵ for IR compounds.

BR/Sulfur/TMTD/Stearic Acid

The thermogram of this system was similar to that of the sulfur/TMTD system, with the exception of an endotherm at 40°C (not shown), which represented the dissolution of stearic acid in BR (Fig. 3). Stearic acid delayed the dissolution of TMTD in the

rubber by about 20°C and this indicated a TMTD/stearic acid interaction, as suggested earlier.¹⁹ Crosslink densities and the percentage polysulfidic crosslinks were unchanged as compared to compounds without stearic acid (Table I).

BR/TMTD

It is well known¹³ that TMTD can function both as an accelerator and as a sulfur donor and, although crosslinking was observed in BR (Table I), the DSC vulcanization thermogram was poorly defined (Fig.

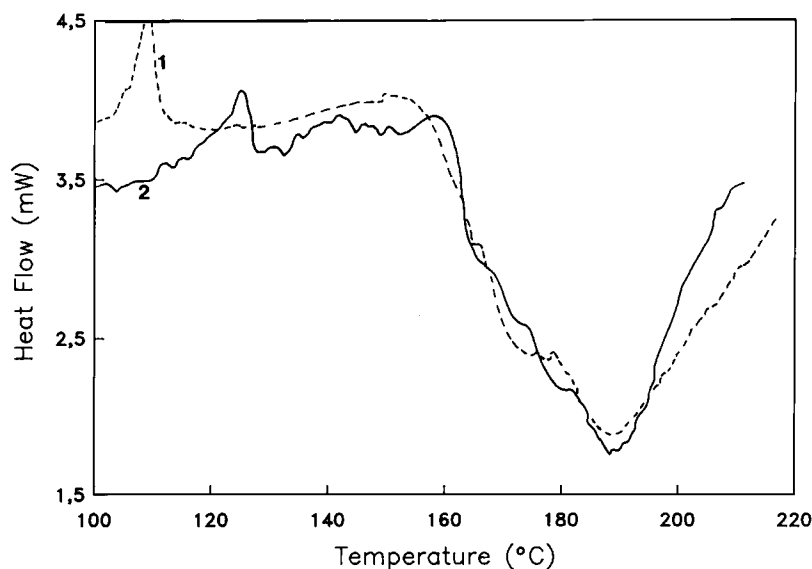


Figure 3 DSC spectra: (1) BR (100)/sulfur (9.46)/TMTD (8.87), $\Delta H = 13 \text{ J/g}$ rubber and (2) BR (100)/sulfur (9.46)/TMTD (8.87)/stearic acid (10.53) $\Delta H = 21 \text{ J/g}$ rubber.

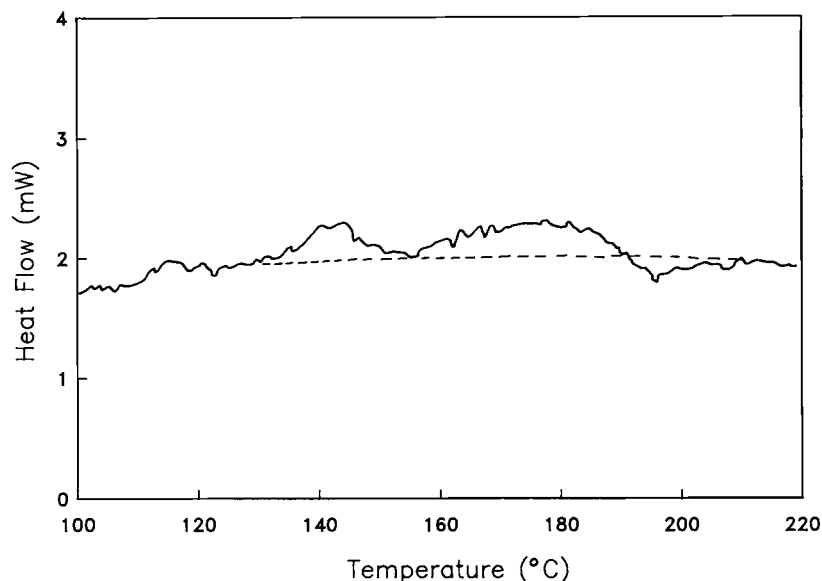


Figure 4 DSC spectrum: BR (100)/TMTD (8.87).

