

Dimethylammonium Dimethyldithiocarbamate-Accelerated Sulfur Vulcanization. II. Vulcanization of Rubbers and Model Compound 2,3-Dimethyl-2-butene

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

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

Received 26 August 2000; accepted 29 September 2001

ABSTRACT: Rubber and model compound 2,3-dimethyl-2-butene were vulcanized for various times with dimethylammonium dimethyldithiocarbamate [(dma)dmtc]-accelerated sulfur formulations in the absence of ZnO. Model compound systems were analyzed by HPLC, and no reaction intermediates containing pendent groups were found. Crosslinked sulfides, characterized by $^1\text{H-NMR}$, were found to be essentially bis(alkenyl). Residual curatives were extracted from rubber compounds vulcanized for various times and analyzed by HPLC. Compounds, cured to various crosslink densities, were found to crystallize readily in a density column at subambient temperatures. This supports evidence from model compound systems that pendent groups are largely absent from vulcanizates. It is suggested that a reaction mechanism, similar to that applicable to zinc dimethyldithiocarbamate-accelerated sulfur vulcanization, may be applicable with (dma)dmtc accelerated formulations. Very limited crosslinking occurred on heating compounds under vacuum, and this can be attributed largely to the rapid loss of (dma)dmtc from rubber at elevated temperatures. However, the slower rate of crystallization on cooling of the gels, compared to the rate in press-cured vulcanizates of similar crosslink density, was interpreted as evidence that some pendent groups did form during heating with (dma)dmtc/sulfur. Crosslinking of such pendent groups may be inhibited by the loss of (dma)dmtc, that, like zinc dimethyldithiocarbamate, may catalyze their crosslinking, and/or to the loss under vacuum of dimethyldithiocarbamic acid that would form thiol pendent groups that would rapidly crosslink with thiuram pendent groups. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3074–3083, 2001

Key words: vulcanization; dimethylammonium dimethyldithiocarbamate; mechanism; crystallization; rubber; crosslinking

INTRODUCTION

Amines (aniline)¹ were the first compounds used as accelerators for sulfur vulcanization. The for-

mation of complexes between sulfur and secondary amines have been reported,² while several workers have suggested that the accelerating effect of amines is due to the liberation of active sulfur.^{3,4} However, Moore and Saville⁵ considered such liberation unlikely. They showed that at 140°C reaction of cyclohexene with diethylamine and sulfur gave a high yield of sulfurated products consisting mainly of dicyclohexyl monosulfide and smaller amounts of disulfide. The fully saturated nature of the products contrasts with

Correspondence to: W. J. McGill (chawjm@upe.ac.za).

Contract grant sponsors: the South African National Research Foundation, the South African Institute of Race Relations for financial assistance, and the University of Fort Hare.

Journal of Applied Polymer Science, Vol. 82, 3074–3083 (2001)
© 2001 John Wiley & Sons, Inc.

the alkyl alkenyl polysulfides obtained in unaccelerated sulfur vulcanization of cyclohexene.⁶ Essentially, similar reactions were reported with trialkylethylenes⁷ while with 1 : 5 diolefin cyclic sulfides also form.⁸ Opening of the cyclic sulfur ring, followed by homolytic scission of the amino polysulfanes formed, giving sulfur radicals, has been suggested.^{9,10} Krebs⁹ considered the accelerating properties of amines to be related to their base strength.

Very early on the toxicity of amines led to the development of guanidines, now used largely as secondary accelerators,^{11,12} and later to various other accelerators, including thiurams and zinc dimethyldithiocarbamate [$\text{Zn}_2(\text{dmtc})_4$], the reactions of which have been studied extensively.^{11,13-16} With $\text{Zn}_2(\text{dmtc})_4$ -accelerated sulfur vulcanization coordination of amines with the zinc complex is considered to have a distinct influence on its reactivity.^{11,13-16} Zinc accelerator complexes, which are sparingly soluble in rubber and amines, are considered to render these complexes more soluble by coordination to the zinc atom.¹⁵ Amine coordination also enhances their reactivity, coordination rendering the Zn—S bond more ionic.¹⁴

Dimethylammonium dimethylthiocarbamate [(dma)dmtc, $(\text{CH}_3)_2\text{NC}(\text{S})\text{S}^-(\text{CH}_3)_2\text{NH}_2^+$], the complex of dimethylamine with dimethyldithiocarbamic acid (Hdmtc), is a well-known accelerator, particularly for latices.¹² Very little scientific data on its reactions has been published. It is thermally stable,¹⁷ and its high reactivity may lead to scorch.¹⁸ This article examines the nature of crosslinked products formed in (dma)dmtc-accelerated sulfur vulcanization of model compound 2,3-dimethyl-2-butene (TME) and the crystallizability of rubber vulcanizates at subambient temperatures. The behavior of the rubber on crystallization relates to the regularity of the polymer chain in the vulcanizate, in particular to its modification by pendent groups.^{19,20} ZnO was not added to formulations, as it readily reacts with (dma)dmtc to form $\text{Zn}_2(\text{dmtc})_4$.^{17,21,22}

