The Role of Dimethyldithiocarbamic Acid in Accelerated Sulfur Vulcanization

S. R. SHELVER, M. SHUMANE, M. H. S. GRADWELL, W. J. MCGILL

Polymer Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa

ABSTRACT: Polyisoprene/tetramethylthiuram disulfide (TMTD)/sulfur compounds were vulcanized under a variety of conditions. TMTD does not decompose to tetramethylthiourea (TMTU) at vulcanization temperatures as has been suggested, neither is it formed as an integral part of the crosslinking process. Instead, it results from the attack of dimethylamine, released on decomposition of dimethyldithiocarbamic acid (Hdmtc), on TMTD. It is demonstrated that the formation of TMTU in vulcanizates may be overlooked, as it is readily lost in the work-up for HPLC analysis. Hdmtc is shown to play an essential role in the crosslinking process in polyisoprene/TMTD/sulfur formulations, and its removal from the system during vulcanization severely impedes crosslinking. Polysulfidic thiuram-terminated pendent groups are formed, in part, by the interaction of tetramethylthiuram polysulfides with the polymer chain, but largely by an exchange between Hdmtc and polysulfidic thiol pendent groups. The latter are formed when sulfurated Hdmtc reacts with the polymer chain. Crosslinking of thiuram-terminated pendent groups is slow, and in the absence of ZnO crosslinking results from reaction between polysulfidic thiuram pendent groups and thiols. Crosslinking is delayed until the bulk of the accelerator is bound to the polymer chain, at which point the concentration of free thiuram groups, in the form of Hdmtc, is low, and exchanges between newly formed thiol pendent groups and Hdmtc is less frequent, permitting crosslinking of thiuram pendent groups with these newly formed thiol pendent groups. Data to support the proposed reaction mechanism is presented. Hdmtc on its own accelerates sulfur vulcanization and acts as a catalyst for the reaction, being regenerated in the crosslinking process. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1371–1379, 1999

Key words: vulcanization; mechanism; tetramethylthiuram disulfide; dimethyldithiocarbamic acid; tetramethylthiourea; polyisoprene

INTRODUCTION

The accelerated sulfur vulcanization of polyisoprene (IR)[1] and of model compounds[2,3] by tetramethylthiuram disulfide (TMTD), in the absence of ZnO, has been the subject of a number of studies. It is generally agreed[1,4–6] that accelerator polysulfide intermediates react with the olefin in a substitution reaction, leading to the formation of accelerator terminated polysulfidic pendent groups and the liberation of dimethyldithiocarbamic acid (Hdmtc). Crosslinking is said to result from the interaction of accelerator terminated pendent groups or from reaction between pendent groups and the polymer chain.[5,7] Geyser and McGill[3] suggested that crosslinking involved reaction between polysulfidic pendent groups terminated by thiurams, and polysulfides, terminated by a dimethylamine salt.
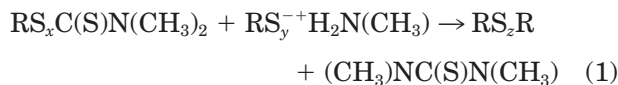
$$RS_xC(S)N(CH_3)_2 + RS_y^{-+}H_2N(CH_3) \rightarrow RS_zR$$
$$+ (CH_3)NC(S)N(CH_3) \quad (1)$$

According to this mechanism tetramethylthiourea (TMTU) forms as a by-product of the crosslinking process. TMTU has been reported by some[1,3] but not all[2] authors as being present in the extractable products at the end of the vulcanization process.

TMTU may form in a side reaction independently of the vulcanization process.[5] Various authors[8–10] have reported that, upon heating, TMTD will yield TMTU. No such breakdown has been observed at vulcanization temperatures in the absence of rubber in any studies in these laboratories.[11,12] Versloot et al.,[2] also, did not report TMTU formation on heating TMTD. The addition of dimethylamine to TMTD leads to the production[13] of dimethylammonium dimethyldithiocarbamate (dma.dmtc) and TMTU, and it has been suggested[5] that differences in TMTU formation may be ascribed to the presence of an impurity, such as an amine, that may or may not be trapped in the system, depending on the experimental setup employed.

