Dimethylammonium Dimethyldithiocarbamate-Accelerated Sulfur Vulcanization. I. Thermal Stability and Reactions with Curatives

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ABSTRACT: To investigate its thermal stability and reactivity towards other accelerators dimethylammonium dimethyldithiocarbamate ((dma)dmtc) was heated at programmed heating rates in sealed and open pans in a differential scanning calorimeter and on a thermobalance. (Dma)dmtc was heated on its own, in rubber compounds and in mixes with tetramethylthiuram disulfide, zinc dimethyldithiocarbamate, and ZnO. In open systems (dma)dmtc readily sublimes at temperatures well below its melting point, and it is almost as rapidly lost when compounded on its own with rubber. No decomposition is observed at vulcanization temperatures and (dma)dmtc is unreactive towards tetramethylthiuram disulfide and zinc dimethyldithiocarbamate. Moisture does not promote its decomposition. Reaction with ZnO to give zinc dimethyldithiocarbamate is restricted to the surface of ZnO particles. (Dma)dmtc is soluble in water in which it dissociates. It must be concluded that when its is included in formulations, (dma)dmtc, per se, would act as a vulcanization accelerator; it does not decompose to dimethyldithiocarbamic acid and dimethylamine, both of which are known accelerators. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3067–3073, 2001

Key words: dimethylammonium dimethyldithiocarbamate; stability; accelerators; tetramethylthiuram disulfide; amines; differential scanning calorimetry; thermal properties; vulcanization; thermogravimetric analysis

INTRODUCTION

Dimethylammonium dimethyldithiocarbamate [(dma)dmtc, $(CH_3)_2NC(S)S^-(CH_3)_2NH_2^+$] is a well-known accelerator, particularly for latices. It is highly reactive, and its reactivity may lead to scorch.[1,2] (Dma)dmtc is the amine complex of dimethylamine (dma) and dimethyldithiocarbamic acid (Hdmtc), both of which are accelerators in their own right. Amines were the first compounds to be used as accelerators, but because of their toxicity, amine complexes are now used mainly as secondary accelerators.[1,3–6] Hdmtc is a highly reactive accelerator.[7] It is liberated during tetramethylthiuram disulfide (TMTD)-accelerated vulcanization, and plays an important role in the TMTD-accelerated reaction. Little scientific data has been published on the reactivity of (dma)dmtc towards other curatives and its function as an accelerator. Solutions of (dma)dmtc in organic solvents are known to exchange with ZnO, giving zinc dimethyldithiocarbamate $(Zn_2(dmtc)_4)$.[8,9] The catalytic decomposition by amines of TMTD to tetramethylthiourea and CS_2 is known, and the proposed mechanism (Scheme 1) involves the formation of (dma)dmtc as an intermediate.[10] This implies decomposition of (dma)dmtc at vulcaniza-
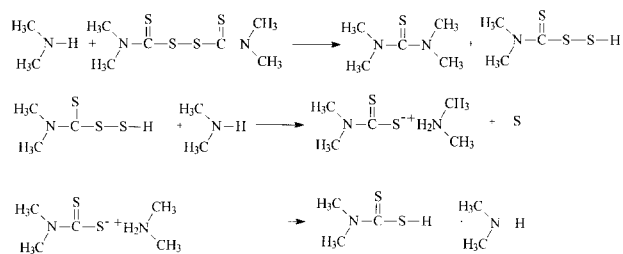
Scheme 1 Formation of tetramethylthiourea catalyzed by dimethylamine liberated on decomposition of (dma)dmtc as proposed by Nieuwenhuizen et al.[10]

tion temperatures. Pentamethyleneammonium pentamethylenedithiocarbamate ((pip)pmtc) has been shown to decompose to piperidine and pentamethylenedithiocarbamic acid (Hpmtc) at vulcanization temperatures.[11] It is, therefore, important to establish whether (dma)dmtc per se, acts as an accelerator, or whether, on heating, it decomposes to dma and Hdmtc, which then act as accelerators.

