

Reactions of 2-(4-Morpholiniothio)- and 2-(4-Morpholinodithio)benzothiazole in the Presence of Polyisoprene

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Received 27 November 1996; accepted 16 January 1997

ABSTRACT: 2-(4-Morpholiniothio)benzothiazole (MOR) and 2-(4-morpholinodithio)benzothiazole (MDB) were reacted, in combination with sulfur and ZnO, in the presence of polyisoprene (IR). Samples were heated in a DSC at 2.5°C/min and characterized by swelling experiments. The products formed at various temperatures were analyzed by HPLC. Crosslinking only occurred once all the benzothiazole sulfenamide had been consumed, the onset of vulcanization characterized by a considerable increase in 2-mercaptobenzothiazole (MBT) concentration. Crosslinking occurred earlier in all corresponding MDB formulations. Higher crosslink densities were recorded with addition of ZnO. The delayed action experienced in MOR systems was attributed to an exchange reaction between benzothiazole-terminated pendent groups and MOR and not due to the stability of the disulfide, MDB. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1093–1099, 1997

Key words: 2-(4-morpholiniothio)benzothiazole; 2-(4-morpholinodithio)benzothiazole; polyisoprene

INTRODUCTION

Benzothiazole sulfenamides are commercially important delayed-action accelerators. The basicity of amines and the steric hindrance of the amine structure affect the delayed action,^{1,2} and primary amines have been shown² to cure faster than secondary amines. It is generally agreed that all of the sulfenamide must be consumed before the onset of crosslinking.^{3–11} The 2-bisbenzothiazole-2,2'-disulfide (MBTS) concentration in the rubber increases initially but decreases again prior to crosslinking while 2-mercaptobenzothiazole (MBT) forms on crosslinking, the maximum crosslink density coinciding with the maximum MBT pro-

duced in the reaction.^{4,5} Campbell and Wise⁴ suggested that, as no 2-(4-morpholiniothio) benzothiazole (MOR) was present when crosslinking started, it did not act directly in crosslinking but played a preparatory role. The intermediary reacted with MOR rather than with the rubber chain and more MOR would thus further inhibit crosslinking. Morita and Young⁶ concluded that the rate of sulfur–sulfenamide reaction and the stability of intermediates influence the delayed action. The formation of 2-(4-morpholinodithio)benzothiazole (MDB), which is sufficiently stable to be isolated, was considered to delay crosslinking. Scheele and Cherubin⁷ also proposed the rapid formation of accelerator complexes that reacted slowly with rubber. Coran⁸ suggested a kinetic scheme that involved the formation of a chelate of the accelerator–zinc complex, the chelate being a more reactive form of the accelerator. More recently, Gradwell and McGill⁹ proposed an exchange reaction between benzothiazole termi-

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Contract grant sponsor: South African Foundation for Research Development.

Journal of Applied Polymer Science, Vol. 66, 1093–1099 (1997)

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CCC 0021-8995/97/061093-07

nated pendent groups and *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS), forming amine-terminated pendent groups. The lower reactivity of the amine-terminated pendent groups was said to account for the delay action experienced in CBS vulcanization.

The decomposition of MOR and its interaction with sulfur and ZnO in the absence of rubber has been described.¹²⁻¹⁴ MDB has been shown to be thermally less stable than MOR.¹⁴

This article reinvestigates the vulcanization of polyisoprene (IR) accelerated by MOR systems. Specifically, it looks at MDB as an intermediate that may cause a delayed reaction and further examines the deactivation of pendent groups by the sulfenamide (as proposed by Gradwell and McGill for CBS⁹) as a reason for the delayed action in MOR vulcanization.

EXPERIMENTAL

The MOR was produced by Bayer (Barcelona) and the polyisoprene by Karbochem, Division of Sentrachem (South Africa). Compounds were prepared on a Brabender Plasticorder, and vulcanized by heating samples to various temperatures at 2.5°C/min in a differential scanning calorimeter (DSC). The network was characterized by swelling in benzene, and extractable curatives were analyzed by high-performance liquid chromatography (HPLC). Experimental details have been described earlier.¹² The amount of curative in parts per hundred rubber (phr) added to the rubber is in the form IR(100)/MOR(9.8)/sulfur(9.5). The curatives were used in the ratio of 1 mol : 1 mol unless stated otherwise. All of the curatives were added as 33.5×10^{-5} mol/mL rubber.

