The Role of Thiol Intermediates in 2-Mercaptobenzothiazole Accelerated Sulfur Vulcanization of Rubber Model Compounds

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ABSTRACT: The model compound, 2,3-dimethyl-2-butene (TME), was vulcanized using 2-mercaptobenzothiazole (MBT) and sulfur. MBT was not consumed during the vulcanization reaction. The resultant crosslink products were bis(alkenyl) in nature. 2,3-Dimethyl-2-buten-1-thiol (TME-SH) was identified as being present in the vulcanization mixture by a postcolumn derivatization technique. The appearance of thiol was coincident with crosslinking. Polysulfanes (H_2S_n) were formed on crosslinking. Studies of the reaction of TME-SH and sulfur indicated a rapid reaction to form crosslink products and polysulfanes. No monosulfidic crosslink species were formed in these reactions. Closer investigation revealed the presence of small quantities of what appeared to be highly reactive polysulfidic thiols. This is the first time that such species have been identified in vulcanization systems. Consequently, MBT-accelerated vulcanization of TME is proposed to occur via the reaction of MBT and S_8 to form polysulfidic MBT, which then reacts with TME to form polysulfidic thiols. These thiols then rapidly react via a metathesis reaction pathway to provide crosslink products and polysulfanes. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 47–54, 2003

Key words: vulcanization; 2-mercaptobenzothiazole; 2,3-dimethyl-2-butene; model compound; thiol

INTRODUCTION

2-Mercaptobenzothiazole (MBT) has been shown to be capable of vulcanizing elastomers, only in the presence of sulfur.[1–3] It has been proposed that the active sulfurating agents are 2-hydropersulfide-benzothiazole species (BtS_xH, $x > 1$) that form when MBT and sulfur react with each other.[3–6] In none of these studies is the formation of 2-hydropersulfide-benzothiazole species conclusively proven, but it is merely suggested to take place. It is argued that where such species do form, they are very short-lived and have consequently eluded detection.[6] Morgan and McGill[6] studied the MBT-accelerated sulfur vulcanization of the model compound 2,3-dimethyl-2-butene (TME), which has often been used as a model compound for polyisoprene, and proposed 2,3-dimethyl-2-butene-1-polythiols ($TME-S_xH$, $x \geq 1$) as intermediates in the vulcanization mechanism. The presence of these thiols was not directly observed but rather inferred by noting the formation of crosslink products on oxidation of a reaction mixture with hydroperoxides. Morgan and McGill[6] propose that these polythiols react with each other to produce H_2S and crosslink products (Scheme 1).

Because 2,3-dimethyl-2-butene-1-thiol (TME-SH) is UV-inactive, it is not readily detectible by conventional reversed-phase high performance liquid chromatographic (RP-HPLC) systems. Consequently we have applied a derivatization technique, where thiol compounds are subjected to reaction with 5,5'-dithiobis(2-nitrobenzoic acid) (Ellman's reagent) to render them UV-active, to mixtures prepared by reacting MBT, TME, and sulfur to elucidate the role of the thiol intermediates proposed by Morgan and McGill.[6] Not only can we report the presence of thiol intermediates, we show that monothiols are unreactive towards each other. Crosslinking occurs as a consequence of metathesis reactions between short-lived, highly reactive polythiols to produce crosslink products and polysulfanes rather than H_2S as proposed by Morgan and McGill.[6] Both the polythiols and polysulfanes have been identified in the reaction mixture.
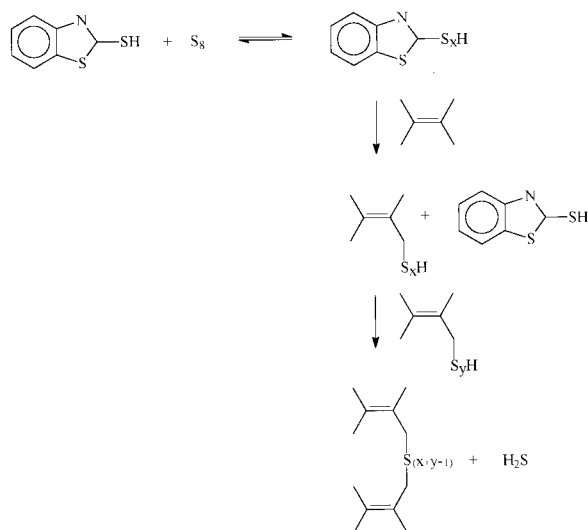
EXPERIMENTAL

Materials

2,3-Dimethyl-2-butene (TME; Aldrich Chemical Company, Milwaukee, WI; 99% purity), 2-mercaptobenzothiazole (MBT; Thiotax, Flexsys, Belgium), sulfur (S_8; AECI, South Africa), and thiourea (Saarchem, Johannesburg, South Africa) were used. MBT and sulfur were purified by recrystallization from hot benzene.

