

Tetramethylthiuram Disulfide and 2-Mercaptobenzothiazole as Binary Accelerators in Sulfur Vulcanization. IV. Vulcanization of Polyisoprene in the Presence of ZnO

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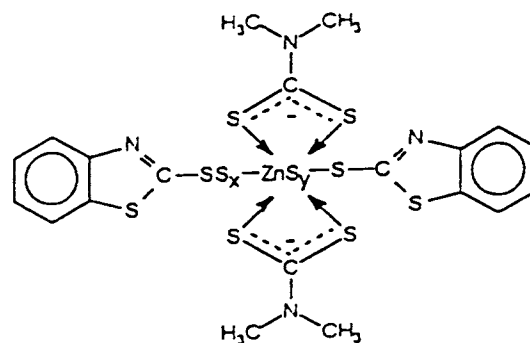
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SYNOPSIS

Polyisoprene was vulcanized with binary accelerator systems comprising mixtures of the zinc salts of tetramethylthiuram disulfide (TMTD) and 2-mercaptobenzothiazole (MBT). Samples were heated in a DSC at a programmed rate, the reaction was stopped at points along the thermal curve, and the system was analyzed. Extractable curatives and reaction intermediates were analyzed by HPLC and the crosslink density of samples measured by swelling. DSC curves for the different systems displayed similar characteristics and their similarity to the curve obtained with the zinc salt of TMTD rather than to the curve obtained with the zinc salt of MBT suggested that the reaction was dominated by the former accelerator. This conclusion was supported by HPLC analyses of extractable curatives. A reaction mechanism for the binary system is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In a previous article,¹ we reported on the vulcanization of polyisoprene (IR) by the binary accelerator system tetramethylthiuram disulfide (TMTD)-2-mercaptobenzothiazole (MBT) in the absence of ZnO. However, most binary accelerator systems have been studied in the presence of ZnO, the greatest synergistic effect in the TMTD-MBT system² occurring at a mol ratio of 1.0/1.315. It has been reported^{3,4} that two-thirds of the TMTD is converted to bis(dimethyldithiocarbamato)zinc(II) [$Zn_2(dmtc)_4$] in the early stages of the reaction [i.e., the $Zn_2(dmtc)_4$ /MBT ratio is 0.67 : 1.315]. In the early stages, MBT and ZnO will also react to form bis(2-mercaptobenzothiazolo)zinc(II) [$Zn(mbt)_2$], and since 2 mol of MBT are involved in forming $Zn(mbt)_2$, the greatest activation coincides with the formation of a $Zn(mbt)_2(dmtc)_2$ complex (I) in which the TMTD/MBT ratio becomes 1 : 1. The authors² argued that this provides evidence for complex I.



Complex I

To explain the TMTD activation of MBT, it was suggested that the $Zn_2(dmtc)_4$ anion ligand will weaken the bond between zinc and the BtS_{x-} groups. Duchacek⁵ found that the scorch time of a TMTD-MBT system reached a maximum at a $Zn_2(dmtc)_4/Zn(mbt)_2$ ratio of 1 : 1 and also concluded that complex I formed. Skinner and Watson⁶ reported synergism in TMTD-MBT and 2-bisbenzothiazole-2'-2'-monosulfide (MBTM)-2-bisbenzothiazole-2,2'-disulfide (MBTS) systems. Pal et al.^{7,8} subscribed to the view that synergism occurs via more reactive intermediates.