MOR was found to react with sulfur at room temperature, and for this reason the rubber could not be extracted for long periods of time. The data for 2-(4-morpholinopolythio)benzothiazoles (MORPs) and 2-bisbenzothiazole-2,2'-polysulfides (MBTPs) reported in the text are the total polysulfide concentrations and include the trisulfides, tetrasulfides, and any higher polysulfides detected by HPLC. MDB was synthesized according to the method described by Hardman.¹⁵

RESULTS

IR/MOR

The vulcanization of IR by MOR, in the absence of sulfur, occurred in the same temperature region

as that in which decomposition of MOR occurred.¹⁴ The vulcanization exotherm of the IR(100)/MOR(9.8) mix started at 215°C and peaked at 225°C (Fig. 1). Prior to crosslinking, little MBT and MBTS were formed, the MBTS concentration peaking with gel formation (Fig. 1 and Table I). As noted in an earlier article,¹⁴ some MBT was present as an impurity in MOR. Crosslinking only commenced once all the MOR had been consumed, at which time the amount of MBT extracted from the compound increased considerably. Some 2-bisbenzothiazole-2,2'-monosulfide (MBTM) and 2-(4-morpholino)benzothiazole (MB), both which are thermally more stable than the other species, formed above 215°C. Approximately 40 mol % of the benzothiazole groups were unaccounted for and were presumably bound to the rubber chain. These could be present as monosulfidic pendent groups that are unreactive and do not lead to crosslink formation. As this system did not contain elemental sulfur, the crosslink density was very low, reaching a maximum crosslink density of 0.212×10^{-5} mol/mL (Table I).

IR/MOR/Sulfur

The DSC curve of the IR(100)/MOR(9.8)/sulfur(9.5) mix shows a single exotherm, starting at 158°C and peaking at 169°C (Fig. 2). MDB formed in small amounts and reached a maximum concentration just prior to vulcanization, after which it rapidly disappeared. Crosslinking only commenced once both the MOR and MDB had been completely consumed, reaching a maximum crosslink density of 7.33×10^{-5} mol/mL at 170°C (Table I). A small amount of MBTPs (<2 mol %) was found before crosslinking and a little MBTM (<2 mol %) after crosslinking. The concentration of MBTS increased slightly at the temperature at which crosslinking occurred. MBT, however, rapidly formed once crosslinking began, then remained at a constant concentration (Fig. 2). A small amount of MB was also observed after the onset of crosslinking. At the onset of crosslinking only 23 mol % of the sulfur was bound to the rubber.

IR/MDB/Sulfur

The vulcanization curve of the IR(100)/MDB(9.85)/sulfur(9.5) mix was broader than that for IR/MOR/sulfur and occurred at lower temperatures, starting at 145°C and peaking at 164°C (Fig. 3). Prior to the crosslinking exotherm

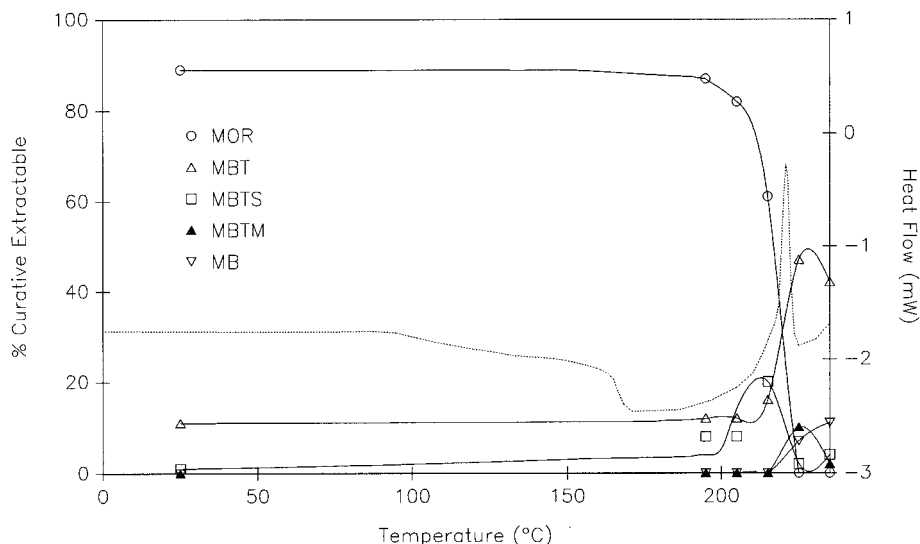


Figure 1 Percentage extractable curatives and DSC curve (· · · · ·) for the IR/MOR system.

