

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

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SYNOPSIS

Polyisoprene was vulcanized with the binary accelerator system tetramethylthiuram disulfide-2-mercaptobenzothiazole (TMTD-MBT) in the absence of ZnO. 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. Two cross-linking reaction sequences were identified, the first being initiated by polysulfides of the mixed accelerator *N,N*-dimethyldithiocarbamylbenzothiazole disulfide, and the second by MBT. All the TMTD is consumed in the first reaction sequence. Synergism of the reaction is discussed in terms of recent work detailing a reaction mechanism for TMTD-accelerated vulcanization. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Combinations of accelerators are frequently used by the rubber industry. Dogadkin et al.^{1,2} first introduced the categorization of binary accelerator systems into three groups, namely (1) synergistic systems, (2) systems in which the activity of the pair does not exceed that of the most active accelerator, and (3) systems with an additive functioning of the accelerators. Originally, the higher activity of binary accelerator systems was explained by the formation of either eutectic mixes or salt-forming compounds that possess better solubility in rubber and greater chemical reactivity.³⁻⁵ Later, reaction mechanisms applicable to particular binary systems were proposed. The system tetramethylthiuram disulfide-2-mercaptobenzothiazole (TMTD-MBT) was studied by Bandyopadhyay and Banerjee⁶ who proposed a mechanism for the vulcanization of natural rubber in the presence of dicumyl peroxide. The detailed reaction mechanism was dependent on the ratio of the accelerators in the compound.

Sulfide-exchange reactions between disulfides and mercaptans occur very readily² and in the TMTD/MBT system lead to the formation of a mixed accelerator *N,N*-dimethylthiocarbamylbenzothiazole disulfide (P2).⁷ Unless removed by reaction with ZnO, the presence of the exchange product dimethyldithiocarbamic acid (Hdmtc) favors the formation of the polysulfides of TMTD and P2.^{7,8} Polysulfides of the accelerators are attributed to having an important role in initiating vulcanization.^{9,10} Most binary formulations studied contain ZnO. This article reports on the vulcanization of polyisoprene (IR) by the binary accelerator system TMTD/MBT in the absence of zinc.

EXPERIMENTAL

Materials

Sulfur CP from Halpro, TMTD and 2-bisbenzothiazole-2,2'-disulfide (MBTS) from Orchem (South Africa), MBT from Monsanto, and 2-bisbenzothiazole-2,2'-monosulfide (MBTM) (Vulkacit MS) from Bayer were used.

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Methods

Compounds were mixed in a Brabender Plasticorder fitted with a W30-type mixing head of 30 mL bowl volume using a fill factor of 0.8. The rubber was masticated for 6 min at 40 rpm, after which the vulcanization ingredients were added and blending was continued for a further 6 min at 30 rpm. Use of a refrigerated thermostat ensured that the temperature of the head did not exceed 45°C during compounding. On dumping, the mix was passed through a two-roll mill seven times, each time folding the compound once.

The number of moles of curatives per hundred parts of rubber is shown in the text in the following form: IR-TMTD(1)-MBT(1). Curatives were used in 1 : 1 mol ratios unless otherwise stated. Curative loadings of 33.5×10^{-5} mol/mL of rubber were used. Abbreviations are as follows:

[dma] ⁺ [dmtc] ⁻	dimethylammonium dimethyldithiocarbamate
DMABT	dimethylaminobenzothiazole
DMBSA	<i>N,N</i> -dimethylbenzothiazole-2-sulfenamide
DMTBS	<i>N,N</i> -dimethylthiocarbamylbenzothiazole sulfide
Hdmtc	dimethyldithiocarbamic acid
MBT	2-mercaptobenzothiazole
MBTM	2-bisbenzothiazole-2,2'-monosulfide
MBTP	2-bisbenzothiazole-2,2'-polysulfides
MBTS	2-bisbenzothiazole-2,2'-disulfide
P1	unresolved peak of DMTBS and/or DMABT and/or DMBSA
P2	<i>N,N</i> -dimethylthiocarbamylbenzothiazole disulfide
P3	<i>N,N</i> -dimethylthiocarbamylbenzothiazole trisulfide
PP	<i>N,N</i> -dimethylthiocarbamylbenzothiazole polysulfide
T3	tetramethylthiuram trisulfide
T4	tetramethylthiuram tetrasulfide
TME	tetramethylethene
TMTD	tetramethylthiuram disulfide
TMTM	tetramethylthiuram monosulfide

Compounds were vulcanized by heating in a DuPont DSC or TG at 5°C/min. The reaction was stopped at points along the thermal curve and residual curatives and reaction intermediates were extracted and analyzed by HPLC.^{7,11} The identi-

fication of reaction intermediates has been ascribed.⁷

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^{7,8} in this series, changes in concentration of selected species only are presented by smoothed curves. The concentrations of all reactants and products are shown in tables and these must be read in conjunction with the figures.

