

Differential Scanning Calorimetric Study of the Interaction of 2,2'-Dibenzothiazole, Sulfur, Zinc Oxide, and Stearic Acid in the Presence of Polyisoprene

ADRIAAN S. LUYT

Department of Chemistry, Vista University (Soweto Campus) Private Bag X09, Bertsham, 2013, South Africa

SYNOPSIS

The interactions between mixtures of 2,2'-dibenzothiazole (MBTS), sulfur, ZnO, and stearic acid were studied by DSC in the presence of polyisoprene (IR). In the absence of ZnO, the onset of vulcanization was at a lower temperature than in its presence, and the crosslink densities were relatively low. ZnO as well as stearic acid did not influence the consumption of MBTS, but the amount of MBT in the sample after vulcanization increased in the presence of ZnO and still more when ZnO and stearic acid were present—the same applied for the crosslink densities. In view of these results, interaction mechanisms are proposed for the different systems.

INTRODUCTION

There have been a number of studies on the interaction of the vulcanization accelerator 2,2'-dibenzothiazole (MBTS) with sulfur, stearic acid, and ZnO in the absence of rubber. Morita, D'Amigo, and Young¹ investigated various sulfur-sulfenamide blends thermoanalytically, while Coran² used infrared to establish complex formation between MBTS and zinc stearate. Milligan³ tried to prepare benzene-soluble complexes of MBTS and zinc carboxylates, and Langenbeck and Rhiem^{4,5} investigated sulfur-MBTS interaction. Kruger and McGill⁶ gave a detailed description of and explanation for most of the MBTS interactions.

Few studies on the interactions in the presence of rubber have been reported. Campbell and Wise^{7,8} investigated NR-sulfur-MBTS and NR-sulfur-MBTS-zinc stearate vulcanization systems using ultraviolet spectrophotometric and polarographic methods. They found that 2,2'-dibenzothiazole polysulphides (MBTP) were formed in the cure delay period prior to vulcanization. Craig, Juve, and Davidson⁹ found that organic acids, such as salicylic and palmitic acids, delay vulcanization when MBTS

is present. This study reports on a DSC study of the interactions of MBTS, sulfur, ZnO, and stearic acid in the presence of polyisoprene (IR).

EXPERIMENTAL

2,2'-Dibenzothiazole was supplied by Karbochem in South Africa, while the other curatives were commercially available AR grade materials. Experimental details were given in a previous study.¹⁰ The amounts of ingredients mixed into the rubber are summarized in Table I.

RESULTS AND DISCUSSION

Figure 1 shows the heating of polyisoprene in the presence of MBTS-ZnO and MBTS-stearic acid-ZnO, respectively. In both cases no vulcanization occurred. In the presence of MBTS-ZnO two endotherms were observed. The first indicates the melting of MBTS, while the second, which falls outside the temperature range for vulcanization, probably indicates the reaction of MBTS with Zn²⁺ to form zincbenzothiazole 2-thiolate (ZMBT). With stearic acid also present, an endotherm at about

Table I Grams of Ingredients in Compounds Investigated

Compound	IR	MBTS	Sulfur	ZnO	Stearic Acid
1	21.8	2.74	2.06		
2	21.8	2.74		0.65	
3	21.8	2.74		0.65	2.29
4	21.8	2.74	2.06	0.65	
5	21.8	2.74	2.06	0.65	2.29

60°C indicating the melting of stearic acid is followed by an exotherm indicating reaction between stearic acid and ZnO to form zinc stearate. The second endotherm, characteristic of zinc stearate melting, is followed by a third endotherm in the temperature region where MBTS melts.

Figure 2 shows the dynamic vulcanization of polyisoprene in the presence of MBTS-sulfur, and Figure 3 shows the vulcanization in the presence of MBTS-sulfur-ZnO. Unlike the situation where MBT was used as accelerator,¹⁰ vulcanization started at approximately the same temperature in both cases, although the reaction was faster but less energetic (smaller ΔH) when ZnO was present. Figure 4 shows the vulcanization in the presence of

MBTS-sulfur-stearic acid-ZnO. Again vulcanization started in the same temperature region, but the reaction proceeded still faster with an even smaller reaction enthalpy.