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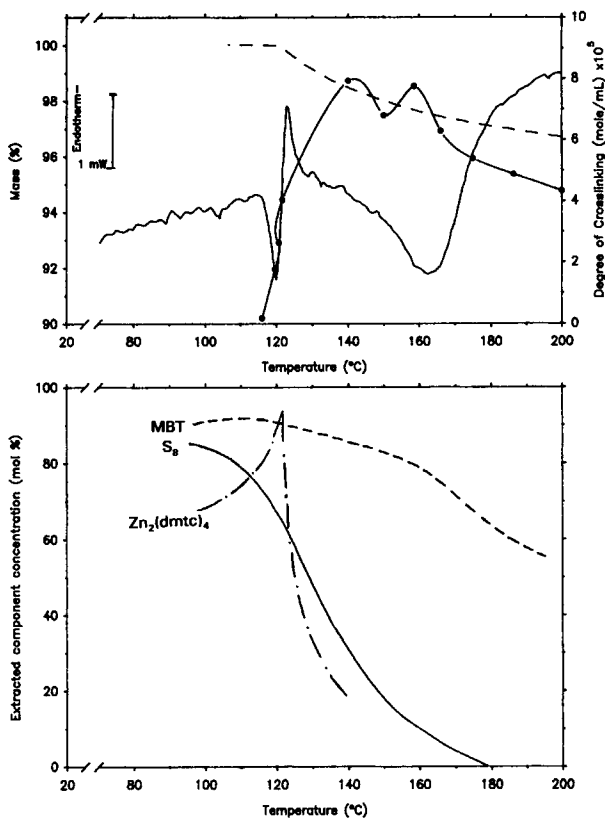


Figure 1 Upper figure: (—) DSC; (---) TG; (-·-) degree of crosslinking. Lower figure: HPLC analysis of IR- $\text{Zn}_2(\text{dmtc})_4$ (0.33)-MBT (0.67)-sulfur (1) heated at 2.5°C/min.

This article reports on the vulcanization of IR by the binary accelerator system TMTD-MBT in the presence of ZnO. Exchange reactions between these accelerators and their zinc complexes in the absence of rubber have been described.⁹

EXPERIMENTAL

Materials

Bis(dimethyldithiocarbamato)zinc(II) [$\text{Zn}_2(\text{dmtc})_4$] and bis(2-mercaptobenzothiazolo)zinc(II) [$\text{Zn}(\text{mbt})_2$] were from Bayer, and ZnO, from BDH. Other materials used were detailed earlier.¹

Compounds were mixed in a Brabender plasticorder and vulcanized by heating at a programmed rate in a DSC.¹ The reaction was stopped at points along the thermal curve and residual curatives and extractable reaction intermediates were analyzed by HPLC as described.^{1,10,11}

RESULTS AND DISCUSSION

Due to the large number of product species formed, detailed plots of their concentration vs. reaction time or temperature become cluttered and difficult to interpret; hence, as in previous articles^{9,11} in this series, changes in concentration of selected species only are presented by smooth curves. The concentrations of all reactants and products are shown in the tables and these must be read in conjunction with the figures.

DSC cure curves for all the formulations studied have the same general features although there are differences in detail (Figs. 1-5). In all cases, the vulcanization exotherm is interrupted by an overlapping endothermic event associated with a mass loss as reflected in the TG curves. As the temperature is increased, the loss of a volatile species from the system continues, but the highly exothermic nature of the reactions associated with vulcanization soon result in the curve resuming its overall exothermic character after a temporary reversal. The general features reflected in the DSC curves parallel

