The Effect of Carbon Black on Tetramethylthiuram Disulfide Accelerator Sulfur Vulcanization of Polyisoprene

W.J. MCGILL* and S.R. SHELVER

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

SYNOPSIS

Polyisoprene was vulcanized with the tetramethylthiuram disulfide/sulfur/ZnO system in the presence and absence of N330 carbon black. Crosslinking was carried out in a DSC at a programmed heating rate, the reaction stopped at points along the thermal curve, and the system analyzed. Residual curatives and reaction intermediates were determined by HPLC and crosslink densities by swelling in benzene. Combinations of the powdered curatives were also heated with and without carbon black and analyzed. It is shown that the step in the vulcanization sequence, influenced by carbon black, is the formation of tetramethylthiuram polysulfides that act as the active sulfurating agent in vulcanization. Carbon black catalyzes their formation, and to a lesser extent, the formation of accelerator terminated polysulfidic pendent groups on the chain. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that carbon black reduces the scorch time and increases the rate of crosslinking in the accelerated sulfur vulcanization of rubbers.[1,2] Carbon black increases the apparent crosslink density as evidenced by its restriction on the swelling of the vulcanizate in a solvent. However, straight line plots of the Kraus equation[3] obtained with filled compounds show that, in many vulcanizates, the true crosslink densities are unaffected by the addition of carbon black to the compound. This does not apply in all cases; Porter[4] showed that in a 2-mercaptobenzothiazole accelerated natural rubber compound carbon black increased the maximum crosslink density by 25% while Pal, Bhomwick, and De[5] reported a 20% increase in crosslink density in a compound that they studied. In addition to their having a large surface area with which the rubber and curatives may interact, carbon blacks have a high surface reactivity occasioned by a variety of reactive oxygen-containing groups.[3,6,7,8]

DSC studies of the interaction of tetramethylthiuram disulfide (TMTD), sulfur, and ZnO in the

absence of rubber[9,10] as well as the vulcanization of polyisoprene (IR) accelerated by TMTD[11,12] have been reported. This article seeks to identify the step in the vulcanization reaction sequence that is accelerated by carbon black. To allow direct comparison with earlier work, done in the absence of carbon black, vulcanization was conducted at a programmed heating rate in a DSC.

EXPERIMENTAL

Materials

Materials were: cis-1,4-Polyisoprene (Afprene, Karbochem S.A., 97% cis-), sulfur (Holpro Analytics Ltd, 99.94% purity), tetramethylthiuram disulfide (Orac TMTD, Orchem S.A.), ZnO (Zinc Process, S.A.), bis(dimethyldithiocarbamato)zinc(II) (Vulcazit L, Bayer S.A.), and carbon black (N330 HAF, Algorax (Pty) Ltd, S.A.)

The compounds were mixed in a Brabender Plasticorder filled with a W30 type head of 30 mL capacity using a fill factor of 0.85. To prevent reaction during compounding, the head temperature was kept below 50°C by circulating chilled water. All the rubber was added to the mixing head and masticated at 40 rpm for 6 min prior to the addition of carbon black and curatives. Mixing continued for a further

6 min at 40 rpm. On removal from the mixer, the compound was passed through the mill 5 times, each time being folded once.

DSC experiments were performed using a Du Pont 910 standard DSC cell and module connected to a Du Pont 9000 Thermal Analyser. Nitrogen, at a flow rate of 80 mL/min, was used as purge gas. Samples (10 mg) were sealed in aluminium pans, with an empty pan being used as reference sample. To follow the progress of the reaction, samples were heated at 2.5°C/min and the reaction stopped at points along the thermogram by opening the cell and rapidly removing and cooling the sample. To determine the crosslink density of these samples, they were swollen in benzene for 48 h, weighed, deswollen, and reweighed. Crosslink densities were calculated using the Flory–Rehner equation.[13] The filler will restrict swelling in the vicinity of the particles, leading to a higher volume fraction of rubber in the swollen vulcanizate (V_r). V_r values were converted to V_{r0} values (volume fraction that would apply in the absence the restricting influence of the filler) using the equation derived by Pal, Bhomwick, and De.[5]

$$V_{r0}/V_r = 0.56 \exp(-z) + 0.44$$

where z is the mass fraction of carbon black in the filled vulcanizate. The percentage polysulfidic crosslinks was determined with a $0.4M$ propane-2-thiol-piperidine chemical probe in n-heptane, which cleaves di(2-alkenyl) polysufidic crosslinks.[14]

Extractable curatives in these samples were determined by HPLC. The benzene used to extract the uncrosslinked rubber in the swelling experiments also extracts the curatives and reaction intermediates not bound to the rubber. The benzene was allowed to evaporate, depositing a thin film of uncrosslinked rubber over the surface of the pill vial. The curatives and reactive intermediates were reextracted from the rubber film for 48 h in the dark, using analytical grade methanol, the methanol being replaced after 24 h. These methanol solutions were made up to 100 mL with pure methanol for HPLC analysis.