For the system IR-MBTS-S an endotherm is observed immediately before the start of vulcanization. It probably represents the dissolution of MBTS in S with formation of 2,2'-dibenzothiazole polysulfides (MBTP).⁶⁻⁸ Table II shows that the monosulfidic crosslink densities are very low, while the polysulfidic crosslink densities have values approximately 10 times higher. In both cases the expected reversion occurs after the peak maximum. The extracted amount of MBTS remains nearly constant, while MBT was also extracted. The amounts of extracted MBT and sulfur decreased with increasing termination temperature.

The endotherm in the DSC curve of the system IR-MBTS-S-ZnO can be explained in a similar way. The monosulfidic crosslink densities are considerably higher than those in the system IR-MBTS-S, but the values for the polysulfidic crosslink densities were only about a factor 2 higher than those for the monosulfidic crosslink densities. Again the expected reversion occurs after the peak maximum. A general increase in the amount of extracted MBT was observed, while the amount of extracted MBTS remained nearly constant at a lower value

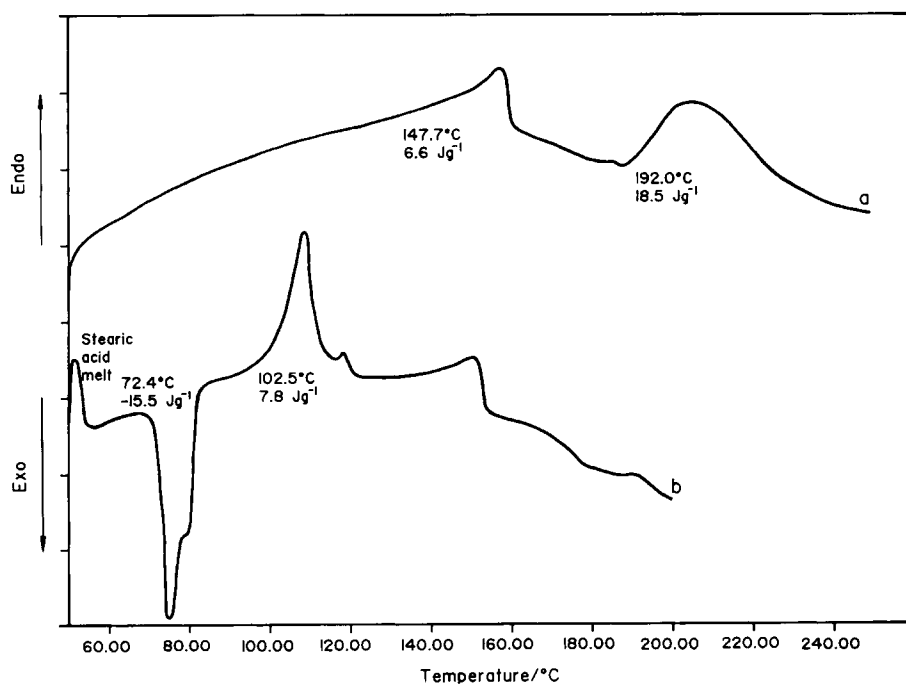


Figure 1 DSC curves for (a) IR-MBTS-ZnO (17.00 mg) and (b) IR-MBTS-stearic acid-ZnO (17.67 mg).