EXPERIMENTAL

Hydroperoxides, which may interfere with the crosslinking process in 2,3-dimethyl-2-butene (TME) (chemical purity 99%, Aldrich Chemical Co., Milwaukee, WI), were removed by shaking with aqueous ferrous sulfate.²³ Other materials and equipment used were detailed in the previous publication.¹⁷ Samples of incompletely dried po-

lybutadiene (BR), used to prepare some compounds, were supplied by the manufacturer. Mixes were compounded on a Brabender Plastimeter and vulcanized in a DSC at a programmed heating rate and isothermally in a press for various times as described earlier.^{24,25} The reaction was stopped at various stages, residual curatives were extracted,^{24,25} and analyzed by HPLC^{25,26} on a C18 Reverse Phase-Bondapak column with 80/20 (v/v) : methanol/water as elution solvent. In gradient elution studies the solvent was changed linearly from 80/20 (v/v) methanol/water to 100% methanol over a period of 120 min. Crosslink densities were determined by swelling²⁴ and the percentage polysulfidic crosslinks by treatment with triphenylphosphine.²⁷ For model compound studies masterbatches of curatives were prepared by mixing the required curatives using a mortar and pestle and transferring the appropriate mass of the compounded mixture and volume of TME required into glass tubes.^{23,28} The contents were frozen and tubes sealed under vacuum. Tubes were fully immersed in an oil bath at 130 or 150°C for various times and residual curatives, reaction intermediates, and products characterized by HPLC^{26,28} and NMR.²⁹⁻³¹ For NMR analysis crosslinked products were separated by TLC and the appropriate band lifted. Formulations for rubber compounds are listed in parenthesis in the text as parts per hundred rubber (phr) and for model compounds in moles. The extinction coefficient of TMTD was used to compare the relative concentrations of crosslinked polysulfides formed with model compounds. The low-temperature crystallization of BR was followed at -16°C using a density column as described by van der Merwe et al.^{19,20} Certain vulcanizates were crystallized by cooling in the DSC at 5°C/min to -50°C, where samples were held isothermally for 30 min to complete the crystallization process, before reheating at 5°C/min to 20°C.²⁰ The onset of crystallization was determined from the intersection of a line drawn through the steeply rising part of the exotherm with the extension of the baseline. The percentage crystallinity was calculated from the area under the melting endotherm, using a value of 75 J/g for a sample that develops 100% crystallinity.²⁰ Table I lists acronyms used.

RESULTS

Polyisoprene(IR)(100)/(dma)dmtc(6.15)/sulfur(9.46)

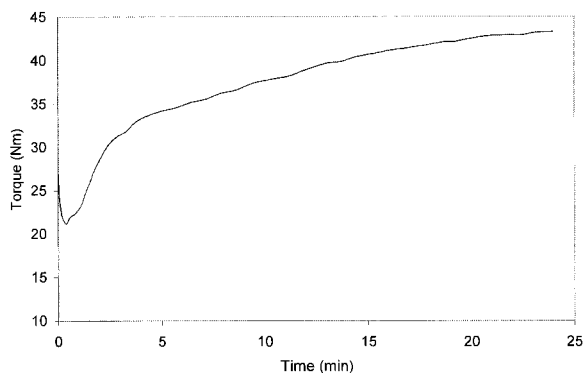
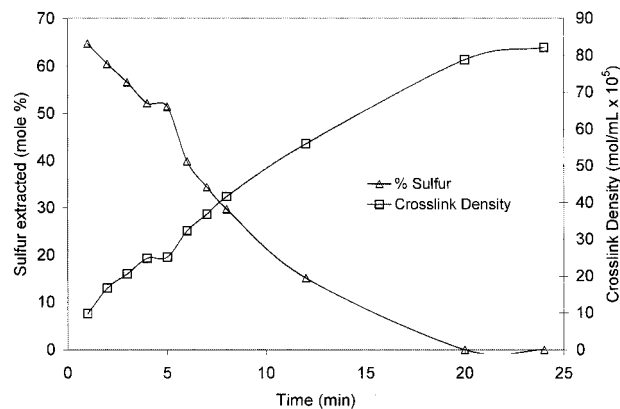
The shape of the DSC curve obtained on heating IR/(dma)dmtc/sulfur at 5°C/min is very similar to

Table I Acronyms

Acronym	Name
BR	polybutadiene
(dma)dmtc	dimethylammonium dimethyldithiocarbamate
Hdmtc	dimethyldithiocarbamic acid
IR	polyisoprene
TME	2,3-dimethyl-2-butene
TMTD	tetramethylthiuram disulfide
TMTP	tetramethylthiuram polysulfide
TMTU	tetramethylthiourea
X	methylthiocarbamyl
Zn ₂ (dmtc) ₄	zinc dimethyldithiocarbamate

that for tetramethylthiuram disulfide(TMTD)/sulfur vulcanization.³² It shows a broad, badly defined endotherm at 114°C due to the melting of sulfur and the onset of a crosslinking exotherm at about 140°C. The only difference is that the sharp endotherm at the onset of crosslinking (150°C), attributed to the loss of volatiles (Hdmtc, H₂S) on pendent group formation prior to crosslinking in the IR/TMTD/sulfur, is absent in the IR/(dma)dmtc/sulfur system.

Rheometer cure curves at 150°C show crosslinking from the onset with a marching cure and no reversion (Fig. 1), while on heating in a press at 150°C crosslinking occurred from the outset (Fig. 2). Treatment of vulcanizates with triphenylphosphine²⁷ showed that most of the crosslinks are polysulfidic (65% at 12 min, 68% at 24 min). (Dma)dmtc is very insoluble in benzene used to extract residual curatives, and could not be extracted from vulcanizates (nor from unheated compounds), and the only extractable detected in HPLC analysis was sulfur, the concen-

**Figure 1** Rheometer cure curve for IR(100)/(dma)dmtc(6.15)/sulfur(9.46) at 150°C.**Figure 2** Crosslink density and percentage sulfur extracted from IR(100)/(dma)dmtc(6.15)/sulfur(9.46) vulcanized in a press at 150°C for various times.

tration of which decreased progressively as the reaction progressed (Fig. 2). No tetramethylthiourea (TMTU) was detected. HPLC analysis of the benzene extract from rubber compounds, after drying and redissolving in dichloroethane/methanol, showed the presence of small amounts of TMTD. Likewise, TME heated with (dma)dmtc/sulfur (see below) and analyzed in dichloromethane/methanol, showed the formation of TMTD. However, this appears to have resulted from the workup procedure, rather than from the vulcanization reaction. When an IR/(dma)dmtc/sulfur compound was heated and the benzene extract injected directly (via a guard column) into the HPLC, no TMTD was found, while when the benzene was evaporated and the residue dissolved in dichloroethane/methanol, some TMTD was detected. (Dma)dmtc, dissolved overnight in benzene/methanol, gave a small TMTD peak.