Crosslinked samples were extracted for 48 h, the benzene evaporated, and the precipitated curatives redissolved in methanol. Powdered samples of curatives studied in the absence of IR were likewise heated to various temperatures, weighed on a microbalance, dissolved in a small amount of dichloromethane, and made up to 50 mL using pure methanol.

A Waters HPLC system comprising of a Model 510 pump and a Model 484 Tunable Absorbance Ultraviolet (UV) detector was used. This was connected to a Baseline 810 Chromatography Workstation via a WD22 Chromatography Interface. Separation was affected on micro-Bondapak C18 reverse phase radial-Pak column (Waters, 8 mm × 100 mm, particle size 10 μm) contained in a Waters Radial Compression Module (RCM) 8 × 10 mm. The column temperature was maintained at 30°C and the UV detector set at a wavelength of 280 nm. Methanol (100%) was used as the mobile phase at a flow rate of 1.0 mL/min.

Peak identification of tetramethylthiuram monosulfide (TMTM), TMTD, bis(dimethyldithiocarbamato)zinc(II) ($Zn_2(dmtc)_4$), and sulfur was done by injecting pure samples dissolved in methanol. Data by Geyser and McGill[15] was used for peak identification in the case of tetramethylthiuram polysulfides (TMTP). The concentrations of reactants and soluble products are expressed in terms of the mole percentage remaining, or of the total that could have formed if 100% of the reactants were converted to that product. Approximate molar absorbtivities as calculated by Geyser and McGill[15] were used for TMTP.

Cure curves for the compounds were obtained on a Monsanto MDR 200 oscillating disc rheometer at 140°C.

RESULTS

Rheometer Cure Curves

Table I contains data extracted from the rheometer cure curves for different compounds. Carbon black can be seen to decrease the scorch time and to increase the rate of vulcanization in all cases.

Crosslink Density

Figure 1 shows that crosslinking commenced at lower temperatures in the filled than in the unfilled samples. Rapid reversion set in at higher temperatures but, with each of the three formulations, the maximum crosslink density prior to reversion was independent of the presence of carbon black. This correlates well with the results obtained by Porter[4] and Kraus[3] that the number of chemically formed sulfur crosslinks formed are not influenced by the presence of filler. Clearly, carbon black accelerates the crosslinking reaction but does not increase the overall crosslink density, i.e., it acts as a catalyst for the reaction.

Table I Analysis of Rheometer Cure Curves Obtained at 140°C

IR Compounded With	Scorch Time Taken at 10% Cure (min)	Time to 50% Cure (min)	Time to 90% Cure (min)	Torque at 90% Cure (dN · m)
TMTD	4.20	6.29	7.59	3.39
TMTD + CB	2.42	4.09	5.33	8.85
TMTD + S	2.03	3.51	5.30	3.73
TMTD + S + CB	1.07	2.45	3.21	9.61
TMTD + S + ZnO	2.20	3.04	3.78	12.77
TMTD + S + ZnO + CB	0.31	0.52	1.30	25.43
ZDMC + S	1.33	2.15	4.03	8.45
ZDMC + S + CB	0.40	1.22	3.44	23.22

CB = carbon black.

Initially, all crosslinks are polysulfidic, and the change in the percentage of polysulfidic crosslinks at higher temperatures shows little difference between the filled and unfilled mixtures (Fig. 2). This is in accordance to carbon black having purely a catalytic effect on sulfur vulcanization, the nature of the reactions involved essentially remaining the same for filled and unfilled IR samples.

Curative Interactions in Absence of Rubber

To establish the effects of carbon black on the interactions of curatives themselves, analyses were done on mixes of curatives with carbon black, but no IR.

