

# Effect of Water and Hydrogen Sulfide in Zinc Dimethyldithiocarbamate Accelerated Sulfur Vulcanization

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**ABSTRACT:** Rubber and the model compound 2,3-dimethyl-2-butene (TME) are vulcanized with zinc dimethyldithiocarbamate [ $Zn_2(dmtc)_4$ ] accelerated sulfur formulations. When heated in dry nitrogen,  $Zn_2(dmtc)_4$  is stable at vulcanization temperatures. However, it shows a mass increase when heated in moist nitrogen, indicating strong coordination with water; in a nitrogen/ $H_2S$  atmosphere rapid degradation to dimethyldithiocarbamic acid (Hdmtc) and ZnS occurs. Model compound studies show that crosslinked sulfides are essentially bis(alkenyl) and confirm the absence of accelerator terminated pendant groups in the vulcanizates, while the ease with which rubber vulcanizates crystallize on cooling in a density column also suggests that pendant groups are largely absent. However, the rates of crystallization, measured as the time for the crystallization process to go to 50% completion, are slower in lightly crosslinked gels than in peroxide cures of similar crosslink density, particularly in the vulcanizates cured in a vacuum; this is interpreted as an indication that some residual pendant groups are present in  $Zn_2(dmtc)_4$  vulcanizates. Water

promotes the rate of crosslink formation in both rubber and TME systems, and it is suggested that the strong coordination of water with zinc in  $Zn_2(dmtc)_4$  promotes its reactivity. The  $H_2S$  liberated in the vulcanization process promotes decomposition of  $Zn_2(dmtc)_4$  to Hdmtc, and this reaction makes an important contribution to the amount of Hdmtc that is formed *in situ*. The importance of Hdmtc as an accelerator and its role in providing alternative routes to crosslink formation in  $Zn_2(dmtc)_4$  accelerated sulfur vulcanization are discussed. It is suggested that water, which is liberated when Hdmtc reacts with ZnO to form  $Zn_2(dmtc)_4$ , activates newly formed  $Zn_2(dmtc)_4$  molecules; and this accounts for the beneficial influence of ZnO in  $Zn_2(dmtc)_4$  formulations. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1516–1531, 2002

**Key words:** vulcanization; zinc dimethyldithiocarbamate; dimethyldithiocarbamic acid; hydrogen sulfide; water; pendant groups; coordination

## INTRODUCTION

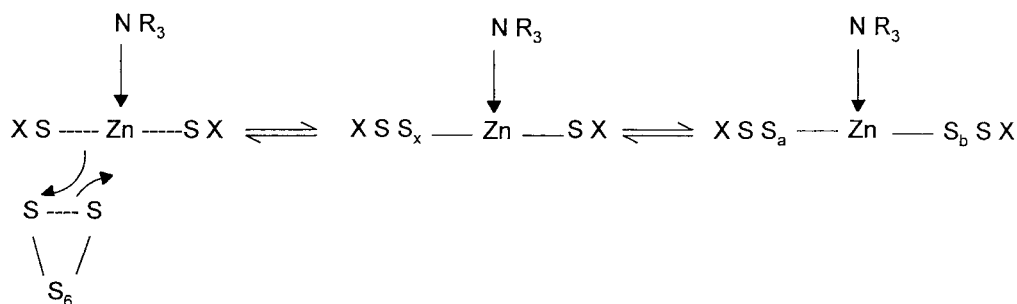
Zinc dimethyldithiocarbamate [ $Zn_2(dmtc)_4$ ] is a well-known ultraaccelerator for sulfur vulcanization. However, the mechanism of the reaction remains unclear, despite extensive literature on the subject. It is commonly suggested<sup>1–4</sup> that the reaction is initiated by sulfuration of the accelerator to give a polysulfidic zinc complex, although such complexes have not been separated.  $Zn_2(dmtc)_4$  is only sparingly soluble in rubber but is said to be rendered more soluble through coordination with nitrogen bases or zinc carboxylates.<sup>3,5</sup> Amine coordination is suggested to enhance the reactivity, the nucleophilic character of  $Zn_2(dmtc)_4$  being increased because of the amine coordination, rendering the Zn—S bonds more ionic.<sup>6</sup> Bateman et al.<sup>2</sup> pictured cleavage of the  $S_8$  ring and nucleophilic attack by the sulfur atoms on the  $Zn_2(dmtc)_4$  complex

(Scheme 1). The suggestion was later supported by Porter.<sup>3</sup>

Chelate ring expansion was found to occur in a reaction of certain metal dithiolates with sulfur.<sup>7,8</sup> The mechanism of sulfur insertion is not known, and for nickel dithiolato complexes sulfur appears to insert into the C—S rather than in the Ni—S bond<sup>8</sup> and the addition is limited to one sulfur atom in the chelate ring.<sup>9</sup> The incorporation of a single sulfur atom would not account for the formation of polysulfidic crosslinks, the observation that prompted the original suggestion of sulfurated  $Zn_2(dmtc)_4$  formation.<sup>2,3</sup> Indirect evidence for the formation of sulfurated  $Zn_2(dmtc)_4$  is supplied by exchange reactions between accelerators and zinc-accelerator complexes in the presence of sulfur. Thus, the rate of exchange between  $Zn_2(dmtc)_4$  and radioactive sulfur at 130°C in xylene solution was accelerated by the presence of small amounts of tetramethylthiuram disulfide (TMTD),<sup>10</sup> which may suggest an exchange of dialkyldithiocarbamyl moieties between TMTD and  $Zn_2(dmtc)_4$ .<sup>11</sup> The nucleophilic character of the Zn—S coordination bond, even in the absence of amines, is held responsible for the very fast exchange reactions between zinc dialkyldithiocarbamates and TMTD in solution,<sup>11,12</sup> as

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**Scheme 1** The formation of Zn<sub>2</sub>(dmtc)<sub>4</sub> polysulfides as proposed by Bateman et al.<sup>2</sup>

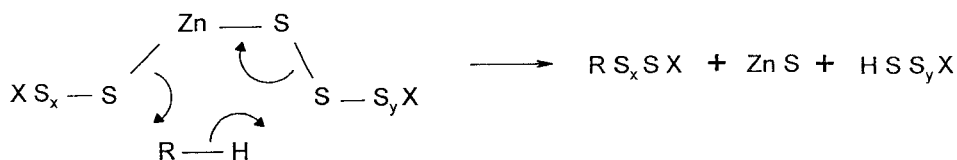
well as for the increased solubility of sulfur in benzene when Zn<sub>2</sub>(dmtc)<sub>4</sub> is added. Giuliani and McGill<sup>13</sup> found that neither TMTD nor 2-mercaptobenzothiazole undergo exchange reactions with the zinc-accelerator complexes Zn<sub>2</sub>(dmtc)<sub>4</sub> and zinc mercaptobenzothiazole in solution at room temperature, but rapid exchange occurs with the addition of sulfur. This suggests the formation of polysulfidic zinc-accelerator complexes that can exchange with ligands. Tagged TMTD and Zn<sub>2</sub>(dmtc)<sub>4</sub> exchange at elevated temperatures,<sup>14</sup> which is under conditions where tetramethylthiuram polysulfides (TMTPs) can form.<sup>2-4,15,16</sup> McCleverty et al.<sup>17</sup> also reported ligand exchange at elevated temperatures. Recent evidence for sulfur-rich zinc(II) complexes was demonstrated in theoretical density functional calculations, where it was also shown that the addition of further sulfur atoms to the zinc dithiocarbamate chelate ring is energetically more favorable than insertion of the first sulfur.<sup>18</sup> Mass spectrographic data confirm the incorporation of a number of sulfur atoms into Zn<sub>2</sub>(dmtc)<sub>4</sub> when the mix is held at elevated temperature.<sup>18</sup> However, Coleman et al.<sup>19</sup> did not detect any changes that can be ascribed to the creation of new sulfur-sulfur bonds in the Raman spectrum of a sulfur/Zn<sub>2</sub>(dmtc)<sub>4</sub> (2:1 mole ratio) mixture after heating to 125 and 145°C. [This does not preclude the transient formation of sulfured Zn<sub>2</sub>(dmtc)<sub>4</sub> at elevated temperatures and its breakdown on cooling.] No exchange between <sup>35</sup>S<sub>8</sub> and Zn<sub>2</sub>(dmtc)<sub>4</sub> was found when heating a sulfur/Zn<sub>2</sub>(dmtc)<sub>4</sub> mixture at 140°C for 60 min,<sup>11</sup> which suggests that any sulfur atoms incorporated into the chelate ring are again readily exuded. Labeling studies showed that with nickel complexes the sulfur atom that is added is the same sulfur that is subsequently removed by triphenylphosphane.<sup>20</sup> However, exten-

sive scrambling is said to take place with Zn<sub>2</sub>(dmtc)<sub>4</sub>,<sup>20</sup> which contrasts with the work of Craig et al.,<sup>11</sup> which reported no exchange.

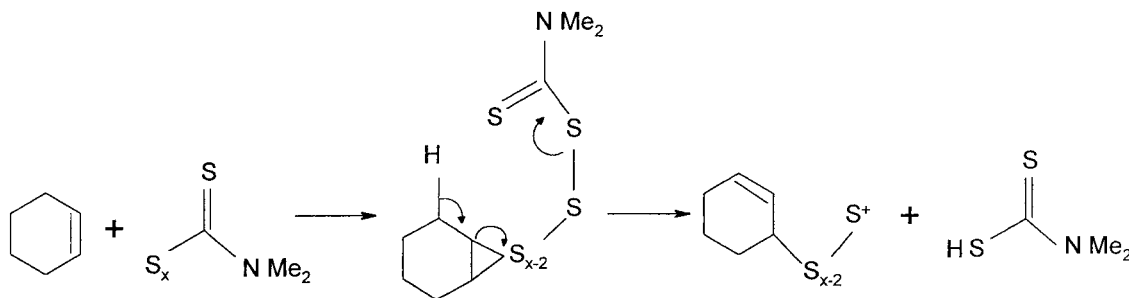
On balance, accumulated evidence supports the formation of sulfured Zn<sub>2</sub>(dmtc)<sub>4</sub> at vulcanization temperatures. It would appear that in the presence of accelerators like TMTD, the rapid exchange between accelerator polysulfides (TMTP) and Zn<sub>2</sub>(dmtc)<sub>4</sub> could be a major route to Zn<sub>2</sub>(dmtc)<sub>4</sub> sulfuration.

