Effect of Carboxylic Acids on 2-Bisbenzothiazole-2,2′-Disulfide- and Tetramethylthiuram Disulfide-Accelerated Sulfur Vulcanization. I. Reaction Between the Acids and Accelerators

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ABSTRACT: Benzoic and stearic acids are shown to react with 2- bisbenzothiazole-2,2′-disulfide (MBTS) and its polysulfides (MBTP) at vulcanization temperatures to form acid-accelerator complexes 2-benzoylthiobenzothiazole (BzM) and stearicthiobenzothiazole (StM), respectively. At higher temperatures MBTS, MBTP, BzM, and StM are decomposed by the acids. Analogous reactions are observed with tetramethylthiuram disulfide (TMTD) and its polysulfides (TMTP). Lesser amounts of acid-accelerator complexes 2-benzoyldimethyldithiocambamate and stearicdimethyldithiocarbamate are formed, but TMTP are more susceptable to decomposition at higher temperatures. The destruction of MBTP and TMTP by carboxylic acids will reduce the concentration of accelerator polysulfides available in compounds, and should impact negatively on vulcanization. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 999–1006, 1999

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

INTRODUCTION

Aliphatic acids, notably stearic acid, are commonly used in accelerated sulfur vulcanization formulations. Its retarding effect on vulcanization, as well as the activating effect of acids on certain accelerators, is well recognized.[1,2] Stearic acid melts below compounding temperatures, and already at this stage will readily react with ZnO. Because ZnO is normally present in excess, there will be no free acid in the compound, only ZnO and zinc stearate. Thus, the addition of zinc stearate is reported[3] to decrease the rate but to in-crease the extent of crosslinking in 2-bisbenzo-thiazole-2,2′-disulfide (MBTS)/sulfur systems.

We[4–7] have conducted extensive studies on the MBTS and tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization of polyisoprene (IR) in the presence and absence of ZnO. It is well known that accelerators MBTS[4,8–11] and TMTD[5,7,9–16] react with sulfur to form accelerator polysulfides that act as active sulfurating agents in the absence of ZnO. Kruger and McGill[17] reported that sulfur and stearic acid were immiscible and that stearic acid delayed the MBTS/sulfur interaction, while TG and DSC studies[13] of TMTD and stearic acid indicated decomposition of TMTD above 146°C, 90% of the TMTD decomposing by 180°C. Craig et al.[18] found that TMTD reacted slowly with palmitic acid at 130–140°C.

As part of a study into the effect of stearic acid on the vulcanization process, the effect of the acid,

Table I Abbreviations

BzM	2-benzoylthiobenzothiazole
BzT	2-benzoyldimethyldithiocarbamate
DMA	dimethylamine
dma.dmtc	dimethylammonium dimethyldithiocambamate
Hdmtc	dimethyldithiocarbamic acid
IR	polyisoprene
MBT	2-mercaptobenzothiazole
MBTS	2-bisbenzothiazole-2,2′-disulfide
MBTM	2-bisbenzothiazole-2,2′-monosulfide
MBTP	2-bisbenzothiazole-2,2′-polysulfide
StM	stearicthiobenzothiazole
StT	stearicdimethyldithiocarbamate
TMTD	tetramethylthiuram disulfide
TMTM	tetramethylthiuram monosulfide
TMTP	tetramethylthiuram polysulfide
TMTU	tetramethylthiourea

in the absence of ZnO, was first studied. This article reports on the interaction of the acid with MBTS, TMTD, and their polysulfides in the absence of rubber. The next article in the series examines the effect of the acid on MBTS and TMTD accelerated vulcanization of IR.

EXPERIMENTAL

Orac MBTS (chemical purity 93%) and Orac TMTD (chemical purity 97%) Orchem South Africa; sulfur (chemical purity 99.9%) Holpro Analytics; stearic acid (Marine Oil Refiners); benzoic acid (Saarchem).

Curatives in equimolar ratios were ground together using a mortar and pestle to yield a homogeneous powder.[19] Samples (20 mg) were heated in sealed aluminium pans in a standard Du Pont DSC cell, connected to a Du Pont 9000 Thermal Analyzer. Heating rates of 2.5°C/min were used, and once the desired temperature had been reached, samples were rapidly removed from the cell and placed on cold metal to cool. High purity nitrogen, at a flow rate of 80 mL/min, was used as a purge gas.