IR-TMTD-MBT

In an IR-TMTD(1)-MBT(1) mix, the TMTD-MBT melt/dissolution endotherm (Fig. 1 and Table I) occurs at 100°C. Crosslink density measurements show that crosslinking initiates at a lower temperature than in the IR-TMTD system,¹⁰ but there is no event in the DSC thermal curve that identifies with crosslinking. It is interesting that a poorly defined exotherm is associated with the desulfuration of polysulfidic crosslinks. A similar exotherm is observable in the IR-TMTD system.¹⁰ In most systems, the "vulcanization exotherm" appears to be attributable to the concurrent desulfuration processes, rather than to crosslink formation.

In samples heated to below 100°C, the concentration of extractable species detected by HPLC is dependent upon the equilibrium set up by the accelerators in solution,⁷ i.e., no accelerator-IR interaction occurs. The spectrum of extractable products changes at temperatures above that at which melting occurs and a different analysis is obtained. This points to a reaction other than that between the curatives in solution. An exchange reaction between TMTD and MBT would lead to the formation of P2 and Hdmtc⁷:



where X = (CH₃)₂NCS and Bt = benzothiazole.

The mass loss that commences coincident with the melting endotherm can be ascribed to the liberation of Hdmtc. At temperatures above the melting endotherm, the concentrations of P2 and TMTD decrease, while that of MBT, 2-bisbenzothiazole-2,2'-monosulfide (MBTM), and P1 increase. (P1 refers to a peak that may be ascribed to *N,N*-dimethyldithiocarbamylbenzothiazole sulfide [DMTBS] and/or dimethylaminobenzothia-

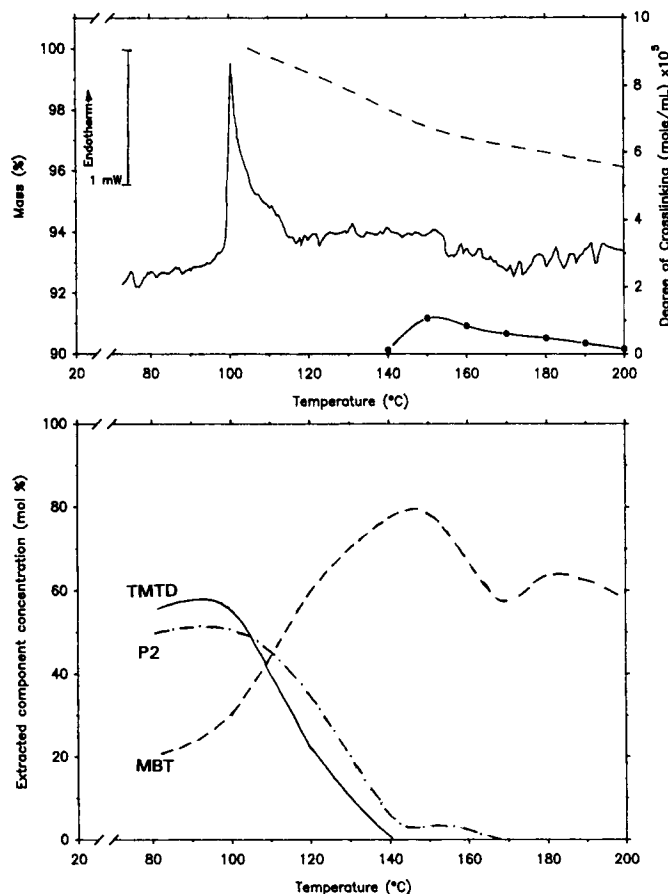
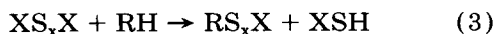
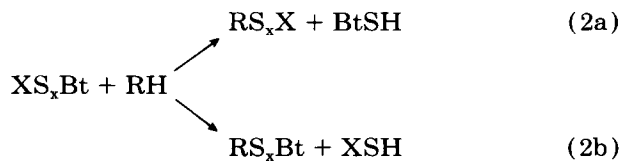