The next step in the vulcanization process is the interaction of the sulfured zinc-accelerator complexes with rubber, which is widely considered to involve the formation of polysulfidic thiuram terminated pendant groups,<sup>2-4</sup> similar to those found with TMTD accelerated formulations.<sup>2-4,21-25</sup> Bateman et al.<sup>2</sup> proposed pendant group formation via a concerted reaction (Scheme 2), and Wolfe<sup>26</sup> proposed the heterolytic cleavage of sulfured Zn<sub>2</sub>(dmtc)<sub>4</sub> and the dmtc-polysulfenium ion attack of the double bond (Scheme 3).

The liberation of ZnS is characteristic of Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated sulfur vulcanization,<sup>1,2,4,26-29</sup> although, in general, the ZnS content of vulcanizates is not a measure of the crosslink density<sup>2,30-32</sup> and the increased formation of ZnS in the latter stages of the reaction appears to be associated with network degradation reactions. The Zn<sub>2</sub>(dmtc)<sub>4</sub> plays two roles in vulcanization reactions: that of an accelerator, in which case its concentration decreases during the reaction, and that of a catalyst for the crosslinking of thiuram pendant groups, during the reaction in which it is not consumed.<sup>2,4,26,29,33-35</sup> On vulcanizing in a differential scanning calorimetry (DSC) apparatus, where the escape of volatiles is possible, the Zn<sub>2</sub>(dmtc)<sub>4</sub> concentration drops markedly during vulcanization.<sup>27,35</sup> In formulations containing ZnO, the dimethyldithiocar-



**Scheme 2** The formation of pendant groups via a concerted reaction as proposed by Bateman et al.<sup>2</sup>



**Scheme 3** The formation of pendant groups following the heterolytic scission of sulfurated  $Zn_2(dmtc)_4$  as proposed by Wolff.<sup>26</sup>

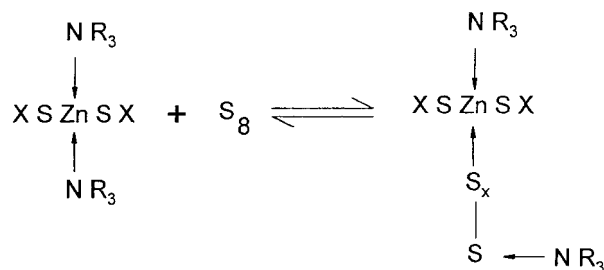
bamic acid (Hdmtc) that is liberated is readily trapped as  $Zn_2(dmtc)_4$ ,<sup>27,33,36</sup> but its reaction with ZnS is slower and, as noted, the  $Zn_2(dmtc)_4$  concentration decreases during vulcanization. In completely sealed model compound systems Hdmtc is more readily trapped by ZnS and reforms  $Zn_2(dmtc)_4$ .<sup>24</sup> However, no thiuram pendant groups were observed in model compound studies with  $Zn_2(dmtc)_4$  accelerated sulfur vulcanization,<sup>21,22,29</sup> and the ease with which  $Zn_2(dmtc)_4$  vulcanizates of polybutadiene (BR) crystallize on cooling<sup>37</sup> also points to the absence of pendant groups. Thus, the proposals for the involvement of pendant groups in the vulcanization process are based on circumstantial evidence.<sup>1-4</sup> Geysler and McGill<sup>33</sup> proposed that the reaction proceeds via a concerted mechanism without the formation of a true intermediate, the crosslinking of polysulfidic thiuram pendant groups being immediate in the presence of  $Zn_2(dmtc)_4$ , which catalyzes their crosslinking. The catalytic crosslinking by  $Zn_2(dmtc)_4$  (and zinc stearate) of pendant groups formed in compounds containing TMTD and sulfur was demonstrated by a number of authors.<sup>5,25,33,34,38</sup> As an alternative to thiuram pendant group formation, it was proposed that sulfurated  $Zn_2(dmtc)_4$  inserts sulfur into the allylic C—H bond.<sup>29</sup> The formation of thiol pendant groups was not detected, but the ability of  $Zn_2(dmtc)_4$  to catalyze the crosslinking of thiol groups on synthetic model compounds was demonstrated. As in the case where crosslinking via thiuram pendant groups is proposed, it is suggested that the inability to detect thiol intermediates in vulcanization studies can be ascribed to the rapid catalytic crosslinking of thiols by  $Zn_2(dmtc)_4$ .

An alternative to the formation of sulfurated  $Zn_2(dmtc)_4$  is the suggestion of Krebs et al.<sup>39</sup> who noted the accelerating properties of amines and suggested opening of the sulfur ring by the amine-zinc accelerator complex (Scheme 4). This could lead to an ionic mechanism similar to that proposed by Bateman and coworkers<sup>2</sup> for unaccelerated sulfur vulcanization. The  $Zn_2(dmtc)_4$  accelerated vulcanization is inefficient, which may be suggestive of an ionic mecha-

nism that involves the double bond.<sup>3</sup> Gregg and Katrenick,<sup>40</sup> on the other hand, suggested that the inefficient use of sulfur reflected cyclic sulfide formation and that this accounted for  $Zn_2(dmtc)_4$  vulcanizates failing to crystallize on cooling. Kruger and McGill<sup>27</sup> suggested that much of the sulfur was present in pendant groups, which they thought were highly sulfurated in  $Zn_2(dmtc)_4$  formulations. However, van der Merwe et al.<sup>37</sup> reported that  $Zn_2(dmtc)_4$  vulcanizates of BR crystallize readily on cooling, although less rapidly than peroxide cures with similar crosslink density. This implies that if cyclic sulfides formation occurs it must be limited, and it certainly conflicts with the suggestion that sulfur is present in pendant groups.

The crosslinking of polysulfidic pendant groups is generally considered to occur via a reaction of a pendant group with the polymer chain or by disproportionation of pendant groups.<sup>4,41-44</sup> Radical, ionic, and concerted mechanisms were suggested, as detailed in a comprehensive table by Nieuwenhuizen et al.<sup>38</sup> In the presence of  $Zn_2(dmtc)_4$  the exchange of ligands with  $Zn_2(dmtc)_4$ , followed by a reaction of the rubber-zinc accelerator complex with an olefin, was also proposed.<sup>2,45</sup>

Furthermore, Hdmtc is a good accelerator<sup>46</sup> and if the  $Zn_2(dmtc)_4$  reaction occurs via sulfurated  $Zn_2(dmtc)_4$ , as discussed above, Hdmtc will be liberated upon pendant group formation and upon crosslinking of thiuram pendant groups. Indeed, Ver-



**Scheme 4** The opening of the sulfur ring aided by the zinc-accelerator complex as proposed by Krebs et al.<sup>39</sup>

sloot et al.<sup>22</sup> found dimethylammonium dmtc (a Hdmtc decomposition product) on the edges of the reaction vessel in studies of the model compound system 2,3-dimethyl-2-butene (TME)/sulfur/Zn<sub>2</sub>(dmtc)<sub>4</sub> but not in the presence of ZnO, which would trap the acid as Zn<sub>2</sub>(dmtc)<sub>4</sub>. Likewise, DSC cure curves of polyisoprene (IR)/sulfur/Zn<sub>2</sub>(dmtc)<sub>4</sub> show a large endotherm, which is attributed to the evaporation of Hdmtc.<sup>27</sup> The endotherm is absent when ZnO is added. Hdmtc could therefore be expected to contribute to the overall vulcanization process that is suggested to occur in TMTD accelerated vulcanization,<sup>46</sup> certainly in the absence of ZnO. It was reported that the stability of metal dithiocarbamates is pH dependant, and under acid conditions they readily decompose to CS<sub>2</sub> and amine.<sup>47</sup> Baldwin<sup>48</sup> suggested that an equilibrium exists between H<sub>2</sub>S/Zn<sub>2</sub>(dmtc)<sub>4</sub> and ZnS/Hdmtc [reaction (1)].



Shelver<sup>35</sup> passed moist nitrogen over Zn<sub>2</sub>(dmtc)<sub>4</sub> contained in a tube immersed in an oil bath at 150°C. Dimethylammonium dmtc, which was attributed to the condensation of Hdmtc, was found on the cold sections of the tube outside the bath. A mass loss of 3.7% was found, corresponding to the decomposition of 5 mol % Zn<sub>2</sub>(dmtc)<sub>4</sub>. The breakdown is more rapid in the presence of H<sub>2</sub>S<sup>35</sup> and may be accelerated by H<sub>2</sub>S liberated in Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated vulcanization.<sup>4,29,33,35,49</sup>

This article examines the effect of water and H<sub>2</sub>S on the decomposition of Zn<sub>2</sub>(dmtc)<sub>4</sub> to Hdmtc and the role in the overall Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated sulfur reaction that is played by Hdmtc. It also examines the effect of vulcanizing compounds containing Zn<sub>2</sub>(dmtc)<sub>4</sub> under a vacuum. A vacuum will remove Hdmtc, which can act as an accelerator, and H<sub>2</sub>S, which is liberated in the Zn<sub>2</sub>(dmtc)<sub>4</sub> reaction.<sup>4,29,33,35,49</sup> Removal of H<sub>2</sub>S will prevent the further formation of Hdmtc by attack on Zn<sub>2</sub>(dmtc)<sub>4</sub>.<sup>35</sup>

## EXPERIMENTAL

### Materials

The Zn<sub>2</sub>(dmtc)<sub>4</sub> used in the study was purchased from Vulcazit L Bayer (Leverkusen, Germany), and the TMTD (chemical purity 97%) was purchased from Flexsys (Brussels, Belgium). Active grade ZnO (99.72% purity) was procured from Zinc Process (Cape Town, South Africa), and sulfur (98% soluble in CS<sub>2</sub>) was procured from AECI (Johannesburg, South Africa). The IR (Afprene IR80) and BR (Neodene, 98% cis-BR) were from Karbochem (Newcastle, South Africa), who also supplied samples of incompletely dried BR containing varying amounts of water. Hydroperoxides, which may interfere with the crosslinking process in