Scheme 1 MBT-accelerated sulfur vulcanization of TME according to Morgan and McGill.[6]

The presence of hydroperoxides in TME was determined with a Merck Merkoquant® 1001 peroxidase enzyme test kit with detectable concentrations in the range 1–25 mg/L. TME was transferred onto sticks tipped in peroxidase and exposed to water vapor, and then peroxide concentrations were determined by a color intensity comparison against a reference chart. It is essential that hydroperoxides are removed from TME when working with MBT-accelerated vulcanization studies because hydroperoxides are able to oxidize alkyl thiols (RSH) readily to alkyl disulfides (RSSR).[7] Were they not removed, they would make the identification of thiols more difficult as well as leading to the anomalous formation of crosslink products (RSSR). Hydroperoxides were removed by shaking TME with an aqueous ferrous sulfate solution. Although the alcohols formed remained in the TME phase, it has previously been shown that these alcohols do not interfere with the vulcanization mechanism. TME stock solution was stored at −10°C to keep further peroxide formation at a minimum.

Synthesis of 2,3-dimethyl-2-butene-1-thiol (TME-SH)

First, 150 mL of oxygen-free ethanol together with 15.81 g of purified thiourea were added to a 500-mL round-bottomed flask. To ensure that the ethanol was oxygen free, it was boiled and flushed with nitrogen. Next, 22.74 g of synthesised 1-bromo-2,3-dimethyl-2-butene[8] were added in a dropwise manner to the reaction mixture, and the mixture was refluxed under a nitrogen atmosphere for 48 h. Once cooled, the ethanol was removed under reduced pressure at 30°C with a rotary evaporator, leaving behind a crystalline residue. Ten, 100 mL of basic aqueous solution (4.8 g

sodium hydroxide in 100 mL water) were added to the crystalline residue and refluxed for 1 h under a nitrogen atmosphere. The pH of the solution was adjusted to a value of 2 by the addition of concentrated hydrochloric acid, and the solution was then shaken for 10 min. The 2,3-dimethyl-2-butene-1-thiol formed was extracted from the aqueous solution by the addition of five successive aliquots of 10 mL of dichloromethane. Excess dichloromethane was removed under reduced pressure at 25°C with a rotary evaporator. Distillation of the remaining solution under reduced pressure and collection of the second fraction that came off yielded 2,3-dimethyl-2-butene-1-thiol. Proton nuclear magnetic resonance (^{1}H-NMR) spectra of the product showed peaks at 1.28 ppm (triplet, 1H), 1.59 ppm (singlet, 3H), 1.64 ppm (singlet, 3H), 1.67 ppm (singlet, 3H), and 3.11 ppm (doublet, 2H). The spectrum obtained corresponded with the spectra obtained by Morgan and McGill[6] and Nieuwenhuizen.[9]

Model compound vulcanization reactions

To study the different vulcanization systems, pre-weighed vulcanization components were placed in 8-mL ampules and sealed under vacuum. The ampules were evacuated to prevent oxidation and bursting of the ampules. The ampules were heated by being fully immersed in an oil bath at 150 ± 0.5°C and shaken mechanically for specified reaction times. They were then removed and placed in liquid nitrogen to quench the reactions. TME, MBT, and sulfur were reacted in a molar ratio of 33.9:1.1:1.[6] A volume of 0.5 mL of TME was used in each experiment. For reactions between TME-SH and sulfur, a TME-SH solution was prepared by adding 5.86×10^{-3} mol TME-SH quantitatively to a 25-mL volumetric flask and diluting to 25 mL with hexane. Then, 0.5 mL of this thiol solution and 3.20×10^{-5} mol S_8 were reacted. The TME-SH/MBT/S_8 system was studied in a similar way by reacting 0.5 mL of the same stock TME-SH solution, 3.20×10^{-5} mol S_8 and 3.50×10^{-5} mol MBT.

RP-HPLC analysis of vulcanization mixtures

The contents of the quenched reaction mixtures were allowed to equilibrate to room temperature, and then they were dissolved in 40 mL of dichloromethane and quantitatively transferred to a 100-mL volumetric flask. The solution was then made up to 100 mL with methanol. Both the dichloromethane and methanol were sonicated prior to use to remove any dissolved oxygen. All vulcanization reactions were conducted in duplicate. One sample was immediately analyzed by conventional RP-HPLC, a procedure for the identification of curatives and their derivatives that has been described.[10–12] The other sample was subjected to RP-HPLC with postcolumn derivatization.[13]
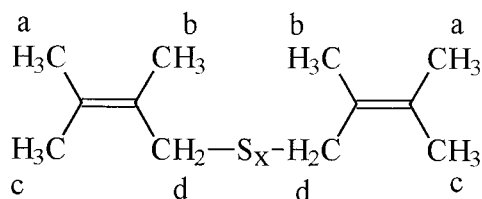
Figure 1 The bis(alkenyl) nature of crosslink products.