Figure 1 Upper figure: (—) DSC; (---) TG; (●—●) degree of crosslinking. Lower figure: HPLC analysis of IR-TMTD(0.5)-MBT(0.5) heated at 2.5°C/min.

zole [DMABT] and/or *N,N*-dimethylbenzothiazole-2-sulfenamide [DMBSA]. See ref. 7). *N,N*-Dimethylcarbonylbenzothiazole trisulfide (T3) and tetramethylthiuram tetrasulfide (T4) were seen to form in the absence of rubber⁷ but are not detected here. These *N,N*-dimethylthiocarbonylbenzothiazole polysulfide (PP) and tetramethylthiuram polysulfide (TMTP) are highly reactive toward IR and would rapidly add to the polymer chain, forming pendent groups, as in eqs. (2) and (3). The TMTD concentration is zero by the time crosslinking starts and the P2 concentration is very low:



RH = rubber hydrocarbon.

The fact that crosslinking initiates considerably earlier than in either TMTD- or MBT-accelerated systems points to the higher reactivity of PP compared to TMTP, i.e., reaction (2a) would lead to pendent group formation, with a corresponding decrease in P2 and increase in MBT concentration. Almost all the MBT is released by the time crosslinking starts. This shows that P2 addition occurs mainly as in eq. (2a) and not as benzothiazole pendent groups [eq. (2b)]. Such benzothiazole pendent groups would liberate more MBT once crosslinking commences.¹² It is generally suggested¹³ that crosslinking involves reaction between pendent groups or between pendent groups and neighboring chains. Versloot et al.¹⁴ claimed that crosslinking resulted only from reaction between pendent groups. Geysler and McGill¹⁵ supported this and their more detailed scheme [reaction (4)] of the reaction sequence proposed that, on vulcanization of the model compounds in the presence of sulfur, an exchange compound occurs between thiuram-terminated pendent reaction groups and Hdmtc, leading to unreactive thiol pendent groups. Dimethylamine, resulting from the

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

Compound	Temp (°C)	$1/2M_c \times 10^5$ (mol/mL)	Extracted Component Concentration (mol %)								
			S8	TMTD	T3	T4	MBT	MBTM	MBTS	P1	P2
IR-											
TMTD (0.5)-											
MBT (0.5)											
	25			59				20	2	5	61
	80			55				21	2	3	50
	100			55			37	31	2		51
	120			22	1			60	6	14	34
	140	0.11	2		3			78	3	6	6
	150	0.99	1					78	3	3	4
	160	0.79						67	4	1	3
	170	0.57						57	5	2	1
	180	0.45					1	64	2	1	1
	190	0.32					2	63	3	2	1
	200	0.15	12				2	58	1	1	2
IR-											
TMTD (0.5)-											
MBT (0.5)-											
sulfur (1)											
	25		40	55	48			17	4		42
	80		49	53	48			15	4		44
	90		55	52	42			17	5		44
	110		78	31	30			21	5	5	40
	130		67	1	1			69	3	1	22
	140	3.57	66					79			3
	145	3.68	66					83			2
	150	4.22	59					79		1	2
	160	5.47	29					73			
	166	6.64	8					71		1	1
	170	5.52						78			4
	180	5.27						73		1	1
	190	3.22						67		1	1
	200	2.59						51		2	1
IR-											
TMTD (0.62)-											
MBT (0.38)-											
sulfur (1)											
	25		69	71 ^a	38	21		^a			48
	80		80	77 ^a	39	18		^a		2	49
	94		71	74 ^a	32	18		^a		2	49
	110		81	68 ^a	33	18		^a		8	54
	130	0.01	78	32 ^a	19	24		^a	6	1	16
	140	1.67	80							2	7
	150	2.99	62	^b				18 ^b	1	1	3
	155	3.13	50	^b				16 ^b	1	1	4
	168	3.95	6	^b				14 ^b	1	4	3
	175	2.73		^b				13 ^b		6	3
	185	1.68		^b				13 ^b		9	1
	200	1.41		^b				16 ^b		10	4

decomposition of thiuram radicals, interacts with thiol pendent groups to form dimethylammonium-terminated pendent groups. Finally, crosslinking results from reaction between these groups and thiuram pendent groups, liberating tetramethylthiourea (TMTU):