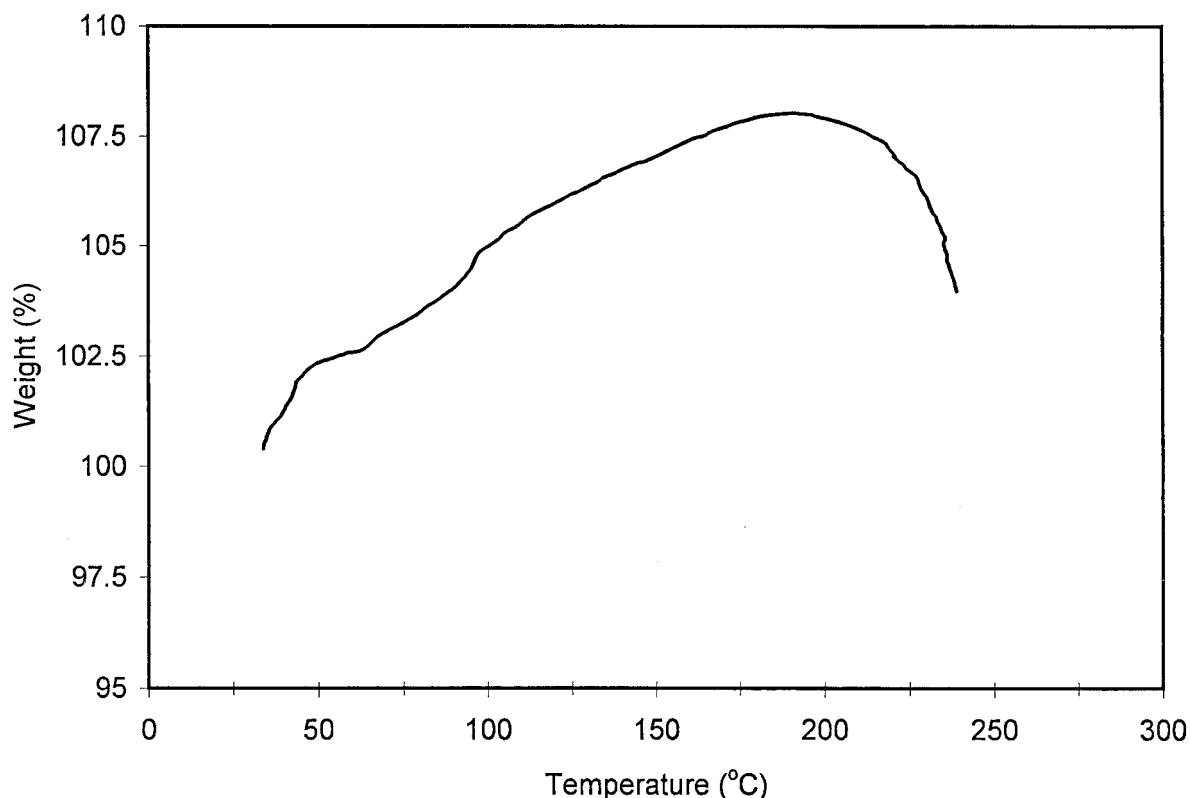
TME (99% chemical purity, Aldrich Chemical Co., Milwaukee, WI), were removed by shaking with aqueous ferrous sulfate.<sup>50</sup>

The effect of moisture and H<sub>2</sub>S on the thermal stability of Zn<sub>2</sub>(dmtc)<sub>4</sub> was determined by heating samples on a Du Pont 915 thermogravimetric (TG) analyzer in a flow of dry nitrogen, moist nitrogen, and a N<sub>2</sub>/H<sub>2</sub>S (90:10 v/v) mixture. The compounds were mixed in a Brabender Plasticorder as described earlier.<sup>51</sup> The formulations are indicated in text in parentheses as parts per 100 rubber (phr). The compounds were vulcanized in three ways: in a press at temperatures as indicated; by heating at 5°C/min in open pans in a DSC 10 cell connected to a TA Instruments Thermal Analyst 2000 system under a flow of nitrogen and under a vacuum; and as thin films, which were precipitated onto the walls of a tube and heated at 120°C under a vacuum in an oil bath. The crosslink densities were determined by swelling.<sup>35,51</sup> The crystallization of vulcanizates was followed on a density column at -16°C.<sup>37,52</sup> Crystallization was allowed to occur over a period of 3000–6000 min, although only the initial portions of the crystallization curves are reproduced in the figures. The TME formulations were prepared as described in two studies<sup>24,50</sup> and reacted in evacuated sealed tubes fully immersed in an oil bath at 150 ± 0.5°C for various times; the reaction was then quenched and the products analyzed by HPLC on a C18 reverse phase μ-Bondapak column with 80/20 (v/v) methanol/water as the eluent.<sup>50</sup> In the gradient elution studies the eluent was changed linearly from 80/20 (v/v) methanol/water to 100% water over a period of 120 min. The HPLC retention times of the crosslinked products were assigned by a comparison with HPLC<sup>49,50,53</sup> and <sup>1</sup>H-NMR spectra<sup>23,49,50</sup> of the reaction products of unaccelerated sulfur and TMTD accelerated sulfur vulcanization of TME. For NMR analysis the crosslinked products were separated by thin layer chromatography and the appropriate band was lifted. The molar ratios of TME to the curatives are indicated.

## RESULTS

### Interaction of Zn<sub>2</sub>(dmtc)<sub>4</sub> with H<sub>2</sub>O and H<sub>2</sub>S

The TG analysis (TGA) shows that Zn<sub>2</sub>(dmtc)<sub>4</sub> is stable when heated in dry nitrogen and decomposition occurs only at temperatures well above 150°C. When heating Zn<sub>2</sub>(dmtc)<sub>4</sub> in a stream of nitrogen, which was moistened by passage through water, a minimal mass loss was recorded after 1 h at 150°C. The purge gas intake to the TG instrument was modified to allow nitrogen moistened by passage through hot water to enter close to the sample. The TGA now showed a mass increase commencing below the vulcanization temperatures (Fig. 1) and a mass loss due to decomposition only at high



**Figure 1** TGA of  $\text{Zn}_2(\text{dmtc})_4$  heated at  $5^\circ\text{C}/\text{min}$  in a TG apparatus modified to allow moist nitrogen to impinge directly onto the sample.

temperatures, similar to where decomposition was observed under dry nitrogen. The effect that sulfuration of  $\text{Zn}_2(\text{dmtc})_4$  may have on its decomposition in moist nitrogen was investigated by heating an equimolar mixture of sulfur and  $\text{Zn}_2(\text{dmtc})_4$  at  $150^\circ\text{C}$  (i.e., at a temperature above the melting point of sulfur). The mass loss varied considerably (Table I) but essentially decreased with the increase in sample size. There was no correlation between the mass loss and moisture in the purge gas, and variations in the percentage of loss must be ascribed to the more ready evaporation of sulfur from smaller samples, where the surface to mass ratio is larger. Sulfur addition did not enhance  $\text{Zn}_2(\text{dmtc})_4$  decomposition in moist nitrogen at  $150^\circ\text{C}$ , although when melted the sulfur surrounds the  $\text{Zn}_2(\text{dmtc})_4$  particles and it may be questioned whether the  $\text{Zn}_2(\text{dmtc})_4$ /sulfur interface [where sulfuration of  $\text{Zn}_2(\text{dmtc})_4$  would occur]

**TABLE I**  
Mass Loss from  $\text{Zn}_2(\text{dmtc})_4$ /Sulfur Heated for 1 h at  $150^\circ\text{C}$  in Flow of Dry and Moist Nitrogen

Purge gas	Mass $\text{Zn}_2(\text{dmtc})_4$ (mg)	Mass loss (%)
Moist nitrogen	5.025	33.9
Dry nitrogen	6.546	33.4
Dry nitrogen	7.137	29.4
Moist nitrogen	10.505	21.7

is accessible to the water. A  $\text{Zn}_2(\text{dmtc})_4$ /sulfur mix (1:5 molal ratio) was moistened with water and the paste heated in the TG analyzer at 20 and  $50^\circ\text{C}/\text{min}$ . Water was rapidly lost from the paste; but very little mass loss, which could be attributed to  $\text{Zn}_2(\text{dmtc})_4$  decomposition, occurred below  $180^\circ\text{C}$ .

The solubility of  $\text{Zn}_2(\text{dmtc})_4$  in rubbers is limited but increases at the temperatures of interest for decomposition.<sup>54</sup> Moreover, in a further attempt to increase the contact of  $\text{Zn}_2(\text{dmtc})_4$  and sulfur with water, a moistened mixture of  $\text{Zn}_2(\text{dmtc})_4$  and sulfur were compounded with IR and heated in the TG analyzer. When compared to a dry mix, no enhanced mass loss was recorded, which could be attributed to the decomposition of  $\text{Zn}_2(\text{dmtc})_4$ .

The TGA showed rapid decomposition of  $\text{Zn}_2(\text{dmtc})_4$  above  $150^\circ\text{C}$  when heating in a flow of  $\text{H}_2\text{S}$ /nitrogen (10/90, v/v), and by  $200^\circ\text{C}$  complete conversion to ZnS is indicated (Table II). This is in agreement with Shelver<sup>35</sup> who reported that  $\text{Zn}_2(\text{dmtc})_4$  decomposed more rapidly when heated at  $150^\circ\text{C}$  in a  $\text{H}_2\text{S}$  atmosphere than when heated in moist nitrogen.

#### Effect of water on vulcanization of IR/ $\text{Zn}_2(\text{dmtc})_4$ /sulfur

It is extremely difficult to dry rubber completely; instead, the effect of adding more water on the rate of

**TABLE II**  
Mass Loss of Zn<sub>2</sub>(dmtc)<sub>4</sub> Heated to 200°C at 5°C/min in 90/10 Nitrogen/H<sub>2</sub>S Purge Gas Atmosphere

Mass Zn <sub>2</sub> (dmtc) <sub>4</sub> (mg)	Mass Loss (%)
5.593	63.76
6.917	65.44
9.069	65.07

The loss for complete conversion to ZnS is 68.25%.

vulcanization was examined. Ca(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>) · 3H<sub>2</sub>O, which loses its water of crystallization at 110°C, was compounded into an IR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(11.27)/sulfur(9.46) mix as a method of adding water to the compound *in situ*. Figure 2 shows that the addition of the hydrate led to an increase in the rate of crosslinking at 120°C compared to the rate in its absence. In another compound Zn<sub>2</sub>(dmtc)<sub>4</sub> was moistened with water before its addition to the mix as a paste, and this also led to an increase in the rate of crosslinking (Fig. 2). As reported previously,<sup>27</sup> the addition of ZnO to the compound also had a marked accelerating effect on the rate of the reaction (Fig. 2).