MBT, sulfur, benzothiazole-pendent group compounds, and crosslink products were identified with the conventional RP-HPLC system. Gradient elution was controlled by a Waters Automated Gradient Controller 680. The mobile phase was varied linearly over 120 min from 90:10 methanol/water (v/v) to 100% methanol. Reaction products were separated on a Waters Symmetry C18 reversed-phase column (250 mm × 4.6 mm i.d., 5 μm) and detected at $\lambda = 280$ nm. Thiol compounds were detected by postcolumn derivatization, where compounds were separated on a Nucleosil C18 reversed-phase column (250 × 4.6 mm i.d., 5 μm) using a 90:10 methanol/water (v/v) mobile phase flowing at 1 mL/min and buffered with 0.1 mol/L tris(hydroxymethyl)aminomethane (Tris) to a pH of 7.5. The separated thiol compounds were then mixed with a parallel stream of 7.08×10^{-4} mol/L 5,5′-dithiobis(2-nitrobenzoic acid) in 50:50 methanol/water (buffered as already described) flowing at 0.3 mL/min. The resultant derivatized mixture was allowed to react for 1 min by inserting an appropriate length of HPLC tubing before being analyzed at $\lambda = 420$ nm.

Identification of TME crosslink products

The crosslink products formed from the MBT-accelerated sulfur vulcanization of TME can be expected to be simple in nature due to the symmetry of the TME molecule. The same crosslink products as produced when 2-bis(benzothiazole)-2,2′-disulfide (MBTS) is used as accelerator are expected in the TME/MBT/S$_8$ system. Because MBTS reacts more completely and faster than MBT, crosslink products were prepared from an MBTS system.

A TME/MBTS/S$_8$ (33.9:1.1:1 molar ratio) sample was isothermally heated at 150°C for 40 min. The reaction products were separated by thin-layer chromatography using silica gel. The bands lifted from the plate were analyzed by ^{1}H-NMR and HPLC. The band R_f 0.89^{CH_2}Cl$_2$ was found to contain the crosslink products. ^{1}H-NMR (CDCl$_3$) confirmed that crosslinks were bis(alkenyl) in nature (Figure 1).

^{1}H-NMR spectral peaks were recorded at (a), (b), (c) 1.71 ppm (singlet), 1.78 ppm (singlet) and (d) varying with the number (x) of S atoms in the bridge between the two TME molecules as follows: $x = 2$, singlet at 3.47 ppm, $x = 3$, singlet at 3.62 ppm, $x = 4$, singlet at

3.71 ppm, and $x \geq 5$ singlet at 3.74 ppm. The spectrum of the crosslink products corresponded to the spectra obtained by Versloot.[8]

Crosslink products were identified in the reaction mixtures studied by comparing retention times with the crosslink products produced by the aforementioned method. Ten crosslink products with sulfur atoms, numbering from 1 to 1,0 were detected after separation by HPLC. The adjusted response factor (Y) of dimethyl disulfide was used to calculate the amount of individual crosslinks present. The response was adjusted according to the number of sulfur atoms (X) present in the sulfur bridge between the two TME molecules. The adjustment was done as follows:

$$\text{response of crosslink} = (XY)/2$$

This adjustment was done to compensate for the fact that sulfur is the main chromatophore present in the crosslinks. The UV absorption was assumed to be proportional to the amount of sulfur atoms present in the crosslink. This treatment differs from that of Morgan and McGill,[6] where it was assumed that all crosslink species have the same response factor. Such an approach tends to overestimate the importance of crosslink products with more sulfur atoms.