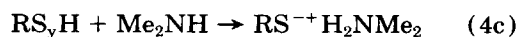
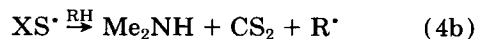
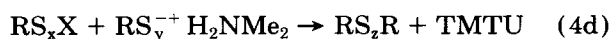


Table I Continued

Compound	Temp (°C)	$1/2M_c \times 10^5$ (mol/mL)	Extracted Component Concentration (mol %)								
			S8	TMTD	T3	T4	MBT	MBTM	MBTS	P1	P2
IR-											
TMTD (0.23)- MBT (0.77)- sulfur (1)	25		71	b	36	22	72 ^b				22
	80		70	b	38	19	66 ^b				22
	96		72	b	33	18	67 ^b		1	1	25
	120		77	b	18		53 ^b		3	3	13
	130	0.10	79	b	11		66 ^b		2	2	5
	140	0.12	74	b			62 ^b		2	2	3
	150	2.73	60	b			62 ^b				1
	160	3.80	34	b			57 ^b				1
	168	4.66	6	b			56 ^b				1
	175	3.82	1	b			70 ^b				
	185	3.04		b			66 ^b				
	200	2.53		b			60 ^b				
IR-											
DMBTS (1)- sulfur (1)	25								4	70	7
	80		68						3	67	7
	100		74						4	70	8
	120		79						3	76	7
	140		71	4			5	1	3	73	8
	150	3.86	68	1			9		16	58	4
	155	7.90	41				44		17	4	3
	163	6.44	5			2	48		18		2
	175	4.51				1	48		24		2
	200	2.71	3				42		19		1

^a TMTD and MBT not separated. Denoted as TMTD.

^b TMTD and MBT not separated. Denoted as MBT.



TMTU was not detected in the binary system. Hdmtc can escape from the DSC at vulcanization temperatures (TG curve Fig. 1). As most of the Hdmtc would be produced in the formation of P2 [reaction (1)], i.e., prior to pendent group formation, the exchange between pendent groups and Hdmtc would be very limited and TMTU would not result in crosslinking. In this system, crosslinking would occur between two thiuram-terminated pendent groups. Crosslinking would also be earlier as deactivation of the pendent groups [reaction (4a)] is less extensive.

IR-TMTD-MBT-Sulfur

The IR-TMTD(0.5)-MBT(0.5)-sulfur(1) system (Fig. 2 and Table I) has a melt/dissolution endotherm at 93°C, considerably lower than in the IR-

TMTD(1)-sulfur(1) compound.¹⁰ The crosslinking exotherm initiates at 138°C, much the same temperature as for IR-TMTD(1)-sulfur(1). A high TG mass loss of 58% of the curatives is observed at 200°C. This can be equated to the loss of most of the TMTD in the compound (60% of the accelerator mix) as Hdmtc. The formation of TMTP is favored relative to that of PP, which corresponds to the situation in the powder mixes.⁷ As in the absence of sulfur, the reaction commences immediately after the endotherm and the concentration of TMTD, T3, T4, and P2 decrease. HPLC analysis shows an increase in free sulfur in the early stages of the reaction. This does not reflect a reaction with IR but must be ascribed to changes in the equilibria set up between the different species in solution.⁷ Reaction in the powder mix showed the maximum TMTP concentration at 100°C, but the formation of pendent groups in rubber removes TMTD, TMTP, P2, *N,N*-dimethyldithiocarbamylbenzothiazole trisul-