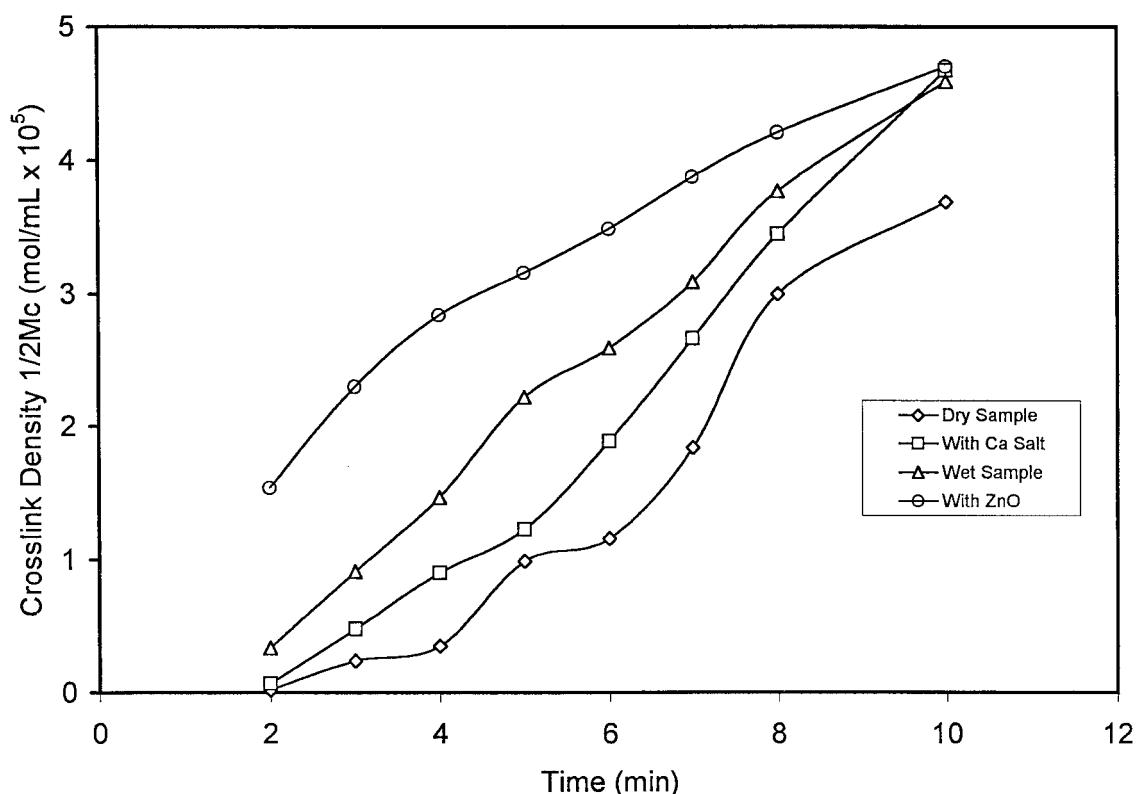
#### Effect of water on vulcanization of BR/Zn<sub>2</sub>(dmtc)<sub>4</sub>/sulfur

Samples of incompletely dried BR were vulcanized at 120°C with a Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated system. At 120°C

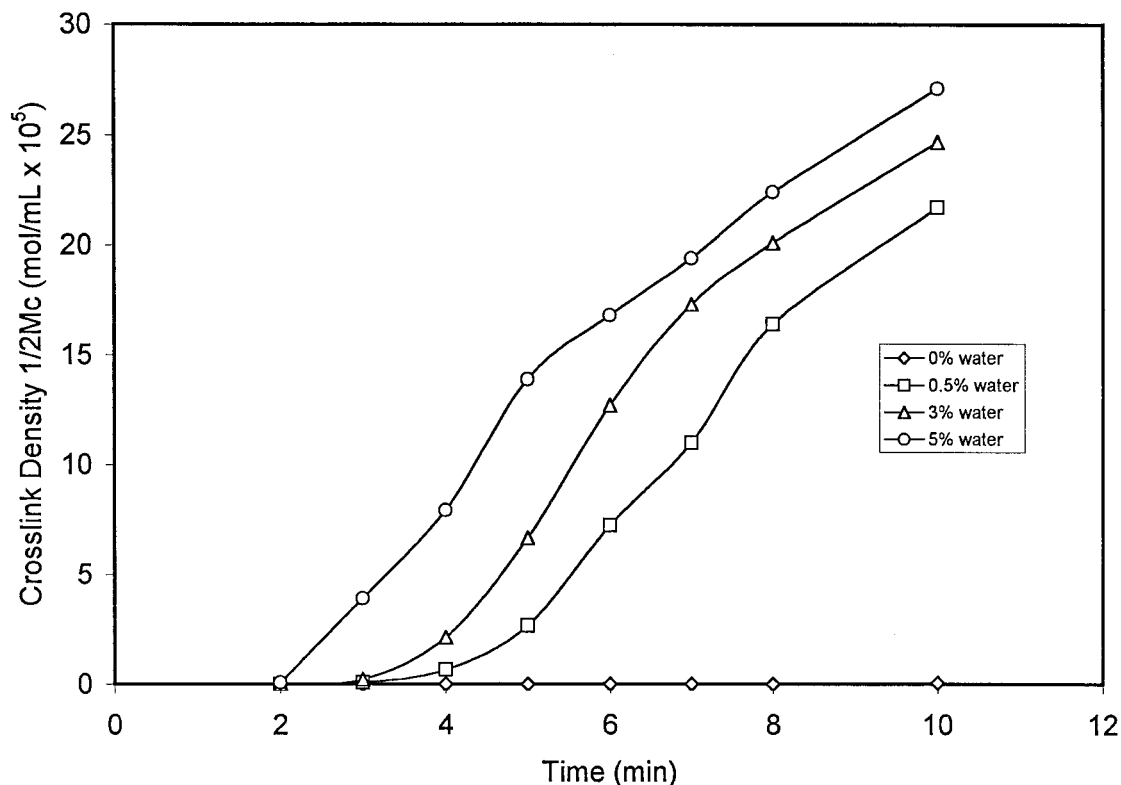
the compounds with dry BR showed no crosslinking after 10 min, compounds containing 0.5 mass % water reacted readily, and mixtures containing higher amounts of water (3 and 5 mass %) gave still higher rates of crosslink formation (Fig. 3). The differences in the crosslinking of dry IR (Fig. 2) and dry BR (Fig. 3) suggest the BR sample was completely dry, unlike the IR sample.

#### Effect of water on vulcanization of TME/Zn<sub>2</sub>(dmtc)<sub>4</sub>/sulfur

The use of moistened instead of dry Zn<sub>2</sub>(dmtc)<sub>4</sub> likewise accelerated the formation of crosslinked products in the TME(33.9)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(1.1)/sulfur(1) model compound system (Table III). The <sup>1</sup>H-NMR resonances at 3.46–3.73, 1.77, and 1.70 ppm allow the major crosslinked polysulfides to be identified as bis(alkenyl).<sup>22,23,49</sup> Weak resonances in the NMR at 0.98–0.99 and 1.33–1.34 ppm show the formation of trace amounts of alkyl alkenyl and bis(alkyl) sulfides. As reported earlier,<sup>22,29,33</sup> HPLC analysis showed that no pendant groups, which are readily detected in TMTD accelerated systems,<sup>16,22,24,49</sup> were observed at any stage in the reaction. The Zn<sub>2</sub>(dmtc)<sub>4</sub> and sulfur concentrations decreased slowly with time as reported by Geyser and McGill.<sup>33</sup>



**Figure 2** The crosslink densities of IR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(11.27)/sulfur(9.46) vulcanized at 120°C for various times: (◇) dry compound, (■) compounded with 4.13 phr Ca(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> · 3H<sub>2</sub>O, (△) compounded with wet Zn<sub>2</sub>(dmtc)<sub>4</sub>, and (○) compounded with 3 phr ZnO.



**Figure 3** The crosslink densities of BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(11.27)/sulfur(9.46) compounds containing varying percentages of water and vulcanized at 120°C.

#### Effect of vacuum on vulcanization

The effect of the vacuum removal of volatiles (Hdmtc and H<sub>2</sub>S) liberated during vulcanization<sup>4,22,24,27,28,33,34,36,55</sup> on the vulcanization process was investigated. Heating under a vacuum would remove some water, as well as volatiles like Hdmtc, which would result if thiuram pendant group formation occurred via sulfurated Zn<sub>2</sub>(dmtc)<sub>4</sub> and H<sub>2</sub>S, which is reported as a product of vulcanization.<sup>4,29,33,56</sup> Vulcanization of thin films of IR/Zn<sub>2</sub>(dmtc)<sub>4</sub>/sulfur, which were precipitated from benzene solution onto the walls of a tube and vulcanized by heating under a vacuum in an oil bath at 120°C, led to a marked reduction in the rate of

vulcanization compared to vulcanization in a press (Table IV). Likewise, heating precipitated films of dry BR compounds under a vacuum at 130°C showed limited crosslinking compared to compounds vulcanized in a press (Table V); at 140°C, where volatilization would be faster, the formation of a gel only was detected when vulcanized under a vacuum (Table VI).

It was noted above that moisture promoted the rate of crosslink formation, and the precipitation of thin films from benzene solution would reduce the amount of water in such films. It may be suggested that the drastically reduced rate of crosslinking in benzene precipitated films, which were heated under a vac-

**TABLE III**  
Relative Areas under HPLC Peaks Ascribed to Di-, Tri-, and Tetrasulfidic Crosslinked Products

Time (min)	Disulfide		Trisulfide		Tetrasulfide	
	Dry	Moist	Dry	Moist	Dry	Moist
3	0	0.9	0	1.0	0	1.0
5	0	2.2	0	1.3	0	0.8
7	0.8	4.6	0.8	5.7	0.9	3.0
9	2.5	17.6	2.9	9.7	1.5	4.7
11	1.1	15.1	1.7	11.1	1.5	4.9
16	14.3	30.7	10.2	15.1	4.0	6.4
20	19.0	47.2	10.4	22.9	4.9	10.5

The products were obtained on heating dry and moist TME(33.9)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(1.1)/sulfur(1) mixes at 150°C for various times.

TABLE IV  
Crosslink Densities of IR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(11.27)/  
Sulfur(9.46) Vulcanized at 120°C

Time (min)	Press vulcanized	Vacuum vulcanized
	(m) $1/2M_c \times 10^{-5}$ (mol/mL)	$1/2M_c \times 10^{-5}$ (mol/mL)
2	0.02	0.04
3	0.24	0.13
4	0.35	0.22
5	0.99	0.22
6	1.16	0.48
7	1.84	0.54
8	3.00	0.68
10	3.69	1.35

uum, may be ascribed to the removal of moisture from the films. Two Zn<sub>2</sub>(dmtc)<sub>4</sub> compounds were prepared on the Brabender using dry BR and BR containing 0.5 mass % water. These were heated at 5°C/min to 180°C in open pans in the DSC apparatus. In one series of experiments nitrogen was passed over the samples, and in a second series vulcanization was conducted under a vacuum. Figures 4 and 5 show that the onset of the vulcanization exotherm occurred earlier in compounds containing 0.5 mass % water when vulcanized under nitrogen and under a vacuum. Under the vacuum the vulcanization exotherms are smaller and lower crosslink densities develop (Table VII), although crosslinking is not as severely impeded as in benzene precipitated films (Tables V, VI). (The latter films were thinner than the DSC samples and this would facilitate the loss of volatiles under the vacuum.)