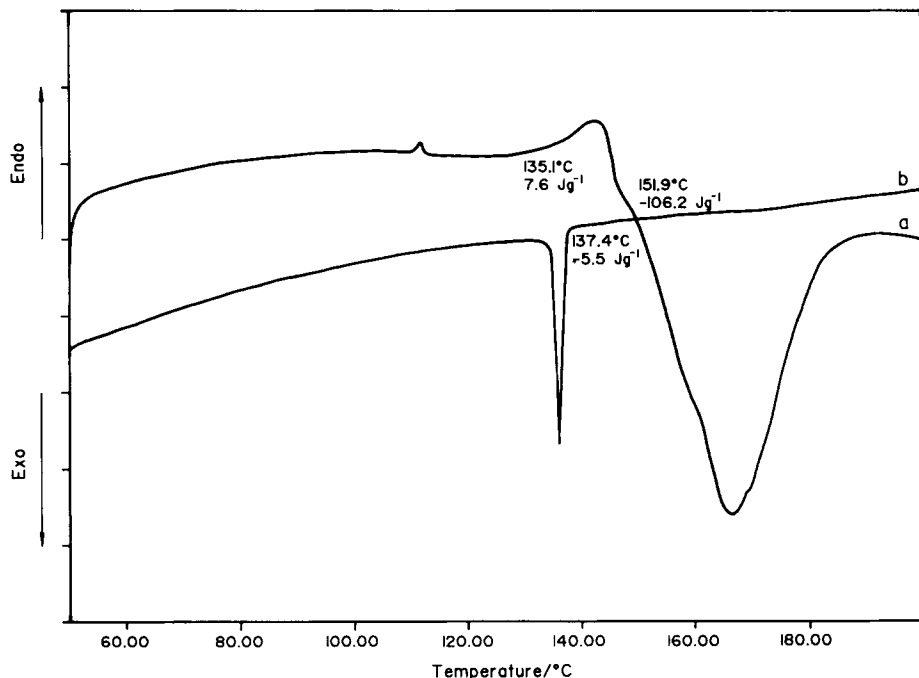


Figure 2 (a) DSC cure curve for IR-MBTS-S (17.34 mg) and (b) cooling curve after curing.

than in the previous case. The amounts of extracted sulfur were also lower.

For the system IR-MBTS-S-stearic acid-ZnO a zinc stearate melting endotherm was observed im-

mediately after the sulfur melting endotherm. As described before, the third endotherm probably represents the dissolution of MBTS in sulfur. The monosulfidic crosslink densities decreased from the

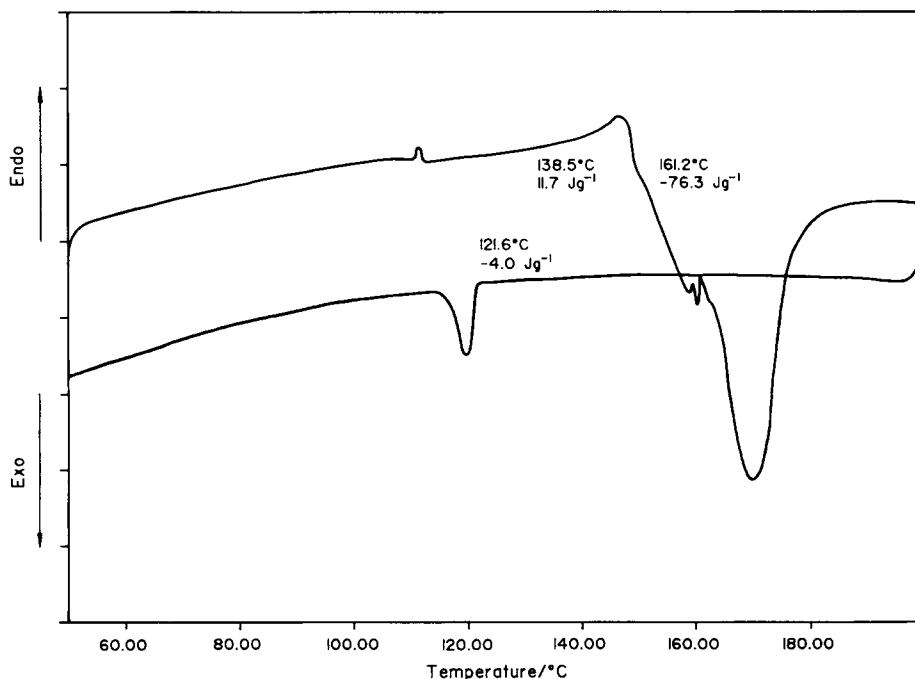


Figure 3 (a) DSC cure curve for IR-MBTS-S-ZnO (16.40 mg) and (b) cooling curve after curing.