Kruger and McGill,[1] who vulcanized IR/TMTD/sulfur compounds in a DSC at programmed heating rates, attributed TMTU formation to the decomposition of Hdmtc, released during pendent group formation, the amine produced attacking residual TMTD. TMTU does not form in vulcanizates where Hdmtc is trapped by ZnO.[14] As noted above, Geyser and McGill[3] considered TMTU formation as an integral part of the crosslinking reaction, although in a similar study of model compound vulcanization by TMTD/sulfur, Versloot et al.[2] did not report TMTU. Furthermore, Versloot et al.[2] noted that in model compound studies thiuram pendent groups crosslinked very slowly in the absence of ZnO, although zinc-free IR/TMTD/sulfur systems are known to crosslink readily,[1,15] and Geyser and McGill[3] found rapid crosslinking with model compounds in the absence of ZnO. They proposed a mechanism in which the amine participated in crosslinking . These discrepancies prompted us to revisit the question of TMTU formation and the role of Hdmtc, released on pendent group formation, on the vulcanization of compounds cured in the absence of ZnO.
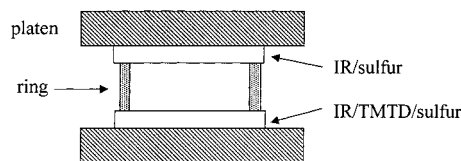

Figure 1 Schematic of system used for the vulcanization of thin films in which Hdmtc vapor diffuses from the lower to the upper film.

EXPERIMENTAL

Materials

Polyisoprene (Afprene IR80) Karbochem; Orac TMTD (purity 97%), was supplied by Orchem, South Africa; sulfur (purity 99.94%), Holpro Analytics, tetramethylthiourea, was supplied by Fluka.

Compounds (IR 100 phr, TMTD 12.27 phr, sulfur 9.46 phr, and IR 100 phr, sulfur 9.46 phr) were prepared in a Brabender Plasticorder as described earlier[16] and contained 1:1 molar ratios of curatives. Various systems were used to vulcanize samples. Some samples were vulcanized in sealed pans in a DSC, either isothermally at 150°C or at a programmed heating rate of 2.5°C/min.[16,17] Other samples were vulcanized in a press at 150°C. Thin films of compounds that had been precipitated on the walls of a tube, were heated in an oil bath at 150°C under a variety of conditions as described in the text. In other experiments, thin films of compounds were formed on the upper and lower platens of a small press as shown in Figure 1. A metal ring prevented physical contact between films. On heating, volatiles, mainly from the lower film, were absorbed into the upper film, and their influence on vulcanization of the upper film was monitored. TG experiments were conducted at 2.5°C/min in a flow of high purity nitrogen.

Residual curatives and soluble intermediates were extracted from the rubber at various stages of the reaction and analysed by HPLC as described earlier.[16,17] In the figures, concentrations of reactants, intermediates, and products are expressed in terms of the initial concentration of reactant, i.e., as the mol % of reactant remaining, or mol % intermediate/product formed from that reactant. Crosslink densities were determined by swelling.[17]

Hdmtc was synthesized by the drop-wise addition of HCl to a saturated aqueous solution of the sodium salt of Hdmtc in an ice bath. TMTD, a

Table I Acronyms

Acronym	Name
dma.dmtc	Dimethylammonium dimethyldithiocarbamate
Hdmtc	Dimethyldithiocarbamic acid
IR	Polyisoprene
MBT	2-Mercaptobenzothiazole
MBTS	2-Mercaptobenzothiazole-2,2′-disulfide
PAN	N-phenyl-1-naphtylamine
TME	2,3-Dimethyl-2-butene
TMTD	Tetramethylthiuram disulfide
TMTM	Tetramethylthiuram monosulfide
TMTP	Tetramethylthiuram polysulfide
TMTU	Tetramethylthiourea

by-product of the reaction, was removed by filtration. However, Hdmtc proved to be unstable upon drying, and difficulty was experienced in extracting buffered solutions into chloroform, as described in the literature.[18] A low product yield was obtained after extraction into methanol and removal of NaCl. The very hygroscopic product produced a single sharp peak at 3.30 min on the HPLC. After vacuum drying over P_2O_5 for 24 h and dissolution in $CDCl_3$, ^{1}H-NMR analysis showed two signals, one at 2.7 ppm due to the equivalent hydrogens on the dimethylcarbamato group and one at 8.3 ppm due to the thiol hydrogen.

Table I lists acronyms used.