TMTD/Sulfur

In DSC scans of TMTD/sulfur, three endothermic peaks are observed (Fig. 3). The first, initiating at

109.5°C, is due to a sulfur solid-solid phase transition, the second peaking at 115°C is due to the sulfur melting,[9] and the third is due to TMTD dissolving in the molten sulfur and interacting to form TMTP.[10] With carbon black, only two peaks are resolved, the first commencing at 106°C is due to the solid-solid phase transition, and the second due to the sulfur melting and immediately interacting with the TMTD.

TMTP3 (TMTD plus one sulfur atom) and TMTP4 are formed in higher concentrations than any of the other TMTP [Fig. 4(a)]. This accords with the findings of Geyser and McGill[15] who studied the isothermal reaction between TMTD and sulfur at 130 and 150°C. They showed that TMTPs are sulfurated by the successive addition of sulfur atoms and not by the incorporation of S_8. Thus, higher TMTPs are slower to form, and the delay in the appearance of the higher order TMTPs (TMTP6–TMTP10) is highlighted by the dynamic heating
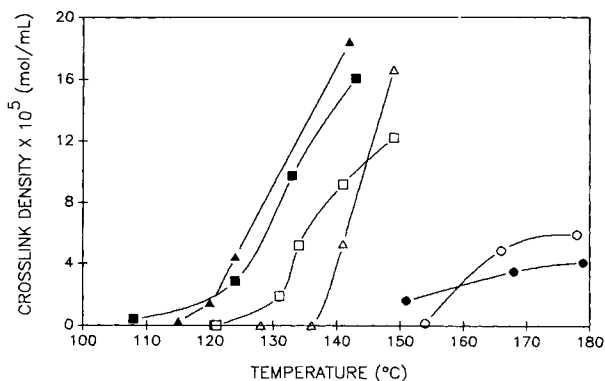

Figure 1 Crosslink density for IR/TMTD/sulfur (O), IR/TMTD/sulfur/ZnO (△), and IR/Zn₂(dmtc)₄/sulfur (□) compounds with (filled symbols) and without (open symbols) carbon black, heated to various temperatures in the DSC.
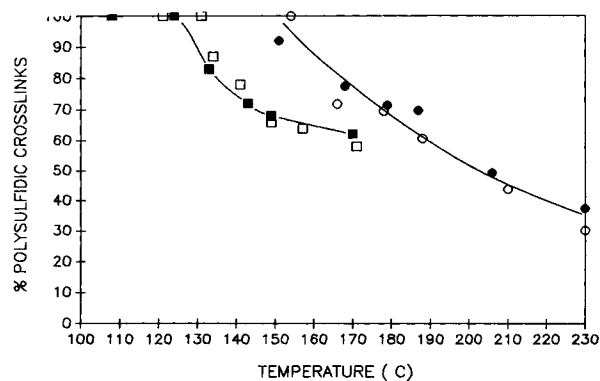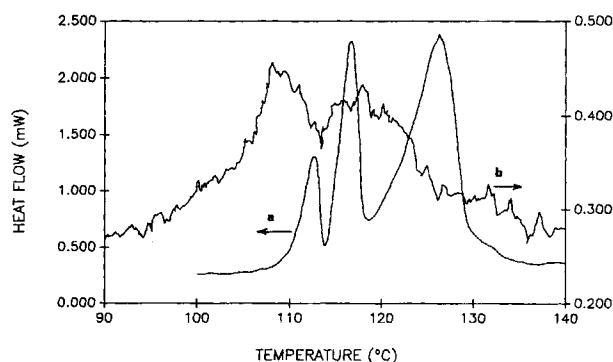

Figure 2 Percentage polysulfidic crosslinks for IR/ TMTD/sulfur (O) and IR/Zn₂(dmtc)₄/sulfur (□) compounds with (filled symbols) and without (open symbols) carbon black, heated to various temperatures in the DSC.

Figure 3   DSC curve for a TMTD/sulfur mixture heated at 2.5°C/min (a) without and (b) with carbon black.

program used in this work. In the presence of carbon black TMTP formation is very rapid, and a similar delay in the formation of the higher TMTPs is not observed [Fig. 4(b)].

The role of carbon black is purely that of a catalyst, as is evident by the concentration of the various species reaching similar equilibrium values. In some cases, concentrations are slightly lower in the presence of carbon black, and this may be due to their adsorption onto the carbon black surface. As is well known, carbon blacks have surface areas of the order of magnitude of 100 m²/g. That of N330 HAF is given[17] as 82 m²/g.