Product analysis was done by HPLC and, because stearic acid cannot be detected by the UV analyzer of the HPLC, benzoic acid, which can be detected, was substituted for stearic acid in various instances. It will be shown below that the reactions of stearic acid parallel those of benzoic acid. Where differences are noted, these can be

ascribed to differences in the solubility of the components in the acids.

Product identification and HPLC analysis procedures have been described before.[20] Products were separated on a Waters μ-Bondpak C18 Reverse Phase Radial-Pak column (8 i.d. × 100 mm) with 15% water:85% methanol as mobile phase. To obtain a better separation of stearicthiobenzothiazole (StM) and 2-benzoylthiobenzotiazole (BzM) from MBTS and stearicdimethyldithiocarbamate (StT) and 2-benzoyldimethyldithio-carbamate (BzT) from TMTD (see below) an Alltech Nucleosil C18 Reverse Phase column (4.6 i.d.× 25 mm) with 20% water:80% methanol was used. Products not commercially available for use in HPLC identification and analysis were synthesized. BzM and BzT were synthesized from benzoyl chloride and the sodium salt of 2-mercaptobenzothiazole (MBT) and dimethyldithiocarbamic acid (Hdmtc), respectively. Dimethylammonium dimethyldithiocarmamate (dma.dmtc) was synthesized by adding CS_2 to an aqueous solution of dimethylamine (DMA). Dma.dmtc formed was extracted from the water layer into chloroform. ^{1}H-NMR signals at 3.57 and 2.78 ppm as reported[14] for dma.dmtc were obtained. Hdmtc was synthesized by the dropwise addition of HCl to Nadmtc in an ice bath. A low product yield was obtained after extraction into methanol and removal of NaCl. In the figures, the concentrations of reactants, intermediates, and products are expressed in terms of the initial mol concentration of reactants, i.e., as the mol % of reactant remaining, or mol % intermediate/product formed from the reactant.

RESULTS AND DISCUSSION

MBTS/Benzoic Acid

On heating in the DSC at 2.5°C/min the melting of MBTS at 168°C is followed by the formation of 2-bisbenzothiazole-2,2′-monosulfide (MBTM) and 2-bisbenzothiazole-2,2′-polysulfides (MBTP). The DSC curves and reaction have been discussed.[8,17] In a MBTS/benzoic acid mixture the melting point of benzoic acid (121°C) is suppressed to 100°C (Fig. 1) and is accompanied by the dissolution of MBTS in the melt. A very broad endotherm between 114 and 153°C represents the reaction of MBTS to form MBTM and MBTP, as shown by HPLC analysis of the system (Fig. 2). Above 150°C the benzoic acid concentration decreases as

Figure 1 DSC curve for MBTS/benzoic acid heated at 2.5°C/min.

it reacts with MBTP to give MBT and a series of products that give rise to peaks at slightly longer retention times than MBTP on the HPLC column. On increasing the polarity of the mobile phase from 12% water : 88% methanol to 20% water : 80% methanol, an increase in the separation of these peaks was achieved. No second peak could be seen adjacent to the accelerator monosulfide peak, but, because separation between peaks increases with the higher MBTP, the possibility of product peak coinciding with the MBTM peak cannot be ruled out.

The ready exchange between disulfidic accelerators to form mixed accelerator species has been demonstrated.[21]

$$BtSSBt + XSSX \leftrightarrow 2BtSSX$$

Bt = benzothiazole and X = dimethylthiuram

and the possibility of the following accelerator–acid reaction was considered:

$$BtS_xBt + RCO_2H \leftrightarrow BtS_{x-1}O_2CR + BtSH$$

RCO_2H = benzoic or stearic acid

An exchange beween MBTS and benzoyl peroxide should yield the same accelerator–acid complex as is obtained with benzoic acid.

$$BtSSBt + RCO_2 - O_2CR \leftrightarrow$$

$$2\ BtSO_2CR\ (Product\ A)$$

Heating a MBTS/benzoyl peroxide (1 : 1 mol ratio) mix isothermally at 120°C led to the complete reaction of benzoyl peroxide to give benzoic

acid and product A, that eluted before MBTM on the HPLC. The source of the proton required to form the acid is not clear. Product A is quite stable, and was separated by TLC. NMR analysis showed the aromatic hydrogens of the benzothiazole and benzoic acid group between 7.2 and 8.2 ppm on the proton spectrum, the aromatic carbons between 122 and 138 ppm and the carbonyl carbon at 188 ppm in the C13 spectrum. Product A was a sticky liquid that could not be handled by our CHN analysis facility and, as its retention time was quite different to that of the white solid products obtained in the MBTS/benzoic acid reaction, it was not studied further.