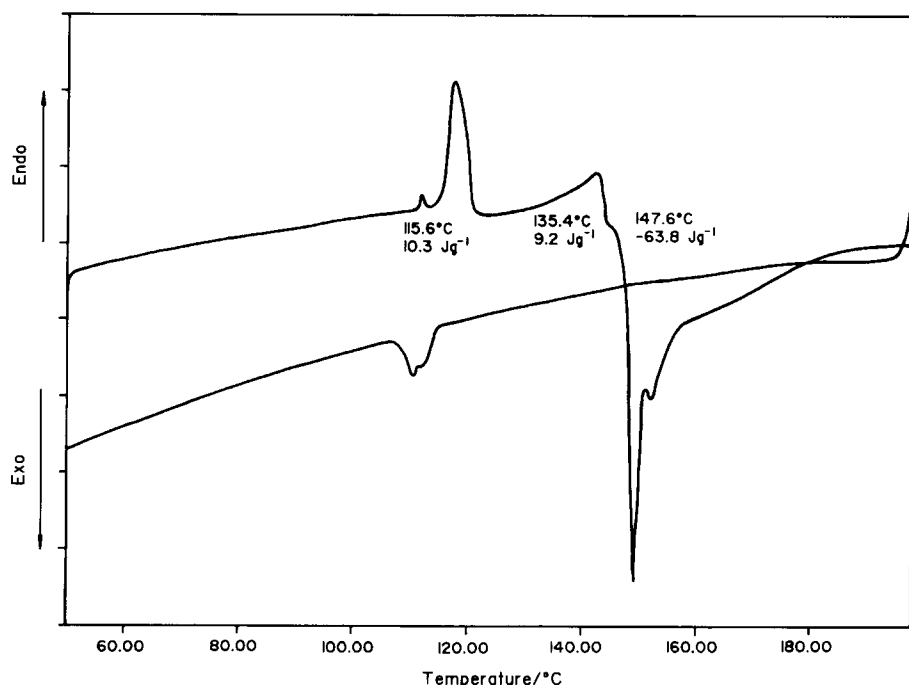
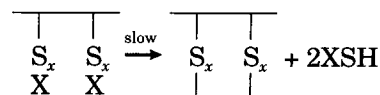
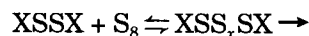


Figure 4 (a) DSC cure curve for IR-MBTS-S-stearic acid-ZnO (13.64 mg) and (b) cooling curve after curing.

start of vulcanization, but the polysulfidic crosslink densities increased until well after the peak maximum. Their values were also noticeably higher, especially in the region of the start of vulcanization. The amount of extracted MBT was even higher than in the previous case, with the amounts of extracted MBTS even lower. The amounts of extracted sulfur seem to be lower, although the difference is relatively small.

The proposed reaction mechanism for the system IR-MBTS-S is



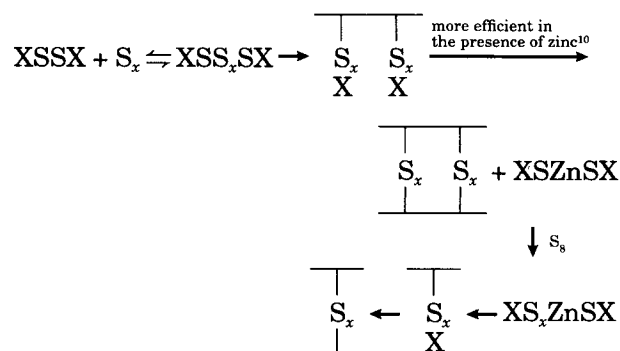
XSH (better known as MBT) will then react further as described in a previous publication.¹⁰ All the

Table II Crosslink Densities and Amounts of Extractables during Vulcanization of (a) IR-MBTS-S, (b) IR-MBTS-S-ZnO, and (c) IR-MBTS-S-Stearic Acid-ZnO