### Crystallization of vulcanizates

The density column shows that the initial densities of more heavily crosslinked BR compounds, which were vulcanized in a press at 130 and 140°C, increase with the vulcanization time (Figs. 6, 7; Tables V, VI). The rates of crystallization, which are the time required for the crystallization process to go to 50% completion ( $t_{1/2}$ ), increase with the crosslink density (Tables V,

VI). Samples heated under a vacuum have much lower crosslink densities (Tables V, VI) than samples cured in a press for similar times and their initial densities progressively decrease with increased cure time (Figs. 8, 9). The rates of crystallization of vacuum-cured samples are much slower than those for samples cured to similar crosslink densities in a press (Tables V, VI).

## DISCUSSION

### Nature of crosslinked products

Accelerated sulfur vulcanization involves a substitution mechanism, as opposed to the unaccelerated sulfur reaction which is an additive process<sup>1-5</sup>; it is also generally considered that the crosslinked polysulfides formed in Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated model compounds are bis(alkenyl), similar to those formed in TMTD accelerated systems. The NMR data confirmed that after 30 min at 130°C the crosslinked products of Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated sulfur vulcanization of TME are indeed similar to those of TMTD accelerated formulations and are mainly bis(alkenyl) in nature.<sup>23,49</sup> Trace amounts of alkyl alkenyl and bis(alkyl) sulfides form, possibly as a result of unaccelerated sulfur vulcanization by the high sulfur loadings in the formulations.

### Pendant groups

As reported earlier,<sup>22,29,33</sup> the formation of crosslinked products in Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated TME systems occurs without the formation of detectable amounts of thiuram pendant groups. The data discussed below for vulcanizates placed in the density column also point to pendant groups being largely absent from the rubber vulcanizates. First, the density column showed that the initial densities of compounds vulcanized in a press for short periods at 130°C were very similar (Fig. 6, Table V); in TMTD and 2-bisbenzothiazole-2,2'-disulfide (MBTS) accelerated vulcanizates, where crosslinking occurs via pendant groups, the initial

TABLE V  
Comparison of Crosslink Densities, Crystallization Rates ( $t_{1/2}$ ), and Initial and Final Densities at -16°C of BR(100)/  
Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/Sulfur(3) Vulcanized at 130°C

Time (min)	Press vulcanized				Vacuum vulcanized			
	$1/2M_c \times 10^5$ (mol/mL)	$t_{1/2}$ (min)	Density (g/mL)		$1/2M_c \times 10^5$ (mol/mL)	$t_{1/2}$ (min)	Density (g/mL)	
			Initial	At 2870 min			Initial	At 2780 min
5	0	30	0.9600	0.9968	0	29	0.9623	0.9944
10	0	31	0.9587	0.9962	0	60	0.9475	0.9792
15	Gel	33	0.9602	0.9966	0.16	74	0.9439	0.9804
18	0.04	64	0.9595	0.9934	0.02	107	0.9399	0.9803
24	0.67	99	0.9597	0.9927	0.40	200	0.9322	0.9770
30	12.1	∞	0.9658	0.9662	0.47			



TABLE VI  
Comparison of Crosslink Densities, Crystallization Rates ( $t_{1/2}$ ), and Initial and Final Densities at  $-16^{\circ}\text{C}$  of BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/Sulfur(3) Vulcanized at  $140^{\circ}\text{C}$

Time (min)	Press vulcanized				Vacuum vulcanized			
	$1/2M_c \times 10^5$ (mol/mL)	$t_{1/2}$ (min)	Density (g/mL)		$1/2M_c \times 10^5$ (mol/mL)	$t_{1/2}$ (min)	Density (g/mL)	
			Initial	At 2580 min			Initial	At 2580 min
2	0	41	0.9551	0.9816	0	53	0.9486	0.9762
4	0.2	90	0.9569	0.9783	0	44	0.9496	0.9783
6	10.8	$\infty$	0.9608	0.9608	0	56	0.9470	0.9721
12	11.3	$\infty$			Gel	90	0.9515	0.9775
15	11.5	$\infty$			Gel			

densities of compounds heated for short periods decreased with the cure time.<sup>37,52</sup> This decrease was attributed to pendant groups increasing the free volume of the vulcanizates. At longer heating times, where high crosslink densities develop, further changes in the initial density of TMTD and MBTS vulcanizates were minimal, while the initial density of Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated compounds cured at both at 130 and  $140^{\circ}\text{C}$  were noticeably increased (Figs. 6, 7; Tables V, VI). This is in agreement with the work of van der Merwe et al.<sup>37,52</sup> who reported a progressive increase in the density of vulcanizates heated for longer times and attributed the increase to the formation in the compound of ZnS, which has a higher density (4.09 g/mL) than the Zn<sub>2</sub>(dmtc)<sub>4</sub> (1.79 g/mL)

from which it forms. It is well known that compounds shrink on vulcanization, a reaction leading to some physical bonds between the components being replaced by chemical bonds in which the bond distance is shorter. Thus, the increase in density of the heavily crosslinked compounds that do not crystallize can be ascribed partly to shrinkage from vulcanization and partly to ZnS formation.

Second, the limited influence of vulcanization (except at high crosslink densities) on the rate of crystallization (Tables V, VI) supports model compound data indicating that the vulcanizate contains very few pendant groups. However, the rates of crystallization of vulcanizates with progressively higher crosslink densities are slightly slower than reported<sup>37</sup> for peroxide

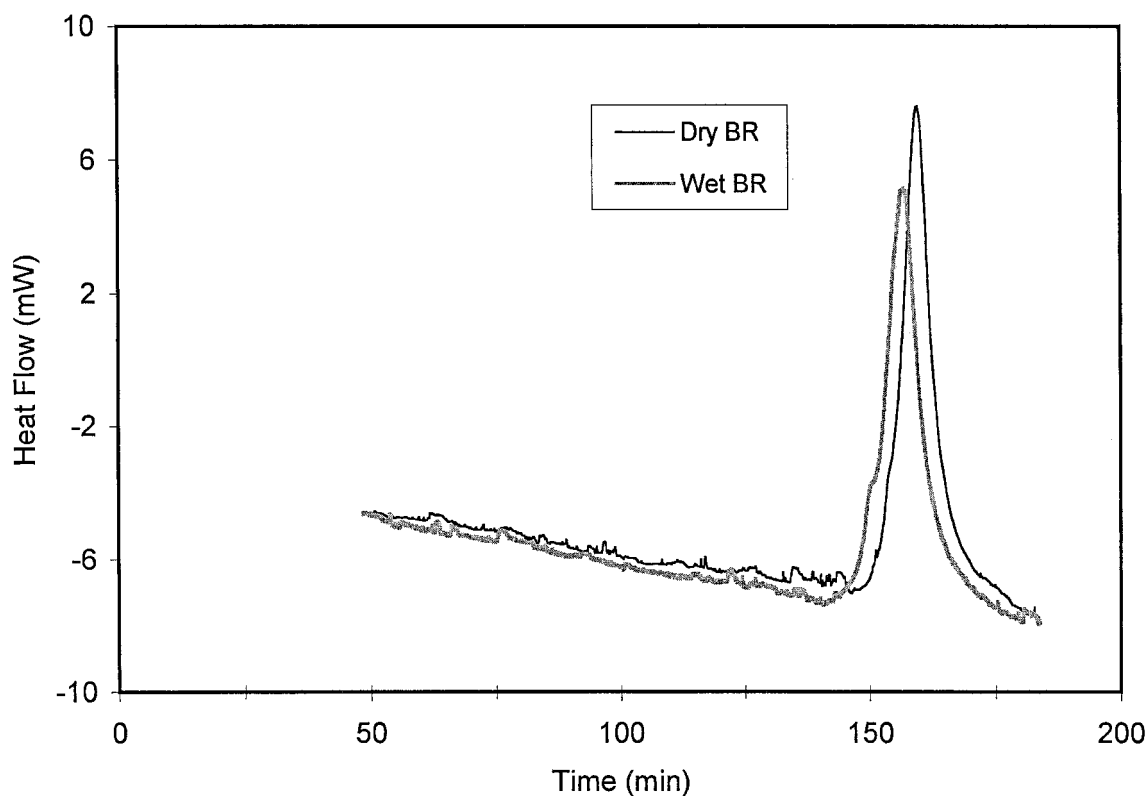
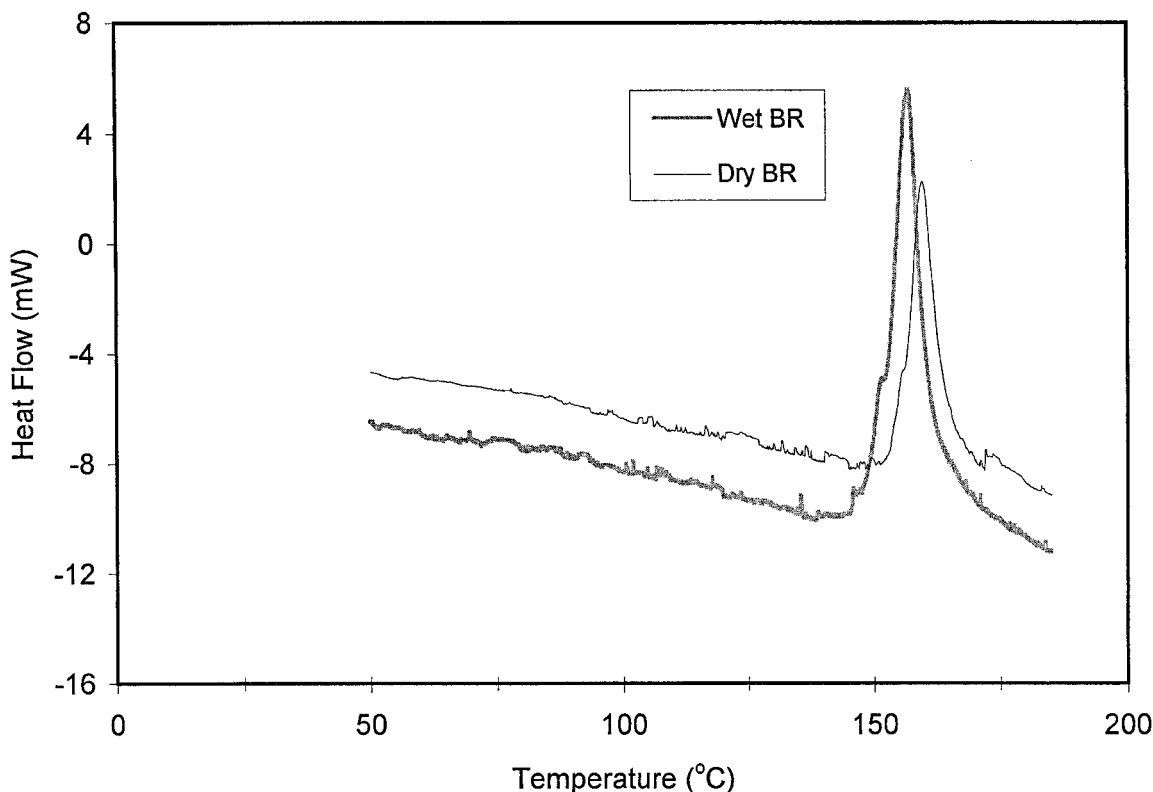


Figure 4 DSC curves of BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/sulfur(3) compounds prepared with dry BR and BR containing 0.5 mass % water and heated at  $5^{\circ}\text{C}/\text{min}$  in open pans in a flow of nitrogen.