BzM, a compound (white solid) containing one oxygen atom less than the assumed product A, was synthesized as described above and, on injection into the HPLC, eluted at the same time as MBTM. Despite changing the polarity of the mobile phase it could not be separated from MBTM on the HPLC. On heating BzM/sulfur to 170°C in the DSC, HPLC analysis revealed the reaction of 60% of the BzM with 40% of the sulfur to form a series of peaks that eluted at similar times to the additional peaks obtained from the reaction of benzoic acid with MBTP. This suggests that these may be polysulfides of BzM. In the absence of sulfur, BzM does not form its polysulfides, although with time, two decomposition product peaks are obtained in the HPLC. Quantitative separation of MBTP and the corresponding BzM polysulfides was unsatisfactory, and the concentrations of MBTM, MBTS, and MBTP presented in the figures are, in each case, based on the combined peak areas.

MBTP are stable in the absence of benzoic acid but in the presence of acid MBTP and the BzM

Figure 2 HPLC analysis of reactants and products obtained on heating MBTS/benzoic acid in a DSC at 2.5°C/min: (◆) benzoic acid; (○) MBTM; (▲) MBTS; (▽) MBTP; (□) MBT.

Figure 3 HPLC analysis of reactants and products obtained on heating MBTS/stearic acid in a DSC at 2.5°C/min: (○) MBTM; (▲) MBTS; (▽) MBTP; (□) MBT.

Figure 5 DSC curve of MBTS/sulfur/benzoic acid heated at 2.5°C/min.

polysulfides decompose above 150°C (Fig. 2). No sulfur is liberated but the increased mass loss indicates the formation of volatile species.

MBTS/Stearic Acid

MBTS does not dissolve as readily in molten stearic acid as it does in benzoic acid and, on heating in the DSC, minimal decomposition occurs before completion of the broad poorly defined melt-dissolution endotherm at 157°C. HPLC analysis (Fig. 3) shows that above 157°C MBT forms, together with the development of shoulders to the MBTP peaks in the HPLC. It is suggested that these shoulders are attributable to StM poly sulfides that have a stearic instead of a benzoyl group in the molecule. Rapid decomposition of MBTP and StM by stearic acid occurs above 180°C.

The interaction of benzoic acid and stearic acid with MBTS appears to be similar, differences in

the temperature of reaction being dependent on the higher solubilities of MBTS in benzoic acid than in stearic acid.

MBTS/Sulfur/Benzoic Acid

When sulfur is present, MBTS dissolves in molten sulfur well below its melting point (168°C) and MBTP form at lower temperatures (Fig. 4). MBTP are stable up to at least 190°C. Limited amounts of MBTM are formed as discussed by Gradwell et al.[8]

When benzoic acid is added to the mixture a double endotherm, attributed to two events, the melting of sulfur followed by that of benzoic acid, is observed (Fig. 5). Endothermic events between 116 and 150°C are ascribed to the formation of MBTP and BzM polysulfides that appear as shoulders to MBTP peaks, and MBT (Fig. 6). Above 150°C continued growth of the combined

Figure 4 HPLC analysis of reactants and products obtained on heating MBTS/sulfur in a DSC at 2.5°C/min: (○) MBTM; (▲) MBTS; (▽) MBTP; (●) sulfur.

Figure 6 HPLC analysis of reactants and products obtained on heating MBTS/sulfur/benzoic acid in a DSC at 2.5°C/min: (◆) benzoic acid; (○) MBTM; (△) MBTS; (▽) MBTP; (□) MBT; (●) sulfur.

Figure 7 HPLC analysis of reactants and products obtained on heating MBTS/sulfur/stearic acid in a DSC at 2.5°C/min: (○) MBTM; (▲) MBTS; (▽) MBTP; (□) MBT; (●) sulfur.

MBTM/BzM peak in the HPLC is probably due to BzM. High temperature decomposition of MBTS and BzM species is limited, even at 180°C.