TMTD/Sulfur/ZnO

TMTD and ZnO do not interact[10] in the absence of rubber, and on heating a TMTD/sulfur/ZnO mixture in the absence of carbon black, three endothermic events are again resolvable, the sulfur α-β solid-solid phase transition, the melting of sulfur and of TMTD and interaction of the latter with the molten sulfur to form TMTPs. The latter peak is at 128°C. In the presence of carbon black all three events are coalesced into one endotherm with its peak at 113°C. Figure 5 shows that the amounts of residual sulfur and TMTD in the mix decrease at much lower temperatures in carbon black-filled samples. TMTPs form correspondingly earlier. Figures 6(a) and (b) show that carbon black catalyzes the formation of all TMTPs.

It is interesting to note that, in the absence of rubber, no $Zn_2(dmtc)_4$ is produced. This correlates with the mechanism of thiuram-accelerated sulfur vulcanization suggested by Kruger and McGill[10,16] where Hdmtc is liberated as a by-product in the formation of pendent groups via TMTP. Hdmtc spontaneously reacts with ZnO to form $Zn_2(dmtc)_4$.
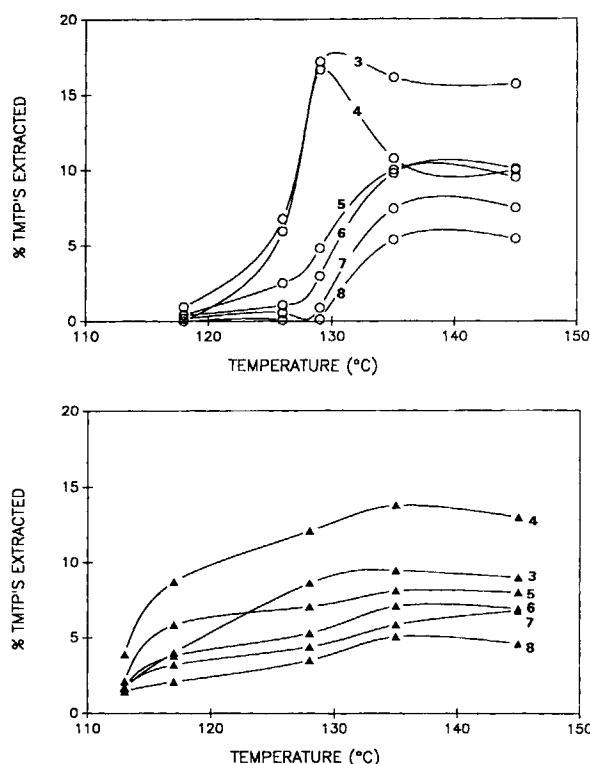

Figure 4   Percentage TMTPs extracted from a TMTD/sulfur mixture heated to different temperatures in the DSC, (a) without and (b) with carbon black. Numerals reflect the number of sulfide sulfur atoms in each TMTP.

Curative Interactions in Rubber

IR/Sulfur

The DSC curve for an IR/S compound, cured at 2.5°C/min, was similar to curves for IR/S compounds reported by Kruger and McGill.[11] The ad-
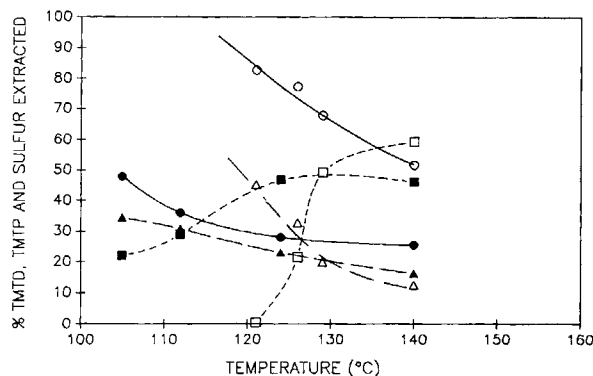