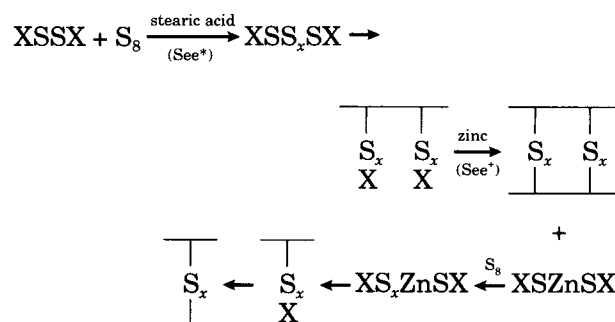
Termination Temp. (°C)		10 ³ Crosslink Density (mmol/mL)			10 ² Extractables (mmol/mL)		
		Mono-S	Poly-S	Total	MBT	MBTS	S
150	(c)	71.3	66.7	138	24.5	2.05	3.45
160	(a)	2.60	26.4	29.0	18.3	6.33	10.7
	(b)	10.1	25.9	36.0	6.79	3.00	4.38
	(c)	33.4	94.8	128	25.5	2.53	0.19
170	(a)	2.65	35.1	37.8	10.9	4.93	4.90
	(b)	45.9	92.4	138	17.0	1.61	0.80
	(c)	43.5	105	149	20.5	3.75	0.00
180	(a)	0.86	6.62	7.48	2.28	8.18	0.00
	(b)	18.4	63.1	81.5	18.6	5.18	0.00
	(c)	27.6	66.5	94.1	16.4	5.02	0.00
190	(a)	0.55	2.81	3.36	2.31	6.18	0.00
	(b)	17.1	36.3	53.4	14.9	5.81	0.00

MBTS is not consumed because of the formation of MBT, which preferably reacts with S_8 .

The reactions within the system IR-MBTS-S-ZnO may be described by



The proposed mechanism for IR-MBTS-S-stearic acid-ZnO is



In this system even more MBT is extracted because more ZMBT will be present, which provides stearic hindrance and inhibits the reaction of MBT.

In all three vulcanization systems described, the cure curves started in the same temperature region. The reason for this is probably that MBTS reacted first in all the cases, with the differences in curve shape attributed to the differences in mechanism

* According to Kruger and McGill⁶ organic acids, such as stearic acid, will delay the vulcanization. It does, however, not happen in this case because the stearic acid reacts with ZnO to form zinc stearate, which accelerates vulcanization after the initial reaction occurred.

† This part of the reaction is more efficient in the presence of zinc stearate because of the greater availability of Zn^{2+} ¹⁰

after the initial reaction. In Figures 2 through 4 the cooling curves showed crystallization exotherms that represents the crystallization of MBT¹¹ and MBTS.⁶ This confirms the HPLC results that there was still unreacted MBT and MBTS after vulcanization.

If this system is compared with the one where MBT acted as accelerator,¹⁰ the following can be concluded:

1. Generally the same vulcanization mechanism describes the process.
2. In this case MBT, which also partakes in the vulcanization process, is formed during the curative interaction.
3. The crosslink densities are much higher than those reported for MBT as accelerator, probably because both MBT and MBTS are now available to accelerate the process.

I wish to thank Professor W. J. McGill of the Department of Chemistry at the University of Port Elizabeth for the compounding of the rubber samples.

REFERENCES

1. E. Morita, J. J. D'Amigo, and E. J. Young, *Rubber Chem. Technol.*, **41**, 721 (1968).
2. A. Y. Coran, *Rubber Chem. Technol.*, **42**, 110 (1969).
3. B. Milligan, *Rubber Chem. Technol.*, **39**, 1115 (1966).
4. W. Langenbeck and H. C. Rhiem, *Chem. Abstr.*, **30**, 8688 (1936).
5. W. Langenbeck and H. C. Rhiem, *Chem. Ber.*, **68**, 2304 (1935).
6. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.*, to appear.
7. R. H. Campbell and R. W. Wise, *Rubber Chem. Technol.*, **37**, 635 (1964).
8. R. H. Campbell and R. W. Wise, *Rubber Chem. Technol.*, **37**, 650 (1964).
9. D. Craig, A. E. Juve, and W. L. Davidson, *J. Polym. Sci.*, **6**, 13 (1951).
10. A. S. Luyt, *J. Appl. Polym. Sci.*, to appear.
11. A. S. Luyt, W. J. McGill, and D. Shillington, *British Polym. J.*, **23**, 135 (1990).

Received March 11, 1991

Accepted May 14, 1991