4). TMTD is more soluble in BR than in IR¹⁸ and did not produce a sharp melting endotherm, as in IR.⁵ The evaporation process, associated with the loss of accelerator fragments, such as dimethylamine and CS₂, occurred over a broader temperature range and was accompanied by an increase in the number of crosslinks. The crosslink density was higher in IR and there was no evidence of reversion at high temperatures. The presence of TMTD at 155°C was confirmed by TLC, but no traces of TMTD, TMTM or sulfur were evident at higher temperatures (Table II).

BR/TMTD/ZnO

DSC vulcanization thermograms were similar to those for IR,^{7,8} but the TMTD melting endotherm (132°C) and the reaction exotherm were less sharply

defined (Fig. 5). TGA showed a lower mass loss (0.76%) than in the absence of ZnO (7%), indicating that ZnO trapped DMDCA, as was also evident in the formation of ZDMC. As reported by Kruger and McGill,^{7,8} ZDMC formation accompanied crosslinking and was a product of crosslinking, not a precursor.

The inclusion of ZnO led to a considerable increase in the crosslink density (Table I), as pendent group destruction reactions were prevented.^{7,8} TLC showed that TMTM and ZDMC were formed during the crosslinking process, but no TMTD was detected after crosslinking had commenced (Table II). In IR compounds, TMTD was detected at all stages of the reaction.⁸

BR/Sulfur/TMTD/ZnO

The thermogram (Fig. 6) for the system contained essentially the same elements as for the IR compound,¹¹ but the peaks were less clearly resolved; the onset of vulcanization was earlier and the process was completed at lower temperatures. Following the endotherm attributed to the melting and interaction of sulfur and TMTD, the first exotherm could be attributed to the crystallization of ZDMC,¹¹ the formation of which accompanied crosslinking. TGA showed an evaporation process that initiated at 125°C and coincided with the onset of crosslinking. The rate and extent of evaporation was less than in the absence of ZnO, due to ZnO trapping DMDCA to form ZDMC. Table I shows that a high crosslink density was obtained early in the reaction (132°C)

Table II Analysis of Compounds by TLC

Compound (Parts per 100 BR)	Temperature (°C)	Component Detected in Extract
TMTD (8.87)	155	TMTD
	175	No TMTD
	210	No TMTD
TMTD (8.87) ZnO (3.00)	133	TMTD
	143	TMTM and ZDMC
	155	TMTM and ZDMC
	175	ZDMC

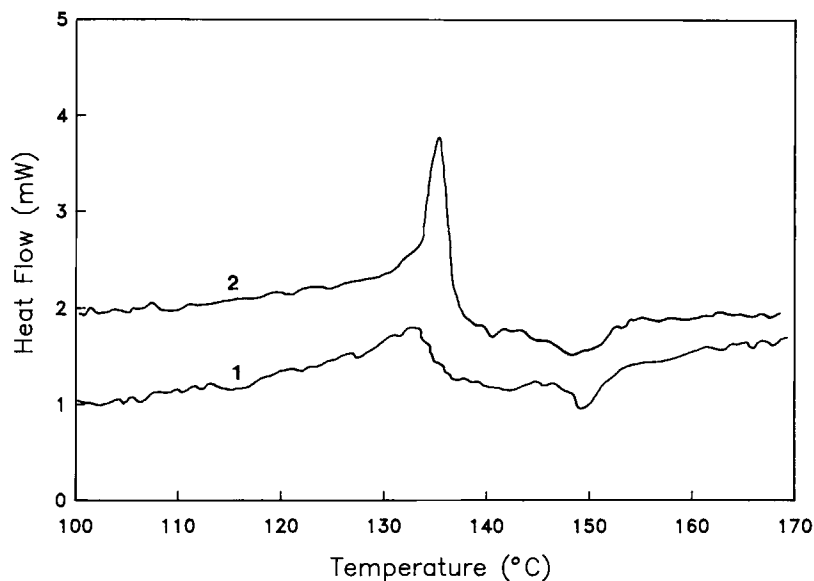


Figure 5 DSC spectra: (1) BR (100)/TMTD (8.87)/ZnO (3.00) and (2) IR (100)/TMTD (8.87)/ZnO (3.00) (Ref. 6).

and thereafter the crosslink density increased only slightly. As with other BR vulcanizates, crosslink densities were higher than in IR compounds and the percentage of polysulfidic crosslinks was lower.⁵⁻¹² These remained fairly constant until the end of the reaction, when the percentage of polysulfidic linkages fell to only 9%. HPLC analysis showed that, at 136°C, 63 mol % of the TMTD could be accounted for as ZDMC, 17% as TMTM, and 6% as TMTD.