RESULTS AND DISCUSSION

TME/MBT/S$_8$ vulcanization system

The results of the analysis of the TME/MBT/S$_8$ system heated isothermally at 150°C are presented in Figure 2. Compounds that have been shown not to play a significant role in crosslinking were omitted from Figure 2 (e.g., the monosulfidic benzothiazole terminated pendant group, TME-S$_1$-Bt).[6]

The MBT concentration initially showed a small decrease till a minimum was reached after 6 min. This decrease was followed by a slight rise in concentration and then the concentration remained relatively con-
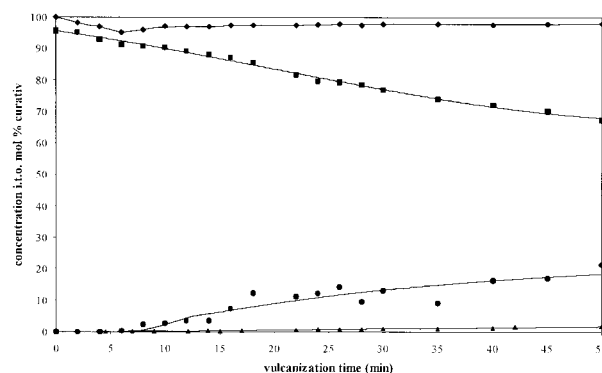

Figure 2 HPLC analysis of the TME/MBT/S$_8$ (33.9:1.1:1 mol) system, heated at 150°C. Key: (♦) MBT; (■) sulfur; (▲) TME-SH; (●) sum of TME-S$_x$-TME ($x = 1$–6).
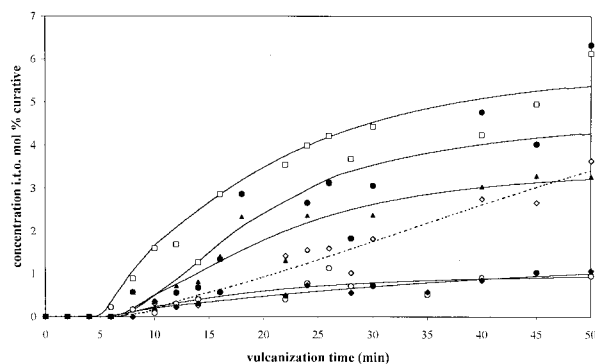
Figure 3 HPLC analysis of bis(alkenyl) crosslink products formed in the TME/MBT/S_8 (33.9:1.1:1 mol) system, heated isothermally at 150°C. Key: (◇) TME-S-TME; (□) TME-S_2-TME; (●) TME-S_3-TME; (△) TME-S_4-TME; (○) TME-S_5-TME; (◆) TME-S_6-TME.

stant at 98%. The sulfur concentration decreased fairly linearly to reach 66% of the original concentration after 50 min. The first crosslinks were detected after 6 min. The nature of the crosslink products was determined by HPLC and ^{1}H-NMR to be bis-alkenyl rather than alkyl-alkenyl or bis-alkyl. Of these, the pentasulfidic crosslink was the first crosslink product to be detected. From 8 min onwards, the disulfidic crosslink was the most numerous, with the penta- and hexasulfidic crosslinks being the least numerous (Figure 3). Similar observations were made by Morgan and McGill.[6]

It is apparent that the shape of the TME-S_1-TME formation curve is different from that of the other bis(alkenyl) crosslinks. Firstly, monosulfidic crosslinks are detected after 10 min (3–4 min later than the other crosslink species). Furthermore the TME-S_1-TME concentration appears to increase in a linear fashion, whereas the shape of the curves for the other crosslinks is sigmoidal. Morgan and McGill[6] also observed delayed formation of TME-S-TME but did not account for this observation.

Small amounts of bis(alkyl) and alkyl-alkenyl crosslinks were detected when the samples were heated for >16 min. The presence of these crosslinks and their late formation indicate that unaccelerated sulfur vulcanization of TME does take place in the presence of MBT. This reaction, however, is limited and does not contribute significantly to the overall vulcanization reaction.

Small amounts of 2-disulfide-2,2′-disulfide (Bt-S_2-Bt) and 2-bis(benzothiazole)-2,2′-trisulfide (Bt-S_3-Bt) were detected in samples heated for 8 min and longer. No benzothiazole-terminated pendant groups (except TME-S_1Bt) were detected in this system.

TME-SH was detected, albeit in small quantities. TME-SH was first detected after 6–7 min of heating. The amount of TME-SH present increased linearly with time and reached 1.7% (i.t.o. mol % TME) after 50

min of heating. No other thiol compounds were detected in this vulcanization system. The detection of TME-SH appeared to be coincident with the formation of the first crosslink species. The thiol-specific derivatization chromatography employed also indicated the presence of H_2S once crosslinking had occurred. In most samples, additional peaks appeared between the H_2S and TME-S_1H peaks in the HPLC chromatograms. These peak(s) varied from a sharp single peak (Figure 4) to a broad band of smaller peaks. These peak(s) disappeared if the sample was reanalyzed after the sample had been allowed to stand at room temperature, whereas the H_2S peak had increased in size. It could be thought that these peaks are due to TME-S_xH ($x > 1$). Mockel[15] has shown that polysulfidic compounds would elute later than their monosulfidic analogues using similar mobile phase conditions. It is consequently postulated that these peak(s) are due instead to the presence of polysulfanes (H_2S_n).