MBTS/Sulfur/Stearic Acid

Besides showing the melting of stearic acid, the DSC curve for MBTS/sulfur/stearic acid (Fig. 7) is essentially similar to that for MBTS/sulfur, although the MBTS/sulfur interaction was somewhat delayed. Kruger and McGill[17] attributed this to the insolubility of sulfur in stearic acid. Above 147°C MBTP react with stearic acid to produce StM polysulfides. Only the tri- and tetrapolysulfidic species could be detected as shoulders on the corresponding MBTP peaks in the HPLC, but at higher temperatures the formation of MBT is a clear indication of reaction, and is accompanied by a decrease in the overall concentration of MBTP.

TMTD

On heating TMTD at 2.5°C/min in the DSC tetramethylthiuram monosulfide (TMTM) and tetramethylthiuram polysulfides (TMTP) form above the melting endotherm as described by Kruger[13] and Geyser,[12] no tetramethylthiourea (TMTU) being detected below 160°C.

TMTD/Benzoic Acid

As in the case of MBTS, the accelerator depresses the melting point of benzoic acid. Melting at 103°C (Fig. 8) is accompanied by dissolution of TMTD in benzoic acid and the formation of TMTM and TMTP. These reactions occur much earlier when dissolution is the acid is possible.

Figure 8 DSC and TG curves for TMTD/benzoic acid heated at 2.5°C/min.

The second endotherm, below 120°C, represents the reaction of benzoic acid with TMTP, as evidenced by the decrease in benzoic acid concentration (Fig. 9) and the development of secondary peaks adjacent to TMTP peaks on the HPLC chromatogram. BzT was synthesized, and its HPLC retention time was found to be identical to that of TMTD, not to that of the monosulfide, as in the case of MBTM and BzM. This would require that the shoulder that appears on the thriuam trisulfide peak be ascribed to the BzT disulfide, and so on. BzT heated with sulfur, unlike in the case of BzM, did not produce a series of peaks that can be ascribed to BzT polysulfides. This does not disprove the existence of BzT polysulfides, but rather indicates that these are preferentially formed from the interaction of benzoic acid with TMTP, rather than by sulfuration. The low concentrations of these species made their separation from TMTP and their positive identification impossible. TG (Fig. 8) shows a rapid mass loss above

Figure 9 HPLC analysis of reactants and products obtained on heating TMTD/benzoic acid in a DSC at 2.5°C/min: (◆) benzoic acid; (○) TMTM; (▲) TMTD; (▽) TMTP; (●) sulfur. (◇) Mass loss from DSC pans.

Figure 10   DSC and TG curves for TMTD/stearic acid heated at 2.5°C/min.

100°C that can be attributed to the evolution of Hdmtc, the formation of which would accompany StT production (see below). In the absence of benzoic acid rapid evaporation of TMTD and TMTP commences only above 150°C.

The DSC shows a third endotherm at 141°C (Fig. 8), and this is associated with the degradation of TMTM, TMTD, TMTP, and BzT polysulfides (Fig. 9). Decomposition is associated with a rapid mass loss, even from DSC pans.

In the MBTS-acid reaction the major product was MBT. In the TMTD-acid reaction the corresponding species would be Hdmtc, which is volatile and would not remain in DSC pans. TMTD/benzoic acid was heated in a tube partially immersed in an oil bath at 150°C, and HPLC analysis of volatiles that precipitated on the cold parts of the tube revealed benzoic acid, Hdmtc, and dma.dmtc. When dry, Hdmtc decomposes to dma.dmtc and CS_2. It can be concluded that the TMTD–acid reaction is analogous to the MBTS–acid reaction, BzT and Hdmtc being produced below 140°C, while at higher temperatures TMTD, TMTP, and BzT polysulfides are degraded by the acid.