Figure 5   Percentage TMTD ($\triangle$), TMTP ($\square$) and sulfur ($\bigcirc$) extracted from a TMTD/sulfur/ZnO mixture heated to various temperatures in the DSC with (filled symbols) and without (open symbols) carbon black.
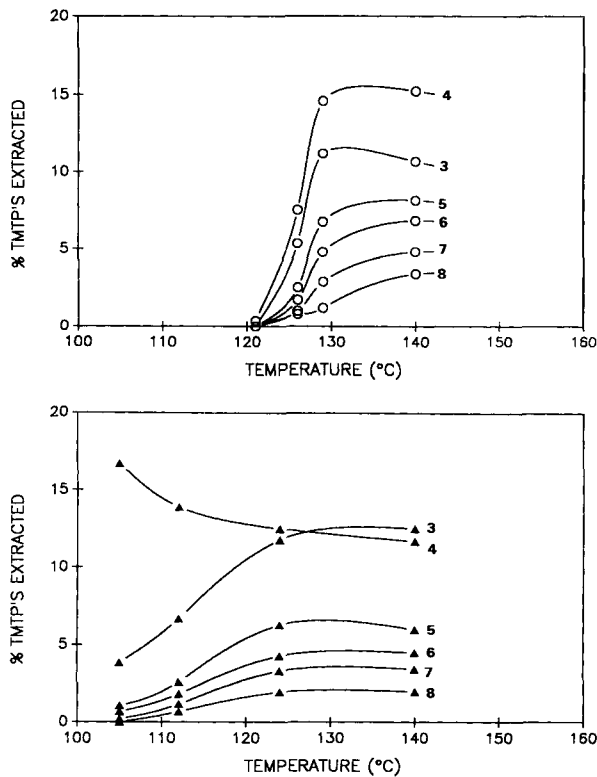
Figure 6 Percentage TMTPs extracted from a TMTD/ sulfur/ZnO mixture heated to different temperatures in the DSC (a) without and (b) with carbon black. Numerals reflect the number of sulfide sulfur atoms in each TMTP.

dition of carbon black did not in anyway shift the position of the vulcanization exotherm.

IR/TMTD

The DSC curves of IR with TMTD only are not well defined, but a comparison of such curves with and without carbon black (Fig. 7) run at 2.5°C/min,
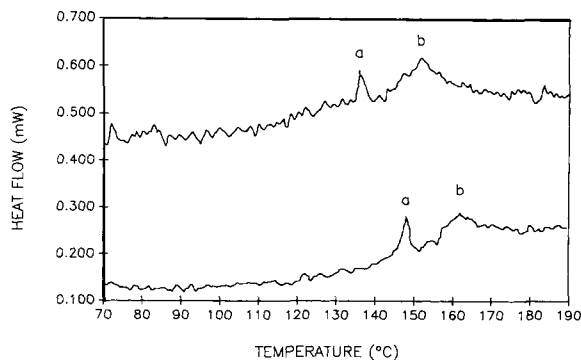

Figure 7 DSC curves for a IR/TMTD compounds heated at 2.5°C/min with (upper curve) and without (lower curve) carbon black. (a) TMTD melt endotherm and (b) onset of broad vulcanization exotherm.[11]
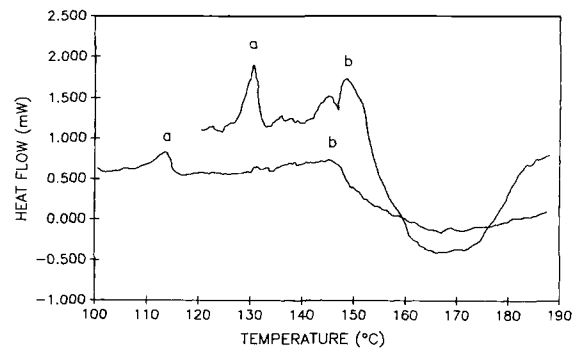

Figure 8 DSC curve for a IR/TMTD/sulfur compound heated at 2.5°C/min without (upper curve) and with (lower curve) carbon black. (a) TMTD/sulfur interaction, (b) onset of vulcanization.

shows that the TMTD melt-reaction endotherm shifts from 147 to 136°C upon addition of carbon black. This endotherm is associated with the formation of TMTM and TMTP the moment TMTD melts.[18] The position of the vulcanization exotherm, relative to the melt endotherm, appears to be essentially uneffected, i.e., both the melting and cross-linking events shifted by about 10°C.

IR/TMTD/Sulfur

DSC curves of IR/TMTD/S with and without carbon black (Fig. 8) show that the peak temperature of the endotherm associated with the melting and interaction of TMTD/sulfur, to form the activated sulfurating complex, TMTP, is shifted from 132°C to 115°C by the presence of the filler. Vulcanization commences at 151 and 145°C in the presence and absence of carbon black, respectively.