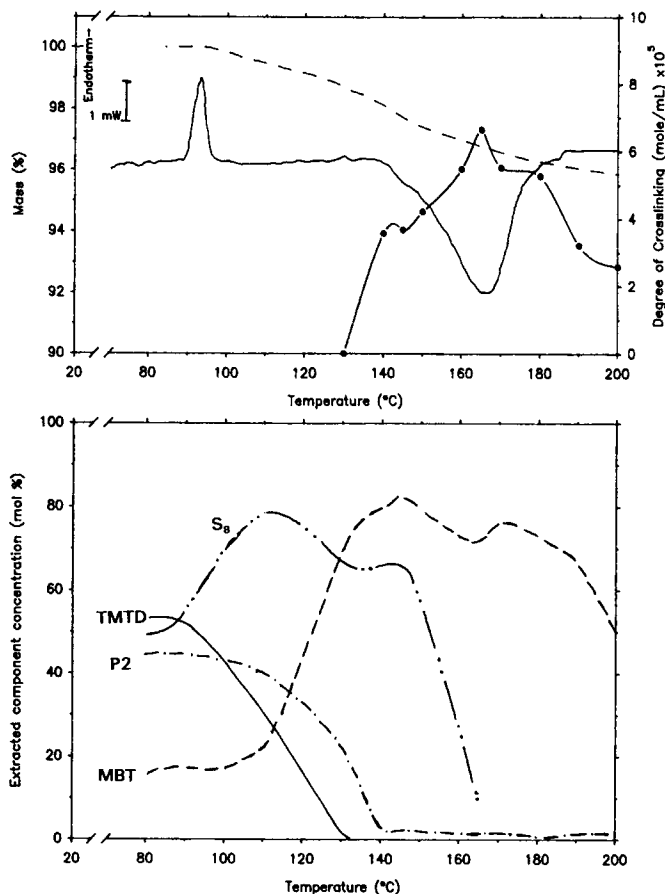


Figure 2 Upper figure: (—) DSC; (---) TG; (●—●) degree of crosslinking. Lower figure: HPLC analysis of IR-TMTD(0.5)-MBT(0.5)-sulfur(1) heated at 2.5°C/min.

fide (P3), etc., thus influencing the amount of sulfur present as polysulfides when the curatives are extracted into the solvent. As in the absence of sulfur, the MBT concentration, which is initially low due to its incorporation in P2, increases as pendent groups are formed [reaction (2a)], while Hdmtc liberation results in the TG mass loss observed. Liberation of most of the MBT prior to the onset of crosslinking again suggests that most pendent groups are formed via reactions (2a) and (2b). Neither dimethylammonium dimethyldithiocarbamate ($[\text{dma}]^+[\text{dmtc}]^-$) nor TMTU, reported¹⁵ to form on reaction with 2,3-dimethyl-2-butene (TME)-TMTD-sulfur in a closed system, was detected. These species will not form when Hdmtc and dimethylamine can escape from the system.

Kruger and McGill,¹⁰ who used a similar DSC curing system to the above, reported the formation of TMTU during crosslinking in both IR-TMTD and IR-TMTD-sulfur compounds. In TMTD systems, Hdmtc is released during pendent group formation [reaction (3)] and this Hdmtc and the pen-

dent groups are in close proximity. Thus, reactions (4), which lead to TMTU, will occur more readily than where Hdmtc is liberated in forming P2 prior to pendent groups being present. Crosslinking begins slightly earlier than in the absence of sulfur (cf. Figs. 1 and 2) and may be ascribed to the higher concentration of TMTP. In this system, not all the P2 had been consumed by the time crosslinking started and some MBT was released in the pendent group formation that occurred concurrently with crosslinking.

Two crosslinking reactions apply, the first of which can be explained in terms of a series of reactions initiated by PP and/or TMTP. Crosslinking is rapid above 130°C but reaches a plateau at 140°C. The exotherm has a very slight shoulder near its beginning, which coincides with the number of crosslinks reaching the plateau value. All TMTD, TMTP, and P2 are consumed at the onset of the crosslink density plateau and the maximum MBT concentration is attained. The concentration of sulfur remains virtually constant over this plateau and decreases only once crosslinking recommences. It is

suggested that the second crosslinking process occurs via an MBT-accelerated mechanism, with a slow decrease in the MBT concentration as expected.¹⁶ The crosslink density is a maximum at the DSC exotherm maximum and coincides with the complete consumption of sulfur, akin to the single-accelerator IR-TMTD(1)-sulfur(1)¹⁰ and IR-MBT(1)-sulfur(1)¹¹ systems. The second reaction is much less efficient; it consumes 70% of the sulfur, yet forms the same number of crosslinks as does the first reaction.