Unbound sulfur comprised 46% of the original sulfur. At 160°C, there was 62 mol % ZDMC and 5 mol % TMTD, while no TMTM was detected and all of the sulfur had been consumed.

BR/Sulfur/TMTD/ZnO/Stearic Acid

Upon the addition stearic acid to the previous compound, the sulfur/TMTD interaction/dissolution

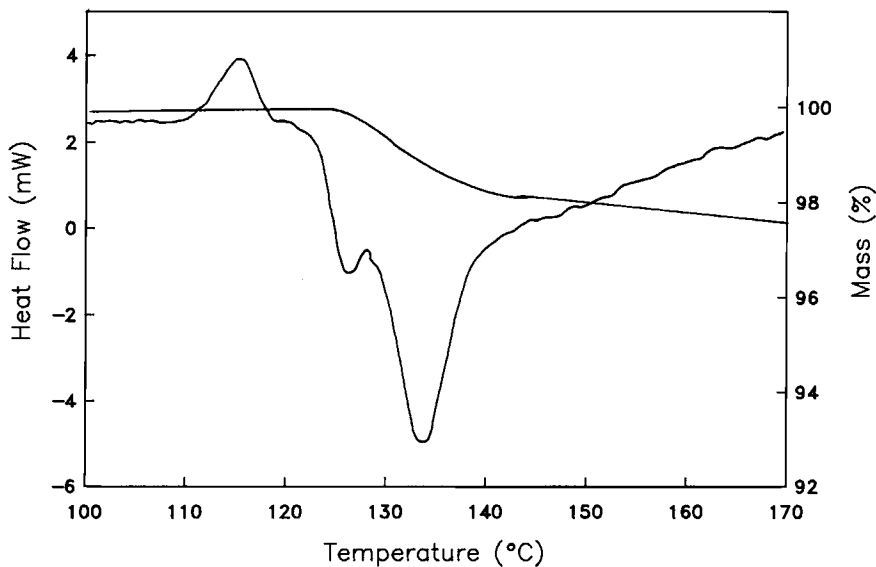


Figure 6 DSC spectrum and TGA curve for BR (100)/sulfur (9.46)/TMTD (8.87)/ZnO (3.00).

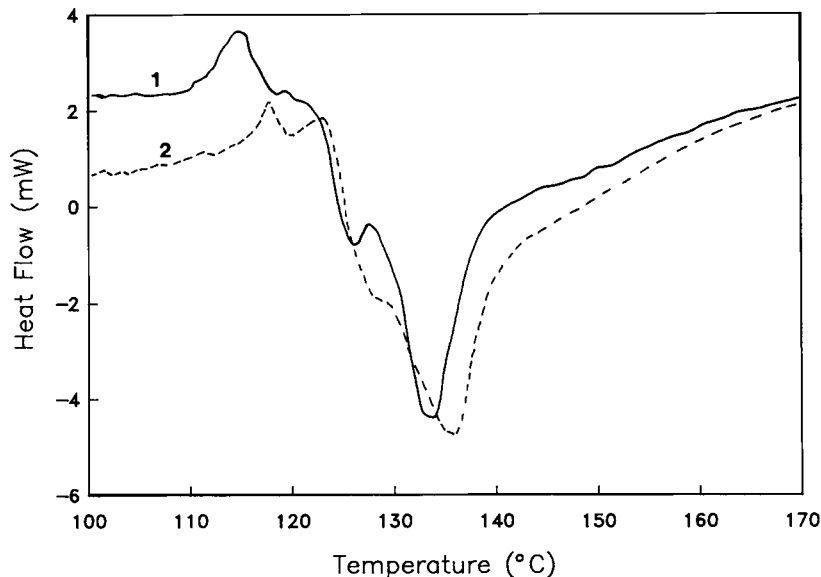


Figure 7 DSC spectra: (1) BR (100)/sulfur (9.46)/TMTD (8.87)/ZnO (3.00), $\Delta H = 14$ J/g rubber and (2) BR (100)/sulfur (9.46)/TMTD (8.87)/ZnO (3.00)/stearic acid (10.53), $\Delta H = 9$ J/g rubber.

endotherm (Fig. 7) was less pronounced, pointing to a TMTD/stearic acid interaction, which in turn inhibited the sulfur/TMTD interaction to form TMTP. Kruger and McGill¹⁹ demonstrated that, in the absence of rubber, stearic acid delayed the sulfur/TMTD interaction. The delay in forming TMTP would account for the delay in crosslinking. In the presence of stearic acid, no crosslinks had formed at 125°C (Table I), as evident by the fact

that the sample dissolved completely in benzene. In all, slightly fewer crosslinks formed in the presence of stearic acid and no reversion was apparent.