HPLC analysis of the percentage sulfur and accelerator remaining unreacted is shown in Figure 9. At 152°C in the filled samples the sulfur and accel-
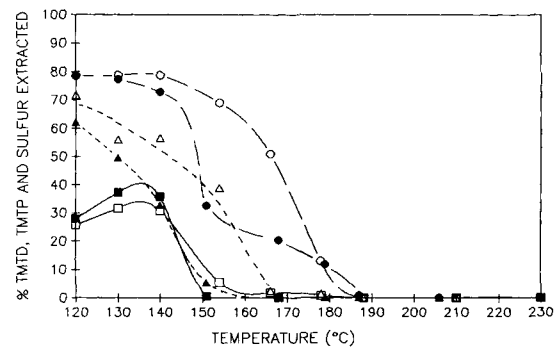

Figure 9 Percentage TMTD (△), TMTP (□) and sulfur (○) extracted from a IR/TMTD/sulfur compound heated to various temperatures in the DSC with (filled symbols) and without (open symbols) carbon black.
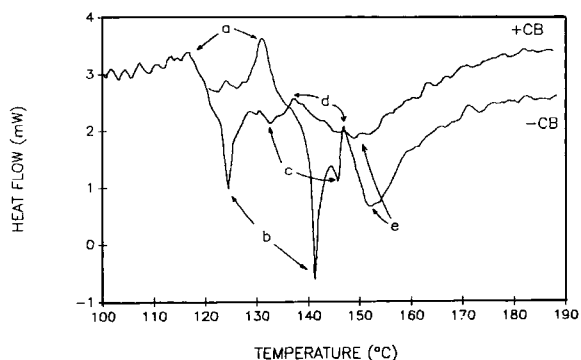
Figure 10 DSC curve for a IR/TMTD/sulfur/ZnO compound heated at 2.5°C/min with and without carbon black. (Corresponding thermal events are indicated by a, b, c, d.)

erator are practically consumed, whereas in the unfilled sample, the curatives are still present in high concentrations. Initially, the concentration of TMTP is higher in the filled compound, but as TMTP is highly reactive in the presence of IR, its concentration drops (Fig. 9) as it adds to the chain to form pendent groups.[11] The more rapid decrease in TMTP concentration shows that carbon black also activates pendent group formation. By 152°C (the onset of crosslinking), all the TMTP in the filled compound has been converted to polysulfidic pendent groups, whereas in the unfilled sample, 10% TMTP still has to be converted into pendent groups.

IR/TMTD/Sulfur/ZnO

The DSC curve of the IR/TMTD/sulfur/ZnO system (Fig. 10) is similar to that reported by Kruger and McGill,[12] who interpreted the curve as follows. The initial endotherm is attributed to the TMTD/ sulfur interaction, and this is followed by the vulcanization exotherm commencing at about 135°C. Hdmtc, which is a by-product of crosslinking, reacts with ZnO to form $Zn_2(dmtc)_4$. As $Zn_2(dmtc)_4$ has a low solubility in IR, it crystallizes from the rubber, and the sharp exotherm, superimposed on the vulcanization exotherm, is attributed to this process. This is followed by furthur less clearly characterized vulcanization events. The point where vulcanization commences is not well defined on the curve but TG curves of Kruger and McGill[12] and crosslink density measurements show that it occurs just before the shoulder prior to the steeply rising exotherm. The addition of carbon black does not change the general features of the DSC curve but merely shifts the temperatures at which events occur. The TMTD melt-reaction endotherm is very poorly defined (Fig. 10),

and crosslink density measurements show that vulcanization occurs at 104°C on heating at 2.5°C/min, i.e., immediately after the TMTD-sulfur melt-reaction endotherm, there being no delay. Figure 11 reveals the reasons for this phenomenon. By 115°C, 90% of the accelerator (TMTD) has already reacted with sulfur to form TMTP, which readily reacts with IR to form polysulfidic pendent groups. By contrast, at 128°C (the onset of crosslinking for the unfilled sample), only 39% of the TMTD has reacted in the unfilled sample. Carbon black not only catalyzes the reaction of TMTD with sulfur to form polysulfidic pendent groups, but also promotes the formation of polysulfidic pendent groups. In the filled sample, the TMTP concentration is only 5% at 115°C and readily drops to zero while in the unfilled sample, the TMTP concentration increases to 25% before decreasing as a result of its addition to the polymer chain. HPLC analysis shows the formation of $Zn_2(dmtc)_4$, coincident with the sharp exotherm in the DSC curve (Fig. 10) at the onset of crosslinking.