TME(100)/(dma)dmtc(1.1)/sulfur(1)

On heating TME/(dma)dmtc/sulfur at 150°C, the sulfur and (dma)dmtc concentrations decrease rapidly (Table II), but no peaks that can be ascribed to thiuram pendent groups were detected in the HPLC chromatograms of systems heated for 2 min to 20 min. Thiuram pendent groups can readily be detected in TMTD-accelerated systems.^{28,30} Three broad peaks with retention times of 5.22, 6.04, and 6.56 min, slightly longer than that of (dma)dmtc (4.42 min), developed in mixes heated for 2 min, and on heating for longer times the 5.22 min peak grew slightly while the other two peaks diminished in magnitude. Similar peaks were not found on heating (dma)dmtc/sul-

Table II Percentages of Residual Curatives and Soluble Reaction By-products in TME(33.9)/(dma)dmte(1.1)/sulfur(1) Heated for Various Times at 150°C

Time (min)	(Dma)dmte (mol %)	Sulfur (mol %)	TMTU (mol %)
2	22.4	35.2	0
5	17.5	26.5	0
7	18.8	18.3	0.8
10	18.4	12.4	6.2
13	31.2	9.7	5.8
16	16.2	8.0	1.3
20	11.1	6.1	4.5

fur in the absence of TME.¹⁷ The decrease in (dma)dmte and sulfur concentrations in the absence of detectable pendent groups suggests that these broad peaks may represent sulfurated (dma)dmte species that are stabilized in TME solution. With TMTD and other accelerators, peaks due to accelerator polysulfides occur at higher retention times than the disulfide accelerator peak.^{26,29,30,33} However, these broad peaks were not positively identified. The formation of a range of polysulfidic crosslinked products (TME-S_x-TME, x = 1–7, retention times 39 to 100 min) was detected in mixes heated for 2 min and longer (Fig. 3). These peaks were identified by NMR (see below) and by comparison with the retention times of peaks that develop in the HPLC chromatogram of TME/TMTD/sulfur vulcanizates, where the formation of a range of polysulfidic crosslinked products has been demonstrated.^{23,28,30} After 2 min further crosslink formation occurs without the equivalent loss of (dma)dmte and sulfur, i.e., there is a large increase in the concentrations of crosslinked products between 2 and 5 min (Fig. 3) while the decrease in (dma)dmte and sulfur concentrations is less than that which occurs during the first 2 min (Table II). This supports the suggestion that sulfur and (dma)dmte may, in part, be present in the system as polysulfidic complexes that give rise to the peaks observed in the HPLC chromatogram at 5 to 7 min. A small TMTD peak is present in the chromatogram of mixes heated for 2 min and longer and, as noted above, it appears to form in the workup of solutions for HPLC analysis. Small amounts of TMTU were detected in mixtures vulcanized for 10 min and longer (Table II). As reported earlier,¹⁷ (dma)dmte is stable at vulcanization temperatures, and does not decompose to

Hdmte and dimethylamine. Instead, it is suggested that TMTU results from limited decomposition of Hdmtc¹⁷ and attack by the amine on TMTD produced in the workup procedure.

Nature of Crosslinked Products

Crosslinked products may be alkyl alkenyl, bis(alkenyl), or bis(alkyl) sulfides (Fig. 4),^{11,15,16} and were identified by comparison of the ¹H-NMR spectra^{17,31} and HPLC chromatograms of (dma)dmte vulcanizates with those of unaccelerated sulfur and TMTD accelerated sulfur formulations.^{28,30,31}

TME(33.9)/sulfur(1) was vulcanized in sealed tubes at 150°C for 40 min. Crosslinked products were separated by TLC and the ¹H-NMR spectra obtained. In addition to resonances at 1.77 and 1.70 ppm [Fig. 4(a)–(c)] and 3.46–3.73 ppm (d), common to alkyl alkenyl and bis(alkenyl) sulfides,^{30,31} shifts ascribed to groups [(e),(f)] (1.28–1.33 ppm) and [(g),(h)] (0.98–0.99 ppm) in alkyl alkenyl and bis(alkyl) sulfides can be seen. The chemical shifts of methylene groups were shown by Versloot et al.^{30,31} to move from low to high field on going from a long sulfur chain towards a disulfide, (S₂) = 3.46, (S₃) = 3.61, (S₄) = 3.70, (S_{>5}) = 3.73 ppm. The resonances for other protons were similarly dependent on the number of sulfur atoms in the crosslink.

