# Effect of Carboxylic Acids on 2-Bisbenzothiazole-2,2'-Disulfide- and Tetramethylthiuram Disulfide-Accelerated Sulfur Vulcanization. II. Vulcanization of Polyisoprene in the Absence of ZnO

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ABSTRACT: Polyisoprene was vulcanized by 2-bisbenzothiazole-2,2'-disulfide (MBTS)/ sulfur and tetramethylthiuram disulfide (TMTD)/sulfur in the absence and presence of benzoic and stearic acids. It was found that the crosslink density of MBTS vulcanizates is halved by the addition of carboxylic acids and this can be explained in terms of the attack of the acids on the accelerator polysulfides. TMTD polysulfides are more reactive toward polyisoprene than are MBTS polysulfides, and their addition to the polymer chain occurs before significant attack by the carboxylic acids can reduce the polysulfide concentration. Consequently, the acids have little effect on the crosslink density of TMTD vulcanizates. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1007–1012, 1999

**Keywords:** vulcanization; polyisoprene; carboxylic acids; 2-bisbenzothiazole-2,2'-disulfide; tetramethylthiuram disulfide

## **INTRODUCTION**

It is well established that the first step in the vulcanization of polyisoprene (IR) with 2-bisbenzothiazole-2,2'-disulfide (MBTS)/sulfur and with tetramethylthiuram disulfide (TMTD)/sulfur is the formation of the polysulfides of MBTS<sup>1-3</sup> and TMTD<sup>3-6</sup>, respectively. It is generally agreed<sup>3,6-9</sup> that tetramethylthiuram polysulfides (TMTP) react with the polymer chain in a substitution reaction, liberating dimethyldithiocarbamic acid (Hdmtc), but the addition of 2-bisbenzothiazole-2,2'-polysulfides (MBTP) to the chain is unclear. Many authors<sup>10-12</sup> have reported that 2-mercaptobenzothiazole (MBT) is liberated, but others<sup>1,13</sup> suggested that MBT is formed only on crosslinking. Further reaction of pendent groups leads to crosslinking.  $^{8,10,14}$ 

In a previous article,<sup>15</sup> it was shown that, in the absence of rubber, benzoic and stearic acids react with the accelerators to decrease the concentrations of MBTP and TMTP that form on heating with sulfur. With MBTS, much of the MBTP is converted to 2-benzoylthiobenzothiazole (BzM) and stearicthiobenzothiazole (StM) and their polysulfides, while at higher temperatures, the carboxylic acids initiate decomposition of MBTS, BzM, StM, and their polysulfides. With TMTD, lesser amounts of 2-benzoyldimethyldithiocarbamate (BzT) and stearicdimethyldithiocarbamate (StT) are produced on reaction with carboxylic acids, but the acid-initiated decomposition of TMTD, BzT, StT, and their polysulfides occurs more readily.

Accelerator polysulfides initiate reaction with the polymer chain and this article examines the influence of carboxylic acids, in the absence of

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IR	MBTS	TMTD	Sulfur	Benzoic Acid	Stearic Acid
100	12.27		9.46		
100	12.27		9.46	4.51	
100	12.27		9.46		10.49
100		8.86	9.46		
100		8.86	9.46	4.51	
100		8.86	9.46		10.49

 
 Table I
 Compound Formulations in Parts per Hundred Rubber

ZnO, on the MBTS- and TMTD-accelerated sulfur vulcanization of IR.

#### **EXPERIMENTAL**

The materials used were the following: IR (Afprene IR80; Karbochem, Newcastle, South Africa); Orac MBTS (chemical purity 97%) and Orac TMTD (chemical purity 99.9%) (Orchem, Sasolburg, South Africa); sulfur (chemical purity 99.9%); and benzoic acid (Riedel-de-Haën, Seelze, Germany); and stearic acid (Marine Oil Refiners, Capetown, South Africa).