RESULTS AND DISCUSSION

The crosslink density and HPLC analysis of a study of IR/TMTD/sulfur compounds, vulcanized by heating in a DSC at 2.5°C, are presented in Figure 2. Above 110°C the TMTD concentration decreased rapidly and tetramethylthiuram polysulfides (TMTP) formed. The subsequent decrease in their concentration is attributed to their attachment to the rubber chain as pendent groups. At the point at which crosslinking initiated (140°C at the heating rate used) the TMTD concentration was low and soon dropped to zero. At 160°C 70 mol % of the sulfur was still extractable but, despite the TMTD concentration being negligible, was rapidly consumed in further crosslinking reactions. Kruger and McGill[1] also reported high sulfur and low TMTD concentrations at the onset of crosslinking. Little TMTU was detected upon crosslinking, unlike in the work of Kruger and McGill[1] and Geyser and

McGill,[3] who reported TMTU formation as accompanying crosslinking. Two questions must be addressed, viz. discrepancies in the detection TMTU on crosslinking and the consumption of sulfur in further crosslinking reactions despite the absence of free TMTD accelerator. DSC curves[1] show that unaccelerated sulfur vulcanization is rapid only at 175°C, and cannot account for the consumption of sulfur observed in Figure 2.

TMTU Formation from TMTD

No TMTU was found on heating TMTD at 140°C in a sealed tube for 2 h, TMTU being produced only at higher temperatures. As noted above, TMTD decomposition to TMTU may require the presence of an amine impurity.[5] Such an impurity was clearly absent from the present TMTD sample, and where TMTU was found on vulcanization, the species responsible for initiating TMTU formation must be generated in the vulcanization process or TMTU must result form the crosslinking reaction.

TMTU Formation in Vulcanizates

Kruger and McGill[1] suggested that TMTU resulted from the attack of dimethylamine, formed upon decomposition of Hdmtc, on TMTD and thiuram pendent groups, while Geyser and McGill[3] suggested that, because TMTU was produced coincident with crosslinking, it may be formed as in integral part of the crosslinking reaction. This did not exclude degradation reactions contributing to TMTU.
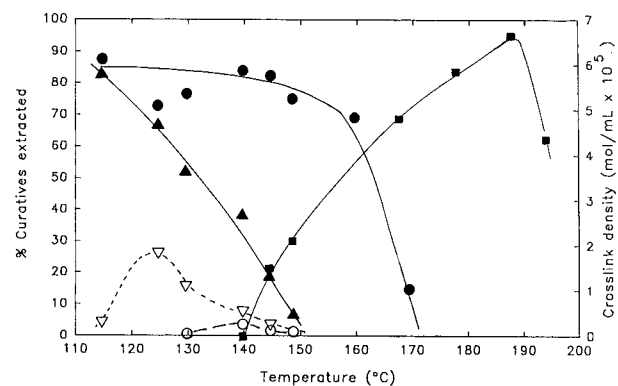

Figure 2 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur heated at 5°C/min: crosslink density, TMTM, TMTD, TMTP and sulfur.

Table II   TMTU and Crosslink Formation in IR/TMTD/Sulfur[1] and TME/TMTD/Sulfur[3] Vulcanizates Cured to Different Temperatures or for Different Times at 150°C

Temp. (°C)	TMTU (mol/mL $\times 10^5$)	Crosslinks (mol/mL $\times 10^5$)	TMTU/Crosslink
		IR/TMTD/Sulfur	
143	11.6	0.41	28.3
151	20.1	4.97	4.0
164	22.5	6.31	3.6
		TME/TMTD/Sulfur	
14	50	1.0	50.0
15	60	5.0	10.0
16	55	5.2	6.6

On heating a thin film of IR/TMTD/sulfur in an evacuated, sealed tube, totally immersed in an oil bath at 150°C for 10 min, HPLC analysis of soluble compounds extracted with dichloromethane from the contents of the tube revealed the presence of TMTD, Hdmtc, dma · dmtc, and considerable amounts of TMTU. When the tube was only partially submerged, no TMTU was detected in the material that precipitated on the cold section of the tube. TMTU was extracted from both films, and the large amounts of TMTU formed in the vapor phase in the totally immersed reaction tubes points to TMTU resulting from a high temperature reaction involving Hdmtc. TMTU formation is prevented when condensation of the volatiles occurs on the cold walls of the tube. In this event only dma · dmtc results. Attack on TMTD by dimethylamine, formed on decomposition of Hdmtc, will give TMTU.[5] Such an attack could occur on TMTD present in the film and in the vapor phase.