It is known that polysulfanes (H_2S_n) rapidly establish an equilibrium with H_2S and S8.[16] It is most likely that H_2S_n converts to H_2S between analysis and reanalysis of the sample. Furthermore the equilibrium is shifted towards H_2S because H_2S is volatile and thus escapes from the sample solution as a gas.

TME-SH/S_8 vulcanization system

The results obtained on heating the TME-SH/S_8 system isothermally at 150°C are represented in Table I. TME-SH is rapidly consumed in the first 2 min of reaction, after which there is a more gradual decrease in the concentration. The sulfur concentration showed a rapid decrease that coincided with the decrease in TME-SH concentration (first 2 min), and then its concentration did not change. The rate of crosslink formation is also initially rapid followed by a decrease in the rate of formation.

The crosslinks formed are only bis(alkenyl) in nature. This observation was confirmed by HPLC and
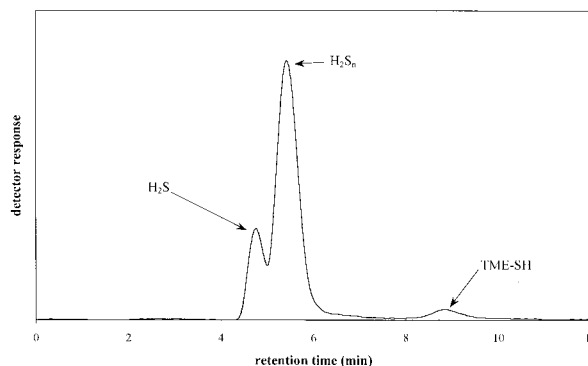

Figure 4 A typical chromatogram obtained for the TME/MBT/S_8 (33.9:1.1:1 mol) vulcanization system using postcolumn derivatization HPLC.

TABLE I
Degree of Reaction Achieved for the TME–SH/S$_8$
Vulcanization System at 150°C

Species	Amount Present after 2 min, %	Amount Present after 10 min, %
Sulfur	80.7	81.2
TME–SH	63.8	55.3
TME–S$_2$–TME	10.5	3.9
TME–S$_3$–TME	10.0	18.3
TME–S$_4$–TME	4.3	11.8
TME–S$_5$–TME	2.1	4.7
TME–S$_6$–TME	1.0	1.9
Total crosslinks	27.7	40.6

^{1}H-NMR. That only bis(alkenyl) crosslinks are formed is indicative that thiol–thiol interactions are responsible for crosslink formation. If addition of a thiol to an alkene had occurred, a loss of unsaturation would have taken place[17,18] and Markovnikov products would have formed.[18]

The trisulfidic crosslink species is the most abundant crosslink formed, whereas the hexasulfidic crosslink is the least abundant crosslink formed. Importantly, no monosulfidic crosslinks were detected in this system. Note that 100% of the original TME-SH is not accounted for by the data in Table I because of the difficulties involved with analyzing such systems. After quenching with liquid N$_2$, samples had to be reheated to allow sulfur to dissolve for analysis. Crosslinking, however, was observed to increase the longer the samples were allowed to stand prior to analysis (it even continued when samples were placed at $-20°$C in a freezer for storage). Every effort was hence made to analyze as rapidly as possible. Unfortunately, because of the chromatographic systems used, thiol compounds were determined from one vulcanization mixture and sulfur, crosslinks, and other species from a duplicate vulcanization experiment. Thus, because of continuing crosslinking during sample preparation for HPLC, any difference in preparation time would lead to variation in results.

The postcolumn derivatized chromatograms of this system revealed the presence of H$_2$S and polysulfanes (H$_2$S$_n$). Careful analysis of these chromatograms revealed small peaks to be present as shoulders on the TME-SH peak when an undiluted vulcanization mixture was injected. These compounds eluted after TME-SH (Figure 5) and were deduced to be less polar because less polar compounds elute later than polar compounds in reversed-phase HPLC.[15]

Compounds with a higher sulfur rank in a homologous series will elute later than compounds with lower sulfur rank under reversed-phase conditions. A plot of the logarithm of the retention times versus the sulfur rank of a homologous series of olefinic thiol compounds should yield a linear relationship when elution is performed isocratically.[15] This phenomenon
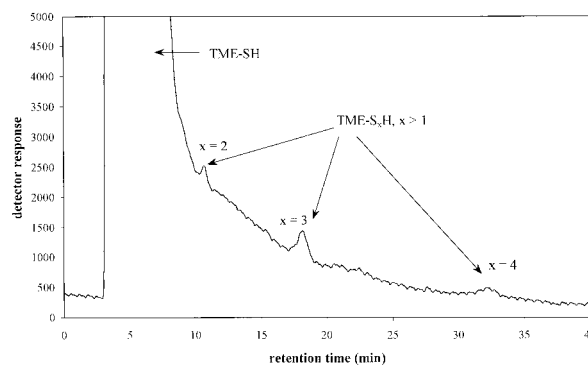