This article examines the thermal stability of (dma)dmtc and its reactions with other curatives [TMTD, ZnO, $Zn_2(dmtc)_4$ and sulfur], while the next article reports on (dma)dmtc as an accelerator for the sulfur vulcanization of rubber and model compound 2,3-dimethyl-2-butene (TME).

EXPERIMENTAL

Materials

TMTD (chemical purity 97%) Flexsys, Brussels, Belgium; $Zn_2(dmtc)_4$, Vulcazit L Bayer, Leverkusen Germany; ZnO (active grade, 99.72% purity) Zinc Process, Cape Town, South Africa; sulfur (98% soluble in CS_2) AECI, Johannesburg, South Africa; polyisoprene, Afprene IR80, and polybutadiene, Neodene 98% cis-BR, Karbochem, Newcastle, South Africa, who also supplied samples of incompletely dried polybutadiene containing varying amounts of water. (Dma)dmtc was synthesized[12,13] by the addition of carbon disulfide to an aqueous solution of dma at room temperature under continuous stirring. (Dma)dmtc was extracted from the aqueous solution with chloroform, from which solution a white solid was obtained on evaporation. ^{1}H-NMR data in $CDCl_3$ (3.57 ppm, 2.78 ppm) agreed with that of Versloot et al.[13]

When studying mixtures (dma)dmtc was ground together with other curatives using a mor-

tar and pestle to yield homogeneous mixtures. (Dma)dmtc and sulfur were compounded with rubber in a Brabender Plasticorder as described.[14] (Dma)dmtc, mixes of curatives and rubber compounds containing (dma)dmtc were heated at a programmed rate of 5°C/min in sealed and open DSC pans in a standard differential scanning calorimeter DSC10 cell connected to a TA Instruments Thermal Analyst 2000 system and on a Du Pont 915 Thermogravimetric analyzer (TG). The reaction was stopped at various temperatures, the mixture rapidly cooled and analyzed by HPLC.[14,15] Table I lists acronyms used.

RESULTS

Thermal Stability of (dma)dmtc

(Dma)dmtc is reported[13,16] to have a melting point of 125°C, which is just below the temperature region where vulcanization is normally performed. Three endotherms are observed on heating (dma)dmtc in a closed DSC pan at 5°C/min (Fig. 1). The first small peak at about 84°C recurs on reheating, and is attributed to the melting of an unidentified impurity that could not be removed by recrystallization from benzene. On reheating of samples cooled from just above the melting endotherm (peak temperature 140°C) a similar DSC curve to that found on the first heating was obtained, confirming the endotherm to be associated with a reversible process that is ascribed to the melting of (dma)dmtc. The melting of (dma)dmtc is followed by a third endotherm. DSC pans did not seal hermitically, and were found to be empty once samples reached 165°C. On rapidly heating (dma)dmtc in a closed DSC pan to 100°C

Table I Acronyms

| Acronym	Name
CPTD	N,N'-dipentamethylenethiuram disulfide
dma	dimethylamine
(dma)dmtc	dimethylammonium dimethyldithiocarbamate
Hdmtc	dimethyldithiocarbamic acid
Hpmtc	pentamethylenedithiocarbamic acid
(pip)pmtc	pentamethyleneammonium pentamethylenedithiocarbamate
TME	2,3-dimethyl-2-butene
TMTD	tetramethylthiuram disulfide
$Zn_2(dmtc)_4$	zinc dimethyldithiocarbamate
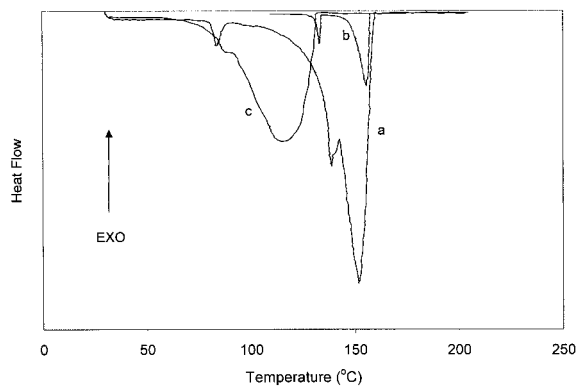
Figure 1 DSC curves of (dma)dmtc heated (a) at 5°C/min in a closed pan, (b) rapidly to 100°C and then at 0.5°C/min in a closed pan, and (c) at 5°C/min in an open pan.