In both IR[1] and TME[3] vulcanizates the TMTU/crosslink density ratio is far in excess of one (Table II), and it is evident that the bulk of the TMTU must result from reactions other than crosslinking. On further reaction the crosslink density increased more rapidly than did TMTU evolution These ratios, read in conjunction with the above data, do not disprove the crosslinking mechanism proposed by Geyser and McGill,[3] but suggest that its contribution to the to the overall crosslinking process must be reviewed.

The data reported for IR films above is consistent with studies of model compound vulcanization. Geyser and McGill,[3] who reported TMTU, completely submerged the reaction tubes in the oil bath at 150°C, while Versloot et al.,[2] who employed partially submerged reaction tubes, did not report TMTU in the products that precipitated on the cold sections of the reaction tubes. Dma · dmtc was detected, which implies that some Hdmtc escaped being trapped by ZnO present in the system, yet as volatiles could precipitate on the upper sections of the reaction tube, TMTU was not produced, only dma · dmtc.

Extraction of TMTU from Vulcanizates

In some experiments conducted in these laboratories TMTU was detected[1] upon vulcanization of rubber compounds in a press or in sealed DSC pans, while in other cases[15] little or no TMTU was found. These inconsistencies in detecting TMTU needed further investigation. In model compound experiments residual curatives, products, and the unreacted model compound were dissolved in dichloromethane and solutions for HPLC analysis prepared in dichloromethane/methanol (5 v/95 v).[3] The same procedure was followed for the analysis of products that collected on the walls of the reaction tube when thin films of rubber were heated in sealed tubes.[15] With rubber compounds, residual curatives and reaction intermediates were extracted from the vulcanizate with benzene, the solution evaporated, the precipitate redissolved in dichloromethane, and solutions for HPLC analysis made up in dichloromethane/methanol.[1,15,17] Prolonged extraction or swelling of a vulcanizate in benzene or cyclohexane, as is required in experiments aimed at measuring crosslink densities, may lead to the slow degradation of the network in certain cases.[19] Equilibrium swelling values can thus not be attained. The addition of the stabilizer N-phenyl-1-naphtylamine (PAN) to the swelling solvent was found to prevent such degradation.[17,19] A careful review
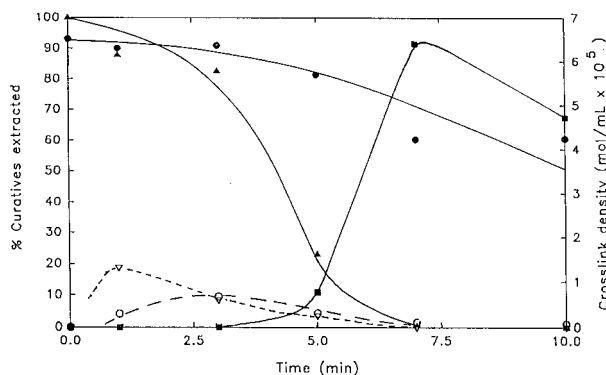
Figure 3 Crosslink density and HPLC analysis of reactants and products in the vulcanization of IR/TMTD/sulfur at 150°C: crosslink density, TMTM, TMTD, TMTP, and sulfur.

of experimental procedures followed by different workers in the laboratories revealed that TMTU was not detected when the addition of PAN to the extracting solvent was omitted. In control experiments TMTU (0.5–3 mg) was dissolved in benzene, the solvent evaporated overnight, the residue redissolved in dichloromethane and analysed by HPLC. TMTU losses of 85 to 96 mol % were observed. When PAN was added to TMTU solutions before evaporation of the solvent, much smaller losses ($\approx$ 25 mol %) of TMTU were found. When residual curatives and reaction products of compounds vulcanized in DSC pans were not extracted with benzene but, after opening the pan and its contents were placed directly into dichloromethane, the solution made up with methanol and analysed by HPLC, TMTU (14–38 mol %) was detected. It would appear that the small amount of PAN added to the extraction solvent coats the precipitate formed on evaporation, preventing its sublimation. It is interesting to note that Moore et al.[20] separated TMTU by sublimation at 60°C *in vacuo*. Only TMTU sublimed during solvent evaporation; HPLC analysis of control experiments with TMTD and other curatives showed no noticeable loss on evaporation of the solvent.