Figure 5 The additional peaks, postulated to be TME-S$_x$H ($x > 1$), observed in the TME-SH/S$_8$ system. The chromatogram was obtained using postcolumn derivatized HPLC. Note that the TME-SH peak has a height of $1.1 = 10^6$ units.

is due to the relationship between the standard free energy change of the transition between the mobile and stationary phases, and the number of atoms in a homologous series being linear (under isothermal and isocratic conditions).[19] Such a plot was performed for the peaks that were proposed to be TME-S$_x$H (Figure 6). A linear relationship ($R^2 = 0.9999$) was observed. Thus, it is very likely these peaks are indeed indicative of TME-S$_x$H being present. It should be noted that only —SH-containing compounds will give a detector response using the postcolumn derivatization with Ellman's reagent and detection at 420 nm; thus, these shoulders are definitely the consequence of the presence of thiol compounds. This is the first time such polysulfidic thiols have been identified in any vulcanization system. Unfortunately, because of their very low concentration and high reactivity, such species were not quantifiable.

TME-SH/MBT/S$_8$ vulcanization system

HPLC analysis of the TME-SH/MBT/S$_8$ system (Figure 7) revealed that very little or no MBT is consumed
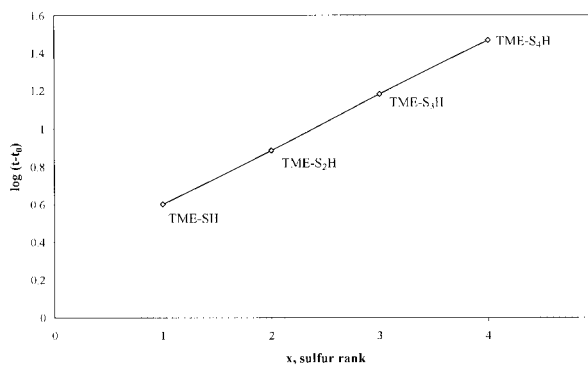

Figure 6 The linear relationship resulting from plotting the log of retention times versus proposed sulfur rank of TME-S$_x$H. TME-S$_1$H (known) is taken as the first compound in the homologous series.
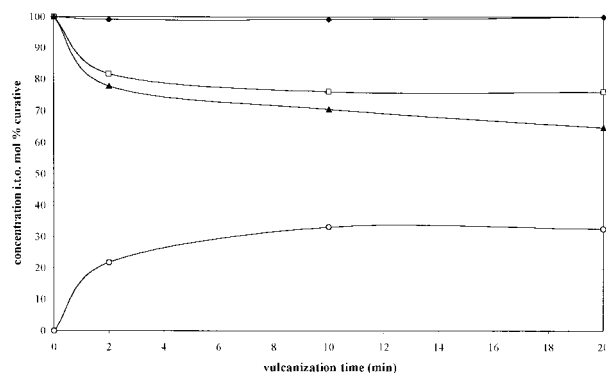
Figure 7 HPLC analysis of TME-SH/MBT/S_8 system, heated isothermally at 150°C. Key: (◆) MBT; (□) sulfur; (▲) TME-SH; (○) sum of TME-S_x-TME ($x = 2$–6).

during the reaction and that this system is similar to the TME-SH/S_8 system in terms of TME-SH uptake and crosslink formation. Similar to the TME-SH/S_8 system, only bis(alkenyl) crosslinks were formed (TME-S_2-TME to TME-S_6-TME).

The most abundant crosslink species is TME-S_3-TME (Figure 8). Except for the disulfidic crosslink, all species increase in concentration with time. The disulfidic species peaks in concentration at 2 min, after which it decreases in concentration. A similar result was obtained in the TME-SH/S_8 vulcanization system, where TME-S_2-TME acts as a source of sulfur for higher rank crosslinks after initially being rapidly formed. The reaction appears to be complete by 10 min.