(140°C), 53 mol % of MDB had converted to MBTS, MBTPs, and MBTM, together with a small amount of MBT (Fig. 3). The concentrations of all accelerator species, other than MBT, however, rapidly decreased to zero when vulcanization started. MDB did not desulfurate to form MOR. Crosslinking only began once all the MDB had been consumed and was accompanied by the release of more MBT. The maximum crosslink density (5.55×10^{-5} mol/mL) coincided with the apex

of the exotherm, i.e., 164°C (Table I). At the onset of vulcanization (gel state) 23 mol % of sulfur had been bound to the rubber. A small amount of MB (<3 mol %) was found after crosslinking had commenced.

IR/MOR/Sulfur/ZnO

The addition of ZnO to the IR/MOR/sulfur system changed the single vulcanization exotherm into

Table I Comparison of Crosslink Densities $1/2 M_c$ (mol/mL $\times 10^5$) at Different Temperatures for Vulcanization Systems Studied

Temp (°C)	IR/MOR	IR/MOR/Sulfur	IR/MDB/Sulfur	IR/MOR/Sulfur/ZnO	IR/MDB/Sulfur/ZnO
25	0	0	0	0	0
130		0		0	0
135					15.3
140		0	0	0	
145			0	0	18.1
150		0	0	0	20.5
155		0	4.3	0.63	
160		4.77	5.32	22.1	8.77
165			5.55		8.39
170		7.33	4.22	12.81	4.97
180		3.78		7.64	4.37
185			1.43		
190		2.56			
205	0				
215	0				
225	0.19	1.45	1.96	1.15	2.97
235	0.21				

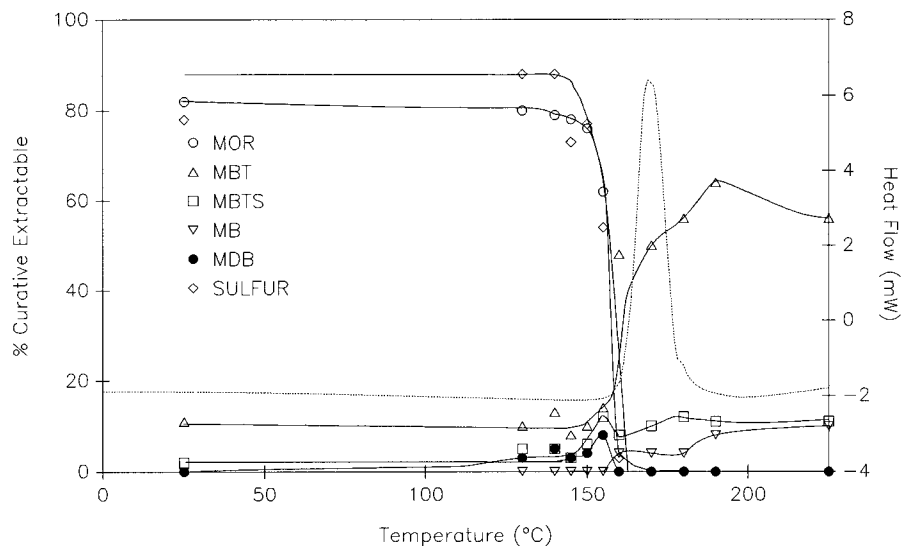


Figure 2 Percentage extractable curatives and DSC curve (· · · · ·) for the IR/MOR/sulfur system.

two exotherms. The DSC curve of the IR(100)/MOR(9.8)/sulfur(9.5)/ZnO(3) mix showed the first exotherm starting at 153°C and peaking at 158°C, and the second peaking at 167°C (Fig. 4). The second exotherm occurred in much the same temperature range as the single exotherm found in the absence of ZnO (Fig. 2), the exotherm preceding it being very narrow. Rapid crosslinking occurred during the first exotherm while reversion reactions dominated during the second exotherm. It can be seen from Table I that the cross-

link density increased very rapidly, reaching a maximum of 22.1×10^{-5} mol/mL at 160°C (Table I), at which stage most of the sulfur had been consumed, and then decreased gradually.