and then at 0.5°C/min, these two endotherms were completely resolved (Fig. 1). The third endotherm is attributed to the evaporation from the closed pans of (dma)dmtc or of its degradation products. TG showed that when (dma)dmtc was not confined to a closed system, heating at 5°C/min in a flow of nitrogen resulted in all of the compound being lost from the TG pan before the melting point is reached (Fig. 2). On heating (dma)dmtc in an open DSC pan at 5°C/min a broad endotherm confirmed the rapid loss of (dma)dmtc without melting (Fig. 1). The shape of the DSC curve obtained on heating (dma)dmtc in open pans suggests that two processes may be involved, viz. sublimation and/or, at higher temperatures, decomposition. Decomposition may in itself involve two stages, viz. decomposition to Hdmtc and dma, which evaporate, or evaporation after the further breakdown of Hdmtc.

$$(Dma)dmtc \rightarrow dma + Hdmtc$$

$$Hdmtc \rightarrow dma + CS_2$$
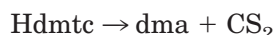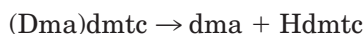
However, TG curves show no change in slope that may be associated with a two-stage process (Fig. 2). Nevertheless, if an alternative mass loss process, for example, decomposition, as opposed to its sublimation, became possible at a higher temperature, this would be indicated by a change in the activation energy of the mass loss process. An increase in the slope of the activation energy plot would indicate the onset of this higher temperature process. Samples of (dma)dmtc were heated in the TG at different heating rates and the activation energy of the mass loss process at different

stages calculated using the method of Flynn and Wall.[17] Figure 3 shows activation energy plots for the mass loss process at different degrees of decomposition or sublimation. Straight line plots, the slopes of which could be identified with the activation energy of the process, were not obtained. However, no increase in slope, indicating the onset of an alternative mass loss reaction commencing above a particular temperature is indicated, and it is concluded that the TG mass loss curves are associated with a single process.

The possibility that moisture present in the nitrogen purge gas could initiate decomposition in an open pan DSC and in the TG balance, was considered. The purge gas input to the TG balance was modified to permit a stream of nitrogen, moisturized by passage through hot water, to impinge directly onto the sample. However, this had no effect on the mass loss curve (Fig. 2).

TG shows that (dma)dmtc can escape from rubber almost as readily as when heated in an open system on its own (cf. Figs. 2 and 4), most of the accelerator having been lost from a polyisoprene (IR) sample by 145°C [4.86 mass % loss, equal to 88% of the (dma)dmtc]. The continued slower mass loss from rubber compounds at higher temperatures (Fig. 4) is probably due to the loss of volatiles (H_2S) formed in the vulcanization process, accelerated by residual (dma)dmtc. In IR/TMTD/sulfur compounds essentially no mass loss (0.06%) is detected prior to the onset of pendent group formation, when a rapid mass loss initiates[18] due to the escape from the open system of Hdmtc and H_2S formed (Fig. 4). When (dma)dmtc is compounded into polybutadiene (BR) containing water (0.5 and 6 mass %) the mass loss (after
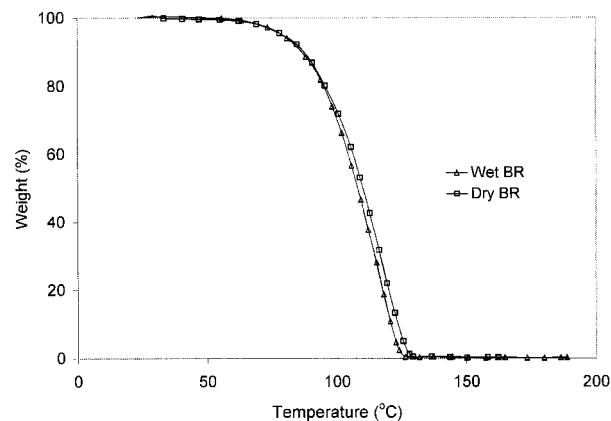