BR/ZDMC

BR compounds with ZDMC produced a featureless thermogram and no crosslinks formed as indicated by the complete dissolution of the sample in benzene.

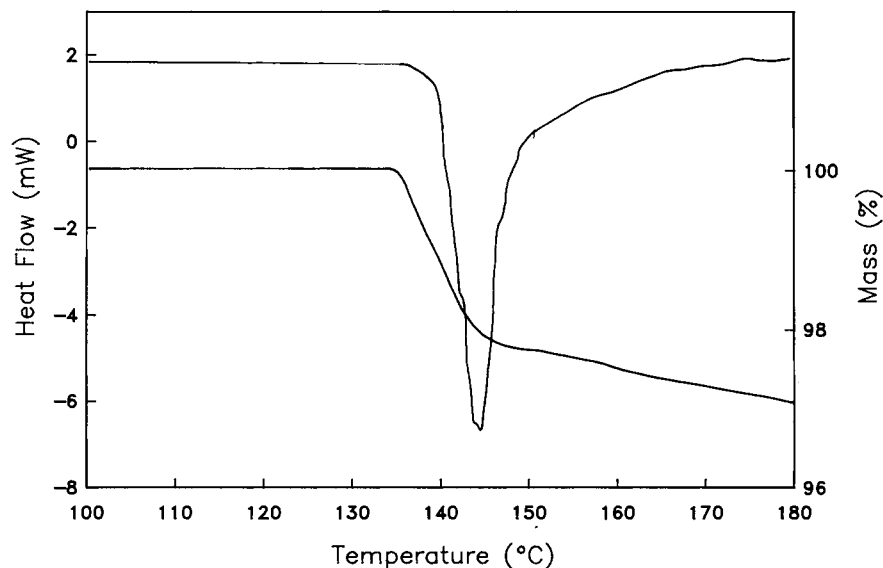


Figure 8 DSC spectrum and TGA curve for BR (100)/sulfur (9.46)/ZDMC (11.27), $\Delta H = 10$ J/g rubber.

BR/Sulfur/ZDMC

ZDMC is an ultra-accelerator.¹⁴ Vulcanization of the corresponding IR compound was slow,⁹ but the reaction in BR was rapid, as shown by the narrow exotherm in Figure 8. TGA showed the loss of volatiles from the system, but no definite endotherm, associated with the evaporation process, was observed, as in IR compounds. The onset of crosslinking was delayed, compared to TMTD compounds containing ZnO, and crosslink densities were slightly lower.

BR/Sulfur/ZDMC/Stearic Acid

The inclusion of stearic acid allowed vulcanization to proceed at considerably lower temperatures, but otherwise the thermograms (Fig. 9) were similar to those already discussed. Crosslink densities were of the same order of magnitude, though stearic acid seemed to favor the formation of polysulfidic linkages very slightly (Table I). The reduction in the induction period might be brought about by the neutralization of amines, which would otherwise attack polysulfidic pendent groups.

BR/Sulfur/ZDMC/ZnO

The inclusion of ZnO in the compound allowed vulcanization to occur at somewhat lower temperatures (*cf.* Figs. 8 and 10) and the resulting exotherm was broader than in the absence of ZnO. ZnO trapped fragments of the accelerator, as made evident by the

lower mass loss of 1.8% compared to 3.5% in the absence of ZnO. TGA showed that the bulk of the mass loss occurred during the latter part of the exotherm. This may indicate that the surface of the ZnO particles had become encrusted with ZDMC and was no longer available to trap DMDCA. The delay in the onset of vulcanization in the absence of ZnO could be ascribed to destruction of pendent groups by dimethylamine, formed on decomposition of DMDCA liberated in the crosslinking reaction.⁸