Only 1% of the MOR was extractable as MDB (just prior to crosslinking), in contrast to the 8% in the absence of ZnO (Fig. 2). Again, rapid crosslinking occurred once most of the MOR had been consumed and the release of MBT accompanied crosslinking (Fig. 4). Small amounts of MBTS were formed throughout the reaction.

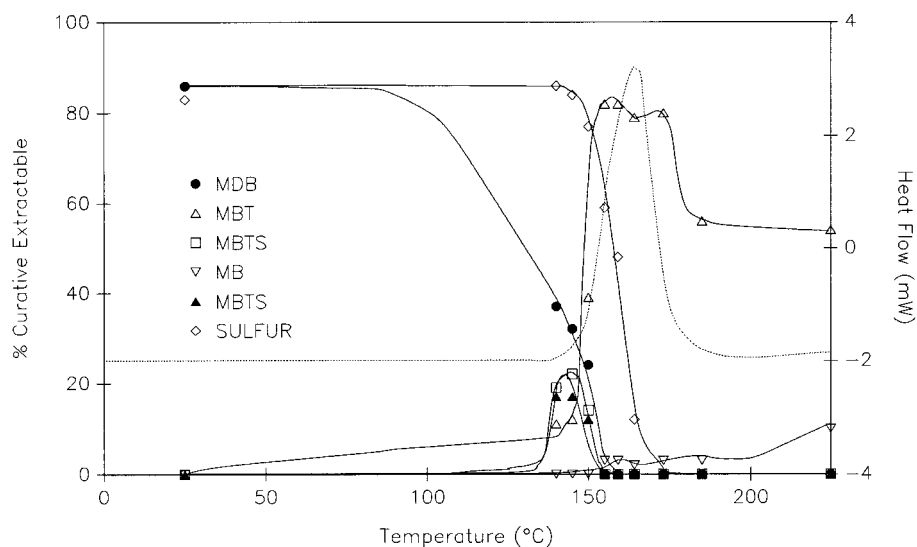


Figure 3 Percentage extractable curatives and DSC curve (· · · · ·) for the IR/MDB/sulfur system.

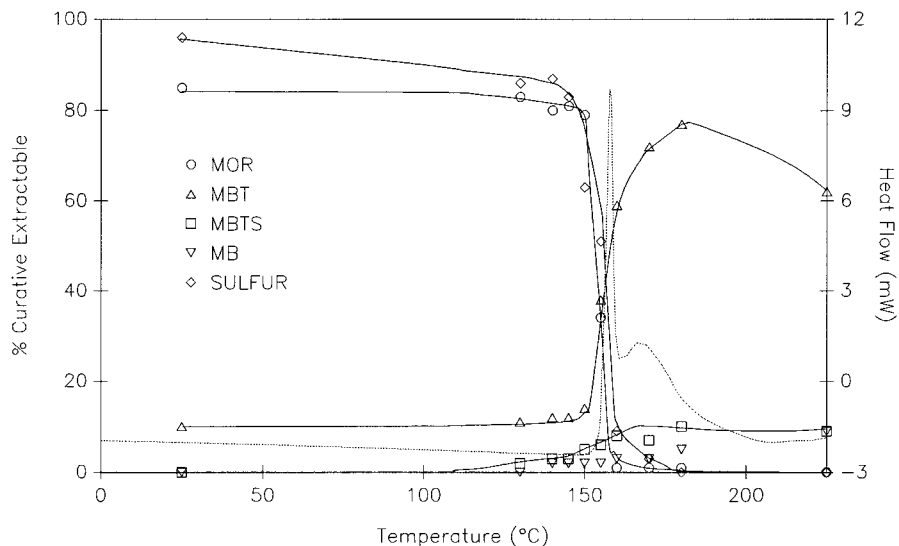


Figure 4 Percentage extractable curatives and DSC curve (· · · · ·) for the IR/MOR/sulfur/ZnO system.

IR/MDB/Sulfur/ZnO

The DSC curve and HPLC data for this system, IR(100)/MDB(9.85)/sulfur(9.5)/ZnO(3) are given in Figure 5. Changes in the extractable products were analogous to those obtained with the corresponding MOR system (cf. Figs. 4 and 5). As with all MDB formulations, crosslinking occurred earlier than with MOR.