¹H-NMR analysis of the reaction products of TME(33.9)/(dma)dmte(1.1)/sulfur(1), heated at 130°C for 30 min and separated by TLC, show resonances at 1.77 and 1.70 ppm, which were

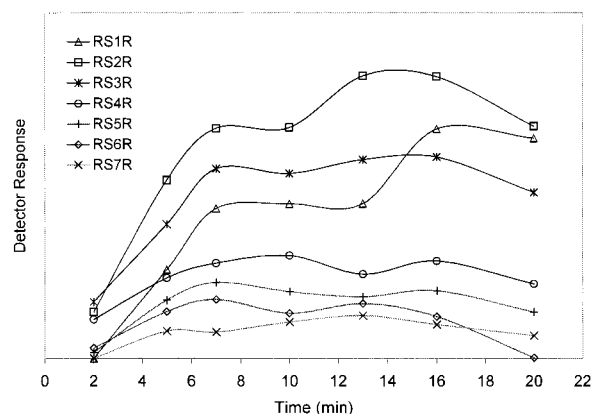


Figure 3 Relative concentrations of crosslinked polysulfides (TME-S_x-TME) in TME(33.9)/(dma)dmte(1.1)/sulfur(1) heated in sealed tubes at 150°C for various times. The extinction coefficient of TMTD was used to determine the relative concentration of all sulfides.

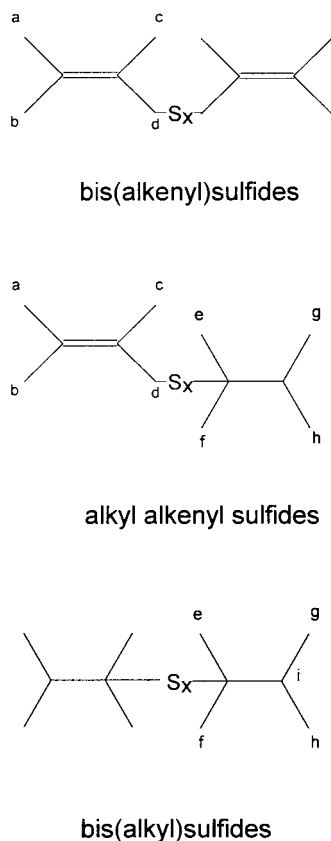


Figure 4 Crosslinked bis(alkenyl), alkyl alkenyl and bis(alkyl) sulfides of TME. (a,b) 1.77 ppm; (c) 1.70 ppm; (d) 3.46–3.73 ppm; (e,f) 1.20–1.33 ppm; (g,h) 0.98–0.99 ppm.^{30,31}

assigned to the methyl groups [Fig. 4(a)–(c)] and between 3.73–3.46 ppm, assigned to methylene groups (d) next to sulfur.^{30,31} Weak resonances in the NMR at 1.28–1.33 ppm [(e),(f)] and 0.98–0.99 ppm [(g),(h)] show evidence for the formation of small amounts of alkyl alkenyl and bis(alkyl)sulfides.

The ¹H-NMR spectrum of TME(33.9)/TMTD-(1.1)/sulfur(1) heated at 130°C for 20 min is very similar to that obtained with (dma)dmtc vulcanizates. In addition to resonances attributable^{30,31} to bis(alkenyl) sulfides (1.77, 1.70, and 3.46–3.73 ppm), there is evidence for the formation of small amounts of alkyl alkenyl and bis(alkyl) sulfides ($\delta = 1.28$ – 1.33 ppm and $\delta = 0.98$ – 0.99 ppm).

HPLC analysis of TME(33.9)/sulfur(1), using 80/20:methanol/water as the mobile phase, showed a series of peaks attributed to crosslinked product species (TME-S_x-TME) of sulfur rank 1 to 7.^{28,30} Using a dilution gradient on the HPLC peaks for each crosslinked sulfide could be sepa-

rated into three peaks, two relatively large and one minor. In unaccelerated sulfur vulcanization alkyl alkenyl sulfides form first, and these disproportionate to bis(alkenyl) and bis(alkyl) sulfides.^{11,30} Following Versloot,³¹ the major peaks are ascribed to bis(alkenyl) sulfides, the secondary peaks to alkyl alkenyl sulfides, and the minor peaks to bis(alkyl) sulfides. Likewise, HPLC analysis of TME(33.9)/(dma)dmtc(1.1)/sulfur(1), using a dilution gradient, allowed crosslinked products to be separated into a series of major peaks, each accompanied by two minor peaks. In the early stages of TMTD accelerated sulfur vulcanization peaks due to accelerator polysulfides (TMTP) and to thiuram pendent groups (TME-S_xX), reported earlier,^{28,30} were detected in the HPLC chromatogram of TME(33.9)/TMTD(1.1)/sulfur(1). These have been discussed fully, and will not be referred to here; only peaks attributed to crosslinked products will be considered. Use of a dilution gradient resulted in three peaks for each of the seven crosslinked polysulfides detected, a major peak, a second very much smaller peak, and a third extremely small peak. The HPLC is similar to that for (dma)dmtc vulcanizates. In terms of our understanding of TMTD accelerated sulfur vulcanization^{11,13,15,16} and the interpretation by Versloot³¹ of the HPLC data for unaccelerated sulfur vulcanization, the major peak in each triplet of peaks must be attributed to the bis(alkenyl) sulfides. The retention times for these major peaks correspond to those attributed to bis(alkenyl)sulfides in sulfur vulcanizates. The two minor peaks associated with each of the bis(alkenyl) sulfides in the (dma)dmtc and TMTD accelerated systems may arise from the fact that formulations contain large amounts of sulfur that may lead to the formation of some alkyl alkenyl sulfides via unaccelerated sulfur vulcanization. Some disproportionation would give bis(alkenyl) sulfides. The retention times of the minor peaks correspond to those of the second and third largest peaks in sulfur vulcanizates. Unlike the two minor peaks found in (dma)dmtc and TMTD systems, Versloot³¹ reported only a single minor peak associated with each of the crosslinked sulfide peaks in the HPLC chromatogram of TME/TMTD/sulfur/ZnO. Preparative HPLC allowed them to accumulate sufficient of the minor product for NMR analysis, from which the sulfide isomers (2,3-dimethyl-2-butene-1-yl)(2,3-dimethyl-1-butene-3-yl) were identified and ascribed to the minor peak.^{29,31}