TMTD/Stearic Acid

Stearic acid is not a good solvent for TMTD and a DSC scan (Fig. 10) of the mixture shows the melting of stearic acid (60°C) followed only at 140°C by that of TMTD and its reaction to produce TMTM and small amounts of TMTP. The rapid mass loss (attributed to Hdmtc) from DSC pans is also seen in TG experiments (Fig. 10) and indicates the reaction of stearic acid with TMTD above 140°C. In the absence of stearic acid the mass loss is negligible. In some samples shoulders that could

be attributed to StT polysulfides were observed on TMTP peaks in the HPLC. The extent to which TMTD reacts with stearic acid is not very reproducible, as shown in Figure 11, the amounts of TMTD reacted and TMTP formed being quite varied from experiment to experiment. These inconsistencies may arise from the incompatability of TMTD with stearic acid resulting in nonuniformity of the melt being reacted. The low TMTP concentration (5 mol %) compared to that in the absence of stearic acid (20 mol %) at 144°C indicates the stearic acid initiated decomposition of TMTP. A third endotherm at 144°C occurs immediately after the TMTD melt/reaction endotherm and is due to the stearic acid initiated degrdation of TMTM, TMTD, TMTP, and StT polysulfides. Sulfur is liberated.

TMTD/Sulfur/Benzoic Acid

As described earlier[12,13] on heating TMTD/sulfur mixes in the DSC, TMTD dissolves in the sulfur as soon as it melts, leading to TMTP, the concentrations of which remain constant at higher temperatures.

The accelerator depresses the melting point of benzoic acid and melting-dissolution of benzoic acid–TMTD occurs at 104°C (Fig. 12). The formation of relatively large amounts of TMTM in the presence of sulfur (Fig. 13) suggests that sulfur has not dissolved in the TMTD/benzoic acid melt. Benzoic acid does not react at this stage, its concentration remaining constant. The second endotherm (Fig. 12) is due to the reaction of TMTD and sulfur to form TMTP, as confirmed by the consumption of sulfur (Fig. 13). No further TMTM is produced. As soon as TMTP start forming above

Figure 11   HPLC analysis of reactants and products obtained on heating TMTD/stearic acid in a DSC at 2.5°C/min: (○) TMTM; (▲) TMTD; (▽) TMTP; (●) sulfur. (◇) Mass loss from DSC pans.

Figure 12 DSC and TG curves for TMTD/sulfur/benzoic acid heated at 2.5°C/min.

Figure 14 HPLC analysis of reactants and products obtained on heating TMTD/sulfur/stearic acid in a DSC at 2.5°C/min: (○) TMTM; (▲) TMTD; (▽) TMTP; (●) sulfur.

115°C, interaction with benzoic acid occurs, as seen by the decrease in extractable benzoic acid. Very limited amounts of BzT polysulfides were detected as shoulders to TMTP peaks.

Above 140°C the benzoic acid initiated decomposition of TMTP is observed and sulfur is liberated and the rate of mass loss increases (Fig. 12).

TMTD/Sulfur/Stearic Acid

Besides the melting of stearic acid the DSC curve of TMTD/sulfur/stearic acid is almost identical to that of TMTD/sulfur up to 138°C. HPLC analysis shows the formation of comparable amounts of TMTP (50 to 60 mol %) as in the absence of the acid. No StT species were detected. TMTD is essentially insoluble in stearic acid, and it appears that sulfur further suppresses its dissolution. Above 138°C stearic acid initiates breakdown of TMTP, liberating sulfur (Fig. 14).

Figure 13 HPLC analysis of reactants and products obtained on heating TMTD/sulfur/benzoic acid in a DSC at 2.5°C/min: (◆) benzoic acid; (○) TMTM; (▲) TMTD; (▽) TMTP; (●) sulfur.

CONCLUSIONS

At vulcanization temperatures interaction between accelerator polysulfides and carboxylic acids leads to the partial decomposition of the polysulfides and the formation of MBT (with MBTS) of Hdmtc (with TMTD) and polysulfide complexes of the accelerators and acids (BzM, BzT, StM, and StT). This interaction reduces the amount of accelerator polysulfides available for vulcanization. At higher temperatures the slow, acid-initiated degradation of accelerator polysulfides and the polysulfides to the accelerator-acid complexes leads to their complete destruction. With TMTD, lesser amounts of the TMTD–acid complexes (BzT, StT) are produced, but the complexes are more rapidly degraded by acids than are the MBTS–acid complexes (BzM, StM). The former liberate sulfur on degradation. MBTS–acid complexes are stable up to 180°C in the presence of sulfur. In the absence of rubber, incompatability between reactants, particularly between stearic acid and TMTD, reduces the rate of reaction, but such restrictions will not apply in a compound where the rubber acts as solvent for the curatives, and destruction of TMTP will occur more readily.

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