**Figure 5** DSC curves of BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/sulfur(3) compounds prepared with dry BR and BR containing 0.5 mass % water and heated at 5°C/min in open pans under a vacuum.

cures of similar crosslink density. (The half-life for crystallization of a peroxide-cured gel is 28 min and for a crosslink density of  $3.10 \times 10^{-5}$  mol/mL the  $t_{1/2}$  is 52 min.<sup>37</sup>) The slower rate of crystallization in Zn<sub>2</sub>(dmtc)<sub>4</sub> vulcanizates points to some main chain modification. In TMTD and MBTS accelerated formulations of IR and BR the rate of crystallization of the gels is greatly reduced at subambient temperatures and this is largely attributed to the effect of residual pendant groups, the influence of crosslinks becoming important only at high crosslink densities.<sup>37,52</sup> When zinc stearate is added to the formulation, higher crosslink densities develop, yet crystallization occurs more readily as zinc stearate catalyzes the crosslinking of pendant groups, reducing the number of residual pendant groups in the compound.<sup>37</sup> The ability of Zn<sub>2</sub>(dmtc)<sub>4</sub> to catalyze the crosslinking of pendant

groups is well established<sup>5,25,33,34,38</sup> and a rapid catalytic crosslinking reaction may well account for the undetected involvement of pendant groups in the reaction. Thus, in accord with previous studies, we concluded that Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated sulfur vulcanization occurs rapidly without the detection of pendant groups in the model compounds. However, the decrease in the rate of crystallization of lightly crosslinked vulcanizates suggests that in these compounds a limited number of pendant groups escaped essentially bis(alkenyl) in nature.

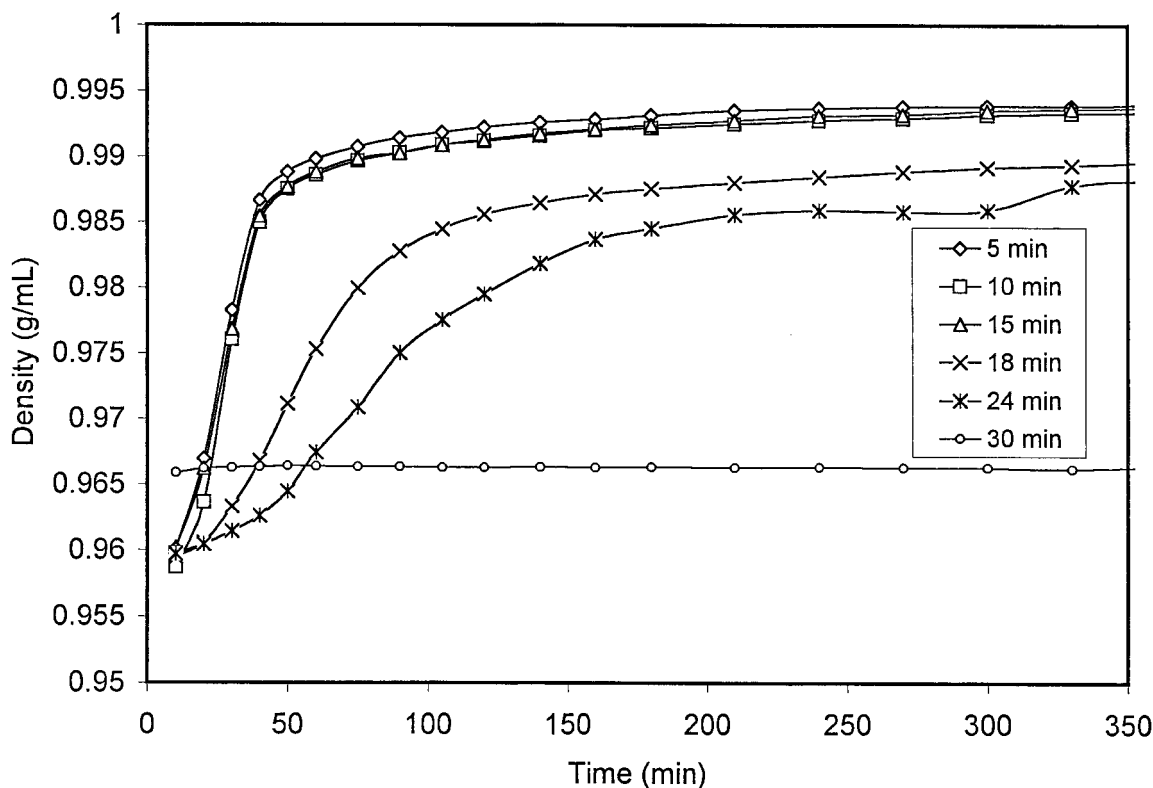
Two contributions in this article that need discussion are the promotion of crosslinking by moisture and the reduced ability of compounds to crosslink when heated in a vacuum.

#### Effect of water on vulcanization

The addition of water to formulations accelerates crosslink formation with IR, BR, and TME (Figs. 2, 3; Table III). Hdmtc was shown to be a good accelerator for sulfur vulcanization<sup>46</sup> and, if liberated by the action of moisture on Zn<sub>2</sub>(dmtc)<sub>4</sub>, a sequence of reactions leading to Hdmtc accelerated sulfur vulcanization may be envisioned [reactions (2)–(5)]. Sulfurated Hdmtc would form hydrogen terminated polysulfidic pendant groups [reaction (2)].

**TABLE VII**  
Crosslink Density of BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/Sulfur(3) Compounds with Dry and Wet BR Heated at 5°C/min to 180°C in Apparatus

Atmosphere	Dry BR $1/2M_c \times 10^5$ (mol/mL)	BR with 0.5 mass % water $1/2M_c \times 10^5$ (mol/mL)
Nitrogen	7.06	29.90
Vacuum	5.23	13.70



**Figure 6** The initial portions of the density versus the time curves for BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/sulfur(3) heated at 130°C in a press for various times.



Exchange between such thiols and Hdmtc would give thiuram pendant groups [reaction (3)].



Crosslinking could result from the reaction between thiol pendant groups [reaction (4)]<sup>29,50</sup> and from the reaction between thiuram and thiol pendant groups [reaction (5)].<sup>46</sup> Reactions (4) and (5) are also catalyzed by Zn<sub>2</sub>(dmtc)<sub>4</sub>.<sup>5,25,33,34,38</sup>



Morgan et al.<sup>50</sup> reported H<sub>2</sub>S evolution on crosslinking between thiols, but Nieuwenhuizen et al.<sup>29</sup> suggested a metathesis reaction with H<sub>2</sub>S liberation only in the Zn<sub>2</sub>(dmtc)<sub>4</sub> catalyzed reaction.

However, as shown above, attempts to increase the Zn<sub>2</sub>(dmtc)<sub>4</sub> decomposition by increasing or improving the contact between water and Zn<sub>2</sub>(dmtc)<sub>4</sub> had little effect on its rate of decomposition. Therefore, one must conclude that water initiated decomposition of Zn<sub>2</sub>(dmtc)<sub>4</sub> to give Hdmtc plays a minor role in the vulcanization process. Instead it is suggested that wa-

ter activates Zn<sub>2</sub>(dmtc)<sub>4</sub> by coordination with zinc, which supposedly occurs with amines and carboxylic acids,<sup>3,5</sup> and larger amounts of water ensure the activation of more Zn<sub>2</sub>(dmtc)<sub>4</sub>. The mass gained when Zn<sub>2</sub>(dmtc)<sub>4</sub> is heated in moist nitrogen (Fig. 1) may be an indication of the strong coordination between Zn<sub>2</sub>(dmtc)<sub>4</sub> and water. The association is sufficiently strong for a mass increase to be recorded, even at 150°C, well above the boiling point of water. Thus, weakening of the Zn—S bond, as suggested by Higgins and Saville,<sup>6</sup> may initiate the formation of thiuram<sup>2-4</sup> or thiol<sup>29</sup> pendant groups, the crosslinking of which is catalyzed by Zn<sub>2</sub>(dmtc)<sub>4</sub>.<sup>5,25,29,33,34,38</sup> A reaction via thiuram pendant groups will liberate Hdmtc (Scheme 2); Nieuwenhuizen et al.,<sup>29</sup> who suggested the formation of thiol pendant groups, thought Hdmtc was formed during the Zn<sub>2</sub>(dmtc)<sub>4</sub> catalyzed crosslinking of thiol pendant groups. Thus, Hdmtc, formed *in situ* at this point, becomes available to act as an accelerator [reactions (2)–(5)] in parallel with Zn<sub>2</sub>(dmtc)<sub>4</sub>. Further, H<sub>2</sub>S may form in the exchange between Hdmtc and thiol pendant groups [reaction (3)] or via any of a number of other routes reported in the literature.<sup>4,29,33,56</sup> The liberation of H<sub>2</sub>S will accelerate Zn<sub>2</sub>(dmtc)<sub>4</sub> decomposition and the formation of more Hdmtc; the TGA shows that the decomposition of Zn<sub>2</sub>(dmtc)<sub>4</sub> by H<sub>2</sub>S [reaction (1)] is rapid. The importance of H<sub>2</sub>S in Zn<sub>2</sub>(dmtc)<sub>4</sub> decomposition was recog-