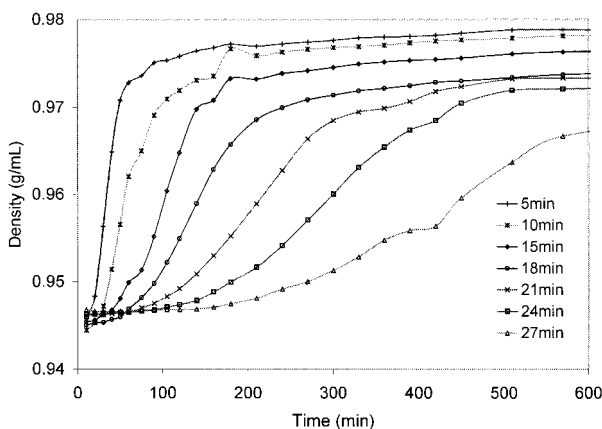


Figure 5 Initial portion of curve showing the change in density of BR(100)/(dma)dmtc(2.18)/sulfur(3) with time at -16°C for compounds heated in a press at 130°C for various times.

Crystallization of Vulcanizates

It was shown earlier^{19,20} that crystallization is markedly reduced in natural rubber (NR) and polybutadiene (BR) vulcanizates in which pendent groups form during crosslinking. BR crystallizes more readily on cooling than NR and, therefore BR, rather than NR compounds, were used to study the effect of vulcanization on the crystallizability of vulcanizates. BR(100)/(dma)dmtc(2.18)/sulfur(3) compounds, heated in a press at 130°C for various times to achieve different degrees of vulcanization, were crystallized in a low-temperature (-16°C) density column.^{19,20} Compounds crystallized rapidly (Fig. 5), even when cured to relatively high crosslink densities, although rates of crystallization, expressed as $t_{1/2}$, the time taken

for crystallization to go to 50% completion, increased with crosslink density (Table III). The initial densities of samples vulcanized for longer times did not show a progressive decrease, as found with TMTD and MBTS accelerated formulations,^{19,20} but their densities varied randomly over a range of 0.0025 g/mL (Fig. 5).

Effect of Vacuum on Vulcanization

Thin films of compounds precipitated from solution onto the walls of a tube were vulcanized under vacuum by heating in an oil bath at 130°C . Crosslinking was delayed and lower crosslink densities developed than in a press (Table III). Despite the very low crosslink densities that develop, rates of crystallization in the density column at -16°C decreased progressively with longer cure times (Fig. 6), rates ($t_{1/2}$) for vulcanizates with similar crosslink densities being slower than found on vulcanization in a press (Table III). The initial density of samples, when placed in the density column, showed a decrease (0.944, 0.940, and 0.938 g/mL) with increased cure time (Fig. 6).

(Dma)dmtc is volatile at elevated temperatures¹⁷ and may be lost from thin films during drying. In a second series of experiments thin sections of a BR(100)/(dma)dmtc(2.18)/sulfur(3), compounded on the Brabender, were rapidly heated to 130°C under vacuum in open DSC pans and held at that temperature for various times. As with solution-cast films, the rate of volatilization of (dma)dmtc and the loss of volatile reaction products will depend on the film thickness.

Table III Comparison of the Crosslink Densities and Rates of Crystallization ($t_{1/2}$) in a Column at -16°C for BR(100)/(dma)dmtc(2.18)/sulfur(3) Vulcanized in a Press and under Vacuum at 130°C for Various Times

Cure Time (min)	In Press		Under Vacuum	
	$1/2M_c \times 10^5$ (mol/mL)	Rate $t_{1/2}$ (min)	$1/2M_c \times 10^5$ (mol/mL)	Rate $t_{1/2}$ (min)
5	Gel	40	Soluble	55
10	0.29	60	Gel	95
15	0.93	110	0.25	100
18	1.45	150		
21	2.10	225		
24	3.22	310		
27	4.62	460		

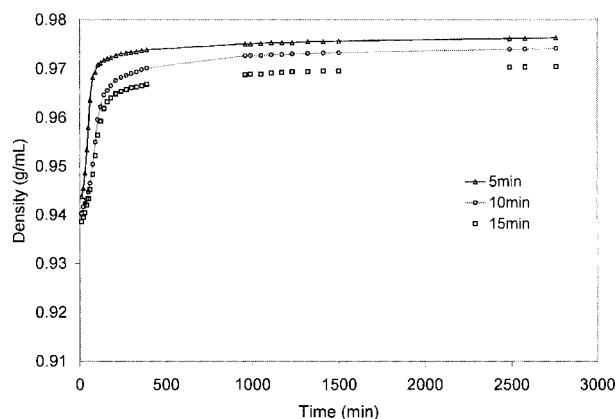


Figure 6 Change in density of BR(100)/(dma)dmtc(2.18)/sulfur(3) with time at -16°C for compounds heated under vacuum at 130°C for various times.