Reactivity of Pendent Groups

Using model compounds, Versloot et al.[2] showed that thiuram-terminated pendent groups crosslink only very slowly in the absence of zinc. In this study, an IR/TMTD/sulfur compound was heated at 150°C for 3 min to a point just prior to the onset of crosslinking (cf. Fig. 3). Soluble curatives were

extracted and, after drying, the sample was reheated at 150°C. Crosslinking, attributable to the reaction of thiuram terminated pendent groups, occurred slowly, the rate and extent of the reaction being less than one-third that when the reaction was not interrupted by extraction. This implies that interruption of the reaction and extraction removes an agent essential for the crosslinking process.

Effect of Removal of Hdmtc on Crosslinking

When ZnO is present, Hdmtc will be trapped as bis(dimethyldithiocarbamato)zinc(II),[14] which in turn, may act as an accelerator, but the role of Hdmtc in zinc free systems has been ignored. It will be shown below that removal of Hdmtc from an IR/TMTD/sulfur compound during vulcanization delays the onset of crosslinking and reduces the crosslink density.

That accelerator-terminated pendent groups do not, on their own, lead to rapid crosslinking, and the importance of Hdmtc, is demonstrated by the following experiment. A thin film of IR/TMTD/sulfur was heated at 150°C for 10 min under vacuum to remove Hdmtc immediately it was produced in a pendent group formation. The rubber sample dissolved completely in benzene, although data in Figure 3 suggest that a crosslink density of 6×10^{-5} mol/mL would have been achieved in a system from which Hdmtc could not escape. The rubber from the vacuum-heated sample was reprecipitated as a thin film. The residual curatives (unreacted TMTM, TMTD, TMTP, and sulfur) were extracted with methanol for 48 h, the methanol being replaced after 24 h, leaving behind only thiuram-terminated pendent groups attached to the polymer chain. Half of the sample was reheated for 10 min at 150°C, and when placed in benzene, it was found that the sample had formed a loose gel, further indicating that thiuram-terminated pendent groups do not readily interact with each other or with the chain to form crosslinks. The addition of zinc stearate to the other half of the sample, followed by reheating for 10 min at 150°C, resulted in a compound with a crosslink density of 11×10^{-5} mol/mL. This is considerably higher than is achieved when vulcanization is not interrupted (Fig. 3). It was illustrated earlier[22] that zinc stearate promotes crosslinking of pendent groups, and the high crosslink density achieved highlights the large number of pendent groups on the chain that do

Table III Crosslink Densities in IR/Sulfur Compounds Exposed to Hdmtc Vapor at 150°C

Time (min)	Crosslink Density 1/2Mc (mol/mL Rubber $\times 10^{-5}$)		
	Run 1	Run 2	Average
5	0.34	0	0.17
7	1.72	0.54	1.13
9	3.70	2.38	3.04
11	3.64	1.08	2.36
13	9.87	6.49	8.18
15	6.09	9.17	7.63

not participate in crosslinking in the absence of zinc.

Hdmtc as Accelerator

Because Hdmtc was found to be very unstable when dried, a few mg of incompletely dried Hdmtc was added to a thin film of unvulcanized IR/sulfur and folded into the compound by hand. Upon heating in a DSC at 2.5°C/min, the vulcanization exotherm initiated at 146°C, considerably earlier than the exotherm at 177°C for an IR/sulfur compound.[1] After heating samples isothermally for 10 min at 150°C it was found that, upon swelling in benzene, an IR/sulfur compound had formed a loose gel of immeasurably low crosslink density, while an IR/Hdmtc/sulfur compound provided an extremely highly crosslinked vulcanizate (20 $\times 10^{-5}$ mol/mL).

In a second series of experiments Hdmtc vapor was allowed to absorb into a heated IR/sulfur compound and the crosslink density measured as a function of time. Hdmtc, liberated during pendent group formation in IR/TMTD/sulfur compounds, can readily escape from thin films of rubber. A sandwich system (Fig, 1) was used in which Hdmtc, evolved from an IR/TMTD/sulfur compound upon heating, was allowed to absorb into an IR/sulfur film held at 150°C, and the crosslink density of the latter films examined as a function of time. Reproducible results are difficult to obtain, as the amount of Hdmtc available for acceleration depends on the thickness of the IR/TMTD/sulfur film from which it escapes as well as on the thickness of the IR/sulfur film into which diffusion occurs. Nevertheless, it is clear that diffusion of Hdmtc into the IR/sulfur film leads to a substantial increase in crosslink density (Table III)

compared to an IR/sulfur film heated for similar times in the absence of Hdmtc vapor where essentially no crosslinking occurred. Crosslink densities in Table III are similar to those obtained with IR/TMTD/sulfur (Figs. 2 and 3). Treatment with 0.4 M propane-2-thiolpiperidene in n-pentane,[17,23] showed that 95% of crosslinks were polysulfidic. HPLC analysis of extractable curatives revealed only sulfur, no thiuram containing species being extracted. This would imply that little TMTD was absorbed from the lower film or that all such absorbed TMTD had reacted.