IR/Zn₂(dmtc)₄/Sulfur

The percentage $Zn_2(dmtc)_4$ and sulfur extracted shows that, for the filled sample, the $Zn_2(dmtc)_4$ starts to react about 12°C earlier than in the unfilled sample (Fig. 12), although the sulfur decrease is only slightly advanced in the filled sample. No polysulfides of TMTD were observed in either system. Carbon black has a greater effect on the IR/TMTD/ sulfur/ZnO vulcanization than a IR/Zn₂(dmtc)₄/ sulfur reaction as is observed from Table I, where the former mixture has a slightly shorter scorch time but the rate of the vulcanization reaction is nearly three times faster than the filled $Zn_2(dmtc)_4$ mixture. The unfilled $Zn_2(dmtc)_4$ mixture has a scorch
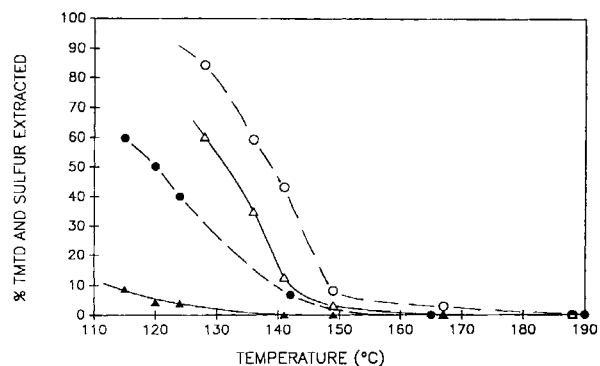

Figure 11 Percentage TMTD (△) and sulfur (○) extracted from a IR/TMTD/sulfur/ZnO compound heated to various temperatures in the DSC with (filled symbols) and without (open symbols) carbon black.

Figure 12 Percentage $Zn_2(dmtc)_4$ (△) and TMTP (□) extracted from a IR/TMTD/sulfur/ZnO compound heated to various temperatures in the DSC with (filled symbols) and without (open symbols) carbon black.
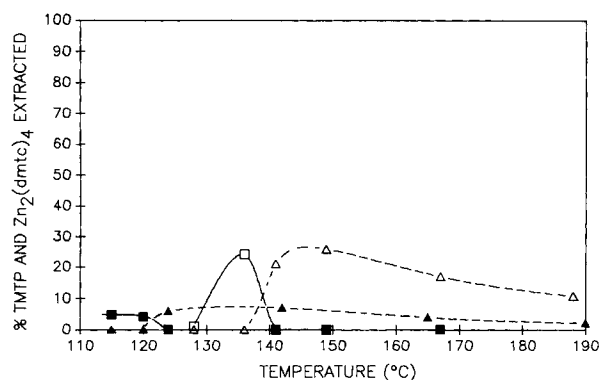
time almost half that of the IR/TMTD/sulfur/ZnO unfilled mixture, and the rates of the vulcanization reaction are very similar.

Comparison of the HPLC extraction results for the mixtures of IR/TMTD/sulfur/ZnO and IR/$Zn_2(dmtc)_4$/sulfur (Figs. 11 and 12) show that carbon black has a greater affect on the reactivity of TMTD with sulfur than on the reactivity of $Zn_2(dmtc)_4$ with sulfur. At the onset of the vulcanization reaction, 90% of the TMTD has already been sulfurated, whereas the $Zn_2(dmtc)_4$ from the IR/$Zn_2(dmtc)_4$/sulfur mixture is still unreacted at the onset of crosslinking. No TMTPs were detected at any stage of the reaction.

DISCUSSION

It is clear that carbon black has a twofold effect on TMTD accelerated sulfur vulcanization. Rheometer curves show that (1) it reduces the scorch period, i.e., it accelerates the reactions prior to crosslink formation, and (2) it increases the rate of the actual crosslinking process. While on heating at 2.5°C/min the position of the vulcanization exotherm in the IR/TMTD/sulfur system is only slightly changed, the lowering by carbon black of the temperatures at which the TMTD/sulfur interaction and the onset of the vulcanization exotherm occur in the IR/TMTD and the IR/TMTD/sulfur/ZnO systems are very clear. Swelling experiments show that the maximum crosslink densities of the vulcanizate and the proportion of polysulfidic crosslinks formed are of the same order of magnitude, both in the presence and absence of the filler. All of the above indicate that the effect that carbon black has on the thiuram accelerated sulfur vulcanization is purely catalytic.