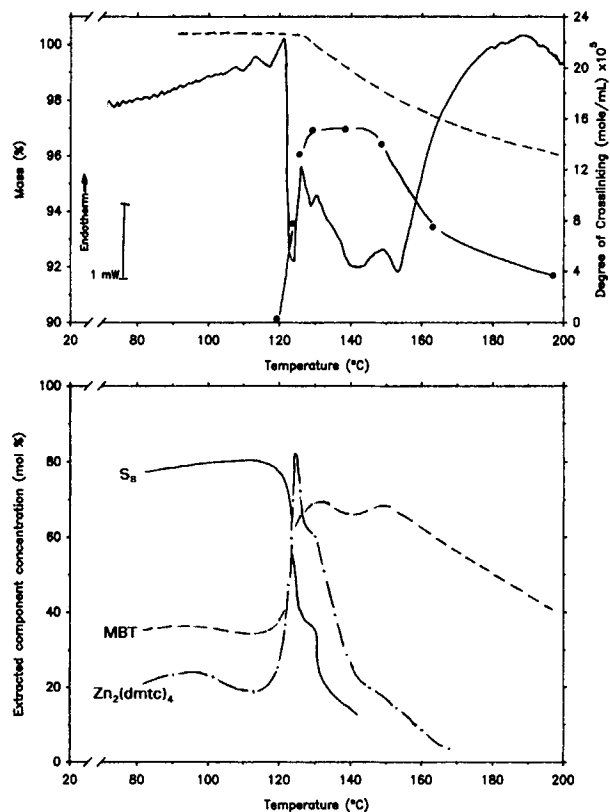


Figure 2 Upper figure: (—) DSC; (---) TG; (-·-) degree of crosslinking. Lower figure: HPLC analysis of IR- $\text{Zn}_2(\text{dmtc})_4$ (0.5)-MBTS (0.5)-sulfur (1) heated at 2.5°C/min.

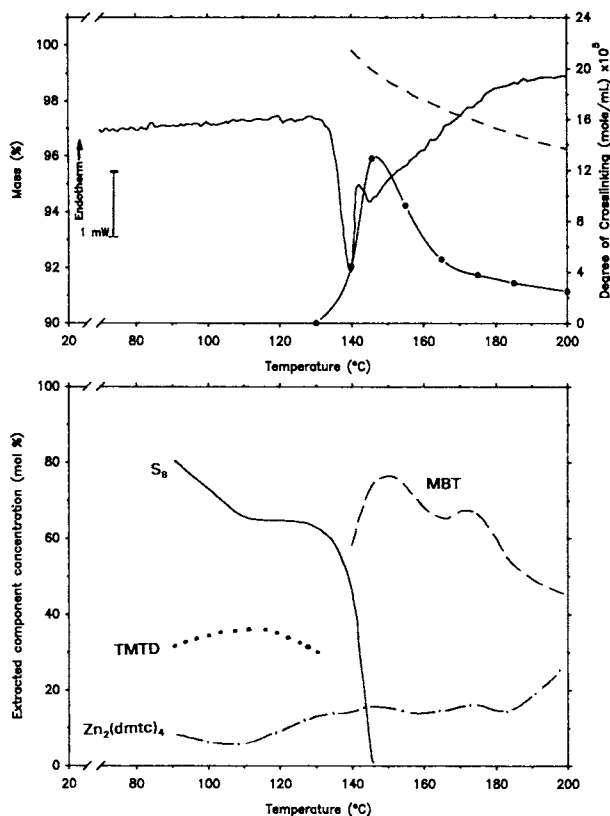


Figure 3 Upper figure: (—) DSC; (---) TG; (-·-) degree of crosslinking. Lower figure: HPLC analysis of IR- $\text{Zn}_2(\text{dmtc})_4$ (0.5)- $\text{Zn}(\text{mbt})_2$ (0.5)-sulfur (1) heated at $2.5^\circ\text{C}/\text{min}$.

those found in that of the IR- $\text{Zn}_2(\text{dmtc})_4$ sulfur system.¹² The endothermic event, attributed to the evaporation of dimethyldithiocarbamic acid (Hdmtc) (or its degradation products), can be eliminated by the inclusion of ZnO in the compound.¹² ZnO traps Hdmtc as $\text{Zn}_2(\text{dmtc})_4$. The similarity between the DSC curves and their resemblance to that of the IR- $\text{Zn}_2(\text{dmtc})_4$ -sulfur system suggests that the crosslinking process is dominated by the accelerator $\text{Zn}_2(\text{dmtc})_4$.

The similarity in the reaction mechanism applicable to the different systems is reinforced by the analyses of curatives and intermediates extracted from the rubbers at different stages of the reaction (Figs. 1-5 and Table I). On extracting curatives from the unheated rubber, a wide spectrum of products is obtained. This can be ascribed to the interaction between curatives on dissolution and is consistent with data reported earlier in studies of the interactions of curatives in the absence of rubber.^{9,11} It is impossible to say whether these interactions occur when the curatives dissolve in the rubber during compounding or only when they are extracted

into the HPLC solvent. Coincident with, or immediately prior to the onset of crosslinking, there is a change in the spectrum of products extracted, indicating that the equilibrium between the species is disturbed and this must be ascribed to the interaction of some species with the polymer chain. The concentrations of most species decrease, but that of MBT increases rapidly and later starts to decrease very slowly, while that of $\text{Zn}_2(\text{dmtc})_4$ increases to a maximum coincident with the onset of the endothermic event in the DSC curve. Thereafter, the $\text{Zn}_2(\text{dmtc})_4$ concentration decreases rapidly, the decrease being accompanied by a mass loss as reflected in the TG curves.