In a control experiment, an IR/TMTD film was used in place of an IR/TMTD/sulfur film in the setup shown in Figure 1. In the absence of sulfur, limited TMTP and pendent group formation,[1] and therefore limited Hdmtc evolution, will occur from this film, but the loss of TMTD to the upper IR/sulfur film will still be possible. Analysis of the upper IR/sulfur film showed a crosslink density of 0.3×10^{-5} mol/mL after 15 min, indicating that the amount of TMTD absorbed into the IR/sulfur film was insufficient to account for the increase in crosslink density observed in films exposed to Hdmtc. Control experiments failed to lead to crosslink densities comparable with those found with Hdmtc, and the observed increase in crosslink density in Table III must, therefore, be attributed to Hdmtc.

Mechanism of TMTD Accelerated Sulfur Vulcanization

It is suggested that the main route to crosslinking in TMTD-accelerated sulfur vulcanization is not via pendent group–pendent group reaction, nor via pendent group–chain reaction,[5,7] nor via the reaction sequence suggested by Geyser and McGill.[3] Instead, the following reaction sequence is proposed. In the first step, accelerator polysulfides form accelerator-terminated pendent groups and Hdmtc, as has frequently been reported.[1,4−6]

$$XSSX + S_8 \rightarrow XS_xX \text{ ----RH----> } RS_yX + HSX \quad (2)$$
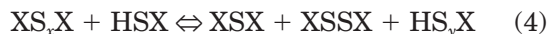
where

$$X = (CH_3)/NC(S)—$$

It is suggested that Hdmtc reacts with sulfur to form polysulfidic species that, like TMTP, interact with the polymer chain (RH), in this event to yield thiol pendent groups.

$$HSX + S_8 \rightarrow HS_xX \cdots RH \cdots> RS_yH + HSX \quad (3)$$

Polysulfidic Hdmtc species also results from exchange reactions between Hdmtc and TMTP.

$$XS_xX + HSX \Leftrightarrow XSX + XSSX + HS_yX \quad (4)$$

TMTD and sulfur were heated at 150°C and the mixture analyzed by HPLC. Within 5 min equilibrium had been established between sulfur, TMTD, and the various TMTP species.[12] The addition of a small amount of Hdmtc solution and reheating at 150°C for 5 min, changed the HPLC product spectrum, the TMTM and TMTD concentrations increasing at the expense of TMTP. This is attributed to an exchange between Hdmtc and TMTP as depicted in eq. (4). Even in the absence of heat, the addition of Hdmtc produced some degradation of TMTP. Some TMTU was also detected, and can be attributed to attack by dimethylamine from Hdmtc decomposition. Exchange reactions of this nature are well known. The more rapid sulfuration of 2-bisbenzothiazole-2,2′-disulfide (MBTS) when 2-mercaptobenzothiazole (MBT) is added to a MBTS/sulfur mix, has likewise been ascribed to an exchange between polysulfides of MBT and MBTS.[24] A similar exchange between TMTD and MBT has been demonstrated.[25]

In another experiment an equilibrium mixture of sulfur and TMTP was prepared by heating sulfur and TMTD for 5 min at 150°C. The mixture was placed on the lower platen of the setup depicted in Figure 1, with an IR/TMTD/sulfur film adhering to the upper platen. After heating for 13 min at 150°C, the mixture was analyzed by HPLC. Again, a decrease in TMTP and an increase in TMTM and TMTD indicated an exchange, as represented by eq. (4).

In the isothermal vulcanization at 150°C the rapid formation of TMTP can be seen by 1 min (Fig. 3). Their interaction with the polymer chain will liberate Hdmtc, which participates in an exchange reaction with TMTP, leading to a sharp decline in TMTP concentration, i.e., the decrease in TMTP is not simply due to their addition to the chain, but is in part due to the exchange with Hdmtc. Note the formation of TMTM and the sudden rapid decrease in TMTP concentration (Fig. 3).

