Effect of Carboxylic Acids on 2-Bisbenzothiazole-2,2'-Disulfide- and Tetramethylthiuram Disulfide-Accelerated Sulfur Vulcanization. III. Reaction Between Accelerators and Zinc Salts of the Acids

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ABSTRACT: Stearic and benzoic acids were heated with 2-bisbenzothiazole-2,2'-disulfide (MBTS)/sulfur/ZnO and tetramethylthiuram disulfide (TMTD)/sulfur/ZnO isothermally at 150°C and in a DSC at 2.5°C/min, in the absence of rubber. The acids readily reacted with ZnO, and at vulcanization temperatures, little or no free acid remains. The zinc salts are less reactive toward the accelerators and accelerator polysulfides than are the acids, although with benzoic acid/ZnO, MBTS formulations produced small amounts of the accelerator-acid complex 2-benzoylthiobenzothiazole and 2-mercaptobenzothiazole, while with TMTD formulations, limited 2-benzoyldimethyldithiocarbamate formation was detected. These small amounts of the reaction can be attributed to the incomplete consumption of benzoic acid, zinc benzoate restricting the acceleratoracid complexes is limited, the zinc salts do promote the slow decomposition of MBTS and TMTD above 150°C. It can be concluded that in the presence of ZnO carboxylic acids should not detrimentally effect the vulcanization reaction. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1013–1020, 1999

Key words: vulcanization; stearic acid; benzoic acid; 2-bisbenzothiazole-2,2'-disulfide; tetramethylthiuram disulfide; ZnO

INTRODUCTION

Carboxylic acids, notably stearic acid, are commonly used as coactivators with ZnO in accelerated sulfur vulcanization.¹ Kapur et al.² suggested a reaction between 2-bisbenzothiazole-2,2'-disulfide (MBTS) and ZnO to form bis(2-mercaptobenzothiazolo)zinc(II) [Zn(mbt)₂] at vulcanization temperatures, but DSC studies,^{3,4} in the absence of rubber, show no evidence for such a reaction. Craig⁵ ob-

tained a reaction in the presence of H₂S. Various authors⁶⁻⁹ supported a reaction between tetramethylthiuram disulfide (TMTD) and ZnO to give bis(dimethyldithiocarbamato)zinc(II) [$Zn_2(dmtc)_4$] prior to vulcanization, while others 10-14 showed that such a reaction is very limited. Zinc-accelerator complexes do form during vulcanization, but as a result of secondary reactions, and do not initiate the crosslinking process.¹⁵⁻¹⁷ Interaction with the rubber chain is initiated by accelerator polysulfides.^{1,15,18,-20} In an earlier article,²¹ it was shown that benzoic and stearic acids react with MBTS and TMTD and their respective polysulfides form accelerator-acid complexes, thus reducing the concentration of accelerator polysulfides available for reaction with the rubber. In the absence of ZnO, this

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Figure 1 HPLC analysis of reactants and products obtained on heating MBTS/sulfur/ ZnO/benzoic acid at 150°C: (\blacklozenge) zinc benzoate; (\bigcirc) MBTM; (\blacktriangle) MBTS; (\bigtriangledown) MBTP; (\square) MBT; (\blacklozenge) sulfur.

has a detrimental effect on the crosslink density of MBTS vulcanizates.²² Tetramethylthiuram polysulfides (TMTP) are more reactive toward polyisoprene (IR) than are 2-bisbenzothiazole-2,2'-polysulfides (MBTP) and add rapidly to the chain before significant attack by carboxylic acids can occur.²²

Carboxylic acids will readily react with ZnO during compounding, and since formulations generally contain an excess of ZnO, there will be no free acid in the compound. This article examines the effect of the zinc salts of benzoic and stearic acids on the interaction of curatives in MBTSand TMTD-accelerated sulfur formulations in the absence of rubber.

EXPERIMENTAL

Materials and experimental procedures were detailed in a previous article in this series.²¹ Curatives, mixed in an equimolar ratio, were heated in a DSC at 2.5°C/min and analyzed by HPLC at various points along the DSC curve. In the figures, concentrations of the reactants, intermediates, and products are expressed in terms of the initial mol concentration of the reactant.

RESULTS AND DISCUSSION

MBTS/Sulfur/ZnO

MBTS does not react with ZnO.^{3,4} This was confirmed by the similarity in the DSC curves obtained on heating MBTS/sulfur and MBTS/sulfur/ZnO at a programmed heating rate and by HPLC analysis of the system after heating at 150°C for up to 20 min. (Balls of insoluble polymeric sulfur were observed in the workup of HPLC solutions of samples heated to above 150°C, which means that the sulfur analysis in the figures are erroneously low.)