TMTD accelerated vulcanization is initiated via polysulfidic accelerator-terminated pendent groups formed when a polysulfidic form of the accelerator reacts with the polymer chain.[11,12] HPLC analysis shows that, in the absence of rubber, the major effect of carbon black is to facilitate the formation of TMTPs. The decomposition of TMTD is normally relatively slow.[19] However, the promotion of TMTD decomposition by carbon black would result in a high concentration of species that can participate in the exchange reaction,[15] leading to a much more rapid formation of TMTPs. The nature of the species on the carbon black surface responsible for the catalytic effect is not known and would require the study of a variety of carbon blacks with different surface characteristics.[3,6-8]

In the presence of IR, high concentrations of TMTPs likewise form at lower temperatures in carbon black-filled compounds. Furthermore, while TMTP concentrations build up more rapidly in the presence of carbon black, they also decrease more rapidly, i.e., pendent group formation is more rapid. In TMTD-containing mixes crosslinking involves reaction between pendent groups,[20] and this exchange, too, is accelerated by carbon black.

In TMTD compounds containing ZnO, crosslinking is also initiated via polysulfidic pendent groups[10] and, hence, the scorch period is likewise greatly reduced.

The $Zn_2(dmtc)_4$ accelerated reaction is also catalyzed by carbon black. Through sulfurated complexes of $Zn_2(dmtc)_4$ are commonly considered to form during vulcanization, they have never been isolated, and how carbon black would influence this reaction is not clear.

CONCLUSION

Polysulfides of TMTD are the active sulfurating agent in TMTD accelerated sulfur vulcanization. Carbon black does not in any way change the mechanism of the reaction, but its role in reducing the scorch time and increasing the rate of crosslink formation can be identified with it catalyzing the formation of these polysulfides. To a lesser extent, it also increases the rate of accelerator terminated polysulfidic pendent group formation.

REFERENCES

1. B. B. Boonstra, *Rubber Technology and Manufacture,* C. M. Blow, Ed. Newnes–Butterworth, London, 1971, Chap. 7.
2. M. L. Studebaker, *Reinforcement of Elastomers,* G. Kraus, Ed., Interscience Publishers, London, 1965, Chap. 12.
3. G. Kraus, *Reinforcement of Elastomers,* G. Kraus, Ed., Interscience Publishers, London, 1965, Chap. 4.
4. M. Porter, *Rubber Chem. Technol.,* **40,** 866 (1967).
5. P. K. Pal, A. K. Bhowmick, and S. K. De, *Rubber Chem. Technol.,* **55,** 23 (1982).
6. N. Tsubokawa, *Prog. Polym. Sci.,* **17,** 417 (1992).
7. D. Riven, *Rubber Chem. Technol.,* **36,** 729 (1963).
8. R. L. Collins, M. D. Bell, and G. Kraus, *J. Appl. Physiol.,* **30,** 56 (1959).
9. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **42,** 2643 (1991).
10. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **42,** 2669 (1991).
11. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **44,** 587 (1992).
12. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **45,** 1545 (1992).
13. P. J. Flory and J. Rehner, *J. Chem. Phys.,* **11,** 512 (1943).
14. B. Saville and A. A. Watson, *Rubber Chem. Technol.,* **40,** 100 (1967).
15. M. Geyser and W. J. McGill, *J. Appl. Polym. Sci.,* **55,** 215 (1995).
16. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **45,** 749 (1992).
17. Algorax (Pty) Ltd. South Africa, Product specification data sheet.
18. F. W. H. Kruger and W. J. McGill, *J. Appl. Polym. Sci.,* **42,** 2661 (1991).
19. G. A. Blokh, *Rubber Chem. Technol.,* **33,** 1005 (1960).
20. P. Versloot, J. G. Haasnoot, J. Reedijk, M. van Duin, E. F. J. Duynstee, and J. Put, *Rubber Chem. Technol.,* **67**(2), 252 (1994).