The results obtained for the TME-SH/MBT/S_8 system were not significantly different from those of the TME-SH/S_8 and thus it seems that MBT is merely responsible for the production of the thiols in the first place and takes no direct role in the thiol–thiol crosslinking reaction. In fact, the extent of crosslinking was slightly reduced when MBT was present compared with when it was not present.
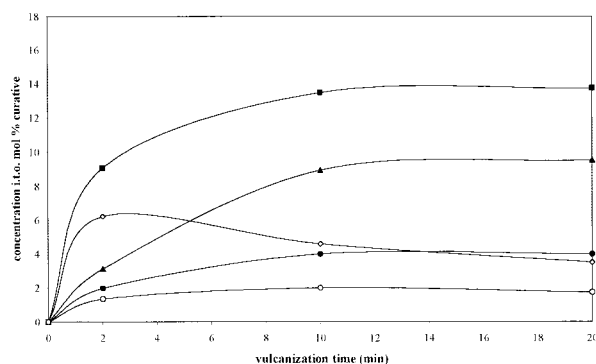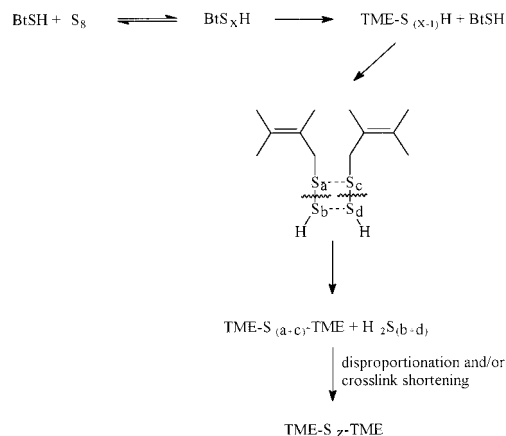

Figure 8 HPLC analysis of the bis(alkenyl) crosslinks formed in the TME-SH/MBT/S_8 system, heated isothermally at 150°C. Key: (◇) TME-S_2-TME; (■) TME-S_3-TME; (▲) TME-S_4-TME; (●) TME-S_5-TME; (○) TME-S_6-TME.

Scheme 2 Proposed major reaction pathway for MBT-accelerated sulfur vulcanization of TME ($z \geq 1$).

Proposed crosslinking reaction

Morgan and McGill[6] proposed that MBT forms MBT polysulfides (Bt-S_xH) on reaction with sulfur. These polysulfides would then interact with TME to form polysulfidic thiols of TME (TME-S_xH) and regenerate MBT. They propose that reaction of TME-S_xH with each other results in crosslink formation (TME-S_x-TME) and H_2S (Scheme 1).

The reaction scheme proposed by Morgan and McGill[6] is possible in a system where an oxidizing agent, such as peroxide, is present. In such a system, monosulfidic thiol does in fact react with itself to produce monosulfidic crosslinks and H_2S. Where TME-SH is heated in the presence of TME alone, however, no crosslinking is observed. Morgan and McGill's[6] mechanism would also predict the formation of monosulfidic crosslink products.

We agree with Morgan and McGill[6] that MBT reacts with sulfur to form MBT polysulfides (Bt-S_xH), which subsequently react with TME to form polysulfidic thiols of TME (TME-S_xH). MBT is regenerated in this process. In contrast to Morgan and McGill,[6] it is postulated that TME-S_xH react with each other via a metathesis pathway to form TME-S_z-TME and H_2S_n (Scheme 2). This scheme is similar to that proposed by Nieuwenhuizen et al.[20] for zinc dithiocarbamate (ZDMC) vulcanization, although these authors did not provide any supporting evidence for such a mechanism and the presence of polythiols. It should be noted that Nieuwenhuizen et al.[20] consider scission in the metathesis reaction to occur terminally (i.e., in the —S—SH bond) and did not consider scission in any of the other S—S bonds. We propose scission in all S—S bonds to generate a range of crosslink products.

Monosulfidic crosslinks are the result either of disproportionation reactions involving higher sulfur rank crosslinks or the interaction of monosulfidic benzothiazole pendant groups and polysulfidic thiols to produce crosslinks and MBT (or polysulfidic MBT).

Supporting evidence for proposed pathway

Although there is no direct evidence to prove the existence and presence of MBT polysulfides (Bt-S_xH), the presence of Bt-S_2-Bt and Bt-S_3-Bt may be used to infer the presence of Bt-S_xH species. Morgan and McGill[6] ascribe the formation of the bis-benzothiazole sulfides to air oxidation of MBT. If, however, Bt-S_xH undergoes a similar metathesis reaction to that proposed for TME-SH, Bt-S_z-Bt would be formed. Indeed, small amounts (<1.5%) of Bt-S_1-Bt, Bt-S_2-Bt and Bt-S_3-Bt are formed together with H_2S (or polysulfane) when BtS_xH and S_8 are reacted together at 150°C. The transient nature of Bt-S_xH results in only small amounts of Bt-S_z-Bt being formed.