It is proposed that crosslinking results from the interaction of thiuram terminated pendent groups and thiols, regenerating Hdmtc that can react further, ultimately consuming the remainder of the sulfur that had not yet bound to the polymer and remained extractable when the TMTD concentration decreased to zero (Fig. 2).

$$RS_xX + RS_xH \rightarrow RS_yR + HSX \quad (5)$$

Morgan and McGill[25] have shown that, in the absence of sulfur, disulfidic benzothiazole pendent groups are unreactive, as are monothiols. By analogy, it would imply that thiuram and thiol pendent groups involved in reaction 5 must be polysulfidic. They also demonstrated rapid crosslinking between thiols in the presence of sulfur, but that reaction between benzothiazole groups and thiols dominated when both species were present.

Induction Period Prior to Crosslinking

Another reaction must be included in the overall vulcanization process suggested above, because pendent groups form early in the reaction (Figs. 2 and 3), yet crosslinking is delayed until most of the TMTD has been consumed. An explanation is required for the delay in the onset of the crosslinking process.

Geyser and McGill[3] suggested that Hdmtc exchanged with thiuram pendent groups to form thiols, thus accounting for the low constant concentration of Hdmtc observed during vulcanization of model compounds. TMTD would be regenerated in the process, and the observed decrease in TMTD concentration as the reaction proceeded could not be explained. The involvement of Hdmtc in thiol formation via the reaction of HS_xX with the polymer chain will equally explain the Hdmtc concentration remaining constant. Geyser suggested that thiols were inactive, and were activated by dimethylamine to form the amine salt, which then crosslinked with thiuram-terminated pendent groups to yield TMTU [(eq. (1)]. It was proposed that dimethylamine formed only when the TMTD concentration, and therefore the thiuram sulfenyl radical concentration, became sufficiently low for the decomposition of these radicals, leading to dimethylamine, to become competitive with radical recombination. However, Morgan and McGill[26] have recently shown that in the presence of sulfur, thiols are very reactive and crosslink rapidly with the liberation of H_2S.

$$RS_xH + HSX \cdots> RS_xX + H_2S \quad (6)$$

It is suggested that the induction period results from an exchange between Hdmtc and thiol groups.

In this study, as well as in that of Kruger and McGill,[1] TG showed a mass loss prior to the crosslinking exotherm. Kruger attributed this to the evaporation of Hdmtc, but it could equally be due to the escape of H_2S from the exchange reaction between Hdmtc and thiol groups. The lead acetate test showed the formation of H_2S.

The exchange depicted in eq. (6) will result in the bulk of the pendent groups on the polymer chain being thiuram groups, accounting for the observed decrease in TMTD as the reaction progresses. Only when the Hdmtc concentration decreases, reducing the probability of an exchange with newly formed thiols , will crosslinking result in accordance with eq. (5). The high concentration of thiuram pendent groups in the compound at this point will also favor crosslinking with thiol pendent groups as soon as they form.

The importance of thiuram pendent group formation via the exchange of thiols with Hdmtc (reaction 6) is demonstrated in the following experiment. A 2-g sample of IR/TMTD/sulfur was vulcanized in a tube immersed in an oil bath at 150°C, and volatiles removed by a nitrogen purge were absorbed in $AgNO_3$. The 0.0351 g of AgS formed in this reaction equates to 6.5×10^{-5} mol of H_2S per mL of rubber compound. The crosslink density of the sample was 7×10^{-5} mol/mL. Thus, the amount of H_2S liberated closely equates to the crosslink density, suggesting that thiuram terminated pendent groups resulted largely via reaction of HS_xX with the polymer chain [(eq. (3)], followed by an exchange of thiol groups with HSX .

If reaction between pendent groups led to crosslinking, the data in Figs. 2 and 3 would require that crosslinking occurred much earlier, and was not delayed until most of the TMTD had been consumed. Also, crosslinking by disproportionation via pendent group–pendent group interaction would regenerate TMTD. Figures 2 and 3 show no such regeneration once crosslinking commences, although TMTD formed could, of course, react further.