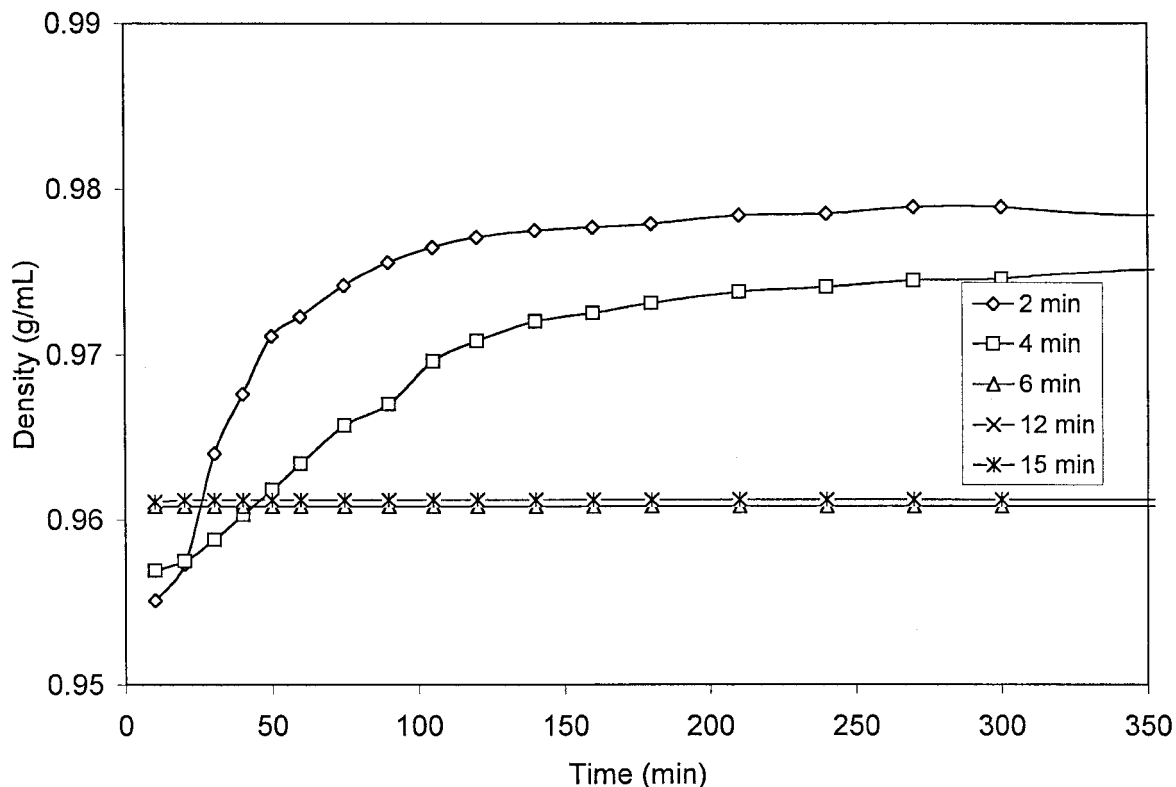


Figure 7 The initial portion of the density versus the time curves for BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/sulfur(3) heated at 140°C in a press for various times.

nized by Bedford and Gray<sup>56</sup> who reported that cures were greatly retarded if stocks containing Zn<sub>2</sub>(dmtc)<sub>4</sub> were placed in an atmosphere of H<sub>2</sub>S before curing.

However, their experiments were performed under conditions where the Hdmtc from Zn<sub>2</sub>(dmtc)<sub>4</sub> decomposition would escape from the compound before it

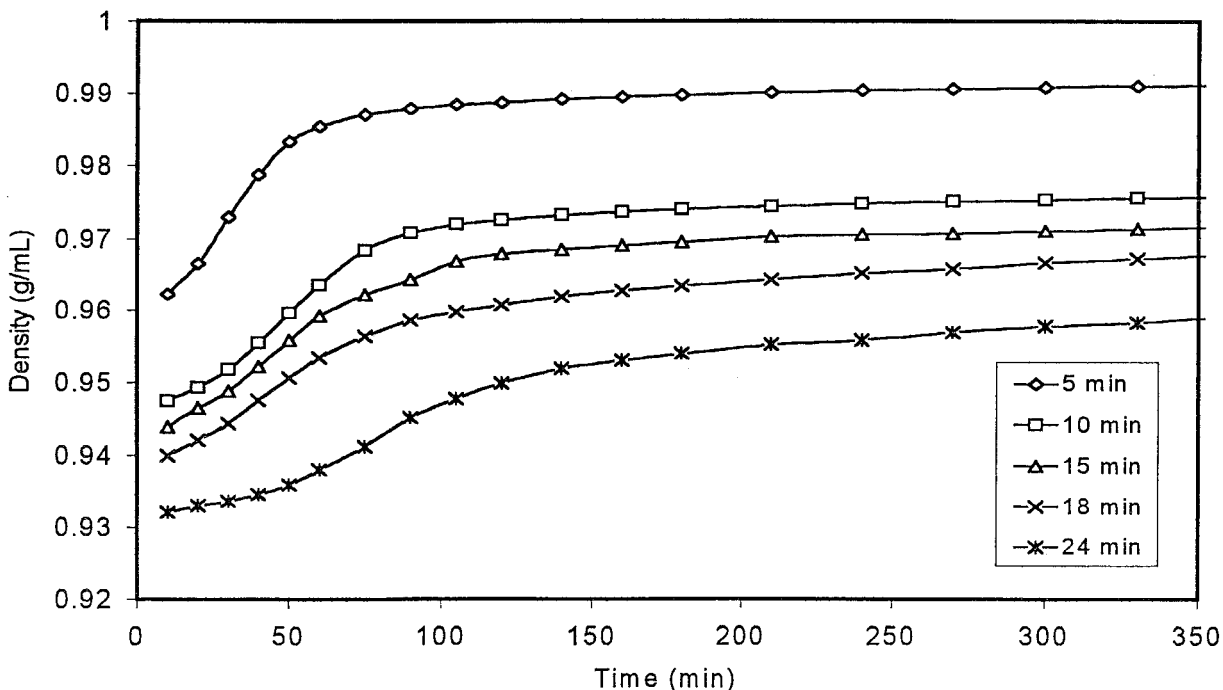
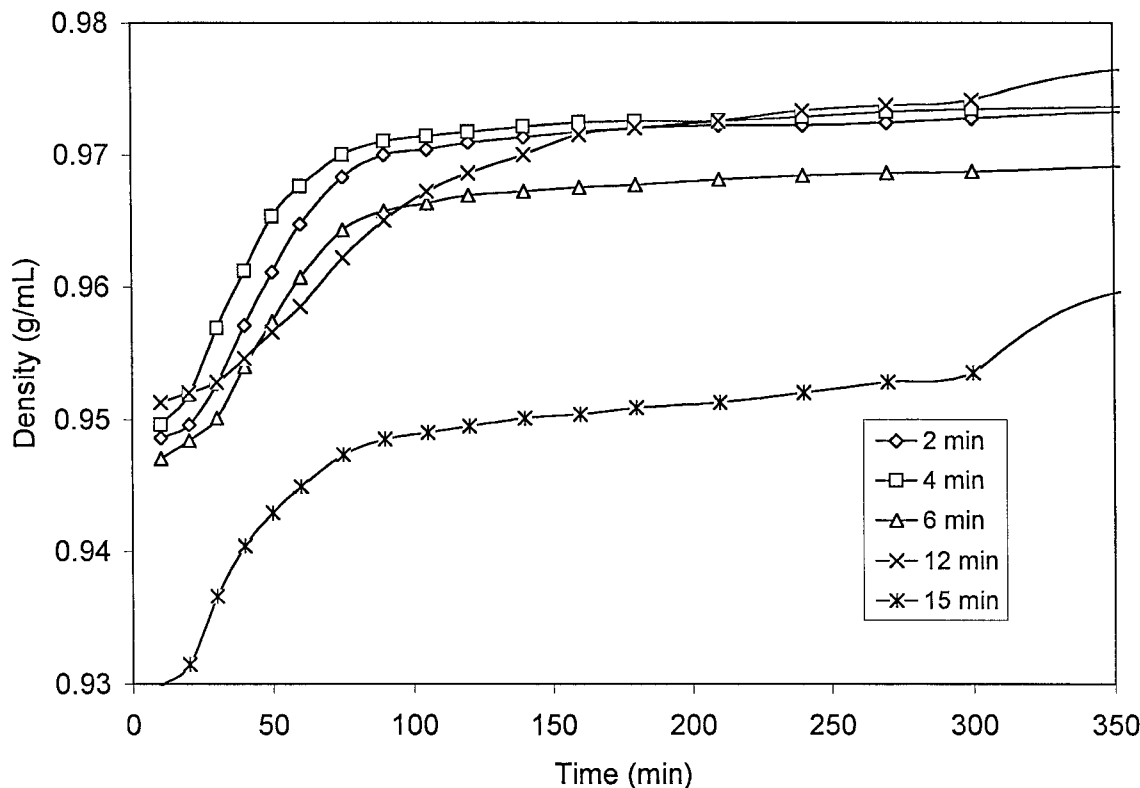


Figure 8 The initial portion of the density versus the time curves for BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/sulfur(3) heated at 130°C under a vacuum for various times.



**Figure 9** The initial portion of the density versus the time curves for BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>/sulfur(3) heated at 140°C under a vacuum for various times.

was placed in the vulcanization press. Hdmtc would therefore not be available as an *in situ* accelerator; that is, H<sub>2</sub>S would partly decompose the primary Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerator without the Hdmtc accelerator produced *in situ* being available for reaction.

The diversity of crosslinking reactions, coupled with the presence of Zn<sub>2</sub>(dmtc)<sub>4</sub> that catalyzes crosslinking, could ensure a pendant group concentration too low to detect in model compound studies or to significantly influence the crystallization of vulcanizates. Even samples with a crosslink density of  $0.67 \times 10^{-5}$  mol/mL crystallize fairly rapidly (Fig. 6), unlike TMTD vulcanizates, where pendant groups have a strong affect on the crystallization rates, even prior to gel formation.

#### Effect of vacuum on vulcanization

Two factors need consideration: the reduced extent of crosslinking under the vacuum (Tables IV–VI) and the slower rates of crystallization of vulcanizates with similar crosslink densities (Tables V, VI).

#### Reduced rate of crosslinking under vacuum

Vulcanization under a vacuum drastically reduces the rate and extent of crosslink formation (Tables V, VI). Zn<sub>2</sub>(dmtc)<sub>4</sub> is a nonvolatile solid; if vulcanization re-

sulted solely via the water activated Zn<sub>2</sub>(dmtc)<sub>4</sub> initiated and catalyzed crosslinking of thiuram or thiol pendant groups, there is no apparent reason why the application of a vacuum should reduce the extent of the reaction. Neither the formation of thiuram<sup>2-4</sup> (or thiol<sup>29</sup>) pendant groups by sulfurated Zn<sub>2</sub>(dmtc)<sub>4</sub> nor their catalytic crosslinking by Zn<sub>2</sub>(dmtc)<sub>4</sub> should be impeded.