Surprisingly, the crosslink density was slightly lower than in the absence of ZnO (Table I). One would have expected a higher crosslink density since reactions that destroy pendent groups were reduced. Noticeably higher crosslink densities were also found in IR with sulfur/ZDMC compounds containing ZnO.⁹

DISCUSSION

The vulcanization reactions in BR can be ascribed to the same sequence of reactions found for IR.⁵⁻¹² In sulfur/TMTD compounds, TMTD would lead to pendent group formation, followed by crosslinking. DMDCA, liberated in pendent group formation and in crosslinking, would decompose to dimethylamine and CS₂ and the former would attack pendent groups, delaying the onset of crosslinking. Existing crosslinks would likewise be degraded by the amine. In the presence of ZnO, which acted as a trap for DMDCA, ZDMC formed and less pendent group and crosslink destruction resulted. This was evident in a reduction in the induction period (*cf.* Figs. 4 and

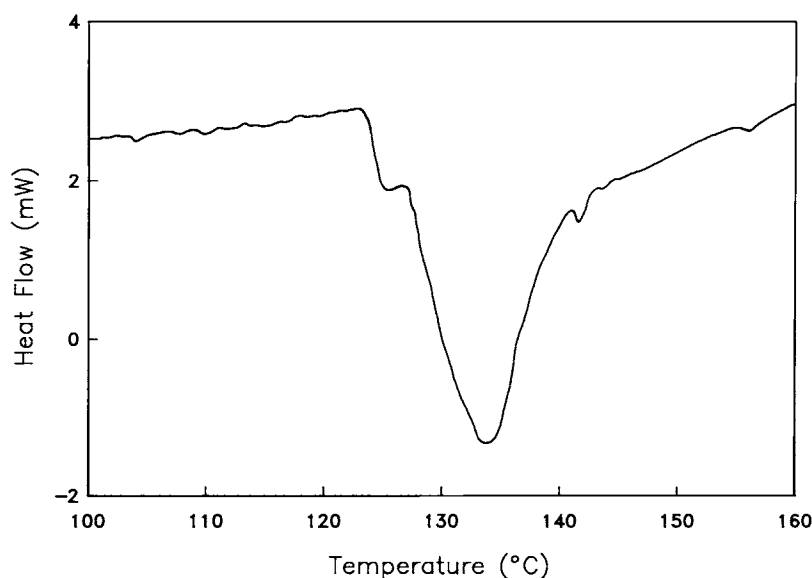


Figure 9 DSC spectrum: BR (100)/sulfur (9.46)/ZDMC (11.27)/stearic acid (10.53), $\Delta H = 7 \text{ J/g rubber}$.

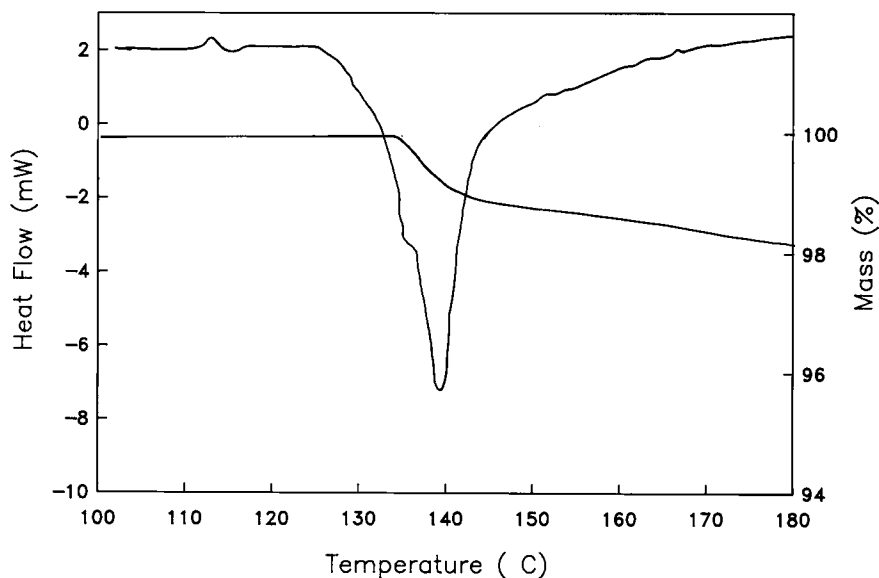


Figure 10 DSC spectrum and TGA curve for BR (100)/sulfur (9.46)/ZDMC (11.27)/ZnO (3.00), $\Delta H = 12$ J/g rubber.