Crosslinking under vacuum was limited to the formation of a loose gel, while samples heated in sealed DSC pans under nitrogen developed higher crosslink densities (Table IV). Samples were crystallized by cooling in the DSC at $5^{\circ}\text{C}/\text{min}$.²⁰ Even in samples where gel formation only was detected, the onset temperature of crystallization, which is a measure of the rate of nucleation,²⁰ was delayed to lower temperatures for films heated under vacuum (Table IV). The DSC crystallization data is consistent with crystallization data in the column, and suggests that in the lightly crosslinked gel sufficient main chain modification, possibly in the form of pendent groups, is present to influence crystallization. For samples heated in sealed pans, where high crosslink densities developed, crystallization was delayed to a greater extent than occurred with samples heated under vacuum. This longer delay can be ascribed to the higher degree of crystallization in

such samples.²⁰ Samples were held at -50°C for 30 min to allow for the completion of the crystallization process²⁰ and were then reheated at $5^{\circ}\text{C}/\text{min}$. The areas under the melting endotherms decreased progressively for compounds having higher crosslink densities (Table IV).

Effect of Water on Vulcanization

Dissociation of (dma)dmtc occurs in water,¹⁷ and water is seen to decrease the rate and extent of crosslink formation in compounds prepared with incompletely dried BR (Fig. 7).

DISCUSSION

Absence of an Ionic Reaction

(Dma)dmtc is not decomposed on heating in moist nitrogen but ionizes in water, as indicated by the high conductivity of aqueous solutions of (dma)dmtc.¹⁷ Nevertheless, in compounds containing larger amounts of water the crosslink density developed on vulcanization decreased rather than increased (Fig. 7), indicating that crosslinking does not involve an ionic reaction. If an ionic mechanism were to apply, increased ionization in water should accelerate the reaction. Furthermore, an ionic reaction, as has been suggested^{13,16,34–36} as a mechanism in unaccelerated sulfur vulcanization, would imply that sulfur cations attack the carbon double bond, giving alkyl alkenyl crosslinked polysulfides that disproportionate to bis(alkenyl) and bis(alkyl) sulfides.^{37–39} As with TMTD vulcanizates, the predominantly bis(alkenyl) nature of crosslinked products, as characterized by NMR and HPLC, indicates a substitutive, rather than an additive reaction, as

Table IV Crosslink Densities, Onset Temperatures of Crystallization on Cooling in the DSC at $5^{\circ}\text{C}/\text{min}$ and Percentage Crystallinity of BR(100)/(dma)dmtc(2.18)/sulfur(3) Heated at 130°C in Open DSC Pans under Vacuum and in Sealed DSC Pans under Nitrogen

Time (min)	Open Pans under Vacuum		Sealed Pans under Nitrogen		
	$1/2\text{Mc} \times 10^5$ (mol/mL)	Crystallization Onset ($^{\circ}\text{C}$)	$1/2\text{Mc} \times 10^5$ (mol/mL)	Crystallization Onset ($^{\circ}\text{C}$)	Crystallinity (%)
10	Gel	-24.6	2.28	-29.4	21
15	0.02	-29.0	4.14	-30.7	17
18	Gel	-29.8	4.40	-32.6	16
21	Gel	-30.1	6.39	-35.0	15
25	Gel	-29.7	6.06	-34.6	15

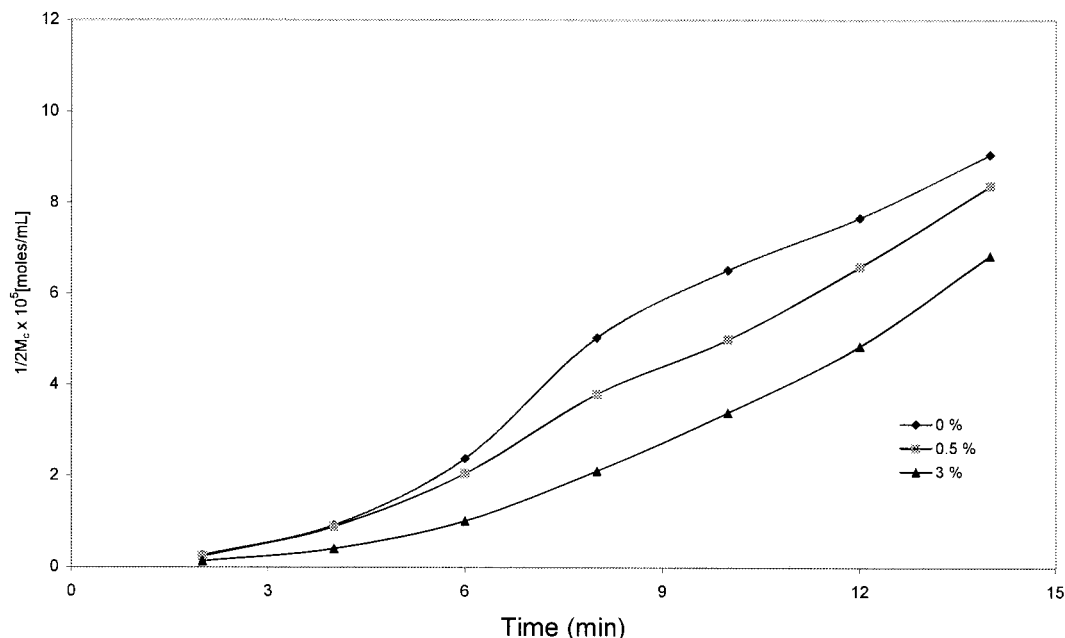


Figure 7 Crosslink density ($1/2M_c$) as a function of cure time at 150°C for BR(100)/(dma)dmtc(4.61)/sulfur(3) compounds with different amounts of water.

is found with unaccelerated sulfur vulcanization. Note, too, that crosslinked products are not fully saturated, as found by Moore and Saville⁵ for diethylamine-accelerated sulfur vulcanization of cyclohexene.