It is possible that in benzene precipitated BR films (Tables V, VI) the moisture content is too low to activate Zn<sub>2</sub>(dmtc)<sub>4</sub>, although in benzene precipitated IR films (Table IV) a measurable degree of crosslink formation was recorded under the vacuum. Nevertheless, even where a solvent was not used in preparing the compound, as in the vacuum vulcanization in the DSC of small BR samples compounded on the Brabender, lower crosslink densities were also obtained than when heating to the same temperature without a vacuum being applied (Table VII). It may be argued that the rapid loss of water under the vacuum reduced the activation of Zn<sub>2</sub>(dmtc)<sub>4</sub> and affected the vulcanization, yet the onset and completion of the vulcanization exotherms for both the dry BR and BR compounds containing 0.5 mass % water were unaffected by the vacuum (Figs. 4, 5), which means the vacuum did not remove the water rapidly enough to influence the reaction in either compound. This suggests that the lower crosslink densities that develop under a

vacuum must be attributed to a second crosslinking process that is inhibited by the vacuum. Crosslinking via *in situ* formed Hdmtc was discussed above. The vacuum removal of the Hdmtc and H<sub>2</sub>S volatile reaction by-products would influence the reaction. As noted earlier, there are various routes<sup>3,29,33,56</sup> to the formation of H<sub>2</sub>S that, as shown in Table II, are very efficient in decomposing Zn<sub>2</sub>(dmtc)<sub>4</sub> to Hdmtc. Hdmtc may also result during pendant group formation (if the reaction occurs via thiuram pendant groups<sup>2-4</sup>) or with crosslinking (if the reaction occurs via thiols<sup>29</sup>). Hdmtc is an efficient accelerator<sup>46</sup> and its removal will decrease the rate of crosslink formation. It is suggested that the reduced crosslink density obtained on vulcanization under a vacuum supports the above contention that Hdmtc, and H<sub>2</sub>S via its decomposition of Zn<sub>2</sub>(dmtc)<sub>4</sub> to Hdmtc, contribute significantly to crosslink formation in Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated sulfur vulcanization via reactions (2)–(5).

#### Rate of crystallization of vacuum-cured compounds

As noted earlier, the initial density of Zn<sub>2</sub>(dmtc)<sub>4</sub> compounds vulcanized in a press increase slightly with increased vulcanization time (Figs. 6, 7; Tables V, VI) and can be attributed to the formation of ZnS that has a high density. However, on vulcanization under a vacuum at 130°C, the initial densities of the compounds decrease with increased vulcanization times (Fig. 8, Table VI). It may be argued that these decreases represent the vacuum loss of thiuram groups and sulfur as Hdmtc and H<sub>2</sub>S, respectively. If the thiuram groups in Zn<sub>2</sub>(dmtc)<sub>4</sub> and all of the sulfur were removed, leaving only ZnS, a decrease in density of 0.0065 g/mL can be calculated. The calculation is based on the masses and densities of components in BR(100)/Zn<sub>2</sub>(dmtc)<sub>4</sub>(4)/sulfur(3) and BR(100)/ZnS(1.27), assuming volumes to be additive and neglecting volume changes resulting from mixing and from chemical reactions in the second compound that will be crosslinked. The experimentally obtained density decreases are larger (0.03 g/mL at 24 min). In TMTD and MBTS accelerated sulfur vulcanizates the decreases in the initial density, particularly during the induction period, were ascribed to the formation of pendant groups on the chain that increase the free volume of the sample. The maximum recorded decreases in density were 0.0057 g/mL in BR(100)/TMTD(4)/sulfur(3) and 0.0095 g/mL in BR(100)/MBTS(4)/sulfur(3) vulcanizates.<sup>37</sup> According to this interpretation, the decrease in the initial density of samples heated under a vacuum at 130°C would suggest the formation of some pendant noncrosslinked groups in the Zn<sub>2</sub>(dmtc)<sub>4</sub> vulcanizates. At 140°C, where the reaction would be faster, a decrease in the initial densities of compounds heated under the vacuum is not evident (Table VI).

It was noted earlier in this article that the rates of crystallization ( $t_{1/2}$ ) of press-cured Zn<sub>2</sub>(dmtc)<sub>4</sub> vulcanizates are slower than those of peroxide cures of similar crosslink density, which suggests the presence of some residual pendant groups in these vulcanizates. The rates of crystallization of compounds vulcanized under a vacuum are slower when compared to vulcanizates of similar crosslink density and heated in a press (Tables V, VI). This supports the contention that residual pendant groups are present in Zn<sub>2</sub>(dmtc)<sub>4</sub> compounds heated under a vacuum and are responsible for the decrease in the initial density.

#### Role of Hdmtc in crosslink formation

Crosslinking by disproportionation of thiuram pendant groups is slow,<sup>22,25</sup> but Zn<sub>2</sub>(dmtc)<sub>4</sub> is not volatile and should remain in the compound to catalyze<sup>5,25,33,34,38</sup> the crosslinking of Zn<sub>2</sub>(dmtc)<sub>4</sub> initiated pendant groups. Yet on vulcanization under a vacuum the vulcanizates have lower crosslink densities, lower initial densities, and slower crystallization than press-cured vulcanizates of similar crosslink density. This suggests that under a vacuum the pendant groups do not crosslink as rapidly as in a press. McGill, Shelver, and coworkers<sup>34,35,46</sup> showed that in TMTD accelerated sulfur vulcanization there is little crosslinking that occurs when Hdmtc is removed from the system under a vacuum, and they suggested<sup>46</sup> that sulfurated Hdmtc was required to supply thiol pendant groups with which thiuram groups could crosslink [reaction (5)]. When Hdmtc remains in the compound it can form thiol pendant groups [reaction (2)] that can rapidly crosslink with thiuram pendant groups [reaction (5)], and the catalytic<sup>29</sup> and noncatalytic<sup>29,50</sup> crosslinking of thiols [reaction (4)] was demonstrated. Exchange reactions with pendant groups, giving groups that may more readily crosslink, are also possible [reaction (3)]. Thus, when it is not removed by a vacuum, Hdmtc not only acts as an accelerator but also provides alternative routes with which pendant groups originating from the Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerator can crosslink. Catalytic amounts (1%) of Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerate the crosslinking of thiuram pendant groups in model compounds by a factor of 4–6.<sup>25</sup> Yet in formulations containing both TMTD and Zn<sub>2</sub>(dmtc)<sub>4</sub>, where TMTD polysulfides will give rise to thiuram pendant groups, such thiuram pendant groups can be detected in model compound studies<sup>33</sup>: although a large loading of Zn<sub>2</sub>(dmtc)<sub>4</sub> that can act as a catalyst for crosslink formation is present, its catalytic reactivity is not sufficient to suppress the detection of the large amount of thiuram pendant groups originating from TMTD. When Hdmtc remains in the Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerated compound, alternative routes become available for crosslink formation [reactions (2)–(5)]

and these routes permit the efficient removal of pendant groups from the polymer chain.

### Role of ZnO in vulcanization

The marked increase in the rate of crosslinking obtained on the addition of ZnO (Fig. 2) was attributed to the Hdmtc being trapped by the ZnO, which prevents its degradation and attack by amines on pendant groups.<sup>55</sup> The endotherm in the DSC cure curve, attributed to Hdmtc evaporation, was eliminated with the addition of ZnO, which traps Hdmtc as Zn<sub>2</sub>(dmtc)<sub>4</sub>.<sup>27</sup> It is suggested here that the role of ZnO lies in its trapping of Hdmtc with the formation of water [reaction (6)] within the compound and that the *in situ* formation of water enhances the role of Zn<sub>2</sub>(dmtc)<sub>4</sub>.



Although Hdmtc, an important *in situ* accelerator liberated in pendant group formation and/or in crosslinking in the Zn<sub>2</sub>(dmtc)<sub>4</sub> system, is removed by ZnO, a molecule of water is formed with every molecule of Zn<sub>2</sub>(dmtc)<sub>4</sub> produced. Thus, a high concentration of water activated Zn<sub>2</sub>(dmtc)<sub>4</sub> develops in ZnO-containing compounds, ensuring their more rapid vulcanization. It is suggested that in ZnO-containing compounds the role of Hdmtc as an accelerator is minimal but the primary Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerator, which is reformed in the reaction, is activated in the reformation process by the parallel formation of water. This ensures that its contribution to crosslinking is correspondingly increased. H<sub>2</sub>S rapidly decomposes Zn<sub>2</sub>(dmtc)<sub>4</sub> and Bedford and Gray<sup>56</sup> postulated that the addition of ZnO protected the Zn<sub>2</sub>(dmtc)<sub>4</sub> by trapping the H<sub>2</sub>S formed during vulcanization<sup>4,29,33,56</sup> as ZnS. This reaction also liberates water and could further contribute to the activation of Zn<sub>2</sub>(dmtc)<sub>4</sub>. The use in compounds of ZnO in conjunction with stearic acid is preferred to the addition of zinc stearate in industry. It is interesting to speculate that the release of water, resulting from the *in situ* formation of zinc stearate, could offer an explanation for the preferred use of the ZnO/stearic acid combination.

### CONCLUSIONS

Although crosslink formation can result from various reactions, it is important to identify reactions that occur with sufficient rapidity to significantly contribute to the overall vulcanization process in real vulcanizates. We suggest that for Zn<sub>2</sub>(dmtc)<sub>4</sub> to act as an efficient accelerator it must be activated and water can provide such activation and that the accelerator Hdmtc formed *in situ* plays a major role in the overall vulcanization process. When ZnO is absent, Hdmtc

acts as an accelerator in its own right, forming thiol pendant groups that can crosslink and promote the crosslinking of thiuram pendant groups. The decomposition of Zn<sub>2</sub>(dmtc)<sub>4</sub> by H<sub>2</sub>S promotes Hdmtc formation and its importance as an accelerator. In ZnO-containing compounds the Hdmtc is trapped and not only is Zn<sub>2</sub>(dmtc)<sub>4</sub> reformed but also, water, which activates the Zn<sub>2</sub>(dmtc)<sub>4</sub> accelerator, is liberated as a by-product, which is more important. When Hdmtc is removed by the application of a vacuum, the number of alternative routes to crosslink formation are reduced, the crosslink densities are lower, and crystallization studies suggest the presence of residual pendant groups that were not crosslinked by the catalytic action of Zn<sub>2</sub>(dmtc)<sub>4</sub>. This article does not contribute to the question of whether crosslinking occurs via thiuram or thiol pendant groups.

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