Figure 2 TG of (dma)dmtc heated at 5°C/min in a flow of dry and wet nitrogen.
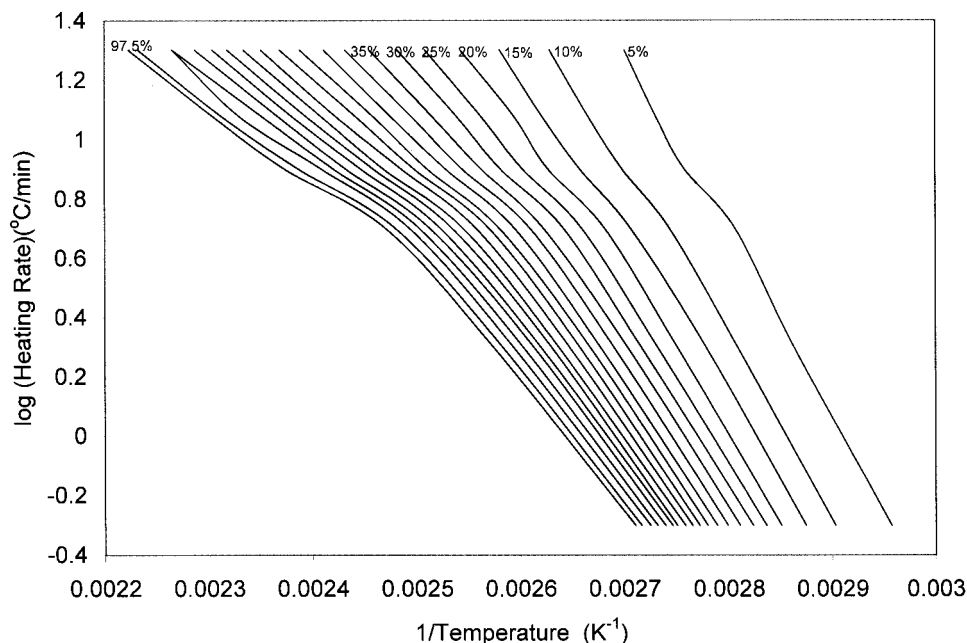
Figure 3 Activation energy plots according to Flynn and Wall[17] for (dma)dmtc at different mass % decomposition.

correcting for the increased loss of water from the wetter samples during heating) is slightly more rapid than from dry polybutadiene (Fig. 5).

Interaction with Curatives

(Dma)dmtc/ZnO

To further investigate the stability of (dma)dmtc its reaction with ZnO to give $Zn_2(dmtc)_4$ was con-

sidered. Mixtures of ZnO and (dma)dmtc of mole ratios 5 : 1 and 1 : 1 were heated in the TG at 5°C/min. Table II shows that the experimentally observed mass loss at equilibrium (200°C) was less than that expected if (dma)dmtc simply sublimed, but greater than that expected if (dma)dmtc fully converted to $Zn_2(dmtc)_4$. X-ray diffraction analysis of the residual mixture after heating showed the presence of ZnO and $Zn_2(dmtc)_4$. Diffraction pat-
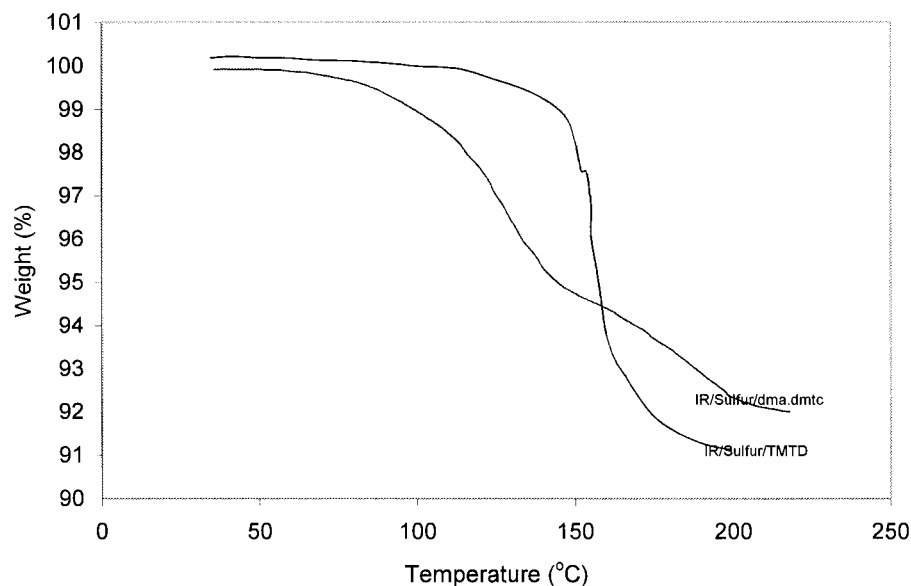