Similarity to $\text{Zn}_2(\text{dmtc})_4$ -Accelerated Vulcanization

Model compound studies show the absence of thiuram pendent groups prior to crosslink formation, while the ease with which vulcanizates crystallize on cooling (Fig. 5) indicates that pendent groups are largely absent from rubber compounds. The density column showed that the initial density of compounds, vulcanized in a press for different times, were very similar (Fig. 5), and this, too, points to pendent groups being largely absent in the vulcanizates. In TMTD and 2-bisbenzothiazole-2,2'-disulfide accelerated vulcanizates the initial density of samples decrease substantially (0.01 g/mL)^{19,20} with increased vulcanization times, and was associated with an increase in free volume in the compounds due to the formation of pendent groups on the polymer chain.^{19,20} If pendent groups did form in dma/dmtc vulcanizates, they were immediately consumed in crosslink formation, which occurs without the involvement of a marked induction period (Figs. 1, 2, and 3). In $\text{Zn}_2(\text{dmtc})_4$ -accelerated sulfur formulations crosslinking is rapid, it occurs without an induction period, pendent groups have

not been detected in model compound studies,^{30,41,42} and vulcanizates readily crystallize on cooling.²⁰ Crosslinking in (dma)dmtc-accelerated sulfur vulcanization has many similarities, and it is suggested that it may occur via a mechanism similar to that applicable to $\text{Zn}_2(\text{dmtc})_4$ -accelerated sulfur vulcanization where polysulfidic $\text{Zn}_2(\text{dmtc})_4$ species^{11,15,16,41,43} are considered to lead to thiuram-terminated pendent groups^{11,13,15,16} or to thiols.⁴² Failure to detect thiuram or thiol groups in model compound studies is attributed to the rapid $\text{Zn}_2(\text{dmtc})_4$ -catalyzed crosslinking of such pendent groups.^{30,41,42,44-47}

Evidence for Pendent Groups

(Dma)dmtc is readily lost from rubber at elevated temperatures,¹⁷ and the development of low crosslink densities on heating thin films under vacuum (Table III) and the formation of a loose gel on heating thin sections under vacuum in the DSC (Table IV) may be attributed largely to the loss of the accelerator from the compound. However, the rates of crystallization ($t_{1/2}$) in the density column of films heated under vacuum are slower than are found with press-heated samples of similar crosslink density (Table III). Clearly, main-chain modification, sufficient to affect crystallization, had occurred. Even in press-cured samples where crosslinking occurs more rapidly,

and fewer residual pendent groups should be present, the rate of crystallization is slower than in peroxide cures.²⁰ In peroxide vulcanizates, where there are no pendent groups, the crystallization half-life $t_{1/2}$ was found to increase more slowly than recorded in Table III. At the point at which gel formation was recorded (5 min) the half-life was 28 min, and this increased to 31 and 60 min at crosslink densities of 0.54 and 4.28×10^{-5} mol/mL, respectively.²⁰ In TMTD-accelerated vulcanizates, where pendent group formation is well recognized, $t_{1/2}$ is 150 min once gel formation is obtained, and increases to 260 min at a crosslink density of 0.64 mol/mL.²⁰ The decrease in the initial density of (dma)dmtc samples heated under vacuum for longer times probably largely reflects the loss of accelerator, although it may, in part, be an indication of an increase in free volume associated with the presence of some pendent groups.^{19,20} The decrease in the temperature at which the crystallization commences on cooling thin sections heated under vacuum in the DSC for longer periods (Table IV) also points to main-chain modification. It has been shown^{19,20} that pendent groups have a larger effect on the onset of crystallization than does crosslink formation. Thus, in TMTD vulcanizates the crystallization onset temperature of compounds heated to points prior to gelation decreased progressively to -26.7°C , the onset temperature falling to -28.7°C at a crosslink density of 0.46×10^{-5} mol/mL.²⁰ The onset of crystallization of a (dma)dmtc sample heated in a sealed pan for 10 min and having a crosslink density of 2.28×10^{-5} mol/mL, was -29.4°C , comparable to that of samples heated under vacuum for 18 to 25 min where gel formation only was detected (Table IV). This also points to the delay in the onset of crystallization of gels being due to main chain modification. Thus, it is proposed that crystallization data for compounds heated under vacuum can be interpreted as indicative of pendent group formation in (dma)dmtc-accelerated sulfur vulcanization. (Dma)dmtc, that is less readily lost from press-cured samples, may catalyze crosslinking, as is found with $\text{Zn}_2(\text{dmtc})_4$,^{30,41,45} while the release during pendent group formation of Hdmtc will lead to thiol pendent groups that can readily crosslink with thiuram pendent groups.⁴⁴ Under vacuum both (dma)dmtc and Hdmtc will be removed, and this may account for sufficient pendent groups remaining on the chain to more noticeably influence the crystallization of compounds.

CONCLUSIONS

There is no detectable induction period before the onset of crosslink formation in (dma)dmtc-accelerated sulfur vulcanization, while model compound studies, and the ease with which vulcanizates crystallize on cooling, point to the absence of pendent groups in press-cured compounds. Crosslinked sulfides are essentially bis(alkenyl). It is suggested that (dma)dmtc may lead to crosslink formation via a mechanism similar to that applicable to $\text{Zn}_2(\text{dmtc})_4$ -accelerated formulations. The ready volatilization of (dma)dmtc leads to low crosslink densities in compounds heated under vacuum. Nevertheless, the crystallization of compounds heated under vacuum is slower than in press-cured compounds, and may indicate the presence in such compounds of pendent groups that have not been able to crosslink, either due to the absence of (dma)dmtc needed to catalyze crosslinking, or to the removal of Hdmtc, which will give polysulfidic thiols that can crosslink with thiuram pendent groups.