The compounds (Table I) were prepared in a Brabender Plasticorder as described earlier<sup>16,17</sup> and vulcanized in sealed pans in a DSC, either isothermally at 150°C or at a programmed heating rate of 2.5°C/min.<sup>16,17</sup> The compounds contained 1:1 molar ratios of curatives. Residual

curatives and soluble intermediates were extracted from the rubber at various stages of the reaction and analyzed by HPLC.<sup>15–17</sup> In the figures, concentrations of the reactants, intermediates, and products are expressed in terms of the initial mol concentration of reactant. Crosslink densities were determined by swelling.<sup>17</sup>

#### **RESULTS AND DISCUSSION**

#### **MBTS Vulcanization**

In a dynamic thermal study involving heating samples in a DSC at a programmed rate and stopping the reaction at various temperatures, Gradwell and McGill,<sup>1</sup> in contrast to many other researchers,<sup>11,12</sup> only detected MBT at the onset of crosslink formation. Campbell and Wise<sup>13</sup> also reported that MBT formation paralleled the crosslink concentration. An isothermal study of IR/MBTS/sulfur (Fig. 1) shows that there is a considerable decrease in the concentration of extractable MBTS before the onset of crosslinking and, indeed, most of the accelerator is consumed prior to the formation of crosslinks. Accelerator consumption involves the formation of MBTP, which is reactive and, in the presence of IR, readily forms benzothiazole-terminated polysulfidic pendent groups. MBT formation coincides with the onset of crosslinking, in agreement with the findings of Gradwell and McGill<sup>1</sup> and Campbell and Wise<sup>13</sup> and suggests that pendent group



**Figure 1** Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/MBTS/sulfur at 150°C: ( $\blacksquare$ ) crosslink density; ( $\triangle$ ) MBTS; ( $\bigcirc$ ) MBTM; ( $\bigtriangledown$ ) MBTP; ( $\bullet$ ) sulfur; ( $\Box$ ) MBT.



**Figure 2** Crosslink densities for  $(\blacksquare)$  IR/MBTS/sulfur,  $(\bullet)$  IR/MBTS/sulfur/benzoic acid, and  $(\blacktriangle)$  IR/MBTS/sulfur/stearic acid vulcanized at 150°C.

formation is an additive and not a substitutive reaction, as in the case of TMTD-accelerated sulfur vulcanization.<sup>8</sup> It is not clear how the addition of benzothiazole groups to the chains occurs.<sup>1</sup>

Figure 2 compares the crosslink density of IR/ MBTS/sulfur with and without carboxylic acids and reveals substantial differences in the presence of the acids. Not only is there a 2.5-min delay in the onset of crosslinking when vulcanization is conducted in the presence of benzoic acid, but the maximum crosslink density is more than halved. Although crosslinking is only detected after 10 min in this system, MBT production already occurs after 5 min (Fig. 3). In the absence of benzoic acid, MBT formation was detected only at the onset of crosslinking (Fig. 1). It is clear that the earlier formation of MBT is not associated with pendent group formation, but is due to the interaction between MBTP and benzoic acid to form BzM polysulfides and MBT, as demonstrated in an earlier article.<sup>15</sup> Due to the small concentration of curatives in the rubber, HPLC separation of BzM species from MBTP was not possible, nor was detection of benzoic acid possible due to its low concentration in the rubber and low UV extinction coefficient.



**Figure 3** Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/MBTS/sulfur/benzoic acid at 150°C: ( $\blacksquare$ ) crosslink density; ( $\blacktriangle$ ) MBTS; ( $\bigcirc$ ) MBTM; ( $\bigtriangledown$ ) MBTP; ( $\bullet$ ) sulfur; ( $\Box$ ) MBT.



**Figure 4** Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/MBTS/sulfur/stearic acid at 150°C: ( $\blacksquare$ ) crosslink density; ( $\triangle$ ) MBTS; ( $\bigcirc$ ) MBTM; ( $\bigtriangledown$ ) MBTP; ( $\bullet$ ) sulfur; ( $\Box$ ) MBT.