Figure 4 TG curves for polyisoprene/(dma)dmtc(6.15 phr)/sulfur (9.46 phr) and polyisoprene/TMTD(8.86 phr)/sulfur(9.46 phr) heated at 5°C/min.
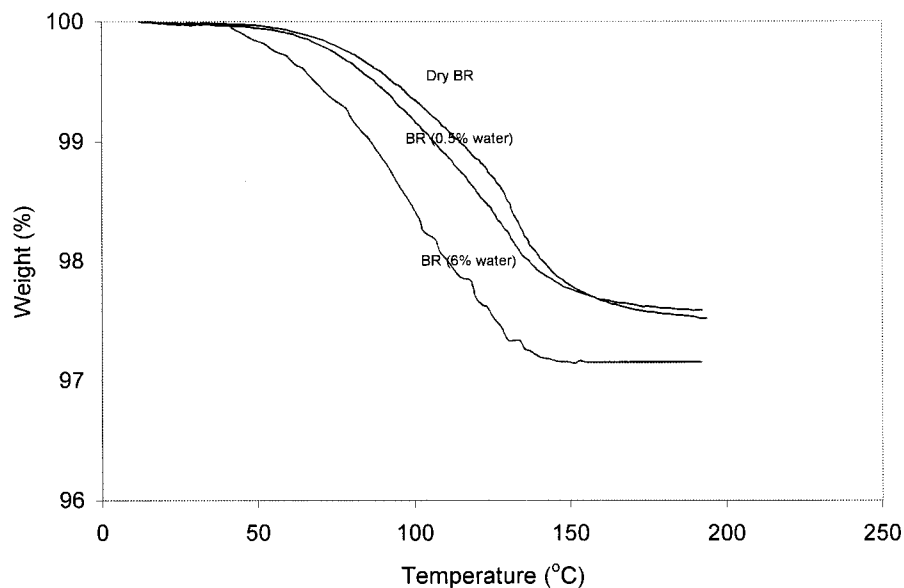
Figure 5 TG curves showing the decrease in the mass of samples due to the loss on heating at 5°C/min of (dma)dmtc from polybutadiene/(dma)dmtc(6.15 phr) containing 0, 0.5 and 6.0 mass % water. These curves were calculated by correcting mass loss curves for samples containing water and (dma)dmtc for the mass loss that occurred in samples containing corresponding amounts of water only.

terns of ZnO and $Zn_2(dmtc)_4$ allowed diffraction peaks at $2\theta = 12.2$ and $15.2°$ in the mixture to be attributed to $Zn_2(dmtc)_4$ and at $2\theta = 32.0$, 34.6, and 36.4° to ZnO. HPLC could not be used for analysis of $Zn_2(dmtc)_4$, as it coelutes with (dma)dmtc. On treatment with $CoCl_2$[19] both compounds convert to Co-$(dmtc)_2$. The incomplete conversion of (dma)dmtc to $Zn_2(dmtc)_4$ is interpreted to imply that limited reaction between ZnO and (dma)dmtc occurred and that the remainder of the (dma)dmtc sublimed. Hdmtc very readily reacts with ZnO[9,20,21] and, if (dma)dmtc decomposed to Hdmtc and dma, most of the Hdmtc should have been tapped with a 5 : 1 mol ratio of ZnO : (dma)dmtc.