DISCUSSION

IR/MOR/Sulfur and IR/MDB/Sulfur

Rapid crosslinking occurred in the same temperature range (155–160°C) as with CBS.⁹ Gradwell and McGill⁹ found that crosslinking commenced when at 155°C the CBS concentration had decreased to 10 mol %, while 57 mol % MBTS had

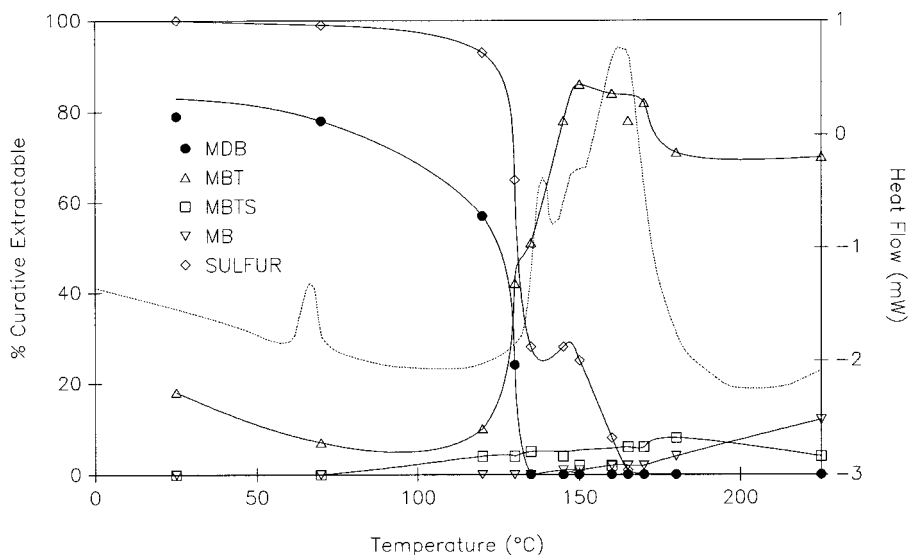
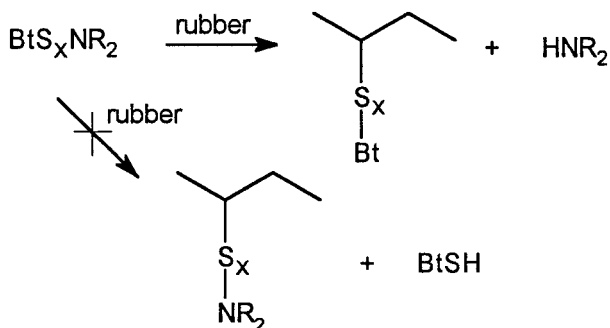
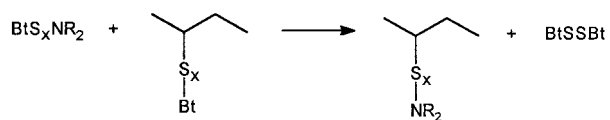


Figure 5 Percentage extractable curatives and DSC curve (· · · · ·) for the IR/MDB/sulfur/ZnO system.

formed. As no MBT formation was detected prior to crosslinking, it was suggested that MORPs added to the chain as benzothiazole pendent groups.

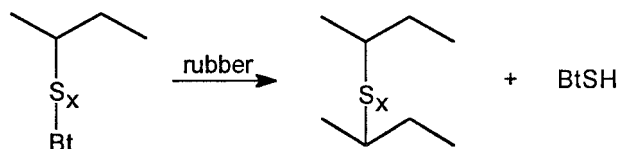


Scheele and Helberg⁵ reported the presence of the free amine in a CBS vulcanizate, the amine concentration reaching a maximum at the onset of crosslinking. An increase in MBTS accompanied the decrease in the CBS concentration. Gradwell⁹ ascribed the delayed crosslinking with CBS to an exchange reaction between CBS and a benzothiazole pendent group, the amine terminated groups thus formed being less reactive.



At 155°C, where the formation of a very loose gel was detectable, 98% of the benzothiazole groups added to the compound as MOR could be accounted for in the extract as MOR or MBTS, i.e., no benzothiazole terminated pendent groups existed, in line with the suggested mechanism.⁹ This supports the contention that an exchange reaction occurs. Crosslinking in CBS systems commences once CBS has been consumed^{6,9,16} when, according to Gradwell and McGill,⁹ the deactivation of new benzothiazole pendent groups no longer occurs. With MOR the events leading up to crosslinking were not as readily distinguishable and, while 62 mol % MOR remained at 155°C (where a lightly crosslinked gel was detected), the accelerator concentration dropped to zero, immediately crosslinking began ($1/2\text{Mc} = 4.77 \times 10^{-5} \text{ mol/mL}$ at 160°C). MBTS resulting from pendent group exchange as described above reacts with sulfur to form MBTPs, and these can add to the rubber to form benzothiazole pendent groups. Once all the MOR has been consumed and BtS_x —

pendent groups are no longer deactivated they react with neighboring chains to produce crosslinks and MBT. The appearance of MBT coincided with the onset of crosslinking in CBS⁹ and in MOR-accelerated compounds.