BzM was synthesized<sup>15</sup> and added to an IR/ sulfur compound. After 60 min at 150°C, a crosslink density (1/2 Mc) of  $1 \times 10^{-5}$  mol/mL was measured, compared to a value of  $0.9 \times 10^{-5}$ mol/mL in an IR/sulfur compound in the absence of BzM. BzM is clearly not an accelerator and the formation of BzM polysulfides may be envisaged as a wastage of the MBTS accelerator.

The trends observed in the IR/MBTS/sulfur/ stearic acid compound (Fig. 4) are analogous to trends in the benzoic acid compound (Fig. 3). The delay in the onset of crosslinking is even more apparent in the presence of stearic acid and the maximum crosslink density is halved (Fig. 2). As in the presence of benzoic acid, MBT formation occurs prior to the formation of crosslinks (Fig. 4) and is not due to the formation of pendent groups, but is due to the interaction between stearic acid and MBTP to form StM, as demonstrated earlier.<sup>15</sup> There is less reversion in the presence of the carboxylic acids, particularly in the case of benzoic acid (Fig. 2), and this may be due to the higher concentrations of sulfur available to MBT, which is a slow accelerator compared to MBTS



**Figure 5** Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur at 150°C: ( $\blacksquare$ ) crosslink density; ( $\triangle$ ) TMTD; ( $\bigcirc$ ) TMTM; ( $\bigtriangledown$ ) TMTP; ( $\bullet$ ) sulfur.



**Figure 6** Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur at 2.5°C/min: ( $\blacksquare$ ) crosslink density; ( $\blacktriangle$ ) TMTD; ( $\bigcirc$ ) TMTM; ( $\bigtriangledown$ ) TMTP; ( $\bullet$ ) sulfur.

and will continue the process once all the MBTS has reacted.

#### **TMTD Vulcanization**

TMTD is more reactive toward IR than is MBTS. At 150°C, MBTS-accelerated sulfur vulcanization occurs after 7.5 min (Fig. 1), while a similar TMTD compound vulcanizes after 5 min (Fig. 5). Crosslinking is also faster in the case of TMTD vulcanizates. With TMTD, lesser amounts of the accelerator-acid complexes BzT and StT are produced on reaction with carboxylic acids than in the case of the MBTS systems.<sup>15</sup> Hdmtc, liberated when BzT and StT form as a result of acid–accelerator interaction, is an efficient accelerator,<sup>18</sup> more so than MBT<sup>16</sup> liberated when BzM and StM form in MBTS formulations. Thus, the influence of carboxylic acids on TMTD-accelerated vulcanization is expected to be limited. Furthermore, although the acid-initiated decomposition of TMTP occurs above 140°C,<sup>15</sup> vulcanization at a programmed rate showed that most of the TMTD



**Figure 7** Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur/benzoic acid at 150°C: ( $\blacksquare$ ) crosslink density; ( $\blacktriangle$ ) TMTD; ( $\bigcirc$ ) TMTM; ( $\bigtriangledown$ ) TMTP; ( $\bullet$ ) sulfur.



**Figure 8** Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur/stearic acid at 150°C: ( $\blacksquare$ ) crosslink density; ( $\blacktriangle$ ) TMTD; ( $\bigcirc$ ) TMTM; ( $\bigtriangledown$ ) TMTP; ( $\bullet$ ) sulfur.

had already been added to the rubber chain by this temperature (Fig. 6). Comparison of Figures 6-8 shows that, while crosslinking is slightly more rapid in the presence of carboxylic acids, the maximum crosslink density achieved is not noticeably affected.

### **CONCLUSIONS**

The rapid reaction of MBTP with carboxylic acids at vulcanization temperatures reduces the concentration of MBTP available for participation in the vulcanization reaction. This increases the induction period and decreases the maximum crosslink density obtained in MBTS vulcanizates. TMTP is less reactive toward carboxylic acids and adds to the polymer chain more readily than does MBTP. Consequently, carboxylic acids have little influence on the crosslink density of TMTD-accelerated vulcanizates.

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