In their study of the $\text{Zn}_2(\text{dmtc})_4$ -accelerated crosslinking of model compounds, Geysler and McGill¹³ suggested that interaction between the octagonal S_8 ring and $\text{Zn}_2(\text{dmtc})_4$ will weaken the Zn-S bond, which, in the presence of rubber or a model compound with a labile hydrogen atom, will lead to the formation of a pendent group of high sulfur rank, ZnS and Hdmtc:

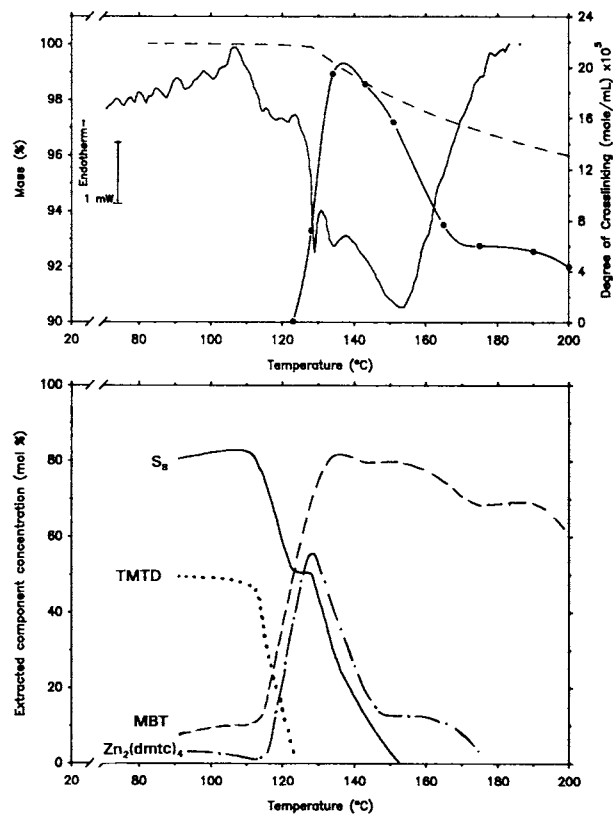
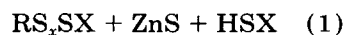
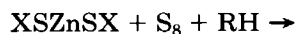


Figure 4 Upper figure: (—) DSC; (---) TG; (-·-) degree of crosslinking. Lower figure: HPLC analysis of IR-TMTD (0.5)- $\text{Zn}(\text{mbt})_2$ (0.5)-sulfur (1) heated at $2.5^\circ\text{C}/\text{min}$.

Table I Analysis of Compounds Heated in the DSC at 2.5°C/Min to Various Temperatures