The reformation of MBT on the reaction of BtS_xH and TME to form TME-S_xH explains the initial uptake of MBT and then the constant concentration thereafter (as seen in Figure 2). The regeneration of MBT makes it available to once more react with S_8 to form BtS_xH.

The bis(alkenyl) nature of the crosslink products is indicative of thiol–thiol interaction rather than thiol–olefin interaction. As indicated earlier, thiol addition to olefins result in a loss of unsaturation.[17,18] In the absence of peroxides, thiols add to olefins according to Markovnikov's rule, whereas in the presence of peroxides, abnormal addition takes place.[18] Thus, in the reaction of TME-SH and TME, an alkenyl–alkyl product would be formed. TME-SH and sulfur reacted to form only bis(alkenyl) products.

The absence of polysulfidic benzothiazole-terminated pendant groups (TME-S_yBt) eliminates the possibility of TME-S_xH and TME-S_yBt interaction to form bis(alkenyl) crosslinks. Note that the interaction of TME-S_xH and TME-SBt (the monosulfidic pendant group) may react to give small quantities of crosslink products (including TME-S_1-TME) and MBT. Such reactions have been proposed to be important in MBTS vulcanization systems.[21]

The presence of polysulfanes further supports the proposed metathesis pathway. It should be noted that it is impossible to for a monosulfidic crosslink to be formed via the metathesis reaction pathway. Indeed, the delay in and contrasting shape of the monosulfidic crosslink formation curve (figure 3) indicates that it is formed in a different way to that of the other crosslinks (TME-S_2-TME to TME-S_6-TME). A possible formation pathway is via crosslink shortening and disproportionation reactions. Polysulfidic crosslinks (which are thermally unstable) will desulfurate to form shorter more thermally stable crosslinks.[22] Crosslink shortening will also contribute to the formation of the shorter crosslinks (i.e., TME-S_2-TME and TME-S_3-TME) from higher ranked crosslinks. It also causes a decrease in concentration of the longer crosslinks (i.e. TME-S_5-TME and TME-S_6-TME) when free sulfur concentration is low. This effect of crosslink shortening is actually reflected in the crosslink formation in the TME/MBT/S_8 system (Figure 2), where TME-S_2-TME and TME-S_3-TME are still increasing in concentration after 30 min, whereas the TME-S_5-TME and TME-S_6-TME concentrations are more-or-less constant. Note though that such crosslink shortening reactions were not observed in the crosslink products formed when TME-SH and sulfur react. Hence, it is also possible that monosulfidic crosslinks result from the reaction of monosulfidic benzothiazole pendant groups and thiols. This reaction has been observed for polysulfidic pendant groups by Morgan and McGill.[21] The regeneration of MBT in such a reaction would be consistent with the near constant MBT concentration observed.

The reason that TME-SH is observed to slowly increase with time (Figure 2) is that the monothiol is unable to undergo metathesis reactions without the intervention of sulfur to form polysulfidic thiols. However, when polysulfidic thiols are formed directly from the reaction of MBT polysulfides and TME, the resultant polythiols are extremely reactive and rapidly form crosslink products. This sequence of reactions then explains why the appearance of TME-SH and crosslink products appears to be coincident. The initial delay in crosslinking is ascribed to a delay in the formation of MBT polysulfides (BT-S_XH), which is most likely the result of the time taken for the sulfur to convert to a form (possibly ionic) by which polysulfides can form from the reaction of MBT and sulfur.

CONCLUSION

MBT accelerates the sulfur vulcanization of TME through the probable formation of MBT polysulfides (Bt-S_xH). These polysulfides are formed through a reaction between sulfur and MBT. Their presence is inferred from the formation of Bt-S_1-Bt, Bt-S_2-Bt, and Bt-S_3-Bt. These polysulfides (Bt-S_{x+1}H) react with TME to form TME thiols (TME-S_xH) of varying sulfur rank and MBT. The monosulfidic thiol (TME-SH) is present in this system and increases linearly in concentration with reaction time. Evidence for the formation of polysulfidic thiols is inferred from their likely metathesis reaction products although such thiols have been observed in TME-SH/S_8 reaction systems. The TME thiols react extremely rapidly with each other through a metathesis pathway to form polysulfidic bis(alkenyl) crosslinks (TME-S_z-TME) and polysulfanes (H_2S_n), which were detected by postcolumn derivatization HPLC. The formation of monosulfidic crosslinks occurs by a hitherto unknown route, although this may involve the reaction of monosulfidic benzothiazole groups and thiol compounds or crosslink shortening reactions. The overall MBT-accelerated sulfur vulcanization of TME is illustrated in Scheme 2.

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