We wish to thank the South African National Research Foundation and the South African Institute of Race Relations for financial assistance, and the University of Fort Hare for financial assistance and for granting research leave to M. Shumane.

REFERENCES

- Oenslager, G. *Ind Eng Chem* 1933, 25, 232.
- Bedford, C. W. *India Rubber World* 1921, 64, 572.
- Katz, C. D.; Flower, A. H.; Coolidge, C. *Ind Eng Chem* 1920, 12, 317.
- Bedford, C. W.; Scott, W. *Ind Eng Chem* 1921, 13, 126.
- Moore, C. G.; Saville, R. W. *J Chem Soc* 1954, 156, 2082.
- Farmer, E. H.; Shipley, F. W. *J Chem Soc* 1947, 1519.
- Moore, C. G.; Saville, R. W. *J Chem Soc* 1954, 156, 2089.
- Glazebrook, R. W.; Saville, R. W. *J Chem Soc* 1954, 156, 2094.
- Krebs, H. *Rubber Chem Technol* 1957, 37, 962.
- Hodgson, W. G.; Buckler, S. A.; Peters, G. *J Am Chem Soc* 1963, 85, 453.
- Nieuwenhuizen, P. J.; Reedijk, J.; Van Duin, M.; McGill, W. J. *Rubber Chem Technol* 1997, 70, 368.
- Hofmann, W. In *Rubber Technology Handbook*; Hanser Publishers: New York, 1996, Chap 4.
- Coleman, M. M.; Shelton, J. R.; Koenig, J. L. *Ind Eng Chem*, 1974, 13, 154.

14. Higgins, G. M. C.; Saville, B. *J Chem Soc* 1963, 2812.
15. Porter, M. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977, Chapt 3.
16. Bateman, L.; Moore, C. G.; Porter, M.; Saville, B. *The Chemistry and Physics of Rubber-Like Substances*; Maclaren & Sons Ltd.: London, 1963, Chapt 15.
17. Shumane, M.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 2001, 82, 3067.
18. Morrison, N. J. *Rubber Chem Technol* 1984, 57, 86.
19. van der Merwe, M. J.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 2001, 81, 2565.
20. van der Merwe, M. J.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 2001, 81, 2573.
21. Bedford, C. W.; Gray, H. *Ind Eng Chem* 1923, 15, 720.
22. Versloot, P.; Haasnoot, J. G.; Reedijk, J.; Van Duin, M.; Duynstee, E. F. J.; Put, J. *Rubber Chem Technol* 1994, 67, 263.
23. Geysler, M.; McGill, W. J. *J Appl Polym Sci* 1995, 55, 215.
24. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1992, 44, 581.
25. Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 1995, 58, 2185.
26. Giuliani, B. V. M. K.; McGill, W. J. *J Appl Polym Sci* 1995, 57, 1391.
27. Saville, B.; Watson, A. A. *Rubber Chem Technol* 1967, 40, 100.
28. Geysler, M.; McGill, W. J. *J Appl Polym Sci* 1996, 60, 431.
29. Versloot, P.; Haasnoot, J. G.; Reedijk, J.; Van Duin, M.; Duynstee, E. F. J.; Put, J. *Rubber Chem Technol* 1992, 65, 343.
30. Versloot, P.; Haasnoot, J. G.; Reedijk, J.; Van Duin, M.; Duynstee, E. F. J.; Put, J. *Rubber Chem Technol* 1994, 67, 252.
31. Versloot, P. PhD Thesis, Rijks University of Leiden, The Netherlands (1993).
32. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1992, 44, 587.
33. Morgan, B.; McGill, W. J. *J Appl Polym Sci* 2000, 76, 1377.
34. Bateman, L.; Moore, C. G.; Porter, M. J. *J Chem Soc* 1958, 2866.
35. Bateman, L.; Glazebrook, R. W.; Moore, C. G. *J Chem Soc* 1958, 2846.
36. Bateman, L.; Glazebrook, R. W.; Moore, C. G. *J Appl Polym Sci* 1959, 1, 257.
37. Bateman, L.; Glazebrook, R. W.; Moore, G. C.; Porter, M.; Ross, G. W.; Saville, R. W. *J Chem Soc* 1958, 2838.
38. Moore, G. C.; Porter, M. *J Chem Soc* 1965, 6390.
39. Wolfe, J. R.; Pugh, T. L.; Killian, A. S. *Rubber Chem Technol* 1968, 41, 1329.
40. Bristow, G. M.; Tiller, R. F. *Kaut Gummi Kunst* 1970, 23, 55.
41. Geysler, M.; McGill, W. J. *J Appl Polym Sci* 1996, 60, 449.
42. Nieuwenhuizen, P. J.; Ehlers, A. W.; Haasnoot, J. G.; Janse, S. R.; Reedijk, J.; Bearends, E. J. *J Am Chem Soc* 1999, 121, 163.
43. Nieuwenhuizen, P. J.; Ehlers, A. W.; Hofstraat, J. W.; Janse, S. R.; Nielen, M. W. F.; Reedijk, J.; Bearends, E. J. *J Chem Eur* 1988, 4, 1816.
44. Shelver, S. R.; Shumane, M.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 1999, 74, 1371.
45. McGill, W. J.; Shelver, S. R. *J Appl Polym Sci* 1999, 72, 1021.
46. Krebs, H.; Fassbender, M.; Jorgens, F. *Chem Ber* 1957, 90, 425.
47. Nieuwenhuizen, P. J.; Timal, S.; van Veen, J. M.; Haasnoot, J. G.; Reedijk, J. *Rubber Chem Technol* 1998, 71, 750.