(Dma)dmtc/TMTD

The DSC curve obtained on heating an equi-molar mixture of (dma)dmtc and TMTD in a closed pan at 5°C/min showed a melting endotherm peaking at 121°C, lower than when (dma)dmtc (Fig. 1) or TMTD (m.p. 139°C)[22] are heated on their own. The (dma)dmtc evaporation endotherm occurred at 150°C. TG showed a rapid mass loss with all of the (dma)dmtc having been lost from the open system by 110°C (experimental loss, 40.4%, calculated loss 40.9%). The loss from the mix is more rapid than with (dma)dmtc on its own (cf. Fig. 2). HPLC analysis of the system at 120°C showed that some tetramethylthiuram monosulfide had formed. In addition, TMTD, (dma)dmtc, and a small peak, probably due to tetramethylthiuram trisulfide,[23] were detected. There is no evidence of thiourea formation at these temperatures as occurred in the analogous (pip)pmtc/CPTD (N,N'-dipentamethylenethiuram disulfide) system.[11] At 200°C HPLC showed sulfur and large amounts of tetramethylthiourea as expected in terms of the known instability of TMTD above 190°C.[10,11,22–25]

Table II   Mass Loss on Heating (dma)dmtc/ZnO at 5°C/min to 200°C

(Dma)dmtc/ZnO Molar Ratio	Sublimation % Mass Loss	$Zn_2(dmtc)_4$ Formation % Mass Loss	Experimental % Mass Loss
5 : 1	29.01	10.04	16.15
1 : 1	67.14	27.89	41.61

(Dma)dmtc/Zn₂(dmtc)₄

TG showed that in an open system all of the (dma)dmtc had sublimed from an equi-molar mixture of (dma)dmtc and $Zn_2(dmtc)_4$ by 110°C (experimental loss 46.9%, calculated loss 48.45%), slightly earlier than in the absence of $Zn_2(dmtc)_4$ (cf. Fig. 2). The DSC scan of the mixture in a sealed pan at 5°C/min showed a large (dma)dmtc melting peak at 116°C, indicating that the melting point of (dma)dmtc is suppressed by $Zn_2(dmtc)_4$ (cf. Fig. 1). This endotherm is followed by a number of poorly defined peaks attributed to the sporadic escape of (dma)dmtc from the incompletely sealed DSC pans. Rapid evaporation occurred at 150°C. (Dma)dmtc and $Zn_2(dmtc)_4$ coelute in the HPLC, and at all stages of heating a single peak due to these two compounds was the only peak observed. There appears to be little interaction between and $Zn_2(dmtc)_4$.

(Dma)dmtc/sulfur

The DSC scan of an equi-molar mixture of (dma)dmtc and sulfur in a sealed pan at 5°C/min showed endotherms associated with the impurity in (dma)dmtc (81°C), the sulfur solid-solid phase transition (113°C) and melt (118°C),[26] the melting of (dma)dmtc (131°C), and its evaporation above 150°C. TG analysis showed a loss equivalent to all of the (dma)dmtc by 120°C (experimental loss 38.2%, calculated loss 39.3%), the point at which sulfur melted. HPLC analysis of a sample at 200°C revealed sulfur with only a trace of (dma)dmtc. Thus, as in the absence of sulfur, (dma)dmtc is readily lost from open systems on heating. Sulfur evaporated very slowly at higher temperatures. The DSC curve showed no thermal events that could be associated with interaction between (dma)dmtc and sulfur, while HPLC analysis showed no evidence of stable sulfurated products resulting from a reaction between (dma)dmtc and sulfur.

(Dma)dmtc/water

(Dma)dmtc readily dissolves in water, and its dissolution leads to a very marked increase in the electrical conductivity of the solution, indicating ionization of the compound in water. The conductivity of a saturated solution of (dma)dmtc was 8050 μS compared to 42 μS for deionized water.