Compound	Temp (°C)	1/2M × 10 ⁵ c (mol/mL)	Extracted Component Concentration (mol %)											
			S8	TMTD	TMTM	T3	T4	MBT	MBTM	P1	P2	P3	Zn ₂ (dmtc) ₄	
IR-														
Zn ₂ (dmtc) ₄ (0.33)														
-MBT (0.67)														
-sulfur (1)	25		77	a				93 ^a			3			
	95		84	a				87 ^a			3			
	110		81	a				92 ^a	b		3	b	61 ^b	
	116	0.18	50	a				75 ^a	b			b	67 ^b	
	120	1.77	58	a				82 ^a	b			b	74 ^b	
	121	2.64	62	a				88 ^a	b			b	95 ^b	
	122	4.04	59	a				84 ^a	b			b	94 ^b	
	140	7.93	36	a				85 ^a	b		1	b	72 ^b	
	150	6.80	16	a				76 ^a	b		2	b	19 ^b	
	159	7.75	13	a				80 ^a			1			
	166	6.29		a				76 ^a			2			
	175	5.39		a				72 ^a			2			
	186	4.87		a				60 ^a						
	200	4.33	1	a				54 ^a			1			
IR-														
Zn ₂ (dmtc) ₄ (0.5)														
-MBTS (0.5)														
-sulfur (1)	80		77	61 ^c			3 ^d	21	35	2	2	21	9	21 ^d
	100		80	51 ^c	7 ^c		5 ^d	24	36	3	2	24	11	23 ^d
	120		77	58 ^c			4 ^d	13	37	2	2	21	13	26 ^d
	124	7.73	56	27 ^c					60	1			16	81 ^d
	127	13.20	40	5 ^c	8 ^c				66			< 1	26	65 ^d
	131	15.10	33	4 ^c	12 ^c				70			1	20	59 ^d
	140	15.20	15	6 ^c	8 ^c			1	66			1	16	29 ^d
	150	14.00		7 ^c	8 ^c			1	69			1	10	18 ^d
	165	7.39			11 ^c			1	60			2	4	7 ^d
	200	3.66					5 ^d	2	40		1	3		
IR-														
Zn ₂ (dmtc) ₄ (0.5)														
-Zn(mbt) ₂ (0.5)														
-sulfur (1)	25		81	25 ^e					e					10 ^e
	90		80	32 ^e					e					9 ^e
	110		64	37 ^e					e					6 ^e
	130	0.01	63	31 ^e					e					13 ^e
	140	4.45	45	e					57 ^e					14 ^e
	146	12.90	3	e					75 ^e					17 ^e
	155	9.23		e					74 ^e					15 ^e
	165	5.01		e					65 ^e			1		14 ^e
	175	3.77		e					67 ^e			1		16 ^e
	185	3.15	3	e					54 ^e			1		14 ^e
	200	2.51		e					46 ^e			1		28 ^e



where X is $(\text{CH}_3)_2\text{NC}(\text{S})$ and RH is rubber or a model compound.

$\text{Zn}_2(\text{dmtc})_4$ catalyzes the reaction of pendent groups with neighboring rubber chains, leading to rapid crosslinking and the liberation of more Hdmtc .¹⁴ In a closed system, ZnS will retrap¹⁵

Hdmtc as $\text{Zn}_2(\text{dmtc})_4$, but in an open system,¹² Hdmtc is lost from the DSC samples at elevated temperatures. (Kruger and McGill¹² suggested that Hdmtc decomposed to CS_2 and dimethylamine, which escaped from the system. Geysler and McGill¹⁵ showed that Hdmtc was stable at vulcanization temperatures and would evaporate without decomposing.) The rapid mass loss seen in the TG curves of all systems is accompanied by a decrease in the amount of $\text{Zn}_2(\text{dmtc})_4$ extracted from the com-

Table I (Continued from the previous page)

Compound	Temp (°C)	1/2M × 10 ⁵ c (mol/mL)	Extracted Component Concentration (mol %)										
			S8	TMTD	TMTM	T3	T4	MBT	MBTM	P1	P2	P3	Zn ₂ (dmtc) ₄
IR-													
TMTD (0.5)- Zn(mbt) ₂ (0.5) -sulfur (1)	25		79	43		1	1 ^f	6	2		32 ^f	2 ^f	
	90		80	50		1	1 ^f	8	2		36 ^f	4 ^f	
	110		83	48		1		10	2		33 ^f	1 ^f	
	114		77	36				13	1		25 ^f	1 ^f	
	123	0.06	52	1				52				42 ^f	
	128	7.21	50					70				56 ^f	
	134	19.5	29					82				40 ^f	
	143	18.7	12					80			1 ^f	17 ^f	
	151	15.7	2					80			2 ^f	12 ^f	
	165	7.68						75			3 ^f	10 ^f	
	175	6.04						69			2 ^f	1 ^f	
	190	5.60						70			3 ^f		
	200	4.37						60			2 ^f		
IR-													
TMTD (0.5) -MBT (0.5) -ZnO (1) -sulfur (1)	25		68	37	28	^d	21	34		4	39	3	15 ^d
	80		63	35	26	^d	18	34		3	34	4	13 ^d
	100		73	39	26	^d	22	36		4	39	5	15 ^d
	116		63	61	17	^d		46		2	20	10	20 ^d
	125	0.36	37	50	5	^d		36		1	4	7	27 ^d
	140	28.10	10	7	9	^d		68				24	63 ^d
	143	29.80	2	5	10	^d		69			1	24	37 ^d
	155	18.90			11	^d		72			2	14	19 ^d
	165	8.61			13			92			2		
	180	4.65			7			85			5		
	200	2.79									2		