5, 2 and 6, and 8 and 10) and the higher crosslink density in the presence on ZnO (Table I). Stearic acid had little effect on the crosslink density, but slightly retarded the onset of crosslinking (Figs. 3 and 7). This can be ascribed to the interaction between the accelerator and stearic acid.¹⁷ In sulfur/ZDMC compounds, stearic acid accelerated the onset of crosslinking slightly (*cf.* Figs. 8 and 9) and this may be ascribed to neutralization of the amine by the acid, reducing pendent group destruction.

Three features distinguish the vulcanization reactions in BR from those in IR⁵⁻¹²:

1. In all BR vulcanizates, the percentage polysulfidic crosslinks was lower than in IR compounds. In IR, the percentage decreased from 90%, in the early stages of the reaction, to 30–40%, while in BR the decrease was from around 45% to about 10%.
2. The crosslink density in IR vulcanizates was always much lower than in BR. IR vulcanizates showed serious reversion (40–50%) beyond the maximum in the DSC exotherm, while in BR, the final crosslink density generally decreased by less than 10% of the maximum value. Only in the sulfur/TMTD compound was there a large degree of reversion.
3. BR vulcanized faster than IR as gauged by the width of the vulcanization exotherms.

These differences can, in part, be explained. Crosslink making and breaking reactions occur concu-

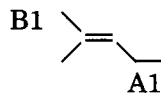
rently. In IR crosslink making, reactions initially exceeded breaking reactions, while after the peak in the exotherm, when all the sulfur had been consumed, crosslink breaking reactions dominated, leading to serious reversion. In BR, the initial rapid formation of crosslinks was followed by a steady-state process, in which making and breaking reactions were in equilibrium. In the sulfur/TMTD/ZnO system, for example, 46 mol % of sulfur remained at 136°C, yet there was no further increase in crosslink density in going to 160°C, when all of the sulfur had reacted. Kruger and McGill⁷ suggested that TMTD was the active desulfurating agent, and not ZDMC, as commonly observed in the literature.^{13,14} TMTM formed in the equilibrium⁶



Rapid removal of TMTP in the vulcanization process would force the equilibrium to the right, yielding a high concentration of TMTM as compared with TMTD. 49 mol % TMTM (expressed as a percentage of the original TMTD in the formulation) and 15 mol % TMTD were found in an IR/TMTD/ZnO compound at 140°C.⁶ In a similar BR compound, thin layer chromatography showed the formation of TMTM, but no TMTD was detected after vulcanization had commenced. In a BR/sulfur/TMTD/ZnO compound, too, TMTM formation was recorded. For example, at 136°C HPLC analysis showed 17 mol % TMTM and 6 mol % TMTD at 136°C. TMTD diffuses 2–4 times faster in BR than

in IR¹⁸ and, if similar diffusion rates apply to TMTM, one may speculate that the more ready availability of TMTM in BR compounds could lead to more rapid desulfuration, yielding vulcanizates with lower percentages of polysulfidic crosslinks. No residual TMTD was detected in any of the IR or BR compounds at the end of the vulcanization exotherm. Desulfuration by TMTM yields TMTP, and more rapid desulfuration would increase the rate of new crosslink formation via this source of TMTP, yielding a higher overall crosslink density in BR.

Crosslink densities may be higher in BR than in IR, as the lower polysulfidic crosslink content in BR would decrease the rate of crosslink destruction by thermal degradation. Furthermore, the high reactivity of the B1 position^{13,20,21} in IR may also lead to the more rapid degradation of crosslinks in IR as compared to BR vulcanizates.



The rapid reaction that occurred in BR after vulcanization had commenced may be ascribed to the fact that all the reaction sites are equivalent, while in IR the reactivities of A1 and B1 positions would be different. These differences in the reactivity of sites along the polymer chain may account for the reaction in IR occurring over a wider temperature range.

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ADDENDUM

Energy changes for the exotherms are noted in the legends to the figures. Enthalpies associated with the formation, degradation, and desulfuration of crosslinks, needed for the further interpretation of this data, are not currently available. The data should be treated with caution as values include energy changes due to the evaporation of volatiles. The

use of sealed DSC pans would eliminate the latter contribution to the overall energy change.

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