The maximum crosslink density measured ($7.33 \times 10^{-5} \text{ mol/mL}$) was similar to that found with the IR/CBS/sulfur system ($7.35 \times 10^{-5} \text{ mol/mL}$ ⁹).

Most of the MOR and MBTS had been consumed at 160°C (Fig. 2), yet 54 mol % of the sulfur remained. It is suggested that, as in the case of the CBS compound,⁹ the remaining sulfur reacted via a MBT accelerated mechanism, this being the only accelerator present.

In the absence of sulfur, degradation of MOR was slow¹⁴ and vulcanization in IR/MOR systems only occurred above 200°C, i.e., in the temperature region at which rapid degradation of MOR occurred. Crosslinking was very limited, as few sulfurated species (MBTPs, MORPs) could form. The behavior of the system was analogous to that found with IR/CBS.⁹ MDB forms from MOR and sulfur on heating. Unlike many other accelerator polysulfides it has sufficient stability to be isolated but the delayed action cannot be attributed to its stability. As shown in a previous article,¹⁴ MDB is less stable than MOR, and crosslinking occurred slightly earlier in the IR/MDB/sulfur system than in the IR/MOR/sulfur system (cf. Figs. 3 and 2).

The vulcanization behavior of the MDB-accelerated system (IR/MDB/sulfur) was similar to that of the MOR-accelerated system. MDB decomposed slowly, forming the same products as in the absence of IR.¹⁴ Most of the MDB had disappeared before any gel was detected, the formation of MBT accompanying crosslinking. As MBTS was not reformed, the amounts of MBT liberated on crosslinking were slightly higher than with MOR (cf. Figs. 3 and 2). The maximum crosslink density measured was slightly lower than that obtained with the MOR system.

Effect of ZnO

The vulcanization curve for the IR/MOR/sulfur/ZnO (Fig. 4) system mimicked that of the corre-

sponding CBS formulation. Crosslinking occurred slightly earlier in the presence of ZnO, and was very rapid reaching a much higher value. Reversion occurred during the second exotherm and was particularly marked. Changes in the extractable products at different temperatures were similar to changes observed in the absence of ZnO. This is not surprising, as MOR and ZnO do not interact.⁸ Crosslinking commenced once all of the MOR had been consumed, and MBT was the main extractable reaction product. The amount of extractable MBT remained high. This is in agreement with data produced by Gradwell⁹ on CBS and with findings of Auerbach.¹⁷ It was earlier suggested that MBT was present as the amine salt and was thus not available for reaction with ZnO.¹³ Recent studies¹⁸ in these laboratories have shown that when the rubber is not subjected to shear, as occurs during compounding, Zn(mbt)₂ formation around ZnO particles is limited.

A satisfactory explanation for the high crosslink densities achieved with ZnO has not yet been forthcoming, although Gradwell⁹ suggested that ZnO may promote crosslinking and reduce cyclization reactions that "waste" pendent groups. In the IR/MDB/sulfur/ZnO system, also, crosslinking started slightly earlier in the presence of ZnO (Fig. 5), and again, very high crosslink densities were attained.

CONCLUSIONS

The same reaction mechanisms applied to the vulcanization of IR with MOR and MDB as were reported earlier for CBS, with MBT forming as a by-product of crosslinking. The scorch delay can be attributed to an exchange reaction between the accelerator and pendent groups, and not to the high stability of MDB, as has been proposed. Indeed, MDB was found to be more reactive than MOR.

ZnO led to an increase in the crosslink density

but did not alter the nature of the extractable reaction intermediates. MBT formed during the reaction does not react with ZnO to form Zn(mbt)₂. This is attributed to Zn(mbt)₂ formed around ZnO particles restricting further reaction.

The authors wish to thank the South African Foundation for Research Development for financial assistance.

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