T3 and T4 = tetramethylthiuram tri- and tetrasulfide; P1, P2, and P3 = *N,N*-dimethyldithiocarbamyl-benzothiazole mono-, di-, and trisulfide.

^a Poor separation TMTD and MBT. Denoted as MBT.

^b Poor separation of Zn₂(dmtc)₄, MBTM, P3, and P4.

^c Poor separation of TMTD and TMTM.

^d Poor separation of Zn₂(dmtc)₄ and T3.

^e Poor separation of Zn₂(dmtc)₄ TMTD and MBT.

^f Poor separation of Zn₂(dmtc)₄, P2, and T4.

pounds and is reflected in the endotherm superimposed on the vulcanization exotherm. ZnO is a better trap for Hdmtc than is ZnS and Kruger and McGill¹² showed that the endothermic event, attributed to the rapid loss of Hdmtc, is not present in compounds containing ZnO.

On heating at 2.5°C/min with the DSC Zn₂(dmtc)₄-accelerated crosslinking initiates below 130°C,¹² while with Zn(mbt)₂, no crosslinks form below 165°C.¹⁰ The latter accelerator gives a single narrow vulcanization exotherm. The DSC curves suggest that crosslinking in the binary accelerator systems is dominated by the Zn₂(dmtc)₄-accelerated reaction sequence. As reported earlier,⁹ accelerators

TMTD, MBTS, and MBT readily exchange with ligands on both thiuram and benzothiazole zinc complexes. Hdmtc, liberated on crosslinking, should, likewise, exchange with Zn(mbt)₂, leading to the observed increase in Zn₂(dmtc)₄ and concentration and to the release of MBT during the early stages of reaction (Figs. 1-5).

ZnS, formed during crosslinking, is a less efficient trap than is ZnO for Hdmtc¹² and the loss of Hdmtc during Zn₂(dmtc)₄-accelerated crosslinking [reaction (1)] will lead to a decrease in Zn₂(dmtc)₄ concentration. The high concentrations of MBT detected also imply that reaction between MBT and ZnS is limited.

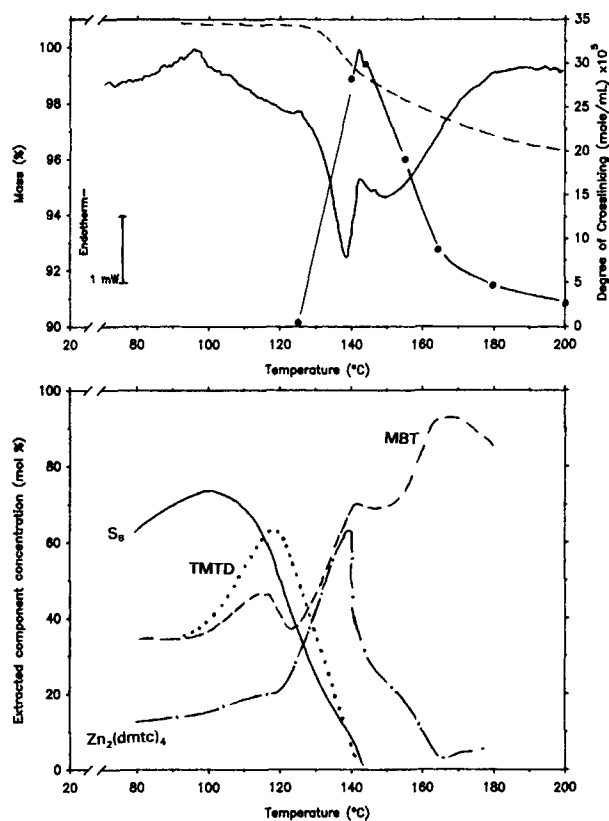


Figure 5 Upper figure: (—) DSC; (---) TG; (· · ·) degree of crosslinking. Lower figure: HPLC analysis of IR-TMTD (0.5)-MBT (0.5)-sulfur (1)-ZnO (1) heated at 2.5°C/min.