IR-TMTD-MBT-Sulfur Varied Ratios

Bandyopadhyay and Banerjee^{6,17} showed that synergism in an NR-TMTD-MBT-sulfur-stearic acid-ZnO system was a maximum at a TMTD : MBT ratio of 0.3 : 0.7 (phr/phr). To determine if, by varying the accelerator ratios, synergism could be found in the absence of zinc (in any of its forms), compounds were prepared in which the mol ratios corresponded to the accelerator ratios used by them,

but at concentration levels consistent with those in this study (a total of 3.34×10^{-4} mol/mL of IR). Difficulties in separating TMTD and MBT were experienced with the HPLC column in these experiments, and the single peak obtained is depicted as TMTD/MBT. Since no measure of the individual concentrations exists, a low concentration of P2 is taken as evidence that TMTD has been completely consumed.

The IR-TMTD(0.62)-MBT(0.38)-sulfur(1) (Fig. 3 and Table I) and IR-TMTD-(0.23)-MBT(0.77)-sulfur(1) (Fig. 4 and Table I) compounds show the same general features as discussed above. The TMTD, TMTP, and P2 concentrations decrease after the endotherm and are accompanied by a mass loss due to Hdmtc liberated when P2 and pendent groups form. Crosslinking commences at a slightly higher temperature when less TMTD is present. When these components have been consumed, there is a change in the mass loss curve and a constant crosslink density prevails until temperature conditions are favorable for the onset of the

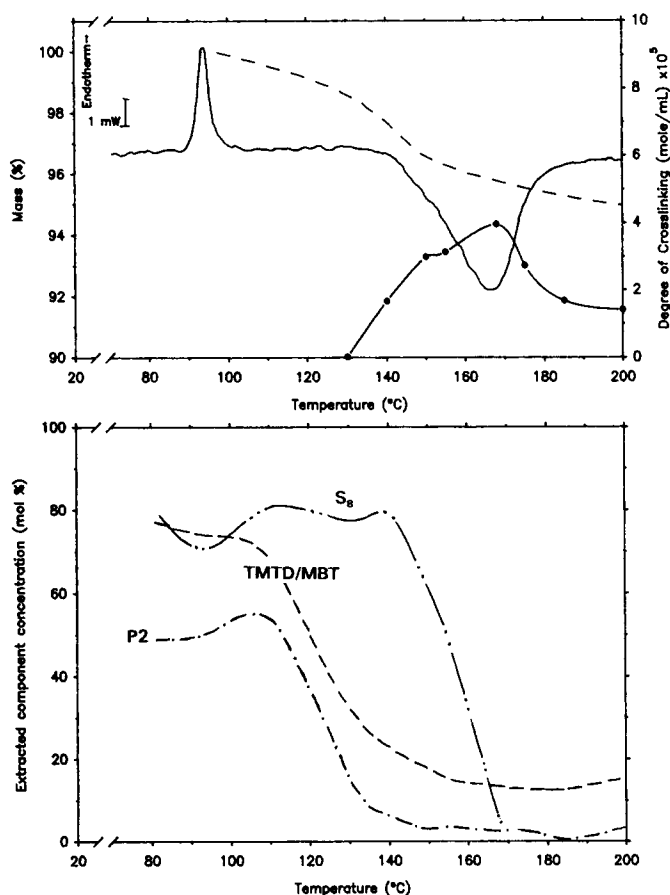


Figure 3 Upper figure: (—) DSC; (---) TG; (●—●) degree of crosslinking. Lower figure: HPLC analysis of IR-TMTD(0.62)-MBT(0.38)-sulfur(1) heated at 2.5°C/min.