MBTS/Sulfur/ZnO/Benzoic Acid

The DSC curves show that benzoic acid reacts with ZnO above 72°C. As compounding occurs above this temperature and in compounds acid concentrations are lower than ZnO loadings, there should be no free acid at vulcanization temperatures. Figure 1 shows that the addition of benzoic acid to an MBTS/sulfur/ZnO mixture at 150°C does not lead to the destruction of MBTP, as occurred with benzoic acid.²¹ The MBTP concentration is only slightly (3%) lower than in the absence of benzoic acid. The formation of 2-benzoylthiobenzothiazole (BzM) is difficult to detect and the clearest $evidence^{21}$ that there is little interaction between MBTP and ZnO/benzoic acid is the formation of only trace amounts of 2-mercaptobenzothiazole (MBT) (Fig. 1).

On heating the mixture in a DSC at 2.5°C/min to 180°C, neither the formation of BzM nor the decomposition of MBTP were observed on HPLC analysis (Fig. 2).

MBTS/Sulfur/ZnO/Stearic Acid

On melting stearic acid, it rapidly reacts with ZnO. As with benzoic acid, the HPLC analysis of



Figure 2 HPLC analysis of reactants and products obtained on heating MBTS/sulfur/ ZnO/benzoic acid in a DSC at 2.5°C/min: (\blacklozenge) zinc benzoate; (\bigcirc) MBTM; (\blacktriangle) MBTS; (\blacktriangledown) MBTP; (\blacklozenge) sulfur.

an isothermal study of this system at 150°C (Fig. 3) shows a slightly lower MBTP concentration than in the absence of acid. The formation of small amounts of MBT are observed. This system was studied using an Alltech HPLC column²¹ and no stearic thiobenzothiazole (StM) species were observed, although separation of minute amounts of StM from MBTS is very difficult. After 5 min, a slight decrease in the MBTP concentration and a continued slow increase in MBT are observed. The liberation of small amounts of sulfur suggests the limited decomposition of MBTP, rather than the formation of StM.²¹ On heating the system to

190°C at a programmed rate, a similar result was obtained, namely, a slight decrease in MBTP, together with the formation of a small amount of MBT and the liberation of some sulfur.

MBTS/Sulfur/Zinc Stearate

HPLC analysis of a study of this system at 150°C (Fig. 4) provided similar results to those of the MBTS/sulfur/ZnO/stearic acid system (Fig. 3). No StM could be detected and the lower MBT concentration than in the ZnO/stearic acid system may indicate that not all of the stearic acid was



Figure 3 HPLC analysis of reactants and products obtained on heating MBTS/sulfur/ ZnO/stearic acid at 150°C: (\bigcirc) MBTM; (\blacktriangle) MBTS; (\bigtriangledown) MBTP; (\square) MBT; (\bullet) sulfur.



Figure 4 HPLC analysis of reactants and products obtained on heating MBTS/sulfur/ zinc stearate at 150°C: (\bigcirc) MBTM; (\blacktriangle) MBTS; (\bigtriangledown) MBTP; (\square) MBT; (\blacklozenge) sulfur.

trapped by ZnO in the latter system.²³ In a rubber compound, where high shearing forces operate during compounding, the ZnO/stearic acid reaction is likely to go to completion.

TMTD/Sulfur/ZnO

A DSC study of this system shows the solid–solid phase transition in sulfur at 106°C, followed by its melting at 111°C. Dissolution of TMTD in sulfur occurs at 116°C. The observed transitions are similar to those described earlier.^{10,11} TMTP forms rapidly once TMTD dissolves in sulfur (Fig. 5). An isothermal study at 150°C shows that the TMTP formed is stable (Fig. 6). After 20 min at 150°C, no $\text{Zn}_2(\text{dmtc})_4$ was detected, in accordance with earlier^{10,11} reports that it forms very slowly when the reactants are thoroughly dried.

TMTD/Sulfur/ZnO/Benzoic Acid

As in the MBTS system, DSC studies show the reaction of benzoic acid with ZnO above 72°C, the remainder of the DSC curve being similar to that for TMTD/sulfur in the absence of benzoic acid. Both the dynamic (Fig. 7) and isothermal (Fig. 8) studies show a decrease in zinc benzoate and TMTP concentrations, indicating their interaction. Peaks in the HPLC, attributed to 2-benzoyl-



Figure 5 HPLC analysis of reactants and products obtained on heating TMTD/sulfur/ ZnO in a DSC at 2.5°C/min: (\bigcirc) TMTM; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\bullet) sulfur.



Figure 6 HPLC analysis of reactants and products obtained on heating TMTD/sulfur/ ZnO at 150°C: (\bigcirc) TMTM; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\bullet) sulfur.

dimethyldithiocarbamate (BzT) and its polysulfides,²¹ were distinguishable.