The rapid decrease in the early stages of crosslinking of accelerator species not containing zinc points to their participation in crosslinking. The formation of polysulfidic pendent groups by these species and their subsequent crosslinking is well established.¹⁶⁻¹⁸ Byproducts of such crosslinking reactions would be MBT and Hdmtc. The concentra-

tion of MBT is seen to increase rapidly while Hdmtc would react with ZnS or exchange with Zn(mbt)₂ to form Zn₂(dmtc)₄.

SYNERGISM

Reversion that occurs at elevated temperatures makes analysis of crosslink density data in different formulations difficult. A limited interpretation, making use of the maximum crosslink densities achieved in different systems, is given below.

As indicated, crosslinking appears to be dominated by Zn₂(dmtc)₄, and in all cases, a synergistic effect is observed in the binary accelerator systems (Table II). Zn₂(dmtc)₄ and sulfur lead to a higher crosslink density than do the equivalent amounts of Zn(mbt)₂ and sulfur (Table II). In the absence of rubber, an exchange between ligands on Zn₂(dmtc)₄ and Zn(mbt)₂ occurs readily.⁹ The conversion of most of the zinc complex to Zn₂(dmtc)₄ via an exchange with Hdmtc produced in the Zn₂(dmtc)₄ crosslinking reaction would result in higher crosslink densities than if the zinc accelerators acted independently. The synergistic effect is further enhanced where the equilibria between species results in high concentrations of *N,N*-dimethylthiocarbamylbenzothiazole disulfide (P2), as reflected in HPLC analyses at 25°C (Table II). Assuming that P2 and *N,N*-dimethylthiocarbamyl-benzothiazole polysulfide (PP) are present in the rubber (and not only in the HPLC solution), it points to the importance of pendent groups, formed via accelerator polysulfides (PP, TMTP) in contributing to the crosslinking reaction. These would crosslink independently and in addition to the Zn₂(dmtc)₄-initiated reaction, although their crosslinking may be catalyzed¹⁴ by Zn₂(dmtc)₄.

Table II Maximum Crosslink Densities ($\frac{1}{2}Mc$) Achieved in Different Compounds

System	$\frac{1}{2}Mc \times 10^{-5}$ Found	mol/mL Calcd.	% P2 at 25°C	Reference or Figure
IR-Zn ₂ (dmtc) ₄ -sulfur	12			Ref. 19
IR-TMTD-sulfur-ZnO	23			Ref. 20
IR-Zn(mbt) ₂ -sulfur	3			Ref. 10
IR-MBT-sulfur-ZnO	4			Ref. 10
IR-Zn ₂ (dmtc) ₄ -MBT-sulfur	8	5.5	< 5	Fig. 1
IR-Zn ₂ (dmtc) ₄ -MBT-sulfur	15	9.5	10	Fig. 2
IR-Zn ₂ (dmtc) ₄ -Zn(mbt) ₂ -sulfur	13	7.5	< 5	Fig. 3
IR-TMTD-Zn(mbt) ₂ -sulfur	20	5	35	Fig. 4
IR-TMTD-MBT-sulfur-ZnO	33		40	Fig. 5

The effect of ZnO, as opposed to Zn-accelerator complexes, in increasing the crosslink density (Table II) is well known^{20,21} although not yet explained (see Table II). This effect is also evident in DMTBS-sulfur-ZnO and TMTD-MBT-sulfur-ZnO compounds (Table II) where ZnO is in excess of the amount required to form the Zn-accelerator complexes.

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