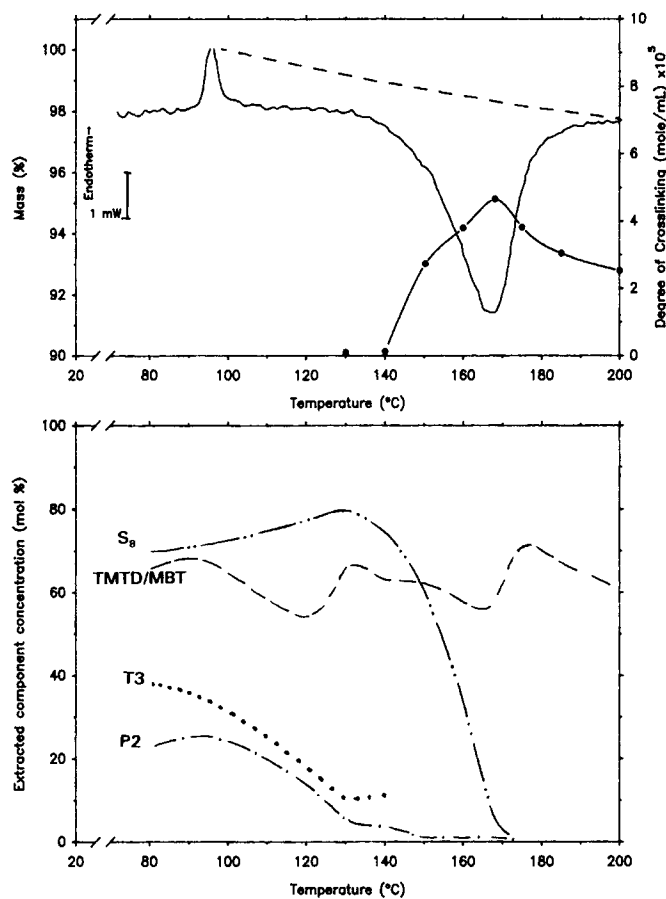


Figure 4 Upper figure: (—) DSC; (---) TG; (●—●) degree of crosslinking. Lower figure: HPLC analysis of IR-TMTD(0.23)-MBT(0.77)-sulfur(1) heated at 2.5°C/min.

MBT-accelerated reaction. The exotherm for the latter reaction reaches its maximum at the same temperature in all three formulations and coincides with the crosslink density maximum. Little sulfur is consumed in the first crosslinking reaction, the concentration dropping rapidly during the second reaction. The sulfur concentration is zero at the maximum of the exotherm.

The crosslink density at the plateau is the highest in the mix with equimolar accelerator concentrations and this points to P2 playing an important role in the reaction. Synergism is discussed below.

IR-DMTBS-Sulfur

The vulcanization reaction of IR-DMTBS(1)-sulfur(1) (Fig. 5 and Table I) occurs well after the melt/dissolution endotherm at 105°C. Only trace amounts of TMTD and MBT are detected prior to crosslinking, indicating limited decomposition of the accelerator:



It should be remembered that as exchange reactions readily occur in solution⁷ the HPLC analysis does not necessarily reflect the equilibria that exist in the rubber; *changes* point to a reaction occurring. There is no mass loss or MBT liberation prior to crosslinking that occurs rapidly at 140°C. PP are not detected in the extract but may form in the rubber where they will rapidly react with the polymer. Removal of P2 (and PP) in pendent group formation [reaction (2a)] will shift the above equilibrium to the right, resulting in more MBTS being detected in the extract. P1 and sulfur decrease rapidly. Reaction (2a) and the crosslinking reactions, detailed by Geyser and McGill,¹⁵ would account for the increase in MBT and a rapid mass loss due to Hdmtc evolution. A high crosslink density is achieved but reversion becomes more important than new crosslinking processes even before all of the sulfur has been consumed at the DSC exotherm peak.