Dimethyldithiocarbamic acid (Hdmtc) produced in the reaction²¹ between zinc benzoate and TMTD should be trapped by ZnO, only half of which is consumed in forming zinc benzoate. However, residual ZnO would be encrusted by zinc benzoate, which is a solid to well above vulcanization temperatures, rendering it unavailable for reaction with Hdmtc. The concentration of $Zn_2(dmtc)_4$ in the residue was too low to determine after exchange with $CoCl_2$.²⁴ TMTD/sulfur/ ZnO/benzoic acid was heated in a sealed tube partially immersed in an oil bath at 150°C for 10 min. HPLC analysis of volatiles precipitated on the cold sections of the tube revealed sulfur, tetramethylthiuram monosulfide (TMTM), TMTD, benzoic acid, a small amount of Hdmtc, and a large peak that could be either dimethylammonium dimethyldithiocarbamate (dma dmtc) or tetramethylthiuram trisulfide. Since only small amounts of tetramethylthiuram tetrasulfide, and no other TMTPs were detected in the volatiles, it is probable that the peak was due largely to dma



Figure 7 HPLC analysis of reactants and products obtained on heating TMTD/sulfur/ ZnO/benzoic acid in a DSC at 2.5°C/min: (\blacklozenge) zinc benzoate; (\bigcirc) TMTM; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\blacklozenge) sulfur.



Figure 8 HPLC analysis of reactants and products obtained on heating TMTD/sulfur/ ZnO/benzoic acid at 150°C: (\blacklozenge) zinc benzoate; (\bigcirc) TMTM; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\bullet) sulfur.

dmtc. Addition of $CoCl_2$ gave a yellow-green solution with an HPLC peak characteristic of $Co_2(dmtc)_4$. As $Zn_2(dmtc)_4$ is not volatile at 150°C, the cobalt compound probably was formed from dma dmtc, produced when Hdmtc decomposed on the cold areas of the tube,²⁵ and it can be concluded that Hdmtc accompanied BzT formation.

This is the only system in which BzT was detected with zinc salts. It is possible that residual benzoic acid, rather than zinc benzoate, is responsible for BzT formation. Benzoic acid is less compatible with TMTD than with MBTS, where mutual compatibility of the components may allow the acid-ZnO reaction to proceed more readily.

Above 130°C in the dynamic study (Fig. 7) and after 1 min in the isothermal study at 150°C (Fig. 8), the zinc benzoate-initiated decomposition²¹ of TMTP and BzT occurs. TMTP concentrations in the figures include BzT polysulfides, as quantitative separation is impossible.²¹ TG analysis shows a very rapid mass loss, attributed to the evaporation of Hdmtc, above 145°C. Sulfur is liberated (Figs. 7 and 8). In the absence of zinc



Figure 9 HPLC analysis of reactants and products obtained on heating TMTD/sulfur/ ZnO/stearic acid in a DSC at 2.5°C/min: (\bigcirc) TMTM; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\bullet) sulfur.



Figure 10 HPLC analysis of reactants and products obtained on heating TMTD/ sulfur/ZnO/stearic acid at 150°C: (\bigcirc) TMTM; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\bullet) sulfur.

benzoate, a mass loss, attributed to the evaporation of TMTP, occurs only above 160°C.

TMTD/Sulfur/ZnO/Stearic Acid

Stearic dimethyldithiocarbamate (StT) and its polysulfides²¹ could not be detected by HPLC, but some decomposition of TMTP is evident above 145°C in the dynamic study (Fig. 9) and after 2 min in the isothermal (Fig. 10) study at 150°C. Sulfur is liberated. Zinc stearate melts at 121°C, which may assist the stearic acid–ZnO reaction in going to completion. Hence, there will be less free acid than in the case of benzoic acid to form StT on interaction with TMTP. In a dynamic study of

TMTD/sulfur/zinc stearate, StT also could not be detected although the zinc stearate-initiated decomposition of TMTP is observed above 145°C (Fig. 11).

CONCLUSIONS

Reaction of benzoic acid with ZnO prevents the MBTS-acid reaction leading to BzM and MBT as well as the high-temperature decomposition of MBTP.²¹ With zinc stearate, no StM is detected, although the slow decomposition of MBTP is indicated by the formation of small amounts of MBT



Figure 11 HPLC analysis of reactants and products obtained on heating TMTD/ sulfur/zinc stearate in a DSC at 2.5°C/min: (\bigcirc) TMTM; (\blacktriangle) TMTD; (\bigtriangledown) TMTP; (\bullet) sulfur.

and the liberation of limited amounts of sulfur above 145° C and after 5 min at 150° C.

In TMTD formulations also, conversion of the acids to their zinc salts limits or inhibits the formation of BzT and StT. In the TMTD/sulfur/ZnO/ benzoic acid system, HPLC peaks attributed to BzT were detected. This is the only zinc-containing system in which peaks attributed to an accelerator-acid complex were found. Zinc benzoate does not melt at vulcanization temperatures, and a crust of benzoate around ZnO particles probably led to an incomplete reaction of the acid (residual acid) rather than to zinc benzoate, being responsible for BzT formation.

In all formulations, the slow decomposition of TMTD and TMTP occurs above 145°C in dynamic runs and after 2 min in isothermal experiments at 150°C. Sulfur is liberated on decomposition and a large mass loss, even from DSC pans, is attributed to the evaporation of Hdmtc. Decomposition is faster than with MBTP where it occurs only above 180°C in dynamic studies and after 5 min at 150°C.

It may be anticipated that the addition of carboxylic acids will not have a negative impact on the vulcanization in formulations containing ZnO.

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