DISCUSSION

The accelerator appears to be stable at vulcanization temperatures although ready sublimation oc-curs at temperatures well below its melting point (125°C). When the escape of (dma)dmtc from DSC pans is restricted its melting is observed (Fig. 1), which suggests that the loss of material that occurs at lower temperatures from open pans [DSC (Fig. 1) and TG (Fig. 2)] cannot be attributed to decomposition, but must be due to sublimation. Activation energy plots also show no evidence for two mass loss processes (evaporation, followed at higher temperatures by decomposition). The decrease in the slope of the plots at higher temperatures and heating rates (Fig. 3) may be associated with some cooling of the particle surface as a result of the increased amounts of latent heat of sublimation required to sustain the more rapid sublimation of (dma)dmtc that occurs at increased temperatures, i.e., the particle surface temperature is slightly lower than the recorded temperature, the difference increasing with temperature, and heating rate. The decrease in slope becomes more marked in the curves where the sample has suffered a higher degree of mass loss, which is consistent with a larger particle surface to volume ratio applicable to small particles where the surface cooling effect would be more marked.

Moisture does not influence the rate of mass loss in TG experiments (Fig. 2), indicating that it does not promote degradation of (dma)dmtc. The accelerator is equally readily volatilized from heated compounds not enclosed in a mold (Figs. 4 and 5). Because water does not appear to promote decomposition of (dma)dmtc when heated in a TG in a stream of moist nitrogen (Fig. 2), the small increase in the rate of mass loss that occurs on heating polybutadiene compounds containing varying amounts of water (Fig. 5) must be ascribed to the plasticizing effect of water in the rubber facilitating the escape of (dma)dmtc.

The accelerator is unreactive towards TMTD and $Zn_2(dmtc)_4$. Amines are known to accelerate the decomposition of tetramethylalkylthiuram disulfides to thioureas and a catalytic mechanism (Scheme 1)[10] has been proposed to account for the rapid decomposition in closed systems, where the amine remains trapped. On heating a (pip)pmtc/CPTD mixture the rapid formation of N,N′-dipentamethylenethiourea was ascribed to the decomposition of (pip)pmtc and the piperidine catalyzed decomposition of CPTD.[11] An analogous reaction was not found on heating (dma)dmtc/TMTD, the formation of tetramethylthiourea being detected only at 200°C. The absence of thiourea at vulcanization temperatures reinforces the contention that

(dma)dmtc is thermally stable. It should be noted that the stability of (dma)dmtc is at variance with details of the catalytic mechanism proposed for thiourea formation in TMTD.[10] The proposed mechanism (Scheme 1)[10] suggests attack on TMTD by dma with the formation of tetramethylthiourea and sulfurated Hdmtc. Reaction of the latter with dma liberates the excess sulfur and (dma)dmtc is reformed. The scheme suggests that (dma)dmtc is unstable and decomposes to CS_2 and dma, which initiates further attack on TMTD. However, in view of the demonstrated stability of (dma)dmtc, the rapid liberation of the excess sulfur by sulfurated Hdmtc and the slow decomposition of Hdmtc to dma and CS_2, as suggested by Reyneke-Barnard et al.,[11] appears a more feasible route. TMTD rapidly forms tetramethylthiourea in systems where Hdmtc is liberated, for example, on heating TMTD/mercaptobenzothiazole to vulcanization temperatures in a closed as opposed to an open system.[15,27] In open systems, from which the escape of Hdmtc is possible, no thiourea forms.

Limited reaction occurs on heating with ZnO, though the formation of $Zn_2(dmtc)_4$ at the ZnO particle surface may restrict the extent to which reaction can occur. Bedford and Gray[8] reported that (dma)dmtc reacted with ZnO in a solvent to form $Zn_2(dmtc)_4$, amine and water, while Versloot et al.[9] demonstrated reaction between (dma)dmtc and ZnO in CD_3Cl at room temperature. As with $Zn_2(dmtc)_4$, neither DSC[22] nor HPLC analysis[13,28] show evidence for the formation of stable accelerator polysulfides on heating (dma)dmtc with cyclic sulfur.

CONCLUSIONS

(Dma)dmtc is volatile but thermally stable at vulcanization temperatures, and sublimation occurs without decomposition. It can, therefore, be expected that (dma)dmtc per se will act as accelerator in vulcanization reactions, and not products resulting from its thermal decomposition. Unlike with the analogous (pip)pmtc/CPTD system thiourea is not formed, confirming the stability of (dma)dmtc. In the melt reaction with ZnO is restricted by the formation of $Zn_2(dmtc)_4$ at the ZnO particle surface.

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