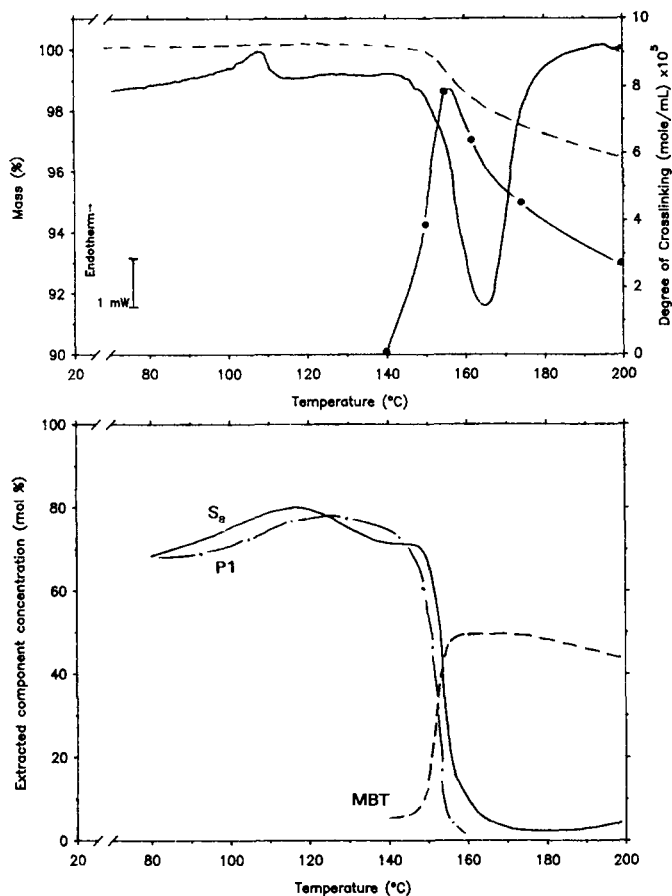


Figure 5 Upper figure: (—) DSC; (---) TG; (●—●) degree of crosslinking. Lower figure: HPLC analysis of IR-DMTBS(1)-sulfur(1) heated at 2.5°C/min.

Synergism

Two crosslinking sequences are involved: In the first, crosslinking is initiated by PP and/or TMTP, and in the second, by MBT. Thiuram pendent groups are deactivated by exchanging with Hdmtc and, unless reactivated by Me_2NH [reactions (4)], do not participate in crosslinking.¹⁵ In the binary acceler-

ated system, much of the Hdmtc is released when P2 forms prior to the formation of pendent groups. Hdmtc can escape from DSC samples as seen by the mass loss that occurs prior to crosslinking (Figs. 1-4) and deactivation of thiuram pendent groups will be limited. Crosslinking between thiuram pendent groups dominates as shown by the absence of TMTU in the system. TMTD, formed on crosslinking, will

Table II Synergism in Binary Systems

System	Degree of Crosslinking ($1/2M_c \times 10^5$ mol/mL)			
	Expected at End of First Stage ^a	Found at End of First Stage	Final	% P2 at 25°C
IR-TMTD (0.5)-MBT (0.5)-S (1)	3.1	3.8	6.9	40
IR-TMTD (0.62)-MBT (0.38)-S (1)	3.9	3.0	4.0	50
IR-TMTD (0.23)-MBT (0.77)-S (1)	1.4	2.8	4.7	20

^a Based on data by Kruger and McGill¹⁰ and Gradwell and McGill.¹¹

exchange with MBT to reform P2 and Hdmtc. At this point, some deactivation of pendent groups becomes possible but the Hdmtc concentration will be lower than in systems accelerated by TMTD only. Furthermore, in TMTD-accelerated systems, Hdmtc is released adjacent to the site at which the pendent group forms and deactivation will be more extensive. PP releases MBT on forming pendent groups. If not all of the thiol groups are reactivated, lower crosslink densities will be obtained than in the compounds where deactivation does not occur and thiuram groups crosslink directly. Table II shows that the ratio of the observed to the expected crosslink density at the end of the first stage of the vulcanization (when P2 = 0) is larger for smaller TMTD concentrations in the binary mixture. This is consistent with a lower extent of pendent group deactivation by Hdmtc. MBT is not consumed in the first stage of the reaction and is available to accelerate crosslinking via the remaining sulfur once the P2 concentration falls to zero.

Equimolar amounts of P1 and TMTD should give the same number of thiuram pendent groups, half of the thiuram groups being released as Hdmtc in the TMTD system. The maximum crosslink density of 7.9×10^{-5} mol/mL achieved with IR-DMTBS-sulfur is higher than the value of 6.3×10^{-5} mol/mL obtained with IR-TMTD-sulfur.¹⁰ This may, in part, be ascribed to there being no Hdmtc present while pendent groups form and therefore their deactivation, prior to their involvement in crosslinking, is limited.

CONCLUSIONS

In vulcanization with the binary accelerator system, pendent groups form via TMTP and/or PP, a polysulfidic species composed of dmtc and mbt groups. A dmtc group is released from the system as Hdmtc in the formation of P2. No further dmtc loss occurs when PP forms pendent groups, the dmtc group preferentially adding to the chain. MBT eliminated in the process can lead to further, albeit slow, crosslinking. The release, in the binary accelerator system, of Hdmtc prior to pendent group formation limits deactivation of thiuram pendent groups and results in higher crosslink densities. With P1, higher

crosslink densities are achieved than with an equimolar amount of TMTD and this is attributed to there being no Hdmtc prior to the onset of crosslinking.

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