2,3-Dimethyl-2-butene(TME)/TMTD/Sulfur

It is worth noting that, in contrast to Versloot et al.,[2] Geyser and McGill [3] found considerable crosslinking with TME/TMTD/sulfur in the ab-

sence of zinc. The difference between Geyserís and Verslootís experimental conditions was that Geyser completely immersed the sample tube in the oil bath, thereby preventing the condensation of Hdmtc on the colder sections of the reaction vessel, as could happen in the case of Verslootís experiments. Versloot found dma · dmtc (a Hdmtc decomposition product) at the top of the reaction vessel. In Geyser's experiments, condensation of Hdmtc was prevented, and it remained available to participate in the reaction, forming thiol pendent groups essential for crosslinking.

CONCLUSIONS

TMTD does not decompose to TMTU at vulcanization temperatures but, where TMTD accelerated sulfur vulcanization is carried out under conditions in which traces of dimethylamine—from Hdmtc decomposition—contacts TMTD at elevated temperatures, it catalyzes TMTU formation. This may occur in the rubber as well as in the vapor phase. When condensation of Hdmtc occurs on the cold walls of the reaction vessel, dma · dmtc forms.

When Hdmtc is removed from the compound during vulcanization, crosslinking of thiuram pendent groups is slow, indicating that it plays an active role in crosslinking. It is proposed that polysulfides of Hdmtc interact with the polymer chain, forming polysulfidic thiol pendent groups, and regenerate Hdmtc. Thiuram-terminated pendent groups result from the reaction of TMTP with the rubber chain, and from exchange reactions between Hdmtc and thiol pendent groups, this exchange constituting the major route in thiuram pendent group formation in TMTD accelerated vulcanization. H_2S is liberated in the exchange. Crosslinking involves reaction between polysulfidic thiuram and polysulfidic thiol groups on the chain. Hdmtc, on its own, can also accelerator for sulfur vulcanization, and is regenerated in the process, thus acting as a catalyst, rather than as an accelerator. Its catalytic action enables residual sulfur, present in the system when all of the TMTD has been consumed, to rapidly participate in crosslinking reactions.

REFERENCES

1. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 44, 587.
2. Versloot, P.; Haasnoot, J. G.; Reedijk, J.; van Duin, M.; Duynstee, E. F. J.; Put, J. Rubber Chem Technol 1994, 67, 252.
3. Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 439.
4. Shelton, J. R.; McDonel, E. T. Rubber Chem Technol 1960, 33, 342.
5. Nieuwenhuizen, P. J.; Reedijk, J.; van Duin, M.; McGill, W. J. Rubber Chem Technol 1997, 70, 368.
6. Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 431.
7. Chapman, A. V.; Porter, M. Natural Rubber Science and Technology; Roberts, A. D., Ed.; Oxford University Press: Oxford, 1988.
8. Dogadkin, B. A.; Shershnev, V. A. Rubber Chem Technol 1960, 33, 401.
9. Graig, D. Rubber Chem Technol 1956, 29, 994.
10. Coleman, M. M.; Shelton, J. R.; Koenig, J. L. Rubber Chem Technol 1973, 46, 956.
11. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1991, 42, 2669.
12. Geyser, M.; McGill, W. J. J Appl Polym Sci 1995, 55, 215.
13. Geyser, M.; McGill, W. J. J Appl Polym Sci 1996, 60, 425.
14. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 45, 749.
15. Gradwell, M. H. S.; McGill, W. J. J Appl Polym Sci 1995, 58, 2185.
16. McGill, W. J.; Shelver, S. R. J Appl Polym Sci, to appear.
17. Kruger, F. W. H.; McGill, W. J. J Appl Polym Sci 1992, 44, 581.
18. Aspila, K. I.; Chakrabarti, C. L.; Sastri, V. S. Anal Chem 1975, 47, 945.
19. Honiball, D.; McGill, W. J. J Polym Sci Polym Phys Ed 1998, 26, 1529.
20. Moore, C. G.; Watson, A. A. J Appl Polym Sci 1964, 8, 581.
21. Craig, D.; Davidson, W. L.; Juve, A. E. J Polym Sci 1951, 6, 177.
22. McGill, W. J.; Shelver, S. R. J Appl Polym Sci 1999, 72, 1021.
23. Saville, B.; Watson, A. A. Rubber Chem Technol 1967, 40, 100.
24. Gradwell, M. H. S.; Morgan, B.; McGill, W. J. J Appl Polym Sci 1995, 56, 1581.
25. Giuliani, B. V. M. K.; McGill, W. J. J Appl Polym Sci 1995, 57, 1391.
26. Morgan, B.; McGill, W. J. J Appl Polym Sci, to appear.